

REACTIONS OF FIFTH GROUP LEWIS ACIDS WITH NITRILES AND IMIDAZOLIUM-BASED COMPOUNDS

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Doctoral Dissertation
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REAKCIJE LEWISOVIH KISLIN PETE SKUPINE Z
NITRILI IN IMIDAZOLIJEVIMI SPOJINAMI

Doktorska disertacija

Supervisor: Asst. Prof. Dr. Gašper Tavčar

Ljubljana, Slovenia, August 2020

Acknowledgments

I would like to thank my partner Neja and my family to whom I am dedicating this thesis. I am grateful for the motivation, energy and understanding that you have given me throughout my doctoral study. Your encouragements and support during the preparation of this thesis were a valuable resource for its successful completion.

Thanks to wonderful individuals that I have amassed over the years and whom I have a privilege to call friends. I would like to thank you for your patience.

Thanks to my past educators and the Slovenian education system for enabling me to achieve this level of education. I would like to express my special gratitude to the members of the evaluation board for the time they have allotted to evaluate the thesis. I am acknowledging the contribution of the Slovenian Research Agency for funding my study.

I am indebted to the colleagues at the Department of Physical and Organic Chemistry and the National NMR Center for their time and resources. Their contributions have elevated the quality of our research.

I would like to thank my friends and acquaintances at the Jožef Stefan Institute, Jožef Stefan International Postgraduate School and beyond for making this academic institution a hospitable working environment. My thanks go especially to my mentor, coworkers and friends at the Department of Inorganic Chemistry and Technology. In these few years we shared many delightful experiences and, unknowing to us all, I have received some lifelong lessons.

Abstract

Coordination chemistry of N-heterocyclic carbenes (NHC) with early transition metals is often overlooked and in the shadow of the reactions done with the flagship NHC complexes with coinage and other mid to late transition metals. The attention toward NHC complexes with fluoride or oxide fluoride reagents of oxophilic metals further diminishes, due to their reactivity as well as special expertise and equipment required for their manipulation. Our intent was to expand the library of NHC-based complexes with group 5 fluorides and to shed some light onto their characteristics. Newly prepared neutral compounds were $[(\text{NHC})\text{VOF}_3]$, $[(\text{NHC})\text{NbF}_5]$ and $[(\text{NHC})\text{TaF}_5]$. Recently, our laboratory synthesized from the NHC substrate a new “naked” fluoride reagent. The goal was to expand the study of fluoride donating capabilities for our imidazolium fluoride $[(\text{NHC})\text{H}][\text{F}]$ from the main group fluorides to transition metal fluorides and oxide fluorides. We correctly predicted that previously established sterically demanding properties of the imidazolium cation could be utilized to prepare and isolate long sought $[\text{VOF}_4]^-$ anion in crystalline form. Furthermore, we also treated the pentafluoride reagents with the $[(\text{NHC})\text{H}][\text{F}]$ salt, which yielded otherwise abundantly represented $[\text{MF}_6]^-$ anions, yet additional tests demonstrated the limits of fluoride donation potential. Isolated aforementioned neutral NHC complexes as well as $[(\text{NHC})\text{H}][\text{VOF}_4]$, $[(\text{NHC})\text{H}][\text{NbF}_6]$ and $[(\text{NHC})\text{H}][\text{TaF}_6]$ salts were structurally characterized and analyzed with NMR and vibrational spectroscopy. Additionally, their stability in solid form and in solution was investigated. In the case of vanadium species, their hydrolysis afforded air stable $[(\text{NHC})\text{H}][\text{VO}_2\text{F}_2]$ salt.

Through careful observation of crystal structures and their comparison to the related compounds, several peculiarities were noted. To help us elaborate on these unusual features, a theoretical approach was employed. Part of calculations was the elucidation of structural difference in conformation of fluoride and chloride moiety in $[(\text{NHC})\text{MX}_5]$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{F}, \text{Cl}$) and shift of fluorine atoms toward the NHC ligand. An especially interesting feature of oxophilic metals in their highest oxidation state is a formally empty valence orbitals and a hypothetically impossible situation for any kind of back-donation to occur urged us to scrutinize the bonding situation in the square pyramidal $[(\text{L})\text{VOF}_3]$ complexes. A minute π -back-donation of fluoride ligands to carbenic carbon atom was theoretically determined. Calculations also showed that elongation of the $\text{V}-\text{F}_{\text{trans}}$ bond is due to the internal crystal packing and should not be oversimplified and invariably ascribed to the trans effect.

Newly prepared salt with the $[\text{VOF}_4]^-$ anion was used for the preparation of relatively rare anionic complexes $[\text{VOF}_4(\text{THF})]^-$, $[\text{VOF}_4(\text{py})]^-$ and $[(\text{VOF}_4)_2(\text{pyz})]^{2-}$. We were able to associate the electron donating ligand onto the $[\text{VOF}_4]^-$ anion, however their instability outside their mother liquor averted analysis beyond structural characterization. As such, the structural data was used to compare and speculate about possible contributing factors to the observed anion–ligand interaction.

Finally, during the preparation of soluble precursors (nitrile adducts of group 5 fluorides) we stumbled upon a system that produced easily and under atmospheric conditions a product of cyclotrimerization of nitriles $[(^{\text{Ph}}\text{TZN})\text{H}][\text{MF}_6]$. Oxonium salt

$[\text{H}_3\text{O}][\text{SbF}_6]$ was used for acidic initiation of the trimerization process. In specific reaction conditions with benzonitrile, we managed to obtain crystals of otherwise only theoretically proposed twice-protonated triazine framework in $[(^{\text{Ph}}\text{TZN})\text{H}_2][\text{SbF}_6]_2$. Interestingly, in the same system *tert*-butylnitrile yielded unusual carbonylamidine in $[(^{\text{tBu}}\text{CA})\text{H}][\text{SbF}_6]$, which is a hydrolyzed by-product in the process of the ongoing cyclotrimerization.

Povzetek

Raziskave koordinacijske kemije N-heterocikličnih karbenov (NHC) s kovinami z začetka d-bloka so pogosto prezrte in v senci kompleksov s kovinami s sredine in konca d-bloka. Zaradi reaktivnosti oksifilnih kovin ter specifičnosti potrebnega znanja in inventarja pri rokovanju z njihovimi fluoridi in oksifluoridi je količina pozornosti namenjene njihovim kompleksom z NHC ligandi še toliko manjša. S tem delom smo želeli razširiti nabor koordinacijskih spojin s fluoridi kovin pete skupine in predstaviti njihove vidnejše značilnosti. V tej disertaciji so opisani sintezni postopki in lastnosti nevtralnih kompleksov $[(\text{NHC})\text{VOF}_3]$, $[(\text{NHC})\text{NbF}_5]$ in $[(\text{NHC})\text{TaF}_5]$. Nedavno je naša raziskovalna skupina pripravila iz NHC substrata nov fluorirni reagent. V prejšnjih poskusih se je ta imidazolihev fluorid, $[(\text{NHC})\text{H}][\text{F}]$, s fluoridi polkovin izkazal za reagent, ki nadvse uspešno donira prosti fluorid, hkrati zaradi velikosti kationa lahko stabilizira doslej še neopaženo koordinacijsko število 5. V tem delu smo predstavili in razširili njegovo uporabno vrednost na reaktante kovin prehoda. Natančneje na fluoride in oksifluoride pete skupine. Naša predvidevanja so se izkazala za pravilna, saj je imidazolihev kation s svojim steričnim učinkom pripomogel k izolaciji v kristalni obliki doslej zgolj indirektno dokazanega $[\text{VOF}_4]^-$ aniona. Uporaba dotičnega reagenta s kovinskimi pentafluoridi pa je privedla do nastanka in izolacije soli z $[\text{MF}_6]^-$ anionom. Dasiravno je v literaturi strukturno okarakteriziranih mnogo soli s takšnim anionom, smo z dodatnimi eksperimenti pridobili dodatne informacije o reaktivnosti (domet fluorirnih sposobnosti) tega novega reagenta. Predstavljene so kristalne strukture soli $[(\text{NHC})\text{H}][\text{VOF}_4]$, $[(\text{NHC})\text{H}][\text{NbF}_6]$ in $[(\text{NHC})\text{H}][\text{TaF}_6]$, kot tudi prej omenjenih nevtralnih kompleksov z NHC. Poleg sinteznih postopkov in kristalnih struktur smo lastnosti novo pripravljenih spojin analizirali tudi z NMR in vibracijsko spektroskopijo. Raziskali smo tudi njihovo stabilnost v kristalni obliki in v raztopinah s polarnimi topili. V primeru vanadijevih spojin je njihova hidroliza privedla do nastanka izjemno stabilne soli $[(\text{NHC})\text{H}][\text{VO}_2\text{F}_2]$.

Natančna določitev strukturnih parametrov kristalnih struktur omenjenih spojin in njihova primerjava s sorodnimi spojinami nam je razkrila mnoge razlike med njimi. Za razlago teh razlik in drugih opaženih nenavadnih detajlov smo se poslužili teoretičnih orodij. S kalkulacijskim pristopom smo pojasnili razlike v konformaciji fluoridnega in kloridnega fragmenta v kompleksu $[(\text{NHC})\text{MX}_5]$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{F}, \text{Cl}$). Prav tako smo razložili premik fluoridnih ligandov proti NHC ligandu. Posebej zanimiva značilnost oksofilnih kovin v najvišjem oksidacijskem stanju so njihove prazne valenčne orbitale, ki v teoriji ne dopuščajo nobene povratne donacije. V študiji podobne spojine s kloridi $[(\text{NHC})\text{VOCl}_3]$ so raziskovalci vseeno dopustili možnost povratne vezave preko klorov, zato smo v našem primeru prispevke h koordinacijski vezi natančno preučili. Pri določitvi le-the prispevkov smo opazili minimalne π -donorske lastnosti fluoridnih ligandov, ki del naboja donirajo karbenskemu atomu NHC liganda. Z izračuni smo tudi uspeli pokazati, da podaljšanje $\text{V}-\text{F}_{\text{trans}}$ vezi ni posledica trans efekta, kot je v literaturi pogosto poenostavljeno razloženo. V našem primeru se je izkazalo, da je podaljšanje vezi odvisno od notranjega kristalnega pakiranja.

Novo sol z $[\text{VOF}_4]^-$ anionom smo uporabili kot izhodni reagent za pripravo redkih anionskih kompleksov $[\text{VOF}_4(\text{THF})]^-$, $[\text{VOF}_4(\text{py})]^-$ and $[(\text{VOF}_4)_2(\text{pyz})]^{2-}$. Pripravljen kompleks med elektron donorskim ligandom in $[\text{VOF}_4]^-$ anionom smo uspešno strukturno okarakterizirali. Na žalost pa zaradi nestabilnosti šibkih aduktov nismo uspeli izvesti analiz, ki zahtevajo dodatno predpripravo vzorca. Primerjava strukturnih informacij naših $[\text{VOF}_4(\text{L})]^-$ kompleksov s primeri iz literature nam je omogočila špekulacije o možnih dejavnikih, ki prispevajo k interakciji anion–ligand.

Za konec je predstavljen sistem, ko smo med pripravo prekurzorjev (nitrilnih aduktov fluoridov pete skupine) naleteli na sistem, ki je pri normalnih pogojih privedel do ciklotrimerizacije nitrilov s strukturo $[(^{\text{Ph}}\text{TZN})\text{H}][\text{MF}_6]$. Ugotovili smo, da je za iniciacijo procesa trimerizacije potrebna oksonijeva sol $[\text{H}_3\text{O}][\text{SbF}_6]$. Ko smo jo uporabili v reakciji z benzonitrilom v diklorometanu, nam je uspelo vzgojiti kristale z dvakrat protoniranim triazinskim obročem v $[(^{\text{Ph}}\text{TZN})\text{H}_2][\text{SbF}_6]_2$. Do sedaj je bila takšna spojina predvidevana samo v teoriji. Pod istimi pogoji je uporaba *tert*-butilnitrila privedla do nastanka karbonilamidinske soli $[(^{\text{tBu}}\text{CA})\text{H}][\text{SbF}_6]$, za katero se je izkazalo, da je produkt hidrolize dimernega intermediata. Ta stranska reakcija je kompetitiven proces ciklotrimerizaciji.

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Abbreviations

FEP	... fluorinated ethylene propylene
Me	... Methyl
Et	... Ethyl
<i>i</i> Pr	... isopropyl (IUPAC: propan-2-yl)
<i>t</i> Bu	... <i>tert</i> -butyl (IUPAC: 2-methylpropan-2-yl)
Ph	... phenyl
Xyl	... xylyl (IUPAC: dimethylphenyl)
Mes	... mesityl (IUPAC: 2,4,6-trimethylphenyl)
Dipp	... 2,6-diisopropylphenyl (IUPAC: 2,6-di(propan-2-yl)phenyl)
Ad	... adamantly
MeCN	... acetonitrile
<i>t</i> BuCN	... <i>tert</i> -butylnitrile (IUPAC: 2,2-dimethylpropanenitrile)
PhCN	... benzonitrile
DCM	... dichloromethane
THF	... tetrahydrofuran (IUPAC: oxolane)
py	... pyridine
pyz	... pyrazine
bipy	... 2,2'-bipyridine
phen	... 1,10-phenanthroline
TMEDA	... <i>N,N,N',N'</i> -tetramethylethane-1,2-diamine
TfOH	... triflic acid (IUPAC: trifluoromethanesulfonic acid)
NHC	... N-heterocyclic carbene
VOF	... vanadium oxide fluoride
TZN	... <i>s</i> -triazine, 1,3,5-triazine
CA	... carbonyl amidine, carbonyl imidamide
DFT	... density functional theory
PBE	... Perdew-Burke-Ernzerhof functional
rxn	... reaction

Symbols

- L . . . ligand moiety in coordination compound indiscriminative of its bonding features or charge
- M . . . central moiety in coordination compound; usually (but not necessarily) describes metal cation
- X . . . halide ligand in coordination compound
- A . . . metal of organic cation in salts

Preface

As part of a PhD study, I familiarized myself with the work of researchers. The journey chemists embark on every new day is both fascinating and awe inspiring. The goal they strive toward is to discover something new, to synthesize a compound that has not been known before or to optimize a reaction in a previously unprecedented way. Nobody knows how and why exactly nature manifests in a certain way, but one can make a guess, an educated guess. I have noted that scientific work comprises six simple steps and one major leap. To work as a scientist, one needs to (1) formulate an idea, (2) test, (3) observe, (4) evaluate, (5) explain, (6) adapt, (7) REPEAT. The true process of learning and knowing more thus never ends.

As synthetic chemists, we heavily rely on the results of the analyses. From our perspective, only so much can be explained with analysis of bond distances, chemical shifts and intensities of bands. This thesis is a result of close collaboration with the theoretical field of chemistry. Now more than ever cooperation is key in providing the world with the most excellent findings and conclusions. Throughout the study, I have realized that no matter how fastidious were the observations of differences in bond distances and NMR shifts, some effects and features could not be interpreted appropriately or correctly without the theoretical contribution. Likewise, it is beneficial if *in silico* theoretical models are supported by observations from real samples. Only with collaboration between traditional chemistry and newer theoretical chemistry we can really step on the shoulders of giants and see further than ever before.

I have realized that our impact and contributions to the accumulated knowledge of the humankind are small, albeit important. First is for the sake of the core nature of the human species that is most certainly full of curiosity and therefore living to the fullest. Second is due to the inclusion of new pieces into the mosaic of the nature's bigger picture, which we might one day see.

Chapter 1

Introduction

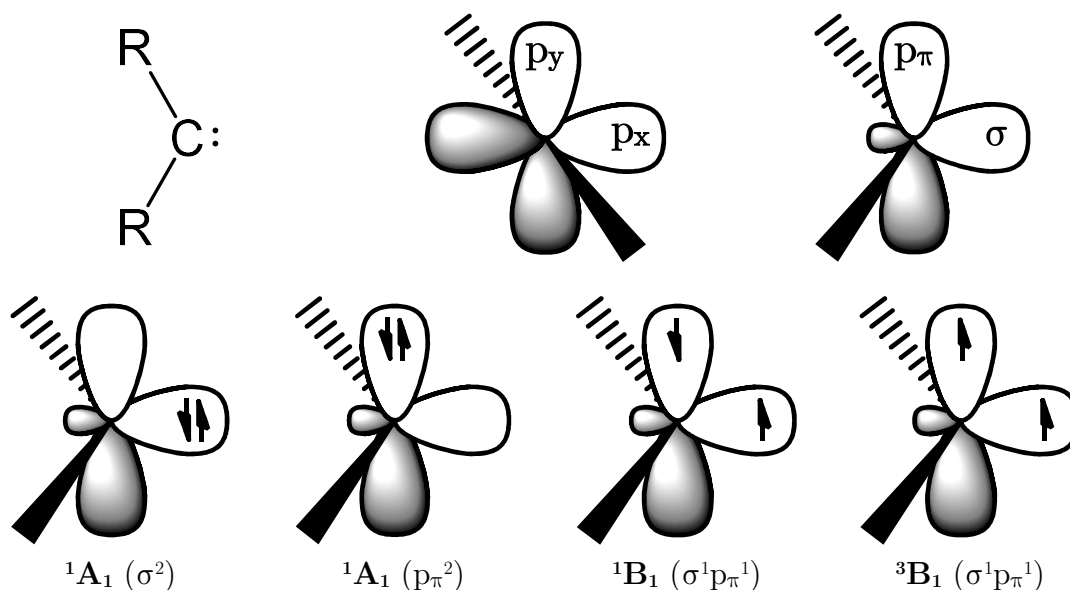
1.1 Carbenes

1.1.1 General overview of carbenes

Carbenes are neutral molecules ($R_2C:$) containing a divalent carbon atom with six electrons in their valence shell. In linear carbenes, carbon atoms are sp hybridized with two degenerate p -orbitals (p_x, p_y) [1]–[3]. Through bending of the sp -orbitals the molecule loses its linearity and p_x -orbital starts to adopt some of the character of the s -orbital and turns into orbital noted as σ -orbital. Therefore, carbene carbon atom is in bent carbene units sp^2 hybridized and retains the remaining p_y -orbital, noted commonly as p_π (Scheme 1). In this situation, two non-bonding electrons of the carbon atom do not contribute to the stabilization of the internal structure of the molecule, but rather they are assigned to two frontier orbitals (σ and p_π). There are four possible electronic configurations: $^1A_1$ singlet state with electron pair in σ -orbital (σ^2), $^1A_1$ high energy demanding singlet state with electron pair in p_π -orbital (p_π^2), $^1B_1$ excited singlet state with one electron in σ and one in p_π , $^3B_1$ triplet state with one electron in σ and one in p_π -orbital (Scheme 1). Spins of the latter state's electrons are parallel and due to their reactivity, such carbenes are regarded as biradicals. Relative stabilities of all four states depend on the neighboring atoms and functional groups bonded to carbenic carbon atom.

Triplet state carbenes exhibit radical behavior and are extremely reactive [4]. Aromatic groups adjacent to carbenic carbon atom do not provide any thermodynamic stabilization, but rather help dispersing electrons from sp^2 -orbitals throughout the conjugated system. Substituents tend to be bulky in order to sterically shield carbenic carbon atom and help reduce reactivity [5], [6].

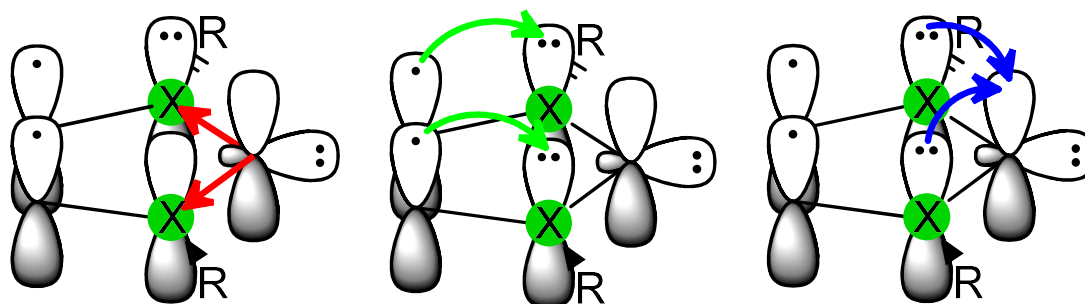
For singlet state to be stable, heteroatoms or functional groups with strong σ -withdrawing (negative inductive) effect and π -donating (positive mesomeric) effect need to be adjacent to carbenic carbon atom (Scheme 2) [7], [8]. Inductive effect attracts electron density and relieves lone electron pair in σ -orbital, while heteroatom participating with mesomeric effect donates its lone electron pair into empty p_π -orbital of carbenic carbon through π -interaction.



Scheme 1: Top row: Representation of carbenic fragment (left), orbitals in sp hybridized carbon atom (middle) and orbitals in sp^2 hybridized carbenic carbon atom (right). Bottom row: Four electronic configurations in carbene moiety.

Several combinations of heteroatoms or functional groups adjacent to the carbenic carbon atom meet the criteria of the “push-pull” stabilization effect and accordingly result in stabilized and less reactive carbenic species, although most of them are usually still not isolable. Meanwhile, introduction of second such moiety yields diamino carbene units and influences the carbene carbon atom with negative inductive along with positive mesomeric features from both sides. This renders them superior in regard to the thermodynamic stabilization of the carbene’s electronic structure and in consequently even less reactive species. Additional thermodynamic stabilizing effects are cyclic structure and aromaticity of the cycle bearing the carbenic carbon. Bulky substituents bonded to the heteroatoms in general provide kinetic stabilization of the carbene.

When all the stabilizing factors are accounted for and the difference between the singlet–triplet energy levels is more than 2 eV (46.12 kcal/mol), then the singlet state is preferred, whereas values below 1.5 eV (34.59 kcal/mol) result in the triplet state [9], [10]. Energy gap in N-heterocyclic carbenes similar to those used in our research is approximately 80 kcal/mol [11], [12].



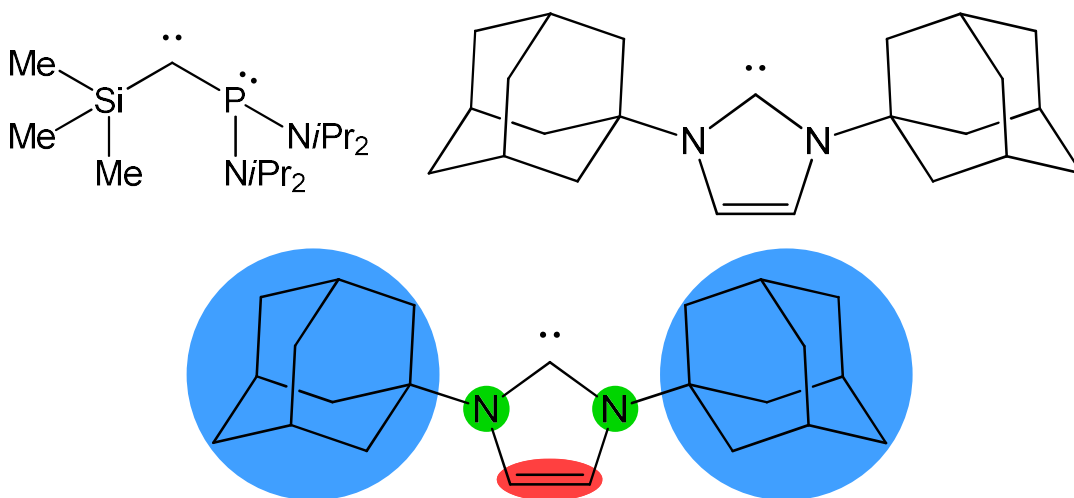
Scheme 2: Inductive (left), π -delocalization from the unsaturated backbone (middle) and mesomeric (right) electronic stabilizing effects within the structure of the unsaturated cyclic carbenes.

1.1.2 N-heterocyclic carbenes

Until 1988 carbenes were viewed as reactive, transient intermediates that could not be isolated. Interestingly, coordination compounds of carbenes and transition metals were reported about three decades earlier through *in situ* preparation of carbenic species and subsequent formation of complexes. The first reported isolated carbenic species was (phosphino)(silyl)carbene [13], although the first crystals of monomeric carbene, i.e. N-heterocyclic carbene (NHC), molecule were prepared three years later (Scheme 3) [14]. Previous efforts to isolate diamino, which a subcategory of NHCs, resulted in dimeric alkene moieties, while crystalline “bottle-able” 1,3-diadamantyl-2,3-dihydro-1*H*-imidazol-2-ylidene showed unusual inertness toward dimerization [15], [16]. Isolated NHC compound is indeed carbenic in character with highly stable singlet state (due to large singlet–triplet energy gap) [11], [17] and with bulky substituents on heterocyclic base (“wingtips”) providing the steric hindrance to prevent the potential dimerization [18], [19]. Inconsistent and conflicting reports regarding the formation of tetraaminoethene from the diaminocarbenes and their congeners sparked a series of publications commenting on the dimerization mechanism [20]–[23]. The most widely discussed was the existence of Wanzlick’s equilibrium (rxn. 1) [24], [25], which proposes a dimeric olefin structure for small enough “wingtips”, whereas larger and sterically demanding substituents discourage and prevent dimerization from taking place.



However, more recent studies suggest that such dimerization process is indeed thermodynamically favorable for most NHC compounds but a prohibitively high energy barrier inhibits the reaction [26], [27], thus negating correlation between bulkiness of “wingtips” and dimerization. Experimentally detected dimeric products of NHCs were attributed to electrophilic contaminants (most commonly proton) in the reaction system. Even though Wanzlick’s equilibrium is not suitable theory for NHCs it is valid for more nucleophilic carbenes, which are less stable and much more prone to afford olefinic compounds [3], [28]–[30].



Scheme 3: Top row: (phosphino)(silyl)carbene (left) [13] and 1,3-diadamantyl-2,3-dihydro-1*H*-imidazol-2-ylidene (right) [14]. Bottom row: Highlighted stabilizing structural features in representative carbene compound.

NHCs are in comparison to other typical carbenes that contain, adjacent to the carbene carbon atom, heteroatoms other than nitrogen noticeably more stable due to the superior stabilizing effects of amino groups [1], [17], [31]. However, cyclic structure and aromatic character of the heterocyclic ring also aid in minor part to the overall stability of the molecule [8], [31]. Cyclic geometry forces N–C–N segment into bent position, which in turn enhances sp^2 hybridization. If double bond is present in the backbone fragment, it allows the small π -delocalization of lone pair of amines, vacant p_π -orbital of carbenic carbon and unsaturated backbone forming a 6 e^- , 5 center aromatic structure (Scheme 2) [7]. All of the presented stabilizing contributors make imidazole and imidazoline-based NHCs among the most stable carbenic compounds, what ultimately led to the first isolation in crystalline form.

Another appealing feature of the NHCs and carbenes in general is their modularity [2]. It is possible to modify, substitute or eliminate several of the constructing parts of the NHCs, e.g. size of the heterocyclic ring [32], [33], use of additional heteroatoms in the ring [34], use of saturated core framework [35], [36], change in size and electronic character of the substituents on the amino groups [18], attachment of functional groups on the backbone [37]. All such alterations allow access to a diverse library of carbenes with various electronic and steric properties.

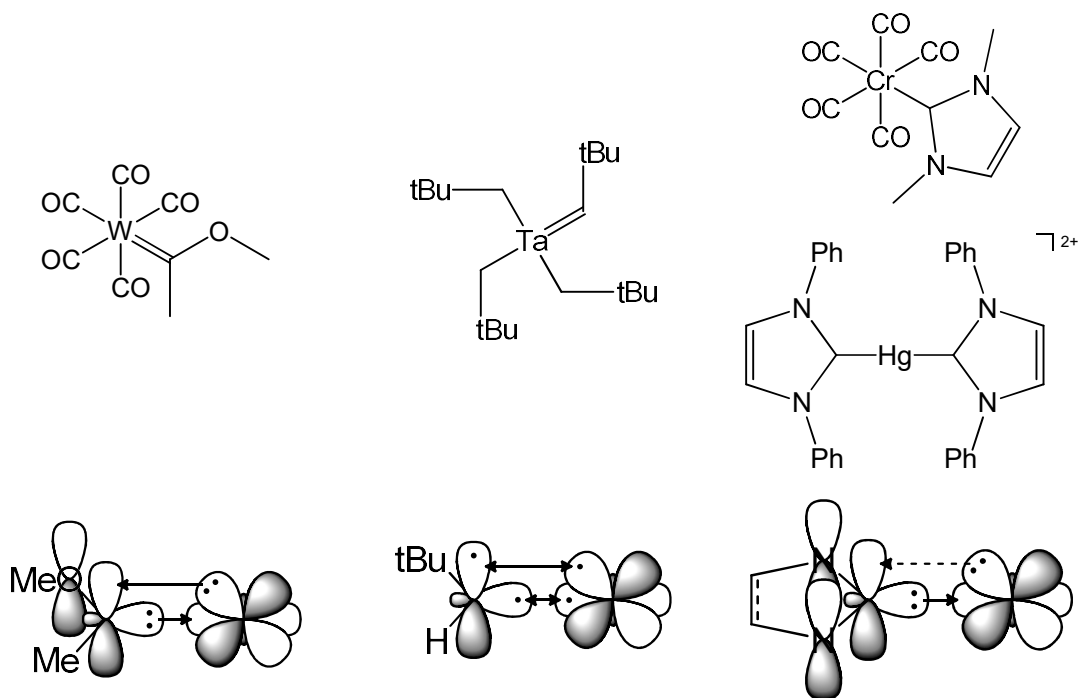
NHCs are strong Brønsted-Lowry bases and have a strong nucleophilic character (Lewis base) [38]–[40]. With formally empty p_π -orbital, electrophilic behavior is also expected, but due to the profound π -back-donation from amine into the p_π -orbital, NHCs do not react in predicted electrophilic fashion. Consequently, in organic reactions they no longer behave as transient singlet carbenes (insertion into C–H bonds, cycloadditions, addition to aldehydes and isocyanides and reactions with nucleophilic reagents), however they gain the ability to act as potent σ -donating ligands in coordination chemistry, rivalling the long established electron rich phosphines [7]. Nevertheless, utility of NHCs has been expanded beyond the role of a ligand [41] and its organocatalytic properties were also established [42]–[44].

1.1.3 NHC–metal complexes

First carbene–metal complex was reported in 1925 [45], however corresponding complexes received recognition a few decades later. Three different models of carbene–metal complexes that are most commonly described in the literature are presented in Scheme 4 [46]. The first group are Fischer carbene complexes where carbenic carbon atom bonds to a metal center by a donor–acceptor bond [47]. π -donating heteroatom adjacent to carbenic carbon atom stabilizes the singlet state and negates the reactivity of an electron-deficient compound. Upon coordination electrophilic carbenic carbon atom donates its lone electron pair from σ -orbital to appropriate metal orbital and in return, metal center uses its full d-orbitals for π -back-bonding into empty p-orbital of carbenic carbon [46], [48], [49]. Metals participating in coordination are mostly late and low valent transition metals that have their d-orbitals filled [50]. Accordingly, Fischer complexes have ordinarily 18 valence electrons and metallic fragment is stabilized by π -electron withdrawing ligands.

Schrock carbene complexes are the polar opposite [51]. Electron-deficient and nucleophilic carbenic carbon atom in triplet state interacts with triplet metal fragment that yields an associative interaction. Carbenes in this setting are bearing alkyl substituents and possess nucleophilic character [46], [48], [49]. Central metal cation is likewise in addition to carbene coordinated by alkyl or cyclopentadienyl ligands [52]. At variance with Fischer complexes, carbenic carbon atom in Schrock complexes coordinates onto an early transition metal generally in its highest oxidation states and the complex has thus less

than 18 valence electrons [50]. Large overlap of d-metal and p-carbenic carbon orbitals allows for effective π -back-donation from formally empty metal fragment to electron-deficient p-orbital of carbene producing a covalent double bond [48]. Although the metal fragment in Fischer complex is composed of low valent metal and is intuitively more suitable for π -back-donation, an unfavorable energy difference between metal d-orbitals and p-orbital due to poor orbital overlap diminishes the π -interaction, which results in $M-C_{\text{carbene}}$ bond being in general longer than in Schrock carbene complexes [52].



Scheme 4: Left column: First reported Fischer carbene complex [47]. Middle column: First reported Schrock carbene complex [51]. Right column: First reported NHC carbene complexes [53], [54]. Bottom row: Representation of contributing effects to the carbene–metal interaction for respective carbene complex.

The third type are NHC–metal complexes, which are nowadays most researched due to NHC’s superb stability and adaptability. Ability to isolate solid deprotonated NHCs in their monomeric form allows for fairly simple preparation procedure of new coordination compounds, however first such complexes were prepared by in situ deprotonation of imidazolium salt [53], [54]. At the first glance, NHC–metal complexes could be classified as Fischer type complexes, since the NHC bond to the metal center with nucleophilic lone pair in σ -orbital and the carbenic carbon atom is situated between two π -donating heteroatoms [1], [7]. However, due to high internal stability, complexes with NHCs lack significant π -back-donating interaction contributing to the $M-C_{\text{NHC}}$ bond and therefore form a unique category [3], [46], [49]. Bonding situation is in practice generalized and most commonly depicted as a strong single bond, while $M-C_{\text{carbene}}$ bond in Fischer and Schrock complexes is presented as a double bond [8]. Such presentation is not unheard of, since potential rotation on bond’s axis was experimentally confirmed. On the other hand, theoretical studies reported that contributions of π -donation (C_{NHC} to M) and π -back-donation (M to C_{NHC}) are not negligible [3], [49]. Depending on characteristics of NHC ligand and metal center used in the complex, degrees of π -interactions in the bond may vary. For example, substitution of one sp^2 hybridized nitrogen atom for sp^3 carbon

atom affords cyclo (alkyl)(amino)carbene (CAAC) [55]. which has modified electronic structure compared to NHC, making it more unstable in monomeric isolated form, but has its nucleophilic character much more expressed. Complexes prepared with CAAC are, with their electronic composition of the coordination bond, an intermediate state between Fischer and NHC complexes. Further electronic properties of carbene complexes and experimental methods for their determination (Tolman electronic parameter, complex probes, redox potentials and NMR experiments) were recently reviewed [56].

Due to their nucleophilic σ -bonding character, they are often associated with analogous phosphine ligands [8], [57]. When comparing the two, NHCs are in general stronger ligands, i.e. better electron donors, and form thermodynamically stronger bonds [58]. This difference was exploited for the preparation of second generation of Grubbs catalysts, which is used for olefin metathesis reactions [59]. While the phosphines can be presented as cones with bulky substituents turned away from the metal, NHCs are described as fan-shaped ligands with the substituents on amino groups pushed toward the metal center and can participate in interactions with remaining ligands. Accordingly, the steric effect of “wingtips” exhibits some influence on the bonding properties of a ligand in addition to the aforementioned electronic interactions between NHC and metal center. Sterically demanding NHC ligands make the synthesis of labile complexes more accessible, which is at variance with phosphines that have their bulky groups turned away from the metal center. NHCs even form complexes that would otherwise be, according to the electronic interactions, perfectly inert. Subsequently, these two classes of ligands have a different buried volume ($\% V_{\text{bur}}$) [60], [61], which is a parameter to determine ligand’s integration within the coordination sphere of metal center.

NHCs as ligands are capable of stabilizing low oxidation state of central moiety, however they are most extensively used as homogeneous catalysts in NHC–transition metal complexes [62], [63]. Ability to tune electronic and steric features of ligand allows NHC complexes much more flexibility and can be designed to fulfil niche requirements. Additionally, strong M–C_{NHC} bond renders complexes stable under catalytic conditions and less likely to decompose [8]. Beyond catalytic properties of the complexes, their applicability as luminescent, medicinal and functionalization materials has also been demonstrated [64]–[70].

1.1.4 NHC–M^{group 5} complexes

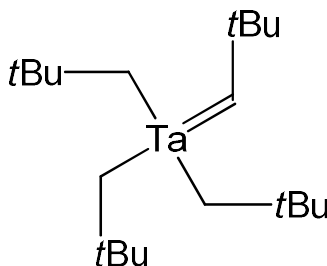
NHCs showed bonding capabilities with elements throughout almost whole periodic table [3], [71]–[75]. NHC complexes with late transition metals have been studied extensively, due to their favorable bonding features and catalytic properties of the complexes [62]. At variance with middle and late counterparts, the NHC coordination chemistry of early transition metals was somehow neglected [76]. The reason is often ascribed to the extreme oxophilic nature of starting material of early metals and their susceptibility for hydrolysis [77]. In group 5 halides water affinity increases from fluoride to iodide [78], but diminishes with introduction of the oxide ligand into the coordination sphere. Peculiarity of early transition metals is their large range of relatively easily accessible oxidation states allowing access to different spin states and versatile coordination geometries. Complexes with metals in their highest oxidation states are compelling for their formally empty valence orbitals and consequential inability to stabilize σ -bond with any kind of back-donation.

In this chapter, overview of the literature with the motif of NHC coordinated to group 5 metals and structurally characterized relevant complexes for later discussion are presented. Since our interest is in NHC complexes with group 5 halides and oxide halides,

attention will be given to those results. Especially to fluorides that are usually underrepresented due to the difficulties with handling of starting materials and specific electronic properties of the fluorides.

Polydentate NHC ligands functionalized with indenyl, fluorenyl (cyclopentadienyl's congener) [79], [80], alkoxy [81], bisaryloxy [82] or bisamide [83] were used to enhance the stability of the group 5 complexes. Another approach to prepare rigid complexes is with the use of multidentate pincer ligand containing two NHC [84]–[88]. Additional bonding moieties are reinforcing coordination onto the metal center, but do not inhibit metal's reactivity as it is shown in some catalytic studies [89], [90].

Although NHC complexes with group 5 metals have only a few features in common with Schrock type complexes, it is interesting to note that first example of the Schrock complex was prepared with tantalum (Scheme 5) [51].

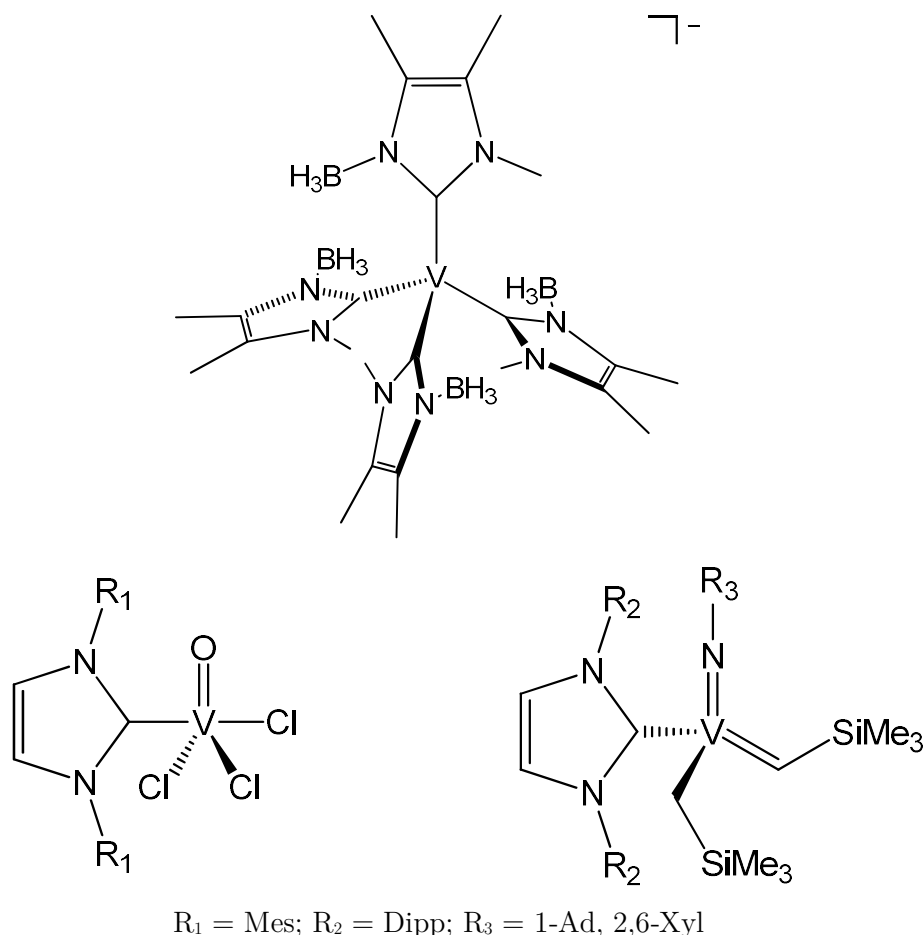


Scheme 5: First reported carbene complex with group 5 metal [51].

First evidence (elemental analysis, ^1H and ^{13}C NMR spectroscopy) of NHC coordination onto the group 5 metals were $[(\text{NHC}^{\text{Me}})_4\text{Vl}_2]$ and $[(\text{NHC}^{\text{Me}})_2\text{MCl}_4]$ ($\text{M} = \text{Nb}, \text{Ta}$) complexes reported in 1994 [91]. First ever structurally characterized vanadium NHC complex was observed in $[\text{V}(\text{NHC}-\text{BH}_3)_4]^-$ anion reported in 2002 [92] and first neutral halide complex was monodentate NHC with VOCl_3 reported in 2003 (Scheme 6) [93]. Authors reported that coordination of the NHC to the VOCl_3 diminished the reactive character and moisture sensitivity of the vanadium moiety. Additionally, NHC electrochemical stabilizing influence is observed with lower electron reduction potential. In respect of the reactivity, the $[(\text{NHC})\text{VOCl}_3]$ complex is surprisingly stable in comparison to other adducts with VOCl_3 even in a DCM solution [94]–[98]. They also proposed that chlorine atoms *cis* to the carbene unit are bent toward carbenic carbon atom, which was contributed to the back-donation of lone pairs of chlorine atoms into the empty p-orbital of the carbon atom.

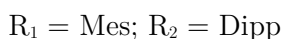
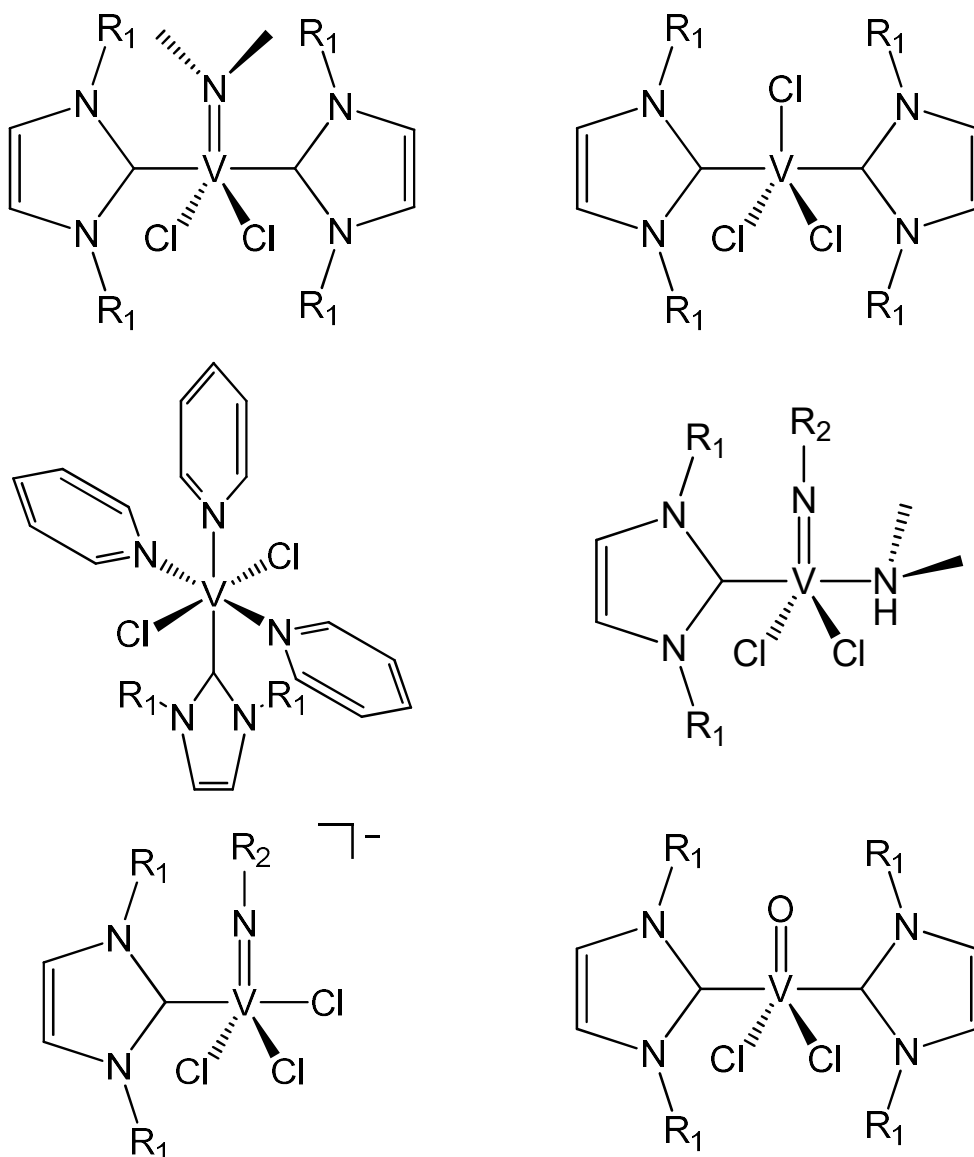
Studies of catalytic activity of $[(\text{NHC})\text{VOCl}_3]$ complexes toward ethylene–propylene copolymerization were also performed [99], [100].

In 2008, two (imido)vanadium alkyl alkylidene complexes with NHC were reported (Scheme 6) [101]. These results most likely later prompted authors to prepare vanadium complex with NHC ligand bonded with weakly coordinating anion (WCA-NHC ligand) (see below).



Scheme 6: Top row: First structurally characterized vanadium(III) complex with modified NHC [92]. Bottom row: First NHC complex with vanadium(V) oxide chloride (left) [93] and representation of vanadium(V) imido NHC complex (right) [101].

Only two other studies regarding NHC complexes with vanadium chloride as common structural motif were published to this date. In 2009, several such complexes were synthesized and most of them characterized with X-ray single crystal analysis (Scheme 7) [102]. Depending on the metal precursor (chloride, amide, imido), a different approach to the synthesis was undertaken. With addition of imidazolium chloride $[(\text{NHC})\text{H}][\text{Cl}]$ to the vanadium amide $[\text{V}(\text{NMe}_2)_4]$ the reaction proceeds with *in situ* deprotonation of the imidazolium salt. To the vanadium chlorides and imido precursors, a neutral NHC was added. In addition, the oxide chloride $[(\text{NHC})_2\text{VOCl}_2]$ complex was obtained either with the addition of NHC to the suspension of $[\text{VOCl}_2(\text{NHMe}_2)_2]$ or with exposure of a solution of $[(\text{NHC})_2\text{VCl}_3]$ to the air. Ligands in most of the prepared complexes occupy pentacoordinated geometry around vanadium center and oxidation state of the vanadium range from II to IV. Based on the experimental observations they proposed that some level of interaction between carbenic carbon atom and chlorine atoms does occur. By comparison of shorter bonds observed in vanadium complexes (d^1) with longer bonds of isostructural titanium complexes (d^0) they proposed that d^1 electron could participate in π -back-donation of NHC, achieving higher bond order, however without computational data they were wary in their assumptions.

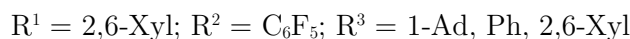
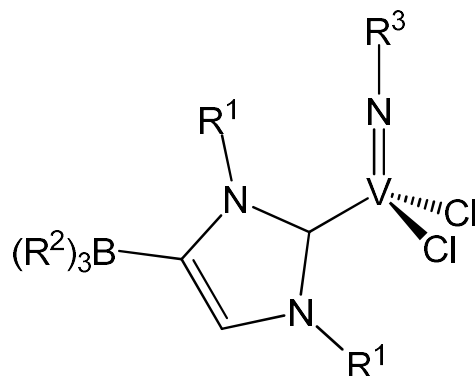


Scheme 7: A series of NHC complexes with vanadium center in different oxidation states [102].

In 2016, three complexes of vanadium(V) imido dichloride with WCA-NHC were reported (Scheme 8) [103]. WCA-NHC are a new class of frustrated carbene-borane Lewis pair resulting in anionic ligand, where weakly coordinating anionic (WCA) borate is bonded to a heterocyclic ring of the neutral NHC. They noted some unusual structural features (short V-C_{NHC} and V-Cl bonds) and contributed them to higher affinity of electron donating species (strong σ -bond and enhanced π -back-donation, respectively) toward the electron deficient cationic [VCl₂(NR)]⁺ fragment. Authors also focused on the application side of the complexes. They established that all [(WCA-NHC)VCl₂(NR)] complexes exhibit ethylene polymerization capabilities and that a specific catalytic system (R = 2,6-Me₂C₆H₃, co-catalyst triisobutylaluminum (AlⁱBu₃)) affords outstanding results.

They have additionally explored effects on the catalytic process with application of different aluminum-based co-catalysts [104] and compared catalytic capabilities of

WCA-NHC to various other nitrogen- and oxygen-based ligands in $[(L)VCl_2(NAr)]$ (L = ligand) complex [105].



Scheme 8: Vanadium(V) imido complex with anionic WCA-NHC [103].

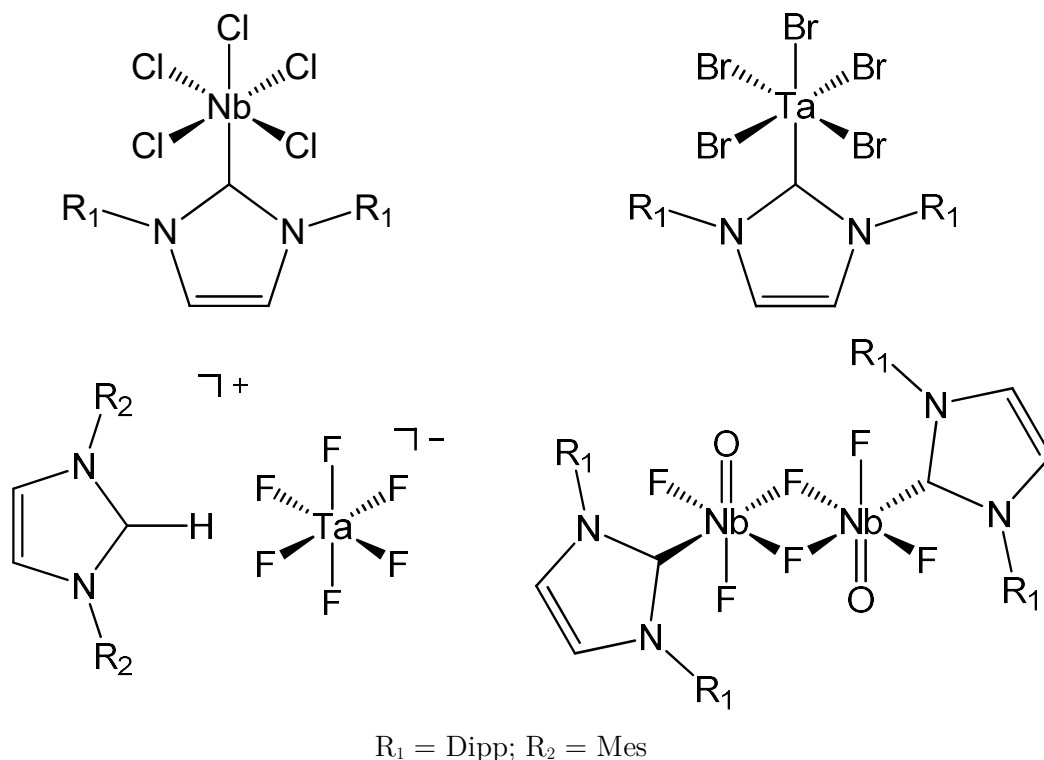
In 2014, first monodentate complex of niobium was prepared in toluene with the reaction between $NbCl_5$ and NHC ligand (Scheme 9) [106]. They determined that stability of this complex increased in regard to the precursor $NbCl_5$. Slightly elongated $Nb-C_{NHC}$ bond was observed, which was attributed to the pure σ -bonding character of the NHC. Using theoretical analysis of DFT calculations, they found no evidence to support any kind of π -interaction between metal and carbene or *cis* ligands and carbene. Results were at variance with more than a decade old findings for $[(NHC)VOCl_3]$, which postulated a π -back-donation of *cis* chlorine atoms into the electron deficient p-orbital of the carbenic carbon atom [93].

Later they extended their research and performed an elaborate computational study on the various bonding effects in the octahedral $[(L)NbCl_5]$ (L = NHC, CO, HCN, $[CN]^-$) complexes with the metal center in its highest oxidation state and therefore with formally empty valence orbitals [107]. Focal point of the study were contributing influences to the $Nb-C_{NHC}$ bond of the $[(NHC)NbCl_5]$ complexes, which were investigated by position of chloride ligands and involved orbitals. Conclusions of the research can be summarized as follows. d^0 metals can partake in the back-donation, since they are only formally empty, however almost the entire electron density comes from chloride atom that is *trans* to NHC molecule and they have reconfirmed that *cis* chlorine atoms do not donate any of their lone pairs into the empty p-orbital of the NHC.

In 2016, the same research group expanded their research of neutral $[(NHC)MX_5]$ complexes to other niobium and tantalum homoleptic pentahalides (fluorides, chlorides and bromides) [108]. They performed elemental and IR analysis on the bulk of the isolated products, which confirmed the formation of neutral complexes, though the majority of the research was based on the NMR spectra of the dissolved complexes. Tracking of the reaction mixture with the NMR spectroscopy showed a presence of two sets of peaks ascribed to backbone protons, which prompted them to perform DFT calculations and compare relative energies of potential intermediates. As a result, they proposed a reaction mechanism for obtaining a neutral coordinated product $[(NHC)MX_5]$ (Scheme 9) from the dimeric starting M_2X_{10} (M = Nb, Ta; X = Cl, Br) and two equivalents of NHC. According to their findings the reaction proceeds *via* $[(NHC)MX_4][MX_6]$ intermediate, which occurs with the asymmetric rapture of the starting dimeric M_2X_{10} . For tetrameric fluorides, formation of the aforementioned ionic intermediate is an endergonic process and not a viable pathway. The proposed initial stage of the reaction proceeds *via* the coordination of

the neutral NHC to the tetrameric fluoride unit, creating a heptacoordinated metallic center and yielding ionic product (Scheme 9).

In the crystallization attempts, during the research of $[(\text{NHC})\text{NbF}_5]$ complex, the dimeric complex $[(\text{NHC})\text{NbOF}_3]_2$ (Scheme 9) was obtained as a by-product of hydrolysis with moist air [78]. Other reaction path feasible for the preparation of such compound, e.g. $(\text{Me}_3\text{Si})_2\text{O}$ used for synthesis of $[(\text{L})\text{NbOCl}_3]$ adducts, resulted in a mixture of unidentifiable products. $\text{Nb}-\text{C}_{\text{NHC}}$ bond is relatively weak as it has pure σ -type character and is reinforced only by electrostatic interaction.

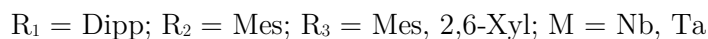
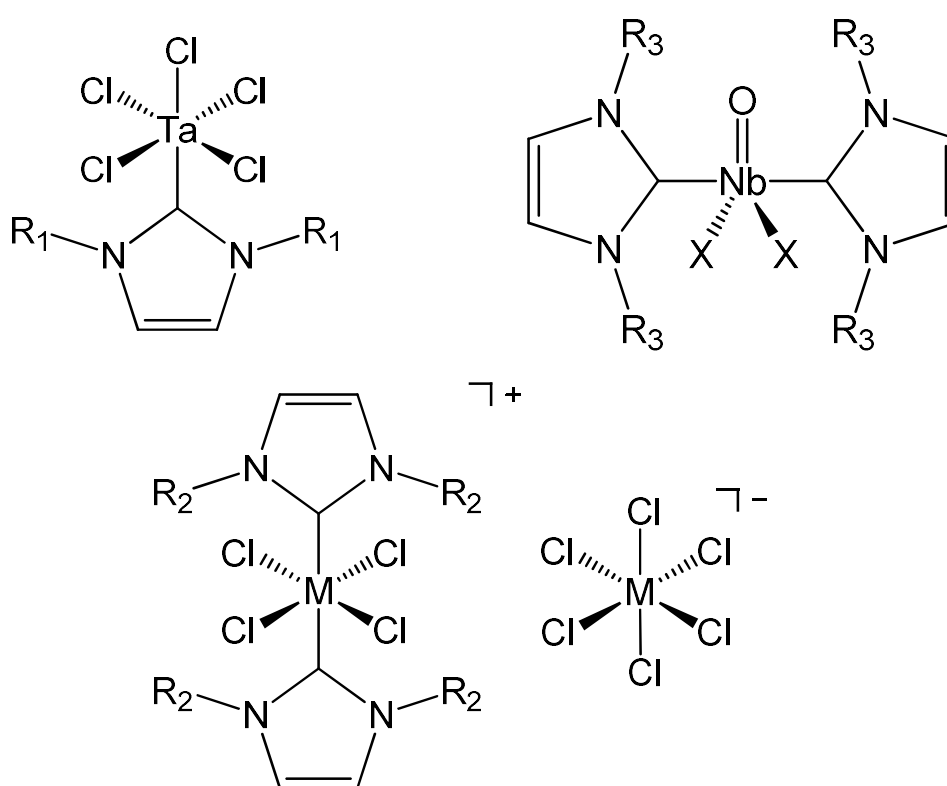


Scheme 9: Top row: Monodentate complexes of NbCl_5 [106] and TaBr_5 with NHC [108]. Bottom row: Incidental by-products in the reactions of MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) and NHC, due to protonation of NHC (left) [108] and oxidation of starting pentafluoride reagent (right) [78].

Later the same year another group reported a molecular structure of $[(\text{NHC})\text{TaCl}_5]$ and bis(NHC) cations with $[\text{MCl}_4]^+$ ($\text{M} = \text{Nb}, \text{Ta}$) fragment, i.e. $[(\text{NHC})_2\text{MCl}_4]^+$ (Scheme 10) [109]. The latter are first examples of NHC cationic species with group 5 metals and their synthesis was attributed to the steric properties of substituent on the heterocyclic base (“wingtips”). In addition, they showed that a neutral complex possesses catalytic capabilities for insertion reaction of CO_2 into the C–O bond of the epoxide molecule. Ionic products show only minor catalytic activity, while the reaction precursors (MCl_5 and NHC) showed almost no activity.

Until recently, only vanadium NHC complexes were prepared with metal center in reduced oxidation states, since vanadium exhibits the most readily accessible and flexible oxidation states among all group 5 metals. However, in 2016 several organic complexes of niobium have been prepared with the metal center in its lower oxidation state through the use of niobium oxide halide moiety [110]. The most interesting of the complexes were $[(\text{NHC})_2\text{NbOX}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) (Scheme 10). Initially, they prepared NbOX_3 from simple

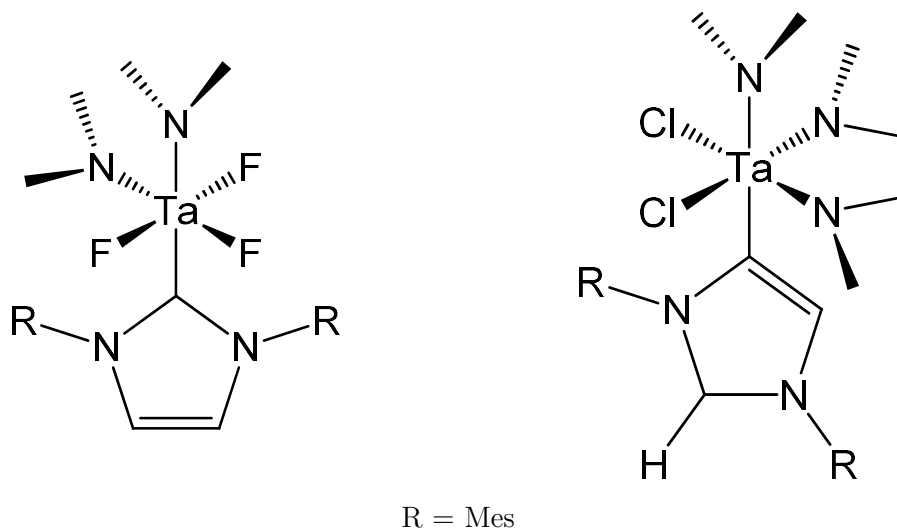
niobium(V) halide with siloxane $(\text{Me}_3\text{Si})_2\text{O}$. With the addition of nitrogen- or oxygen-based ligands (MeCN and 1,2-dimethoxyethane, respectively), adducts with general formula $[\text{NbOX}_3\text{L}_2]$ were obtained and afterwards these adducts were reduced to $[\text{NbOX}_2\text{L}_2]$ with tributyltin hydride (Bu_3SnH). These complexes are extremely air-sensitive and only by use of computational methods it was shown that their structure is most likely dimeric. Addition of NHC-fractured dimeric compound and exchanged previous ligand with two NHC ligands. Stability of complexes significantly improves although the product exposed to air decomposes completely. Complexes are isostructural to previously reported $[(\text{NHC})_2\text{VOCl}_2]$. Crystallographic data and theoretical calculations showed that, with niobium center in its reduced oxidation states, additional electronic process stabilizing the overall energy of the system comes into effect. Due to the filled valence d-orbitals, a π -back-donation from niobium through the halide ligands to the carbenic carbon strengthens the $\text{M}-\text{C}_{\text{NHC}}$ bond.



Scheme 10: Top row: Neutral NHC complex with TaCl_5 (left) [109]. First structurally characterized Nb(IV) oxide halide complex with NHC (right) [110]. Bottom row: Salt forms as a product of auto-ionization of pentahalide reagent [109].

In 2017, $[(\text{NHC})\text{TaF}_3(\text{NMe}_2)_2]$ (Scheme 11) was prepared from $[\text{Ta}(\text{NMe}_2)_5]$ and imidazolium salt $[(\text{NHC})\text{H}][\text{BF}_4]$ [111]. The reaction of tantalum precursor and neutral NHC does not proceed as expected. Authors speculated that high steric demand and strong π -donating properties saturated tantalum center with electron density and render it unreactive toward bulky σ -donating NHC molecule. Instead, metathesis reaction with imidazolium salt, a commonly employed method for transition metal reagents was used and indeed yielded the aforementioned neutral complex. However, in addition to bonding of neutral NHC, tantalum exchanges three of its amides for fluoride ligands from $[\text{BF}_4]^-$ anion,

which depicts tantalum's affinity for fluoride ligands. When imidazolium chloride $[(\text{NHC})\text{H}][\text{Cl}]$ was used, abnormal coordination of NHC occurred. $[(\text{aNHC})\text{TaCl}_2(\text{NMe}_2)_3]$ complex is the first report of abnormally bonded NHC to an early transition metal (Scheme 11). It was suggested that steric hindrance on the tantalum center, since three of the amides remain in the coordination sphere, is crucial to attain such a result.



Scheme 11: Tantalum amido fluoride complexes with NHC with first structurally characterized complex with abnormally coordinated NHC (right) [111].

In this thesis, several additional neutral coordination compounds with group 5 fluorides will be presented. Their synthesis procedure and characterization of the complexes will be described. Structural characterization of single crystals is currently the absolute technique for determination of composition, geometry and structural features of the prepared compounds. Analyses of crystal structures led to the observation of unusual details within the structure, which will be scrutinized by a theoretical study.

1.2 Vanadium Oxide Fluorides

1.2.1 Overview of vanadium oxide fluorides

Vanadium oxide fluorides (VOFs) are a family of compounds composed of a vanadium center coordinated with oxide and fluoride ligands. Oxidation state of central vanadium cation, which in VOFs ranges from III to V, molar ratio of the V, O, F constituents and their arrangement within the compounds vary greatly depending on the starting reagents and reaction conditions employed during the synthesis. All of the mentioned VOF attributes introduce changes in size, topology and charge of the VOFs.

Term VOF commonly refers to the species with higher content of fluoride in regard to the oxide, however compounds with “reversed” molar ratio are also known. Most commonly they are formed from small vanadium(V) oxides such as AVO_3 ($A = [\text{Na}]^+$, $[\text{NH}_4]^+$) [112]–[115], V_2O_5 [116]–[120] or $[\text{VO}(\text{O}t\text{Bu})_3]$ alkoxide [121] and a source of fluoride, which is usually hydrofluoric acid or ammonium fluoride salt. There is no general procedure with the amount of added fluoride source to the vanadium reagent, since some authors reported using a considerable surplus, while others prepared VOF products with a significant deficit of a fluoride donor. Water is the most frequently used solvent [113]–[118], [122]–[124], although polar organic solvents have also been employed, i.e. MeCN [120], [125], [126], DCM [127] or methanol [121].

Interestingly, almost all of the structurally characterized VOF compounds with minor molar content of fluoride compared to oxide are oligomeric in nature with polyoxovanadate core and incorporated fluoride ligand. Vanadium centers of these polyfluorooxovanadates can be in a singular oxidation state of either IV or V, although examples with mixed oxidation states are also represented. Apart from the mentioned syntheses of polyfluorooxovanadates from small vanadium(V) oxides, a straightforward path to their preparation utilizes ammonium fluoride salt to include fluoride into the polyoxovanadate cluster [122], [125], [127]. Fluoride enters the structure through substitution of oxide ligands or is incorporated into the most suitable place between vanadium cations. Changes associated with a smaller size and lower charge of more electronegative fluoride ligand primarily result in building units with different coordination requirements, bridging capabilities and overall stability. On the secondary level, it induces atypical dimensionality to a size and shape of the cage, modifies composition of the cluster and alters its surface charge.

VOFs with their composition in favor of fluoride ligands are vastly more represented as was already established. Herein, they will be sorted in groups according to the overall charge of the species. As such, anions are the largest group, however neutral compounds and cations are known and being actively studied. In regard to the size and geometry of “typical” VOFs, compounds with monomeric, dimeric, oligomeric as well as polymeric topology have been reported. Hitherto, no 3D structure has been described, but greater dimensionalities of the VOF geometry can be obtained with incorporation of transition metal cations and their cationic complexes into the crystal structure. In these examples, fluoride functions as a bridge and establishes $[-\text{V}-\text{F}-\text{M}-]_n$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Zn}, \text{etc.}$) networks. Additional diversification of VOF chemistry can be achieved by conjunction of VOFs with VO_4 units or PO_4 into polymeric structures. Such compounds are not related to the topic of this thesis and therefore will not be further reviewed.

Cationic VOFs comprise the smallest part of the VOF chemistry. The only representatives of cationic species are complexes $[\{\text{VO}(\text{salen})\}_2\text{F}]^+$ ($\text{salen} = N,N'$ -bis(salicylidene)ethylenediamine) [128]–[130] and $[\text{VOF}(\text{bipy})_2]^+$ [131]. Starting $[\text{VO}(\text{salen})]$ oxidizes in air and reacts with $[\text{BF}_4]^-$ to produce dimeric cation bridged by a

fluoride. $[\text{VOF}(\text{bipy})_2]^+$ forms with introduction of fluorine source (HBF_4 , HF or KF) to the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ in water.

The most numerous group of the VOFs are anions. Their topology ranges from discrete monomeric anions to infinite chains and planes made of smaller monomeric or dimeric units. Most commonly, synthesis procedure for the preparation of the anionic VOFs involves dissolution of vanadium oxide (VO_2 and V_2O_5) with appropriate co-reagent or ligand in hydrofluoric acid. Anionic VOFs prepared using this method form either smaller monomeric [132]–[135], dimeric and trimeric units [136], [137], as well as one-dimensional chains [138], [139]. Hydrofluoric acid introduces a fluoride ligand into the oxide framework of the Lewis acid. Fluoride forms strong, highly polar bonds with vanadium center in its highest oxidation state and strong interactions in $\text{M}-\text{F}-\text{M}$ bridges that have drastic consequences on the chemistry of the products as well as the topology of their structures [140]. Fluoride displaces oxide ligand from the coordination sphere. Nevertheless, one or two oxides cannot be supplanted due to the strong oxophilic tendencies of the group 5 metals [77]. Alternatively, similar results can be obtained by using fluoride reagents with various vanadium materials, i.e. AVO_3 ($\text{A} = [\text{Na}]^+$, $[\text{NH}_4]^+$) [128], [141]–[143], VOF_3 [144], [145], VOSO_4 [123], [124], [146] and $[\text{VO}(\text{acac})_2]$ (acac = acetylacetonate) [147].

Regardless of the method used for the preparation of VOF products, their oxidation state always correlates with the oxidation state of the starting vanadium reagent. Nevertheless, addition of the reducing agent SO_2 to the reaction mixture with vanadium(V) oxide in hydrofluoric acid reduces the oxidation state of vanadium to IV [148]–[151]. Interestingly, in all the compounds the resulting vanadium(IV) anion is dimeric $[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]^{2-}$.

In regard to the reduction of the vanadium center it is worth noting that when the vanadium(V) reagent is exposed to ionothermal or solvothermal conditions, the reduction of the vanadium(V) cation is likely to occur. Thermal reactions have been reported for synthesis procedures of the anionic VOF species with either V_2O_5 [152]–[160] or VOF_3 [161]–[163] and have given, in addition to typical small VOF anions and polymeric chains, also 1D ladder-like structures and 2D layers. However, small alterations in the reaction conditions, such as the source of vanadium [159], [162], amount of water [154], [155], organic template added and solvent used [156], [162], lead to considerably different outcomes. Although the results are quite unpredictable, some foretelling patterns have emerged. Use of water as a solvent yields products of lower dimensionality, most commonly monomeric, dimeric or polymeric chains [154], while ionothermal conditions produce more extended structures, some of which are 2D layers [157], [162]. Increase in temperature (affects nuclearity) during the reaction promotes higher dimensionality of the anion, however it also promotes further reduction of the vanadium(IV) to vanadium(III) oxidation states [155]. Hydrothermal syntheses were performed also with vanadium(IV) reagents VF_4 and VO_2 and with careful control of reaction conditions the oxidation state of central vanadium ion did not change [164], [165].

Addition of oxidizing agent into the reaction mixture and exposing it to thermal conditions can alternatively produce oxidized VOF. The sole example of oxidized VOF is neutral $[\text{VOF}_2(\text{H}_2\text{O})]$ prepared by oxidation of VF_3 with selenous acid (H_2SeO_3) [166]. Hexacoordinated vanadium(IV) cation is the center of $[\text{VOF}_4(\text{H}_2\text{O})]$ octahedral unit and is sharing with its neighbors an edge and two corners constructing a layer of $[\text{VO}_2\text{F}_4(\text{H}_2\text{O})_2]_n$, which is the only 2D VOF structure prepared under the hydrothermal conditions. Other instances of neutral VOF obtained by thermal reactions are also known, although they are less common than their anionic equivalents [162], [164], [167], [168]. In principle, thermal conditions suitable for the preparation of neutral VOFs with monodentate ligands must include lower temperatures and shorter reaction times, although reaction with bidentate

and tridentate ligands proceeds also under harsher conditions [164]. Prepared products range from polymeric $[\text{V}_2\text{O}_2\text{F}_4(\text{pyz})]_n$, where the pyz ligand serves as a connector between two VOF chains [162], to dimeric $[\text{V}_2\text{O}_2\text{F}_4(\text{py})_4]$, $[\text{V}_2\text{O}_2\text{F}_4(\text{ONpy})_2(\text{H}_2\text{O})_2]$ (pyNO = pyridine-*N*-oxide) [164] and finally to monomeric $[\text{VOF}_2(\text{H}_2\text{O})_2]$, $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$, $[\text{VOF}_2(\text{L})]$ (L = terpyridine), $[\text{VOF}_2(\text{L})(\text{H}_2\text{O})]$ (L = bipy, phen) [164]. The named monomeric and dimeric complexes are a result of hydrolysis of VF_4 , producing VOF_2 , in the presence of appropriate ligands. Of the reported compounds only $[\text{V}_2\text{O}_2\text{F}_4(\text{ONpy})_2]$ contains oxygen-based organic ligand, while others are coordinated by stronger nitrogen-derived heterocyclic bases. Oxygen donor ligands are in this system most probably too weak ligands and are thus readily displaced from the coordination sphere by water. The mentioned VOFs contain vanadium center in oxidation state IV, but there are also two solvothermally obtained $[\text{V}_2\text{O}_4\text{F}_2(\text{L})_2]$ (L = bipy, phen) complexes with vanadium(V) [167], [168]. Interestingly, the same $[\text{VOF}_2(\text{phen})(\text{H}_2\text{O})]$ [169] and $[\text{V}_2\text{O}_4\text{F}_2(\text{bipy})_2]$ [170], [171] complexes were also synthesized *via* non-thermal route.

Other reactions performed under more extreme conditions, such as high-energy milling or high pressure solid state reactions, yield a layered structure of $[\text{VO}_2\text{F}]_n$ from an equimolar combination of reactants V_2O_5 and VOF_3 [172], [173]. Authors found it could be an interesting new cathode material in lithium batteries. Another example of neutral VOF with layered 2D topology is $[\text{VOF}_3]_n$ [174]. It is prepared with fluorination of V_2O_5 with undiluted F_2 at 475 °C. $[\text{VOF}_3]_n$ is, as shown in this chapter, the origin of VOF_3 synthon for many reactions with the intent to formulate new VOFs.

Polymer of VOF_3 dissolves in polar organic solvents such as MeCN, DCM and THF. This allows for manipulations with a source of vanadium(V) in non-acidic medium as well as making VOF_3 an accessible reagent for further reactions. Currently, there are no crystal structures of VOF_3 complex with any of the solvents, although indications of a possible $[\text{VOF}_3(\text{MeCN})]$ adduct being prepared in a workable solid form were presented [126]. $[\text{VOF}_3(\text{MeCN})]$ was used as a starting reagent for reactions with nitrogen, oxygen, phosphorous, sulphur and arsenic ligands. Strong nitrogen- and oxygen-based ligands, e.g. bipy, phen, py, TMEDA, OPR₃ (R = Me, Ph), pyNO (pyridine-*N*-oxide), managed to push MeCN molecule from the adduct and afford complexes that were more resistant to reduction and hydrolysis. Few of them crystallized as $[\text{VOF}_3(\text{phen})]$, $[\text{VOF}_3(\text{OPPh}_3)_2]$ and $[\text{VOF}_3(\text{ONpy})_2]$. On the other hand, reactions with softer ligands yielded in several decomposition products such as fluorinated ligand, hydrolyzed and reduced VOF_3 synthon.

Reaction between VOF_3 , nitrogen or oxide ligands and $(\text{Me}_3\text{Si})_2\text{O}$ in MeCN gives compounds with a general formula $[\text{VO}_2\text{F}(\text{L})_x]$ ($x = 1, 2$) [171]. However, this system comes with its own peculiarities. VO_2F has a polymeric structure and is quite inert toward organic solvents and hence extremely poorly soluble, but it promptly hydrolyzes with water into unidentifiable polyvanadates. Likewise, the VO_2F complexes are susceptible for hydrolysis with traces of water, which among others produce $[\text{VOF}_4]^-$ and $[\text{VO}_2\text{F}_2]^-$ that exhibit some robustness toward reactions with water. Despite difficulties, researchers obtained crystals of $[\text{VO}_2\text{F}(\text{py})_2]$ and successfully prepared coordination complexes with other nitrogen donor ligands bipy, phen and TMEDA, whereas oxygen-based ligands, e.g. THF, $\text{MeO}(\text{CH}_2)_2\text{OMe}$ and 15-crown-5, were not able to compete with affinity of VO_2F for polymerization.

Lastly, neutral VOF was prepared in metathesis reaction between VOF_3 and $\text{Me}_3\text{SiNPPH}_3$, where the final complex is tetrahedral $[\text{VOF}_2(\text{NPPH}_3)]$ [175]. From the presented overview of coordination chemistry of neutral VOFs we can conclude that the field is dominated by nitrogen-based ligands that form monomeric or dimeric complexes. Another exception to this trend is $[\text{VOF}_2(\text{O}i\text{Pr})(i\text{PrOH})_2]$ ($\text{O}i\text{Pr}$ = isopropoxide, $i\text{PrOH}$ = isopropanol) complex synthesized from $[\text{VO}(\text{O}i\text{Pr})_3]$ alkoxide dissolved in $i\text{PrOH}$ and added equimolar amount of hydrofluoric acid [176].

1.2.2 Small anionic VOFs

Discrete monomeric and dimeric anionic VOFs obtained by either of the previously presented synthesis routes are relatively scarce in comparison to the larger anions. Hitherto the only oxidation states of the vanadium center observed within these smaller discrete anions are either IV or V. Among the presented structurally characterized VOFs in Table 1, the most commonly reported anions are octahedral $[\text{VOF}_5]^{3-}$, $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ as well as their oxidized counterparts $[\text{VOF}_5]^{2-}$, $[\text{VOF}_4(\text{H}_2\text{O})]^-$ and tetrahedral $[\text{VO}_2\text{F}_2]^-$. Table 1 also lists small non-polymeric clusters where VOF anions are not completely isolated, but are weakly associated with the cationic complex. Related polymeric structures, with monomeric or dimeric VOF anion as an integral component of polymeric arrangement and cationic fragment connecting the anions into 1D–3D networks, are not a subject of this introductory chapter. However, they are listed according to their VOF anions in the Appendix (Table A1). Inspection of the crystal structure of dimeric anions revealed that they are a combination of octahedral monomeric units with one, two or three bridging fluorides. Monomeric units in dimers have an octahedral coordination environment if the bridging fluorides are also taken into account, otherwise the coordination number is naturally lower. Dimers with one and three bridging fluorides are somewhat of an exception and the most represented dimers are formed by two bridging fluorides, since they are provided with the most optimal stabilizing effects in the given setting. This might be due to the flexible nature of the dimer with only one bridging fluoride and a trend where more participating fluorides yield a more rigid, constrained and deformed octahedron of an individual vanadium center.

Table 1: Overview of all structurally determined monomeric and dimeric VOF anions.

Oxidation state	Coordination	Monomeric compound	Ref.
IV	6	$[\text{VOF}_5]^{3-}$	[154], [177], [178]
	5 (0.62) ^[a]	$[\text{VOF}_4]^{2-}$	[179]
	6	<i>cis</i> - $[\text{VOF}_4(\text{H}_2\text{O})]^{2-[\text{b}]}$	[154], [156]
	6	<i>trans</i> - $[\text{VOF}_4(\text{H}_2\text{O})]^{2-[\text{b}]}$	[152], [154], [155], [159], [180]–[183]
	6	<i>cis, cis</i> / <i>cis, cis</i> - $[\text{VOF}(\text{L}^1)_2]^{3-[\text{b}, \text{c}]}$	[143]
	6	<i>cis, cis</i> / <i>cis, trans</i> - $[\text{VOF}(\text{L}^1)_2]^{3-[\text{b}, \text{c}]}$	[143]
V	6	$[\text{VOF}_5]^{2-}$	[160], [184]–[186]
	6	<i>trans</i> - $[\text{VOF}_4(\text{H}_2\text{O})]^{-[\text{b}]}$	[132], [155], [187]
	5 (0.03) ^[a]	$[\text{VOF}_2(\text{L}^2)]^{-[\text{b}, \text{d}]}$	[147]
	5 (0.69) ^[a]	$[\text{VOF}_2(\eta^2\text{-O}_2)_2]^{3-}$	[133]
	4	$[\text{VOF}(\eta^2\text{-O}_2)_2]^{2-}$	[135], [188], [189]
	6	$[\text{VO}_2\text{F}_4]^{3-}$	[134]
	4	$[\text{VO}_2\text{F}_2]^{-}$	[122], [128], [141]
	5 (0.72) ^[a]	$[\text{VO}_2\text{F}_2(\text{L}^3)]^{-[\text{b}, \text{e}]}$	[190]
	6	$[\text{VO}_2\text{F}_2(\text{IO}_3)_2]^{3-}$	[191]
	5 (0.45) ^[a]	$[\text{VO}_2\text{F}(\text{L}^1)]^{2-[\text{b}, \text{c}]}$	[113]
	5 (0.48) ^[a]	$[\text{VO}_2\text{F}(\text{IO}_3)_2]^{2-}$	[191]
Dimeric compound			
IV	6	$[\text{V}_2\text{O}_2\text{F}_6(\mu\text{-F})_2]^{4-}$	[124], [154]–[156], [159], [165], [192]
	6	$[\text{V}_2\text{O}_2\text{F}_4(\mu\text{-F})_3]^{3-}$	[136]
	6	<i>cis</i> / <i>cis</i> - $[\text{V}_2\text{O}_2\text{F}_4(\mu\text{-F})_2(\text{H}_2\text{O})_2]^{2-[\text{b}]}$	[123], [148]–[151], [155], [156], [164]
	6	<i>cis, cis</i> / <i>cis, cis</i> - $[\text{V}_2\text{O}_2\text{F}_2(\mu\text{-F})_2(\mu\text{-L}^4)_2]^{4-[\text{b}, \text{f}]}$	[146]
	6	$[\text{V}_{1.5}\text{Mo}_{0.5}\text{O}_3\text{F}_6]^{3-[\text{g}]}$	[193]
V	6	$[\text{V}_2\text{O}_2\text{F}_8(\mu\text{-F})]^{3-}$	[194]
	6	$[\text{V}_2\text{O}_2\text{F}_6(\mu\text{-F})_2]^{2-}$	[144]
	6	<i>trans</i> - $[\text{V}_2\text{O}_2\text{F}_7(\mu\text{-F})(\text{H}_2\text{O})]^{2-[\text{b}]}$	[137]
	5	$[\text{V}_2\text{O}_2\text{F}_2(\mu\text{-F})(\eta^2\text{-O}_2)_2(\mu\text{-}\eta^2\text{-O}_2)]^{3-}$	[195], [196]
	5	$[\text{V}_2\text{O}_2\text{F}(\eta^2\text{-O}_2)(\mu\text{-}\eta^2\text{-O}_2)_3]^{3-}$	[196]
	6	$[\text{V}_2\text{O}_2\text{F}_2(\mu\text{-O})_2(\mu\text{-}\kappa^2\text{-SeO}_3)_2]^{4-}$	[197]
	6	$[\text{V}_2\text{O}_4\text{F}_2(\mu\text{-F})_3]^{3-}$	[136]

^[a] Structural parameter was calculated using $\tau = \frac{\beta - \alpha}{60^\circ}$, where β is the largest of the basal angles and α is the angle between the remaining basal atoms [198].

^[b] Position of ligand relative to the V–O bond.

^[c] L¹ represents bidentate oxalate $[\text{C}_2\text{O}_4]^{2-}$ ligand.

^[d] L² represents bidentate acetylacetonate $[\text{C}_5\text{H}_7\text{O}_2]^{2-}$ ligand.

^[e] L³ represents bidentate 1,2,4-triazol-4-yl $[\text{C}_2\text{H}_2\text{N}_3\text{R}]$ ligand bonded to VOF anion only through one V–N bond.

^[f] L⁴ represents bridging bidentate squarate $[\text{C}_4\text{O}_4]^{2-}$ ligand.

^[g] Severely disordered anion.

1.2.3 $[\text{VOF}_4]^-$ anion and its anion–ligand interactions

In addition to the structurally characterized examples of small anionic VOFs, one of the profoundly researched monomers was $[\text{VOF}_4]^-$. It was also one of the earliest prepared

and analyzed VOFs. Its first NMR report was in 1965 when a symmetrical quintet had been observed in ^{51}V NMR spectrum of V_2O_5 in aqueous HF [199], which was elaborated to be a result of the symmetric square pyramidal anion with the oxide in the apical position. Later reports of salts containing the $[\text{VOF}_4]^-$ anion and different small cations of isolated solid samples predominantly relied on vibrational spectroscopy and X-ray structural analysis, while NMR studies of various VOF species observed in the solution were also published. According to the IR spectra of the solid sample of the $[\text{Cs}][\text{VOF}_4]$ salt, it was initially thought that salt consists of discrete $[\text{VOF}_4]^-$ anions, despite the unusual splitting of the bands in the spectra indicating a polymeric structure [200]. The latter was proven accurate by analysis of crystal structure of the named salt [201]. Ribbon-like structure comprises distorted octahedra connected through fluoride bridges, where $[\text{VOF}_4]^-$ anions function as donors and acceptors of these bridges. V–F bond at the bridge donor anion is only slightly elongated (1.79 Å), whereas the V–F bond at the sixth coordination site of the acceptor is significantly extended (2.31 Å), which may be interpreted as distorted octahedral geometry. Subsequent studies of similar salts with alkali and other small counter ions ($[\text{Na}]^+$, $[\text{K}]^+$, $[\text{Rb}]^+$, $[\text{Tl}]^+$, $[\text{Ag}]^+$, $[\text{Me}_4\text{N}]^+$, $[\text{NH}_3\text{OH}]^+$) reconfirmed the polymeric chain of $[\text{VOF}_4]^-$ anions [145], [201]–[203]. Different interpretations of NMR spectra obtained for VOF species in the solutions of V_2O_5 in HF sparked similar controversy whether quintet in ^{51}V NMR spectra should be assigned to $[\text{VOF}_4]^-$ vs. $[\text{VO}_2\text{F}_4]^{3-}$ [200], [204]–[206]. The former had been regarded flexible and labile in solution, prone to oxidize in aqueous environment and could therefore exist only in a water-free medium, while the latter was viewed as stable in solutions since recrystallization from such a system had been shown [205]. However, a detailed inspection of ^{19}F NMR spectra, additional hydrolysis study of $[\text{VOF}_4]^-$ [206] in organic solvents and reports of salts with $[\text{VOF}_4(\text{H}_2\text{O})]^-$ anion led to a consensus of $[\text{VOF}_4]^-$ presence in a solution [207], [208].

Overview of VOF crystal structures without associated ligands (H_2O) demonstrates that $[\text{VOF}_4]^-$ anions with bare metal counter ions generally adapt polymeric character [145], [201]–[203]. The only exceptions to the polymeric association of $[\text{VOF}_4]^-$ anions are discrete $[\text{V}_2\text{O}_2\text{F}_8]^{2-}$ anions balanced by $[\text{Pb}]^{2+}$ cations [209]. With the organic cations present in the structure, there are only two other $[\text{VOF}_4]^-$ -based anions with a non-polymeric structure, the trimeric $[\text{V}_3\text{O}_3\text{F}_{12}]^{3-}$ [137] and dimeric $[\text{V}_2\text{O}_2\text{F}_8]^{2-}$ [144]. In the former, the combination of alkali and $[\text{Me}_4\text{N}]^+$ cations is in the 1:2 ratio, while the cation in the latter is a large imidazolium-based moiety suggesting the possibility that the size of the cations might affect the topology of the overall structure of the VOF anions. Collection of the crystallographic data of the aforementioned studies could be interpreted as follows: increase in bulkiness of the cation stabilizes and is compensated by ever smaller $[\text{V}_n\text{O}_n\text{F}_{4n}]^{n-}$ anions.

Considering the indications from previous studies regarding the C_{4v} point group for $[\text{VOF}_4]^-$ anion, proposing a square pyramidal geometry presents a possibility to increase a number of coordinated ligands to 6. Dissimilar to other well-established square pyramidal compounds XeOF_4 and BrF_5 that possess an electron pair in their sixth position, vanadium center in the $[\text{VOF}_4]^-$ anion has formally depleted valence orbitals (d^0 , oxidation state V) rendering the region *trans* to V–O bond and below the basal fluorine atoms hypothetically accessible to electron donating ligands. Review of the literature (Table 1) reveals that currently only $[\text{F}]^-$ and H_2O occupy this site. Interestingly, the V–F or V–O bond to the associated sixth ligand is elongated (cca 2.1 Å and 2.3 Å, respectively) in comparison to other present bonds (cca V–O 1.6 Å, V–F 1.8 Å), forming a distorted octahedron. This characteristic has also been observed in the polymeric chain of $[\text{VOF}_4]^-$, where V–F bond to the bridging fluorine is elongated (2.3 Å) [201]. Unfortunately, beyond these few structures there are no other examples with the $[\text{VOF}_4(\text{L})]^-$ motif. A search through crystal structure databases for the discrete $[\text{MOF}_4(\text{L})]$ (M = metal, L = organic ligand) motif for

a representative set of coordination complexes yielded, in addition to known H_2O complexes (Table 1), [210] also py- [211]–[213] and phosphanone- (OPPh_3) [214], [215] based adducts. All of the presented compounds are extremely moisture-sensitive. Predictably, coordination centers in all of the found oxide fluoride complexes are early d-block metals with oxophilic propensities. All of the metal centers, with the exception of some vanadium(IV) examples, are in their highest oxidation states, therefore without valence electrons. Hence, group 5 complexes are anions, while group 6 are neutral compounds. Beyond salts with already mentioned $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ and $[\text{VOF}_4(\text{H}_2\text{O})]^-$ anions (Table 1), only one other related anion has been published – $[\text{NbOF}_4(\text{H}_2\text{O})]^-$ [210]. Interestingly, the metal center of all current aqua oxide fluoride compounds belongs in the same group 5. Other $[\text{MOF}_4(\text{L})]$ complexes are neutral adducts of monodentate py [211]–[213] and OPPh_3 [214], [215] ligands with molybdenum or wolfram center that are, due to their lack of charge, isoelectronic to the $[\text{VOF}_4(\text{H}_2\text{O})]^-$ anion. Their coordination geometry is described as distorted octahedron and inspection of the structures reveals another mutual property that was registered in this collection of complexes, with some inconsistencies for two of the vanadium(IV) anions. The ligand moieties are usually positioned *trans* in relation to the V–O bond, whereas the two exceptions are in *cis* position and the coordination center is shifted from the plane of equatorial fluorides toward the oxide group. Displaced position of the metal ion as well as a bond between the ion and associated *trans* organic ligand is elongated regardless of the ligand type, oxidation state of central ion or charge of the complex. Elongation effect is clearly seen in $[(\text{teta})\text{H}_4][\text{VOF}_4(\text{H}_2\text{O})]_2$ (*teta* = triethylenetetramine) [154], where both *cis*- $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ and *trans*- $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ isomers were determined. V–O and V– $\text{O}_{\text{H}_2\text{O}}$ bonds in *cis* anion are 1.641 Å and 2.035 Å, respectively, and V–F *trans* to the V–O is extended for cca 0.16 Å in comparison to the remaining V–F bonds. In *trans* anion the discrepancies in the length of V–F bonds are negligible, but at the same time the V–O and V– $\text{O}_{\text{H}_2\text{O}}$ bonds are 1.606 Å and 2.305 Å, respectively. In conclusion, ligands in the *trans* position indiscriminately form weaker interactions with the metal center, which was attributed to the *trans* effect [132], [154], [155]. Another proposition for bond lengthening, metal ion displacement and consequential deformation of coordination geometry is a repulsive effect of the M–O bond [211], [216], although newer findings suggest that electronic effects ($d\pi$ – $p\pi$ -interactions) of metal cation and oxide are affecting detected out-of-center distortions [217], [218]. The energy gap between the lowest unoccupied molecular orbital of M^{5+} , M^{6+} cations and the highest occupied molecular orbital of the oxide ligand is sufficiently small for the pseudo Jahn-Teller effect (shortening of bond, displacement of metal ion) to occur. Energy of the metal’s vacant d-orbitals is lowered with decreased size and increased charge of the central cation, thus any other larger cation (M^{3+} , M^{4+}) is unsuitable. Similarly inadequate are energy levels of filled p-orbitals of fluoride as they are lower than the oxide’s. Theoretical models show strengthened M–O bond and weaker M–F bond. The former possesses, in addition to the σ -bond, significant contribution of π -character to the bond, while the latter is mainly σ -type in nature [219].

Herein, we report the synthesis procedure for the preparation of two imidazolium salts with vanadium(V) oxide fluoride anions. Their structural features obtained with X-ray diffraction are depicted in great detail and other compound’s characteristics are elucidated in accordance with their NMR and vibrational spectroscopy. In addition, the documented data is interpreted and compared to the results calculated by theoretic examination of the crystal structures. The research was extended to the anion–ligand adduct and comments of the weak associative interactions observed in the $[\text{VOF}_4(\text{L})]^-$ anionic complex.

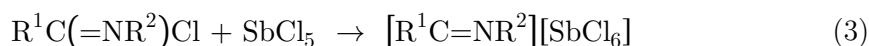
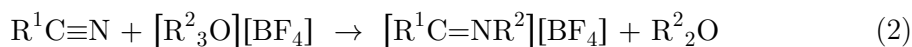
1.3 Nitrile Cyclotrimerization

1.3.1 Nitrilium cations

Adducts of the inorganic reactants with solvent molecules are often used precursors in synthesis as they enhance solubility, yet the metal–solvent bond is reasonably weak and the solvent can be easily replaced by investigated ligand. Group 5 pentafluorides are due to their oligomeric character and strong fluoride bridges scarcely soluble in non-polar solvents, but readily dissolve in polar organic solvents such as MeCN. As such they are suitable to be synthons in subsequent reactions [140]. Although niobium and tantalum fluorides readily dissolve in nitriles, form adducts in solution [220], [221] and can be prepared as white solids [222], the preparation of single crystals is an onerous task [223]. Single crystals are often formed from the last drop of the mother liquor due to their perfect solubility. Crystals are extremely air-sensitive and even if they are submerged in the inert liquid medium, such as octane or perfluorodecalin, they promptly decompose into unidentifiable products. Meager stability of solid adducts deters the possibility of further analysis with different methods. Reactivity and ability to form coordination compounds of group 5 pentafluorides is often associated to their main group counterparts, i.e. arsenic and antimony pentafluorides [224], [225], since they are all strong Lewis acids and have equivalent geometry [226]. Interestingly, crystalline nitrile adducts of the main group pentafluorides have been prepared and successfully structurally characterized [227], [228].

Addition of anhydrous HF to the solid pentafluorides yields a medium known for its exceedingly acidic properties. Dissolution of different alkyl and aryl nitriles in such super-acidic medium comprised of HF/MF₅ (M = As, Sb) protonated nitrile molecule and afforded stable nitrilium cation [229]. Alternatively, nitrilium cations have also been prepared and proved by NMR spectroscopy, when nitriles were treated by similarly strong acids (sulfuric acid, oleum or HSO₃F/SbF₅/SO₂) [230], [231]. Nitrilium ions are long known reactive intermediates that are involved in various transformations in organic chemistry [232]. Protonated nitriles are reactive moieties in the Houben-Hoesch process and are used in order to introduce the acyl group to the phenol substrate [233], [234]. Currently, there are no reported studies that would elaborate on the unusual stability of aforementioned examples of protonated nitriles in super-acidic solution. Their stability is most probably associated with the “inertness” of the employed reaction system and of the anionic part.

Structurally related to the protonated nitriles are nitrilium cations prepared by Meerwein’s reagent [R₃O][BF₄] (R = Me, Et) [235]–[237] (rxn. 2) or by abstraction of chloride from imidoyl chlorides with Lewis acids (rxn. 3) [238], [239]. These are usually referred to as stable nitrilium salts. Interestingly, the majority of stable *N*-alkyl or *N*-aryl nitrilium salts contain weakly coordinating anions or some auxiliary moieties mediating reactive character of nitrilium species [232]. These observations correlate and reconfirm noted peculiar stability of protonated nitriles. Therefore, in future attempts to isolate additional, otherwise reactive species, rigorous water-free reaction conditions must be employed, while in reactions the dual nature of the nitrilium salts can be exploited for nucleophilic additions of appropriate reagents [240]–[243].



Oxonium salt $[\text{H}_3\text{O}][\text{SbF}_6]$ [244], [245] is a derivative of the superb alkylation reagent Meerwein’s trialkyl substituted oxonium salt $[\text{R}_3\text{O}][\text{BF}_4]$ ($\text{R} = \text{Me}, \text{Et}$) as well as a congener of the fluoronium $[\text{H}_2\text{F}]^+$ cation [246], the formation of which is due to the equilibrium processes within the fluoroantimonic acid (rxn. 4) [247], [248]. $[\text{H}_3\text{O}][\text{SbF}_6]$, as an unwanted by-product in fluorine chemistry, did not receive much attention as a potential reactive species in organic reactions and even in a broader sense, the studies of its reactivity are practically non-existent [249].



The simplest of the nitrilium cations are protonated nitriles, which are a crucial intermediates in the acid promoted cyclotrimerization of nitriles. One such example is the modified Houben-Hoesch reaction, where for the source of proton and weakly coordinating anion of conjugate acid, the formally used system of HCl and Lewis acid (ZnCl_2 or AlCl_3) was replaced by TfOH acid and the following synthesis yielded *s*-triazine products [250], [251].

1.3.2 Nitrile cyclotrimerization procedures

Symmetric 2,4,6-trisubstituted-1,3,5-triazines (*s*-triazines) are a class of heterocyclic compounds that are currently being actively studied as a remarkable synthon in supramolecular chemistry due to their ligand properties, hydrogen bonding, electrostatic, charge-transfer and aromatic-stacking interactions. The most prominent fields of research for the covalent triazine framework derivatives of the *s*-triazines are energy storage applications in the form of supercapacitors, electrocatalysis, photocatalysis, hydrogen storage, CO_2 capture and heterogeneous catalysis [252]–[257]. The advances in the synthesis of smaller non-polymeric *s*-triazines are often transferred into the studies of polymeric *s*-triazines frameworks and are thus equally valuable.

For the preparation of the *s*-triazines, the most commonly employed synthesis procedures are the reaction of aldehydes with amidine hydrochlorides [258]–[260], acidly catalyzed trimerization of imidates [261], substitution of chloride ions of cyanuric chloride [262]–[264] and cyclotrimerization of nitriles. All of them require prolonged reaction times, elevated temperatures or in some cases a combination of both. Auto-cyclotrimerization of nitriles requires in addition to high temperatures also extreme pressures and an appropriate solvent [265]–[267], hence in order to improve the efficiency of the trimerization, the use of reagents with catalytic nitrile activating ability is essential.

Use of catalysts in the presence of a basic reagent has been established as one of the viable paths toward the trimerization product *s*-triazine. Cyclotrimerization of nitriles was catalyzed by $[\text{La}(\text{OTf})_3]$ ($\text{OTf} = \text{triflate}$) and ammonia or amine as a co-catalyst, but they still needed temperatures up to 200 °C for the reaction to proceed [268], [269]. Equivalent results were obtained in systems with a similar mixture of catalyst and amine co-catalyst such as $[\text{NH}_4][\text{Br}]$ in ammonia [270], $[\text{Y}(\text{OTf})_3]$ and piperidine [271] and SmI_2 or samarium(II) complexes with *n*-hexylamine, which was heated to 80 °C [272], [273]. Another method for the synthesis of *s*-triazines in basic conditions has been reported. Basicity is ensured by the addition of alkaline AOH ($\text{A} = \text{alkali metal}$) salt and various other reagents are introduced (18-crown-6 or CoCl_2) [274]–[276]. Similarly to the amine procedures, the hydroxide method also requires elevated temperatures. The reaction of nitriles with KOH and 18-crown-6 was performed in refluxing decalin and with LiOH and CoCl_2 solvothermal conditions were maintained for a week. *s*-triazine can also be prepared

with metallic alkali and alkaline reagents or their hydrides although yields are generally low and a mixture of products is obtained [277]–[280]. In addition, elevated temperatures are needed for these reactions. For instance, reaction between nitriles and NaH in benzene had to be heated to 70–85 °C.

Acid-activated cyclotrimerization of nitriles is currently the most prominent method. In the past, pairs of Lewis acids and hydrogen halides were used as initiators of the reaction, whereas most of the contemporary synthesis procedures employ TfOH or triflic anhydride (TfOTf) to activate the nitriles [251], [281], [282]. At variance with the procedures in the basic medium, reactions with TfOH proceed at room temperature and *s*-triazine products can be prepared with excellent yields. A drawback of this method is the extensive number of by-products that can form and contaminate the expected product [283]. Their occurrence and quantity depends on the reaction time and the molar ratio between MeCN and TfOH. In the reaction mixture with an excess of TfOH (MeCN:TfOH = 1:14) the formation of kinetic product twice-protonated iminium cation is favored, which slowly converts to acetamidium cation and protonated acetic acid. Meanwhile, experiments with excess of MeCN (MeCN:TfOH = 20:1) show that a relatively stable primary product twice-protonated *s*-triazine tends to react with another such molecule creating bigger oligomers consisting of several *s*-triazine units. Nevertheless, appropriate nitrile:TfOH ratio yields optimal results. As previously stated, Lewis acids were once the best reagents for the activation of nitrile molecules and ensuing cyclotrimerization process. The most commonly used were aluminum halides (AlCl₃, AlBr₃), BF₃ or PCl₅ with hydrogen halide (HCl, HBr) [284], [285]. Their use was prevalent due to their availability. Use of Lewis acids in HCl as promoters of cyclotrimerization was later expanded to MCl₃ (M = Sb, Bi, Fe) salts, although the acidic conditions yielded salts with *s*-triazinium cations [286]. Lanthanide complexes are also capable of catalyzing trimerization process in benzene even at room temperature [287]. Silica-supported Lewis acids with the addition of nucleophiles such as piperidine or morpholine in microwave-heated system initiate nitrile cyclotrimerization reaction [288] and it has been shown that lithium nitride under solvothermal conditions also produces *s*-triazines [289]. In material and polymer sciences, the addition of Lewis acid to polynitriles leads to their cyclotrimerization, thus forming porous polymer structures mentioned at the beginning of this chapter. Field of covalent triazine frameworks rapidly expanded after initial publications in 2008 describing synthesis details and proposing the applicability of polymers. The cyclotrimerization reaction of functionalized benzonitriles with ZnCl₂ was carried out under ionothermal conditions at temperatures well above the melting point of ZnCl₂, specifically 400–600 °C [290], [291]. Nowadays, several other methods for the preparation of covalent triazine frameworks are available, one of them also being acid-promoted nitrile trimerization by derivatives of TfOH [292].

Unsuccessful attempts to synthesize the complex of metal pentafluoride–nitrile adducts lead us to the unexpected discovery. During the study, we stumbled upon reaction conditions and devised a system that leads to the cyclotrimerization of certain nitriles. Oxonium [H₃O][SbF₆] reagent exhibited strong proton donating capabilities capable of affording nitrilium cation followed by cyclotrimerization. Therefore, we have shifted focus of our research to the reactivity of the oxonium salts with different nitriles.

Chapter 2

Methodology

2.1 Experimental Methods

2.1.1 General information

Many of the reagents and products we were working with were oxygen- and water-sensitive. Thus, we have employed procedures for work under the inert conditions (Schlenk techniques) and used a specialized equipment designed for the manipulations with chemicals under the inert environment. Two of the most essential and valuable pieces of equipment were a glove box and a Schlenk line.

M. Braun's glove box was used for storage and weighting of solid reagents. The main compartment is filled with atmosphere of slightly pressurized argon gas, which continuously circulates through filters and can be additionally purified through water and oxygen absorbent filters. All the required equipment and reagents are brought into the workstation container through air lock, which can be purged with argon or evacuated with a vacuum pump.

Schlenk line is a glass-made dual manifold apparatus connected with low-pressure PVC tubes to a vacuum pump (vacuum line) and source of argon gas (inert gas line). In between the operational part of the vacuum line and the vacuum pump, a cold trap with liquid nitrogen is attached to condense solvent vapors and other volatile compounds and prevents pump contamination. The inert gas line is open on both ends. Before argon enters the line, it is additionally purified with passing through a series of filter columns filled with dehydrating agents: granulated potassium hydroxide and phosphorus pentoxide powder. Oil pressure release valve is placed in the exhaust of the inert gas line that prevents irruption of air into the system and prevents build-ups of potentially dangerous pressure in the line.

The segment of the Schlenk line, which is used the most, is a system of meticulous glass tubing with two Teflon valves (one for each part of the line) called connectors extended further for easier manipulation with a PVC tubes. During the chemist's work, a Schlenk flask is attached to the previously mentioned PVC tubes and valves are used for regulation of atmosphere and pressure in the flask. With other specialized glassware, chemists can perform, under inert conditions, most of the reactions and operations as they would in tabletop chemistry. Most commonly employed procedures are solvent addition through cannula, addition of liquid reagents with a syringe, filtration, isolation of solid samples with removal of a volatile compound in dynamic vacuum and distillation.

Since most commercially obtainable solvents contain moisture, additional dehydration methods were applied prior to their use. The first step in the preparation of ethers, which in the presence of oxygen form explosive peroxides and toluene with its high boiling point,

was the preparation of a mixture of sodium and benzophenone until the solution turned deep purple. Afterwards the solvent was distilled under argon atmosphere, freeze-thawed and stored over dried 3 Å molecular sieves. MeCN, DCM and octane were redistilled under argon atmosphere, degassed by freeze-thawing cycles and stored over dried 3 Å molecular sieves [293]. Deuterated NMR solvents and silicon oil used to transfer crystals in air were stored in a glove box in glass bottles with added dried 3 Å molecular sieves. Molecular sieves as a ubiquitous desiccant and glassware were, dried overnight in an oven at 160 °C prior to their use. Dry reagents were stored in a glove box and no additional purification methods were applied prior to their use. Liquid reagents PhCN and *t*BuCN were transferred and stored over dried 3 Å molecular sieves. Starting reagents (NHC^{Dipp}) [294] and [(NHC^{Dipp})H][F] [295] were prepared according to the reported synthesis procedure.

2.1.2 Synthesis of imidazolium-based products

Routine synthesis reaction for the preparation of neutral NHC complexes (rxn. 5) or ionic imidazolium salts (rxn. 6) comprises of loading solid samples to a reaction vessel of an appropriate material (FEP material if there is a release of HF to be expected), dissolution of the reactants with organic solvent and stirring of the reaction mixture.



If needed, the reaction mixture was warmed or cooled. Unreacted starting material or precipitated products were filtered and analyzed separately, while filtrate was most commonly dried *in vacuo*. The solid product was weighted to determine the yield of the reaction.

Due to the slow decomposition and reduction of some vanadium(V) oxide fluoride reactants in organic solvents [296], associated elimination of HF and etching of the silica-based glassware, we performed these reactions in vessels made from a FEP polymer material, which is resistant to the fluorination. Hence, when necessary, inlays for NMR tubes were produced of the same material.

2.1.3 Synthesis of anionic complexes

Solid [(NHC)H][VOF₄] reagent readily dissolves in liquid THF or py, which acts as a reagent as well as a solvent, whereas solid reagent pyz and [(NHC)H][VOF₄] were loaded in equimolar ratio and dissolved with the addition of MeCN. Crystallization of the reaction mixture yielded single crystals of the [VOF₄][−] anion associated with the ligand molecule [VOF₄(L)][−] in the case of THF and py. pyz molecule is due to the two bonding sites connected to two anions [(VOF₄)₂(pyz)]^{2−}. In all instances, cation is the imidazolium [(NHC)H]⁺ cation.

2.1.4 Synthesis of nitrile-based products

Reactions of liquid nitriles with oxonium [H₃O][SbF₆] salt were initially carried out in a solvent that also acted as a reagent. Synthesis in the case of PhCN proceeded through protonation of the nitrile molecule to the *s*-triazinium salt. Equivalent reaction with MeCN

or *t*BuCN did not afford any product of trimerization. However, crystallization of *t*BuCN with slow diffusion of hexane did afford trimeric product. When nitriles were mixed with oxonium salt in different molar ratios of the reagents and various organic solvents were employed to dilute reagents, other results were obtained. Use of DCM as a solvent yields in the case of PhCN a twice-protonated triazinium salt and for the *t*BuCN a dimeric carbonyl amidinium cation. Reaction in MeCN as a solvent did not generate any product of dimerization or trimerization. All synthesis procedures with the oxonium salts were executed under inert conditions.

2.1.5 Raman spectroscopy

Solid samples were loaded inside the glove box into the 0.3 mm quartz capillaries, which were previously dried in an oven at 160 °C. Raman spectra were recorded at room temperature on a Horiba Jobin Yvon Labram-HR spectrometer coupled with an Olympus BXFM-ILHS microscope. Samples were excited by the 633 nm emission line of a 24.3 mW He-Ne laser with a power output of 14 mW on the sample. The instrument was calibrated to the peak from the silicon wafer. Spectra were recorded and analyzed with LabSpec software [297].

2.1.6 NMR spectroscopy

Samples were loaded into NMR tubes in a glove box under argon atmosphere. Decomposition and reduction of some vanadium(V) oxide fluoride compounds in organic solvents and consequential elimination of HF [296] compelled us to use inlays for NMR tubes made from FEP material. This approach removed otherwise present signals of silicon and boron fluoride species. NMR spectra (^1H , ^{13}C , ^{19}F , ^{51}V , ^{93}Nb) were recorded at the Slovenian NMR Centre at the National Institute of Chemistry, using Agilent Technologies Unity Inova 300 MHz spectrometer with a broadband probe (^1H at 303.0 MHz, ^{13}C at 76.2 MHz, ^{19}F at 285.1 MHz, ^{51}V at 79.6 MHz and ^{93}Nb at 74.0 MHz). Samples were recorded at 298 K. The chemical shifts of ^1H and ^{13}C were referenced to residual signals of deuterated solvent and are reported relative to tetramethylsilane as a primary reference. ^{19}F signals were referenced to CFCl_3 in deuterated benzene as an external standard. ^{51}V signals were referenced according to lock frequency and are given relative to the neat VOCl_3 . ^{93}Nb signals were referenced according to the lock frequency and are given relative to $\text{K}[\text{NbCl}_6]$ in deuterated acetonitrile (CD_3CN). Spectra were prepared with MestReNova software [298].

2.1.7 X-ray structural analysis

Solutions for crystallization were beforehand filtered and concentrated under dynamic vacuum. Crystals suitable for X-ray single crystal diffraction were obtained from a concentrated solution stored in a refrigerator, with slow evaporation of solvent under static vacuum or by lowering of polar character of concentrated solution with slow diffusion of non-polar hexane into it. Crystals, which were usually air-sensitive, were transferred under the microscope immersed in silicon oil, perfluorodecaline or octane. They were handpicked with looped pin and mounted onto the diffractometer.

Crystal data for all compounds were collected on a Gemini A diffractometer equipped with an Atlas CCD detector, using graphite monochromated Cu K α radiation. Crystals were held under a stream of nitrogen gas at 120 K or 150 K.

The data were treated using the CrysAlisPro software suite program package [299]. Analytical absorption correction was applied to all data sets [300]. Structures were solved with the SHELXT [301] and structure refinement was performed with the SHELXL [302], both implemented in the software package Olex2 [303]. Figures were prepared with Diamond 4 software [304].

2.1.8 Elemental analysis

Roughly, 4 mg of dried powder of the products stored in a glove box were transferred into silver foils. Carbon, hydrogen and nitrogen contents were determined using CHNS elemental analyzer Vario EL cube (Elementar) operating in the CHN mode.

2.2 Computational Methods

2.2.1 Calculations of gas phase species and crystal structures

Calculations were performed in the framework of density functional theory (DFT). *In vacuo* molecular calculations were performed with the Gaussian16 program [305] using Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [306] and a D3 empirical dispersion correction of Grimme [307] with Becke-Johnson damping [308]. Electrons were described with all electron basis sets. Triple- ζ basis set with polarization functions, in particular Def2-TZVP, was used [309], [310].

Crystal structures were calculated using the PBE generalized gradient approximation [306], plane-wave basis set with ultrasoft pseudopotential [311], and the PWscf code from the Quantum ESPRESSO distribution [312]. Kohn-Sham orbitals were expanded in a plane-wave basis set up to a kinetic energy cutoff of 50 Ry (400 Ry for the charge-density cutoff); these cutoffs yield well-converged results. Ultrasoft pseudopotentials for H, C, N, O, F, Cl, Br, V and Nb were taken from the Quantum Espresso PseudoPotential library. All degrees of freedom including the unit cell size and shape were relaxed using a variable-cell Broyden-Fletcher-Goldfarb-Shanno optimization. Brillouin-zone integrations were performed using only the gamma k -point. D2 empirical dispersion correction of Grimme [313], [314], was utilized to better describe intermolecular interactions in the crystal structure.

Additionally, when appropriate, the Bader charge analyses [315] were carried out using the Bader code [316] by generating charge densities with Quantum ESPRESSO [312] using the projector-augmented-wave (PAW) potentials [317] and 1000 Ry kinetic energy cutoff for charge density.

Charge density difference plots, molecular graphics and observed interatomic interactions were produced by the XCRYSDEN graphical package [318].

2.2.2 Vibrational calculations

Calculations of vibrational frequencies for geometrically optimized neutral compounds and anions of interest were performed with the Gaussian16 program [305]. Results most comparable to experimental observations were obtained with the DFT method using the

PBE exchange-correlation functional [306]. Electrons were described with all-electron basis sets. Triple- ζ basis sets augmented with polarization and diffuse functions, that is, aug-cc-pVTZ, were used [319]–[322].

Chapter 3

Aims and Hypothesis

Products of N-heterocyclic carbenes (NHC) and late d-block metals have demonstrated superb catalytic activity, hence they have been in the spotlight of coordinative chemistry of the NHCs for the last three decades. However, recently the attention has also been given to the early d-block reagents in their highest oxidation state. Lack of their complexes with NHCs is mostly due to the oxophilic character and moisture sensitivity of the group 5 fluorides. Their stability toward air tends to improve with the formation of the NHC complex, which was continually observed in various reactions between fluorides and NHC ligand. Synthesis and subsequent crystallization were performed in order to expand the library of known coordination products. X-ray structural characterization, as a fundamental characterization method of newly prepared compounds, was employed for the description of single crystals. Peculiar structural effects were elucidated by meticulous examination of the crystal structure and later by findings of the theoretical study. The most interesting was bonding analysis in square pyramidal $[(\text{NHC})\text{VOF}_3]$ complex due to the recently proposed π -back-donation of the fluoride and chloride ligands into an empty p-orbital of carbenic carbon atom.

Fluoride donation capabilities of imidazolium fluoride salt were demonstrated with main group fluorides. Our intention was to show the utility and versatility of the imidazolium salt with the d-block metal fluorides. Reaction, isolation and crystallization was formulated to finally afford crystals of long sought discrete square pyramidal $[\text{VOF}_4]^-$ anion. The role of the sterically demanding imidazolium cation is crucial as the reaction with smaller inorganic or organic cations resulted in octahedral $[\text{VOF}_5]^{2-}$ or dimeric $[\text{V}_2\text{O}_2\text{F}_8]^{2-}$. Geometry of the anion is expected to be square pyramidal, which intuitively allows the addition of ligand at the sixth coordination site and consequently upgrades geometry to octahedral. Determination of the bonding contributors could start the discussion of a relatively unexplored field of weakly coordinated ligands to the anion.

Oxonium $[\text{H}_3\text{O}][\text{SbF}_6]$ salt is a common undesirable by-product in fluorine chemistry. Acidic cation and weakly coordinating anion are related to the super-acidic HF/SbF_5 system, which has been shown to successfully protonate nitrile molecules and form stable salts with the resulting nitrilium cations. Reactivity of the oxonium was never thoroughly studied, even though it is readily available. Herein, its capability to protonate nitrile molecules was explored in various solvents. Surprisingly, the reaction resulted in trimeric products, the crystal structure of which was determined. Equivalent trimers have previously been prepared with TfOH as a proton donor. In addition, dimeric “intermediate” product was isolated and its structure could elaborate the process of acid-activated trimerization. Acquired knowledge could be applied to synthesis of new covalent triazine frameworks.

Chapter 4

Results and Discussion

Results presented in the following chapter are:

- based on the article “The peculiar case of conformations in coordination compounds of group V pentahalides with N-heterocyclic carbene and synthesis of their imidazolium salts” published in Journal of Fluorine Chemistry [323],
- based on the article “Reactivity of VOF_3 with N-heterocyclic carbene and imidazolium fluoride: Analysis of ligand– VOF_3 bonding with evidence of a minute π -back-donation of fluoride” published in Inorganic Chemistry [324],
- part of an article, which is planned for publication in the near future with a working title “[VOF_4][−] anion with weak ligand contact: Coordinated or hydrogen bonded?”,
- part of the unpublished work regarding oligomerization of nitriles into dimeric or trimeric products.

Herein, less relevant information and results that did not fit into the scope of the prepared manuscripts are also described.

My contribution to the cited works was the preparation and execution of experiments, performance of the subsequent analyses, solution of crystal structures and their descriptions. In collaboration with other authors I prepared and interpreted NMR and Raman spectra, critically reviewed experimental data and proposed conclusions from observing similarities and differences with results from the literature. Apart from that, I have coordinated and edited the written work of other authors and prepared the material for the final publication.

Computational results and their interpretations are work of other collaborating authors, but are integral part of the first two articles and are thus presented in this thesis to provide context and explanations to the experimental observations.

(**2**) complexes revealed that they are isostructural, therefore only the structure of the former is provided in Figure 1, whereas the latter is shown in the Appendix (Figure A1). Fluorine atoms and NHC^{Dipp} ligand are placed in an octahedral arrangement around the metal center. The most significant bond distances and angles are presented in Table 2. Crystal collection data and refinement parameters are given in the Appendix (Table A12).

Table 2: Selected bond distances and angles for neutral [(NHC^{Dipp})NbF₅] (**1**) and [(NHC^{Dipp})TaF₅] (**2**) complexes. Table is based on the reference [323].

Ref.	[(NHC ^{Dipp})NbF ₅] (1)	[(NHC ^{Dipp})TaF ₅] (2)
Intramolecular bond distance [Å]		
M–F	1.865(1) (F1)	1.875(2) (F1)
	1.881(1) (F2)	1.888(2) (F2)
	1.872(2) (F3)	1.878(2) (F3)
M–C _{NHC}	2.319(2)	2.309(3)
F–C _{NHC}	2.903(2) (F1)	2.917(4) (F1)
	2.826(2) (F2)	2.844(4) (F2)
F–C _{iPr}	3.165(2) (F1, C13)	3.167(3) (F1, C13)
	3.183(2) (F2, C10)	3.188(3) (F2, C10)
Intermolecular bond distance [Å]		
F2–C3	3.180(2)	3.179(3)
M displacement [Å] ^[a]	0.145	0.124
Angle [°]		
F–M–F _{cis}	90.3(1) (F1, F1 ⁱ) ^[b]	90.5(1) (F1, F1 ⁱ) ^[b]
	89.4(1) (F1, F2 ⁱ) ^[b]	89.5(1) (F1, F2 ⁱ) ^[b]
	89.4(1) (F2, F1 ⁱ) ^[b]	89.5(1) (F2, F1 ⁱ) ^[b]
	89.6(1) (F2, F2 ⁱ) ^[b]	89.5(1) (F2, F2 ⁱ) ^[b]
	95.2(1) (F1, F3)	94.4(1) (F1, F3)
	93.7(1) (F2, F3)	93.1(1) (F2, F3)
F _{cis} –M–C _{NHC}	87.2(1) (F1)	87.8(1) (F1)
	83.9(1) (F2)	84.7(1) (F2)
F–M–F _{trans}	171.1(1)	172.5(1)
F _{trans} –M–C _{NHC}	176.6(1)	176.9(1)
F1–M–C _{NHC} –N1	50.3(2)	50.0(2)
F2–M–C _{NHC} –N1 ⁱ ^[b]	39.4(2)	39.7(2)
plane _{F1-F2-F3} –plane _{NHC}	45.8(1)	45.7(1)

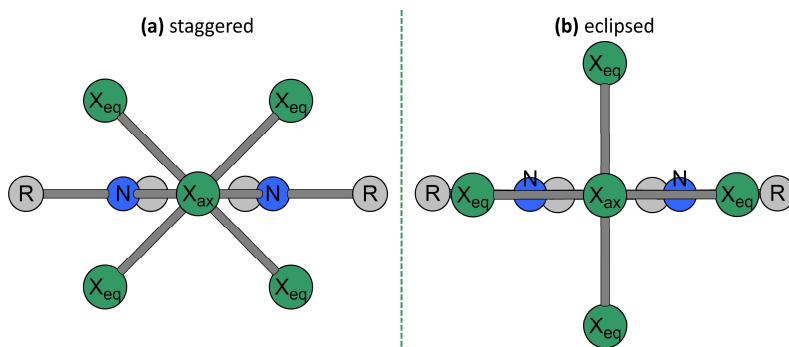
^[a] Displacement of metal center from the plane of the equatorial fluorine atoms.

^[b] Fluorine atoms are generated with symmetry operation. Symmetry code: (i) $x, 1/2-y, z$.

Surprisingly, synthesized fluoride complexes have a differently oriented MF₅ group with respect to the plane of NHC ring than other structurally characterized NHC complexes containing chlorine or bromine atoms (MX₅; X = Cl, Br) [106], [108], [109]. In particular, staggered conformation (Scheme 12a) is observed in [(NHC^{Dipp})NbF₅] (**1**), [(NHC^{Dipp})TaF₅] (**2**) and all other reported [(NHC)MF₅] (M = P, As, Sb) [327]–[330], whereas eclipsed conformation (Scheme 12b) can be seen for the related halide complexes [(NHC^{Dipp})NbCl₅] [106], [(NHC^{Dipp})TaCl₅] [109] and [(NHC^{Dipp})TaBr₅] [108]. DFT calculations of the [(NHC^{Dipp})MX₅] (M = Nb, Ta; X = F, Cl, Br) complexes predict the same conformations (see below) [108]. Additionally, a pair of equatorial chlorine or bromine

atoms of MX_5 unit perpendicular to the NHC ring are bent toward the NHC carbon atom, whereas for the fluorine atoms, such deformation is not that prominent. Initial intuitive explanation for this behavior was attributed to back-donation of the larger halogen atom into the empty p-orbital of the NHC carbon atom [109], but recent DFT calculations discourage such interpretation [107], [108], [324].

Surprisingly, an identical trend is observed in octahedrally coordinated and sterically more restricted $[(\text{NHC}^{\text{Dipp}})_2\text{TiX}_4]$ ($\text{X} = \text{F}, \text{Cl}$) complexes [331]. Examination of the TiF_4 conformation reveals that it is in a staggered position toward one of the *trans* ligands and eclipsed toward opposing second NHC^{Dipp} ligand. Since TiF_4 unit is disordered, conformation of the smaller domain is identical, only *vice versa*. All atoms of the TiF_4 unit are planar and titanium center is surrounded by ligands in a perfect octahedral geometry. On the other hand, octahedron in the $[(\text{NHC}^{\text{Dipp}})_2\text{TiCl}_4]$ complex is heavily distorted due to each pair of chlorine atoms bent toward the NHC carbon atom. TiCl_4 is oriented in the eclipsed position in relation to the planes of both *trans* NHC rings. NHC^{Dipp} ligands are tilted at the 90° angle related to each other in order to reduce the steric effect. Interestingly, the staggered conformation of TiF_4 is preferred even when less sterically demanding 1,3,4,5-tetramethylimidazol-2-ylidenes or 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidenes are used [332].



Scheme 12: Staggered (a) and eclipsed (b) conformation of the MX_5 unit in relation to the plane of the NHC ring in $[(\text{NHC})\text{MX}_5]$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{F}, \text{Cl}$; $\text{R} = \text{NHC}^{\text{Me}}, \text{NHC}^{\text{Ph}}, \text{NHC}^{\text{Mes}}, \text{NHC}^{\text{Dipp}}$) complexes. Due to the top-down view, the M and NHC carbon atoms lie in the plane of the NHC ring and are positioned directly behind the axial X atom. Scheme is based on the reference [323].

$\text{M}-\text{C}$ ($\text{M} = \text{Nb}, \text{Ta}$) distances are similar in both complexes (Nb 2.319(2) Å; Ta 2.309(3) Å), which shows the possible influence of Lewis acidity on the $\text{M}-\text{C}$ bond. While the ionic radii of niobium and tantalum are the same (0.78 Å) [333] and the volumes of the octahedral $[\text{MF}_6]^-$ ($\text{M} = \text{Nb}, \text{Ta}$) anions are fairly similar (Nb 125 Å³, Ta 128 Å³) [334], the marginally shorter $\text{Ta}-\text{C}$ distance could only be ascribed to the somewhat stronger Lewis acidity of the TaF_5 in comparison to NbF_5 [335]. Despite a different orientation of the pentahalide group to the NHC^{Dipp} ligand, comparison of $\text{M}-\text{C}$ ($\text{M} = \text{Nb}, \text{Ta}$) bond in analogous complexes $[(\text{NHC}^{\text{Dipp}})\text{NbCl}_5]$ (2.396(12) Å at 100 K) [106], $[(\text{NHC}^{\text{Dipp}})\text{TaCl}_5]$ (2.373(5) Å at 296 K) [109] and $[(\text{NHC}^{\text{Dipp}})\text{TaBr}_5]$ (2.383(10) Å at 100 K) [108] shows that fluoride complexes $[(\text{NHC}^{\text{Dipp}})\text{MF}_5]$ ($\text{M} = \text{Nb}$ (1), Ta (2)) display a shorter $\text{M}-\text{C}$ bond probably as a consequence of higher Lewis acidity of MF_5 molecule in comparison to MX_5 ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$). Distance of $\text{M}-\text{F}$ ($\text{M} = \text{Nb}, \text{Ta}$) bonds complies with the $\text{M}-\text{F}_{\text{cis}}$ in $[\text{TaF}_4(\text{CH}(\text{SiMe}_3)_2)]_n$ complex (203 K) [336], while $(\text{NPPH}_3)^-$ and 2-[(2,6-diisopropylphenyl)iminomethyl]phenol (dpimpH) ligands form a stronger $\text{M}-\text{L}$ bond

and consequently longer M–F bonds [337], [338]. We did not observe any elongation of the M–F bond *trans* to the NHC molecule, thus negating a possible *trans* effect proposed for [(NHC^{Dipp})TaCl₅] [109].

Octahedral geometry is slightly distorted with Nb or Ta cation being displaced from the plane of four equatorial fluorine atoms (F1-F1ⁱ-F2-F2ⁱ) toward *trans* fluorine atom (F5) by 0.145 Å or 0.124 Å, respectively (Table 2). C2–M–F_{cis} angles in complexes [(NHC^{Dipp})MF₅] (M = Nb (**1**), Ta (**2**)) are smaller than 90°, which might be due to the electron repulsive forces between fluorine atoms. Currently these are the only examples where *cis* fluorine atoms are moved toward an organic ligand in comparison to the aforementioned structurally characterized [(L)MF₅] (M = Nb, Ta; L = CH(SiMe₃)₂, (NPPh₃)[−], dpimpH) complexes [336]–[338].

4.1.2 Structural optimization of [(NHC)NbF₅] and [(NHC)NbCl₅] complexes

Unusual experimental results concerning the orientation of the MX₅ (M = Nb, Ta; X = F, Cl) unit with respect to the NHC ligand prompted us to examine whether theoretical analyses support the observed crystallographic results. We studied the rotation of the NbX₅ group in regard to the use of different bulky substituents (“wingtips”) on the heterocyclic base. Herein, the structural features of the isolated [(NHC)NbX₅] (X = F, Cl; NHC = NHC^{Me}, NHC^{Ph}, NHC^{Mes}, NHC^{Dipp}) products are discussed with the assistance of the DFT calculations. Some previous studies already reported structural optimizations of several pertinent complexes, i.e. [(NHC)NbCl₅] and [(NHC^{Dipp})MX₅] (M = Nb, Ta; X = F, Cl, Br) [106], [108], but they lack some of the currently relevant [(NHC)NbF₅] ones, hence we recalculated them all for easier comparison. Little structural changes were predicted on replacing Nb with Ta [108], therefore we limited our calculations only to the niobium complexes.

NbF₅ remains in a staggered position regardless of the used NHC ligand and its steric factor (Figure 2a–c). On the other hand, NbCl₅ maintains its staggered conformation only with NHC ligand with the smallest methyl “wingtips” (Figure 2d), but for larger phenyl “wingtips”, the transition toward eclipsed conformation can already be observed (Figure 2e). This trend continues to the point that for the largest of the tested ligands (NHC^{Mes}, NHC^{Dipp}) eclipsed conformation is preferred (Figure 2f) and corresponds well to the experimentally determined structure [106].

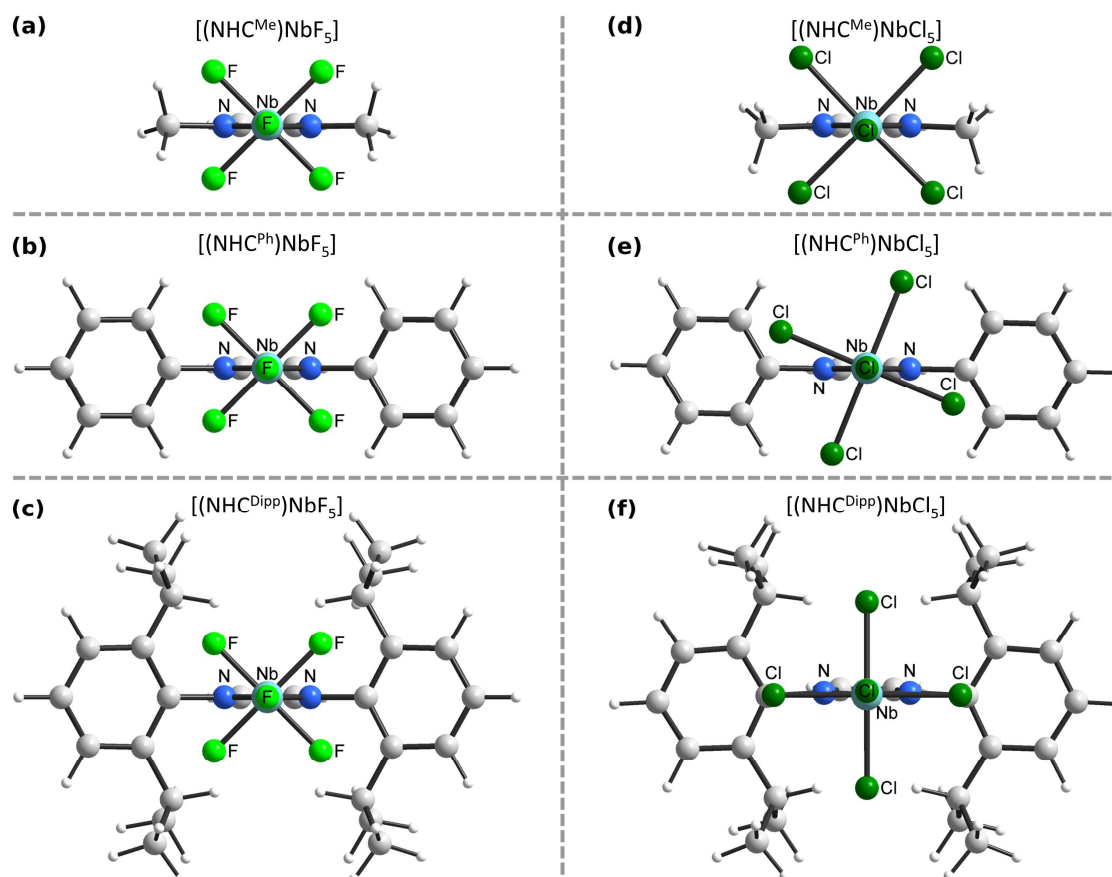


Figure 2: Optimized structures of $[(\text{NHC})\text{NbF}_5]$ ($\text{NHC} = \text{NHC}^{\text{Me}}$ (a), NHC^{Ph} (b), NHC^{Dipp} (c)) and $[(\text{NHC})\text{NbCl}_5]$ ($\text{NHC} = \text{NHC}^{\text{Me}}$ (d), NHC^{Ph} (e), NHC^{Dipp} (f)) complexes. Figure is based on the reference [323].

The calculated Nb–C bond distance for $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (2.38 Å) is noticeably longer than the experimental value (2.32 Å), which can be in part due to the neglect of crystal packing effects in calculations [324]. However, this overestimation of the Nb–C bond length has no effect on the eclipsed *vs.* staggered conformation, because calculations with the Nb–C bond distance constrained to the experimental value predict the same preference. Interestingly, calculations reveal that $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ apparently displays two local minima, i.e. staggered and eclipsed, with almost the same stability (the fact that experimentally only staggered conformation is observed can be therefore attributed to crystal packing effects). To shed more light on the stability of the two conformations, we calculated energy profiles for the rotation of NbX_5 group ($\text{X} = \text{F}, \text{Cl}$) around the Nb–C bond from staggered to eclipsed conformation and Figure 3 shows the corresponding results for $[(\text{NHC}^{\text{Me}})\text{NbX}_5]$ and $[(\text{NHC}^{\text{Dipp}})\text{NbX}_5]$; these calculations were performed by constraining only the rotation angle and relaxing other degrees of freedom. Staggered conformation is clearly more stable in the case of NHC^{Me} for both pentahalides, whereas eclipsed conformation is significantly more stable for $[(\text{NHC}^{\text{Dipp}})\text{NbCl}_5]$. However, for $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$, the energy is rather insensitive to the rotation of NbF_5 around the Nb–C bond, because all the energies are within 0.3 kJ/mol.

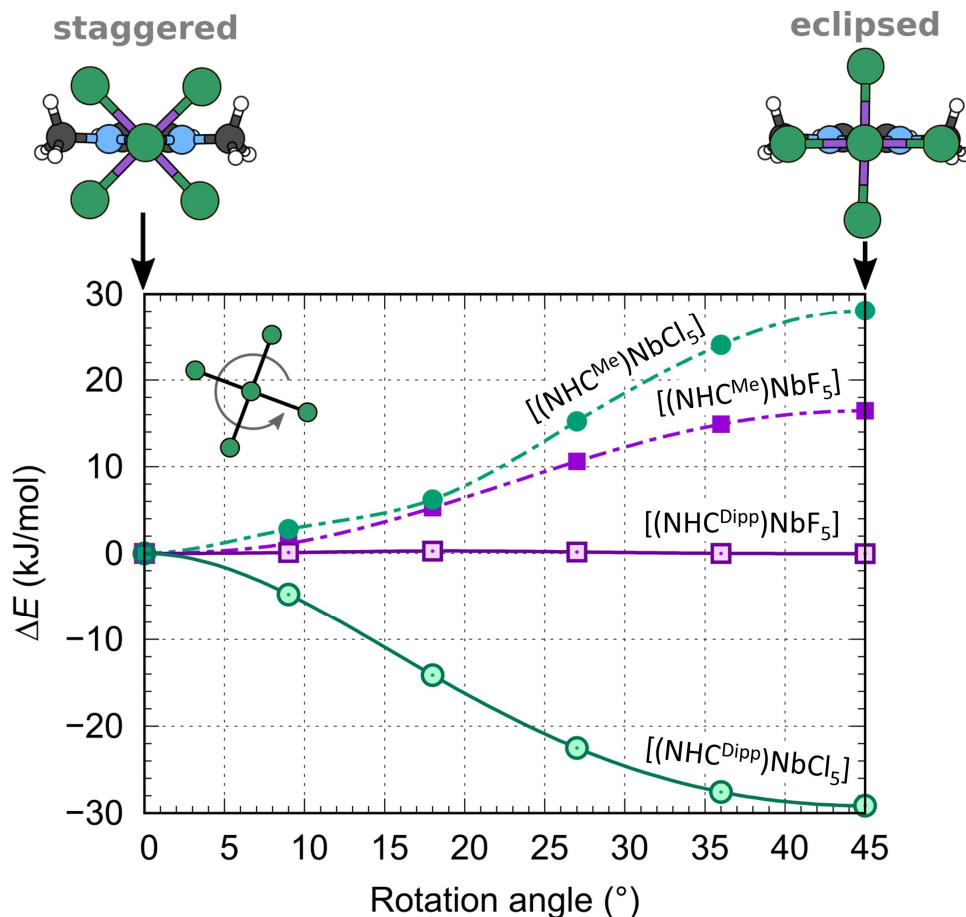


Figure 3: PBE calculated relative stabilities of conformations of $[(\text{NHC}^{\text{Me}})\text{NbX}_5]$ and $[(\text{NHC}^{\text{Dipp}})\text{NbX}_5]$ ($\text{X} = \text{F}, \text{Cl}$) on the rotation angle of the NbX_5 group around the $\text{Nb}-\text{C}$ bond (rotation angle of 0° corresponds to staggered and 45° to eclipsed conformation). Figure is based on the reference [323]. From the obtained results, we can conclude that the size of the “wingtips” has a little effect on the orientation of the NbF_5 group and a strong one for NbCl_5 , because the latter undergoes transition from staggered to eclipsed conformation as passing from small methyl to large mesityl and diisopropylphenyl “wingtips”. Analysis suggests that the orientation of NbX_5 group is due to an interplay between attractive hydrogen bonding interactions of $\text{C}-\text{H} \cdots \text{X}$ type (Figure 4) and steric repulsion between equatorial halogen atoms and “wingtips”. The susceptibility of NbCl_5 conformation on the size of the “wingtips” can be attributed to a larger size of $[\text{Cl}]^-$ anion (ionic radius of $1.81 \text{ \AA}$) compared to $[\text{F}]^-$ anion (ionic radius $1.33 \text{ \AA}$) [333], which causes stronger steric repulsion. This steric repulsion can be appreciated from the structure of (constrained) eclipsed conformation of $[(\text{NHC}^{\text{Me}})\text{NbCl}_5]$ (Figure 5b); the large Cl atoms are apparently too close to methyl “wingtips” and consequently up-shift so significantly as to end up above the Nb cation (this movement is indicated by small red arrows in Figure 5b). In contrast, such a remarkable up-shift does not happen for NbF_5 group (Figure 5a), because F atoms are smaller. This suggests that $[(\text{NHC})\text{NbF}_5]$ complexes opt for a stronger and larger number of $\text{C}-\text{H} \cdots \text{F}$ interactions, which is met by staggered conformation (the reason that for the largest NHC^{Dipp} ligand the staggered and eclipsed conformations are almost energy degenerate can be attributed to large and flexible enough “wingtips” which can adopt to both conformations). In contrast, $[(\text{NHC})\text{NbCl}_5]$ complexes take the conformation which reduces the steric repulsion and this condition is met by staggered conformation for methyl “wingtips” and by eclipsed conformation for larger “wingtips”.

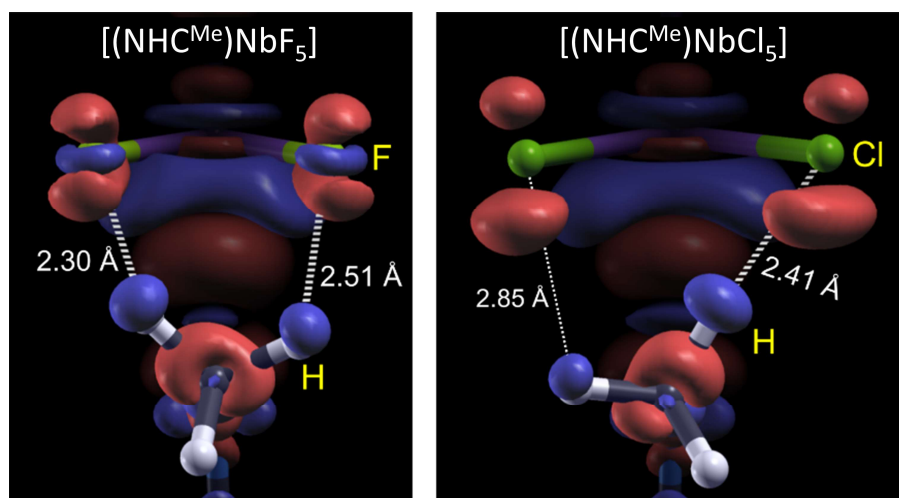


Figure 4: Electron charge density difference of $[(\text{NHC}^{\text{Me}})\text{NbF}_5]$ (left) and $[(\text{NHC}^{\text{Me}})\text{NbCl}_5]$ (right). Electron densities were calculated as $\Delta\rho(\mathbf{r}) = \rho^{[(\text{L})\text{NbX}_5]}(\mathbf{r}) - \rho^{\text{L}}(\mathbf{r}) - \rho^{\text{NbX}_5}(\mathbf{r})$; where $\rho^{[(\text{L})\text{NbX}_5]}(\mathbf{r})$ stands for electron density of the $[(\text{NHC}^{\text{Me}})\text{NbX}_5]$ ($\text{X} = \text{F}, \text{Cl}$) complex, $\rho^{\text{L}}(\mathbf{r})$ and $\rho^{\text{NbX}_5}(\mathbf{r})$ represent the electron densities of the NHC^{Me} and NbX_5 fragments, respectively, having the same geometry as in the complex. Electron excess regions are coloured red, while electron deficit regions are blue (isosurfaces are drawn at $\pm 0.002 \text{ e/Bohr}^3$). The illumination focuses on $\text{H} \cdots \text{X}$ ($\text{X} = \text{F}, \text{Cl}$) interactions (in the front), which are evident from the red kidney-like electron accumulation region below the two halogen atoms and the blue charge deficit regions above the neighbouring H atoms. $\text{H} \cdots \text{X}$ bond lengths are also given. Figure is based on the reference [323].

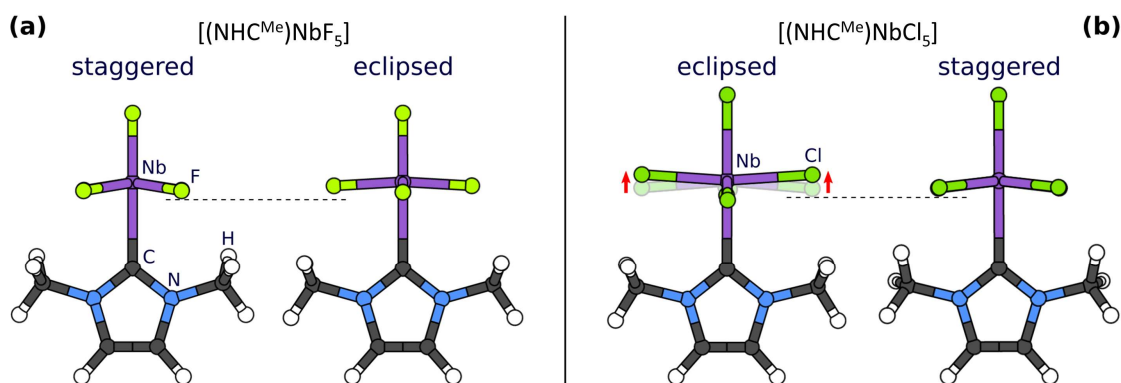


Figure 5: Calculated side-view snapshots of staggered and (constrained) eclipsed structures of $[(\text{NHC}^{\text{Me}})\text{NbF}_5]$ (a) and $[(\text{NHC}^{\text{Me}})\text{NbCl}_5]$ (b). The shaded Cl atoms and red arrows in (b) indicate the up-shift of the two Cl atoms; horizontal dashed lines are drawn for the same purpose. Figure is based on the reference [323].

4.1.3 Synthesis and structural analysis of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ salts

Reaction between MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) and imidazolium fluoride $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ in equimolar ratio in MeCN yields $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{MF}_6]$ ($\text{M} = \text{Nb}$ (**3**), Ta (**4**)) salts. Air-stable

crystals of imidazolium hexafluoride salt form during the crystallization at ambient temperature under static vacuum. Anionic part of the salt is highly disordered despite the high quality of crystals, low temperature of the experiment (120 K) and extensive collection of data. Attempts to obtain crystals of the products from DCM likewise at the ambient temperature yielded only microcrystalline powder. However, crystallization of concentrated solution with either MeCN or DCM at lower temperature ($-30\text{ }^{\circ}\text{C}$) yielded $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{MF}_6]\cdot 2\text{MeCN}$ ($\text{M} = \text{Nb}$ (**3a**), Ta (**4a**)) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{MF}_6]\cdot \text{DCM}$ ($\text{M} = \text{Nb}$ (**3b**), Ta (**4b**)) solvates, respectively. Introduction of solvent molecules in crystal structure wedges the anion into its place and prevents disorder of the anion, which is observed in salts without the presence of solvent molecules. Due to the similarity of the structural characteristics of niobium and tantalum products, only tantalum salts (**4a**, **4b**) will be described and depicted (Figure 6 and Figure 7) here. However, selected bond distances and angles for either of the salts are presented in Table 3 and Table 4. Figures of isostructural niobium salts are shown in the Appendix along with the information regarding the disordered isopropyl group of the imidazolium cation, crystal collection data and refinement parameters for all the salts (Figure A2–Figure A7, Table A3–Table A6, Table A13 and Table A14).

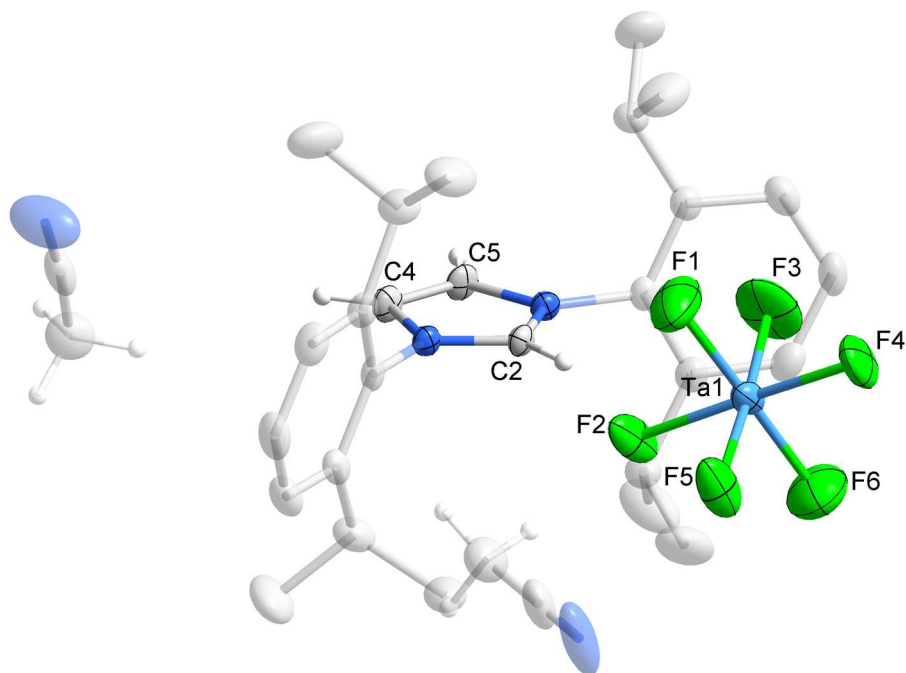


Figure 6: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot 2\text{MeCN}$ (**4a**) salt. Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ are shaded, less relevant hydrogen atoms are omitted and only domain A of the MeCN molecule is shown. Figure is based on the reference [323].

Anion in the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot 2\text{MeCN}$ (**4a**) crystals exhibits octahedral geometry (Figure 6), with Ta–F2 bond being noticeably elongated, probably due to the fairly strong C2–H $\cdots$ F2 interaction (2.997(4) Å). Most *cis* F–M–F angles are of a similar size and only F2–Ta–F5 and F3–Ta–F4 deviate for more than 2° from the ideal angle for octahedral coordination. Interestingly, they are on the opposing side. One MeCN molecule lies neatly in between two cations beside anion with the shortest F5–C31 contact at 3.161(4) Å. The

other MeCN molecule fills the void between diisopropylphenyl wings and has no strong connection with its surrounding, which is probably causing its disordering. Each of the two domains (A, B) has 50 % occupancy.

Table 3: Selected bond distances and angles for $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot 2\text{MeCN}$ (**3a**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot 2\text{MeCN}$ (**4a**) salts. Table is based on the reference [323].

Ref.	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot 2\text{MeCN}$ (3a)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot 2\text{MeCN}$ (4a)
Intramolecular bond distance [$\text{\AA}$]		
M–F	1.873(2) (F1)	1.889(2) (F1)
	1.900(1) (F2)	1.910(2) (F2)
	1.857(2) (F3)	1.863(2) (F3)
	1.876(1) (F4)	1.886(2) (F4)
	1.884(1) (F5)	1.892(2) (F5)
	1.856(2) (F6)	1.868(2) (F6)
Intermolecular bond distance [$\text{\AA}$]		
F–C	3.002(3) (F2, C2)	2.997(4) (F2, C2)
	3.025(3) (F5, C4)	3.027(4) (F5, C4)
	3.195(3) (F5, C5)	3.193(4) (F5, C5)
Angle [$^\circ$]		
F–M–F _{cis}	89.7(1) (F1, F2)	89.4(1) (F1, F2)
	88.9(1) (F1, F3)	89.1(2) (F1, F3)
	89.9(1) (F1, F4)	90.0(1) (F1, F4)
	89.5(1) (F1, F5)	89.1(1) (F1, F5)
	89.5(1) (F2, F3)	89.6(1) (F2, F3)
	87.6(1) (F2, F5)	87.7(1) (F2, F5)
	89.9(1) (F2, F6)	90.0(1) (F2, F6)
	93.8(1) (F3, F4)	93.5(1) (F3, F4)
	91.3(1) (F3, F6)	91.3(2) (F3, F6)
	89.1(1) (F4, F5)	89.2(1) (F4, F5)
	90.6(1) (F4, F6)	90.6(1) (F4, F6)
	90.3(1) (F5, F6)	90.4(1) (F5, F6)
F–M–F _{trans}	179.5(1) (F1, F6)	179.2(1) (F1, F6)
	176.7(1) (F2, F4)	176.8(1) (F2, F4)
	176.7(1) (F3, F5)	176.8(1) (F3, F5)

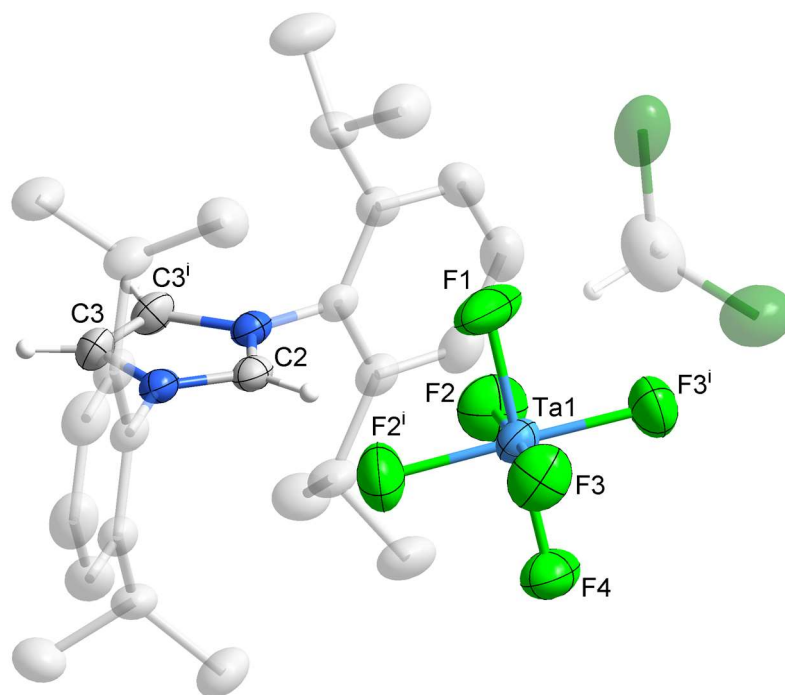


Figure 7: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot\text{DCM}$ (**4b**) salt. Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ are shaded and less relevant hydrogen atoms are omitted. Symmetry code: (i) $x, 3/2-y, z$. Figure is based on the reference [323].

Molecules of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot\text{DCM}$ (**4b**) solvate crystals lie on the mirror plane and are generated with symmetry code: $x, 3/2-y, z$ (Figure 7). $[\text{TaF}_6]^-$ anion is closer to the ideal octahedral geometry than the anion in the MeCN solvate. Fluorine atoms that are in close proximity of imidazolium cation and have possible electrostatic interactions with it ($\text{C2-H}\cdots\text{F2}$ 3.255(3) Å and $\text{C3-H}\cdots\text{F4}$ 3.191(3) Å) make for slightly elongated Ta–F bonds in the anion. $\text{C2-H}\cdots\text{F2}$ interaction of two fluorine atoms to single C–H bond might contribute to a smaller $\text{F2-M-F2}^{\text{i}}$ angle. DCM molecule that lies above the $[\text{TaF}_6]^-$ anion and between four cations does not show any signs of disorder. The shortest contact between DCM and $[\text{TaF}_6]^-$ anion ($\text{F1}\cdots\text{C16}$ 3.122(5) Å) is a consequence of electrostatic interactions.

Table 4: Selected bond distances and angles for $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot\text{DCM}$ (**3b**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot\text{DCM}$ (**4b**) salts. Table is based on the reference [323].

Ref.	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot\text{DCM}$ (3b)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot\text{DCM}$ (4b)
Intramolecular bond distance [$\text{\AA}$]		
M–F	1.872(2) (F1)	1.875(4) (F1)
	1.889(2) (F2)	1.900(3) (F2)
	1.870(2) (F3)	1.880(3) (F3)
	1.891(2) (F4)	1.909(4) (F4)
Intermolecular bond distance [$\text{\AA}$]		
F–C	3.255(3) ^[a] (F2, C2)	3.280(6) ^[a] (F2, C2)
	3.191(3) (F4, C3)	3.199(6) (F4, C3)
Angle [$^\circ$]		
F–M–F _{cis}	90.4(1) (F1, F2)	90.8(2) (F1, F2)
	90.4(1) (F1, F3)	90.5(2) (F1, F3)
	86.8(1) (F2, F2) ^[b]	87.3(2) (F2, F2) ^[b]
	91.4(1) (F2, F3) ^[b]	91.0(2) (F2, F3) ^[b]
	90.3(1) (F2, F4)	89.9(2) (F2, F4)
	90.4(1) (F3, F3) ^[b]	90.7(2) (F3, F3) ^[b]
	88.9(1) (F3, F4)	88.7(1) (F3, F4)
	179.1(1) (F1, F4)	179.0(2) (F1, F4)
F–M–F _{trans}	178.0(1) (F2, F3)	177.8(2) (F2, F3)

^[a] Bond distance larger than sum of van der Waals radii [339].

^[b] Fluorine atoms are generated with symmetry operation. Symmetry code: (i) $x, 1/2-y, z$.

We have further tried to synthesize larger $[\text{MF}_7]^{2-}$ ($\text{M} = \text{Nb}, \text{Ta}$) anion with the addition of one equivalent of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ salt to the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{MF}_6]$ salt or treating one equivalent of initial MF_5 with two equivalents of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ salt. According to the ^{19}F NMR spectroscopy, the signals were of $[\text{MF}_6]^-$ and unreacted imidazolium reagent, however some additional peaks of possible by-products were starting to appear. Crystallization of the reaction mixture did not yield any new compound.

Attempts to prepare mixed halide anions with the addition of imidazolium fluoride to the MCl_5 resulted in a red solution, which gradually lost its intense color and transformed into a pale yellow. Fluoride salt most probably promoted the auto-ionization process of the MCl_5 reagent, since the X-ray analysis of the obtained single crystals revealed imidazolium salt with the $[\text{MCl}_6]^-$. Similar results were obtained in the reaction of the fluoride congener, imidazolium chloride $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{Cl}]$, with the MF_5 .

4.1.4 Raman spectroscopy

Raman spectroscopy was used in order to detect MF_5 and $[\text{MF}_6]^-$ ($\text{M} = \text{Nb}, \text{Ta}$) species in the samples. Because of the large number of bands of the neutral NHC^{Dipp} ligand or $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation, the assignment of the bands related to the M–F vibrations is challenging. Spectra of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) and $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) complexes are presented in Figure 8, while the full range spectra of $[(\text{NHC}^{\text{Dipp}})\text{MF}_5]$ ($\text{M} = \text{Nb}$ (**1**), Ta (**2**)) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{MF}_6]$ ($\text{M} = \text{Nb}$ (**3**), Ta (**4**)) can be found in the Appendix (Figure A14 and Figure A15). Bands for MF_5 in neutral $[(\text{NHC}^{\text{Dipp}})\text{MF}_5]$ are at 677 cm^{-1} ($\text{M} = \text{Nb}$ (**1**)) and 691 cm^{-1} ($\text{M} = \text{Ta}$ (**2**)) and can be assigned to the M–F vibrations. Metal in these

complexes is octahedrally coordinated with five fluorine atoms and additional NHC carbon atom from NHC^{Dipp} . Therefore we compared our results with $[\text{MF}_6]^-$ species in which Raman active vibration ν_1 can be found at 683 cm^{-1} ($\text{M} = \text{Nb}$) and at 692 cm^{-1} ($\text{M} = \text{Ta}$) [340].

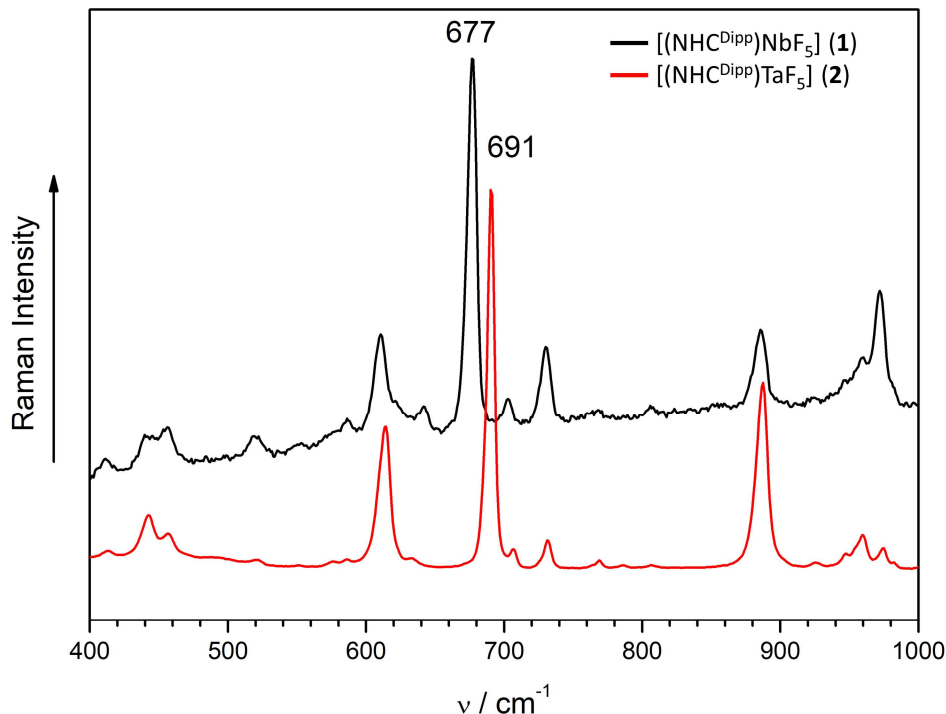


Figure 8: Raman spectra of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) and $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) with assigned bands for M–F vibrations. Figure is based on the reference [323].

4.1.5 NMR spectroscopy

After dissolution of the $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) powder in deuterated benzene (C_6D_6), a characteristic split of isopropyl doublets is seen in the ^1H NMR spectrum. In the ^{19}F NMR spectrum, a signal of the complex (**1**) is at $\delta_{\text{F}} = 152.5\text{ ppm}$ (Table 5), which differs substantially from the value previously reported $\delta_{\text{F}} = 131.4\text{ ppm}$ for the complex (**1**) in deuterated toluene [108]. However, in the experiment with excess NbF_5 , authors measured chemical shift ($\delta_{\text{F}} = 156\text{ ppm}$) that was much closer to our observations. Interestingly, at variance with the aforementioned study we were not able to observe any signal in the ^{93}Nb NMR spectrum that could be assigned to the neutral compound (**1**). According to the ^{19}F and ^{93}Nb NMR spectra, an insignificant amount of $[\text{NbF}_6]^-$ anion is present in every sample, which can be detected as poorly resolved multiplets at $\delta_{\text{F}} = 104.6\text{ ppm}$ and $\delta_{\text{Nb}} = -1550.2\text{ ppm}$. Addition of deuterated acetonitrile (CD_3CN) to the $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) converts it into the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ salt (**3**) as described before [108], [341]. In the ^{19}F and ^{93}Nb NMR spectra, the only observed signals are decet ($\delta_{\text{F}} = 101.9\text{ ppm}$, $J_{\text{F-Nb}} = 336.4\text{ Hz}$) and septet ($\delta_{\text{Nb}} = -1557.7\text{ ppm}$, $J_{\text{Nb-F}} = 336.1\text{ Hz}$) of $[\text{NbF}_6]^-$ anion, respectively. In the ^1H NMR spectrum, the chemical shifts of the NHC backbone protons and the phenyl protons are shifted downfield compared to the neutral complex and are in agreement with the chemical structure of the imidazolium cation $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$. Contrary to expectation, no peak is observed for a proton at the carbene site and the signal of the imidazolium backbone protons remains a singlet. This is likely the result of deuteration of the carbene site through reaction with the deuterated solvent CD_3CN . Since peaks are well

resolved and chemical shifts agree with those of the imidazolium cation, this excludes the possibility of the NHC^{Dipp} being coordinated to the cationic fragment $[\text{MF}_4]^+$ ($\text{M} = \text{Nb}, \text{Ta}$) as it was proposed for auto-ionized compounds $[(\text{NHC})_2\text{NbCl}_4][\text{NbCl}_6]$ [108], [109]. In deuterated dichloromethane (CD_2Cl_2), similar degradation of neutral complex **(1)** proceeds, albeit at a slower rate. In the ^{19}F NMR spectrum, a peak at $\delta_{\text{F}} = 150.5$ ppm was assigned to the complex, but $[\text{NbF}_6]^-$ anion's dectet ($\delta_{\text{F}} = 102.4$ ppm, $J_{\text{F-Nb}} = 333.8$ Hz) is also present. In a matter of weeks, additional signals were detected in the ^{19}F NMR spectrum, while in the ^1H NMR spectrum peaks of the neutral complex **(1)** prevail. In the ^{93}Nb NMR spectrum, only the signal of the $[\text{NbF}_6]^-$ anion ($\delta_{\text{Nb}} = -1553.6$ ppm, $J_{\text{Nb-F}} = 335.1$ Hz) is observed.

Powdered $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ **(2)** dissolved in C_6D_6 shows nearly identical ^1H NMR spectrum as $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ **(1)**. In the ^{19}F NMR spectrum, a major signal at $\delta_{\text{F}} = 82.2$ ppm (Table 5) is assigned to the neutral complex and there is negligible amount of $[\text{TaF}_6]^-$ anion ($\delta_{\text{F}} = 40.3$ ppm). In addition, some other small yet noticeable peaks are detected, which could be ascribed to various imidazolium fluoride compounds, but we were unable to isolate and characterize any of them. These minor peaks are also visible in CD_3CN and CD_2Cl_2 at comparable chemical shifts. Similarly to the previously described deuteration of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ **(1)** in polar CD_3CN , the same reaction takes place with tantalum complex **(2)**, although it advances more gradually. Therefore, we were able to detect in the ^{19}F NMR spectrum a signal for a neutral compound **(2)** at $\delta_{\text{F}} = 79.5$ ppm. However, decomposition of tantalum complex **(2)** in CD_2Cl_2 proceeds faster than for niobium complex **(1)**. In the ^{19}F NMR spectrum, the most intensive signal at $\delta_{\text{F}} = 80.9$ ppm is assigned to complex **(2)**, but after a few days, the peaks of the imidazolium cation in the ^1H NMR spectrum become noticeably more intense same as with the peaks of decomposition products in the ^{19}F NMR spectrum.

^1H NMR spectra of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{MF}_6]$ ($\text{M} = \text{Nb}$ **(3)**, Ta **(4)**) in CD_3CN or CD_2Cl_2 reveal signals of imidazolium cation, as expected. In the ^{19}F NMR spectrum of **(3)** in CD_3CN a well-resolved dectet of $[\text{NbF}_6]^-$ is observed at $\delta_{\text{F}} = 102.1$ ppm ($J_{\text{F-Nb}} = 336.2$ Hz), while in CD_2Cl_2 the dectet is at $\delta_{\text{F}} = 102.8$ ppm ($J_{\text{F-Nb}} = 335.2$ Hz). The ^{93}Nb spectrum shows a septet at $\delta_{\text{Nb}} = -1557.6$ ppm ($J_{\text{Nb-F}} = 336.3$ Hz) and $\delta_{\text{Nb}} = -1553.0$ ppm ($J_{\text{Nb-F}} = 335.0$ Hz), in CD_3CN and CD_2Cl_2 , respectively (Table 5). Signals corresponding to $[\text{TaF}_6]^-$ anion can be detected in the ^{19}F NMR spectrum of **(4)** in CD_3CN at $\delta_{\text{F}} = 38.1$ ppm and in CD_2Cl_2 at $\delta_{\text{F}} = 39.0$ ppm. Interestingly, in ^{19}F NMR spectra of both salts **(3, 4)** in either of the solvents, no additional signals indicating possible decomposition are observed. All NMR spectra can be found in the Appendix (Figure A17–Figure A43).

Table 5: Chemical shifts in ^{19}F NMR spectra of the compounds $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ **(1)**, $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ **(2)**, $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ **(3)**, $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ **(4)** in CD_3CN , CD_2Cl_2 and C_6D_6 . Table is based on the reference [323].

Ref.	$[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (1)	$[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (2)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ (3)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ (4)
δ_{F} [ppm]				
CD_3CN	/[a]	79.5	102.1	38.1
CD_2Cl_2	150.5	80.9	102.8	39.0
C_6D_6	152.5	82.2	/[a]	/[a]

[a] Not applicable due to fast degradation or poor solubility (see text).

4.2 Compounds of Vanadium(V) Oxide Trifluoride with Imidazolium-Based Reagents

This chapter is based on the article “Reactivity of VOF_3 with N-heterocyclic carbene and imidazolium fluoride: Analysis of ligand- VOF_3 bonding with evidence of a minute π -back-donation of fluoride” published in *Inorganic Chemistry* [324].

4.2.1 Synthesis and structural characterization of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (NHC^{Dipp}) is an N-heterocyclic carbene that has become, since its isolation, a widely utilized ligand for late transition metals in low and medium oxidation states, while oxophilic metal species in their highest oxidation states received considerably less attention [76], [110], [342], [343]. Using a bulky neutral NHC^{Dipp} in a reaction with VOF_3 in ethers (THF, diethyl ether) leads to the formation of the expected $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**). To obtain pure crystals of the neutral complex and remove any anionic vanadium oxide fluoride (VOF) species, crystals were washed with small amounts of MeCN. Our $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex is the first reported coordination compound of VOF_3 with NHC and the second structurally determined NHC complex with metal oxide fluoride (MOF). Interestingly, the first reported NHC-MOF compound contained a metal from the same d-block group – niobium [78]. The molecular structure of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex is shown in Figure 9 and selected bond lengths and angles are given in Table 6. Bond valence sum, crystal collection data and refinement parameters are given in the Appendix (Table A2 and Table A15).

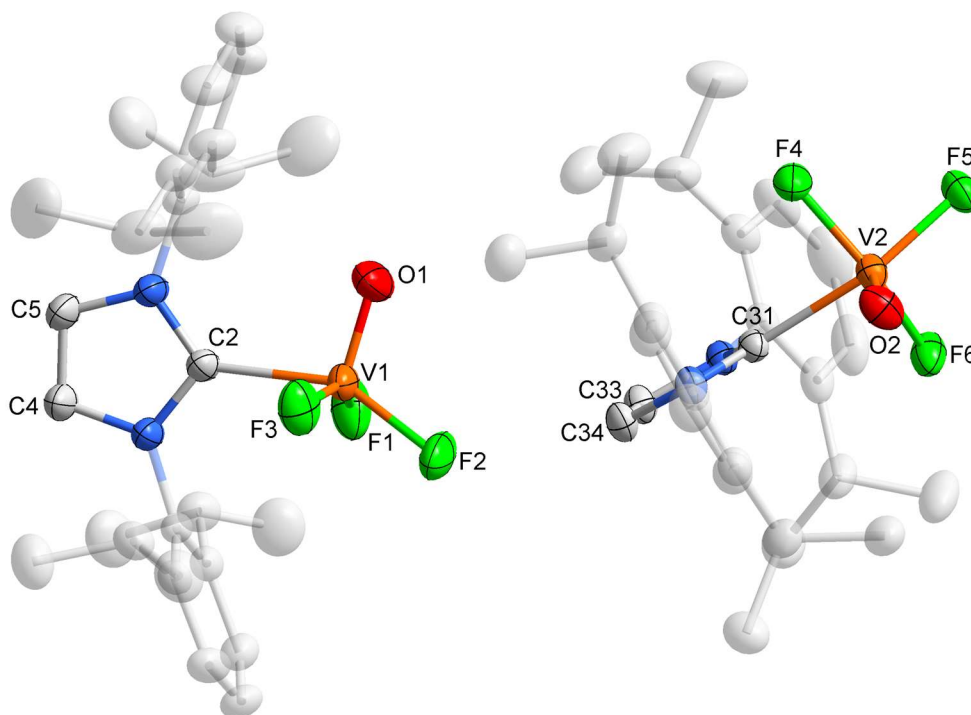


Figure 9: Molecular structure of the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex (both subunits are presented). Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of NHC^{Dipp} are shaded, hydrogen atoms are omitted and only domain A of the isopropyl group is shown. Figure is based on the reference [324].

In the crystal structure, the asymmetric unit consists of two separate $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) subunits with the $86.58(7)^\circ$ dihedral angle between both planes of NHC rings. Both subunits are connected by hydrogen interactions, which consequently prevent disorder. However, positional disorder of two isopropyl groups is present within the first subunit. Interestingly, occupancy of both disordered groups is equivalent, which suggests that observed orientational disorders are somehow related. Additional information of this disorder is provided in the Appendix (Figure A8, Table A7 and Table A8). Due to substantial structural similarities between subunits, only the results of the first subunit are reported here, but the information about the second subunit is available in Table 6. The coordination sphere of vanadium(V) center is distorted square pyramidal, where three fluorine atoms form the corners of the distorted square with the fourth corner being occupied by the C_{NHC} atom from the NHC^{Dipp} ligand. The oxygen atom is in the apical position of the pyramid with the V1-O1 bond length being $1.558(2)$ Å. Although τ_5 index with a value of $6.7 \cdot 10^{-5}$ indicates square pyramidal geometry of the complex, the distances between the opposite basal atoms differ significantly (F1-F3 $3.428(2)$ Å and F2-C2 $3.808(2)$ Å), which is obviously due to different chemical characteristics of F and C atoms. The V-F bond *trans* to the V-C_{NHC} bond is slightly elongated (V1-F2 $1.804(1)$ Å) in comparison to the *cis*-fluorides (V1-F1 $1.771(1)$ Å and V1-F3 $1.781(1)$ Å). Recently, it was shown in the trifluoridoorganogold(III) complex $[(\text{NHC}^{\text{SIMes}})\text{AuF}_3]$ ($\text{SIMes} = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazolidin-2-ylidene}$) that, in contrast to F_{cis} , F_{trans} ligand involved in such elongated $\text{M-F}_{\text{trans}}$ bond is capable of substitution and could be utilized for selective fluorination reactions [344]. However, the elongated $\text{V-F}_{\text{trans}}$ bond could be due to crystal packing effects rather than electron donating nature of the C_{NHC} atom of the NHC^{Dipp} ligand (see Chapter 4.2.7). As for the orientation of the VOF_3 fragment, the axis linking two F_{cis} atoms is almost perpendicular to the plane of the NHC ring and these fluorine atoms are bent toward the NHC^{Dipp} ligand with C2-V1-F angle being $82.79(6)^\circ$ and $82.48(6)^\circ$ for F1 and F3, respectively. Bending of the *cis*-atoms toward the NHC ligand was also observed in the previously published neutral square pyramidal VOCl_3 complex with $\text{NHC}^{\text{IMes}} = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazol-2-ylidene}$ (C1-V1-Cl1 $81.04(6)^\circ$ and C1-V1-Cl3 $82.20(6)^\circ$) [93]. Further comparison of the two analogous structures surprisingly reveals that the V-C_{NHC} distance with uncertainty considered is practically the same in $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) (C2-V1 $2.141(2)$ Å) and in $[(\text{NHC}^{\text{IMes}})\text{VOCl}_3]$ (C1-V1 $2.137(2)$ Å) despite the fact that the fluorine atom is more electronegative than chlorine and has a smaller van der Waals radius (F 1.46 Å; Cl 1.82 Å) [339]. Moreover, literature results with VOCl_3 also report surprisingly short $\text{Cl}_{\text{cis}}\text{-C2}$ distances that could be attributed to unusual interactions between them [93]. However, recent results of theoretical calculations for $[(\text{NHC})\text{NbCl}_5]$ complexes showed that there is no direct back-donation from Cl to C_{NHC} , but rather the niobium metal center exploits the electronic charge of the Cl_{trans} atom for back-donation, yet even this type of back-donation is rather minute [107]. Due to the short $\text{F}_{\text{cis}}\text{-C}_{\text{NHC}}$ distance (F1-C2 $2.601(2)$ Å and F3-C2 $2.599(2)$ Å), the back-donation effect for the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex was elucidated by DFT calculations (see Chapter 4.2.8).

Table 6: Selected bond distances and angles for both subunits of the neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Table is based on the reference [324].

	Subunit 1	Subunit 2
Intramolecular bond distance [$\text{\AA}$]		
V–O	1.558(2)	1.561(1)
	1.771(1) (F1)	1.776(1) (F4)
V–F	1.804(1) (F2)	1.802(1) (F5)
	1.781(1) (F3)	1.784(1) (F6)
V–C _{NHC}	2.141(2)	2.139(2)
F _{cis} –C _{NHC}	2.601(2) (F1)	2.582(2) (F4)
	2.599(2) (F3)	2.629(2) (F6)
F–F _{trans}	3.428(2) (F1, F3)	3.430(2) (F4, F6)
F _{trans} –C _{NHC}	3.808(2) (F2, C2)	3.827(2) (F5, C31)
Intermolecular bond distance [$\text{\AA}$]		
F–C	3.119(2) (F2, C33)	3.145(2) (F5, C5)
	2.919(2) (F2, C34)	3.341(2) (F6, C4) ^[a]
V displacement [$\text{\AA}$] ^[b]	0.478	0.464
$\tau_5^{\text{[c]}}$	0.000	0.056
Angle [$^\circ$]		
	104.61(8) (F1)	104.40(7) (F4)
O–V–F	110.08(7) (F2)	108.77(6) (F5)
	103.99(8) (F3)	105.01(7) (F6)
O–V–C _{NHC}	100.22(7)	98.95(7)
F _{cis} –V–C _{NHC}	82.79(6) (F1)	81.98(5) (F4)
	82.48(6) (F3)	83.66(5) (F6)
F–V–F _{trans}	149.69(7)	148.89(6)
F _{trans} –V–C _{NHC}	149.69(6)	152.24(6)
O–V–C _{NHC} –N	7.8(2) (O1, V1, C2, N1)	19.4(2) (O2, V2, C31, N30)
plane _{O1-V1-F2} –plane _{F1-F2-F3}	89.66(7)	89.63(6)
plane _{NHC} –plane _{O1-V1-F2}	7.95(8)	17.50(6)
plane _{NHC} –plane _{F1-F2-F3}	82.29(7)	74.07(6)

^[a] Bond distance larger than the sum of van der Waals radii [339].

^[b] Displacement of vanadium center from the plane of basal C_{NHC} and fluorine atoms.

^[c] Structural parameter was calculated using $\tau = \frac{\beta - \alpha}{60^\circ}$, where β is the largest of the basal angles and α is the angle between the remaining basal atoms [198].

Increasing the molar ratio between VOF_3 and NHC^{Dipp} ligand to 2:1 did not afford any kind of other possible oligomeric products. According to the ^{19}F NMR spectrum, only $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**), $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and unreacted starting VOF_3 are present in the reaction mixture (see the Appendix Figure A75) showing that the steric effect of the NHC^{Dipp} is prevalent and VOF oligomers or polymers could not be formed despite the indication that oligomeric d-block metal fluorides could be stronger acids than their parent monomers [345]. Likewise, the reaction with the molar ratio of 1:2, with an additional equivalent of NHC^{Dipp} ligand, did not yield any new species. In the ^1H and ^{19}F NMR spectra of the reaction mixture, only signals of neutral complex $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) and unreacted starting NHC^{Dipp} were observed (see the Appendix Figure A76 and Figure A77).

We have also tried to prepare rare molecular VO_2F complex with NHC^{Dipp} in the reaction of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with $(\text{Me}_3\text{Si})_2\text{O}$ following the procedure for the preparation of the known neutral $[(\text{L})\text{VO}_2\text{F}]$ ($\text{L} = \text{py}, \text{bipy}, \text{phen}, \text{TMEDA}$) complexes [171], but the

reaction did not proceed in the proposed MeCN, THF or $(\text{Me}_3\text{Si})_2\text{O}$ as a solvent. NMR spectroscopy showed only the starting material with a small amount of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**).

4.2.2 Synthesis and structural characterization of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$

A reaction of VOF_3 with imidazolium fluoride $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ in MeCN leads to the formation of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) salt in almost quantitative conversion. Crystallization of the product in DCM yields crystals suitable for X-ray analysis, however disorder of the anionic part prevents quality solution of the crystal structure. On the other hand, if the product is recrystallized from the MeCN solution, the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]\cdot 2\text{MeCN}$ (**6a**) crystals are obtained. The structure of one asymmetric unit is presented in Figure 10. Structural details of the salt anion are provided in Table 7, while bond valence sum is given in the Appendix along with crystal collection data and refinement parameters (Table A2 and Table A15). X-ray structural analysis reveals imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation and discrete $[\text{VOF}_4]^-$ anion. To the best of our knowledge, this is the first structural identification of this discrete anion.

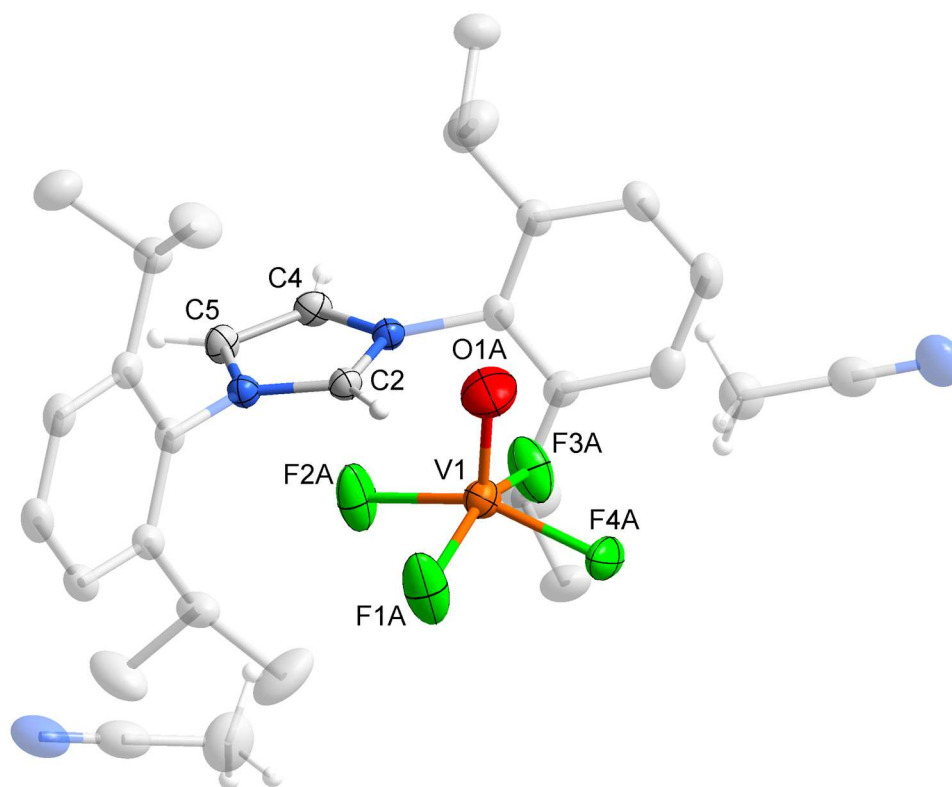


Figure 10: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]\cdot 2\text{MeCN}$ (**6a**) salt. Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ are shaded, less relevant hydrogen atoms are omitted and only domain A of the $[\text{VOF}_4]^-$ anion is shown. Figure is based on the reference [324].

The product crystallizes as a solvate with nitrogen atoms of the MeCN molecules turned away from the vanadium(V) center negating any possibility of the coordination to the vanadium(V) ion like in the aforementioned compound with $[\text{VOF}_4(\text{H}_2\text{O})]^-$ anion [132],

[155]. In contrast, MeCN molecules are not present in non-crystalline powder as revealed by NMR and elemental analysis. In the crystal structure, the orientation of the $[\text{VOF}_4]^-$ anion is disordered. We assume that this orientational disorder is in part due to weak hydrogen bonding interactions that hold anion wedged in organic surrounding. Two preferred orientations of the anion are observed, with occupancy of the first domain (A) being 73 % and of the second domain (B) being 27 %. Graphical representation of orientation of both anion's domains is presented in the Appendix (Figure A9). The O1A–V–O1B angle between domains is $131.51(3)^\circ$. Both domains of the $[\text{VOF}_4]^-$ anion show a square pyramidal arrangement, with the vanadium(V) center having the same position for both orientations. In both domains the oxygen atom is in apical position, while fluorine atoms are in basal position of the pyramidal geometry and vanadium(V) ion is located within the $[\text{VOF}_4]^-$ pyramid. Herein we describe only more representable results of the dominant domain A, for structural characteristic of domain B see Table 7. The V–O bond is close to perpendicular to the plane of the imidazolium ring and basal fluorine atoms are almost parallel to this plane with the dihedral angle between both planes being $10.42(6)^\circ$. The length of the V–O bond is $1.560(2)$ Å and four basal V–F bonds are between $1.776(2)$ Å and $1.815(2)$ Å. O–V–F angles are between $103.1(1)^\circ$ to $107.0(1)^\circ$ and trans F–V–F angles are $149.8(1)^\circ$ and $152.1(1)^\circ$. The corresponding geometry index τ_5 is 0.038 indicating that the geometry of the anion is close to square pyramid although the vanadium(V) ion is dislocated from the plane of basal fluorine atoms toward the center of the pyramid by 0.446 Å.

The addition of another equivalent of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ does not lead to the formation of known discrete $[\text{VOF}_5]^{2-}$ anion [184] but rather a mixture of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and unreacted starting imidazolium fluoride according to ^{19}F NMR spectroscopy (see the Appendix Figure A78). Prolonged reaction times do not yield any additional components. We attribute the lack of observation of the octahedral $[\text{VOF}_5]^{2-}$ anion to the bulkiness of the imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Namely, it was demonstrated in a previous publication [346] that the role of the bulky cation in stabilizing the pentacoordinated monovalent anions against the hexacoordinated divalent ones is due to steric hindrance as well as electrostatic effects.

Table 7: Selected bond distances and angles for both domains of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]\cdot 2\text{MeCN}$ (**6a**) salt. Table is based on the reference [324].

Occupancy	Domain A 72.8(3) %	Domain B 27.2(3) %
Intramolecular bond distance [Å]		
V–O	1.560(2)	1.587(8)
	1.776(2) (F1A)	1.681(9) (F1B)
	1.815(2) (F2A)	1.760(1) (F2B)
	1.807(2) (F3A)	1.690(6) (F3B)
V–F	1.794(2) (F4A)	1.833(4) (F4B)
Intermolecular bond distance [Å]		
F–C	2.97(1) (F1A, C5)	4.10(1) (F1B, C5) ^[a]
	3.07(1) (F2A, C2)	3.15(1) (F2B, C2)
	3.23(1) (F3A, C2)	3.36(1) (F3B, C2) ^[a]
	3.50(1) (F4A, C5) ^[a]	3.60(4) (F4B, C5) ^[a]
V displacement [Å] ^[b]	0.446	0.544
$\tau_5^{\text{[c]}}$	0.038	0.367
Angle [°]		
O–V–F	107.0(1) (F1A)	103.2(5) (F1B)
	104.5(1) (F2A)	110.1(5) (F2B)
	103.1(1) (F3A)	126.5(5) (F3B)
	103.4(1) (F4A)	96.7(4) (F4B)
F–V–F _{cis}	86.1(1) (F1A, F2A)	71.0(5) (F1B, F2B)
	87.3(1) (F1A, F4A)	93.9(3) (F1B, F4B)
	84.0(1) (F2A, F3A)	82.7(4) (F2B, F3B)
	88.3(1) (F3A, F4A)	89.3(3) (F3B, F4B)
F–V–F _{trans}	149.8(1) (F1A, F3A)	129.4(4) (F1B, F3B)
	152.1(1) (F2A, F4A)	151.4(4) (F2B, F4B)
plane _{FA} –plane _{FB} ^[d]	75.2(4)	

^[a] Bond distance larger than the sum of van der Waals radii [339].

^[b] Displacement of vanadium center from the plane of basal fluorine atoms.

^[c] Structural parameter was calculated using $\tau = \frac{\beta - \alpha}{60^\circ}$, where β is the largest of the basal angles and α is the angle between the remaining basal atoms [198].

^[d] Plane of fluorine atoms of domain A (F1A–F2A–F3A–F4A) relative to the plane of fluorine atoms of domain B (F1B–F2B–F3B–F4B).

4.2.3 Synthesis and structural characterization of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$

Compounds with $[\text{VO}_2\text{F}_2]^-$ anion are usually obtained from the reaction between vanadium oxides or other vanadates with hydrofluoric acid [141], [142], [347], but such an approach usually yields an anion in oligomeric or polymeric form in practically all known crystal structures, except $[\text{Ph}_4\text{M}][\text{VO}_2\text{F}_2]$ ($\text{M} = \text{P}, \text{As}$) [141], $[\{\text{VO}(\text{salen})\}_2(\mu\text{-F})][\text{VO}_2\text{F}_2]$ ($\text{salen} = N,N'$ -bis(salicylidene)ethylenediamine) [128], and $[\text{Et}_4\text{N}]_6[\text{HV}_{22}\text{O}_{54}(\text{VO}_2\text{F}_2)]$ [122]. We were able to prepare crystals of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) salt through the reaction of NHC^{Dipp} and VOF_3 in THF. After the initial stirring, the solution was left standing with a slow diffusion of air into the reaction mixture. Apparently moisture from the atmosphere is enough to decompose the neutral complex $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) according to the rxn. 7 (see Chapter 4.2.4). Isolation of pure $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) from a dried combination of salts is possible due to its poor solubility in THF in comparison to the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**).

The crystal structure of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) contains an imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation and a discrete $[\text{VO}_2\text{F}_2]^-$ anion; its asymmetric unit is presented in Figure 11 and measurements of structural features are given in Table 8. Bond valence sum, crystal collection data and refinement parameters are given in the Appendix (Table A2 and Table A15).

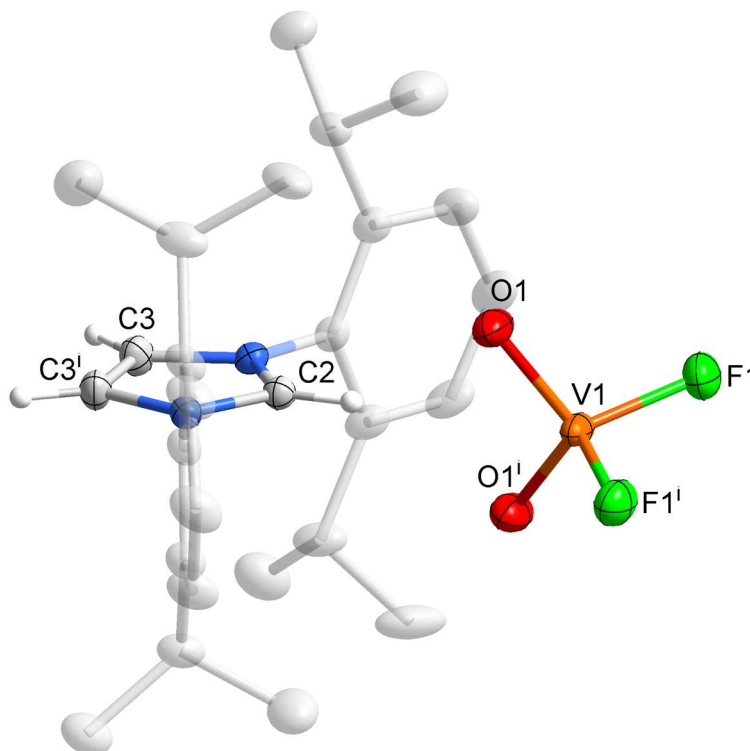


Figure 11: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) salt. Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ are shaded and less relevant hydrogen atoms are omitted. Symmetry code: (i) $1/2-x, 3/2-y, z$. Figure is based on the reference [324].

Bond distances in the tetrahedral anion are 1.615(1) Å for V–O and 1.801(1) Å for V–F. Angles deviate from the ideal tetrahedral angle with the smallest O1–V–O1ⁱ being 106.49(9)° and the largest O1–V–F1ⁱ being 110.94(5)°. Oxygen atoms are facing toward C2–H proton of the cation and least-square plane comprised of the oxygen atoms and vanadium(V) center is rotated by 77.2(3)° from the plane of the imidazolium ring. Fluorine atoms are facing backbone of another imidazolium cation. Least-square plane of fluorine atoms and vanadium(V) center is at the 21.3(9)° angle to the imidazolium plane of that neighboring cation. The distance from vanadium(V) to the closest cation is 3.840(2) Å long V–C2 and V–C3 to the cation on the opposite side is 4.018(2) Å, both of which are within the sum of van der Waals radii (4.19 Å) [339]. Interestingly, the shortest V–C distance in $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**1**) is 4.205(2) Å. In our case, we did not observe any orientational disorder reported in literature with the same anionic species [122], [128], probably because hydrogen interactions locked the anion in position and consequently prevented the disorder.

Table 8: Selected bond distances and angles for the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) salt. Table is based on the reference [324].

Intramolecular bond distance [Å]	
V–O	1.615(1)
V–F	1.801(1)
Intermolecular bond distance [Å]	
O–C2	3.151(2)
F–C3	3.041(2)
Angle [°]	
O–V–O	106.49(9)
O–V–F	109.80(5) (O1, F1)
	110.94(5) (O1, F1 ⁱ) ^[a]
F–V–F	108.88(7)
plane _{O1-V1-O1} –plane _{F1-V1-F1} ^[a]	89.18(5)

^[a] Oxygen and fluorine atoms are generated with symmetry operation. Symmetry code: (i) $1/2-x, 3/2-y, z$.

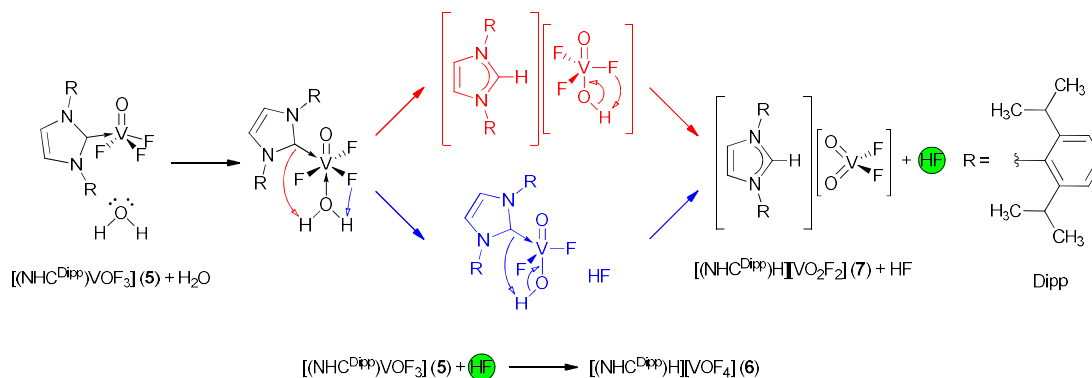
4.2.4 Stability of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$, $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$, $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$

During the assessment of stability of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**), we found that hydrolysis of the complex led to the formation of a mixture of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) (rxn. 7).



In ^{19}F NMR spectrum of the hydrolysis experiment, a signal at $\delta = -139$ ppm can also be observed (see the Appendix Figure A79), which can be explained as the impurity obtained during the decomposition of the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**). The breakdown of the complex proceeds through the formation of HF, which in turn slowly reacts with the glass reaction vessel forming SiF_4 . Decomposition cascade ends with the reaction of SiF_4 with $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ in the solution yielding a $[\text{SiF}_5]^-$ anion. Release of HF during the decomposition of VOF_3 in MeCN solution followed by the formation of SiF_4 was already observed [296]. When the reaction was repeated in the reaction vessel made from FEP, we did not detect the peak at $\delta = -139$ ppm proving not only the in situ formation of HF during the hydrolysis but also that SiO_2 from the glassware is indeed the source of the proposed $[\text{SiF}_5]^-$ impurity.

In the provided Scheme 13 we tried to elaborate the mechanism of hydrolysis of the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. We proposed two possible paths of decomposition, with the first stage being either insertion of water molecule onto the complex or formation of imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. The former might be more plausible since hydrolysis of the $[\text{VOF}_4]^-$ anion in the solution does occur although only imidazolium cations are present in such a system. During the hydrolysis, the formation of HF occurs, which in turn reacts either with another molecule of a neutral complex $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) (bottom row of the Scheme 13) or with silicon oxide species from the glass.



Scheme 13: Proposed mechanism with two possible paths of hydrolysis of the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. HF that is released in the process further reacts with another neutral complex forming $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) as seen in the bottom row. Scheme is based on the reference [324].

Decomposition of the $[\text{VOF}_4]^-$ anion in the solution was observed after prolonged reaction times. In the ^{19}F NMR spectrum in deuterated acetonitrile (CD_3CN), only signals at -34.1 ppm, -138.3 ppm and -151.8 ppm were detected, which were assigned to $[\text{VO}_2\text{F}_2]^-$ anion, $[\text{SiF}_5]^-$ anion and $[\text{BF}_4]^-$ anion, respectively. To further test its stability bulk sample of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) was loaded into a NMR tube made of glass (borosilicate glass 3.3, Hilgenberg) and dissolved with CD_3CN . A drop of CFCl_3 was added into the solution to act as an internal standard. ^{19}F NMR spectrum of the same sample was recorded on the day when it was prepared and after 1, 2, 3, 7, 14, 31 days. NMR spectra were recorded at 298 K. Results are presented in Table 9 and Figure 12. NMR tube was stored in a glove box at room temperature when it was not measured. Integral of the CFCl_3 peak was set to value 1. Values of other peaks are not normalized and are provided to indicate an approximate rate of decomposition and the products thereof.

Table 9: Integrated values of observed peaks in ^{19}F NMR spectra in a study of decomposition of $[\text{VOF}_4]^-$ anion in the CD_3CN solution with time. Values of the integrals are in accordance with the integral of the added internal standard CFCl_3 , the value of which was set to 1. Table is based on the reference [324].

$\delta^{19}\text{F}$ [ppm]	$[\text{VOF}_4]^-$	CFCl_3	$[\text{VO}_2\text{F}_2]^-$	$[\text{SiF}_5]^-$	$[\text{BF}_4]^-$
	129.0	-1.2	-34.1	-138.3	-151.8
Day					
0	16.3	1	/	1.1	/
1	15.1	1	0.4	1.2	/
2	13.8	1	0.5	1.4	0.05
3	13.4	1	0.6	1.8	0.09
7	10.6	1	0.9	2.8	0.3
14	6.8	1	1.6	4.9	0.6
31	2.6	1	1.8	7.8	1.0

To further evaluate the stability of the $[\text{VOF}_4]^-$ anion toward the hydrolysis in the solution, the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) salt was dissolved in MeCN solutions with 10 or 30 equivalents of water (see the Appendix Figure A81–Figure A84). Both experiments were stopped after 16 hours with isolation of products *in vacuo*. Subsequent analysis of their ^{19}F

and ^{51}V NMR spectra revealed that in both instances partial hydrolysis of the $[\text{VOF}_4]^-$ anion does occur and its extent depends on the amount of added water. Decomposition of the anion leads to the formation of the $[\text{VO}_2\text{F}_2]^-$ anion. Interestingly, prolonged reaction times did not completely convert starting $[\text{VOF}_4]^-$ and the initial ratio between $[\text{VOF}_4]^-$ and $[\text{VO}_2\text{F}_2]^-$ anions was kept even after 5 days.

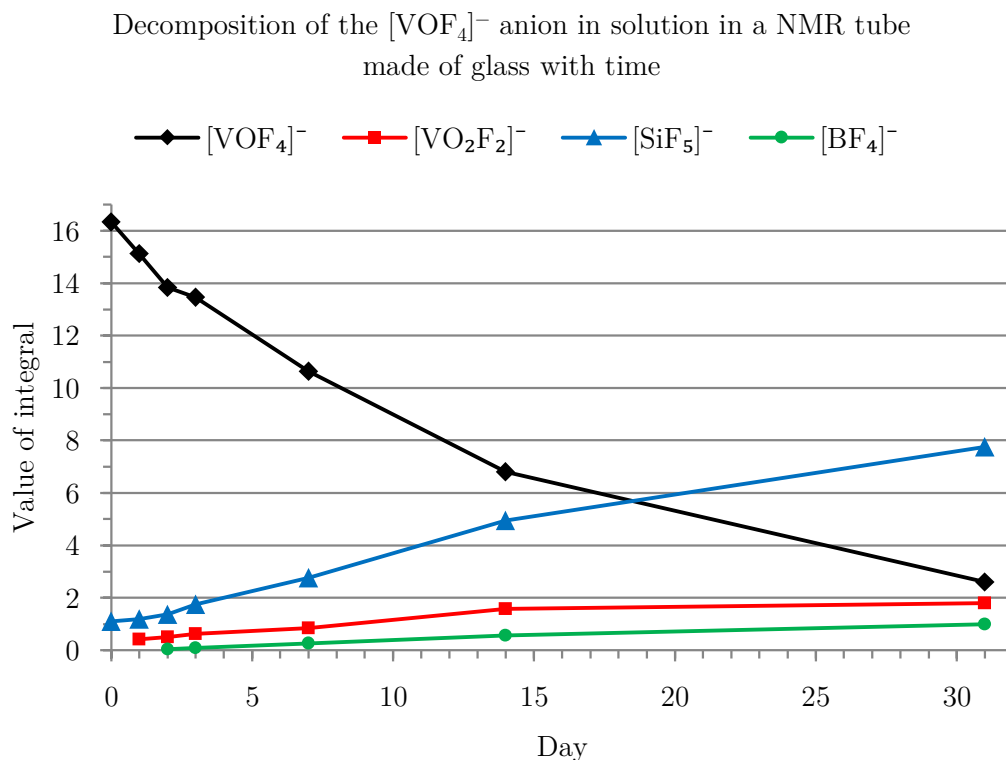


Figure 12: Graphic presentation of integrated values of observed peaks in ^{19}F NMR spectra in a study of decomposition of $[\text{VOF}_4]^-$ anion in the CD_3CN solution with time. Values of the integrals are in accordance with the integral of the added internal standard CFCl_3 , the value of which was set to 1 and is not represented on the chart. Figure is based on the reference [324].

The synthesis of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) was from its inception onward performed in air thus proving that both product salts from rxn. 7 (see above) are air-stable. Still further hydrolysis of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) was tested, but the $[\text{VO}_2\text{F}_2]^-$ anion did not produce any side product or show any other signs of reaction with water after 16 hours according to NMR spectroscopy.

Similar decomposition experiment as with the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) was designed to establish decomposition ratio $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) salt in accordance with time. Even after a month no decomposition of the $[\text{VO}_2\text{F}_2]^-$ anion was observed. Integrals of the $[\text{VO}_2\text{F}_2]^-$ peak are constant to the integral of the internal standard CFCl_3 and no other peaks can be observed. Results are presented in Table 10.

Table 10: Integrated values of observed peaks in ^{19}F NMR spectra in a study of decomposition of $[\text{VO}_2\text{F}_2]^-$ anion in the CD_3CN solution with time. Values of the integrals are in accordance with the integral of the added internal standard CFCl_3 , the value of which was set to 1. Table is based on the reference [324].

$\delta^{19}\text{F}$ [ppm]	$[\text{VOF}_4]^-$ 129.0	CFCl_3 −1.2	$[\text{VO}_2\text{F}_2]^-$ −34.1	$[\text{SiF}_5]^-$ −138.3	$[\text{BF}_4]^-$ −151.8
Day					
0	/	1	7.37	/	/
1	/	1	6.98	/	/
2	/	1	7.08	/	/
3	/	1	7.32	/	/
7	/	1	7.14	/	/
14	/	1	7.34	/	/
31	/	1	6.98	/	/

4.2.5 Raman spectroscopy

Raman spectroscopy was used in order to detect vanadium(V) oxide fluoride species in the samples. Assignment of these species in the spectra was challenging due to the large number of bands of the imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation or neutral NHC^{Dipp} ligand that mask many of the bands contributed by vanadium(V) oxide fluorides species. Raman spectra of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**), $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) are presented in Figure 13 and full range spectra can be found in the Appendix (Figure A16). We compared the spectra of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) with published $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{GeF}_5]$ [346] in order to first identify bands of the cation and in turn determine bands in the spectra contributed by VOF anions. The V–O stretching band can be assigned to the bands at 1030 cm^{-1} for the $[\text{VOF}_4]^-$ anion and at 971 cm^{-1} for the $[\text{VO}_2\text{F}_2]^-$ anion. This is a characteristic region for the identifications of V–O vibrations in VOF species. Bands at 636 cm^{-1} and 631 cm^{-1} can be assigned to V–F vibrations. The most intense bands observed in Raman spectra for V–O and V–F vibrations together with calculated vibrations are listed in Table 11.

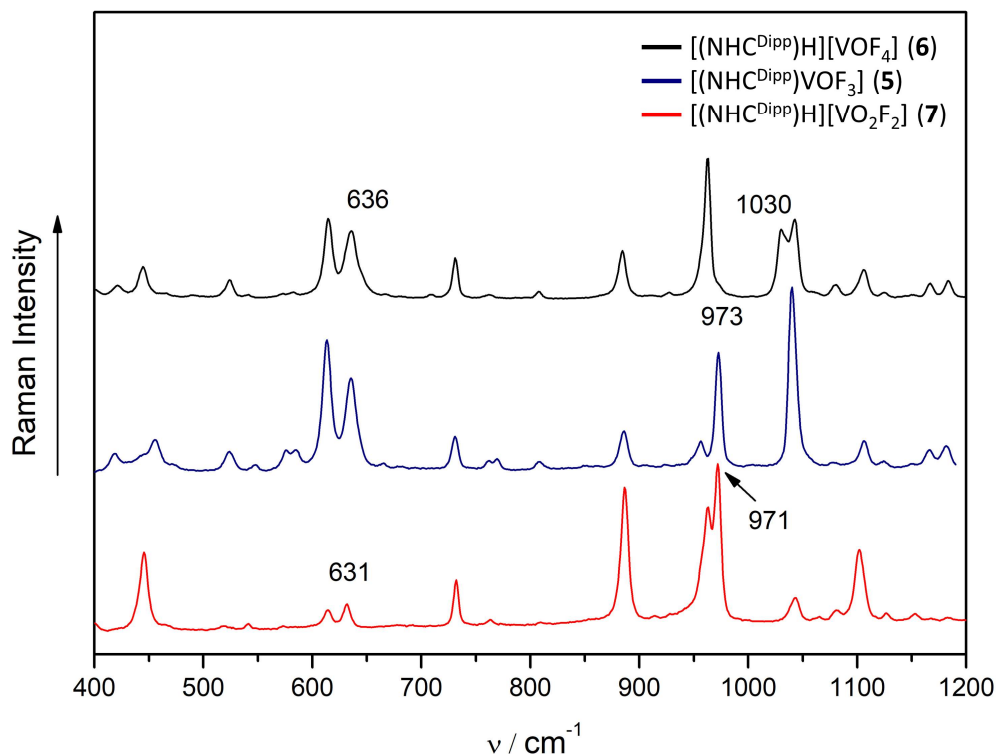


Figure 13: Raman spectra of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**), $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) with assigned bands for V–O and V–F vibrations. Figure is based on the reference [324].

Table 11: Frequencies of the strongest Raman active modes for isolated VOF_3 , $[\text{VOF}_4]^-$ and $[\text{VO}_2\text{F}_2]^-$ moieties according to PBE/aug-cc-pVTZ calculated and experimentally determined values. Table is based on the reference [324].

	PBE (aug-cc-pVTZ)	Experimental
Frequencies [cm^{-1}]		
VOF_3		
$\nu_s(\text{VF}_3)$	698	721.5 ^[b]
$\nu(\text{VO})$	1075, 1044 ^[a]	1057.8 ^[b] , 973 ^[c]
$[\text{VOF}_4]^-$		
$\nu_s(\text{VF}_4)$	609	636, ^[d] 630 ^[e]
$\nu(\text{VO})$	1023	1030, ^[d] 1012 ^[e]
$[\text{VO}_2\text{F}_2]^-$		
$\nu_s(\text{VF}_2)$	615	631 ^[b] , 631 ^[f]
$\nu_a(\text{VF}_2)$	647	664 ^[b]
$\nu_a(\text{VO}_2)$	965	960 ^[b]
$\nu_s(\text{VO}_2)$	966	969 ^[b] , 971 ^[f]

^[a] Corresponds to $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$ complex.

^[b] Reference [340].

^[c] Corresponds to $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex.

^[d] Corresponds to $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) salt.

^[e] Reference [144].

^[f] Corresponds to $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) salt.

4.2.6 NMR spectroscopy

NMR spectra of the dried bulk product obtained from a straightforward VOF_3 and NHC^{Dipp} reaction mixture in deuterated polar solvents acetonitrile and tetrahydrofuran (CD_3CN , THF-d_8 , respectively) show the expected signals of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) and additional signals indicating the presence of impurities in the form of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) salt, which forms with spontaneous decomposition of VOF_3 and release of HF [296]. To eliminate the presence of traces of this salt in solution, crystals of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) were loaded into a NMR tube and deuterated non-polar solvent benzene (C_6D_6) was added, in which impurity $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) is only scarcely soluble. The solution turned pale yellow despite only moderate solubility of the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) product in this non-polar solvent. Doublets are observed in the ^1H NMR spectrum for the two methyl groups in the isopropyl of the NHC^{Dipp} ligand in the complex, which are noticeably split ($\delta_{\text{H}} = 1.42$ and 1.01 ppm). This is in agreement with previously reported values for coordinated NHC^{Dipp} ligand [348]–[350]. Two broad signals are present in the ^{19}F NMR spectrum at $\delta_{\text{F}} = 178.0$ and 173.8 ppm with approximate integral ratio of 1:2, respectively. Our observation is comparable with values reported for neutral VOF_3 complexes with nitrogen-based ligands [126]. The distinct ^{19}F NMR resonances correspond to two fluorine nuclei that are *cis* to the C_{NHC} in heterocyclic ring and one fluorine nucleus, which is in a *trans* position. The latter fluorine atom interacts with solvent molecules as the chemical shift of its peak changes noticeably between solvents (Table 12). Similar ^1H and ^{19}F NMR results can also be observed in much more polar solvents (CD_3CN , THF-d_8), which shows that in solution these molecules do not displace NHC^{Dipp} as a ligand. The ^{51}V NMR spectrum in C_6D_6 shows a broad peak corresponding to the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) at $\delta_{\text{V}} = -733.5$ ppm, which is in line with the shifts reported for other neutral complexes of VOF_3 [126].

The bulk of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) product was transferred to NMR tubes and dissolved in deuterated solvents CD_3CN , dichloromethane (CD_2Cl_2) or THF-d_8 forming a deep orange solution. In the ^1H NMR spectra in all solvents we observed characteristic signals for the imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. A signal is present in the ^{19}F NMR spectrum of CD_3CN at $\delta_{\text{F}} = 129.0$ ppm ($J_{\text{F-V}} = 86.9$ Hz), which is split into an octet by scalar coupling to a quadrupolar ^{51}V nucleus ($I = 7/2$) and a corresponding quintet is observed in the ^{51}V spectrum at $\delta_{\text{V}} = -796.9$ ppm ($J_{\text{V-F}} = 86.9$ Hz). These signals have similar chemical shifts also in other used solvents (Table 12) and their chemical shifts and shapes correspond well to those previously reported for $[\text{Ph}_4\text{As}][\text{VOF}_4]$, despite the use of a different deuterated solvent [126]. Interestingly, it has been reported that the ^{19}F chemical shift of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{VOF}_4]$ in deuterated chloroform (CDCl_3) is $\delta_{\text{F}} = -28.21$ ppm [351]. However, we have assigned this value to $[\text{VO}_2\text{F}_2]^-$ anion instead (see below). The presence of well-resolved multiplets in ^{19}F and ^{51}V NMR spectra implies that $[\text{VOF}_4]^-$ anion in solution retains its symmetrical shape observed in the crystal structure. Note that a similar result was obtained when weakly coordinating CD_2Cl_2 solvent was used (Table 12), meaning that most likely there are no CD_3CN molecules in the coordination sphere of vanadium(V) in the solution.

The slightly crystalline powder of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) obtained after reaction in moist air was transferred from a polyethylene container into a NMR tube and dissolved with the addition of either CD_3CN , CD_2Cl_2 or THF-d_8 , producing an almost colorless solution in all cases. The ^1H NMR spectrum of the salt in any of the solvent is consistent with the presence of the imidazolium cation. In ^{19}F NMR spectrum, a well-defined octet can be observed at $\delta_{\text{F}} = -29.8$ ppm ($J_{\text{F-V}} = 272.1$ Hz) in THF-d_8 , whereas in CD_3CN or CD_2Cl_2 , the chemical shift is similar (Table 12), while the multiplet structure is not resolved. The chemical shift corresponds to ionic compounds with the $[\text{VO}_2\text{F}_2]^-$ anion [128],

[171]. Signals in the ^{51}V NMR spectra support similar conclusions. A well-defined triplet resulting from coupling to two equivalent ^{19}F nuclei is observed in THF- d_8 at $\delta_{\text{F}} = -594.1$ ppm ($J_{\text{V-F}} = 272.9$ Hz), which correlates to previously reported values for $[\text{VO}_2\text{F}_2]^-$ anions [128], [171]. Meanwhile only broad multiplets are observed in CD_3CN or CD_2Cl_2 at a similar chemical shift (Table 12). All NMR spectra can be found in the Appendix (Figure A44–Figure A74).

Table 12: Chemical shifts observed in ^{19}F and ^{51}V NMR spectra of the compounds $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**), $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) given for CD_3CN , CD_2Cl_2 , THF- d_8 and C_6D_6 . Table is based on the reference [324].

Ref.	$[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (6)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (7)
δ [ppm]			
^{19}F			
CD_3CN	177.0 (2F), 142.3 (1F)	129.0	−34.1
CD_2Cl_2	179.5 (2F), 144.6 (1F)	125.6	−29.1
THF- d_8	173.3 (2F), 169.3 (1F)	127.4	−29.8
C_6D_6	178.0 (1F), 173.8 (2F)	/	/
^{51}V			
CD_3CN	−714.9	−796.9	−594.8
CD_2Cl_2	−722.3	−793.5	−597.4
THF- d_8	−728.3	−790.8	−594.1
C_6D_6	−733.5	/	/

4.2.7 Computational crystal structure results

Periodic plane-wave DFT calculations reproduced the crystal structure of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in fair agreement with the experiment. Comparison between the calculated and the experimental unit cell parameters is provided in Table 13 and a few relevant bond lengths and angles are compared in Table 14. Notably, crystal structure calculations reproduce the experimentally observed elongated $\text{V-F}_{\text{trans}}$ bond with respect to V-F_{cis} bonds. Analysis reveals that $\text{V-F}_{\text{trans}}$ bond elongation is due to crystal packing effects rather than the electron donating nature of the C_{NHC} atom from the NHC^{Dipp} ligand. In particular, in the calculated crystal structure three C–H fragments of NHC^{Dipp} ligands from neighboring complexes are within the distance of 2.35 Å from F_{trans} (Figure 14a) and the charge density difference plot clearly shows hydrogen bond like interactions between the three neighboring H atoms and F_{trans} (Figure 14b). If, instead of the whole crystal structure, only an isolated $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex is considered in calculations, then the $\text{V-F}_{\text{trans}}$ distance is reduced by 0.04 Å, thus becoming slightly shorter than the V-F_{cis} distances.

Table 13: Comparison of PBE and PBE-D calculated unit cell parameters of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with experimental data. Table is based on the reference [324].

	PBE	PBE-D	Experimental
Edge length [$\text{\AA}$]			
a	12.93	12.12	12.51
b	16.15	15.26	15.45
c	16.57	15.84	16.04
Angle [$^\circ$]			
α	116.9	118.8	117.8
β	90.6	91.3	91.1
γ	90.8	91.5	91.0
$V [\text{\AA}^3]$	3085	2564	2742

Table 14: Comparison between selected PBE and PBE-D calculated bond distance, C–V–F_{cis} angles and N–C–V–O dihedral angles within the crystal structure of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with experimental data. For comparison, the calculated data for standalone $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex, calculated with the cubic unit cell of 25 $\text{\AA}$ size, are also given. Table is based on the reference [324].

	Crystal structure			Isolated complex	
	PBE	PBE-D	Experimental ^[a]	PBE	PBE-D
Bond distance [$\text{\AA}$]					
V–O	1.575	1.575	1.560	1.577	1.576
V–F _{cis}	1.796	1.801	1.778	1.800	1.804
	1.801	1.809	1.779	1.804	1.809
V–F _{trans}	1.817	1.816	1.803	1.778	1.781
V–C _{NHC}	2.172	2.121	2.140	2.187	2.152
Angle [$^\circ$]					
F _{cis} –V–C _{NHC}	82.2, 82.7	82.2, 82.9	82.2, 83.2	80.2, 80.4	79.9, 80.2
O–V–C _{NHC} –N	12.1	16.1	13.6	13.3	13.7

^[a] Given data is an average over the two subunits in the asymmetric unit.

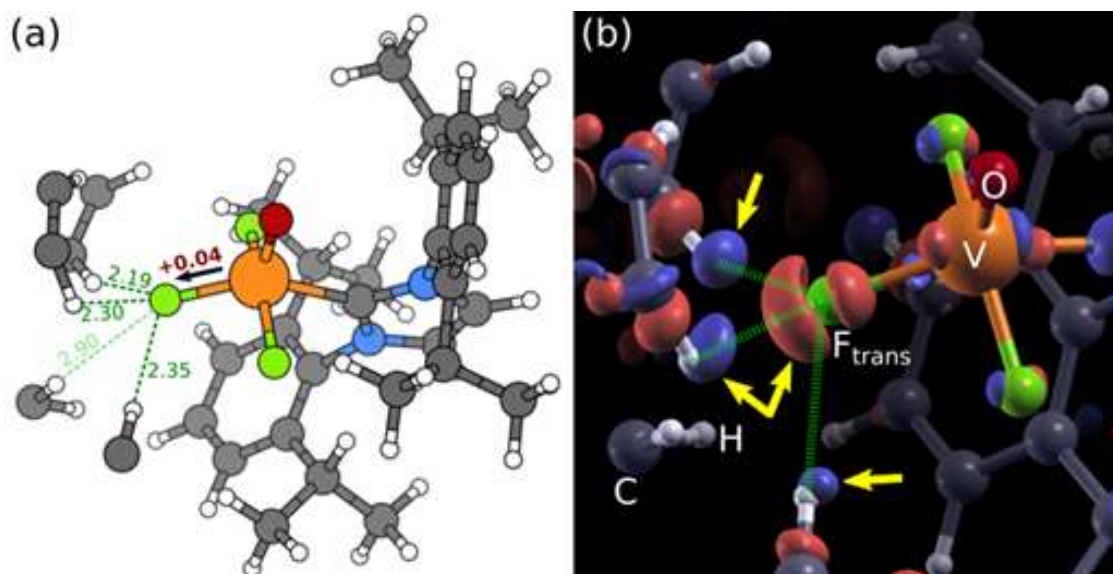
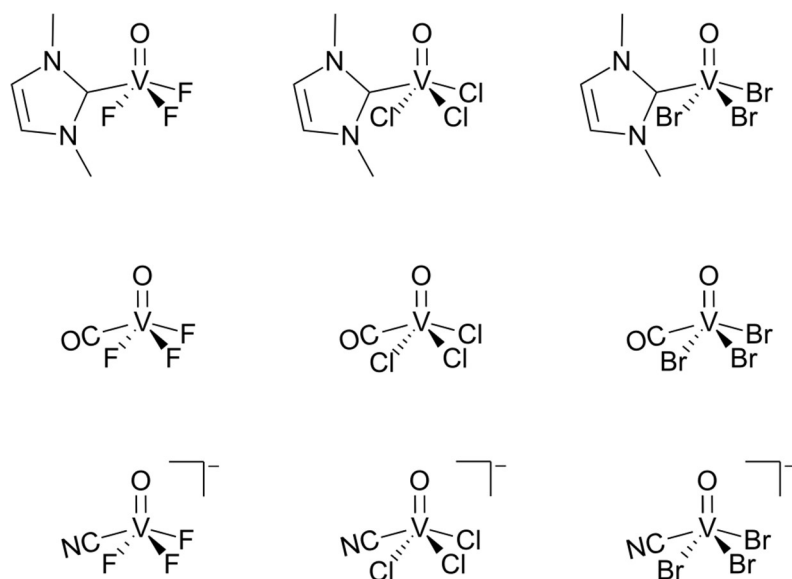


Figure 14: The PBE-D/plane-wave calculated structure of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5). For clarity, only a subset of atoms in the unit cell is drawn (note that atoms are drawn on the basis of atomic and not ionic radii). (a) In the crystal structure, three H atoms of neighboring NHC^{Dipp} ligands are within the distance of 2.35 Å from F_{trans} and these $\text{H}\cdots\text{F}$ interactions cause the $\text{V}-\text{F}_{\text{trans}}$ bond length to elongate with respect to the standalone $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) complex. (b) Electron charge density difference plot, calculated as the difference between the electronic density of the whole crystal minus the density of the individual standalone $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) complexes. Electron excess regions are colored red, while electron deficit regions are blue (isosurfaces are drawn at $\pm 0.002 \text{ e}/\text{Bohr}^3$). $\text{H}\cdots\text{F}$ interactions are evident from the kidney-like electron accumulation region near the F_{trans} atom and the charge deficit regions at the neighboring H atoms (marked by yellow arrows). Figure is based on the reference [324].

4.2.8 Electronic structure and bonding analysis of standalone complexes

We analyzed ligand bonding within $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) and some related complexes, shown in Scheme 14 (most are model complexes used for the sake of argument), by means of PBE/plane-wave calculations.

In this $[(\text{L})\text{VOX}_3]$ setting, it is notable that the rather short distances between C_{NHC} and *cis* halogen atoms, which are well below the sum of respective van der Waals radii [339], have induced some interest and discussion about the type of interactions between them [93], [107]. These include an unusual $\text{C}_{\text{NHC}}\leftarrow\text{Cl}_{\text{cis}}$ back-donation [93] as well as a more standard $\text{C}_{\text{NHC}}\leftarrow\text{metal}$ back-bonding [107]. For the latter type of back-bonding, it is noteworthy that the vanadium ion should not be able to back-donate electron charge, because in current, complexes it is in an oxidation V state and therefore formally without valence electrons. Nevertheless, the charge density plot instead reveals a high valence electron density around the vanadium nucleus, as seen in Figure 15.



Scheme 14: Skeletal structures of standalone $[(L)VOX_3]$ ($L = \text{NHC}^{\text{Me}}$, CO , $[\text{CN}]^-$; $X = \text{F}$, Cl , Br) model complexes, used in the computational analysis to disentangle L-VOX_3 bonding. Scheme is based on the reference [324].

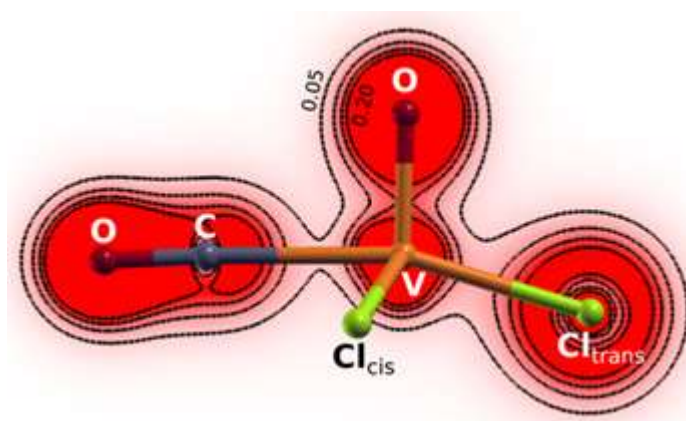


Figure 15: Valence electron density of the $[(\text{CO})\text{VOCl}_3]$ complex plotted on the $\text{C-V-Cl}_{\text{trans}}$ plane. Contours are drawn in a linear scale from 0 to 0.2 e/Bohr^3 with the increment of 0.05 e/Bohr^3 . Notice the high electron density around the vanadium center, although it is formally in an oxidation state V. Bader population analysis reveals that the charge of the vanadium ion in $[(\text{CO})\text{VOCl}_3]$ is $+1.93$, hence it contains about 3 valence electrons. Figure is based on the reference [324].

Bader analysis further reveals that the vanadium(V) ion contains about 3 valence electrons in various currently considered $[(L)\text{VOX}_3]$ complexes (Table 15), standalone VOX_3 molecule and isolated oxide fluoride $[\text{VOX}_4]^-$ and $[\text{VO}_2\text{X}_2]^-$ anions (Table 16). On this basis it is not surprising that back-donation in organometallic complexes with d^0 metal center was observed and is commonly explained for the carbonyl molecule as a model ligand [352]–[354].

Table 15: Bader charges (q) of VOX_3 fragments and their constituent ions as well as π -back-donation ($Q_{\pi^*}^{\text{L} \leftarrow \text{M}}$) and σ -donation ($Q_{\sigma}^{\text{L} \rightarrow \text{M}}$) for standalone high-symmetry $[(\text{L})\text{VOX}_3]$ ($\text{L} = \text{NHC}^{\text{Me}}$, CO , $[\text{CN}]^-$; $\text{X} = \text{F}$, Cl , Br) complexes, calculated at the PBE/plane-wave level of theory. Table is based on the reference [324].

	$q(\text{VOX}_3)$	$q(\text{V})$	$q(\text{O})$	$q(\text{X}_{\text{cis}})$	$q(\text{X}_{\text{trans}})$	$Q_{\pi^*}^{\text{L} \leftarrow \text{M}}$	$Q_{\sigma}^{\text{L} \rightarrow \text{M}}$
$[(\text{L})\text{VOF}_3]$							
$[(\text{NHC}^{\text{Me}})\text{VOF}_3]$	-0.302	+2.209	-0.687	-0.605	-0.615	0.025	0.327
$[(\text{CO})\text{VOF}_3]$	-0.049	+2.265	-0.647	-0.567	-0.533	0.027	0.076
$[(\text{CN})\text{VOF}_3]^-$	-0.344	+2.243	-0.715	-0.619	-0.634	0.000	0.344
$[(\text{L})\text{VOCl}_3]$							
$[(\text{NHC}^{\text{Me}})\text{VOCl}_3]$	-0.320	+1.901	-0.671	-0.515	-0.519	0.051	0.371
$[(\text{CO})\text{VOCl}_3]$	-0.017	+1.929	-0.612	-0.448	-0.438	0.174	0.191
$[(\text{CN})\text{VOCl}_3]^-$	-0.377	+1.944	-0.673	-0.529	-0.588	0.000	0.377
$[(\text{L})\text{VOBr}_3]$							
$[(\text{NHC}^{\text{Me}})\text{VOBr}_3]$	-0.285	+1.794	-0.665	-0.470	-0.473	0.065	0.349
$[(\text{CO})\text{VOBr}_3]$	+0.030	+1.792	-0.621	-0.377	-0.388	0.247	0.217
$[(\text{CN})\text{VOBr}_3]^-$	-0.354	+1.830	-0.674	-0.480	-0.549	0.000	0.354

Table 16: PBE/plane-wave calculated V–X and V–O bond distances and Bader charges of O and X ions of standalone VOX_3 species as well as $[\text{VOX}_4]^-$ and $[\text{VO}_2\text{X}_2]^-$ anions ($\text{X} = \text{F}$, Cl or Br). Table is based on the reference [324].

	$d(\text{V-X})$ [Å]	$d(\text{V-O})$ [Å]	$q(\text{V})$	$q(\text{O})$	$q(\text{X})$
VOF					
VOF_3	1.731	1.570	+2.222	-0.635	-0.543
$[\text{VOF}_4]^-$	1.825	1.601	+2.318	-0.743	-0.644
$[\text{VO}_2\text{F}_2]^-$	1.820	1.635	+2.161	-0.890	-0.689
VOCl					
VOCl_3	2.149	1.569	+1.921	-0.626	-0.431
$[\text{VOCl}_4]^-$	2.291	1.582	+1.946	-0.661	-0.570
$[\text{VO}_2\text{Cl}_2]^-$	2.260	1.625	+1.965	-0.832	-0.656
VOBr					
VOBr_3	2.302	1.569	+1.776	-0.640	-0.375
$[\text{VOBr}_4]^-$	2.460	1.581	+1.801	-0.666	-0.532
$[\text{VO}_2\text{Br}_2]^-$	2.417	1.622	+1.897	-0.823	-0.628

In order to determine whether and to what extent the $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex back-donates the charge into ligand’s unoccupied π^* -states and how this back-donation affects the V–F bond lengths, two preconditions were established: (i) a compound that can be used as a reference for evaluating the back-donation into π^* was determined and (ii) a pool of model compounds large enough to avoid spurious chance correlations was assembled. Furthermore, to make calculations more manageable we utilized a smaller NHC^{Me} ligand ($\text{NHC}^{\text{Me}} = 1,3\text{-dimethylimidazol-2-ylidene}$) in favor of the larger NHC^{Dipp} ligand and consider the symmetrized geometry of the complex within the C_s point group. It should be noted, though, that this symmetry constrained structure is only by 2.4 kJ/mol less stable than the relaxed low-symmetry structure of $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$.

For the first item (i), we started from an existing work [107] that showed a significant back-donation for a model $[(\text{CO})\text{NbCl}_5]$ complex. However, in the current work we consider

vanadium complexes instead. An analogous calculation for the vanadium $[(\text{CO})\text{VCl}_5]$ complex reveals that back-donation is even larger, 0.19 e^- , whereas for the pentacoordinated $[(\text{CO})\text{VOCl}_3]$ back-donation is 0.17 e^- . This latter complex was used as our reference for back-donation. We would use a more closely related $[(\text{CO})\text{VOF}_3]$ instead, however, CO interacts too weakly with VOF_3 ; the resulting C–V bond length is $2.59\text{ \AA}$ and due to such weak interaction back-donation is only 0.03 e^- .

As for the second item (ii), we analyzed the back-donation and bond lengths for nine $[(\text{L})\text{VOX}_3]$ ($\text{L} = \text{NHC}^{\text{Me}}$, CO, $[\text{CN}]^-$; $\text{X} = \text{F}, \text{Cl}, \text{Br}$) complexes (Scheme 14). The choice of these ligands is motivated by the observation that CO is a ligand archetypical for back-donation, whereas for the $[\text{CN}]^-$ ligand little (if any) back-donation is expected [107]. As for halide ions, Cl and Br are less electronegative than F and correspondingly we can expect larger back-bonding for chloride and bromide complexes. Table 15 indeed reveals that these expectations are correct.

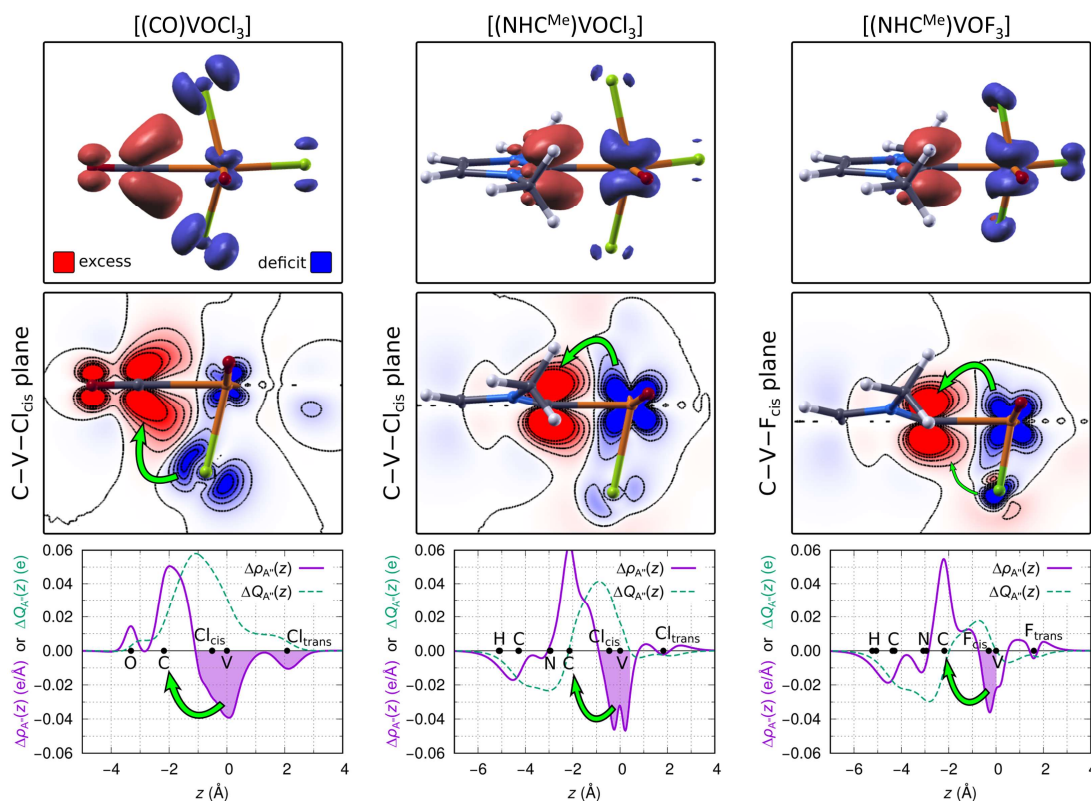


Figure 16: Analysis of $\text{L} \leftarrow \text{M}$ back-donation for $[(\text{CO})\text{VOCl}_3]$ (left), $[(\text{NHC}^{\text{Me}})\text{VOCl}_3]$ (middle) and $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$ (right). Top and middle rows: A'' symmetry resolved charge density differences $\Delta\rho^{A''}(\mathbf{r})$ shown in 3D with isosurfaces at $\pm 0.001\text{ e}/\text{Bohr}^3$ (top row) and in 2D on the C–V– X_{cis} plane ($\text{X} = \text{Cl}$ or F) with nine contours in a linear scale from -0.002 to $+0.002\text{ e}/\text{Bohr}^3$ (middle row); the blue (red) color represents electron deficit (excess) regions, i.e. electron charge moved from blue to red regions (indicated by green arrows). Bottom row: charge displacement analysis along the z axis, i.e. the C–V bond direction. The solid curve represents the A'' component of xy -integrated planar charge density difference $\Delta\rho^{A''}(z)$, whereas the dashed curve represents its integral $\Delta Q_{A''}(z)$. An estimate of the A'' component of charge donated from VOX_3 to the ligand is indicated by the purple colored area (the direction of electron charge flow is marked by a green arrow). Figure is based on the reference [324].

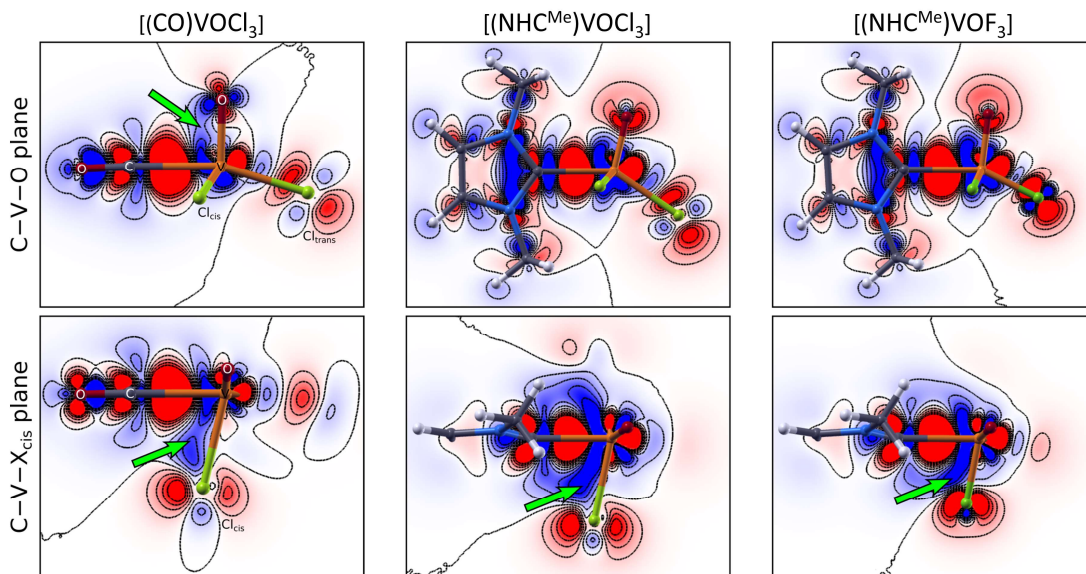


Figure 17: Contour plots of total charge density difference for $[(\text{CO})\text{VOCl}_3]$ (left), $[(\text{NHC}^{\text{Me}})\text{VOCl}_3]$ (middle) and $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$ (right). Charge densities were calculated as $\Delta\rho(\mathbf{r}) = \rho^{\text{L-M}}(\mathbf{r}) - \rho^{\text{L}}(\mathbf{r}) - \rho^{\text{M}}(\mathbf{r})$; where M stands for VOX_3 of selected standalone $[(\text{L})\text{VOX}_3]$ complexes plotted on C-V-O (top row) and C-V- X_{cis} (bottom row) planes. Nine contours are drawn in a linear scale from -0.005 to $+0.005$ e/Bohr^3 ; the blue (red) color represents electron deficit (excess) regions, that is, electron charge moved from blue to red regions. The σ -type of C-V bond is clearly evident by intense red charge accumulation lobe in the midst of the C-V bond. On the left side of the V- X_{cis} bond, notice the blue charge deficit region extending from X_{cis} toward the V ion (marked by green arrow); an analogue charge deficit region on the left side of the V-O bond exists only for the CO ligand (marked by a green arrow), whereas for the NHC^{Me} ligand the red charge accumulation region surrounds the O ion. This difference is due to a different electronic structure of CO and NHC^{Me} ligands, due to which the $\text{CO} \leftarrow \text{O}$ back-bonding is possible only for the CO ligand. Figure is based on the reference [324].

As stated above, $\text{CO} \leftarrow \text{VOCl}_3$ back-bonding of 0.17 e^- is significant, but to disentangle its local characteristics, the symmetry resolved charge density differences, i.e. A'' component, are depicted in Figure 16 (top and middle rows). The $\Delta\rho^{A''}(\mathbf{r})$ plots clearly show that in this case back-bonding mainly stems from Cl_{cis} ions. Note also that the red electron charge accumulation lobes around the C atom point toward Cl_{cis} ions and the blue charge deficit lobes around Cl_{cis} ions point toward the C atom; this is a clear indication of direct $\text{CO} \leftarrow \text{Cl}_{\text{cis}}$ back-bonding interaction. A similar charge difference pattern was previously reported for the $[(\text{CO})\text{NbCl}_5]$ complex [107]. The charge-displacement analysis of $\Delta\rho^{A''}(\mathbf{r})$ gives the value of 0.06 e^- for $\text{CO} \leftarrow \text{VOCl}_3$ (Figure 16, bottom row), which is considerably smaller than the value of 0.17 e^- predicted by orbital projections. The reason for this underestimation is two-fold: (i) the contour plot reveals that the xy -planar integration of $\Delta\rho^{A''}(\mathbf{r})$, underestimates charge transfer, because the border, i.e. zero contour, between electron excess and deficit regions around the V-Cl bond is bent and the red regions extending from C toward Cl_{cis} atoms to some extent penetrate in between the blue regions of Cl_{cis} ; (ii) further analysis reveals that back-donation originates also from the O ion of VOCl_3 , however, due to symmetry reasons $\Delta\rho^{A''}(\mathbf{r})$ cannot show it, because the O ion lies on the A'' nodal plane. However, $\text{CO} \leftarrow \text{O}$ back-donation can be anticipated from the plot of total charge density difference (Figure 17) and also by analyzing the

back-donation onto two degenerate 2π -orbitals of CO; the back-donation onto the 2π -orbital compatible with $\text{CO} \leftarrow \text{Cl}_{\text{cis}}$ back-bonding is 0.11 e^- , whereas the back-donation of the other 2π -orbital, compatible with $\text{CO} \leftarrow \text{O}$ back-bonding, is 0.06 e^- .

In contrast to $[(\text{CO})\text{VOCl}_3]$, where back-donation predominantly comes from Cl_{cis} ions, for the $[(\text{NHC}^{\text{Me}})\text{VOCl}_3]$ complex back-bonding is not only much smaller (0.05 e^-) but overall stems instead from the metal V ion (Figure 16, middle column). The charge-displacement analysis of $\Delta\rho^{\text{A}''}(\mathbf{r})$ gives a back-donation of 0.04 e^- , which is close to the value of 0.05 e^- predicted by orbital projections. The reason for good agreement between the two methods is that in this case, the zero contour between electron excess and deficit regions around the V–Cl bond is rather straight and, moreover, due to symmetry reasons, there is no $\text{NHC}^{\text{Me}} \leftarrow \text{O}$ back-donation, i.e. all π -orbitals of NHC^{Me} have a nodal plane aligned with the plane of the heterocyclic ring. Back-bonding is therefore much smaller for $[(\text{NHC}^{\text{Me}})\text{VOCl}_3]$ compared to $[(\text{CO})\text{VOCl}_3]$; in part larger back-donation for the latter can be attributed to a triple bond of CO and, consequently, doubly degenerated virtual 2π -orbital due to which $\text{CO} \leftarrow \text{O}$ back-bonding is possible.

Finally, for $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$ back-bonding is even smaller; orbital projections result in the value of 0.03 e^- , whereas charge displacement analysis gives 0.02 e^- . Surprisingly, however, the pattern of back-bonding appears to be a combination of the two aforescribed cases. The $\Delta\rho^{\text{A}''}(\mathbf{r})$ plots clearly reveal (Figure 16, right column) that while the majority of back-bonding stems from the metal V ion, there is also a noticeable contribution coming from all three F ions (note the blue charge deficit 3D isosurfaces located at F ions and the intense blue region around the F_{cis} ion in the 2D contour plot). That back-donation in the case of $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$ is smaller than that of $[(\text{NHC}^{\text{Me}})\text{VOCl}_3]$ is reasonable, because Cl is chemically softer (more polarizable) and less electronegative than F. However, for precisely the same two reasons it is counterintuitive why F ions are to a larger extent involved in back-bonding than Cl ions. Perhaps, the larger involvement of F ions in back-donation can be to some extent attributed to a smaller $\text{F}_{\text{cis}}\text{--C}_{\text{NHC}}$ distance ($2.578\text{ \AA}$) compared to $\text{Cl}_{\text{cis}}\text{--C}_{\text{NHC}}$ distance ($2.785\text{ \AA}$). Nevertheless, despite the fact that F ions appear to be more involved in back-donation than Cl ions in $[(\text{NHC}^{\text{Me}})\text{VOX}_3]$, the situation is qualitatively different in the case of the CO ligand; in particular, in $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$ the blue charge deficit lobes of the F_{cis} ions do not point toward the C atom as in the case of the CO ligand (see the contour plots in Figure 16).

Having described the local characteristics of back-donation for the three cases considered in Figure 16, let us now discuss the $[\text{CN}]^-$ ligand and the effect of the type of halide ion $[\text{X}]^-$ ($\text{X} = \text{F}, \text{Cl}$ or Br). The results of the Bader charge analysis of $[(\text{L})\text{VOX}_3]$ complexes and the respective σ -donations and π -back-donations are given in Table 15. For all three $[(\text{CN})\text{VOX}_3]^-$ complexes, orbital projections predict no π -back-donation (the resulting numbers are on the order of 10^{-5} e^-). The order of back-bonding affinity for the three ligands is therefore $\text{CO} \gg \text{NHC}^{\text{Me}} > [\text{CN}]^-$, whereas the order of donating affinity is just the opposite: $[\text{CN}]^- > \text{NHC}^{\text{Me}} \gg \text{CO}$. Notice that for $[\text{CN}]^-$ and NHC^{Me} ligands, σ -donation is considerably larger than the π -back-donation, whereas for CO the two display about the same magnitude. The type of C–V bonding can be further inferred from total charge density plots, shown in Figure 17. Table 15 further reveals that the ability of VOX_3 fragments to back-donate the charge to CO and NHC^{Me} ligands follows the $\text{VOBr}_3 > \text{VOCl}_3 > \text{VOF}_3$ order, which is what one would expect on the basis of chemical softness and electronegativity of Br, Cl and F.

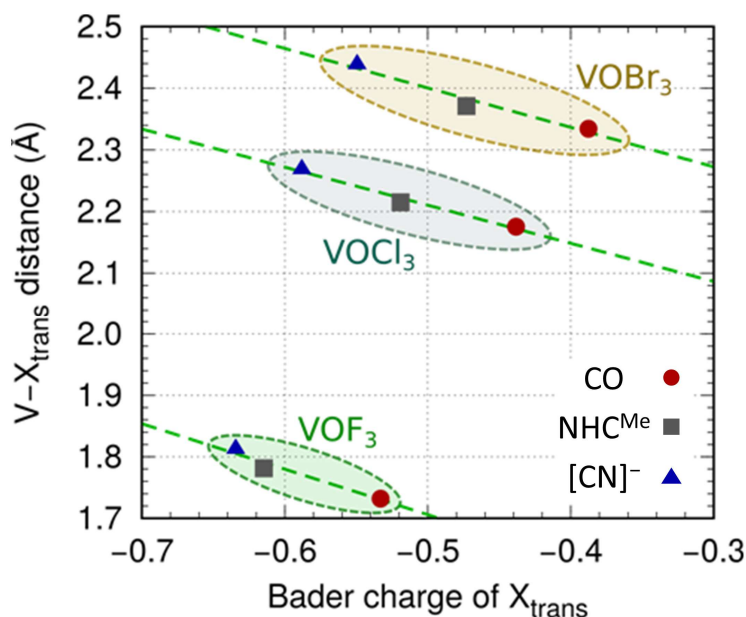


Figure 18: Correlation between the $V-X_{trans}$ bond lengths in $[(L)VOX_3]$ complexes and the Bader charges of X_{trans} ions ($L = CO, NHC^{Me}, [CN]^-$; $X = F, Cl$ or Br). Note that the more the X_{trans} anion is negatively charged, the longer the $V-X_{trans}$ bond. Figure is based on the reference [324].

The results of the population analysis (Table 15) and the structural parameters presented in Table 17 allow us to rationalize the dependence of $V-X_{trans}$ and $V-X_{cis}$ bond distances on donating/back-donating characteristics of the ligand. Figure 18 plots the dependence of the $V-X_{trans}$ bond length on the Bader charge of the X_{trans} ion; this figure clearly reveals that the more the X_{trans} ion is negatively charged, the longer is the $V-X_{trans}$ bond (a similar dependence exists if the Bader charge of VOX_3 is considered instead of the charge of X_{trans} , not shown). Due to different sizes of F, Cl and Br ions, each of them displays its own dependence, but the three regression lines are roughly parallel to each other (the slopes are -0.74 Å/e , -0.62 Å/e and -0.64 Å/e for F, Cl and Br, respectively). This plot further reveals that for a given ligand, the magnitude of the negative charge of X_{trans} increases, as expected, in the order of $F > Cl > Br$. Another notable observation from Table 15 and Table 17 is that for a given VOX_3 counterpart, the larger the back-bonding to the ligand, the smaller the $C-V-X_{cis}$ angle; in other words, the tilting of X_{cis} ions toward the ligand increases with back-donation, thus displaying the $CO > NHC^{Me} > [CN]^-$ trend, i.e. the larger the tilt, the smaller the $C-V-X_{cis}$ angle.

Table 17: V–X_{cis}, V–X_{trans}, V–O and V–C bond lengths and C–V–X_{cis} angles for standalone high-symmetry [(L)VOX₃] (L = NHC^{Me}, CO, [CN][−]) complexes, calculated at the PBE/plane-wave level of theory. Table is based on the reference [324].

	$d(\text{V-X}_{\text{cis}})$ [Å]	$d(\text{V-X}_{\text{trans}})$ [Å]	$d(\text{V-O})$ [Å]	$d(\text{V-C})$ [Å]	$\angle(\text{C-V-X}_{\text{cis}})$ [°]
[(L)VOF ₃]					
[(NHC ^{Me})VOF ₃]	1.797	1.781	1.581	2.184	80.1
[(CO)VOF ₃]	1.751	1.732	1.575	2.592	76.1
[(CN)VOF ₃] [−]	1.798	1.813	1.583	2.119	82.6
[(L)VOC ₃]					
[(NHC ^{Me})VOC ₃]	2.268	2.215	1.572	2.138	78.3
[(CO)VOC ₃]	2.225	2.175	1.572	2.182	76.8
[(CN)VOC ₃] [−]	2.261	2.268	1.573	2.076	80.9
[(L)VOBr ₃]					
[(NHC ^{Me})VOBr ₃]	2.437	2.371	1.570	2.130	78.4
[(CO)VOBr ₃]	2.401	2.334	1.570	2.122	75.3
[(CN)VOBr ₃] [−]	2.425	2.438	1.571	2.076	80.8

To scrutinize the effect of back-bonding on the V–X_{trans} versus V–X_{cis} bond distances, we have compared the two distances to each other in Figure 19a. For the [(CN)VOX₃][−] complexes, which lack any back-donation, the two distances are roughly the same and the respective points lie on the y=x line. In contrast, in [(CO)VOX₃] and [(NHC^{Me})VOX₃] complexes, back-bonding apparently shortens the V–X_{trans} bond with respect to the V–X_{cis} bond and correspondingly these points lie on a dashed line which displays a slightly smaller slope. To further corroborate this observation, Figure 19b shows how the difference between V–X_{cis} and V–X_{trans} bond lengths depends on π -back-donation (the dependence is plotted only for CO and NHC^{Me} ligands, because back-donation is absent for the [CN][−] ligand). It is clearly evident from the figure that for a given ligand, the larger the back-donation, the shorter the V–X_{trans} bond with respect to the V–X_{cis} bond.

Our computational results agree with previous results of [(L)NbCl₅] complexes, where the Nb–Cl_{trans} bond is longer in the presence of σ -donating ligands and shorter in the presence of π -acceptor ligands [107]. But currently we also scrutinized the effect of back-bonding on the difference between the V–X_{cis} and V–X_{trans} bond lengths. There is, however, one provision. Namely, the above rationalization of ligand’s donating and back-donating characteristics on V–X_{trans} and V–X_{cis} bond distances of VOX₃ holds for standalone complexes. We showed above that in the crystal structure, the crystal packing effects may have a significant influence on the V–X bond lengths (Figure 14); for [(NHC^{Dipp})VOF₃] (**5**) they elongate the V–F_{trans} bond by 0.04 Å. An estimate based on the correlation between the V–X_{trans} bond lengths and Bader charges of VOF₃ counterpart (not shown) reveals that such an elongation is equivalent to a ligand’s donation of about 0.15 e[−]. This clearly indicates that care should be exercised when estimating the ligand’s donating power solely from bond lengths obtained from the crystal structure.

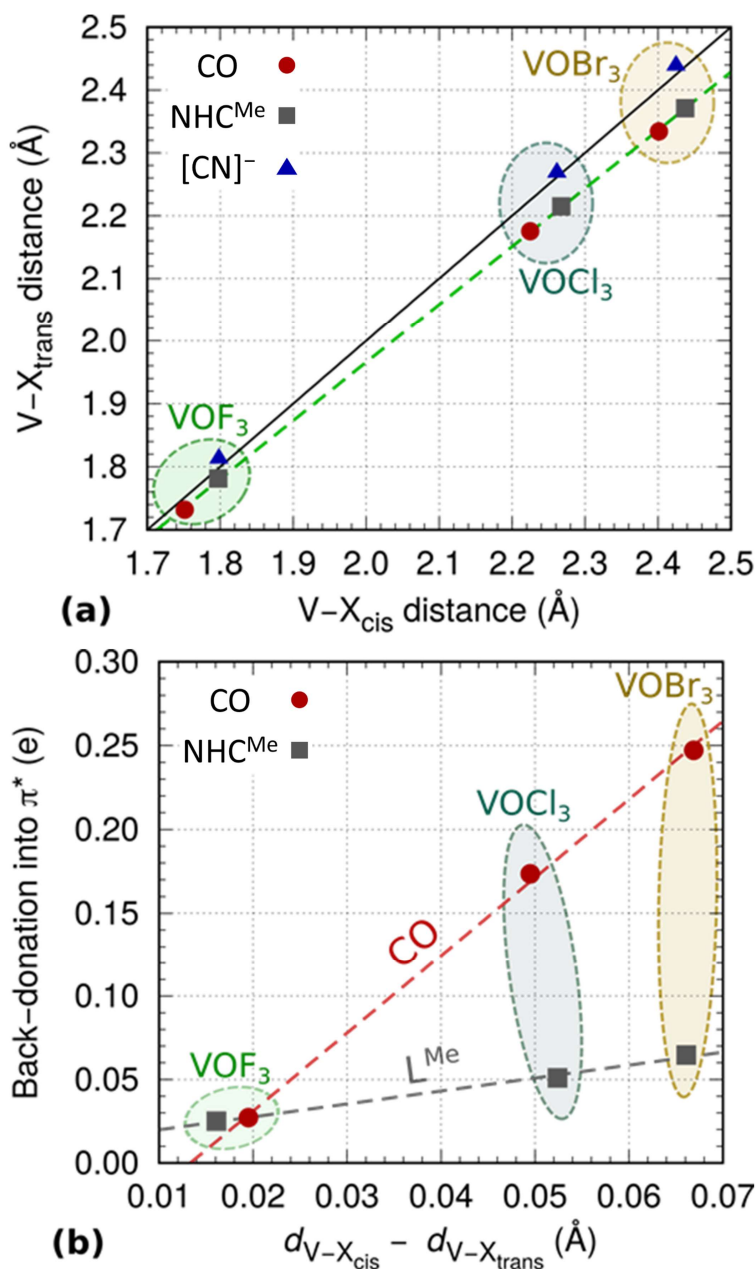


Figure 19: (a) Correlation between the $V-X_{trans}$ and $V-X_{cis}$ bond lengths in standalone $[(L)VOX_3]$ complexes; the solid slanted line represents the slope of 1 and the points of the $[(CN)VOX_3]^-$ complexes lie on it due to the absence of back-bonding to $[CN]^-$ ligand, whereas for CO and NHC^{Me} ligands, the back-bonding shortens the $V-X_{trans}$ bond and correspondingly these points lie on a green-dashed line which displays the smaller slope of 0.93, i.e. the $V-X_{trans}$ bond is slightly shorter than the $V-X_{cis}$ bonds. (b) Correlation between the back-donation into virtual π^* -orbitals and the difference between the $V-X_{cis}$ and $V-X_{trans}$ bond lengths, plotted only for CO (red dashed line) and NHC^{Me} (gray dashed line) ligands, because the back-bonding is absent for the $[CN]^-$ ligand. For a given ligand, the larger the back-donation, the shorter the $V-X_{trans}$ bond with respect to the $V-X_{cis}$ bond. Figure is based on the reference [324].

4.3 Associated Organic Ligands to the Pentacoordinated Tetrafluoride Oxide Vanadium(V)

Structurally characterized salts $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$ and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$ presented in this chapter as well as comparison of their structural features are basis for a yet unpublished manuscript currently titled “[VOF_4] $^-$ anion with weak ligand contact: Coordinated or hydrogen bonded?”. Additional crystal structure of $[(\text{NHC}^{\text{Dipp}})\text{H}]_2[(\text{VOF}_4)_2(\text{pyz})]$ salt and other information are part of the ongoing study.

4.3.1 Synthesis and structural characterization of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$

Crystallization of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) salt was performed with slow evaporation of the MeCN solvent from the mother liquor under static vacuum [244]. Resulting solvate crystals were $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]\cdot 2\text{MeCN}$ (**6a**), with both MeCN molecules turned away from the anion. When isolated bulk powder of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) was dissolved in THF and the solution was slowly concentrated with evaporation of the solvent under inert conditions crystals of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$ (**8**) began to form. Since $[\text{VOF}_4]^-$ reacts with silica from glassware, these reactions were performed in vessels made from FEP. Indiscriminately of the procedure, identical crystals were obtained with the reaction of VOF_3 and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ in THF and equivalent crystallization process. Whereas the isolation of dry reaction product yields only starting $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) as a main product. Similarly, upon transferring the crystals from mother liquor into inert liquid medium (octane, silicon oil, perfluorodecalin), these crystals presumably quickly lose weakly bound THF molecule, manifesting in noticeable weaker diffraction pattern. When crystals are exposed to air, they instantaneously react and decompose into unidentifiable compounds. Selected structural features are outlined in Table 18. However, more structural details, bond valence sum, crystal collection data and refinement parameters are given in the Appendix (Table A2, Table A9 and Table A16).

Analysis of the crystal structure (Figure 20) showed that THF molecule is positioned on the sixth coordination site of the vanadium(V) center in the $[\text{VOF}_4(\text{L})]^-$ anion. It is located *trans* to the oxide ligand and is enclosed with the fluoride ligands. Ligands in the coordination sphere of vanadium(V) adopt distorted octahedral geometry.

Length of the V–O bond in the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$ (**8**) compound is 1.561(2) Å, which is equivalent to the same bond in the larger of the domains in the disordered $[\text{VOF}_4]^-$ anion. Discrepancies in length of V–F bonds are more prominent. In $[\text{VOF}_4(\text{THF})]^-$ anion, their values range between 1.805(1)–1.821(1) Å (mean value 1.813 Å), whereas in the $[\text{VOF}_4]^-$ anion, the mean value is 1.798 Å. THF molecule occupies, due to its flexible nature, several positions with two main domains that are almost evenly represented. Occupancy of the domain A is 46.1(9) % and of the domain B 53.9(9) %. After the components of the disorder were modeled, both domains were in the half-chair conformation (see the Appendix Figure A10) [355]. The length of the V–O_{THF} bond in the domain A is 2.403(7) Å and in the domain B 2.464(6) Å. The distance of both bonds is well within the sum of van der Waals radii (3.92 Å) [339] and some associative interactions are expected. Comparison of the V–O_{ligand} bond in the $[\text{VOF}_4(\text{THF})]^-$ to the structurally related water containing $[\text{VOF}_4(\text{H}_2\text{O})]^-$ anion, which is 2.274(3) Å [155] and 2.333(2) Å [132], unveiled unusually elongated V–O_{ligand} interaction *trans* to the doubly bonded oxide ligand.

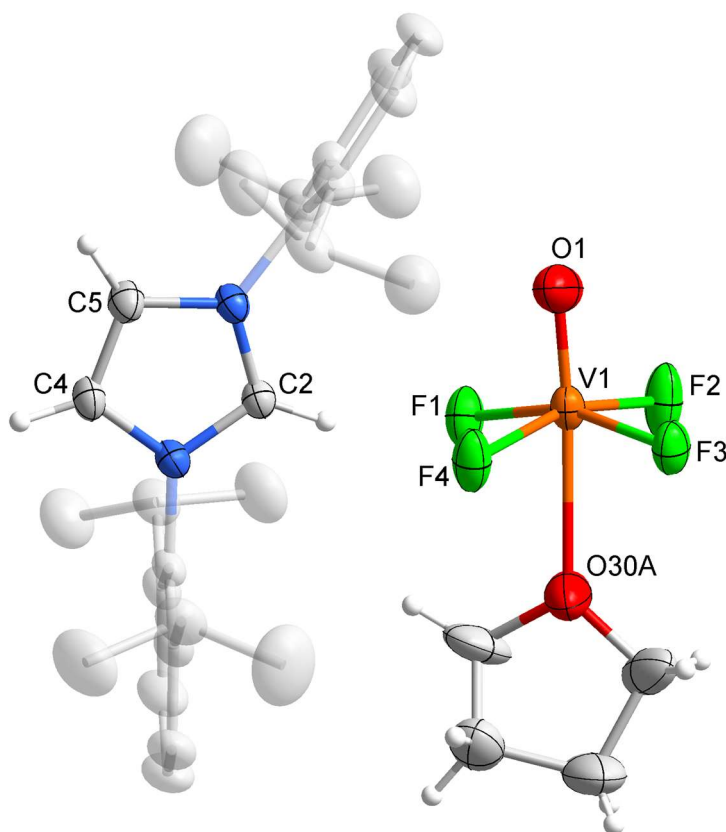


Figure 20: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$ (**8**) salt. Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ are shaded, less relevant hydrogen atoms are omitted and only domain A of the THF molecule is shown.

Fluoride ligands of the $[\text{VOF}_4(\text{THF})]^-$ are pushed slightly more toward ideal octahedral geometry in regard to the discrete square pyramidal $[\text{VOF}_4]^-$, which is observed as a decrease of the O1-V-F angle and consequential displacement of the vanadium(V) center from the plane of the equatorial fluoride ligands. O1-V-F angles in $[\text{VOF}_4(\text{THF})]^-$ range between $98.69(8)$ – $100.53(7)^\circ$ (mean value 99.8°), while mean value of the equivalent angles in $[\text{VOF}_4]^-$ is 104.5° . Angle $\text{O1-V-O}_{\text{THF}}$ is in spite of twisted conformation surprisingly linear with $171.3(2)^\circ$ for domain A and $175.1(2)^\circ$ for domain B. As mentioned, vanadium(V) cation is displaced from the plane of fluoride ligands by $0.309(4)$ Å, suggesting to the disordered octahedral geometry of the anionic $[\text{VOF}_4(\text{THF})]^-$ moiety.

Plane of THF atoms in domain A is according to the plane of O1-F1-F3 and O1-F2-F4 tilted by $40.7(4)^\circ$ and $53.6(4)^\circ$, respectively. Domain B of the THF molecule is in a much more eclipsed position in regard to the same planes, with the dihedral angle being $18.8(3)^\circ$ for O1-F1-F3 and $77.3(3)^\circ$ for O1-F2-F4 .

The shortest contacts of the anion and imidazolium cations are $\text{F1} \cdots \text{C2}$, $\text{F3} \cdots \text{C4}$ and $\text{F4} \cdots \text{C2}$ with the distance being $2.896(2)$ Å, $2.921(2)$ Å and $2.877(2)$ Å, respectively. The plane of equatorial fluorides is with the $87.0(5)^\circ$ almost perpendicular to the neighboring imidazolium plane with C2 atom pointing toward the anion, whereas the angle between the same plane of fluorides and imidazolium cation facing the anion with C4 and C5 is $23.9(6)^\circ$.

4.3.2 Synthesis and structural characterization of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$

Similar synthesis procedure for the preparation of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{L})]$ was attempted with py, since it fits the criteria of cyclic, neutral, electron donating molecule. It is one of the most commonly used ligands in coordination chemistry and its bonding capabilities to the vanadium(V) have been presented in compounds $\text{VOF}_3(\text{py})_2$ [126] and $\text{VO}_2\text{F}(\text{py})_2$ [171]. Ionic $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) readily dissolved in py. Slow evaporation of the solvent under inert conditions from the FEP containers yielded crystals of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$ (**9**), albeit only few. Crystals of much better quality were obtained when equimolar amount of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and py was dissolved in DCM and reaction mixture was slowly concentrated under static vacuum. Crystals are more stable than the congeners with THF, yet they become unsuitable for crystallographic examination if left, immersed in the inert liquid, exposed to air for more than 30 minutes. Selected structural features are outlined in Table 18. However, more structural details, bond valence sum, crystal collection data and refinement parameters are given in the Appendix (Table A2, Table A10 and Table A16).

Examination of the crystal structure reveals that the asymmetric unit comprises two subunits (Figure 21). py molecule is positioned *trans* to the oxide ligand as expected from the results observed for the $[\text{VOF}_4(\text{THF})]^-$ anion. Ligands in the anion form distorted octahedral geometry around the vanadium(V) coordination center.

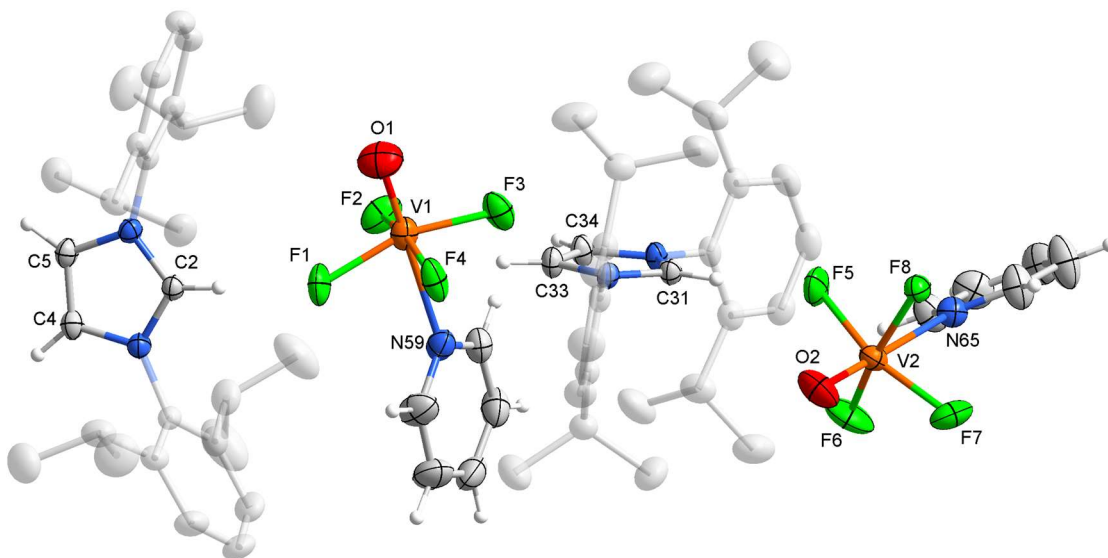


Figure 21: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$ (**9**) salt (both subunits are presented). Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ are shaded and less relevant hydrogen atoms are omitted.

Length of the V–O bond is 1.570(2) Å and 1.574(2) Å for the first and second subunit, respectively. They are just slightly elongated in comparison to the same bond in $[\text{VOF}_4]^-$ anion, which is 1.560(2) Å. V–F bond distances range from 1.804(1)–1.840(1) Å for both subunits (mean value 1.822 Å and 1.818 Å for the first and second subunit, respectively) and are also noticeable longer, when compared to the same bonds in the $[\text{VOF}_4]^-$ anion with a mean value of 1.798 Å. Length of the V–N_{py} bond is 2.399(2) Å and 2.406(2) Å for the first and second subunit, respectively. Both bond distances are well within the sum of

van der Waals radii (4.08 Å) [339]. The length of the V–N_{pyz} bond in anionic complex with pyz ligand is 2.465(2) Å. Unfortunately, there are no other closely related vanadium(V) compounds with aromatic nitrogen-based ligands in *trans* position to oxide ligand, to give us a helpful insight into the py’s interaction with the [VOF₄][−] anion. The most relevant compound is the neutral [WOF₄(py)] complex [213]. The W–N_{py} bond is 2.344(3) Å long and unusual length of M–N_{py} (M = V, W) bond indicates weak interactions within the adduct.

The size of the O–V–F angles in both subdomains ranges within 98.07(8)–100.40(7)° (mean value 99.17° and 99.11° for first and second subunit, respectively). Decrease in O–V–F angle size, when compared to the mean value of 104.5° of parent [VOF₄][−], correlates with the association of the py molecule in the coordination sphere of vanadium(V). However, O–V–F angles shifted from the ideal right angle, which is directly related to the displacement of vanadium(V) cation from the plane of fluoride ligands by 0.291 Å for the first subunit and 0.288 Å for the second subunit, indicate a distorted octahedral geometry of the [VOF₄(py)][−] anion. O–V–N_{py} angle is 179.61(9)° and 176.78(8)° for the first and the second subunit, respectively. These almost ideal values are in part due to the rigid structure of the py molecule.

The plane of the py in the first subunit is tilted in accordance with the plane O1–F1–F3 by 42.04(8)° and with the plane O1–F2–F4 by 47.90(7)°, whereas the plane of the py in the second subunit is slightly pushed from the ideal staggered position and dihedral angle with plane O2–F5–F7 being 56.8(3)° and with plane O2–F6–F8 being 32.9(3)°.

The closest contacts between imidazolium cations and anion of the first subunit are F1···C2, F4···C33 and F4···C34 being 2.896(2) Å, 2.921(2) Å and 2.877(2) Å, respectively. As for the shortest interactions between imidazolium cations and anion of the second subunit, which are F5···C31, F8···C4 and F8···C5 and are of similar lengths; 2.888(2) Å, 3.022(2) Å and 2.984(2) Å, respectively. The plane of the equatorial fluoride ligands of the first subunit is at the 70.31(5)° angle to the imidazolium plane with C2 atom pointing toward the anion and at the 24.14(7)° angle to the imidazolium plane with C33 and C34 atoms faced to the anion. Angles between imidazolium planes of the cations and the plane of equatorial fluoride ligands in the anion of the second subunit are similar to those of the first subunit. The dihedral angle between the imidazolium plane with C31 atom facing anion and fluorides is 76.00(8)° and between the imidazolium plane with C4 and C5 atoms oriented toward anion 20.61(2)°. Planes of fluoride ligands of both subunits are at the dihedral angle of 80.80(6)°.

4.3.3 Synthesis and structural characterization of [(NHC^{Dipp})H]₂[(VOF₄)₂(pyz)]

To the [(NHC^{Dipp})H][VOF₄] (**6**) dissolved in MeCN, a solution of pyz in MeCN was added. Both reagents were added in an equimolar ratio. Evaporation of the solvent under inert conditions produced single crystals. Determination of crystal structures led to the discovery of a solvate crystal with formula [(NHC^{Dipp})H]₂[(VOF₄)₂(pyz)]·4MeCN (**10a**). Interestingly, identical reaction performed in DCM yielded only imidazolium cation and uncoordinated [VOF₄][−] anion. The MeCN molecules are severely disordered as they are filling the gaps between neighboring imidazolium cations and are held in place only by weak interactions. The structure of the [(NHC^{Dipp})H]₂[(VOF₄)₂(pyz)]·4MeCN (**10a**) possesses a center of inversion in the center of aromatic pyz molecule. Selected structural features are outlined in Table 18. However, more structural details, bond valence sum, crystal collection data

and refinement parameters are given in the Appendix (Table A2, Table A11 and Table A16).

The most interesting feature is anionic species, where two $[\text{VOF}_4]^-$ anions capped heterocyclic pyz from both ends, which is shown in Figure 22. The obtained double anion adduct was indeed hypothesized, although the molar ratio for its formation in current reaction conditions was suboptimal. The remaining pyz reagent remained dissolved in the solution.

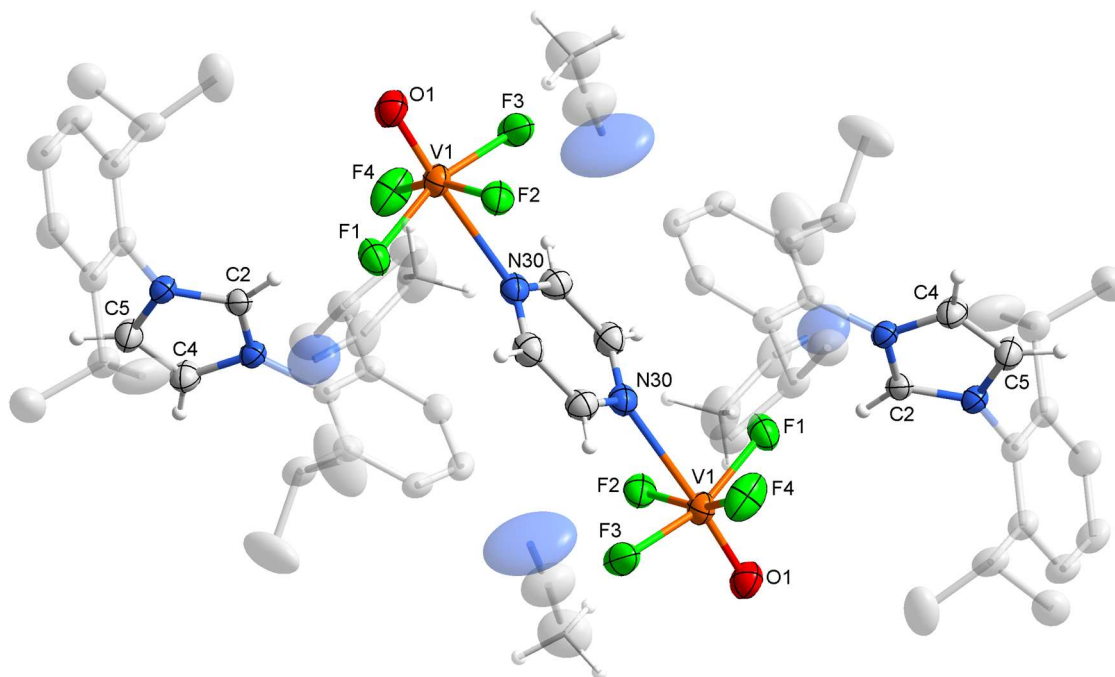


Figure 22: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}]_2[(\text{VOF}_4)_2(\text{pyz})]\cdot 4\text{MeCN}$ (**10**) salt. Ellipsoids are drawn at 50 % probability. For clarity, the “wingtips” of $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ are shaded, less relevant hydrogen atoms are omitted and only domain A of the MeCN molecule is shown. Symmetry code: (i) $-x, -y, 1-z$.

Bond V–O is 1.581(1) Å long and length of V–F bonds ranges between 1.798(1)–1.828(1) Å (mean value 1.814 Å). Comparison bond distances of the same bonds in the $[\text{VOF}_4]^-$ and $[\text{VOF}_4(\text{py})]^-$ anion, the V–O is 1.560(2) Å long and mean value for V–F bonds is 1.798 Å for precursor $[\text{VOF}_4]^-$, while in $[\text{VOF}_4(\text{py})]^-$ anion the V–O is ca. 1.570 Å long and mean value for V–F is ca. 1.820 Å. Bond lengths marginally differentiate from bonds in discrete $[\text{VOF}_4]^-$ anion but they are similar to bonds in the $[\text{VOF}_4(\text{py})]^-$ anion. The length of the V– N_{pyz} bond is 2.465(2) Å, which is noticeably longer than 2.400 Å long V– N_{py} in $[\text{VOF}_4(\text{py})]^-$, yet it is within the sum of van der Waals radii (4.08 Å) [339].

O–V–F angles are in the range 98.13(6)°–100.27(7)° and their size decreases in comparison to the matching angles in $[\text{VOF}_4]^-$ anion with a square pyramidal geometry mean value of 104.5°. This tendency was already observed in $[\text{VOF}_4(\text{py})]^-$ anion and could be in response to the interaction of a larger heterocyclic ligand in the vicinity of fluoride ligands. The consequence of obtuse O–V–F angles is distorted octahedral geometry of ligands, with vanadium(V) center being displaced from the plane of fluoride ligands by 0.288 Å. The size of the O–V– N_{pyz} angle is 176.41(7)°. Non-ideal straight angle could be to some extent a result of encapsulation of pyz molecule by two $[\text{VOF}_4]^-$ units.

The enclosed pyz ligand is slanted in relation to the $[\text{VOF}_4]^-$ moiety as the lines going through N30-N30ⁱ of the pyz molecule and O1-V1 are at the 12.81(7)° angle. The deformation of the pyz ligand could be due to the crystal packing, but its additional contributing factor is π -stacking with one of the imidazolium's phenyl wingtips. The angle between the plane of the pyz and the mentioned phenyl ring is 16.11(7)°. The distance between the centroids of the aromatic rings is 3.643(1) Å. On the other side of the pyz is the same phenyl ring generated through the inversion center. pyz molecule is in regard to the $[\text{VOF}_4]^-$ in an almost staggered conformation with the angle between the plane of pyz and the O1-F1-F3 plane of the anion being tilted by 40.19(6)° and with the O1-F2-F4 plane by 53.09(5)°.

The shortest interaction between the imidazolium cation and the anion is F1···C2 separating two species by 3.032(2) Å. F2···C4 contact of anion with the other imidazolium cation is slightly longer with 3.204(3) Å. The plane of the imidazolium ring is at the 73.8(1)° angle in regard to the plane of the equatorial fluoride ligands of the anion. Solvate molecules of MeCN are squeezed in place by weak C-H···F interactions with the anion. The shortest interactions are C35B···F2 and C38A···F3 with 3.14(1) Å and 3.25(2) Å, respectively. Since interactions with the anion are only stabilizing forces, the observed disorder is a reasonable outcome.

4.3.4 Interaction anion–ligand within the anionic complex

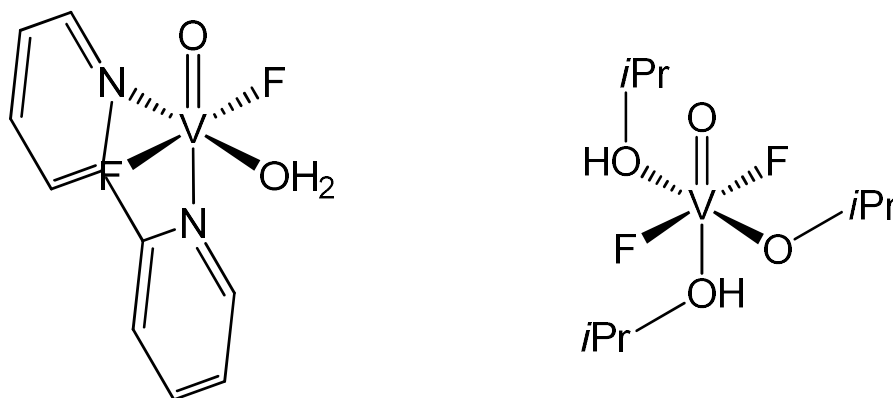
Adduct of the anionic species and neutral molecule is a poorly researched field. Partial contributing factor to this is a modest amount of structurally characterized anionic complexes in comparison to their neutral counterparts. Intuitively, bonding of the electron donating ligand to the anion is an unfavorable process. However, in the literature, interaction between the central cation and the heteroatom from ligand in anionic complexes is defined as coordinative [159], [211], [213]–[215].

Association of the ligand molecule to the $[\text{VOF}_4]^-$ anion with square pyramidal geometry leads to various structural effects described below. Herein structurally equivalent vanadium(V) oxide fluoride isolated complexes will be used for commentary of relevant structural features, however if not available, VOFs with a lower oxidation state or complexes with a different metal center will be discussed. Compounds with vanadium in lower oxidation states possess at variance with the d^0 metal center additional bonding capabilities, due to the valence d-electron. However, overview of the literature showed there are no noteworthy differences in bonds and angles, whether the oxidation state of the coordination center is IV or V. Octahedral geometry of ligands surrounding the metal center is also essential for proper correlations among coordination compounds, as complexes with lower coordination number have vastly different steric effects. Comparison of some of the highlighted structural features among closely related anionic complexes prepared by us and from the literature are given in Table 18.

As seen from our crystal structures with $[\text{VOF}_4(\text{L})]^-$ anion or equivalent moieties from literature, the V–L bond is located *trans* to the V–O bond. Reference for the length of the latter is the largest of the domains for the disordered parent $[\text{VOF}_4]^-$ anion. A small increase in length of the V–O bond is observed with the introduction of heterocyclic ligand into the crystal structure. It is tempting to attribute small differences in V–O bond lengths to bonding capabilities of the specific ligand, nevertheless the subtle discrepancies are in the range of the experimental error and are more likely to occur due to the different experimental temperature. For instance, the longest V–O bond is observed in $[(\text{VOF}_4)_2(\text{pyz})]^{2-}$, yet this is not due to the strongest V–L interaction as the elongation of both bonds is simultaneous. When doubly bonded oxide ligand and neutral organic ligand

are situated *trans* to each other, significant elongation in bonding of the latter is expected, which is reasoned as a consequence of trans effect, intramolecular interactions and steric encumbrance involving cyclic ligand and equatorial fluorides. Bulkiness of the ligand might be the basis for the length of the V–L bond. This explains a slightly shorter bond in case of the smaller water in comparison to the larger THF and py ligands, while other structural features remain almost identical among all anionic complexes. V–L bond for pyz ligand is slightly longer than for the related py, presumably due to the nature of enclosed doubly bonded pyz molecule and lack of stabilizing effects, when one side of the ligand is exposed to the other low strength interactions within the crystal.

Trans effect is observed in complexes with equivalent nitrogen or oxygen ligands on different positions within the complex. Two such known examples are $[\text{VOF}_2(\text{O}i\text{Pr})(i\text{PrOH})_2]$ ($\text{O}i\text{Pr}$ = isopropoxide, $i\text{PrOH}$ = isopropanol) [176] and $[\text{VOF}_2(\text{H}_2\text{O})(\text{bipy})]$ (Scheme 15) [164]. The former has two $i\text{PrOH}$ groups, where the first is *trans* to doubly bonded oxide ligand and the second is *trans* to alkoxide ligand. Average V–O distance to the corresponding $i\text{PrOH}$ ligands is 2.252 Å and 2.159 Å, respectively. Trans effect of the oxide ligand yielded roughly 0.1 Å longer bond. The second example has the bipy ligand in the complex $[\text{VOF}_2(\text{H}_2\text{O})(\text{bipy})]$ positioned with one heterocycle *trans* and another *cis* with relative to the oxide ligand [164]. Coordination environment of heterocycles is different. Across from the *cis* heterocycle is the water ligand and V–N bond is 2.120(4) Å long, whereas the bond distance to the *trans* heterocycle is 2.273(4) Å, making it approximately 0.15 Å longer.



Scheme 15: Two examples of neutral VOF with identical moieties bonded *cis* and *trans* to the oxide group [164], [176], demonstrating that ligand in trans position forms a weaker, elongated bond.

Effects of association of the ligand molecule to the sixth coordination site are more evident in length of V–F bonds and size of O–V–F angles. Repulsive forces of negatively charged oxide and fluoride ligands in discrete $[\text{VOF}_4]^-$ anion are responsible for anion's square pyramidal geometry. Introduction of new ligand is accommodated by marginal elongation of V–F and decrease of the O–V–F angles, which could indicate coordination to the vanadium(V) center. Nevertheless, V–O and V–F bond distances do not significantly expand, angles are still larger than 90° expected for ideal octahedral geometry and V–L bond distances are substantially longer. The sum of all the presented facts motivated us to find alternative explanations. In the absence of significant coordination interactions of water or heterocyclic molecule, hydrogen bonds and crystal packing most likely determine positions of these molecules in the crystal structure. This would rationalize staggered conformation that heterocycles adopted relative to the $[\text{VOF}_4]^-$ moiety determined in our

crystal structures. In staggered conformation, each C–H bond in rigid py and pyz interacts with two fluorides, while THF molecule exhibits such tendencies, but its flexible character does not fully permit optimal orientation. Although the hydrogen atoms were automatically added in the process of solving and refining the crystal structures, locations of residual electron densities were observed in equivalent places as were later added automatically. The proximity of a relatively large ligand molecule and its steric effect onto equatorial fluorides would explain the reduction in the size of the O–V–F angles, which is still at an obtuse angle due to strong aforementioned repulsive forces and minimal changes in the length of V–O and V–F bonds.

Elongated V–L bond is a well-recorded feature in $[\text{MOX}_4(\text{L})]$ (M = transition metal; X = halide; L = organic ligand) neutral and anionic species [132], [155], [210]–[215]. Although the distance is within the sum of van der Waals radii, it is detained in place by evidently rather weak interactions. These are most likely interplay of V–L coordinative bond and C–H $\cdots$ X contacts. Unfortunately, we were unable to elucidate appropriate contributing components. In crystal systems, numerous relatively weak factors, e.g. considerable amount of weak hydrogen bonds, electrostatic interactions, steric effects, crystal packing, are usually neglected, but collectively they can significantly contribute to the final product. Observed elongation of V–N bond in $[(\text{VOF}_4)_2(\text{pyz})]^{2-}$ versus $[\text{VOF}_4(\text{py})]^-$ by ca. 0.6 Å could be explained as follows: pyz molecule is enclosed by two $[\text{VOF}_4]^-$ anions, which isolates and reduces the number of interactions affecting the heterocycle. However, without a theoretical study of this phenomenon we must be cautious in our predictions, since many different positive and negative effects may contribute to the association of neutral moieties.

Study of donor interaction to the $[\text{VOF}_4]^-$ anion was expanded to other possible and commonly available cyclic neutral reagents with the electron donating group. Tested nitrogen donor-based molecules were piperidine, phenazine, bipy and phen, while oxygen containing donor molecules were 1,4-dioxane and benzophenone. Due to the solid nature of most of the reagents, the reactions were performed in MeCN or DCM since these solvents showed no coordination capabilities in the VOF system but have a high tendency to form solvate crystals and in some instances solvent molecules in crystals prevented disorder of the ionic constituents. However, reactions did not proceed as intended and X-ray analysis of crystals or NMR analysis of isolated bulk powder revealed uncoordinated $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ salt, suggesting that $[\text{VOF}_4]^-$ anion coordinates only with molecules that meet certain size and structure-related criteria. Possible applicability of this capability is selective interaction of the anions to specific molecules. Attempts to insert H_2O to the sixth coordination place proved ineffective in previous hydrolysis reactions of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**), since even small amounts of water reacted with the anion.

Table 18: Comparison of selected bond distances and angles for pentacoordinated $[\text{VOF}_4]^-$ anion and related hexacoordinated $[\text{VOF}_4(\text{L})]^-$ anionic complexes.

Ref.	$[\text{VOF}_4]^-$ (6)	$[\text{VOF}_4(\text{THF})]^{-[\text{a}]}$ (8)	$[\text{VOF}_4(\text{py})]^-$		$[(\text{VOF}_4)_2(\text{pyz})]^{2-}$ (10)	[132]	$[\text{VOF}_4(\text{H}_2\text{O})]^-$ [155]	[187]
Temp. [K]	100	150	Subunit 1 (9)	Subunit 2 (9)	150	295	93	100
Intramolecular bond distance [$\text{\AA}$]								
V–O	1.560(2)	1.561(2)	1.570(2)	1.574(2)	1.581(1)	1.577(3)	1.578(3)	1.570(1)
	1.776(2)	1.805(1)	1.804(1)	1.805(1)	1.798(1)	1.769(2)	1.795(2)	1.826(1)
V–F	1.794(2)	1.806(1)	1.811(1)	1.815(1)	1.813(1)	1.776(2)	1.836(2)	1.867(1)
	1.807(2)	1.819(1)	1.831(1)	1.821(1)	1.816(1)	1.830(2)	1.837(2)	1.829(1)
	1.815(2)	1.821(1)	1.840(1)	1.832(1)	1.828(1)	1.858(2)	1.843(2)	1.804(1)
avg. V–F ^[b]	1.798	1.813	1.822	1.818	1.814	1.808	1.828	1.832
V–L ^[c]	/	2.403(7) (O30A) 2.464(6) (O30B)	2.399(2)	2.406(2)	2.465(2)	2.333(2)	2.274(3)	2.374(1)
Angle [$^\circ$]								
	103.1(1)	98.7(1)	98.6(1)	98.1(1)	98.1(1)	98.0(1)	98.1(1)	99.7(1)
O–V–F	103.4(1)	99.6(1)	99.1(1)	98.6(1)	98.8(1)	99.1(1)	98.2(1)	99.5(1)
	104.5(1)	100.2(1)	99.5(1)	99.3(1)	99.4(1)	99.7(1)	98.9(1)	99.9(1)
	107.0(1)	100.5(1)	99.5(1)	100.4(1)	100.3(1)	99.7(1)	100.7(1)	99.7(1)
avg. O–V–F ^[d]	104.5	99.8	99.2	99.1	99.2	99.1	99.0	99.7
O–V–L	/	171.3(2) (O30A) 175.1(2) (O30B)	179.6(1)	176.8(1)	176.4(1)	177.3(1)	178.0(1)	178.1(1)

^[a] THF ligand in the $[\text{VOF}_4(\text{THF})]^-$ anion is disordered, therefore both values regarding O_{THF} are given.

^[b] Average value of all four V–F bonds.

^[c] Distance from vanadium center to electron donating atom of the ligand.

^[d] Average value of all four O–V–F angles.

4.4 Oxonium Induced Cyclotrimerization of Nitriles

Reports, explanations and conclusions in this chapter are part of the unpublished work regarding oligomerization of nitriles into dimeric or trimeric products. Additional research is underway.

4.4.1 Synthesis and structural characterization of $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$

$[\text{H}_3\text{O}][\text{SbF}_6]$ is a white solid salt that is stable under the inert atmosphere and is prepared by the reaction of parent antimony pentafluoride SbF_5 and equimolar amount of water in anhydrous HF as a solvent (rxn. 8) [244], [245].



The salt is poorly soluble in non-polar organic solvents, but it readily dissolves in nitrile solvents. All nitrile reagents used for the following study were liquid at standard conditions. In the reactions they simultaneously served as a solvent as well as a reagent. If the salt is dissolved in dry PhCN in the molar ratio of 1:10 and left undisturbed overnight at ambient temperature, single crystals suitable for X-ray structural analysis start to form. Heating the reaction mixture to 70 °C improves the speed of the crystal growth, without the decrease in their quality, as they start to form after only a few hours. Structural characterization of the single crystals surprisingly revealed salt composed of the protonated product of cyclotrimerization of PhCN solvent *s*-triazine and $[\text{SbF}_6]^-$ anion. Cation of protonated 2,4,6-triphenyl-1,3,5-triazine compound is later referred to as *s*-triazinium $[(^{\text{Ph}}\text{TZN})\text{H}]^+$ cation. The structure is depicted in Figure 23 and a detailed overview of the bond lengths and angles is given in Table 19. Crystal collection data and refinement parameters are given in the Appendix (Table A18). Results can be reproduced if reaction mixture is prepared under inert conditions but is later fully exposed to the air, which demonstrates crystal's stability toward atmospheric oxygen and water. Crystals dissolve nicely in MeCN, while according to NMR spectroscopy, they are only scarcely soluble in DCM and completely insoluble in non-polar solvents. $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (**11**) is the penultimate stage in the preparation of *s*-triazines. Ionic product is a result of acidic character of the oxonium reagent and weakly coordinating anion and is stable due to the rigorously dry reaction conditions. Attempts to deprotonate *s*-triazinium cation were performed in water with Na_2CO_3 and the reaction indeed afforded triazine compound along with some decomposition products, one of which was identified as benzamide.

Bonding-wise the presented structure of $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (**11**) possesses two intriguing details, both of which are related to the proton on the N1 of the $[(^{\text{Ph}}\text{TZN})\text{H}]^+$ frame facing toward the anion. The F6–N1 distance is 2.916(3) Å, whereas the sum of van der Waals radii is 3.12 Å [339], and the F6–H1–N1 angle is 152.6(2)° suggesting relevant hydrogen bond conjoining cation and anion. Consequently, N1–C2 and N1–C6 bonds are 1.357(4) Å and 1.360(4) Å long, respectively. They are the longest among the N–C bonds within the heterocycle and are elongated in comparison to the N–C bonds in neutral *s*-triazine, which are in the range between 1.334(2)–1.343(1) Å [276]. Sb1–F6 bond of the $[\text{SbF}_6]^-$ anion is similarly affected. It is 1.898(2) Å long and it is noticeably longer five Sb–F bonds, which range between 1.868(2)–1.875(2) Å (mean value of non-elongated bonds 1.871 Å). Since it is oriented toward the cation and thus of all six Sb–F bonds the closest to the cation, the

intercationic distances are similar, the elongation of the N1–F6 bond is most probably a result of shorter As–F bonds.

Table 19: Selected bond distances and angles for $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (**11**), $[(^{\text{Ph}}\text{TZN})\text{H}][\text{NbF}_6]$ (**12**), $[(^{\text{Ph}}\text{TZN})\text{H}][\text{TaF}_6]$ (**13**) and $[(^{\text{Ph}}\text{TZN})\text{H}][\text{AsF}_6]$ (**14**) salts.

Ref.	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (11)	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{NbF}_6]$ (12)	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{TaF}_6]$ (13)	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{AsF}_6]$ (14)
Intramolecular bond distance [Å]				
M–F	1.871(2) (F1)	1.877(1) (F1)	1.884(2) (F1)	1.719(2) (F1)
	1.870(2) (F2)	1.876(1) (F2)	1.883(2) (F2)	1.711(2) (F2)
	1.868(2) (F3)	1.872(1) (F3)	1.885(2) (F3)	1.711(2) (F3)
	1.872(2) (F4)	1.885(1) (F4)	1.890(2) (F4)	1.712(2) (F4)
	1.875(2) (F5)	1.882(1) (F5)	1.891(2) (F5)	1.715(2) (F5)
	1.898(2) (F6)	1.928(1) (F6)	1.930(2) (F6)	1.747(2) (F6)
avg. M–F ^[a]	1.876	1.887	1.894	1.719
N–C	1.360(4) (N1, C6)	1.362(3) (N1, C6)	1.360(4) (N1, C6)	1.362(3) (N1, C6)
	1.357(4) (N1, C2)	1.358(3) (N1, C2)	1.355(4) (N1, C2)	1.365(3) (N1, C2)
	1.317(4) (N3, C2)	1.318(2) (N3, C2)	1.321(4) (N3, C2)	1.311(3) (N3, C2)
	1.343(4) (N3, C4)	1.342(3) (N3, C4)	1.341(4) (N3, C4)	1.346(3) (N3, C4)
	1.348(4) (N5, C4)	1.343(3) (N5, C4)	1.348(4) (N5, C4)	1.350(3) (N5, C4)
	1.320(4) (N5, C6)	1.321(2) (N5, C6)	1.317(4) (N5, C6)	1.313(3) (N5, C6)
Intermolecular bond distance [Å]				
F6–N1	2.916(3)	2.849(2)	2.858(3)	2.951(3)
Angle [°]				
plane _{C7–C12} – plane _{N1–C6}	22.1(1)	22.3(1)	22.2(1)	23.1(1)
plane _{C13–C18} – plane _{N1–C6}	18.4(1)	18.5(1)	18.7(1)	17.9(1)
plane _{C19–C24} – plane _{N1–C6}	4.1(1)	4.6(1)	4.5(1)	4.7(1)

^[a] Average value of all six M–F bonds.

4.4.2 Initiation of cyclotrimerization cascade

To establish how the different constituents of the reagent contribute to the process of the unsuspected cyclotrimerization, reactions with a similar setup were explored. From the literature overview, there are several reports of activation of nitrile reagent *via* its protonation (see Chapter 1.3.1). First we had to eliminate a circumstantial generation of trimers due to weakly coordinating $[\text{MF}_6]^-$ anions. $\text{Cd}[\text{NbF}_6]_2$ salt was dissolved in PhCN and stirred overnight at reflux conditions. According to NMR spectroscopy no relevant product was detected, confirming that $[\text{MF}_6]^-$ anion nor “naked” cation cannot start the trimerization. Alternatively, closely resembling to our $[\text{H}_3\text{O}][\text{SbF}_6]$ reagent, a $[\text{NH}_4][\text{SbF}_6]$ salt was prepared and dissolved in PhCN and kept at ambient temperature or heated to 60 °C. In ^1H NMR spectrum, there were only signals of neutral PhCN and ammonium cation impartial of the reaction temperature. Interestingly, the higher basic character of ammonia in comparison to water and consequently larger pK_a value of ammonium cation (9.26 vs. -1.74 , respectively) renders it inert in this system [356], [357]. Basicity of

ammonia prevents its conjugate acid to participate in the crucial first stage by inducing partial positive charge into cyano group of the PhCN. However, when nitrilium cation is activated by acid, it becomes vulnerable to two consecutive nucleophilic attacks that in the last stage forms a stable cycle and produces thermodynamically favorable *s*-triazinium cations. Therefore, the formation of nitrilium cation is essential for initiation and for the cyclotrimerization process to ensue.

A few years ago it was reported that nitriles have been protonated when introduced in super-acidic HF/MF₅ (M = As, Sb) medium [229]. HF/MF₅ was condensed onto frozen nitrile, which was kept at −196 °C. The reaction mixture was warmed to ambient temperature and stirred for a short period of time before it was cooled again and volatile components were removed in *vacuo*. MF₅ was added in slight excess, while anhydrous HF was in significant surplus since it served as a solvent. They achieved quantitative protonation and successfully determined the first crystal structures of different isolated protonated nitrile cations in [(RCN)H][MF₆] salts. Reaction stopped in the initial stage and authors did not report of any possible triazine by-products. From the presented data, the lack of triazinium cations could be attributed to short reaction times or to the excess amounts of protonation source. At first nitrile was frozen and only a small surface was exposed and throughout the whole reaction “free” nitrile was never available due to the strong acidic character of MF₅. There is always a possibility that super-acidic medium does not generate trimeric products as they lack potentially stabilizing H₂O molecule.

Another reagent for the preparation of nitrilium cations is closely related to our [H₃O][SbF₆] salt and is a prominent alkylation agent. Trialkyloxonium salt [R₃O][BF₄] (R = Me, Et) is also known as Meerwein’s reagent. It is highly unstable and reactive [R₃O]⁺ cation promptly transfers [R]⁺ cation onto exposed nitrogen atom of the electron-rich cyano group forming nitrilium cation [R–C=N–R]⁺ [239], [358]. We have synthesized Meerwein’s reagent with [SbF₆][−] replacing the anionic part ([Me₃O][SbF₆]) to resemble [H₃O][SbF₆]. Reaction of [Me₃O][SbF₆] with PhCN afforded, according to structural analysis of single crystals, the [(PhCN)Me][SbF₆] salt. Most likely methyl deactivates the positive charge on the cyano group, maybe through its inductive electron donating proficiency or less likely that it sterically hinders nucleophilic association of another PhCN molecule. Similar results are obtained with the addition of Lewis acids to imidoyl chloride [238], [239], [359].

4.4.3 Synthesis and structural characterization of [(^{Ph}TZN)H₂][SbF₆]₂·DCM

Reaction between [H₃O][SbF₆] and PhCN was performed in DCM in a molar ratio of 1:1, meaning there was an excess of oxonium salt for the preparation of a usual once-protonated *s*-triazine salt. Previously we have established that [H₃O][SbF₆] is only sparsely soluble in dry DCM. However, when the reaction mixture was left undisturbed for a few days, yellow crystalline product started to form. Rhombic single crystals are extremely air and moisture sensitive. When removed from the mother liquor, crystallinity of former crystals starts to degrade in a matter of minutes, which is detected as a loss of diffraction patterns. Successful X-ray structural characterization revealed a salt of twice-protonated *s*-triazine countered by two [SbF₆][−] anions. Twice-protonated *s*-triazine can also be referred to as 2,4,6-triphenyl-1,3,5-triazine-1,2-dium [(^{Ph}TZN)H₂]²⁺ cation. The crystals of [(^{Ph}TZN)H₂][SbF₆]₂·DCM (**15a**) are solvates with DCM incorporated into the crystal structure. The structure of the asymmetric unit is presented in Figure 24 and selected bond distances along with angles are given in Table 20. Crystal collection data and refinement

parameters are given in the Appendix (Table A18). Identical results were obtained when the molar ratio was 2:3, in favor of nitrile reagent, but the quality of crystals was somehow inferior to the reaction with equimolar content of reagents. Likewise, attempts to synthesize a fully protonated *s*-triazine cation with a large excess of $[\text{H}_3\text{O}][\text{SbF}_6]$ in an organic solvent DCM failed and yielded at best only crystals of a twice-protonated trimer of poor quality.

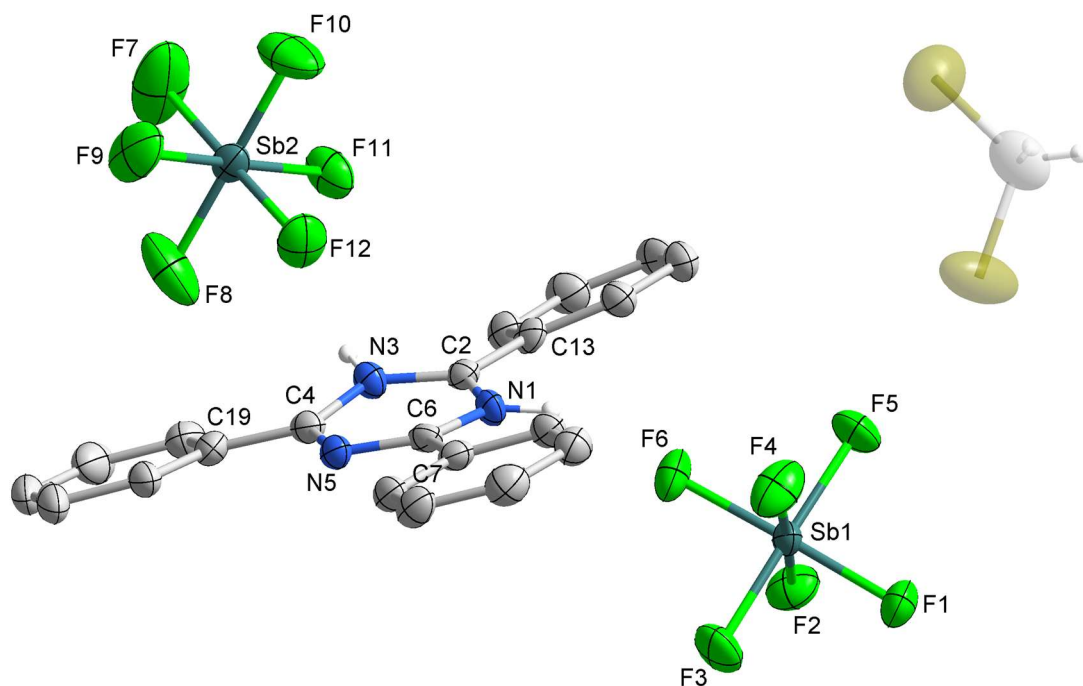


Figure 24: Ionic structure of the $[(^{\text{Ph}}\text{TZN})\text{H}_2][\text{SbF}_6]_2$ (**15**) salt. Ellipsoids are drawn at 50 % probability. For clarity, the less relevant hydrogen atoms are omitted.

Similarly to once-protonated *s*-triazine cation, protons on the N1 and N3 of the heterocyclic frame of the $[(^{\text{Ph}}\text{TZN})\text{H}_2]^{2+}$ cation are facing toward the $[\text{SbF}_6]^-$ anions. Anions are on the opposite side of the dication with one being above and another below the plane of the triazine ring. In the anions, the length of the Sb–F bonds presents two different trends. In the first anion (Sb1), the bonding situation mirrors that of the $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (**11**) salt. Sb1–F6 bond is 1.889(3) Å and is longer in comparison to remaining Sb1–F bonds (mean value of non-elongated bonds 1.868 Å) possibly due to the fairly strong F6–N1 contact with the dication. F6–N1 interaction is 2.722(5) Å long and is well within the sum of van der Waals radii (3.12 Å) [339]. Associated F6–H1–N1 angle between two species is 151.8(3)°, duplicating the circumstances in a once-protonated product. On the other hand, one would expect that stronger, 2.686(5) Å long F12–N3 contact of the second anion (Sb2) with the dication, would be expressed in even greater elongation of the Sb2–F12 bond. On the contrary, Sb2–F12 bond is by consideration of the experimental error within the range of anion’s Sb2–F bond average. Also the F12–H3–N3 angle of 148.7(3)° is slightly smaller than an equivalent F6–H1–N1 angle. This indicates some additional forces influence, prevail and dictate the length of the Sb–F bonds.

Length distortion of the bonds in the triazine ring is also at variance with that seen in the $[(^{\text{Ph}}\text{TZN})\text{H}]^+$ cation and does not follow any predictable pattern that could be easily elucidated from the observations of crystal structure. Additionally, there are perceivable deformations of the *s*-triazine frame in comparison to the non-protonated or once-protonated triazine. Individual constituent atoms of the triazine in $[(^{\text{Ph}}\text{TZN})\text{H}_2]^{2+}$ can

be up to 0.08 Å above or below the mean plane of the heterocycle of twice-protonated triazine, while in the instance of $[(^{\text{Ph}}\text{TZN})\text{H}]^+$ or neutral triazine, the magnitude of the displacement from the plane is much lower, approximately 0.03 Å or 0.009 Å, respectively. This could be the dication's approach to compensate for having anions situated on opposite sides of the plane.

Planes of the phenyl rings on the dication are at the 11.4(1)°, 19.0(1)° and 14.0(1)° angle for phenyls C7-C12, C13-C18 and C19-C24, respectively, in relation to the plane of the triazine ring. For current example, causation for the tilting is unidentified as for the once-protonated triazine and is most probably a sum of several factors. Two of the more obvious causes could be already described contortion of the heterocycle and the presence of two opposing anions.

Table 20: Selected bond distances and angles for $[(^{\text{Ph}}\text{TZN})\text{H}_2][\text{SbF}_6]_2$ (**15**) salt.

	Anion Sb1	Anion Sb2
Intramolecular bond distance [Å]		
Sb–F	1.873(3) (F1)	1.870(4) (F7)
	1.870(3) (F2)	1.840(4) (F8)
	1.877(3) (F3)	1.859(4) (F9)
	1.856(3) (F4)	1.853(4) (F10)
	1.865(3) (F5)	1.870(3) (F11)
	1.889(3) (F6)	1.871(3) (F12)
avg. M–F ^[a]	1.872	1.861
N–C		1.382(6) (N1, C6)
		1.332(6) (N1, C2)
		1.334(6) (N3, C2)
		1.371(7) (N3, C4)
		1.319(6) (N5, C4)
		1.320(6) (N5, C6)
Intermolecular bond distance [Å]		
F–N	2.722(5) (F6, N1)	2.686(5) (F12, N3)
	3.017(6) (F2, N3)	2.793(7) (F10, N1)
	3.071(5) (F2, N5)	2.975(7) (F10, N5)
Angle [°]		
plane _{C7-C12} –plane _{N1-C6}		11.4(1)
plane _{C13-C18} –plane _{N1-C6}		19.0(1)
plane _{C19-C24} –plane _{N1-C6}		14.0(1)

^[a] Average value of all six Sb–F bonds.

4.4.4 Synthesis and structural characterization of $[(^{\text{tBu}}\text{CA})\text{H}][\text{SbF}_6]$

Reaction of $[\text{H}_3\text{O}][\text{SbF}_6]$ in *t*BuCN as a reagent and a solvent, equivalently to the reaction with PhCN, did not yield the product of cyclotrimerization despite countless crystallization attempts from mother liquor. Only with the diffusion of hexane into the concentrated reaction mixture produced crystals of once-protonated *s*-triazine $[(^{\text{tBu}}\text{TZN})\text{H}]^+$ cation and $[\text{SbF}_6]^-$ anion. Unfortunately, the disorder of *tert*-butyl groups and high symmetry of the crystal proved too complex to satisfactorily solve and refine the structure. In addition,

crystals were of inferior quality and much less air stable than the $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (**11**) congener.

Reaction in DCM was performed in a similar manner as with the PhCN in an equimolar ratio of oxonium salt and *t*BuCN. After slow concentration of the reaction mixture in the inert conditions, small square-shaped crystals were obtained, which are rather air stable and readily soluble in MeCN and chlorinated hydrocarbon solvents. X-ray structural analysis of the crystals obtained from the solution showed carbonyl amidinium cation and $[\text{SbF}_6]^-$ anion. Cyclotrimerization surprisingly stopped at the “intermediate” dimeric stage. In further discussion, amidinium cation will also be referred to as the $[(^{\text{tBu}}\text{CA})\text{H}]^+$ cation. Interestingly, from the reactions, where the content of oxonium salt is in deficit to the *t*BuCN reagent, equivalent crystals are formed, however they are of significantly poorer quality.

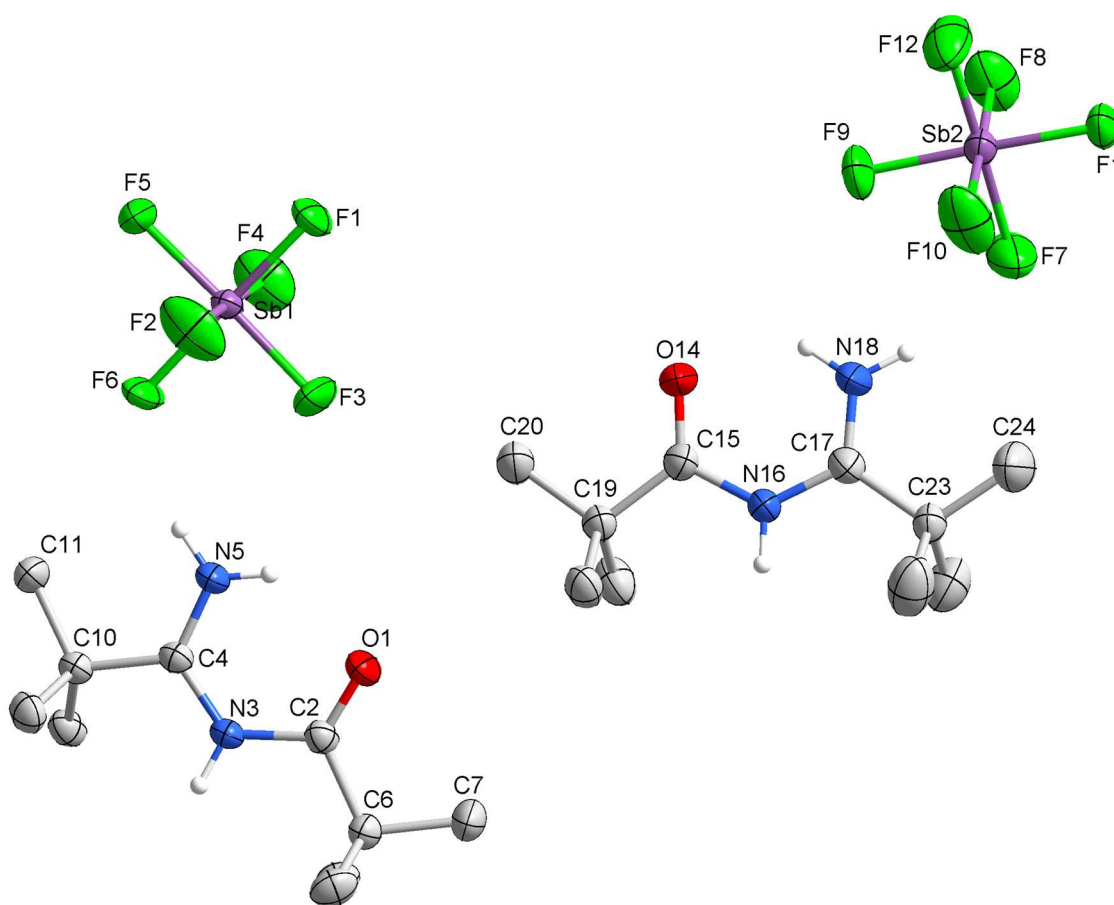


Figure 25: Ionic structure of the $[(^{\text{tBu}}\text{CA})\text{H}][\text{SbF}_6]$ (**16**) salt (both subunits are presented). Ellipsoids are drawn at 50 % probability. For clarity, the less relevant hydrogen atoms are omitted.

In the crystal structure of $[(^{\text{tBu}}\text{CA})\text{H}][\text{SbF}_6]$ (**16**), two subunits of cation–anion pair are observed. The ionic structure is presented in Figure 25 and the selected structural details are given in Table 21. Crystal collection data and refinement parameters are given in the Appendix (Table A18). Although the structural features of each ionic species in both subunits do not deviate significantly, the orientation within the subunit and interaction between the cation and the anion differs greatly. Crystal packing projected along *a* axis shows layers of individual subunits. These layers are composed of columns, where cations

and anions are alternating along the *a* axis. Orientation of the subunits within the columns is different and is consequently correlated to the situation in the subunit itself. There are two F–C contacts, with a distance shorter than the sum of van der Waals radii (3.23 Å) [339] and could be associated with the connection of both subunits. They are F3–C20 and F9–C7 with their length being 3.125(5) Å and 3.060(5) Å, respectively.

Bond distances of $[(^t\text{BuCA})\text{H}]^+$ cations and $[\text{SbF}_6]^-$ anions are comparable between the two subunits and in line with previous observations [360], [361]. Structurally the most relatable is $[(^t\text{BuCA})\text{H}]_2[\text{S}_2\text{O}_7]$ salt, where the cation is as well in the *Z,Z* conformation [360]. In the first subunit, the bond length of the carbonyl group C–O is 1.208(4) Å and of the imine group C–N 1.295(4) Å. This is represented in the C–O bond of the second subunit, which is 1.207(5) Å long, but the C–N bond of the imine group is 1.280(6) Å and is slightly shorter, but both values are still in the range of the experimental error. During refinement of the crystal structure, two residual electron densities corresponding to the hydrogen atoms were observed. Automatic assignment of hydrogens also placed both of them on the imine group. However, there is possible N–H $\cdots$ O intramolecular interaction, but a likelihood of the proton's delocalization with neighboring carbonyl group is quite improbable. The following paragraph will describe only the structural details observed in the cation of the first subunit, due to the high degree of similarity between both cations. Inner C–N bonds of the cationic core are 1.407(4) Å and 1.349(4) Å, where the longer one belongs to the “amide” (RC(O)NHR') and the shorter one to the “amidine” group (RC(NH)NHR'). The longer C–N bond of the former fragment and the relatively short C–O bond [362] negate the feasibility to form a hydroxyl group. Shorter bond distance of amine unit in the “amidine” unit indicates partial conjugation, which is additionally confirmed with planarity of the cation. Torsion angle of O1–C2–C4–N5 is 3.1(3)°. Analogous to the aforementioned method of defining location of the hydrogen atoms, the process was repeated also for the amine hydrogen. Its position in the plane of the cation's frame indicates the sp^2 hybridization of nitrogen. Nitrogen's lone electron pair in the p-orbital reconfirms considerable contribution of delocalization of charge in the “amidinium” part of the cation. The angles in the framework of the cation are at 120.3(3)°, 126.3(3)° and 119.8(3)° for O1–C2–N3, C2–N3–C4 and N3–C4–N5, respectively, which is indeed expected for sp^2 hybridized C2, N3 and C4 atoms. Larger size of the C2–N3–C4 angle is somewhat surprising detail since it deviates from the ideal 120° angle for sp^2 hybridized atom, i.e. the N3 atom. In addition, sterically unfavorable synperiplanar conformation of both *tert*-butyl groups toward carbonyl and imine groups and intramolecular hydrogen bonding are effects that are expected to constrain rather than expand this angle. Corresponding torsion angles were 10.1(5)° and 7.6(5)° for O1–C2–C6–C7 and N5–C4–C10–C11, respectively. In the second subunit, the deviation of carbonyl group from the synperiplanar position is even smaller with O14–C15–C19–C20 being only 5.8(5)°, while the N18–C17–C23–C24 angle is about the same 7.9(6)°. Similar observations of the angle sizes have already been reported [360].

Average Sb–F bond length in the anion is 1.866 Å and is the same for both anions. However, there are some noticeable discrepancies. Bonds Sb1–F1, Sb1–F3, Sb1–F6 and Sb2–F7 are 1.882(2) Å, 1.870(2) Å, 1.888(2) Å and 1.881(3) Å long. They exhibit some unusual elongations, which could be correlated to effective cation–anion interactions similar to the observations made for the $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (**11**) product. Criteria for the herein presented interactions was the sum of van der Waals radii (F–C 3.23 Å, F–N 3.12 Å and F–O 2.96 Å) [339]. F1 is connected through F1 $\cdots$ H–N3 with the neighboring cation above. The F3 and F6 are likewise engaged with the imine group (N5) of the cation below and they in addition form the F $\cdots$ H–C interaction. In the second subunit, the F7 and F9 show an analogous bonding situation to the F1 and F3, respectively. However, contrary to the F1, F6 and F7, the unfavorable geometry of the F3 and F9 makes related contacts rather

weak. Hence, the Sb1–F3 1.870(2) Å and Sb2–F9 1.868(2) Å are not particularly elongated.

There are further F–N and F–C distances between the cation and the anion that need consideration. These are with the atoms of the cation’s framework, but the non-complementary orientation of the contact and the lack of a positive component in the interaction discourage any associative interaction. This is also evident in the relatively large atomic displacement parameter (ADP) of these fluorides, whereas for the other fluorides involved in the constructive intermolecular interaction, their ADP is smaller. Interestingly, oxygen does not form any bonds or noticeable interactions with neither the anion nor another cation.

Table 21: Selected bond distances and angles for $[(^t\text{BuCA})\text{H}][\text{SbF}_6]$ (**16**) salt.

	Subunit Sb1	Subunit Sb2
Intramolecular bond distance [Å]		
Sb–F	1.882(2) (F1)	1.881(3) (F7)
	1.853(3) (F2)	1.851(3) (F8)
	1.870(2) (F3)	1.868(2) (F9)
	1.855(3) (F4)	1.869(3) (F10)
	1.846(2) (F5)	1.868(2) (F11)
	1.888(2) (F6)	1.858(3) (F12)
avg. M–F ^[a]	1.866	1.866
C _{tBu} –C _{carbonyl}	1.523(5) (C6, C2)	1.514(5) (C19, C15)
O–C _{carbonyl}	1.208(4) (O1, C2)	1.207(5) (O14, C15)
C _{carbonyl} –N _{amine}	1.407(4) (C2, N3)	1.410(5) (C15, N16)
N _{amine} –C _{imine}	1.349(4) (N3, C4)	1.351(5) (N16, C17)
C _{imine} –N _{imine}	1.295(4) (C4, N5)	1.280(6) (C17, N18)
C _{imine} –C _{tBu}	1.517(5) (C4, C10)	1.518(5) (C17, C23)
Intermolecular bond distance [Å]		
F–N	3.087(4) (F1, N3)	
	2.987(4) (F2, N3)	3.005(6) (F7, N18)
	3.088(5) (F3, N5)	3.018(4) (F8, N16)
	3.037(4) (F4, N3)	3.026(6) (F9, N18)
	2.898(4) (F6, N5)	
F–C	3.125(5) (F3, C20)	
	3.171(5) (F6, C11)	3.060(5) (F9, C7)
Angle [°]		
O–C _{carbonyl} –N _{amine}	120.3(3) (O1, C2, N3)	119.7(4) (O14, C15, N16)
C _{carbonyl} –N _{amine} –C _{imine}	126.3(3) (C2, N3, C4)	126.5(3) (C15, N16, C17)
N _{amine} –C _{imine} –N _{imine}	119.8(3) (N3, C4, N5)	119.5(4) (N16, C17, N18)
O–C _{carbonyl} –C _{imine} –N _{imine}	3.1(3) (O1, C2, C4, N4)	4.8(4) (O14, C15, C17, N18)
O–C _{carbonyl} –C _{tBu} –C _{tBu}	10.1(5) (O1, C2, C6, C7)	5.8(5) (O14, C15, C19, C20)
N _{imine} –C _{imine} –C _{tBu} –C _{tBu}	7.6(5) (N5, C4, C10, C11)	7.9(6) (N18, C17, C23, C24)

^[a] Average value of all six Sb–F bonds.

Cyclotrimerization of the nitriles in this acidic system most likely proceeds *via* sequential mechanism. Evidence is in the tendency for the reaction to stop in the dimeric form, which suggests the possibility of successive addition of nitrile molecules to the reactive cationic species. This cation is in PhCN less susceptible to the nucleophilic attack

of the water, while the less invested *t*BuCN preferably reacts with it. Since the intermediate stage was inhibited with the addition of the water molecule into the dimeric framework, the event rendered such molecule relatively stable and thus inactive for further addition of nitrile and consequential formation of a full cyclotrimer. Only when the reaction was performed in the hydrophobic solvent hexane, the synthesis yielded the desired trimeric cation. Hence, released water dissolved in DCM took a crucial part in the isolation of the dimeric structure. The incorporation of the water molecule is followed by internal proton–electron reconfiguration of the structure, where carbonyl amidinium $[(^t\text{BuCA})\text{H}]^+$ cation proved to be thermodynamically the most preferable. These results are further supported by the NMR study of the polymerization mechanism of MeCN in TfOH, where similar species among several presented intermediate products demonstrated high stability [283]. A possibility of $[(^t\text{BuCA})\text{H}]^+$ cation being a product of partial hydrolysis of the trimeric structure indeed remains. However, hydrolysis of once fully cyclic trimeric structure showed rather high resistance toward decomposition in air, whereas hydrolysis in water usually concludes with different decomposition products with imide compound being the most prevalent [285], [360], [363].

4.4.5 Attempts to prepare $[(^{\text{Me}}\text{TZN})\text{H}][\text{SbF}_6]$

Reaction between $[\text{H}_3\text{O}][\text{SbF}_6]$ and MeCN did not yield any product of nitrile dimerization or trimerization according to the NMR spectroscopy. Refluxing the reaction mixture for an extended period of time also did not generate hypothesized trimer nor any other reaction by-product. Crystallization of the concentrated reaction mixture produced crystals of the starting $[\text{H}_3\text{O}][\text{SbF}_6]$ reagent. Negative results are surprising since it has been demonstrated that MeCN is capable of protonation and formation of activated nitrilium cation [229].

In line with the previous observation, reaction of $[\text{H}_3\text{O}][\text{SbF}_6]$ and other nitriles (PhCN, *t*BuCN) did not proceed when MeCN was used as a solvent. The reasoning behind it is that MeCN, which was present in large excess, displaced reagent nitriles from the coordination sphere and inhibits further oligomerization reactions with much more susceptible PhCN and *t*BuCN.

4.4.6 Raman spectroscopy

Raman spectroscopy was used in order to demonstrate the presence of different $[\text{MF}_6]^-$ anions in solid samples of triazinium $[(^{\text{Ph}}\text{TZN})\text{H}]^+$, $[(^{\text{Ph}}\text{TZN})\text{H}_2]^{2+}$ and carbonyl amidinium $[(^t\text{BuCA})\text{H}]^+$ salts. Unfortunately, the region where their strongest band (ν_1 ; V–F stretching frequencies) is observed (692–668 cm^{-1}) [340] is populated with bands of triazine framework [364], [365] along with the *tert*-butyl [366] and phenyl [367] groups, thus hampering the band assignation to the anions. Bands belonging to the organic part of the organometallic salts have generally greater intensities than inorganic units have, thus rendering the inorganic anions in our instance unidentifiable. More precisely, in spectra of triazinium salts, a band at $677 \pm 3 \text{ cm}^{-1}$ was assigned to triazine in-plane ring bending and dominates the particular range in the spectrum (Figure 26 and Figure 27) [365], [368]. Likewise, the strongest band in the spectrum of amidinium salt is at 647 cm^{-1} and masks any potential Sb–F band at 668 cm^{-1} (Figure 28) [340]. An exception to this is $[\text{TaF}_6]^-$ anion, whose Ta–F stretching vibrations could be associated with 691 cm^{-1} band (Figure 26), but the spectrum is lacking other observable bands of the anion to unequivocally make such a claim [340]. Remaining bands in spectra are attributed to various vibrational modes of the organic cation [369]. Any deviations from the values in literature could be due to

the protonated character of the cation, whereas the published numbers are given for neutral compounds [370]. A comparison of $[(^{\text{Ph}}\text{TZN})\text{H}]^+$ and $[(^{\text{Ph}}\text{TZN})\text{H}_2]^{2+}$ (Figure 27) is also interesting, where in the spectrum of the latter fewer bands are found and some of the bands are shifted possibly due to the additional highly polarized N–H bond.

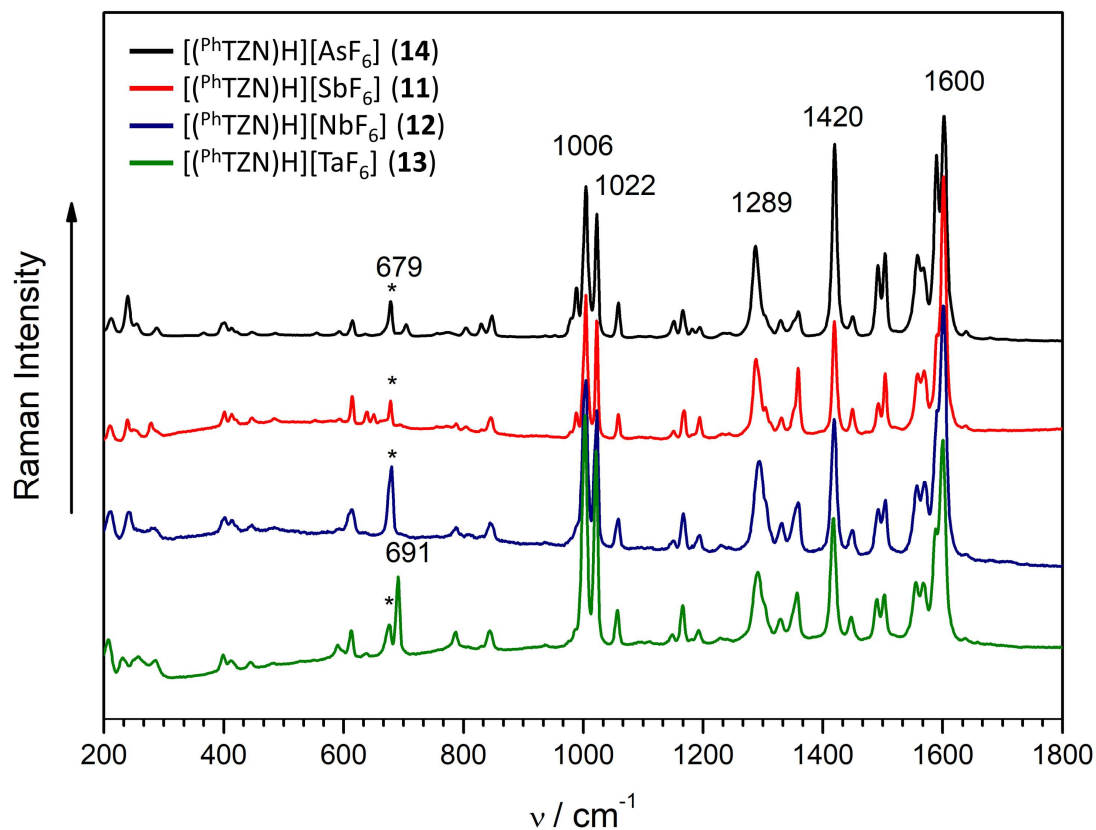


Figure 26: Comparison of Raman spectra of $[(^{\text{Ph}}\text{TZN})\text{H}][\text{MF}_6]$ ($\text{M} = \text{Sb}$ (**11**), Nb (**12**), Ta (**13**), As (**14**)). Potential Ta–F vibrations are marked with *.

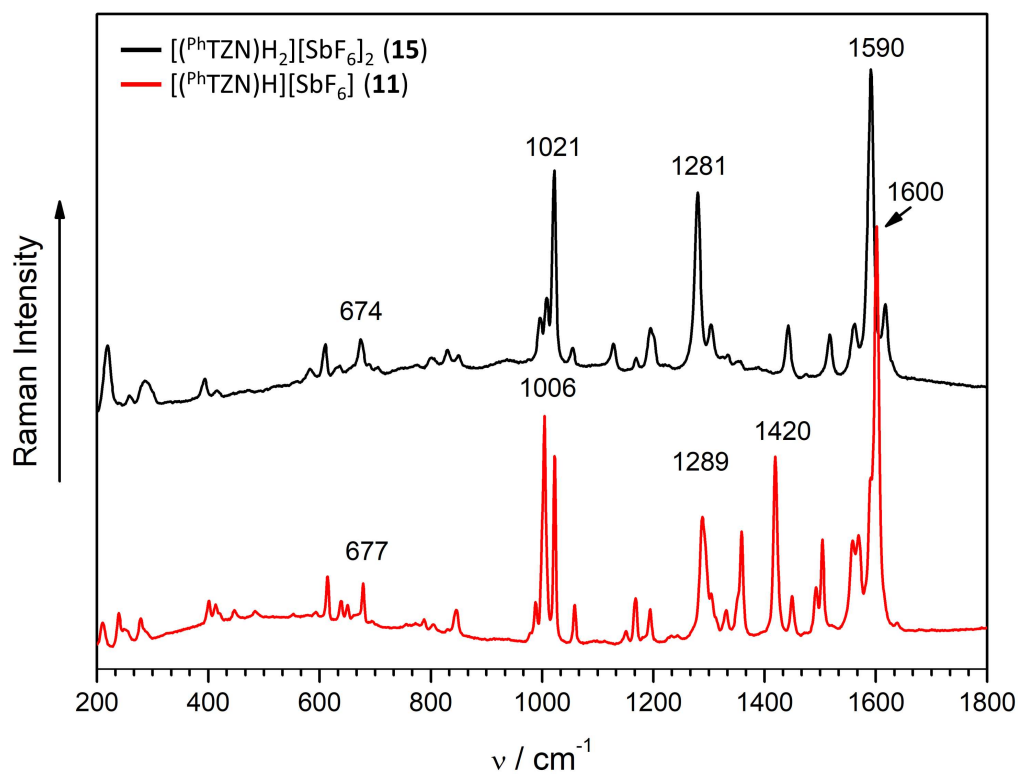


Figure 27: Comparison of Raman spectra of $[(\text{PhTZN})\text{H}][\text{SbF}_6]$ (**11**) and $[(\text{PhTZN})\text{H}_2][\text{SbF}_6]_2$ (**15**).

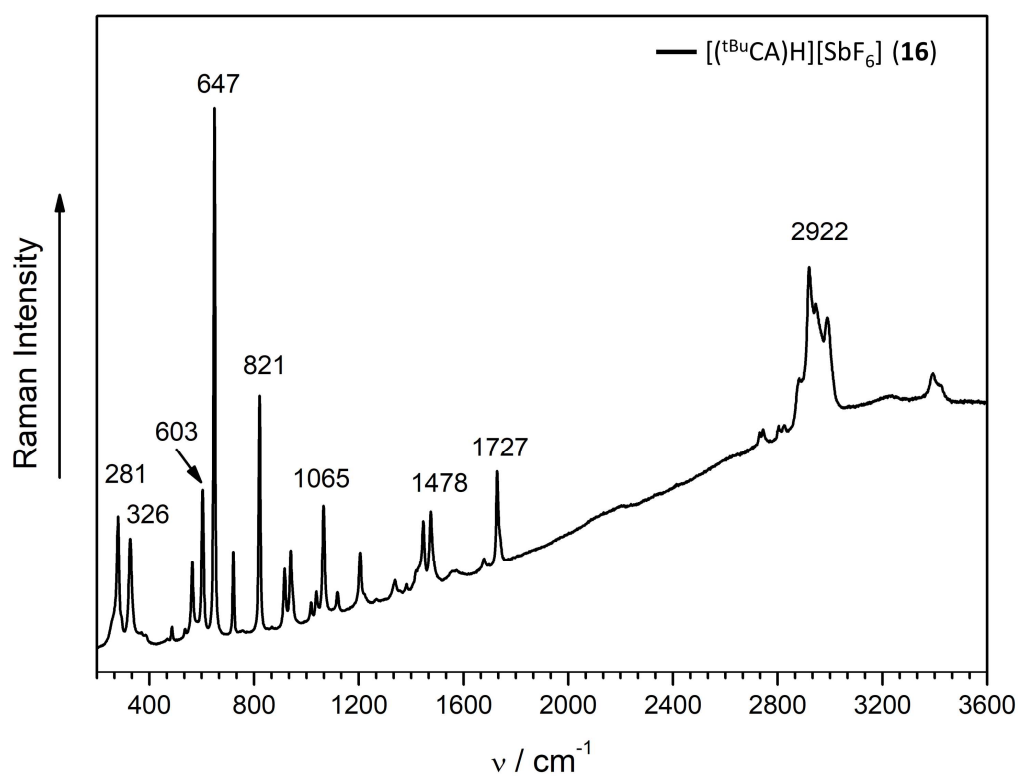


Figure 28: Raman spectrum of $[(\text{tBuCA})\text{H}][\text{SbF}_6]$ (**16**).

Chapter 5

Conclusions

The reaction between group 5 pentafluorides (MF_5 ; $\text{M} = \text{Nb}, \text{Ta}$) and NHC^{Dipp} yielded neutral coordination compounds $[(\text{NHC}^{\text{Dipp}})\text{MF}_5]$ previously characterized only by NMR and IR spectroscopy [108]. However, successful crystallization and structural analysis of these complexes revealed a curious structural characteristic when compared to their heavier chloride and bromide congeners. MF_5 unit is in a staggered position relative to the heterocyclic ring of the NHC ligand, whereas the MX_5 ($\text{X} = \text{Cl}, \text{Br}$) unit in the equivalent setup adopts eclipsed conformation [106], [108], [109]. Although the discrepancy is subtle, it derives from a fundamental difference between the fluoride anion and its heavier counterparts. DFT calculations were utilized to help us investigate and define ensuing effects for the two different conformers. Repulsive steric forces between substituents on heterocyclic base of the NHC moiety (“wingtips”) and equatorial halides of the MX_5 were found to be profoundly implicated. The repelling influence increases with the size of the “wingtips”. The opposing effect are the attractive $\text{C-H} \cdots \text{X}$ interactions, the number of which is maximal in the staggered position. Since small methyl “wingtips” do not pose any restrictions on the staggered conformation nor do they bolster the eclipsed conformation, the MX_5 is, indiscriminately of the halide ion used, in the optimal staggered position. Furthermore, the MF_5 unit is immune to the increase in size of the “wingtips” as it retains its staggered form, while MCl_5 slowly rotates, *via* partially eclipsed position for phenyl “wingtips”, toward fully eclipsed conformation for diisopropylphenyl. The MF_5 unit remained in the staggered position due to the small size of the $[\text{F}]^-$ anion and maximal number of $\text{C-H} \cdots \text{F}$ contacts, whereas repulsive interactions of ever larger “wingtips” pushed the equatorial chlorides into eclipsed conformation.

A neutral coordination compound of vanadium(V) oxide trifluoride with NHC^{Dipp} , $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$, was the second example of the oxide fluoride complex with NHC [78] and first monomeric such complex. Due to its novelty, a stability test of the complex was performed suggesting a rapid degradation into $[(\text{NHC}^{\text{Dipp}})\text{VOF}_4]$ and $[(\text{NHC}^{\text{Dipp}})\text{VO}_2\text{F}_2]$ when exposed to moisture and a slow decomposition in laboratory glassware. Structurally it is related to the vanadium(V) oxide chloride [93], the authors of which interpreted computational results as possible evidence of chlorine π -back-donation into empty p-orbital of carbenic carbon atom. Our computational results of isolated $[(\text{NHC}^{\text{Me}})\text{VOF}_3]$ complex have also provided similar results, suggesting that charge of 0.03 e^- can be contributed to the back-donation, the primary source of which is vanadium ion; however, some extent of this effect does come from the fluoride anions. Furthermore, an occurrence of back-donation and its magnitude in $[(\text{L})\text{VOX}_3]$ ($\text{L} = \text{ligand}, \text{X} = \text{F}, \text{Cl}, \text{Br}$) complexes was correlated to the alterations of the $\text{V-X}_{\text{trans}}$ bond distances as well as the size of the $\text{C}_{\text{NHC}}\text{-V-X}_{\text{cis}}$ angles. Increase in the energy associated with the overall back-donation resulted in shortening of the $\text{V-X}_{\text{trans}}$ bond in relation to the V-X_{cis} . On the other hand, the calculations of experimentally determined structural features of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ complex in single crystal unveiled that noticeable elongation of the $\text{V-F}_{\text{trans}}$ bond is associated with the $\text{C-H} \cdots \text{F}$

interactions within the crystal due to the crystal packing, rather than commonly represented trans effect.

Reaction between group 5 pentafluorides (MF_5 ; $\text{M} = \text{Nb}, \text{Ta}$) with “naked” fluoride reagent $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{F}]$ affords an imidazolium salt with the $[\text{MF}_6]^-$ anion. The salt has solvent molecules incorporated into the crystal structure. Additional equivalent of the fluoride reagent does not yield relatively common $[\text{MF}_7]^{2-}$ anion. Fluoride donating capabilities of this recently prepared reagent toward transition metal fluorides have not been actively researched and these are one of the first examples.

Study of the fluoride donating capabilities of the imidazolium fluoride were extended to the vanadium(V) oxide fluoride, with the intent to structurally characterize discrete $[\text{VOF}_4]^-$ anion for the first time. Similar reactions with a smaller imidazolium cation have already been performed [144], which afforded dimeric $[\text{V}_2\text{O}_2\text{F}_8]^{2-}$. Sterically hindering $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ did stabilize the monomeric anion and single crystals of the appropriate salt were obtained. Analysis of the structure revealed a disordered square pyramidal anion, which has been postulated previously by NMR spectroscopy [199], [200]. Stability of the anion was assessed as mediocre. It is stable in solid under inert conditions, while it slowly hydrolyzes in the presence of moisture. Reaction of VOF_3 with fluoride reagent in the molar ratio of 1:2 unfortunately did not yield $[\text{VOF}_5]^{2-}$ anion, which was rationalized by unfavorable introduction of second bulky cationic moiety.

Imagining the pentacoordinated $[\text{VOF}_4]^-$ anion as octahedron, the empty “sixth” coordination position is readily available for insertion of the electron donating ligand. In literature, this site was occupied by $[\text{F}]^-$ anion [160], [184] or water molecule [132], [155], however we managed to embed a somewhat larger solvent molecule THF or py as well as py’s congener pyz. Dissolution of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ salt with an appropriate electron donor and gradual crystallization yielded extremely labile single crystals, indicating a weak bond between the anion and the organic ligand. Anionic complex formed with the py or THF is $[\text{VOF}_4(\text{L})]^-$ as one would imagine, while the pyz bonded and connected two $[\text{VOF}_4]^-$ anions with its two coordinating nitrogen donor groups into $[(\text{VOF}_4)_2(\text{pyz})]^{2-}$. Introduction of a new neutral molecule *trans* to the V–O bond pushes equatorial fluorides slightly toward the oxide ligand (in comparison to the unbound $[\text{VOF}_4]^-$ anion), although the vanadium center remains displaced from the plane of the fluorides. Geometry of the anionic complex is described as a distorted octahedron mainly due to the elongated V–L bond. Interaction between the cyclic ligand and the anion was concluded to be founded upon attractive C–H contacts with fluorides. Other nitrogen- and oxygen-based cyclic donors, e.g. phenazine, benzophenone, have also been examined but they most likely do not meet the criteria of C–H $\cdots$ F bonds and thus no anionic complexes were prepared.

Reaction of the oxonium salt $[\text{H}_3\text{O}][\text{SbF}_6]$ with nitriles surprisingly activates the oligomerization process producing salts of dimeric or trimeric cations with the $[\text{SbF}_6]^-$ anion. Protonation of the nitrile molecule initiates the cascade reaction that leads to the final ionic products. Synthesis of various protonated oligomers was determined by structural characterization of single crystals and Raman spectroscopy. Symmetric triphenyl triazines were prepared as once- or twice-protonated species with incorporated hexafluoride anion. For the former, the synthesis procedure was successfully repeated with hexafluorides of other pentavalent Lewis acids (As, Nb, Ta) to establish whether any oxonium salt with weakly coordinating anion yields the equivalent results. The latter twice-protonated triazinium compound is the first structural example, the existence of which was speculated in the past but was never confirmed [251]. On the other hand, if the synthesis was performed with *t*BuCN instead of PhCN, the salt with the trimeric cation was observed only in completely non-polar conditions. In any other reaction system, the cation observed was a dimeric product of partial hydrolysis, carbonyl amidinium. The existence and superb stability of the amidinium cation suggests that the substituent on the cyano group

significantly dictates the outcome of the reaction and that water might participate in the reaction, but at a certain stage, it assuredly inhibits the reaction.

Appendix

A.1 Additional Examples of Small VOF Anions

Table A1: Overview of small VOF anionic units linked (most commonly) through metal cations into a polymeric structure.

Oxidation state	Monomeric compound	Ref.
IV	$[\text{VOF}_4]^{2-}$	[179]
	<i>trans</i> - $[\text{VOF}_4(\text{H}_2\text{O})]^{2-[\text{a}]}$	[371]
V	$[\text{VOF}_5]^{2-}$	[209], [372], [373]
	$[(\text{VOF}_4)_3(\text{VF}_6)]^{5-}$	[209]
	$[\text{VO}_2\text{F}_4]^{3-}$	[374]
	$[\text{VO}_2\text{F}_3]^{2-}$	[375]
	$[\text{VO}_2\text{F}_2(\text{L}^1)]^{-[\text{b}]}$	[376]
	$[(\text{VO}_2\text{F})_2(\text{V}_2\text{O}_7)]^{4-}$	[377]
	$[\text{VO}_{3.5}\text{F}_{0.5}]^-$	[378]
Dimeric compound		
IV	$[\text{V}_2\text{O}_2\text{F}_6(\mu\text{-F})_2]^{4-}$	[379], [380]
	$[\text{V}_2\text{O}_2\text{F}_4(\mu\text{-F})_3]^{3-}$	[379]
V	$[\text{V}_2\text{O}_2\text{F}_6(\mu\text{-F})_2]^{2-}$	[209]
	$[\text{V}_2\text{O}_2\text{F}_2(\mu\text{-O})_2(\mu\text{-}\kappa^2\text{-SeO}_3)_2]^{4-}$	[381]
	$[\text{V}_2\text{O}_4\text{F}_4(\mu\text{-F})_2]^{4-}$	[382]
Trimeric compound		
IV	$[\text{V}_3\text{O}_3(\mu\text{-F})_3(\mu_3\text{-F})_3(\mu\text{-L}^2)_3]^{4-[\text{c}]}$	[146]
V	$[\text{V}_3\text{O}_3\text{F}_9(\mu\text{-F})_3]^{3-}$	[137]
Tetrameric compound		
V	$[\text{V}_4\text{O}_6\text{F}_{10}(\mu\text{-O})_2(\mu\text{-F})_2]^{8-}$	[383]
	$[\text{V}_4\text{O}_8(\mu_4\text{-F})(\mu\text{-L}^3)_2]^{-[\text{d}]}$	[120]

^[a] Position of ligand relative to the V–O bond.

^[b] L¹ represents bidentate 1,2,4-triazol-4-yl [$\text{C}_2\text{H}_2\text{N}_3\text{R}$] ligand, bonded to VOF anion only through one V–N bond.

^[c] L² represents bridging bidentate squarate [C_4O_4]²⁻ ligand.

^[d] L³ represents bridging polydentate dicaroxylate [$\text{C}_5\text{H}_6\text{O}_4$]²⁻ ligand.

A.2 Calculations of Bond Valence

Table A2: Calculated bond valences and their sum for structurally determined VOF compounds.

Bond	Bond length [Å]	Bond valence	Bond valence sum
Subunit 1 of [(NHC ^{Dipp})VOF ₃] (5)			
V–O	1.558(2) (O1)	1.939	4.388
	1.771(1) (F1)	0.848	
V–F	1.804(1) (F2)	0.776	
	1.781(1) (F3)	0.825	
V–C _{NHC}	2.141(2) (C2)	/	
Subunit 2 of [(NHC ^{Dipp})VOF ₃] (5)			
V–O	1.561(1) (O2)	1.923	4.359
	1.776(1) (F4)	0.837	
V–F	1.802(1) (F5)	0.780	
	1.784(1) (F6)	0.819	
V–C _{NHC}	2.139(2) (C31)	/	
Domain A of [(NHC ^{Dipp})H][VOF ₄]·2MeCN (6a)			
V–O	1.560(2) (O1A)	1.929	5.084
	1.776(2) (F1A)	0.837	
V–F	1.815(2) (F2A)	0.753	
	1.807(2) (F3A)	0.769	
	1.794(2) (F4A)	0.797	
Domain B of [(NHC ^{Dipp})H][VOF ₄]·2MeCN (6a)			
V–O	1.587(8) (O1B)	1.793	5.521
	1.681(9) (F1B)	1.082	
V–F	1.760(1) (F2B)	0.874	
	1.690(6) (F3B)	1.056	
	1.833(4) (F4B)	0.717	
[(NHC ^{Dipp})H][VO ₂ F ₂] (7)			
V–O	1.615(1) (O1)	1.662	4.888
V–F	1.801(1) (F1)	0.782	
Domain A of [(NHC ^{Dipp})H][VOF ₄ (THF)] (8)			
V–O	1.561(2) (O1)	1.923	5.152
	1.819(1) (F1)	0.745	
V–F	1.805(1) (F2)	0.774	
	1.806(1) (F3)	0.771	
	1.821(1) (F4)	0.741	
V–O _{THF}	2.403(7) (O30A)	0.198	
Domain B of [(NHC ^{Dipp})H][VOF ₄ (THF)] (8)			
V–O	1.561(2) (O1)	1.923	5.122
	1.819(1) (F1)	0.745	
V–F	1.805(1) (F2)	0.774	
	1.806(1) (F3)	0.771	
	1.821(1) (F4)	0.741	
V–O _{THF}	2.464(6) (O30B)	0.168	

Table A2 continued: Calculated bond valences and their sum for structurally determined VOF compounds.

Bond	Bond length [$\text{\AA}$]	Bond valence	Bond valence sum
Subunit 1 of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$ (9)			
V–O	1.570(2) (O1)	1.877	5.072
	1.840(1) (F1)	0.704	
	1.804(1) (F2)	0.776	
	1.831(1) (F3)	0.721	
	1.811(1) (F4)	0.761	
V–N _{py}	2.399(2) (N59)	0.233	
Subunit 2 of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$ (9)			
V–O	1.574(2) (O2)	1.857	5.072
	1.832(1) (F5)	0.719	
	1.805(1) (F6)	0.774	
	1.821(1) (F7)	0.741	
	1.815(1) (F8)	0.753	
V–N _{py}	2.406(2) (N65)	0.229	
$[(\text{NHC}^{\text{Dipp}})\text{H}][(\text{VOF}_4)_2(\text{pyz})]\cdot 4\text{MeCN}$ (10)			
V–O	1.581(1) (O1)	1.822	5.040
	1.828(1) (F1)	0.727	
	1.813(1) (F2)	0.757	
	1.816(1) (F3)	0.751	
	1.798(1) (F4)	0.788	
V–N _{pyz}	2.465(2) (N30)	0.195	

[a] Bond valence analyses were done using the equation $v_{ij} = e^{\left(\frac{R_{ij}^0 - R_{ij}}{B}\right)}$, with parameters $R^0(\text{V–O}) = 1.803 \text{ \AA}$, $R^0(\text{V–F}) = 1.71 \text{ \AA}$, $R^0(\text{V–N}) = 1.86 \text{ \AA}$, $B = 0.37 \text{ \AA}$ [384], [385].

[b] Sum of the bond valences.

[c] Parameter $R^0(\text{V–C})$ is missing in the references, hence the V–C bond is not included in the calculation of the bond valence sum.

[d] VOF anion is composed of two equivalent V–O and V–F bonds, hence the bond valence sum is appropriately multiplied by 2.

A.3 Information of Disordered Crystal Structures

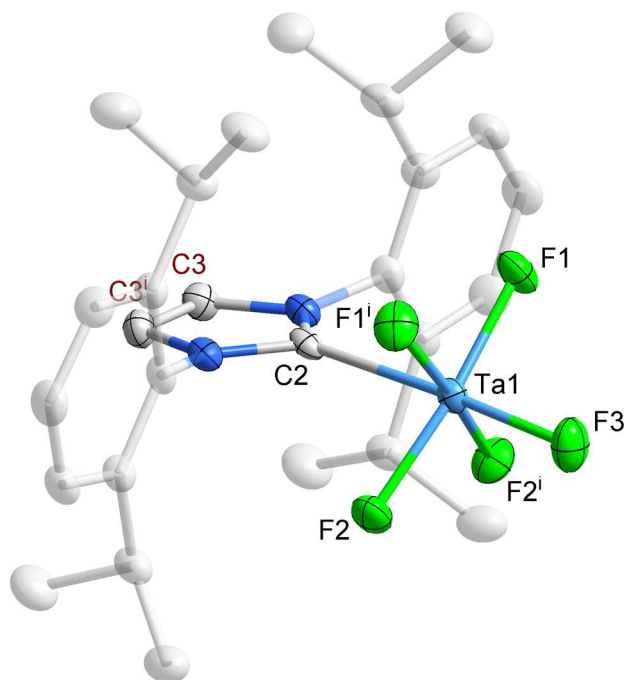


Figure A1: Molecular structure of the neutral $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) complex. Figure is based on the reference [323].

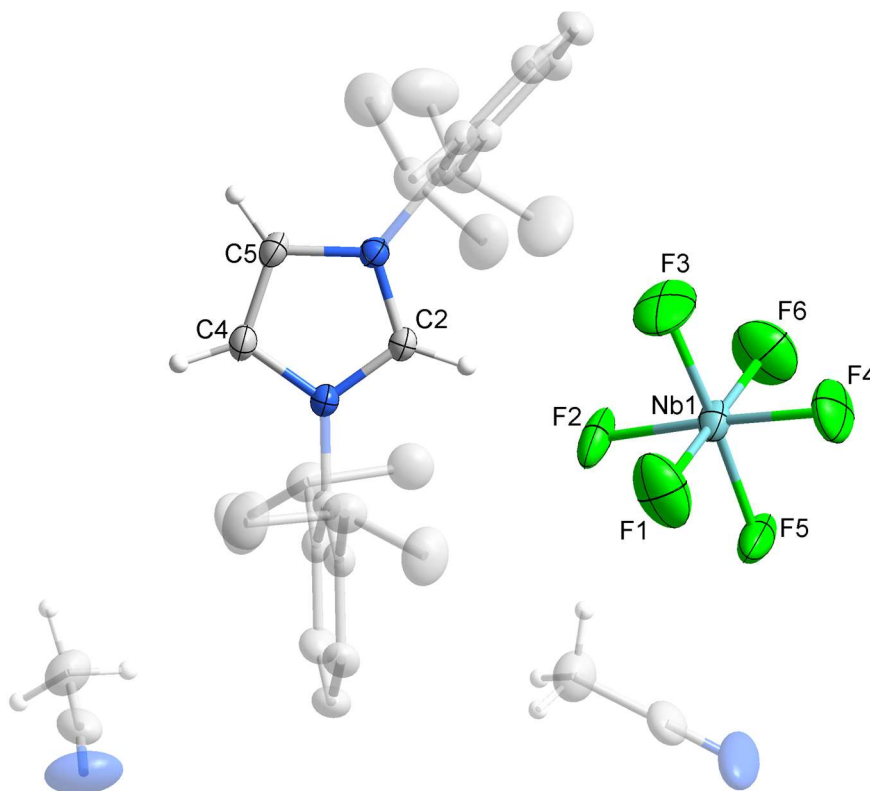


Figure A2: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6] \cdot 2\text{MeCN}$ (**3a**) salt. Figure is based on the reference [323].

Table A3: Structural parameters of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot 2\text{MeCN}$ (**3a**) salt. Table is based on the reference [323].

Occupancy	Domain A 70(2) %	Domain B 30(2) %
Intramolecular bond distance [$\text{\AA}$]		
C–C	1.55(1) (C24, C25A)	1.50(1) (C24, C25B)
	1.50(1) (C24, C26A)	1.61(1) (C24, C26B)

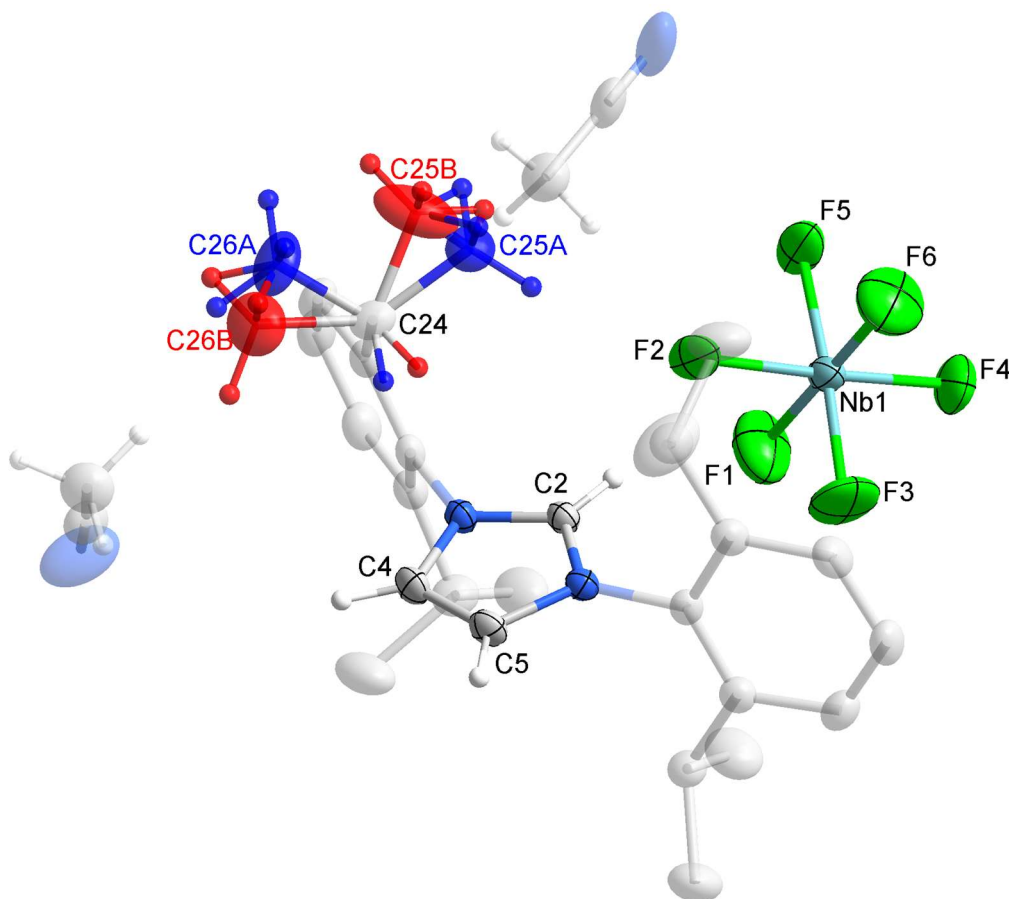


Figure A3: Graphical representation of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot 2\text{MeCN}$ (**3a**) salt. Figure is based on the reference [323].

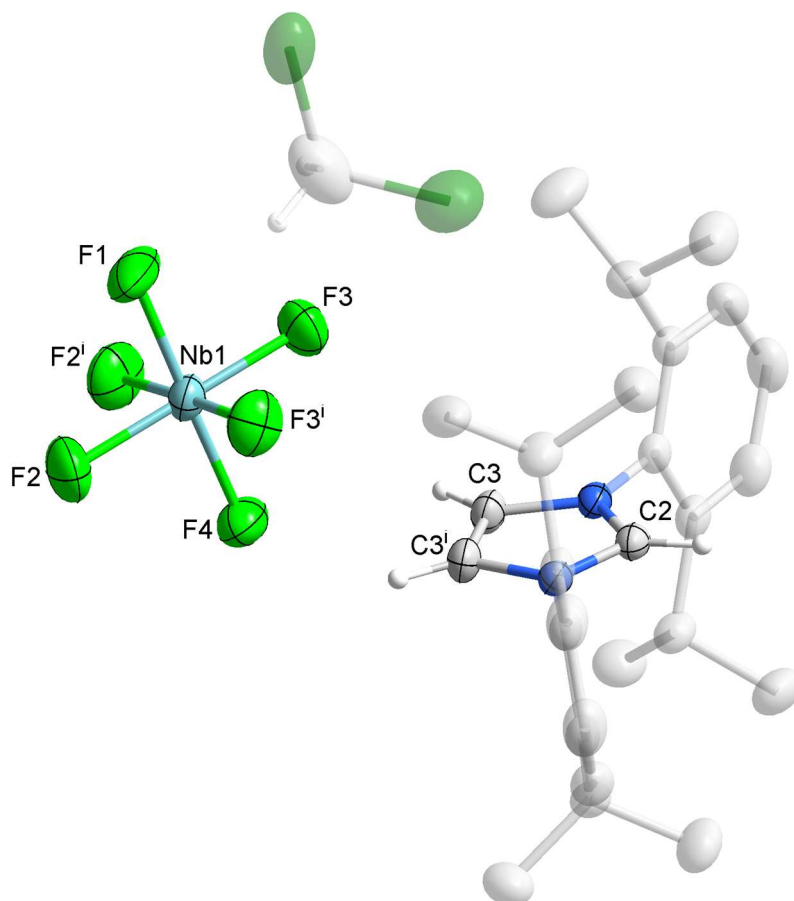


Figure A4: Ionic structure of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot\text{DCM}$ (**3b**) salt. Figure is based on the reference [323].

Table A4: Structural parameters of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot\text{DCM}$ (**3b**) salt. Table is based on the reference [323].

	Domain A	Domain B
Occupancy	53(3) %	47(3) %
Intramolecular bond distance [$\text{\AA}$]		
C–C	1.57(2) (C10, C11A)	1.47(2) (C10, C11B)
	1.50(1) (C10, C12A)	1.58(1) (C10, C12B)

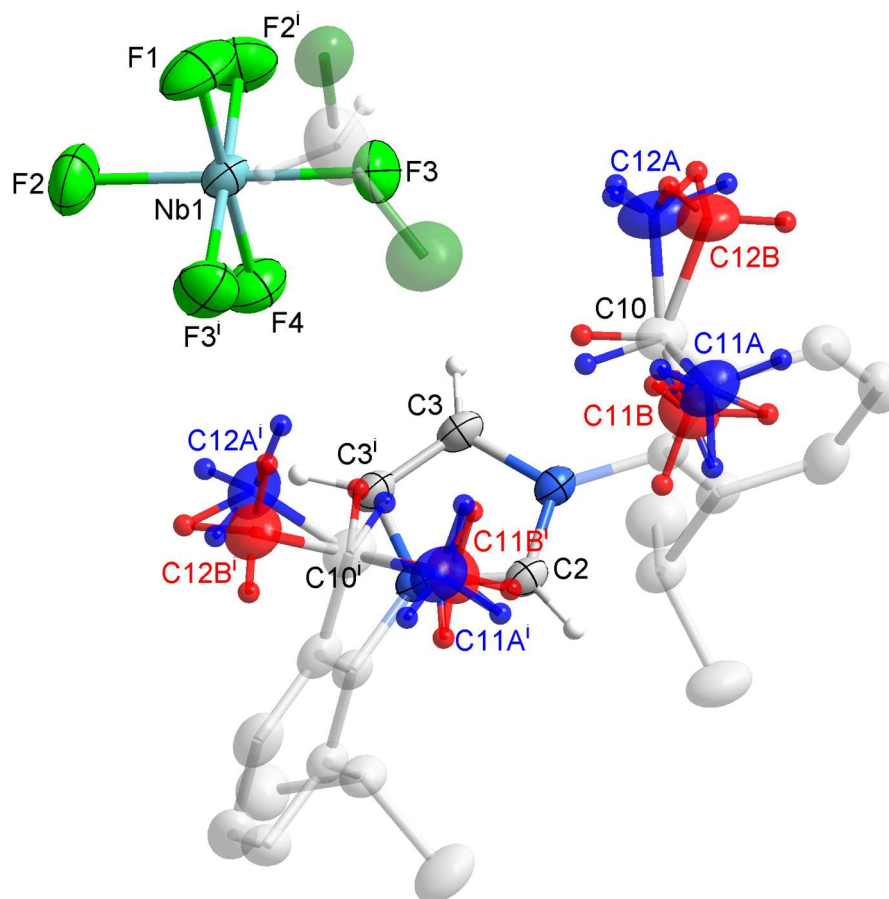


Figure A5: Graphical representation of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot\text{DCM}$ (**3b**) salt. Figure is based on the reference [323].

Table A5: Structural parameters of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot 2\text{MeCN}$ (**4a**) salt. Table is based on the reference [323].

	Domain A	Domain B
Occupancy	68(2) %	32(2) %
Intramolecular bond distance [$\text{\AA}$]		
C–C	1.55(1) (C24, C25A)	1.49(2) (C24, C25B)
	1.50(1) (C24, C26A)	1.61(2) (C24, C26B)

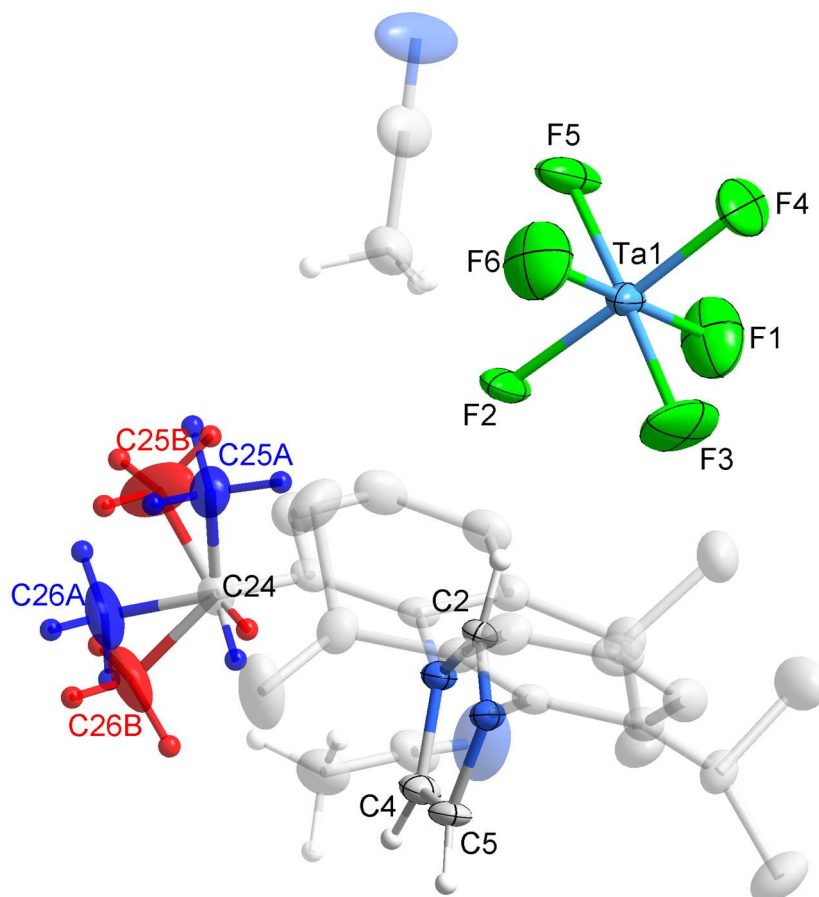


Figure A6: Graphical representation of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6] \cdot 2\text{MeCN}$ (**4a**) salt. Figure is based on the reference [323].

Table A6: Structural parameters of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6] \cdot \text{DCM}$ (**4b**) salt. Table is based on the reference [323].

	Domain A	Domain B
Occupancy	60(5) %	40(5) %
Intramolecular bond distance [$\text{\AA}$]		
C–C	1.57(3) (C13, C14A)	1.47(4) (C13, C14B)
	1.50(1) (C13, C15A)	1.59(2) (C13, C15B)

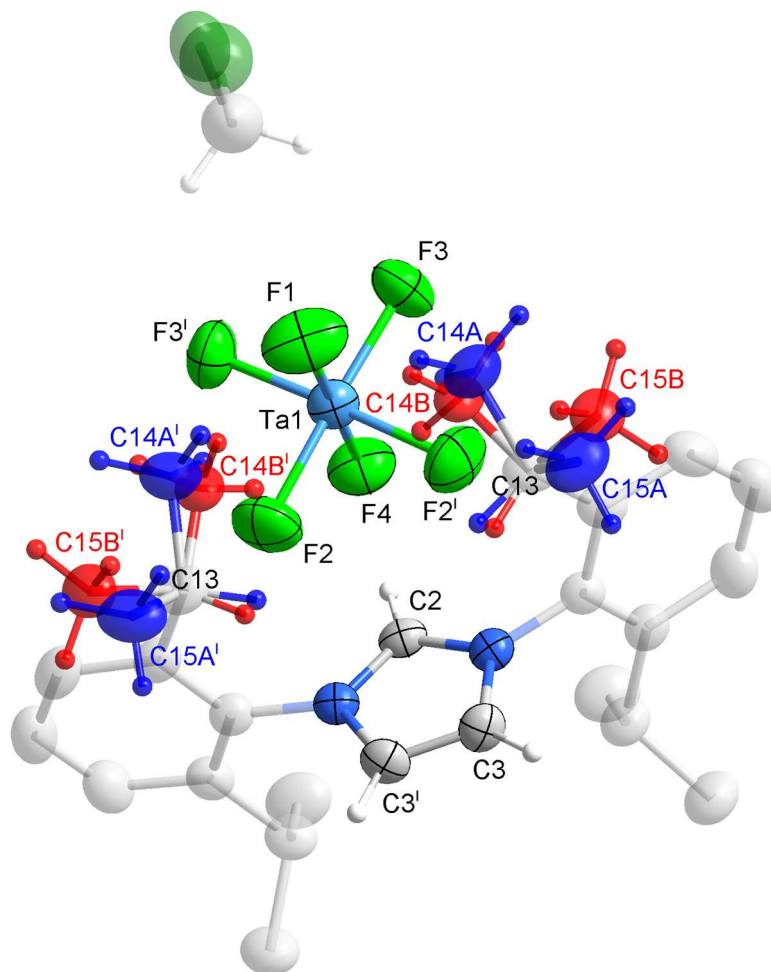


Figure A7: Graphical representation of the disordered isopropyl group of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot\text{DCM}$ (**4b**) salt. Figure is based on the reference [323].

Table A7: Structural parameters of the first disordered isopropyl group of subunit 1 of complex $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**). Table is based on the reference [324].

	Domain A	Domain B
Occupancy	68(3) %	32(3) %
Intramolecular bond distance [$\text{\AA}$]		
C–C	1.62(1) (C12, C13A)	1.32(2) (C12, C13B)
	1.56(1) (C12, C14A)	1.36(3) (C12, C14B)

Table A8: Structural parameters of the second disordered isopropyl group of subunit 1 of complex $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**). Table is based on the reference [324].

	Domain A	Domain B
Occupancy	66(5) %	34(5) %
Intramolecular bond distance [$\text{\AA}$]		
C–C	1.58(2) (C15, C16A)	1.44(5) (C15, C16B)
	1.58(1) (C15, C17A)	1.46(3) (C15, C17B)

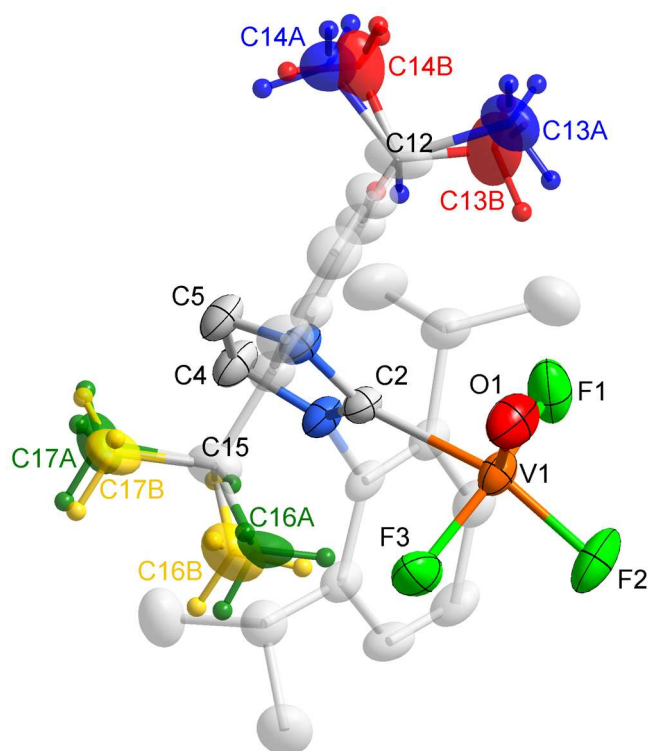


Figure A8: Graphical representation of both disordered isopropyl groups of subunit 1 of complex $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**). Figure is based on the reference [324].

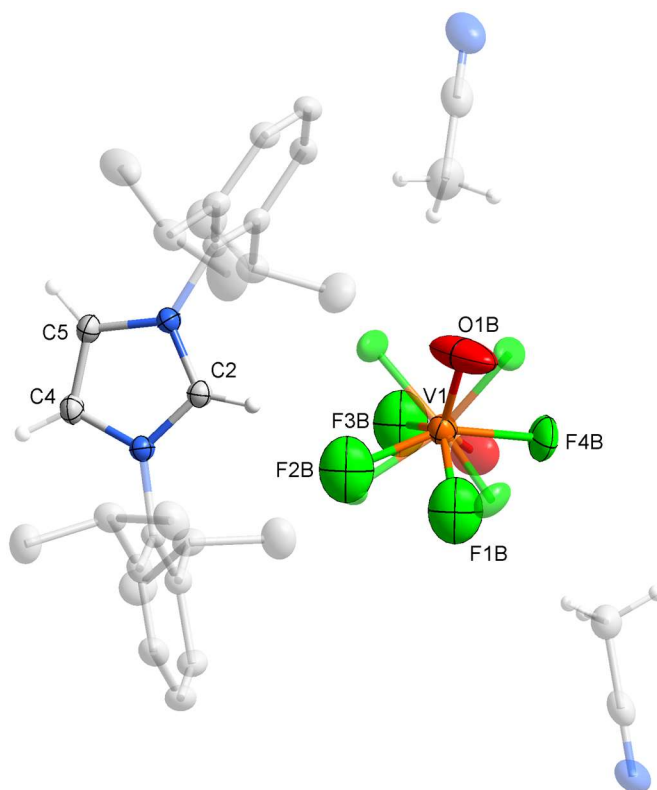


Figure A9: Graphical representation of both disordered domains of the $[\text{VOF}_4]^-$ anion of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]\cdot 2\text{MeCN}$ (**6a**) salt. Figure is based on the reference [324].

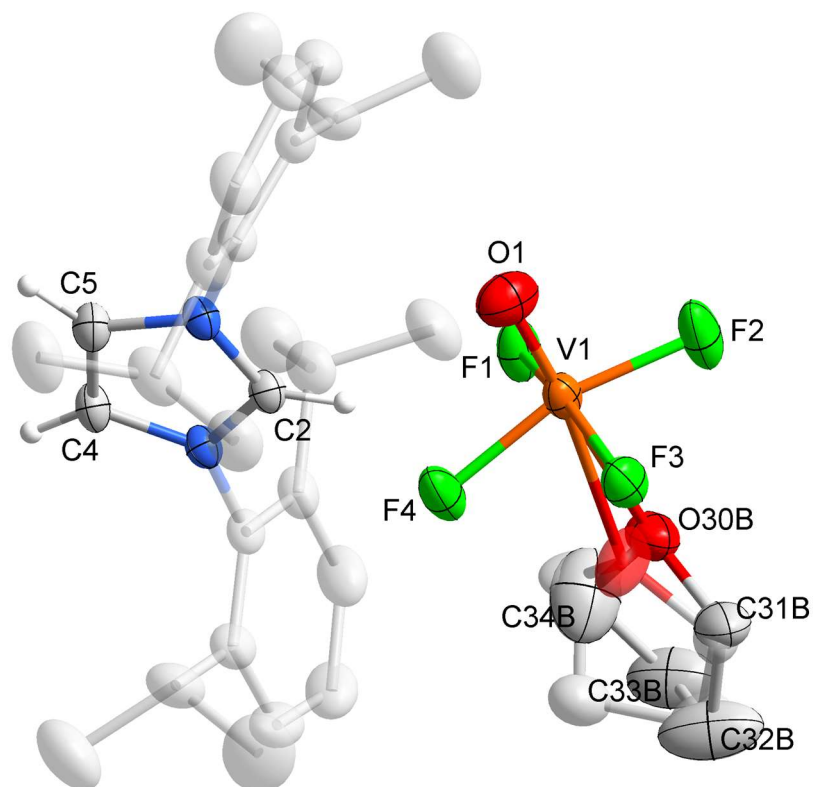


Figure A10: Graphical representation of both disordered domains of THF in the [VOF₄(THF)]⁻ anion of the [(NHC^{Dipp})H][VOF₄(THF)] (**8**) salt. Hydrogen atoms of the THF molecule are omitted for clarity.

Table A9: Selected bond distances and angles for both domains of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$ (**8**) salt.

	Domain A	Domain B
Occupancy	46.1(9) %	53.9(9) %
Intramolecular bond distance [$\text{\AA}$]		
V–O	1.561(2)	
	1.819(1) (F1)	
V–F	1.805(1) (F2)	
	1.806(1) (F3)	
	1.821(1) (F4)	
V–O _{THF}	2.403(7) (O30A)	2.464(6) (O30B)
O _{THF} –C _{THF}	1.42(1) (O30A, C31A)	1.48(1) (O30B, C31B)
	1.49(1) (O30A, C34A)	1.48(1) (O30B, C34B)
	1.50(1) (C31A, C32A)	1.50(1) (C31B, C32B)
C _{THF} –C _{THF}	1.54(1) (C32A, C33A)	1.53(1) (C32B, C33B)
	1.45(1) (C33A, C34A)	1.49(1) (C33B, C34B)
	2.91(1) (F1, C34A)	3.11(2) (F1, C34B)
F–C _{THF}	3.15(2) (F3, C31A)	2.96(2) (F3, C31B)
	3.17(2) (F4, C34A)	3.22(2) (F4, C34B)
Intermolecular bond distance [$\text{\AA}$]		
	3.004(2) (F1, C2)	
	3.081(2) (F2, C5)	
F–C	2.946(2) (F3, C4)	
	3.065(2) (F3, C5)	
	2.986(2) (F4, C2)	
V displacement [$\text{\AA}$] ^[a]	0.309	
τ_3 ^[b]	0.021	
Angle [$^\circ$]		
	99.64(7) (F1)	
O–V–F	100.21(9) (F2)	
	100.53(7) (F3)	
	98.69(8) (F4)	
	88.89(6) (F1, F2)	
F–V–F _{cis}	86.60(5) (F1, F4)	
	88.95(6) (F2, F3)	
	88.96(5) (F3, F4)	
	82.1(2) (F1, O30A)	76.3(2) (F1, O30B)
F–V–O _{THF}	88.3(2) (F2, O30A)	77.1(2) (F2, O30B)
	77.7(2) (F3, O30A)	83.6(2) (F3, O30B)
	72.9(2) (F4, O30A)	83.9(2) (F4, O30B)
O–V–O _{THF}	171.3(2)	175.1(2)
	159.78(6) (F1, F3)	
F–V–F _{trans}	161.05(7) (F2, F4)	
plane _{F1-F2-F3-F4} –plane _{THF}	73.5(3)	76.0(3)
plane _{F1-O1-F3} –plane _{THF}	40.7(4)	18.8(3)
plane _{F2-O1-F3} –plane _{THF}	53.6(5)	77.3(3)

^[a] Displacement of vanadium center from the plane of basal fluorine atoms.^[b] Structural parameter was calculated for hypothetical $[\text{VOF}_4]^-$ anion using $\tau = \frac{\beta - \alpha}{60^\circ}$, where β is the largest of the basal angles and α is the angle between the remaining basal atoms [198].

Table A10: Selected bond distances and angles for both subunits of the $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$ (**9**) salt.

	Subunit 1	Subunit 2
Intramolecular bond distance [$\text{\AA}$]		
V–O	1.570(2)	1.574(2)
	1.840(1) (F1)	1.832(1) (F5)
V–F	1.804(1) (F2)	1.805(1) (F6)
	1.831(1) (F3)	1.821(1) (F7)
	1.811(1) (F4)	1.815(1) (F8)
V–N _{py}	2.399(2) (N59)	2.406(2) (N65)
N _{py} –C _{py}	1.328(3) (N59, C60)	1.327(3) (N65, C66)
	1.341(3) (N59, C64)	1.337(3) (N65, C70)
	1.382(3) (C60, C61)	1.384(3) (C66, C67)
C _{py} –C _{py}	1.381(4) (C61, C62)	1.380(4) (C67, C68)
	1.367(4) (C62, C63)	1.360(4) (C68, C69)
	1.377(4) (C63, C64)	1.383(3) (C69, C70)
	3.043(3) (F1, C64)	3.151(3) (F5, C70)
F–C _{py}	3.047(3) (F2, C60)	2.911(3) (F6, C70)
	3.072(2) (F3, C60)	3.246(3) (F7, C66) ^[a]
	3.171(3) (F4, C64)	3.084(3) (F8, C66)
Intermolecular bond distance [$\text{\AA}$]		
	2.896(2) (F1, C2)	2.888(2) (F5, C31)
	3.100(2) (F3, C34)	3.169(2) (F4, C4)
F–C	2.921(2) (F4, C33)	3.022(2) (F8, C4)
	2.877(2) (F4, C34)	2.984(2) (F8, C5)
	3.116(3) (F2, C68)	3.199(3) (F6, C63)
V displacement [$\text{\AA}$] ^[b]	0.291	0.288
$\tau_5^{\text{[c]}}$	0.008	0.005
Angle [$^\circ$]		
	99.45(9) (F1)	98.62(9) (F5)
O–V–F	99.49(8) (F2)	98.07(8) (F6)
	99.13(9) (F3)	99.34(9) (F7)
	98.61(9) (F4)	100.40(7) (F8)
	80.70(6) (F1, N59)	79.66(6) (F5, N65)
F–V–N _{py}	80.14(6) (F2, N59)	79.25(6) (F6, N65)
	80.73(6) (F3, N59)	82.53(6) (F7, N65)
	81.75(6) (F4, N59)	82.28(5) (F8, N65)
	89.34(6) (F1, F2)	89.54(7) (F5, F6)
F–V–F _{cis}	86.75(5) (F1, F4)	87.53(6) (F5, F8)
	89.00(6) (F2, F3)	90.52(7) (F6, F7)
	89.08(5) (F3, F4)	86.69(6) (F7, F8)
O–V–N _{py}	179.61(9)	176.78(8)
F–V–F _{trans}	161.37(6) (F1, F3)	161.85(7) (F5, F7)
	161.87(7) (F2, F4)	161.53(6) (F6, F8)
plane _{F1-F2-F3-F4} –plane _{py}	83.8(1)	88.8(1)
plane _{F1-O1-F3} –plane _{py}	42.0(1)	56.8(3)
plane _{F2-O1-F3} –plane _{py}	47.9(1)	32.9(3)

^[a] Bond distance larger than the sum of van der Waals radii [339].^[b] Displacement of vanadium center from the plane of basal fluorine atoms.^[c] Structural parameter was calculated for hypothetical $[\text{VOF}_4]^-$ anion using $\tau = \frac{\beta - \alpha}{60^\circ}$, where β is the largest of the basal angles and α is the angle between the remaining basal atoms [198].

Table A11: Selected bond distances and angles for the $[(\text{NHC}^{\text{Dipp}})\text{H}]_2[(\text{VOF}_4)_2(\text{pyz})]\cdot 4\text{MeCN}$ (**10a**) salt.

Intramolecular bond distance [$\text{\AA}$]	
V–O	1.581(1)
	1.828(1) (F1)
V–F	1.813(1) (F2)
	1.816(1) (F3)
	1.798(1) (F4)
V–N _{pyz}	2.465(2)
N _{pyz} –C _{pyz}	1.334(2) (N30, C31)
	1.329(3) (N30, C32)
C _{pyz} –C _{pyz}	1.387(3) (C31, C32) ^[a]
	3.208(2) (F1, C32)
F–C _{pyz}	3.075(3) (F2, C32)
	3.008(3) (F3, C31)
Intermolecular bond distance [$\text{\AA}$]	
F–C	3.032(2) (F1, C2)
	3.204(3) (F2, C4)
V displacement [$\text{\AA}$] ^[b]	0.288
τ_5 ^[c]	0.027
Angle [$^\circ$]	
	99.38(6) (F1)
	98.84(7) (F2)
O–V–F	98.13(6) (F3)
	100.27(7) (F4)
	83.15(5) (F1, N30)
F–V–N _{pyz}	78.66(5) (F2, N30)
	79.30(5) (F3, N30)
	82.31(6) (F4, N30)
	87.79(5) (F1, F2)
F–V–F _{cis}	87.87(6) (F1, F4)
	88.31(6) (F2, F3)
	90.24(7) (F3, F4)
O–V–N _{pyz}	176.41(7)
F–V–F _{trans}	162.44(5) (F1, F3)
	160.85(6) (F2, F4)
plane _{F1-F2-F3-F4} –plane _{pyz}	78.09(6)
plane _{F1-O1-F3} –plane _{pyz}	40.19(6)
plane _{F2-O1-F3} –plane _{pyz}	53.09(6)

^[a] Symmetry code: (i) $-x, -y, 1-z$.^[b] Displacement of vanadium center from the plane of basal fluorine atoms.^[c] Structural parameter was calculated for hypothetical $[\text{VOF}_4]^-$ anion using $\tau = \frac{\beta - \alpha}{60^\circ}$, where β is the largest of the basal angles and α is the angle between the remaining basal atoms [198].

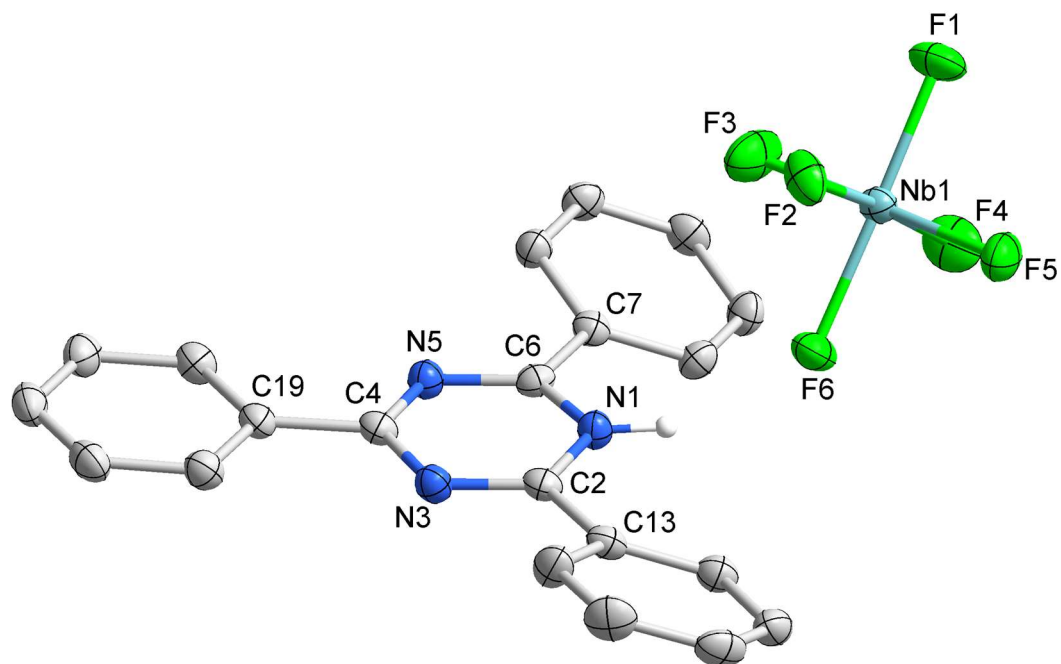


Figure A11: Ionic structure of the $[(^{\text{Ph}}\text{TZN})\text{H}][\text{NbF}_6]$ (**12**) salt.

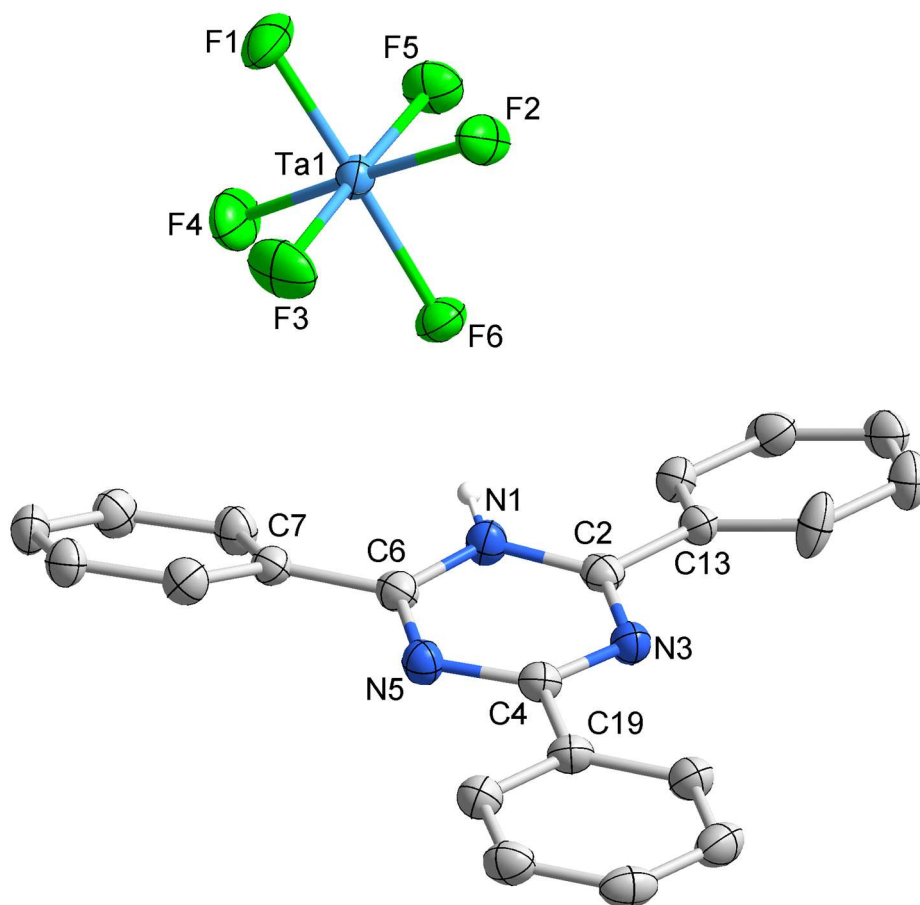


Figure A12: Ionic structure of the $[(^{\text{Ph}}\text{TZN})\text{H}][\text{TaF}_6]$ (**13**) salt.

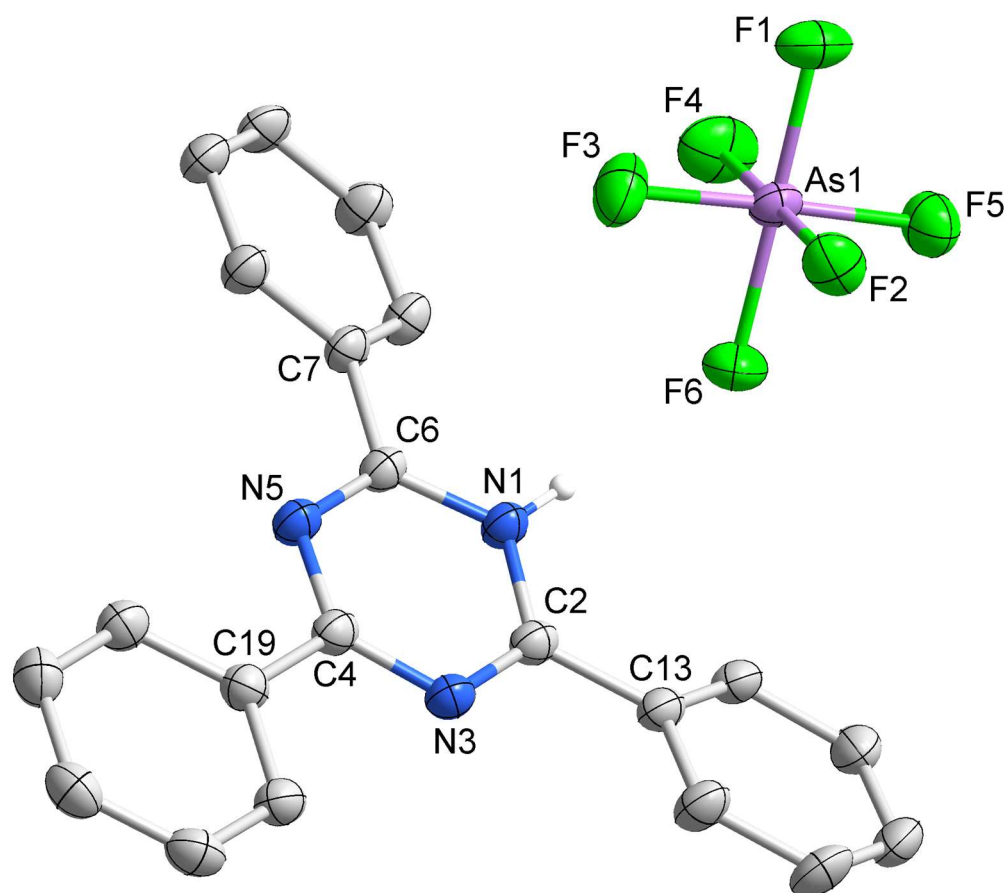


Figure A13: Ionic structure of the $[(\text{PhTZN})\text{H}][\text{AsF}_6]$ (**14**) salt.

A.4 Crystal Collection Data and Refinement Parameters

Table A12: Summary of crystallographic data and structural refinement for neutral $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) and $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) complexes. Table is based on the reference [323].

Compound	$[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$	$[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$
Ref.	(1)	(2)
Formula	$\text{C}_{27}\text{H}_{36}\text{N}_2\text{F}_5\text{Nb}$	$\text{C}_{27}\text{H}_{36}\text{N}_2\text{F}_5\text{Ta}$
F_w	576.49	664.53
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pnma$	$Pnma$
a [Å]	12.7460(1)	12.7947(1)
b [Å]	19.5970(2)	19.5781(2)
c [Å]	11.0652(1)	11.0526(1)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å ³]	2763.90(4)	2768.63(4)
Z	4	4
ρ_{calc} [g/cm ³]	1.385	1.594
Crystal size [mm]	$0.37 \times 0.34 \times 0.2$	$0.39 \times 0.27 \times 0.16$
T [K]	120	120
Radiation type	Cu K α	Cu K α
λ [Å]	1.54184	1.54184
μ [mm ⁻¹]	3.992	7.771
$F(000)$	1192	1320
Θ_{max} [°]	67.072	67.062
Index ranges	$-15 \leq h \leq 15$	$-15 \leq h \leq 15$
	$-23 \leq k \leq 21$	$-23 \leq k \leq 23$
	$-13 \leq l \leq 13$	$-13 \leq l \leq 13$
Reflections collected	32716	90262
Independent reflections	2545	2552
Reflections with $[I > 2\sigma(I)]$	2301	2174
R_{int}	0.0297	0.0439
R_{sigma}	0.0104	0.0088
Data/restraints/parameters	2545/0/167	2552/0/167
$S^{\text{[a]}}$	1.029	1.040
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ $[I > 2\sigma(I)]$	0.0253, 0.0685	0.0226, 0.0567
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [all data]	0.0288, 0.0719	0.0277, 0.0607
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ [eÅ ⁻³]	-0.233, 0.658	-0.377, 0.811

^[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_o - N_p)]^{1/2}$.

^[b] $R_1 = ||F_o| - |F_c||/\Sigma|F_o|$.

^[c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table A13: Summary of crystallographic data and structural refinement for $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot 2\text{MeCN}$ (**3a**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot \text{DCM}$ (**3b**) salts. Table is based on the reference [323].

Compound Ref.	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot 2\text{MeCN}$ (3a)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]\cdot \text{DCM}$ (3b)
Formula	$\text{C}_{27}\text{H}_{37}\text{N}_2\text{F}_6\text{Nb}\cdot 2(\text{C}_2\text{H}_3\text{N})$	$\text{C}_{27}\text{H}_{37}\text{N}_2\text{F}_6\text{Nb}\cdot \text{CH}_2\text{Cl}_2$
F_w	680.60	681.42
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/m$
a [Å]	9.0350(1)	10.2140(2)
b [Å]	22.2940(2)	14.7465(2)
c [Å]	17.4923(1)	10.8761(2)
α [°]	90	90
β [°]	100.970(1)	103.933(2)
γ [°]	90	90
V [Å ³]	3459.03(5)	1589.97(5)
Z	4	2
ρ_{calc} [g/cm ³]	1.303	1.423
Crystal size [mm]	$0.76 \times 0.58 \times 0.38$	$0.57 \times 0.50 \times 0.32$
T [K]	120	120
Radiation type	Cu K α	Cu K α
λ [Å]	1.54184	1.54184
μ [mm ⁻¹]	3.330	5.114
$F(000)$	1408	700
Θ_{max} [°]	67.079	66.968
Index ranges	$-10 \leq h \leq 10$	$-12 \leq h \leq 12$
	$-26 \leq k \leq 26$	$-17 \leq k \leq 17$
	$-20 \leq l \leq 20$	$-12 \leq l \leq 12$
Reflections collected	90266	32731
Independent reflections	6180	2958
Reflections with $[I > 2\sigma(I)]$	5862	2817
R_{int}	0.0383	0.0427
R_{sigma}	0.0112	0.0139
Data/restraints/parameters	6180/0/428	2958/1/215
$S^{\text{[a]}}$	1.023	1.095
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [$I > 2\sigma(I)$]	0.0293, 0.0761	0.0328, 0.0847
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [all data]	0.0308, 0.0772	0.0342, 0.0857
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ [eÅ ⁻³]	-0.573, 0.494	-0.618, 0.408

^[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2) / (N_o - N_p)]^{1/2}$.

^[b] $R_1 = ||F_o| - |F_c|| / \Sigma |F_o|$.

^[c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2)]^{1/2}$.

Table A14: Summary of crystallographic data and structural refinement for $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot 2\text{MeCN}$ (**4a**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot \text{DCM}$ (**4b**) salts. Table is based on the reference [323].

Compound Ref.	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot 2\text{MeCN}$ (4a)	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]\cdot \text{DCM}$ (4b)
Formula	$\text{C}_{27}\text{H}_{37}\text{N}_2\text{F}_6\text{Ta}\cdot 2(\text{C}_2\text{H}_5\text{N})$	$\text{C}_{27}\text{H}_{37}\text{N}_2\text{F}_6\text{Ta}\cdot \text{CH}_2\text{Cl}_2$
F_w	766.64	769.46
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/m$
a [Å]	9.0400(1)	10.2453(2)
b [Å]	22.3063(3)	14.7342(3)
c [Å]	17.5262(2)	10.8780(2)
α [°]	90	90
β [°]	100.976(1)	103.993(2)
γ [°]	90	90
V [Å ³]	3469.49(7)	1593.37(6)
Z	4	2
ρ_{calc} [g/cm ³]	1.468	1.604
Crystal size [mm]	$0.62 \times 0.48 \times 0.38$	$0.61 \times 0.48 \times 0.43$
T [K]	120	120
Radiation type	Cu K α	Cu K α
λ [Å]	1.54184	1.54184
μ [mm ⁻¹]	6.340	8.392
$F(000)$	1536	764
Θ_{max} [°]	67.079	67.080
Index ranges	$-10 \leq h \leq 10$	$-12 \leq h \leq 12$
	$-26 \leq k \leq 26$	$-17 \leq k \leq 17$
	$-20 \leq l \leq 20$	$-12 \leq l \leq 12$
Reflections collected	42899	25285
Independent reflections	6196	2948
Reflections with $[I > 2\sigma(I)]$	5784	2855
R_{int}	0.0368	0.0759
R_{sigma}	0.0178	0.0297
Data/restraints/parameters	6196/0/428	2948/1/215
$S^{\text{[a]}}$	1.062	1.080
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ $[I > 2\sigma(I)]$	0.0263, 0.0646	0.0374, 0.0935
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [all data]	0.0290, 0.0664	0.0385, 0.0944
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ [eÅ ⁻³]	-0.719, 1.124	-0.691, 1.869

^[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_o - N_p)]^{1/2}$.

^[b] $R_1 = ||F_o| - |F_c||/\Sigma|F_o|$.

^[c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table A15: Summary of crystallographic data and structural refinement for neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex, $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]\cdot 2\text{MeCN}$ (**6a**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) salts. Table is based on the reference [324].

Compound	$[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]\cdot 2\text{MeCN}$	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$
Ref.	(5)	(6a)	(7)
Formula	$\text{C}_{27}\text{H}_{36}\text{F}_3\text{N}_2\text{OV}$	$\text{C}_{27}\text{H}_{37}\text{N}_2\text{F}_4\text{OV}\cdot 2(\text{C}_2\text{H}_3\text{N})$	$\text{C}_{27}\text{H}_{37}\text{N}_2\text{F}_2\text{O}_2\text{V}$
F_w	1025.03	614.63	510.52
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	$P-1$	$Pbca$	$Pccn$
a [Å]	12.5134(2)	20.2786(1)	11.1781(1)
b [Å]	15.4535(3)	14.7208(1)	12.5819(1)
c [Å]	16.0382(3)	22.1027(1)	19.8027(1)
α [°]	117.789(2)	90	90
β [°]	91.105(1)	90	90
γ [°]	91.039(1)	90	90
V [Å ³]	2741.9(1)	6598.04(6)	2785.09(4)
Z	2	8	4
ρ_{calc} [g/cm ³]	1.242	1.237	1.218
Crystal size [mm]	$0.92\times 0.61\times 0.24$	$0.60\times 0.41\times 0.27$	$0.67\times 0.60\times 0.47$
T [K]	150	100	100
Radiation type	Cu K α	Cu K α	Cu K α
λ [Å]	1.54184	1.54184	1.54184
μ [mm ⁻¹]	3.369	2.947	3.289
$F(000)$	1080	2592	1080
Θ_{max} [°]	67.077	73.348	67.076
Index ranges	$-14\leq h\leq 14$	$-25\leq h\leq 24$	$-13\leq h\leq 13$
	$-18\leq k\leq 18$	$-18\leq k\leq 18$	$-15\leq k\leq 14$
	$-19\leq l\leq 19$	$-27\leq l\leq 27$	$-23\leq l\leq 23$
Reflections collected	92581	170235	54023
Independent reflections	9786	6613	2488
Reflections with $[I>2\sigma(I)]$	8870	6406	2421
R_{int}	0.0416	0.0313	0.0317
R_{sigma}	0.0171	0.0069	0.0075
Data/restraints/parameters	9786/0/671	6613/22/414	2488/0/160
$S^{\text{[a]}}$	1.041	1.043	1.133
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [$I>2\sigma(I)$]	0.0373, 0.1007	0.0416, 0.1230	0.0338, 0.1013
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [all data]	0.0419, 0.1047	0.0424, 0.1240	0.0345, 0.1020
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ [eÅ ⁻³]	-0.389, 0.475	-0.520, 1.191	-0.443, 0.365

^[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_o - N_p)]^{1/2}$.

^[b] $R_1 = ||F_o| - |F_c||/\Sigma|F_o|$.

^[c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table A16: Summary of crystallographic data and structural refinement for $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$ (**8**), $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$ (**9**) and $[(\text{NHC}^{\text{Dipp}})\text{H}]_2[(\text{VOF}_4)_2(\text{pyz})]\cdot 4\text{MeCN}$ (**10a**) salts.

Compound	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{THF})]$	$[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4(\text{py})]$	$[(\text{NHC}^{\text{Dipp}})\text{H}]_2[(\text{VOF}_4)_2(\text{pyz})]\cdot 4\text{MeCN}$
Ref.	(8)	(9)	(10a)
Formula	$\text{C}_{27}\text{H}_{37}\text{N}_2, \text{C}_4\text{H}_8\text{F}_4\text{O}_2\text{V}$	$\text{C}_{27}\text{H}_{37}\text{N}_2, \text{C}_5\text{H}_5\text{F}_5\text{NOV}$	$2(\text{C}_{27}\text{H}_{37}\text{N}_2), \text{C}_4\text{N}_2\text{F}_8\text{O}_2\text{V}_2, 4(\text{C}_2\text{H}_3\text{N})$
F_w	604.63	1223.25	1309.35
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P-1$	$P-1$
a [Å]	12.6595(1)	12.5745(3)	9.9767(3)
b [Å]	12.7750(1)	12.7175(3)	12.2685(4)
c [Å]	19.6070(2)	20.5561(5)	15.9080(5)
α [°]	90	88.902(2)	92.863(3)
β [°]	93.396(1)	81.187(2)	106.181(3)
γ [°]	90	87.142(2)	110.370(3)
V [Å ³]	3165.38(5)	3244.2(1)	1729.5(1)
Z	2	2	1
ρ_{calc} [g/cm ³]	1.269	1.252	1.257
Crystal size [mm]	$0.49 \times 0.35 \times 0.27$	$0.68 \times 0.29 \times 0.17$	$0.38 \times 0.23 \times 0.13$
T [K]	150	150	150
Radiation type	Cu K α	Cu K α	Cu K α
λ [Å]	1.54184	1.54184	1.54184
μ [mm ⁻¹]	3.066	2.986	2.851
$F(000)$	1280	1288	690
Θ_{max} [°]	67.080	67.073	67.078
Index ranges	$-15 \leq h \leq 15$	$-14 \leq h \leq 15$	$-11 \leq h \leq 11$
	$-15 \leq k \leq 15$	$-15 \leq k \leq 15$	$-14 \leq k \leq 14$
	$-23 \leq l \leq 23$	$-24 \leq l \leq 24$	$-18 \leq l \leq 18$
Reflections collected	71450	34582	16871
Independent reflections	5637	11479	6123
Reflections with $[I > 2\sigma(I)]$	5262	10344	5587
R_{int}	0.0330	0.0228	0.0225
R_{sigma}	0.0117	0.0220	0.0227
Data/restraints/parameters	5637/13/415	11479/0/755	6123/0/463
$S^{[a]}$	1.090	1.032	1.039
$R_1^{[b]}, wR_2^{[c]} [I > 2\sigma(I)]$	0.0376, 0.1004	0.0398, 0.1087	0.0393, 0.1064
$R_1^{[b]}, wR_2^{[c]} [\text{all data}]$	0.0400, 0.1019	0.0449, 0.1131	0.0433, 0.1104
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ [eÅ ⁻³]	-0.356, 0.412	-0.397, 0.684	-0.236, 0.337

^[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_o - N_p)]^{1/2}$.

^[b] $R_1 = ||F_o| - |F_c||/\Sigma|F_o|$.

^[c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table A17: Summary of crystallographic data and structural refinement for $[(^{\text{Ph}}\text{TZN})\text{H}][\text{NbF}_6]$ (**12**), $[(^{\text{Ph}}\text{TZN})\text{H}][\text{TaF}_6]$ (**13**) and $[(^{\text{Ph}}\text{TZN})\text{H}][\text{AsF}_6]$ (**14**) salts.

Compound Ref.	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{NbF}_6]$ (12)	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{TaF}_6]$ (13)	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{AsF}_6]$ (14)
Formula	$\text{C}_{21}\text{H}_{16}\text{N}_3\text{F}_6\text{Nb}$	$\text{C}_{21}\text{H}_{16}\text{N}_3\text{F}_6\text{Ta}$	$\text{C}_{21}\text{H}_{16}\text{N}_3\text{F}_6\text{As}$
F_w	517.28	605.32	499.29
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P-1$	$P-1$	$P-1$
a [Å]	9.4014(4)	9.4075(3)	9.4649(4)
b [Å]	10.6896(3)	10.7005(3)	10.4926(5)
c [Å]	10.7063(3)	10.7228(4)	10.6597(5)
α [°]	94.054(2)	93.970(3)	95.352(4)
β [°]	104.485(3)	104.433(3)	104.723(4)
γ [°]	106.969(3)	107.019(3)	106.125(4)
V [Å ³]	984.33(6)	987.71(6)	968.17(8)
Z	2	2	2
ρ_{calc} [g/cm ³]	1.745	2.035	1.713
Crystal size [mm]	$0.36 \times 0.25 \times 0.10$	$0.30 \times 0.13 \times 0.07$	$0.45 \times 0.22 \times 0.12$
T [K]	150	150	150
Radiation type	Cu K α	Cu K α	Cu K α
λ [Å]	1.54184	1.54184	1.54184
μ [mm ⁻¹]	5.629	10.915	3.036
$F(000)$	516	580	500
Θ_{max} [°]	67.080	67.029	67.075
Index ranges	$-11 \leq h \leq 10$	$-11 \leq h \leq 10$	$-11 \leq h \leq 11$
	$-12 \leq k \leq 12$	$-12 \leq k \leq 12$	$-12 \leq k \leq 12$
	$-12 \leq l \leq 12$	$-12 \leq l \leq 12$	$-12 \leq l \leq 11$
Reflections collected	27091	23491	14898
Independent reflections	3495	3505	3432
Reflections with $[I > 2\sigma(I)]$	3261	3195	3072
R_{int}	0.0362	0.0489	0.0449
R_{sigma}	0.0169	0.0268	0.0286
Data/restraints/parameters	3495/0/280	3505/0/280	3432/0/280
$S^{\text{[a]}}$	1.062	1.050	1.050
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [$I > 2\sigma(I)$]	0.0208, 0.0540	0.0232, 0.0545	0.0382, 0.0994
$R_1^{\text{[b]}}$, $wR_2^{\text{[c]}}$ [all data]	0.0232, 0.0553	0.0274, 0.0560	0.0433, 0.1039
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ [eÅ ⁻³]	-0.285, 0.310	-0.541, 0.898	-0.374, 0.963

^[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_o - N_p)]^{1/2}$.

^[b] $R_1 = ||F_o| - |F_c||/\Sigma|F_o|$.

^[c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table A18: Summary of crystallographic data and structural refinement for $[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (**11**), $[(^{\text{Ph}}\text{TZN})\text{H}_2][\text{SbF}_6]_2 \cdot \text{DCM}$ (**15**) and $[(^{\text{tBu}}\text{CA})\text{H}][\text{SbF}_6]$ (**16**) salts.

Compound Ref.	$[(^{\text{Ph}}\text{TZN})\text{H}][\text{SbF}_6]$ (11)	$[(^{\text{Ph}}\text{TZN})\text{H}_2][\text{SbF}_6]_2 \cdot \text{DCM}$ (15)	$[(^{\text{tBu}}\text{CA})\text{H}][\text{SbF}_6]$ (16)
Formula	$\text{C}_{21}\text{H}_{16}\text{N}_3\text{F}_6\text{Sb}$	$\text{C}_{21}\text{H}_{16}\text{N}_3\text{F}_6\text{Sb}, \text{CH}_2\text{Cl}_2$	$\text{C}_{10}\text{H}_{21}\text{N}_2\text{O}, \text{F}_6\text{Sb}$
F_w	546.12	867.80	421.04
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P-1$	$P2_1/c$	$P2_1/n$
a [Å]	9.4342(2)	10.9716(1)	9.4591(1)
b [Å]	10.6656(3)	16.7569(2)	32.7391(3)
c [Å]	10.7196(3)	15.7098(2)	10.6471(1)
α [°]	94.385(2)	90	90
β [°]	104.433(2)	100.089(1)	97.149(1)
γ [°]	106.737(2)	90	90
V [Å ³]	987.47(5)	2843.58(6)	3271.59(6)
Z	2	4	8
ρ_{calc} [g/cm ³]	1.837	2.027	1.710
Crystal size [mm]	$0.44 \times 0.32 \times 0.20$	$0.52 \times 0.35 \times 0.07$	$0.46 \times 0.26 \times 0.09$
T [K]	150	120	150
Radiation type	Cu K α	Cu K α	Cu K α
λ [Å]	1.54184	1.54184	1.54184
μ [mm ⁻¹]	11.728	17.719	13.951
$F(000)$	536	1664	1664
Θ_{max} [°]	67.057	67.067	67.069
Index ranges	$-11 \leq h \leq 11$	$-13 \leq h \leq 13$	$-11 \leq h \leq 11$
	$-12 \leq k \leq 12$	$-20 \leq k \leq 19$	$-39 \leq k \leq 39$
	$-12 \leq l \leq 12$	$-18 \leq l \leq 18$	$-12 \leq l \leq 12$
Reflections collected	14574	55183	66964
Independent reflections	3503	5060	5842
Reflections with $[I > 2\sigma(I)]$	3299	4495	5561
R_{int}	0.0410	0.1276	0.0460
R_{sigma}	0.0286	0.0395	0.0153
Data/restraints/parameters	3503/0/280	5060/0/370	5842/0/373
$S^{[a]}$	1.070	1.055	1.088
$R_1^{[b]}, wR_2^{[c]} [I > 2\sigma(I)]$	0.0275, 0.0684	0.0454, 0.1215	0.0305, 0.0745
$R_1^{[b]}, wR_2^{[c]} [\text{all data}]$	0.0300, 0.0706	0.0505, 0.1263	0.0323, 0.0756
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ [eÅ ⁻³]	-0.473, 0.804	-1.031, 2.282	-0.503, 0.993

[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2) / (N_o - N_p)]^{1/2}$.

[b] $R_1 = ||F_o| - |F_c|| / \Sigma|F_o|$.

[c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2)]^{1/2}$.

A.5 Raman Spectra

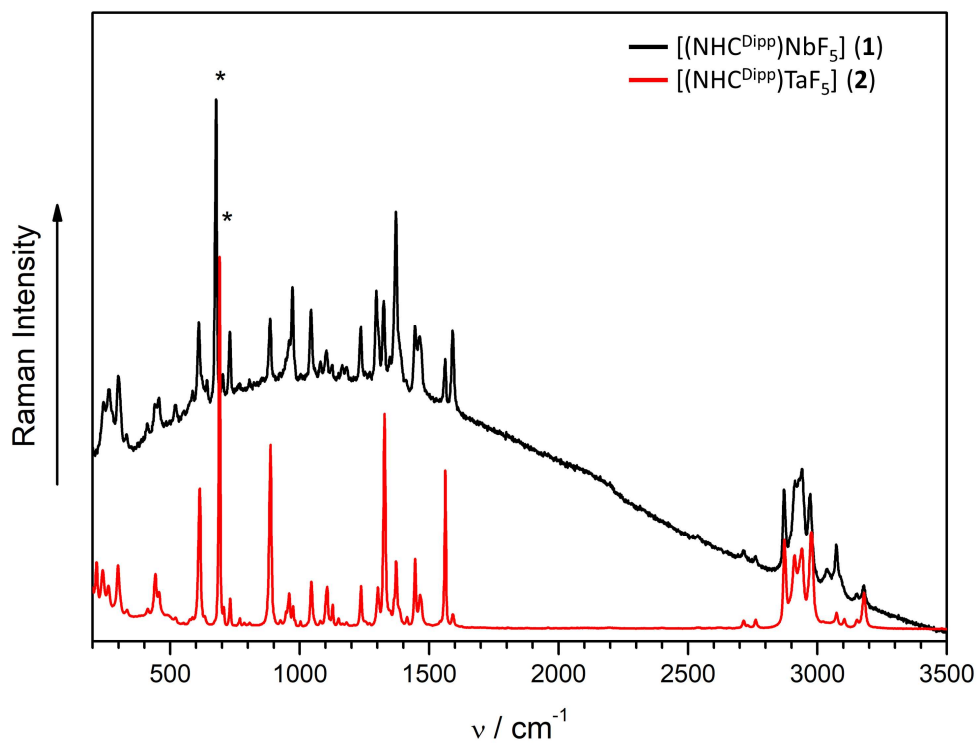


Figure A14: Full range Raman spectra of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (1) and $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (2) complexes. Figure is based on the reference [323].

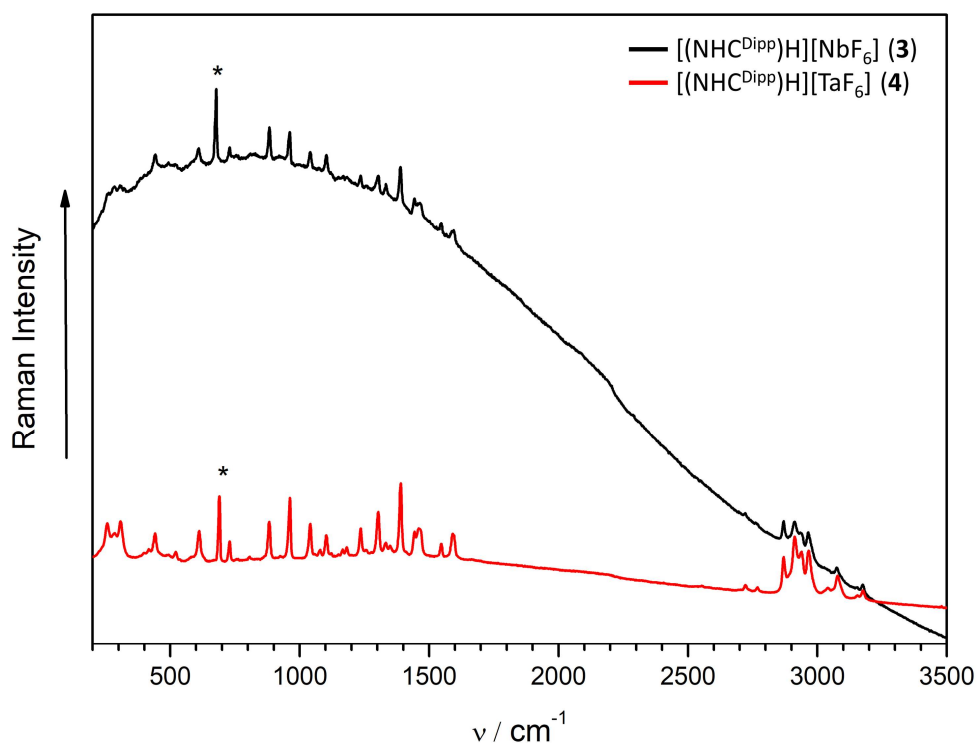


Figure A15: Full range Raman spectra of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ (3) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ (4) salts. Figure is based on the reference [323].

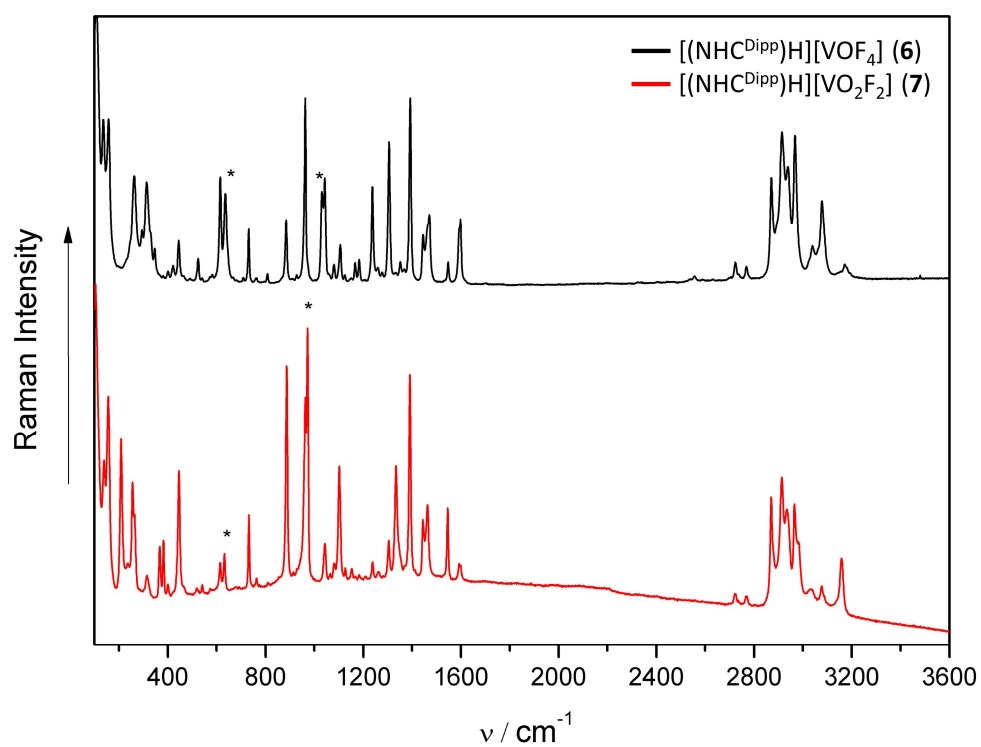


Figure A16: Full range Raman spectra of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) and $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) salts. Figure is based on the reference [324].

A.6 NMR Spectra

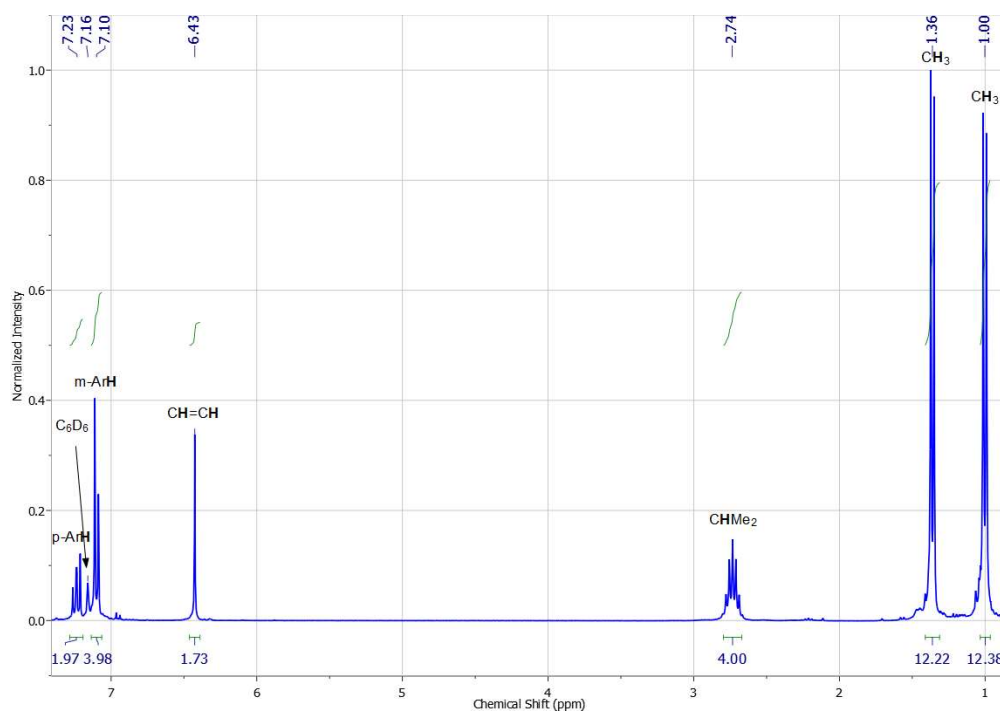


Figure A17: ¹H NMR spectrum of [(NHC^{Dipp})NbF₅] (**1**) in C₆D₆, showing NHC^{Dipp} ligand. Figure is based on the reference [323].

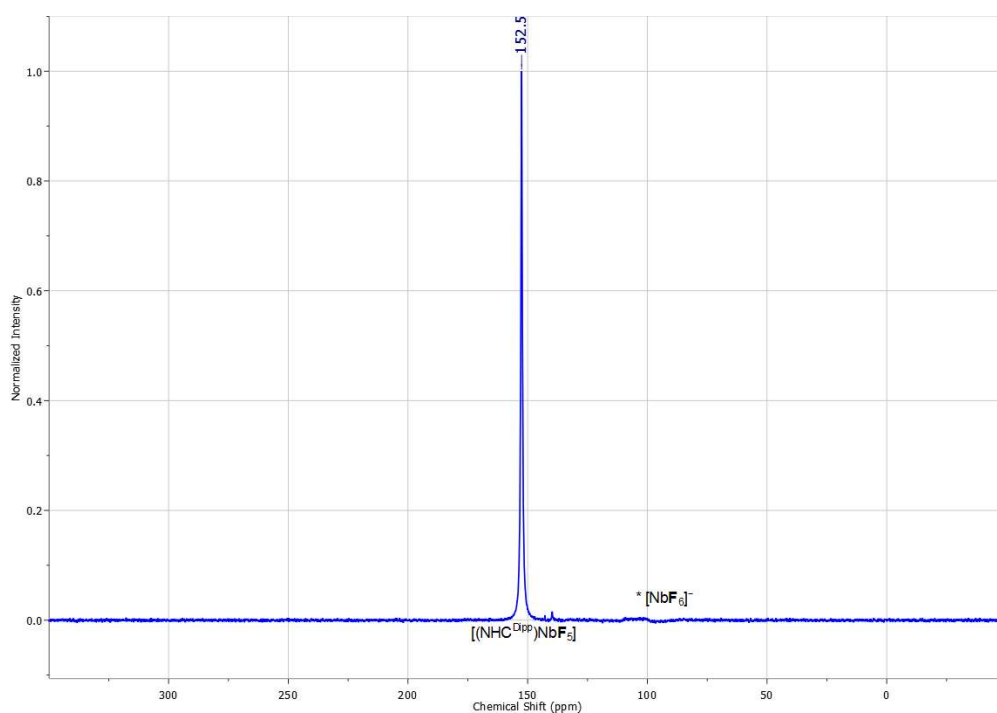


Figure A18: ¹⁹F NMR spectrum of [(NHC^{Dipp})NbF₅] (**1**) in C₆D₆, showing neutral [(NHC^{Dipp})NbF₅] (**1**) complex and a small amount of [NbF₆]⁻ anion impurity. Figure is based on the reference [323].

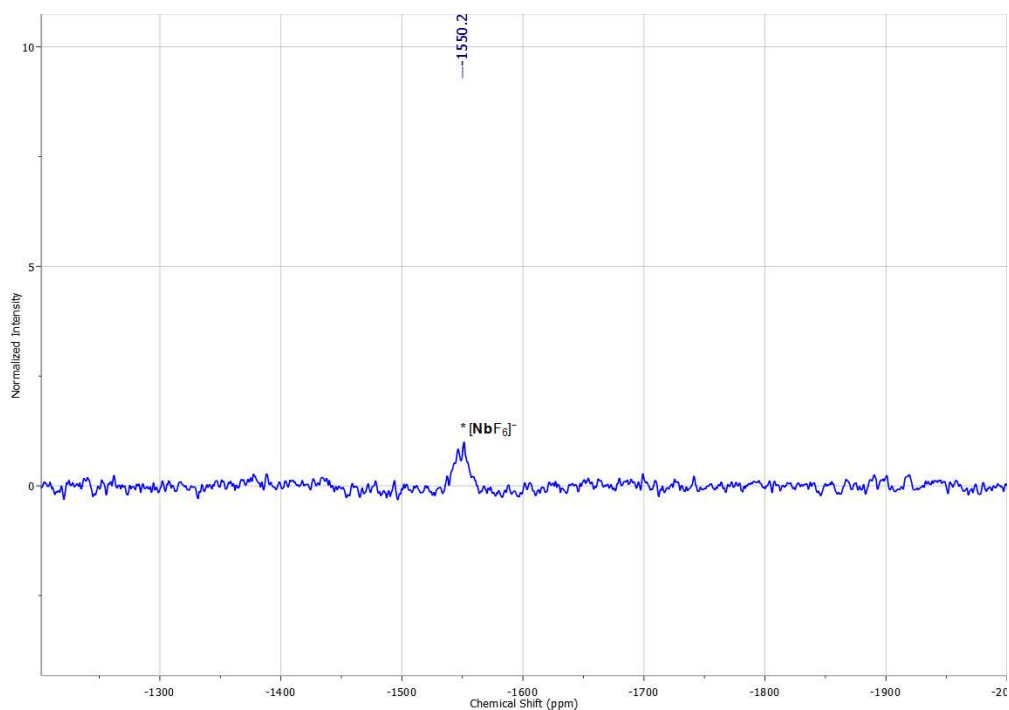


Figure A19: ^{93}Nb NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) in C_6D_6 , showing $[\text{NbF}_6]^-$ anion impurity. Figure is based on the reference [323].

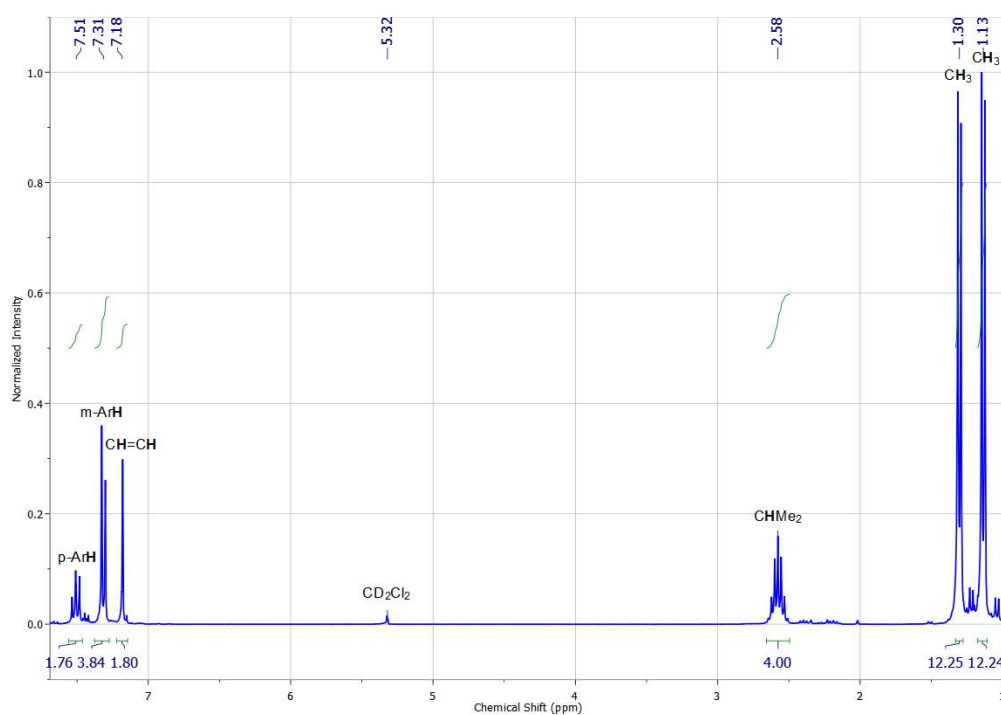


Figure A20: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) in CD_2Cl_2 , showing the bonded NHC^{Dipp} ligand. Figure is based on the reference [323].

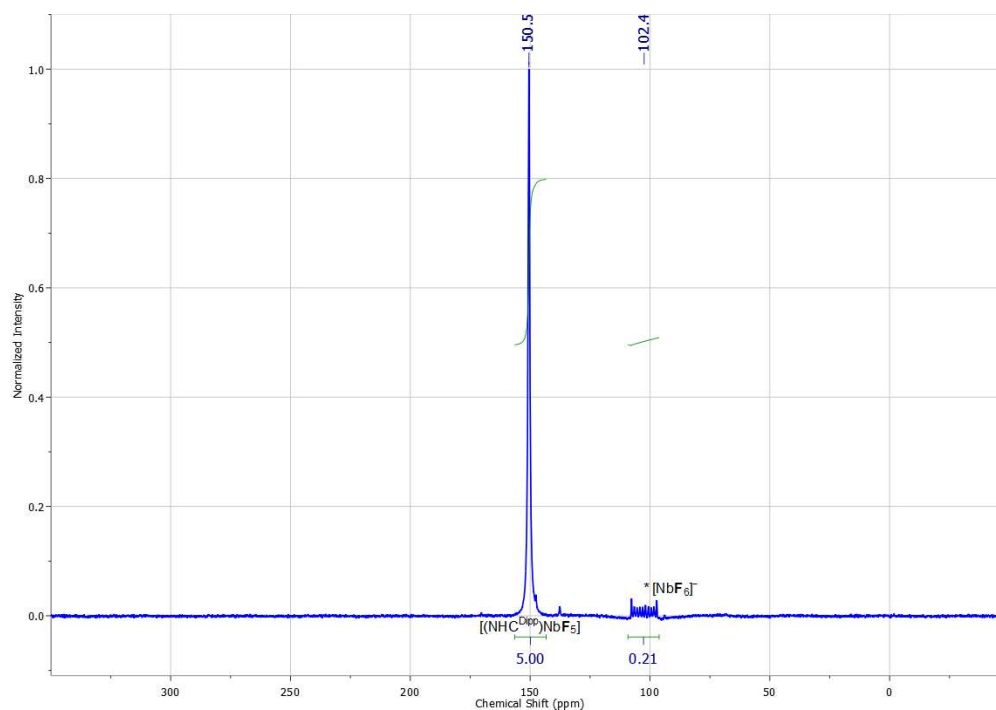


Figure A21: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (1) in CD_2Cl_2 , showing neutral $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (1) complex and a small amount of $[\text{NbF}_6]^-$ anion impurity. Figure is based on the reference [323].

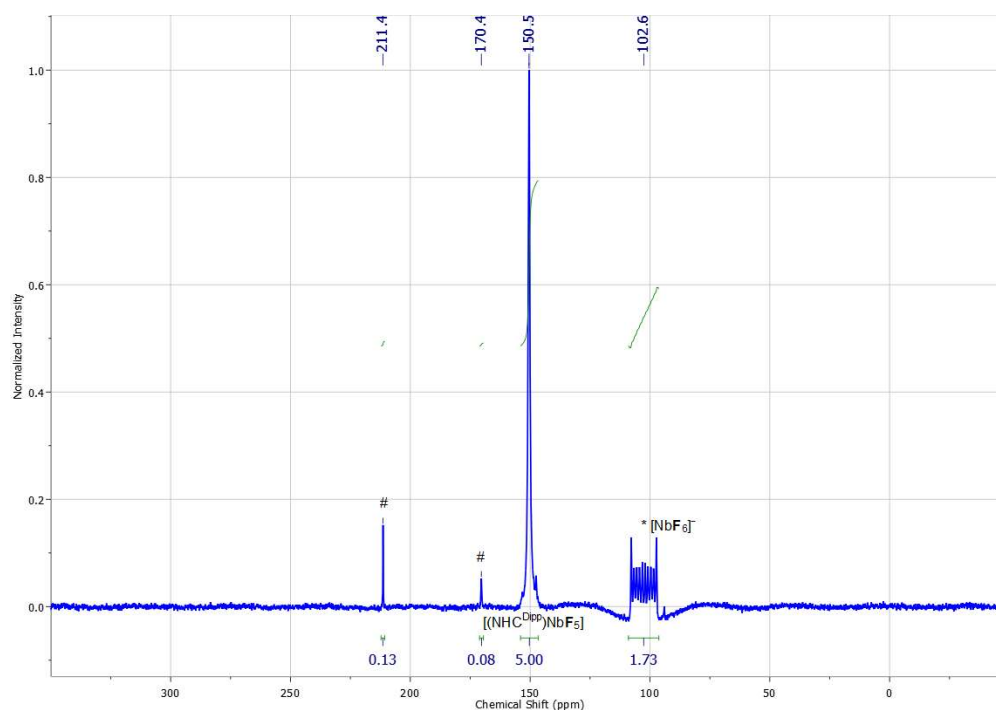


Figure A22: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (1) in CD_2Cl_2 after 20 days, showing neutral $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (1) complex, $[\text{NbF}_6]^-$ anion and other unidentified impurities present due to the slow decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (1) complex. Figure is based on the reference [323].

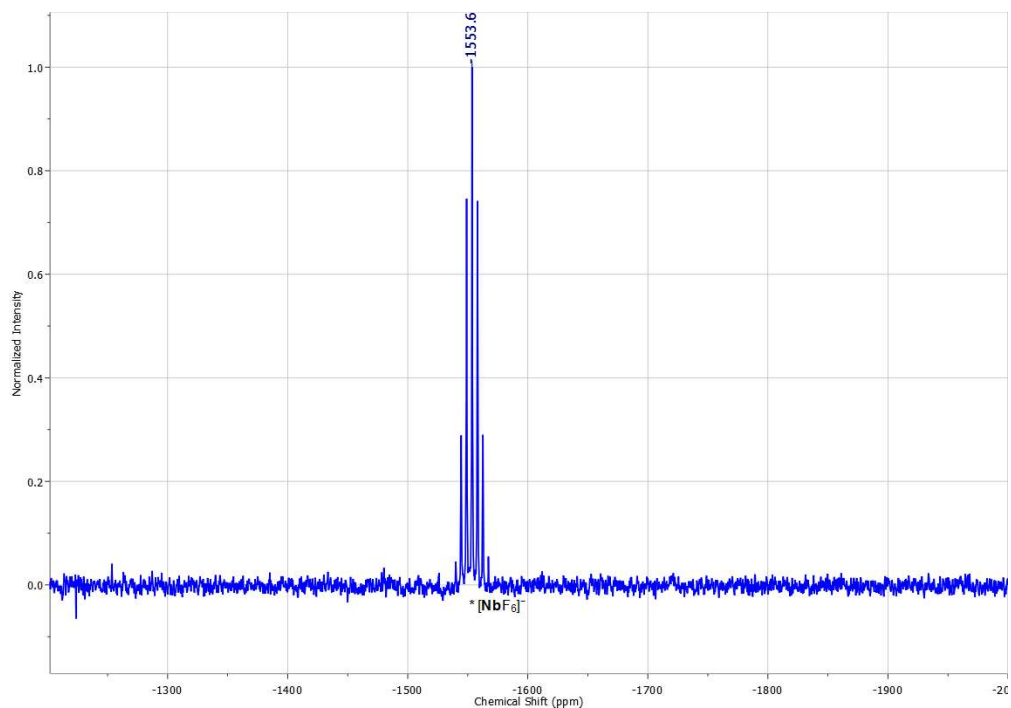


Figure A23: ^{93}Nb NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) in CD_2Cl_2 , showing $[\text{NbF}_6]^-$ anion impurity. Figure is based on the reference [323].

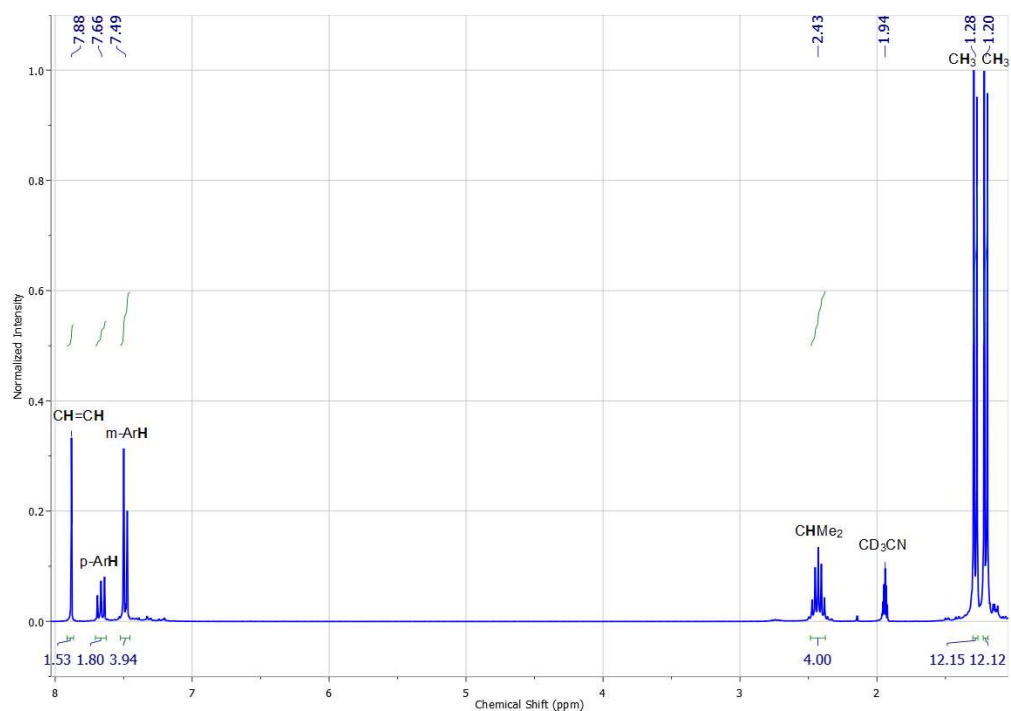


Figure A24: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) in CD_3CN , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{D}]^+$ cation present due to the total decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) complex and deuteration of NHC^{Dipp} with CD_3CN . Figure is based on the reference [323].

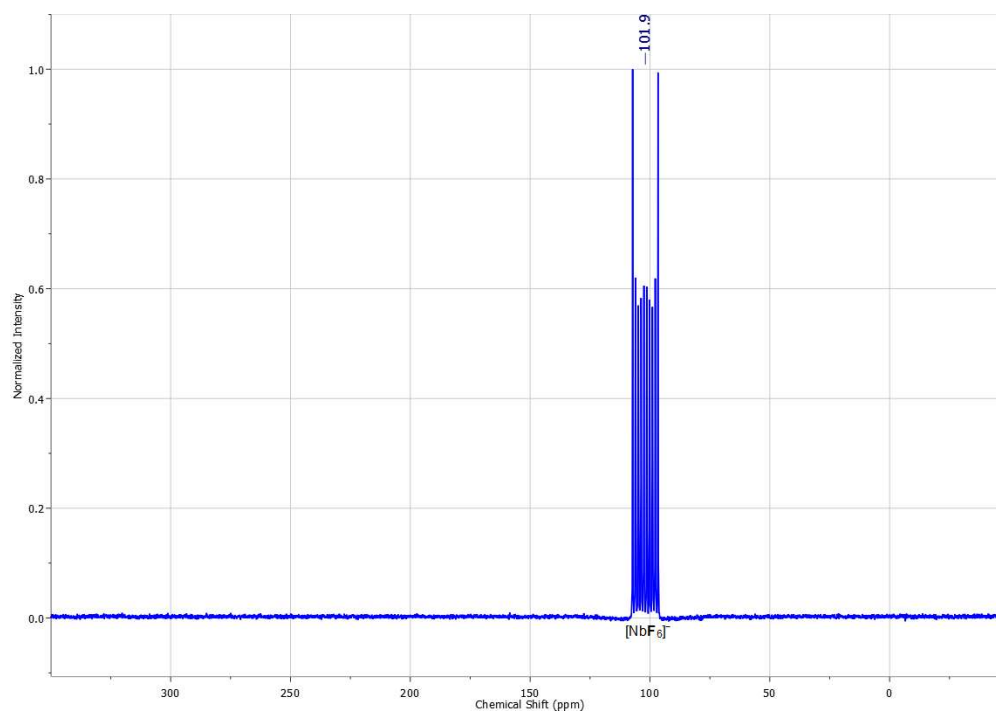


Figure A25: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) in CD_3CN , showing $[\text{NbF}_6]^-$ anion present due to the total decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) complex. Figure is based on the reference [323].

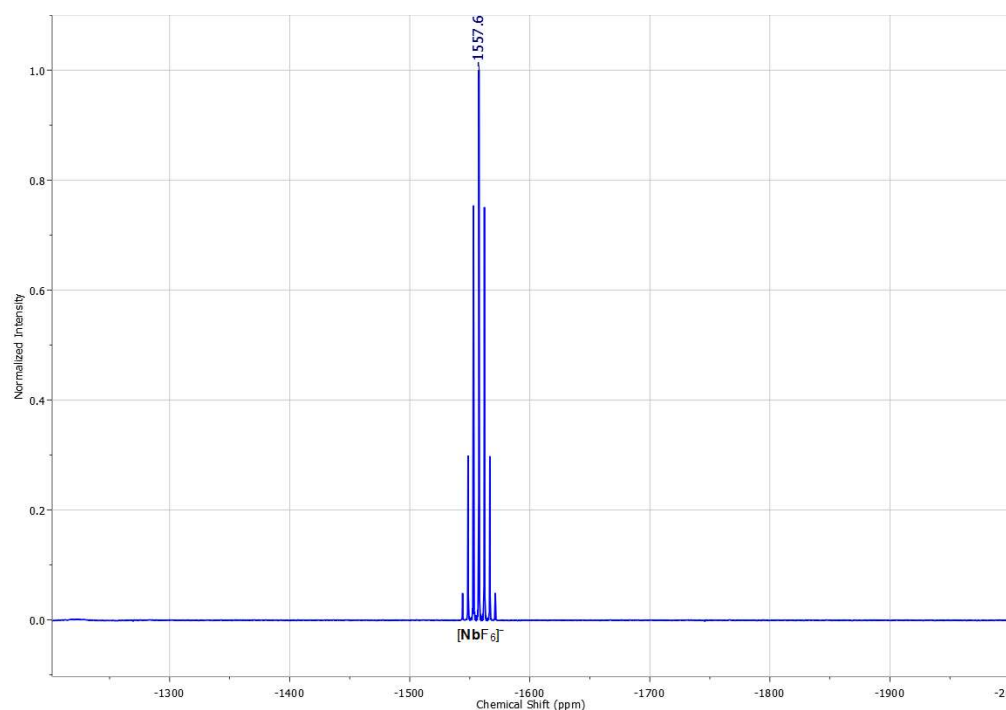


Figure A26: ^{93}Nb NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) in CD_3CN , showing $[\text{NbF}_6]^-$ anion present due to the total decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{NbF}_5]$ (**1**) complex. Figure is based on the reference [323].

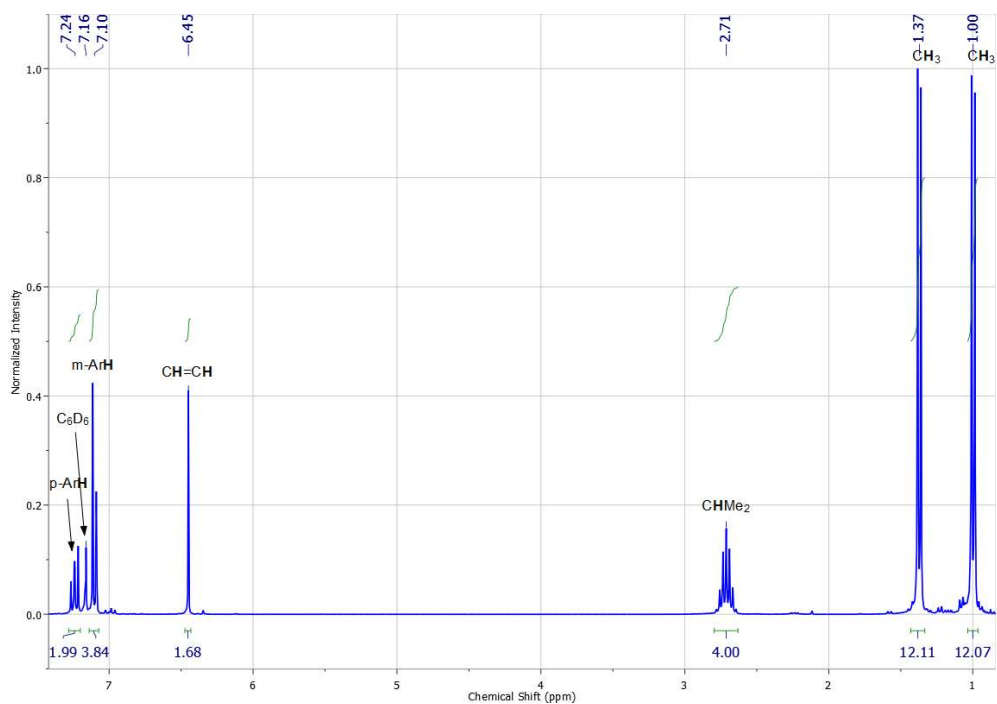


Figure A27: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) in C_6D_6 , showing the bonded NHC^{Dipp} ligand. Figure is based on the reference [323].

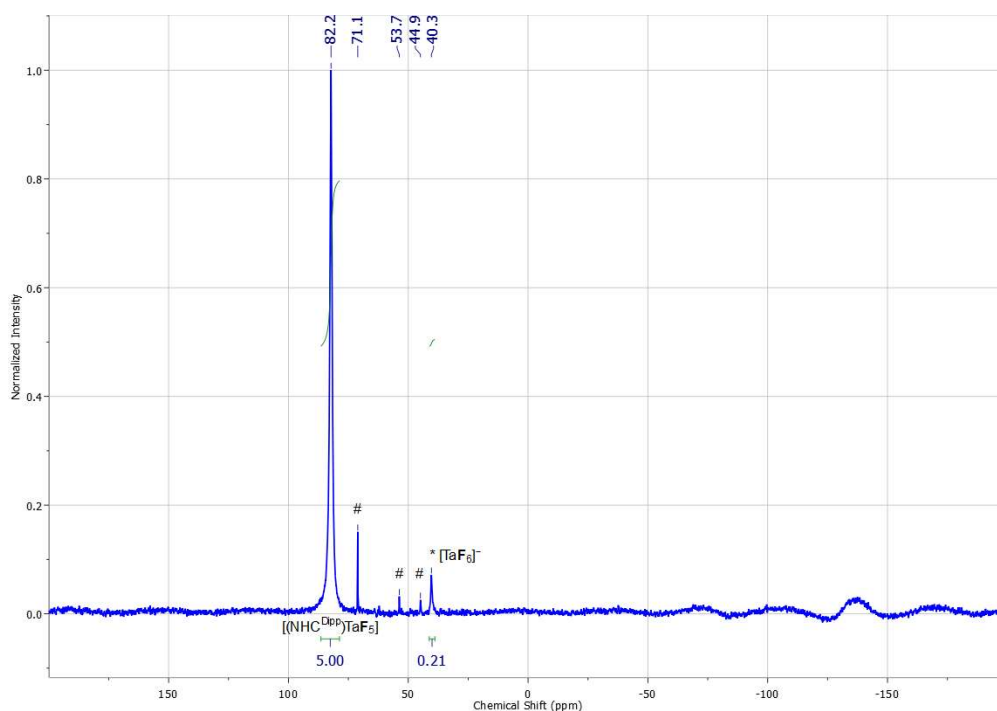


Figure A28: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) in C_6D_6 , showing neutral $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) complex, a small amount of $[\text{TaF}_6]^-$ anion and other unidentified impurities. Figure is based on the reference [323].

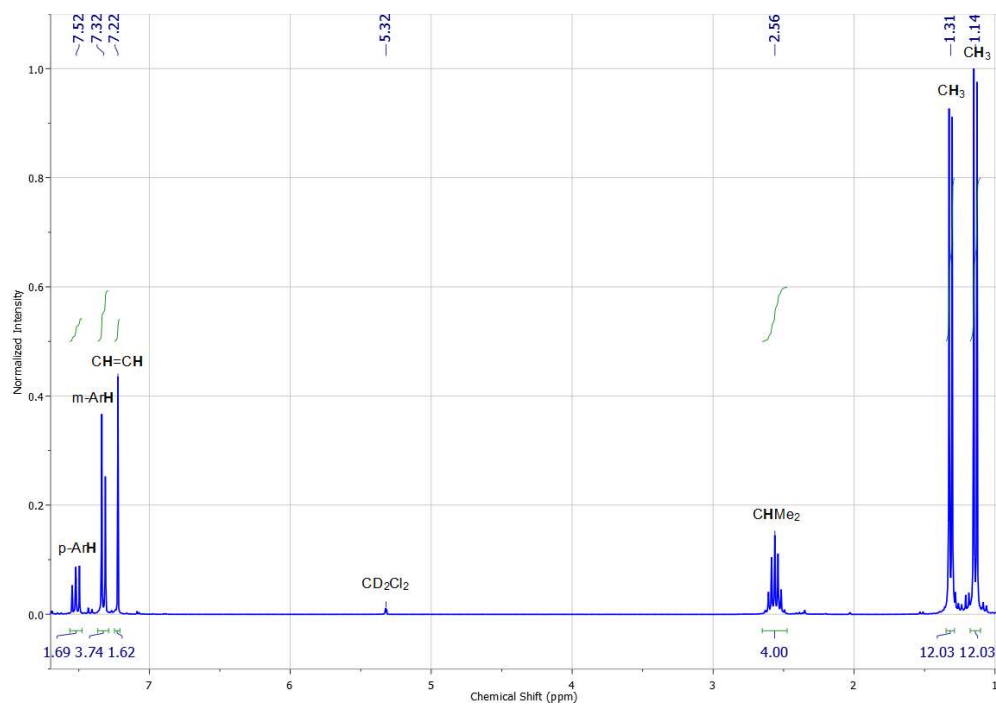


Figure A29: ¹H NMR spectrum of [(NHC^{Dipp})TaF₅] (**2**) in CD₂Cl₂, showing the bonded NHC^{Dipp} ligand. Figure is based on the reference [323].

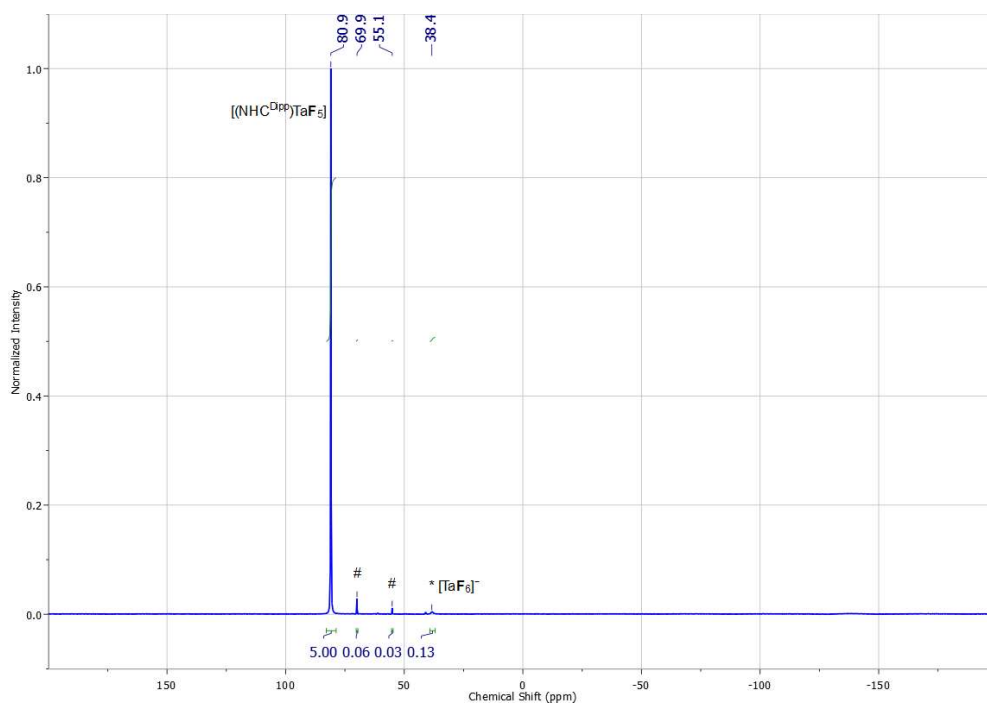


Figure A30: ¹⁹F NMR spectrum of [(NHC^{Dipp})TaF₅] (**2**) in CD₂Cl₂, showing neutral [(NHC^{Dipp})TaF₅] (**2**) complex, a small amount of [TaF₆]⁻ anion and other unidentified impurities. Figure is based on the reference [323].

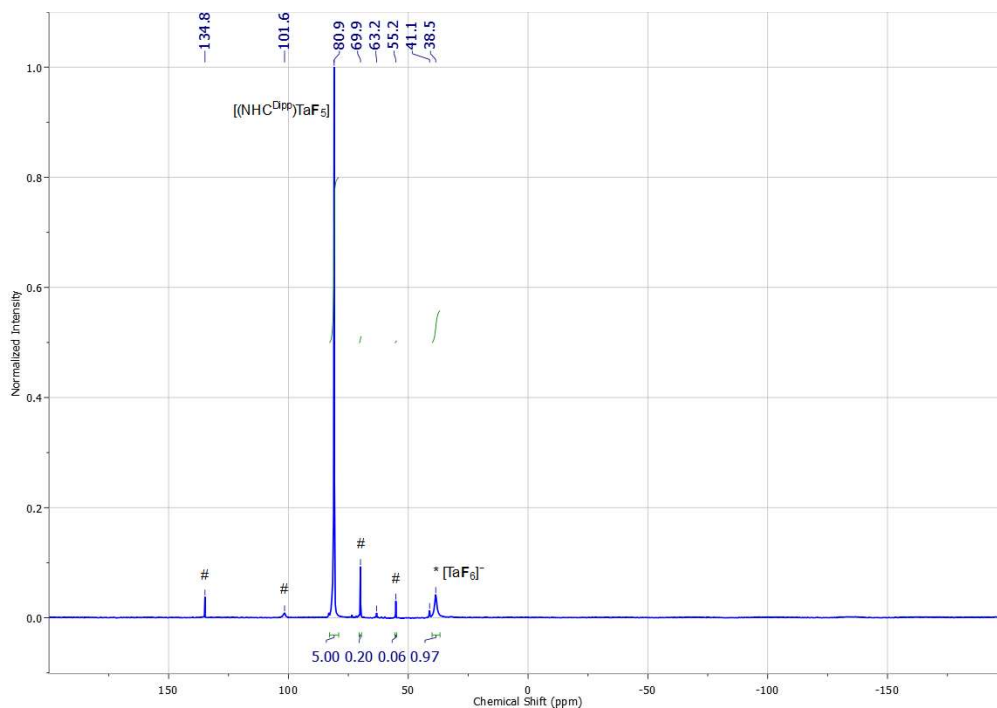


Figure A31: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (2) in CD_2Cl_2 after 5 days, showing neutral $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (2) complex, $[\text{TaF}_6]^-$ anion and other unidentified impurities present due to the decomposition of the neutral $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (2) complex. Figure is based on the reference [323].

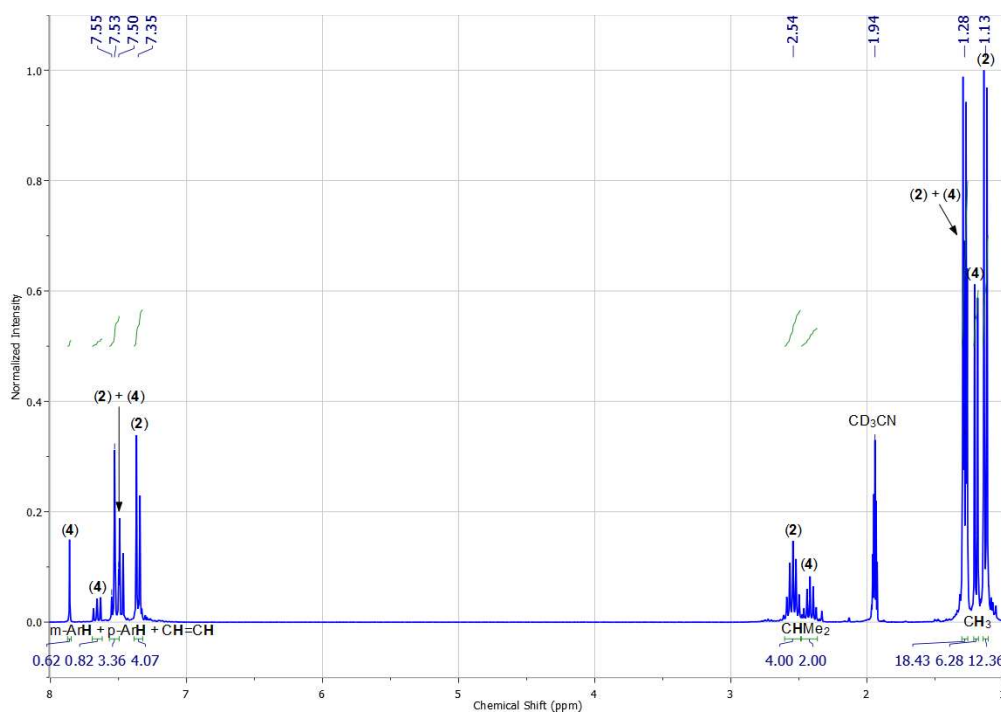


Figure A32: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (2) in CD_3CN , showing a mixture of the bonded NHC^{Dipp} ligand and imidazolium $[(\text{NHC}^{\text{Dipp}})\text{D}]^+$ cation present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (2) complex and deuteration of NHC^{Dipp} with CD_3CN . Figure is based on the reference [323].

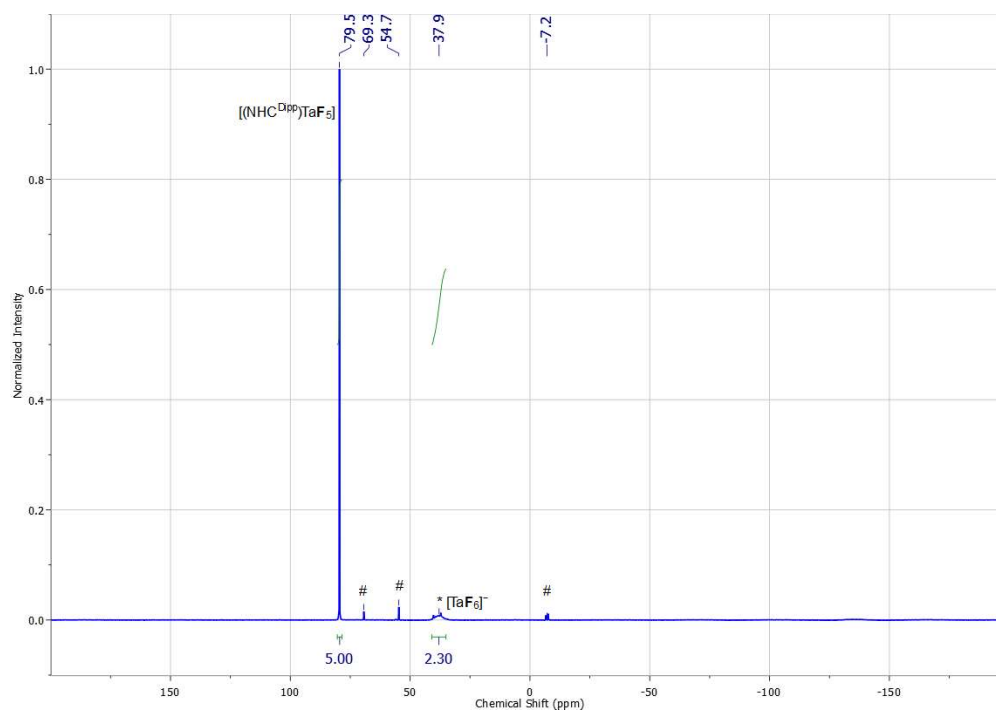


Figure A33: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) in CD_3CN , showing a mixture of neutral $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) complex and $[\text{TaF}_6]^-$ anion present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{TaF}_5]$ (**2**) complex and other unidentified impurities. Figure is based on the reference [323].

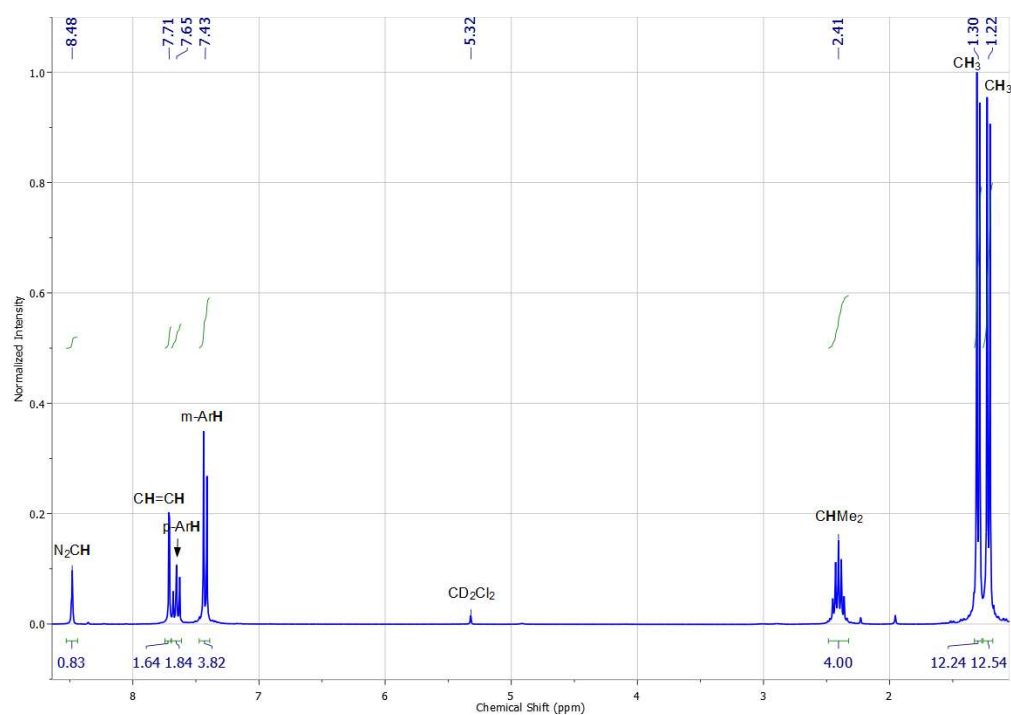


Figure A34: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ (**3**) in CD_2Cl_2 , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Figure is based on the reference [323].

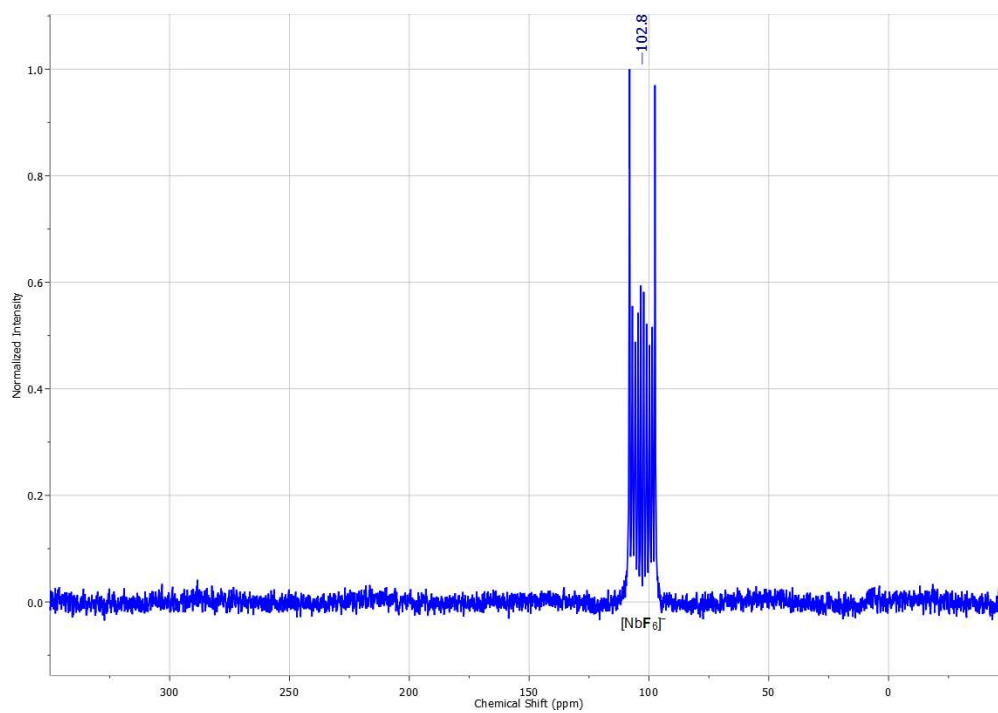


Figure A35: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ (**3**) in CD_2Cl_2 , showing $[\text{NbF}_6]^-$ anion. Figure is based on the reference [323].

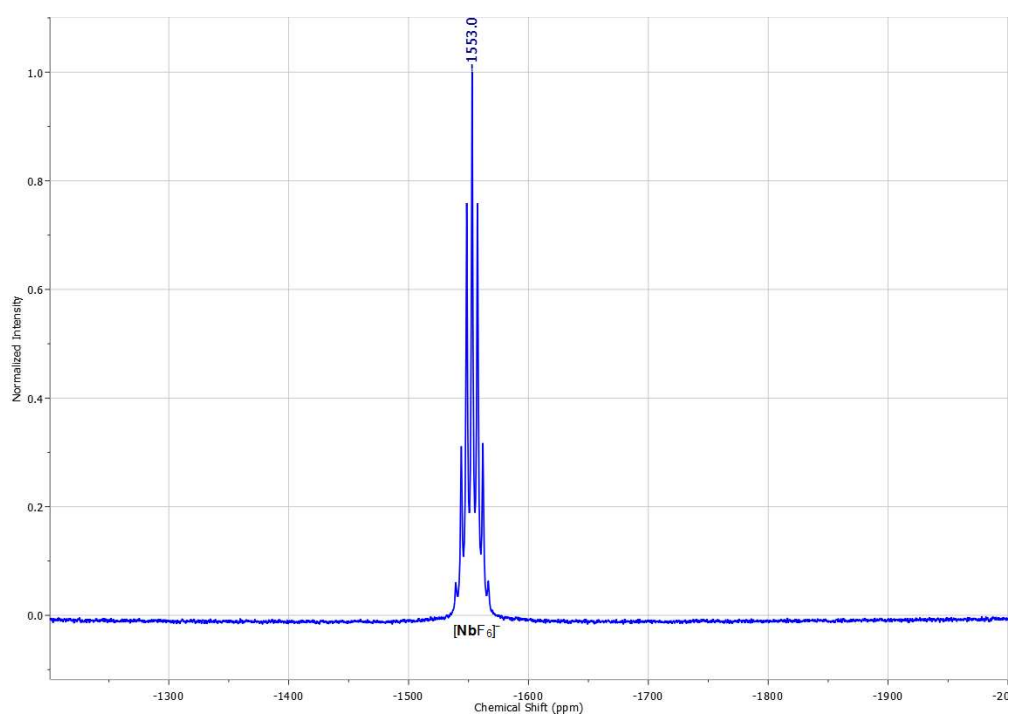


Figure A36: ^{93}Nb NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ (**3**) in CD_2Cl_2 , showing $[\text{NbF}_6]^-$ anion. Figure is based on the reference [323].

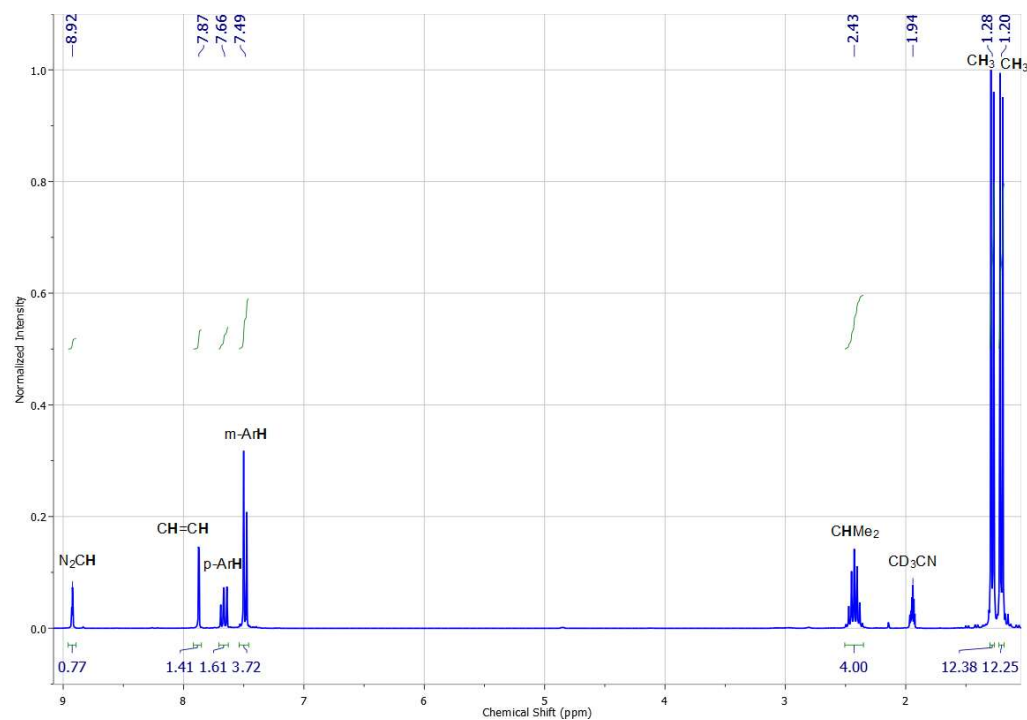


Figure A37: ¹H NMR spectrum of [(NHC^{Dipp})H][NbF₆] (**3**) in CD₃CN, showing imidazolium [(NHC^{Dipp})H]⁺ cation. Figure is based on the reference [323].

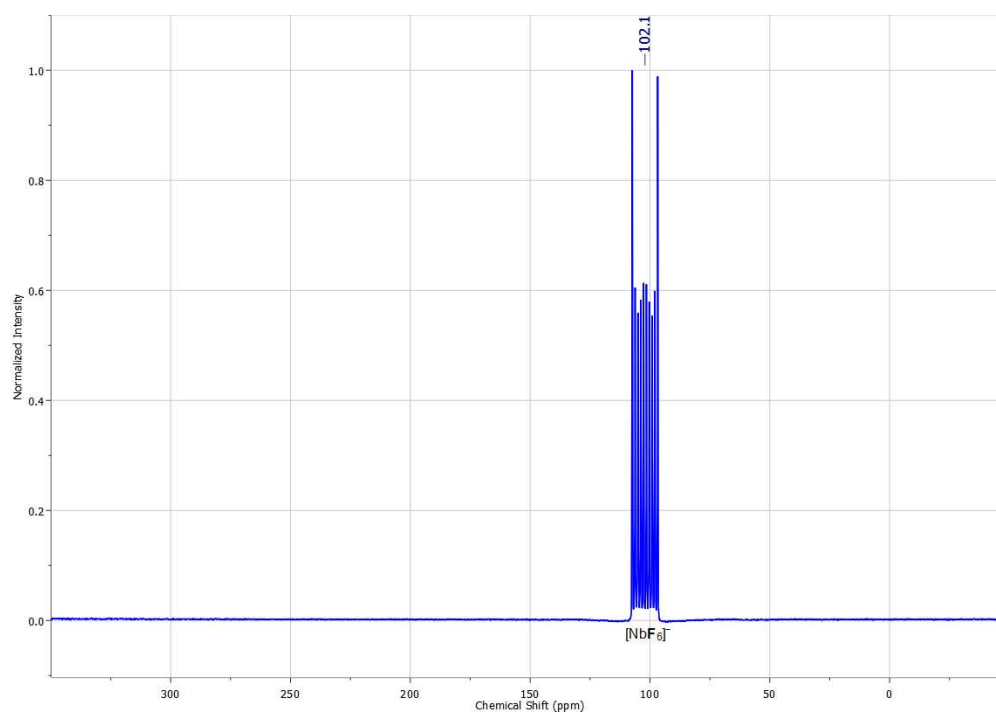


Figure A38: ¹⁹F NMR spectrum of [(NHC^{Dipp})H][NbF₆] (**3**) in CD₃CN, showing [NbF₆]⁻ anion. Figure is based on the reference [323].

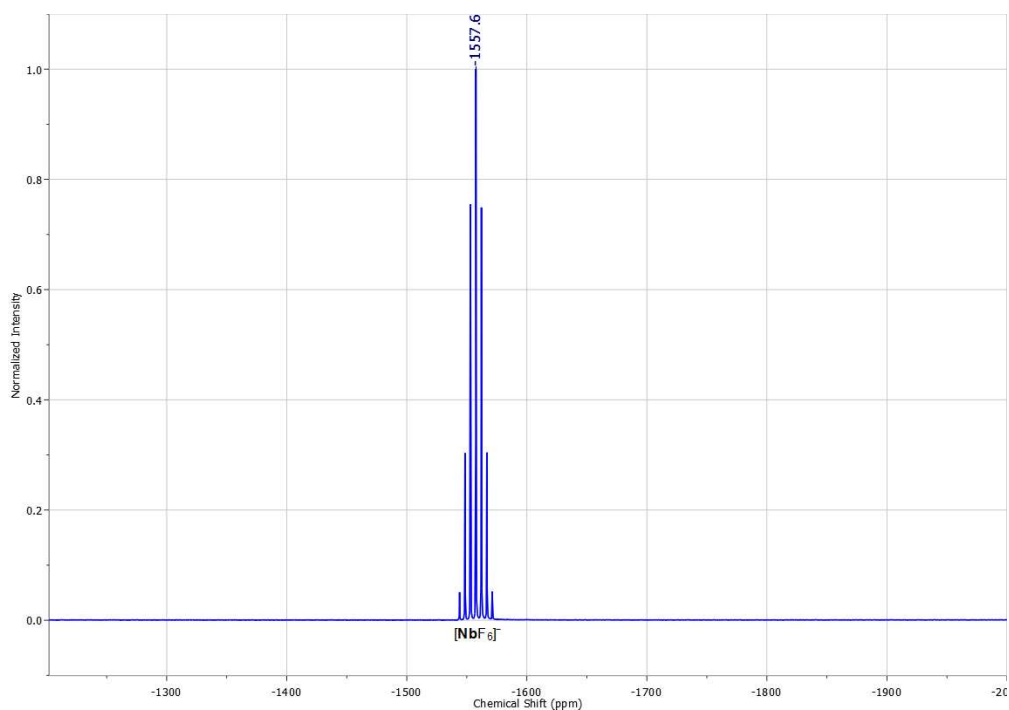


Figure A39: ^{93}Nb NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{NbF}_6]$ (**3**) in CD_3CN , showing $[\text{NbF}_6]^-$ anion. Figure is based on the reference [323].

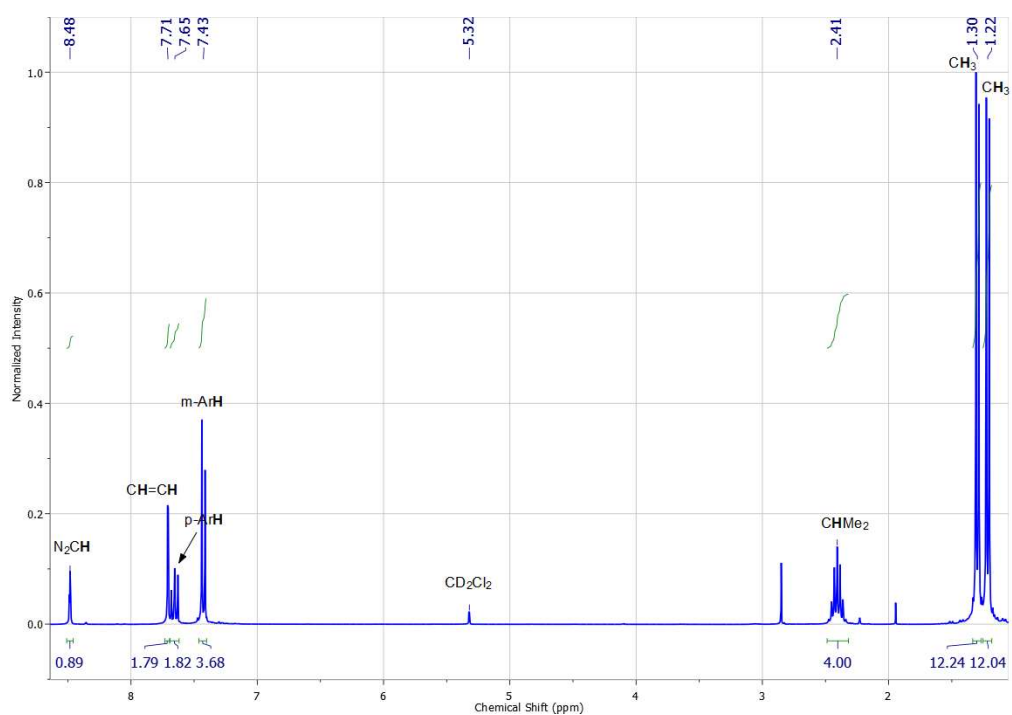


Figure A40: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ (**4**) in CD_2Cl_2 , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Figure is based on the reference [323].

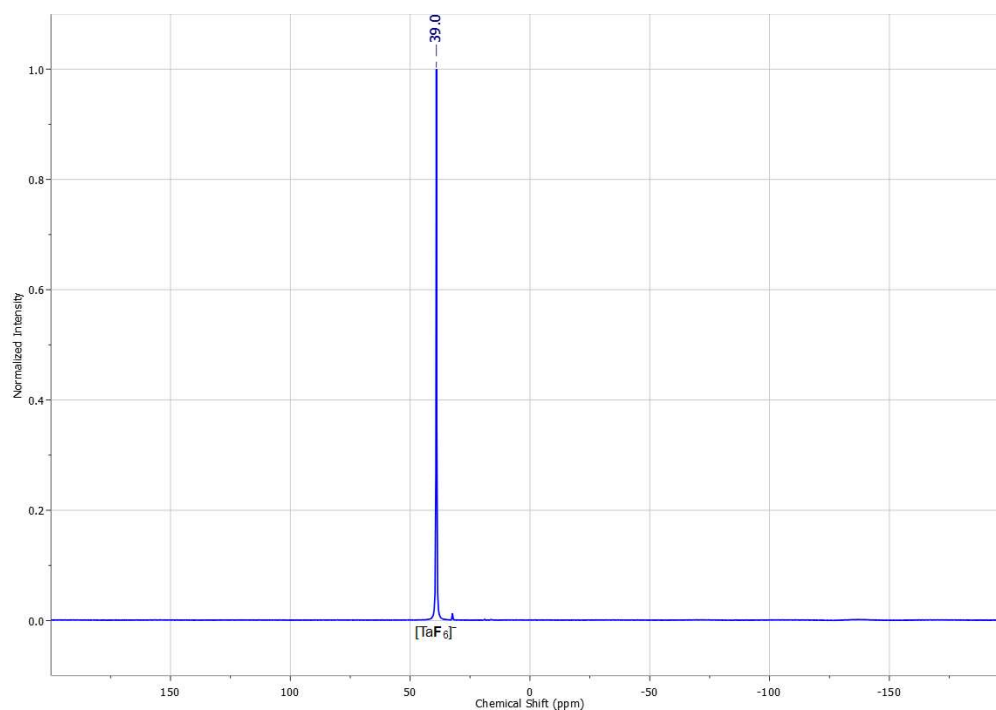


Figure A41: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ (**4**) in CD_2Cl_2 , showing $[\text{TaF}_6]^-$ anion. Figure is based on the reference [323].

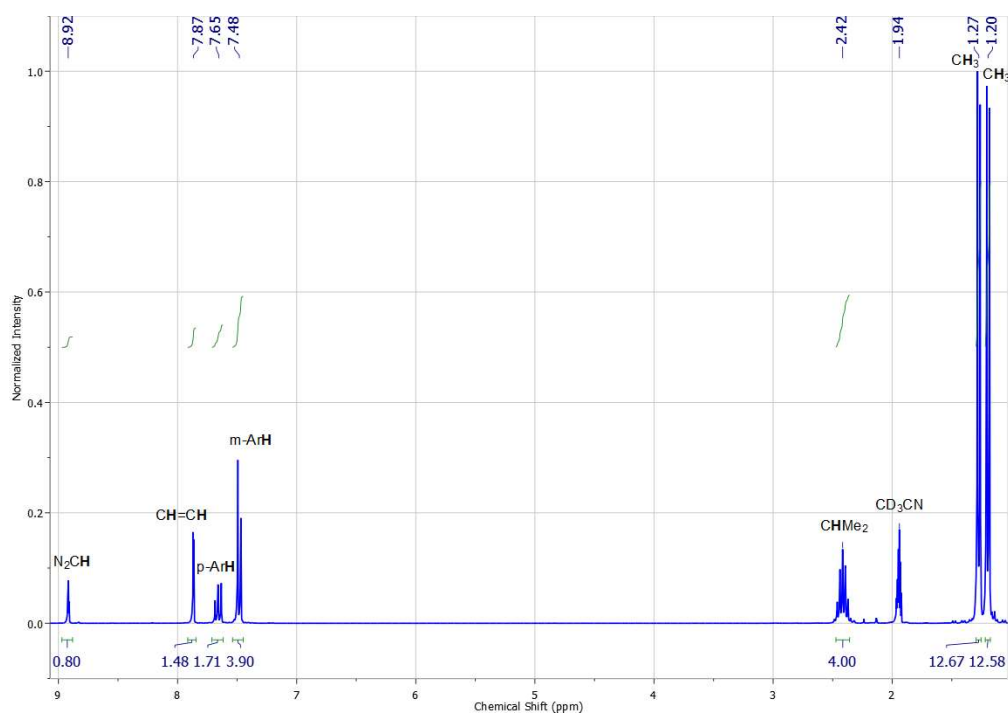


Figure A42: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ (**4**) in CD_3CN , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Figure is based on the reference [323].

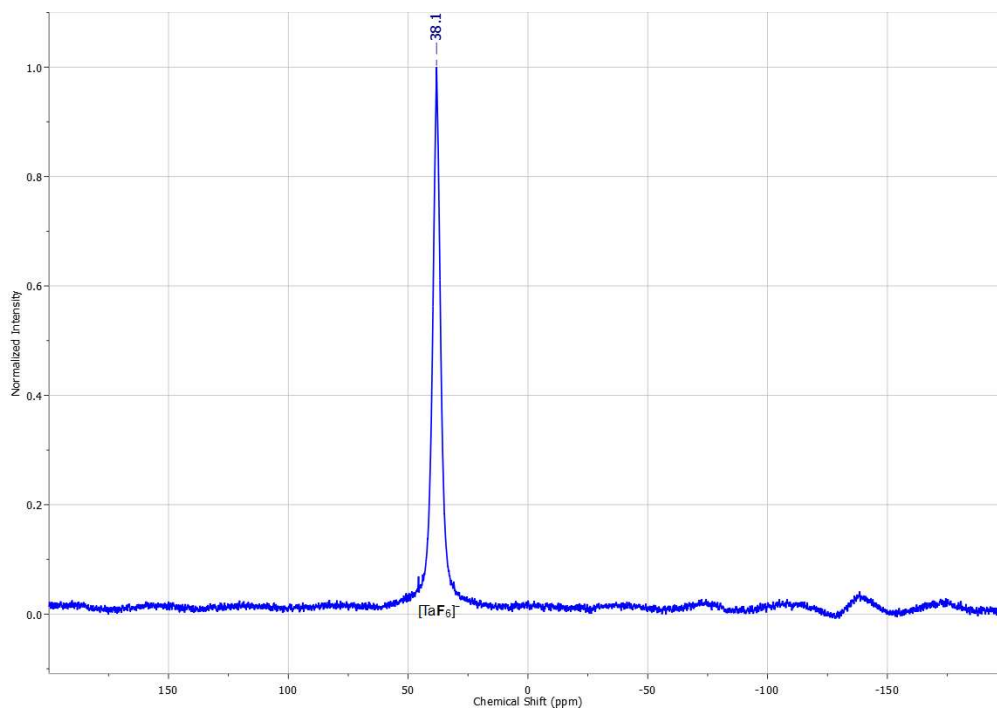


Figure A43: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{TaF}_6]$ (**4**) in CD_3CN , showing $[\text{TaF}_6]^-$ anion. Figure is based on the reference [323].

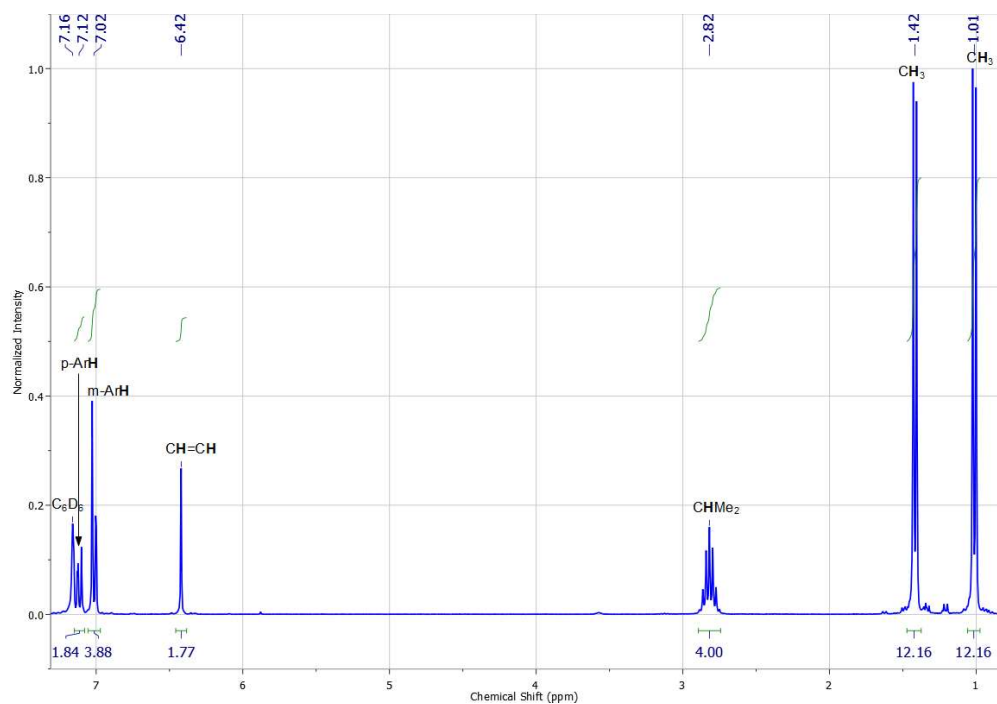


Figure A44: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in C_6D_6 , showing the bonded NHC^{Dipp} ligand. Figure is based on the reference [324].

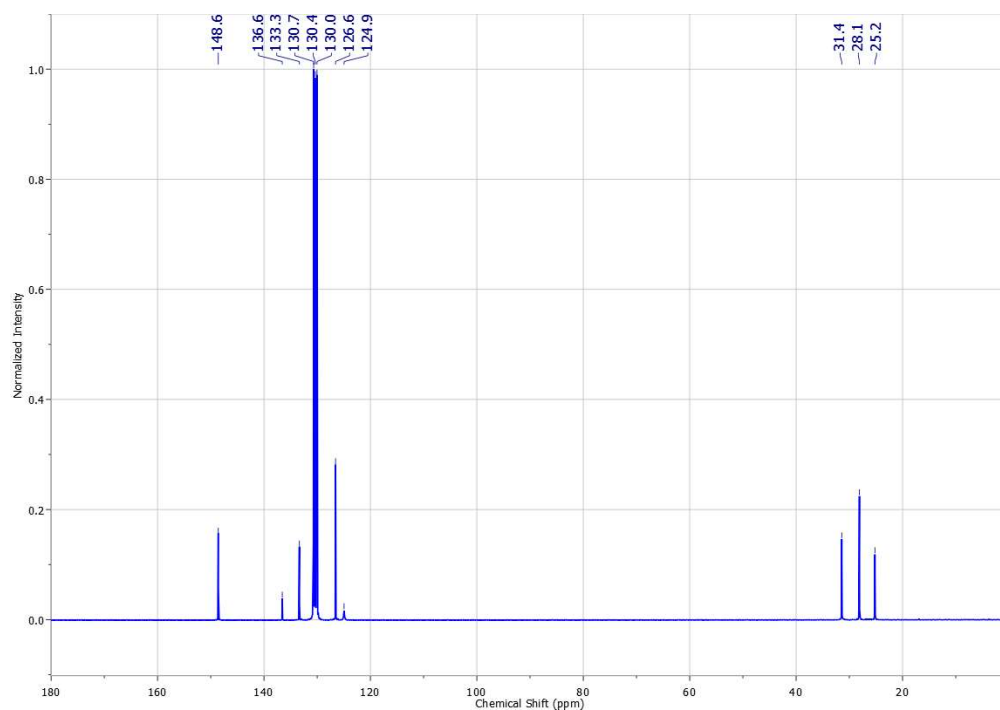


Figure A45: ^{13}C NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in C_6D_6 , showing the bonded NHC^{Dipp} ligand. Figure is based on the reference [324].

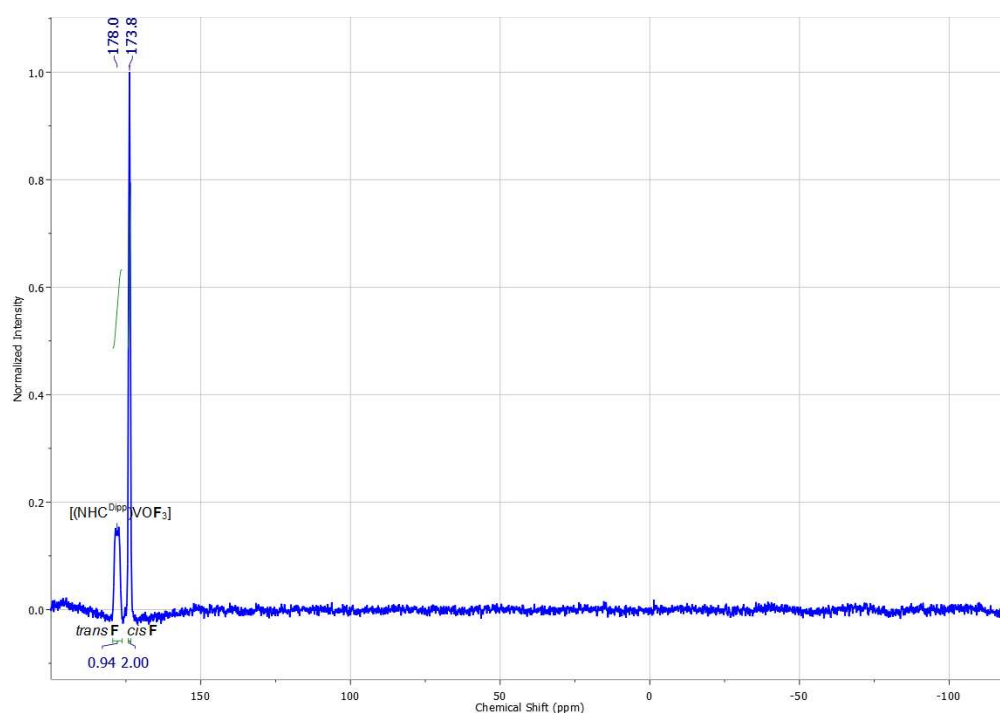


Figure A46: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in C_6D_6 , showing neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

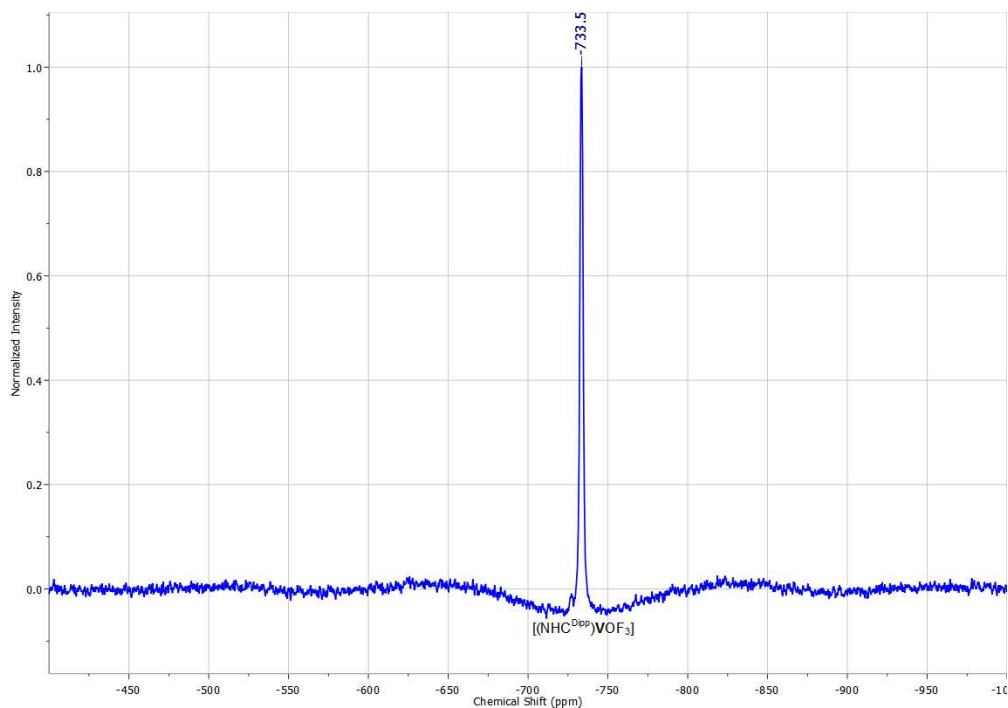


Figure A47: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in C_6D_6 , showing neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

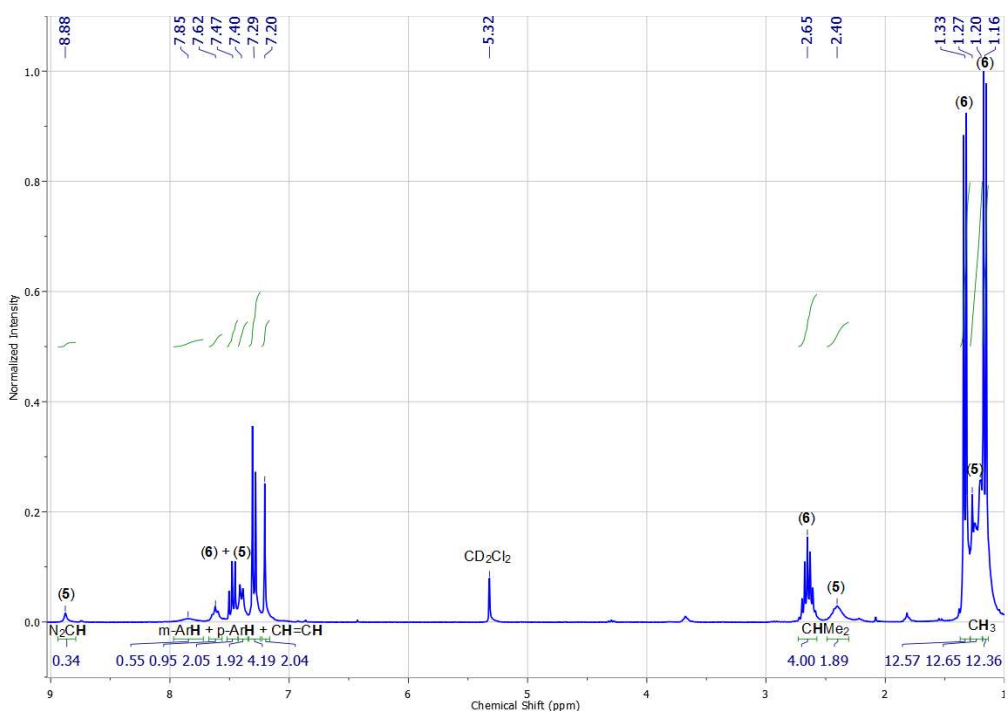


Figure A48: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in CD_2Cl_2 , showing a mixture of the bonded NHC^{Dipp} ligand and imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

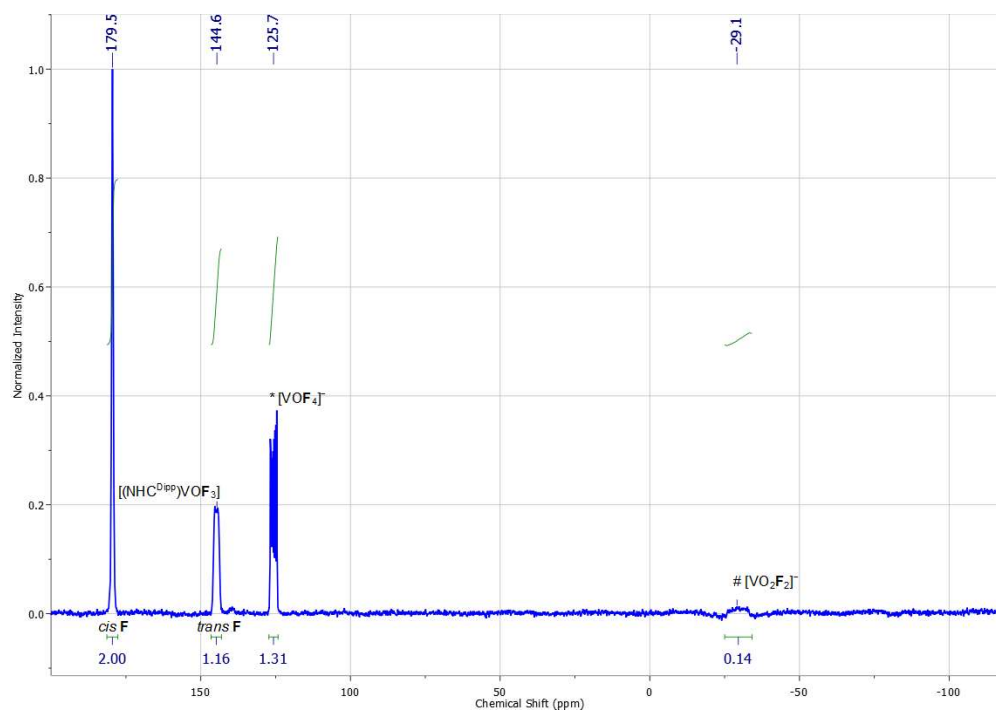


Figure A49: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in CD_2Cl_2 , showing a mixture of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex, $[\text{VOF}_4]^-$ and $[\text{VO}_2\text{F}_2]^-$ anions present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

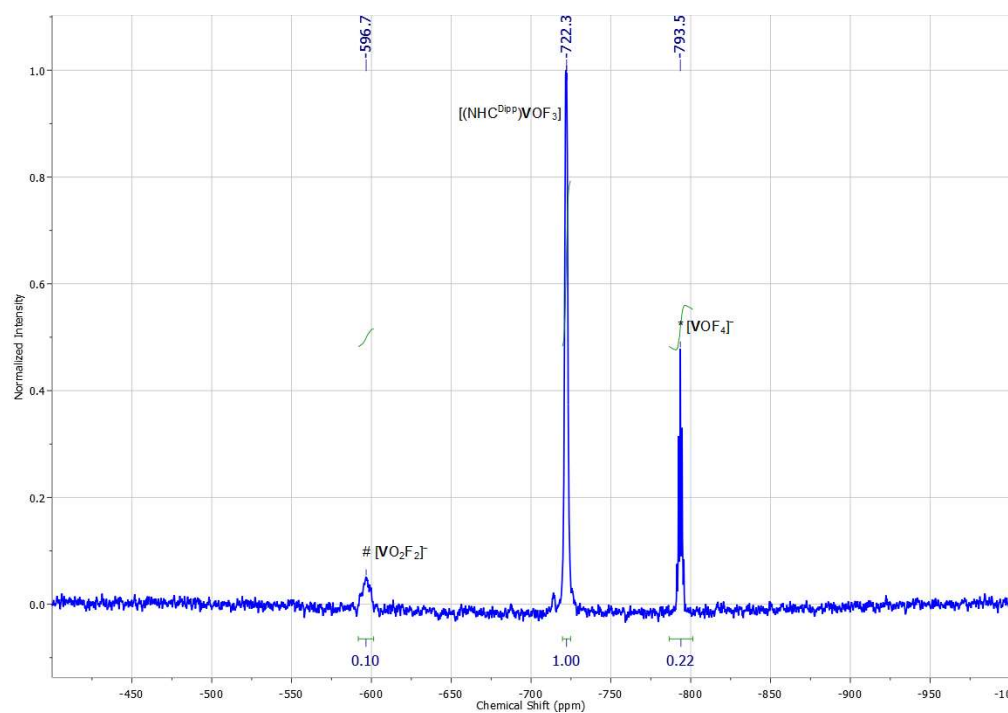


Figure A50: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in CD_2Cl_2 , showing a mixture of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex, $[\text{VOF}_4]^-$ and $[\text{VO}_2\text{F}_2]^-$ anions present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

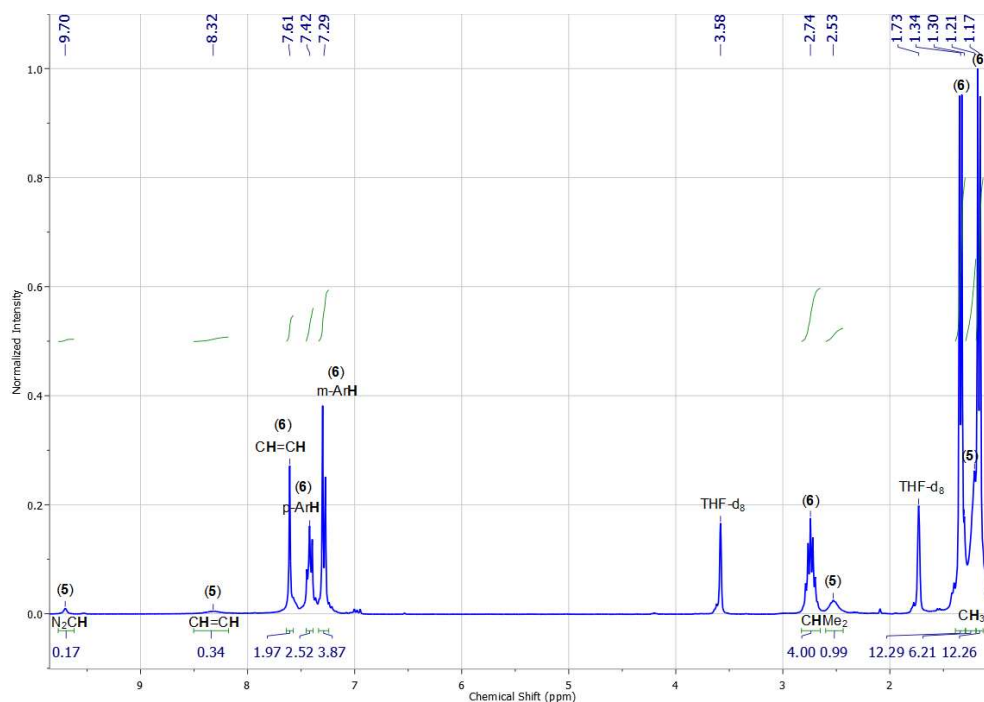


Figure A51: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) in THF-d_8 , showing a mixture of the bonded NHC^{Dipp} ligand and imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) complex. Figure is based on the reference [324].

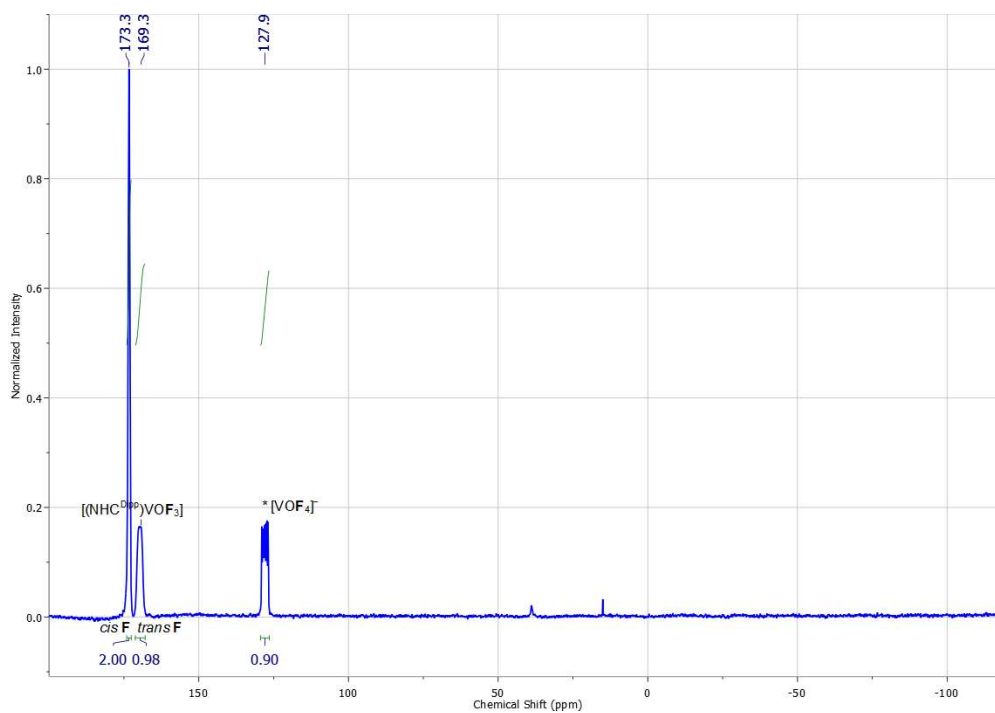


Figure A52: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) in THF-d_8 , showing a mixture of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) complex and $[\text{VOF}_4]^-$ anion present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (5) complex. Figure is based on the reference [324].

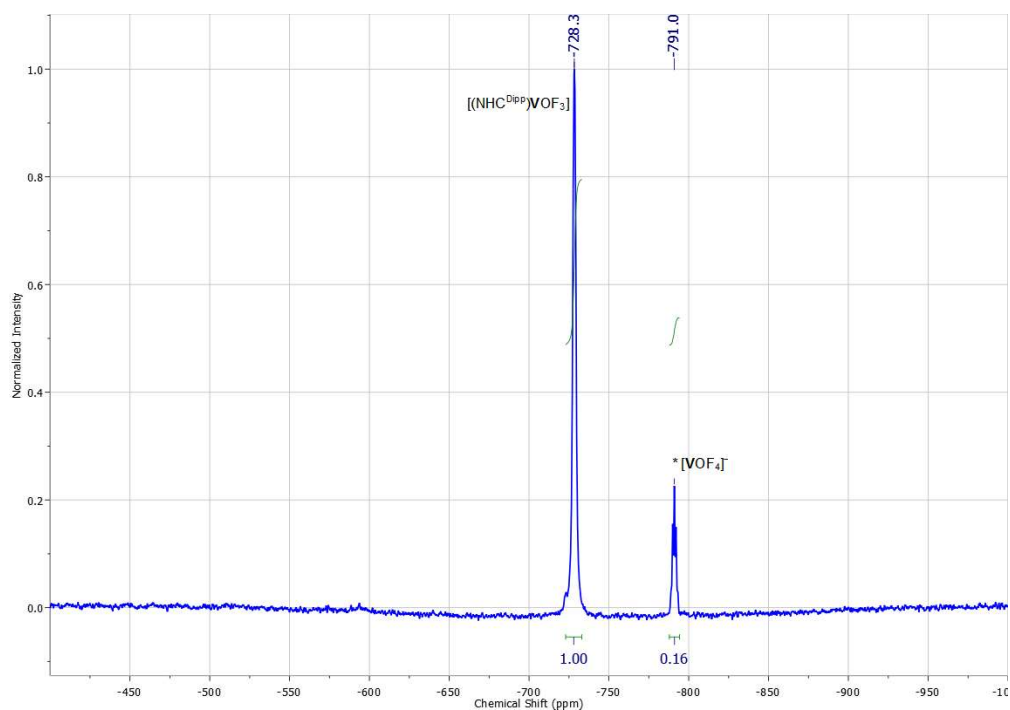


Figure A53: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in THF-d_8 , showing a mixture of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex and $[\text{VOF}_4]^-$ anion present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

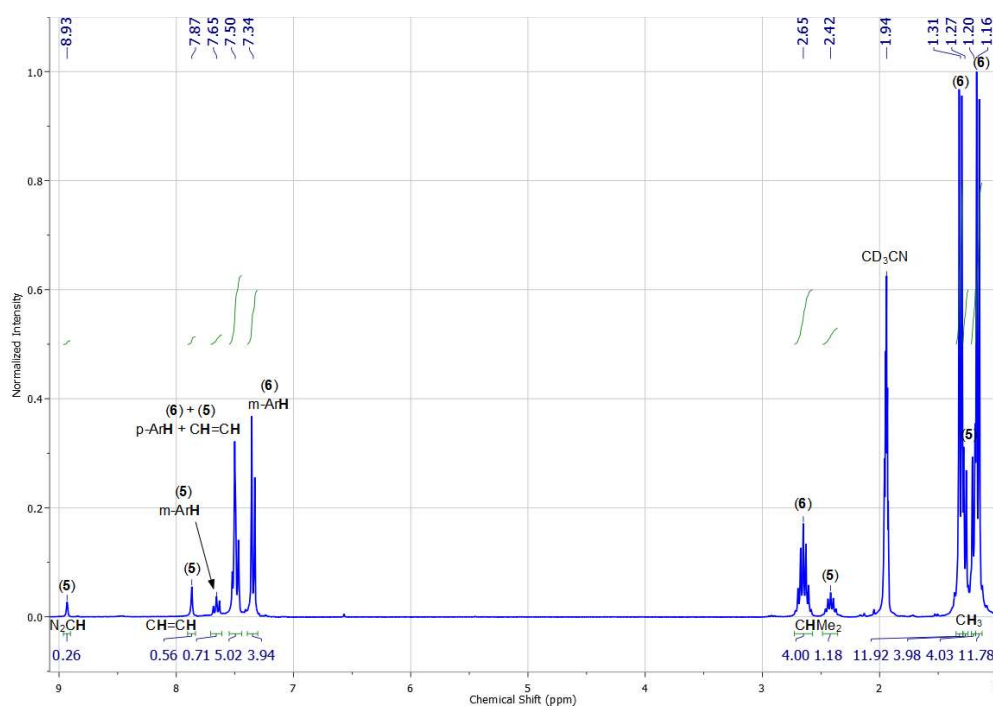


Figure A54: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in CD_3CN , showing a mixture of the bonded NHC^{Dipp} ligand and imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

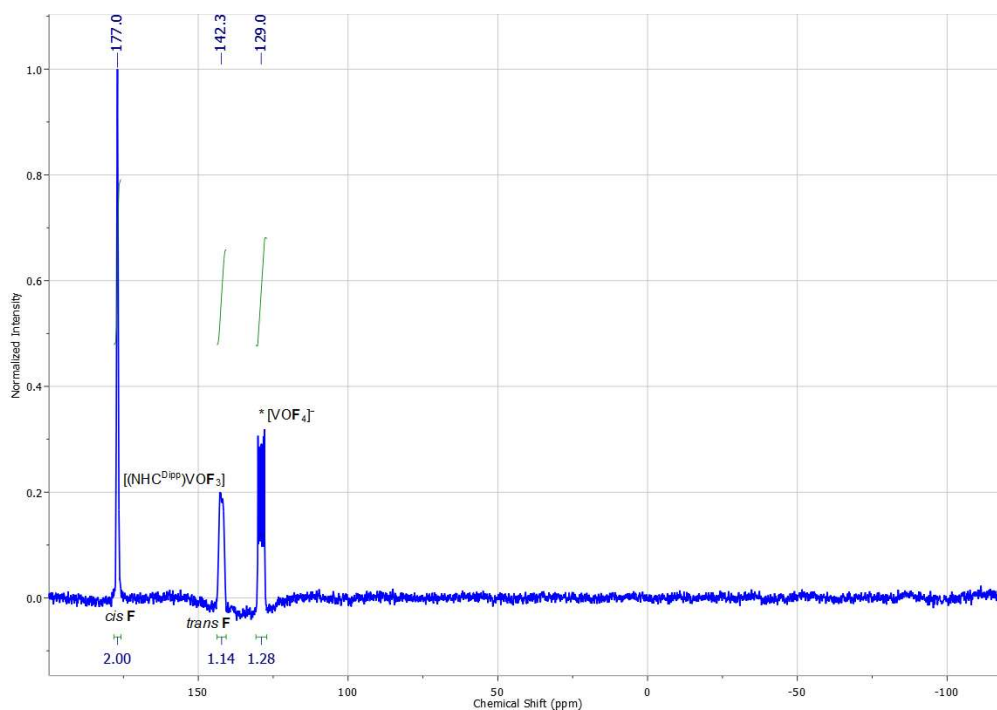


Figure A55: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in CD_3CN , showing a mixture of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex and $[\text{VOF}_4]^-$ anion present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

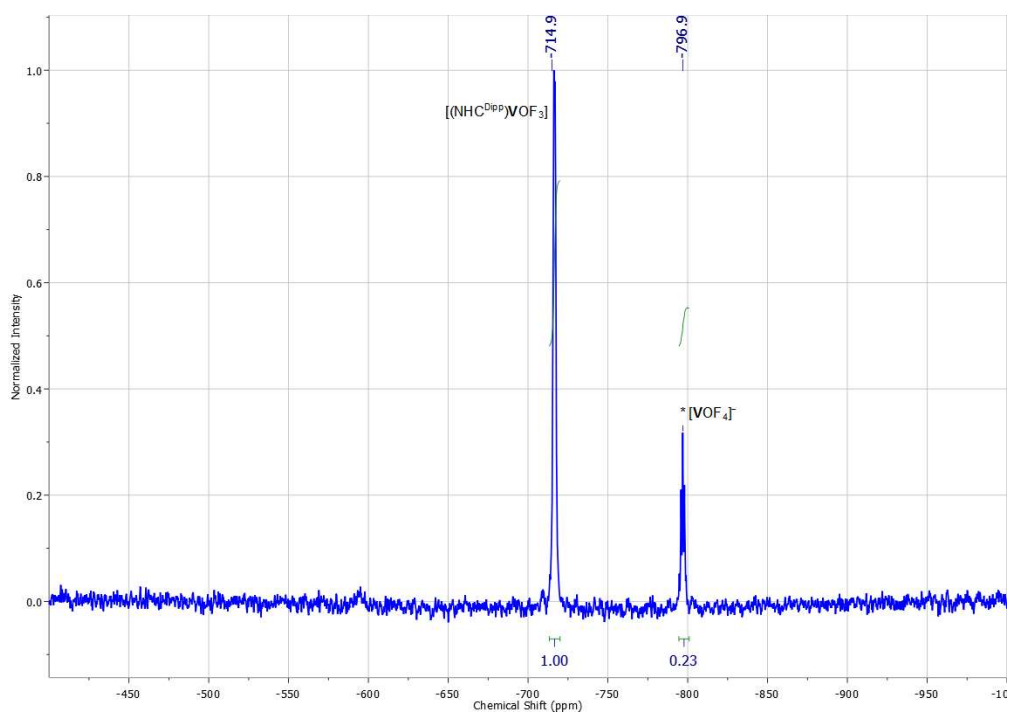


Figure A56: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) in CD_3CN , showing a mixture of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex and $[\text{VOF}_4]^-$ anion present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

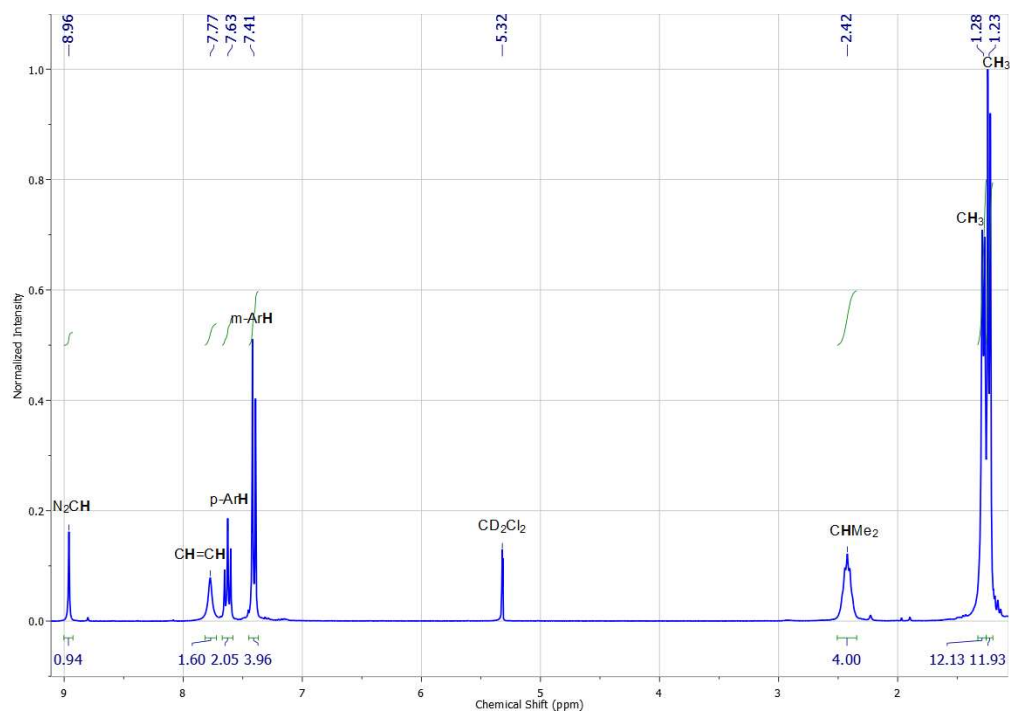


Figure A57: ¹H NMR spectrum of [(NHC^{Dipp})H][VOF₄] (**6**) in CD₂Cl₂, showing imidazolium [(NHC^{Dipp})H]⁺ cation. Figure is based on the reference [324].

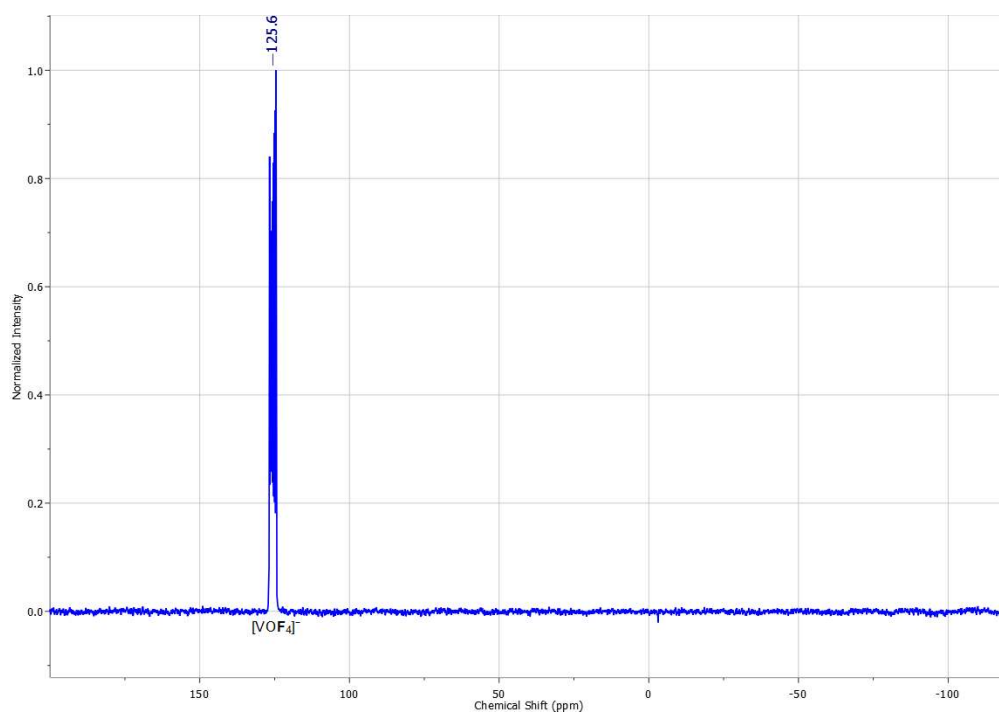


Figure A58: ¹⁹F NMR spectrum of [(NHC^{Dipp})H][VOF₄] (**6**) in CD₂Cl₂, showing [VOF₄]⁻ anion. Figure is based on the reference [324].

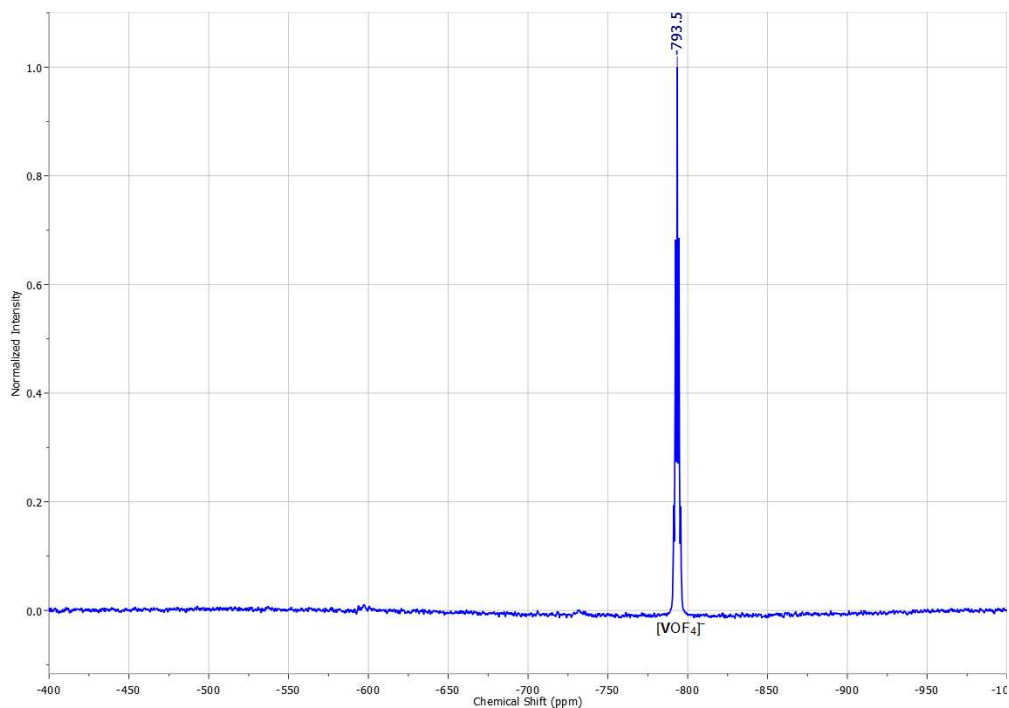


Figure A59: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) in CD_2Cl_2 , showing $[\text{VOF}_4]^-$ anion. Figure is based on the reference [324].

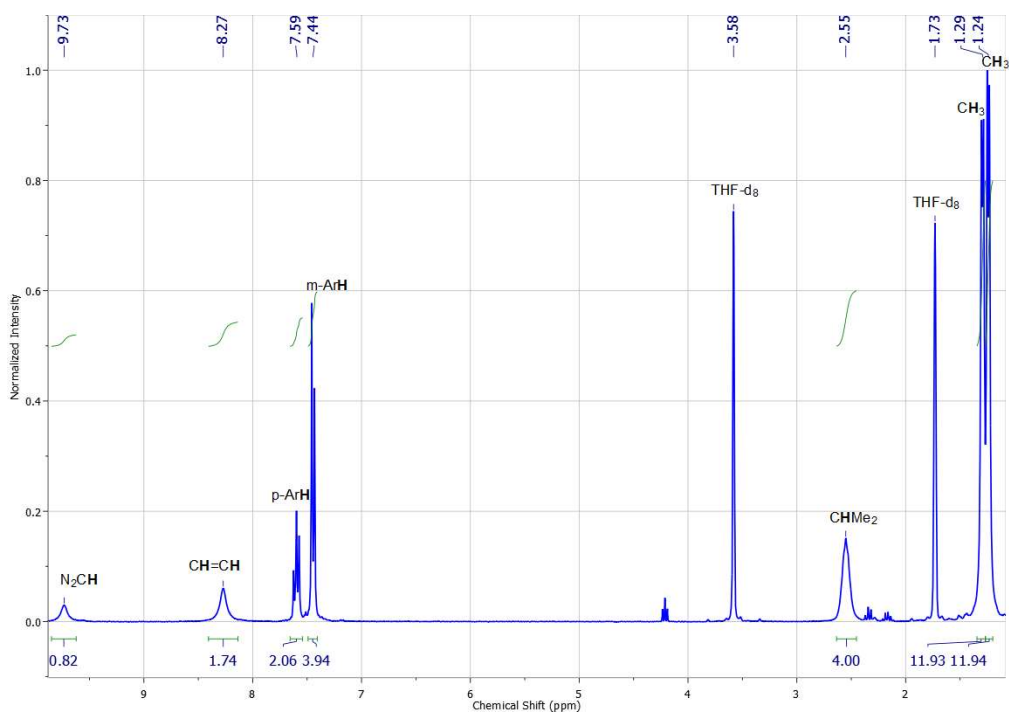


Figure A60: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) in THF-d_8 , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Figure is based on the reference [324].

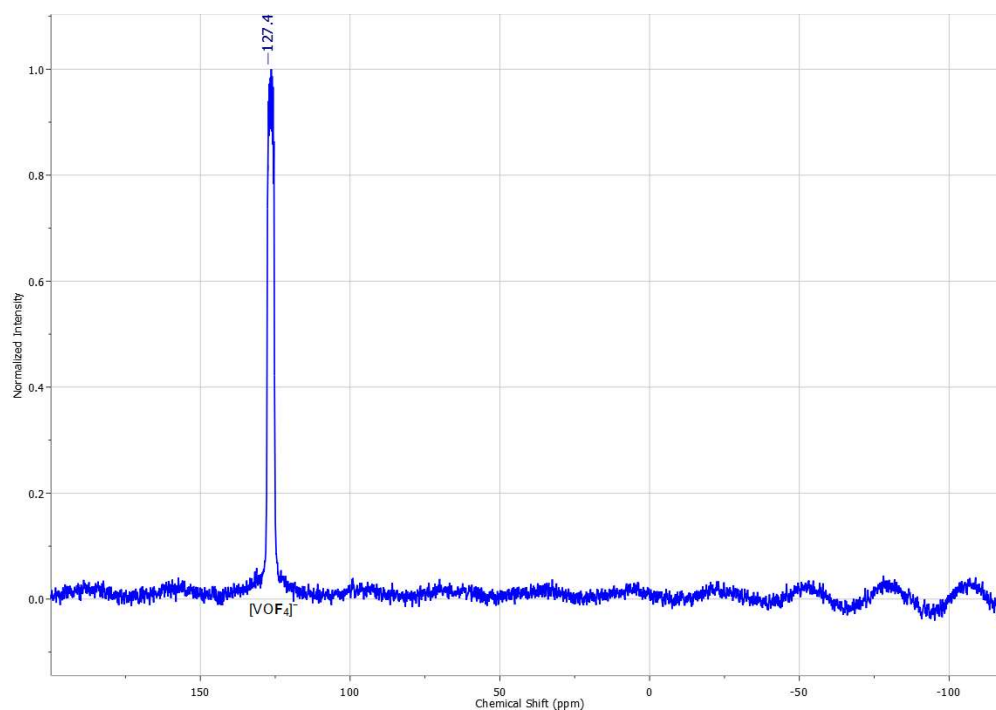


Figure A61: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) in THF-d_8 , showing $[\text{VOF}_4]^-$ anion. Figure is based on the reference [324].

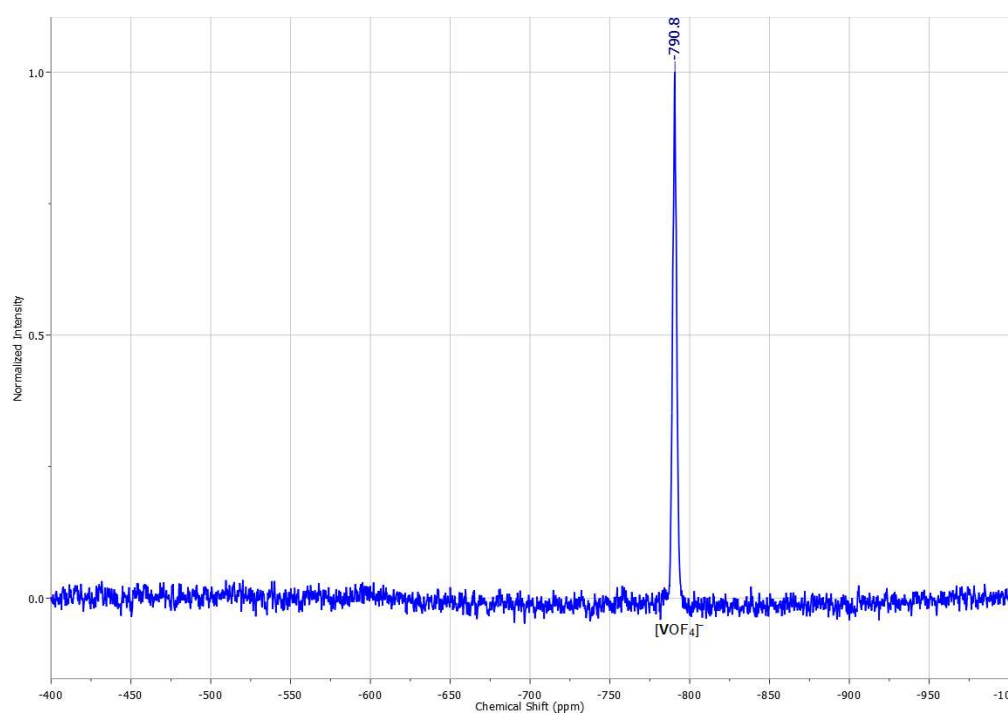


Figure A62: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) in THF-d_8 , showing $[\text{VOF}_4]^-$ anion. Figure is based on the reference [324].

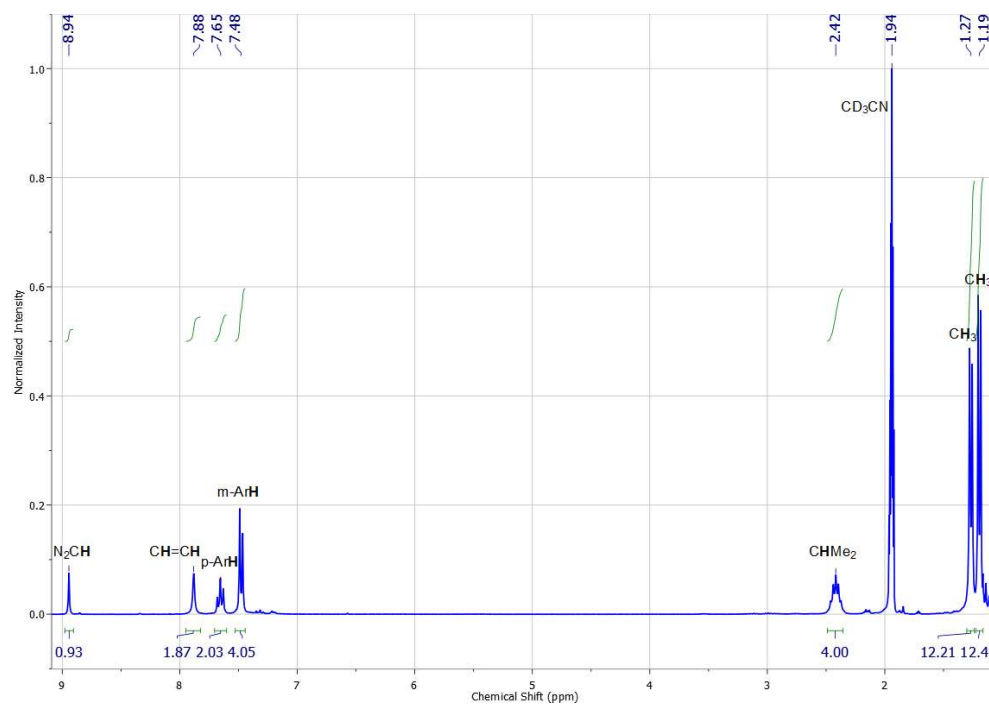


Figure A63: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) in CD_3CN , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Figure is based on the reference [324].

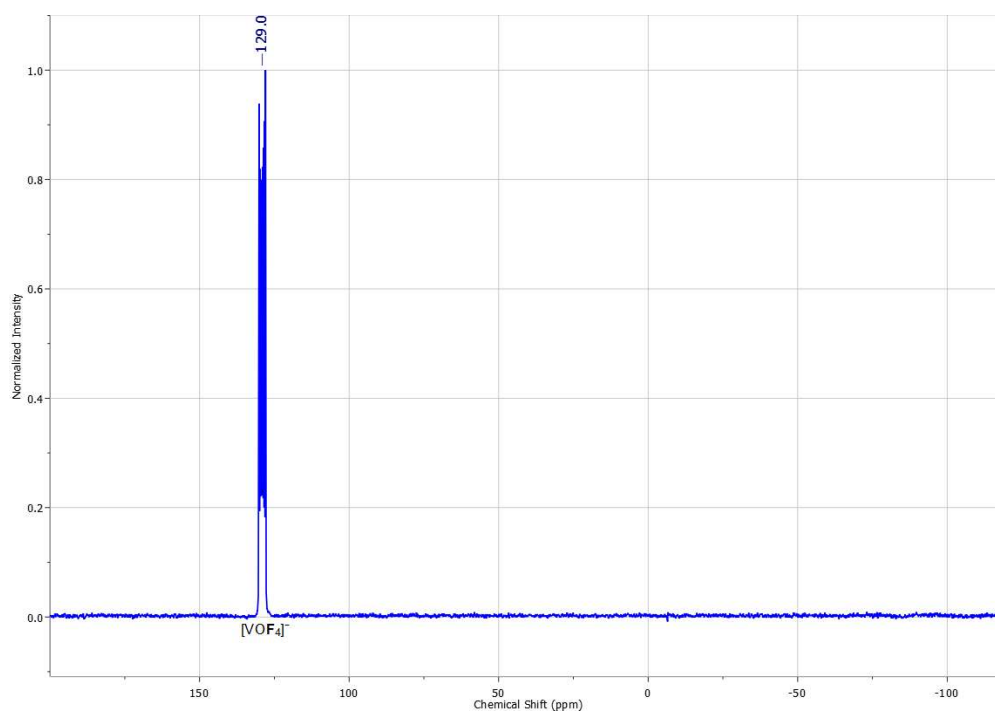


Figure A64: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) in CD_3CN , showing $[\text{VOF}_4]^-$ anion. Figure is based on the reference [324].

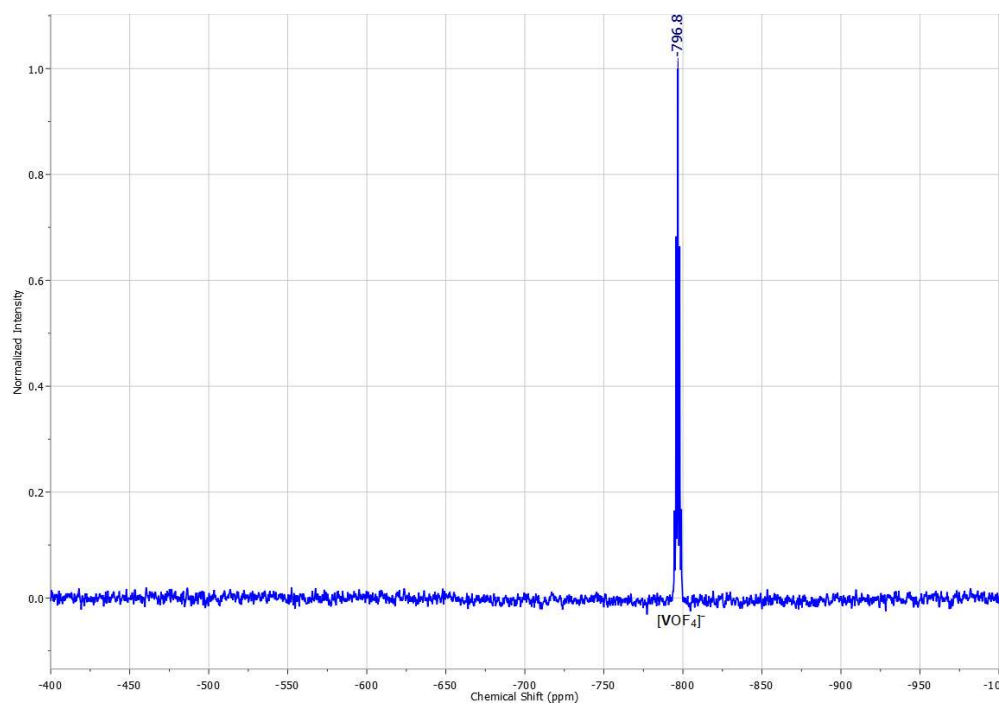


Figure A65: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) in CD_3CN , showing $[\text{VOF}_4]^-$ anion. Figure is based on the reference [324].

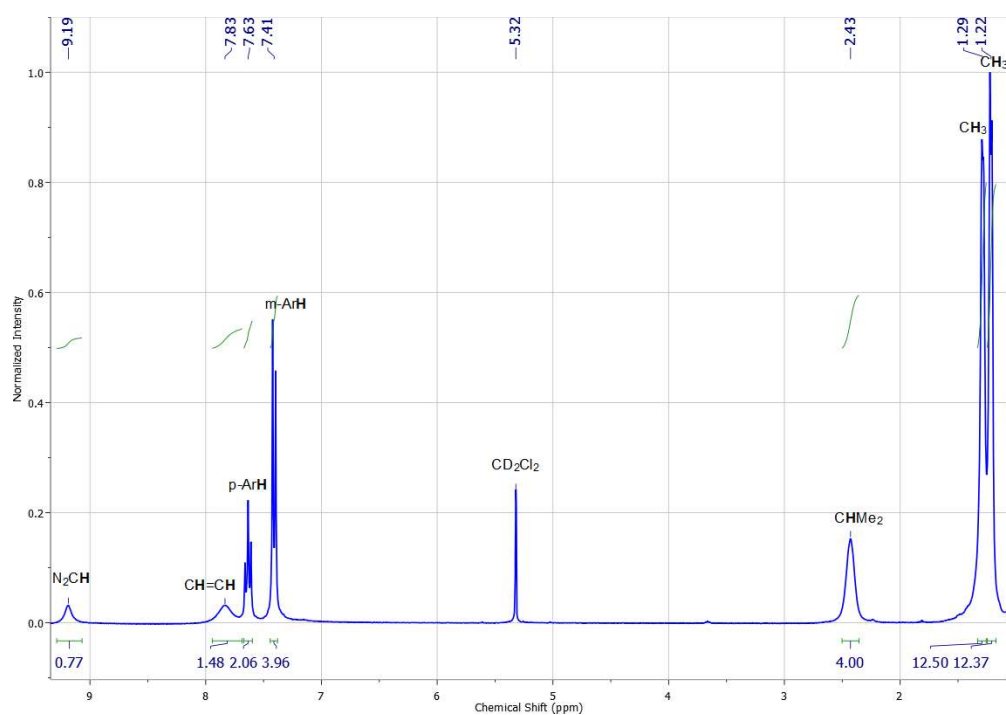


Figure A66: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) in CD_2Cl_2 , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Figure is based on the reference [324].

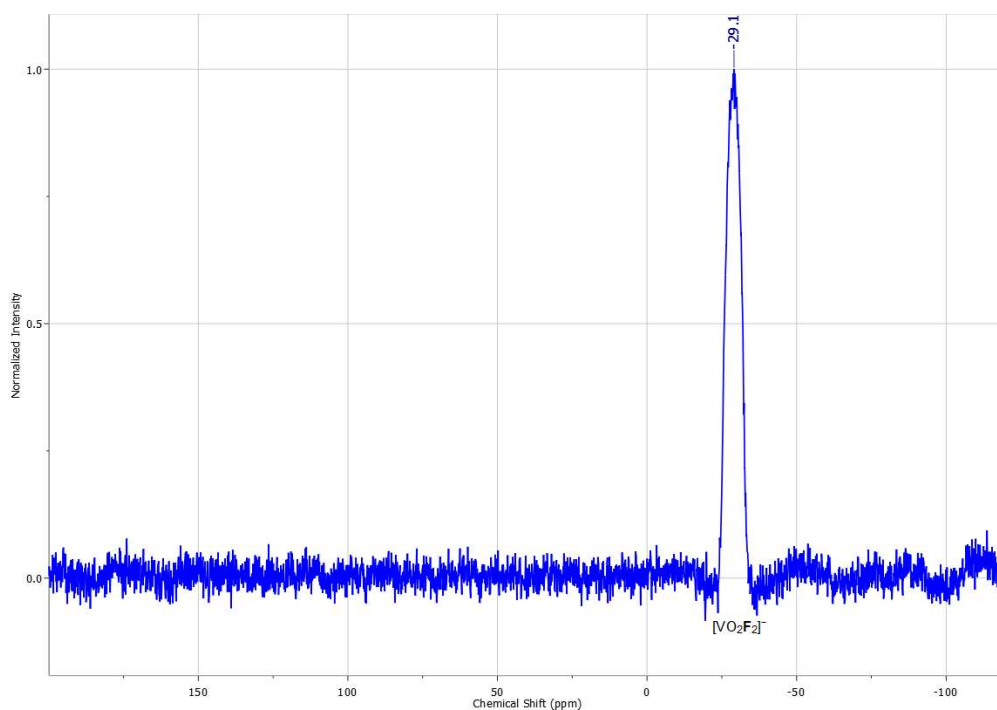


Figure A67: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) in CD_2Cl_2 , showing $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

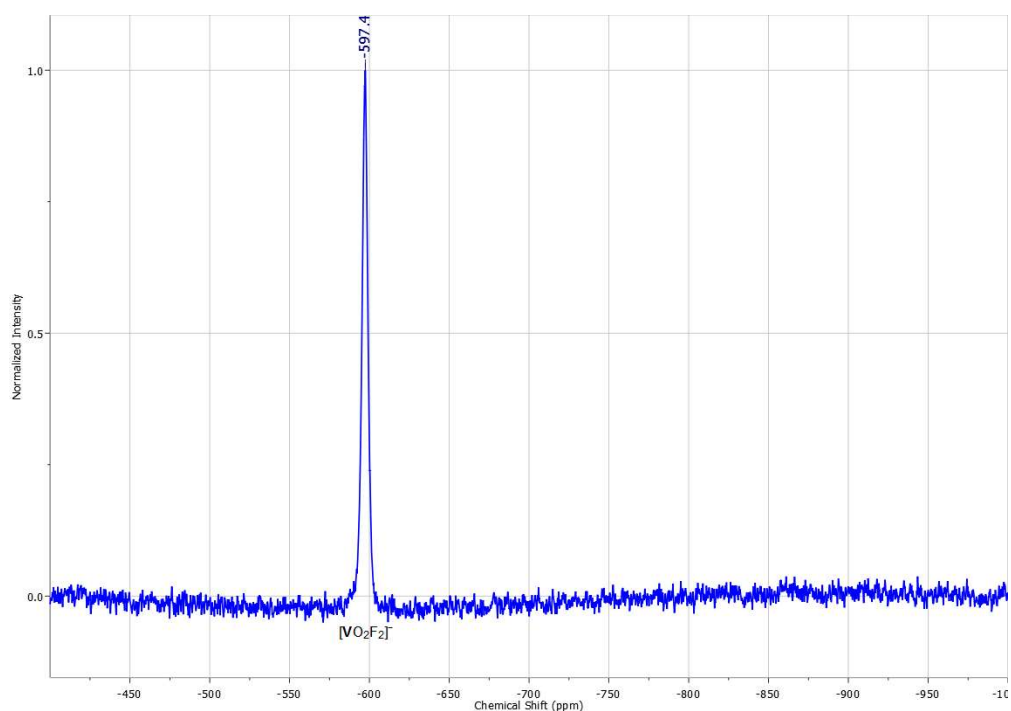


Figure A68: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) in CD_2Cl_2 , showing $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

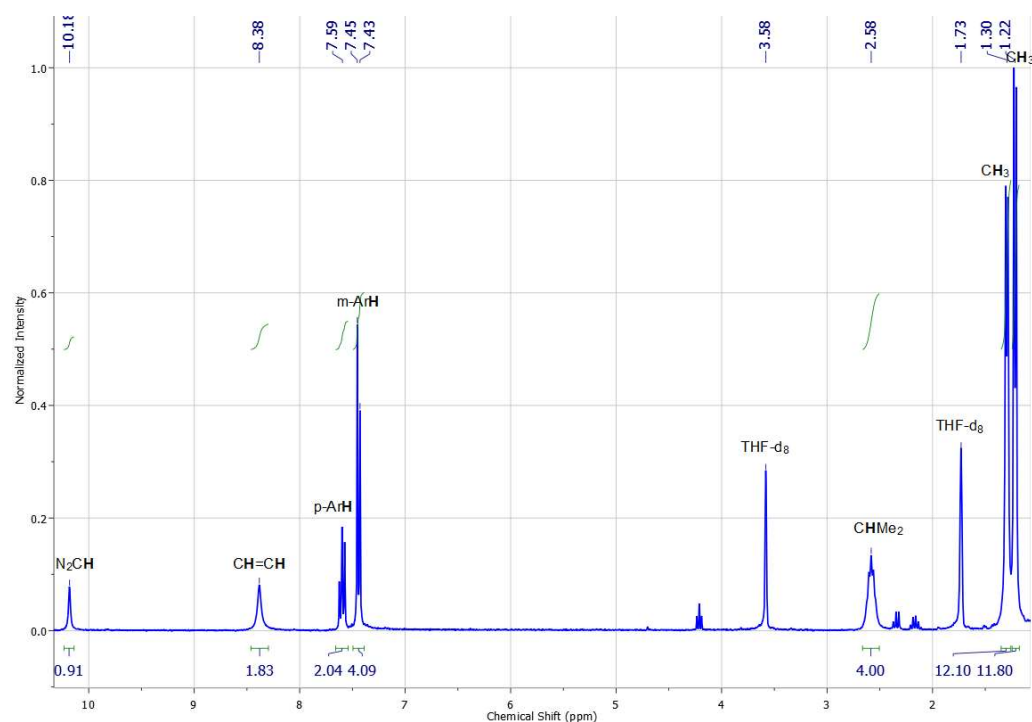


Figure A69: ¹H NMR spectrum of [(NHC^{Dipp})H][VO₂F₂] (**7**) in THF-d₈, showing imidazolium [(NHC^{Dipp})H]⁺ cation. Figure is based on the reference [324].

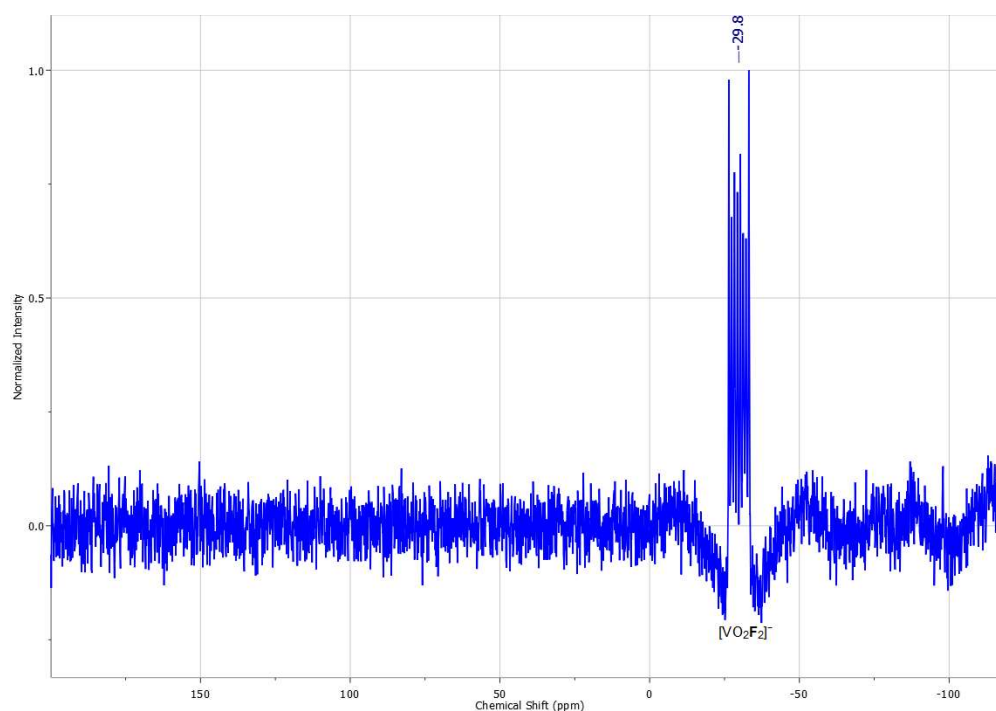


Figure A70: ¹⁹F NMR spectrum of [(NHC^{Dipp})H][VO₂F₂] (**7**) in THF-d₈, showing [VO₂F₂]⁻ anion. Figure is based on the reference [324].

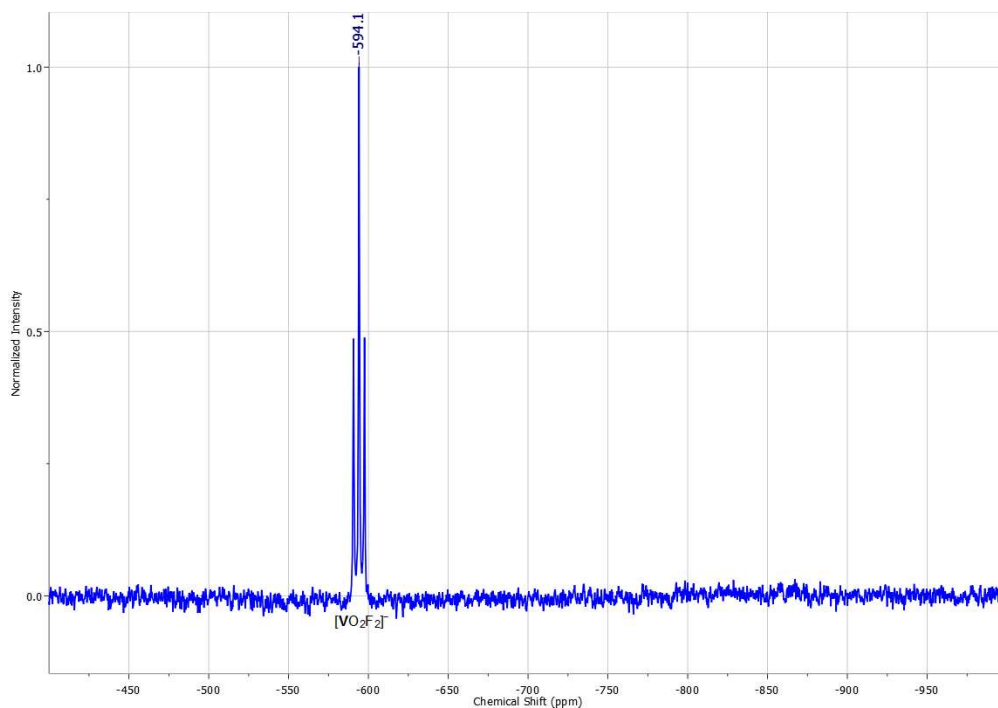


Figure A71: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) in THF-d_8 , showing $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

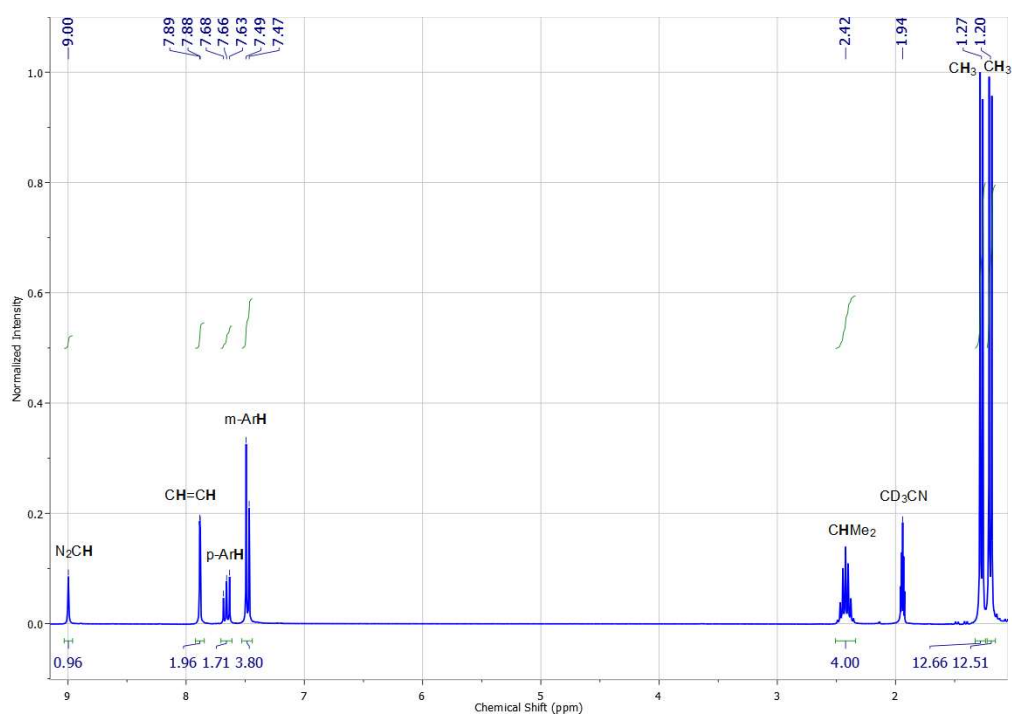


Figure A72: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) in CD_3CN , showing imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation. Figure is based on the reference [324].

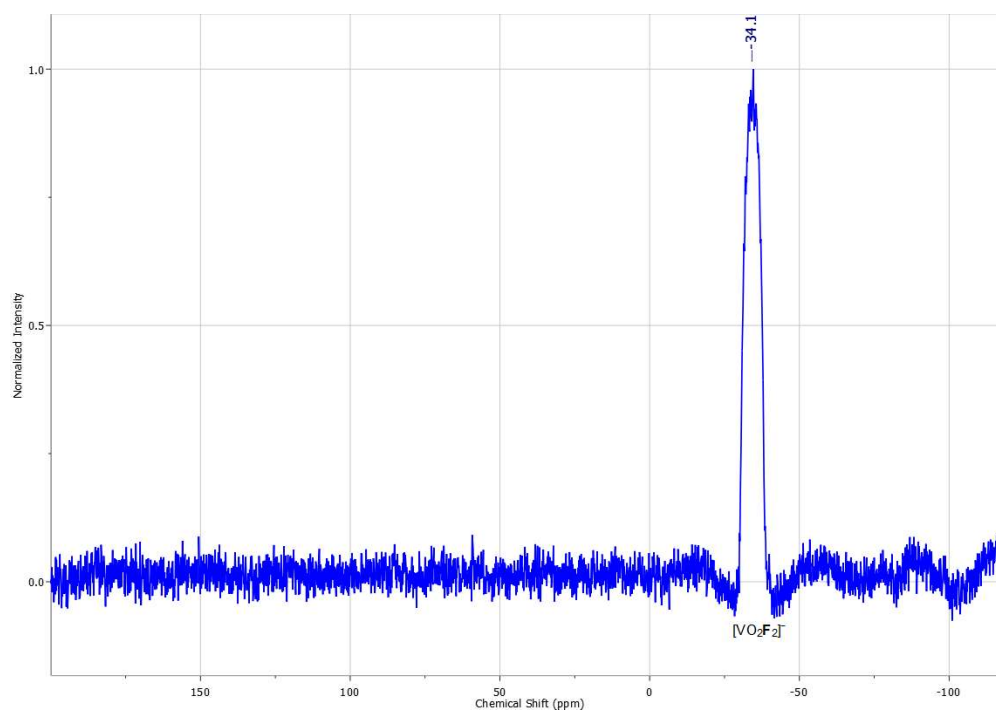


Figure A73: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) in CD_3CN , showing $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

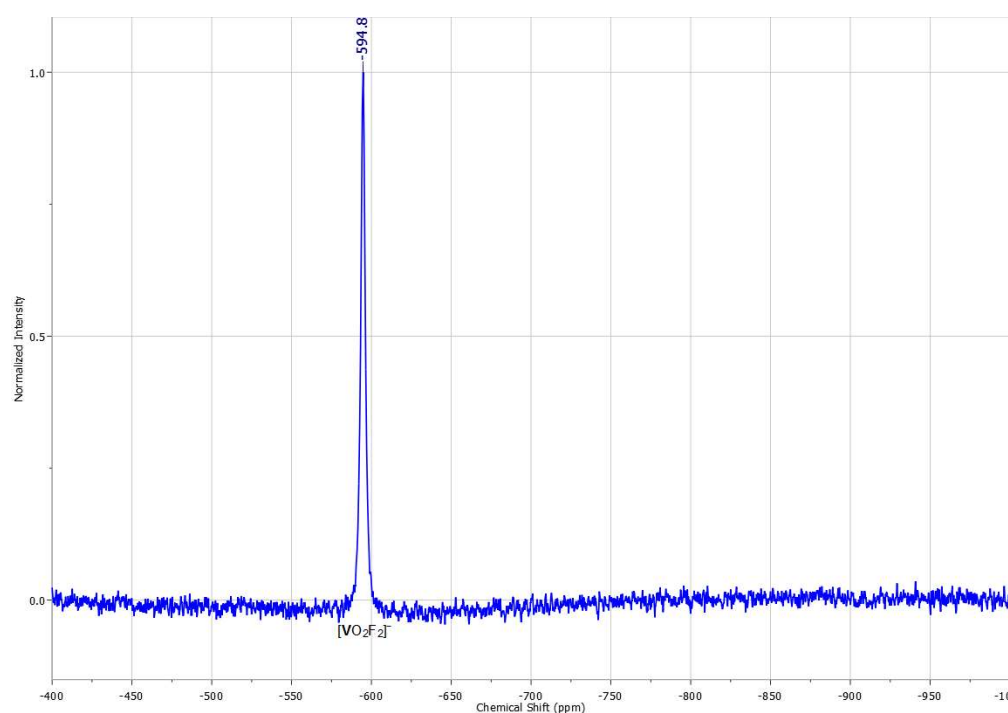


Figure A74: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VO}_2\text{F}_2]$ (**7**) in CD_3CN , showing $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

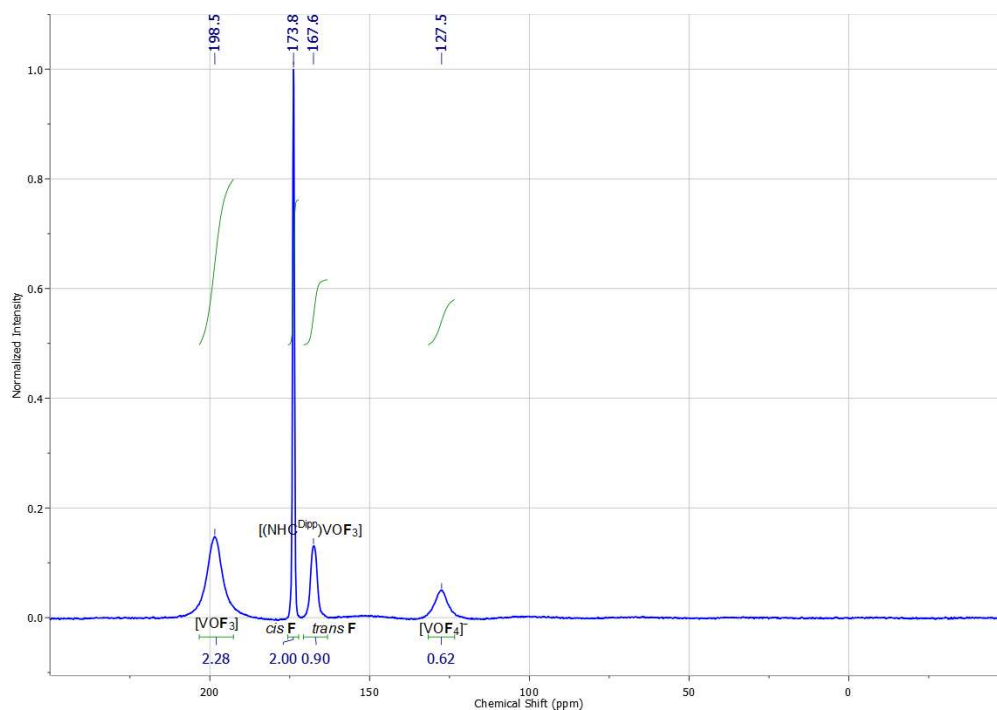


Figure A75: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with one equivalent of VOF_3 in THF-d_8 , showing neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex, $[\text{VOF}_4]^-$ and $[\text{VO}_2\text{F}_2]^-$ anions present due to the decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

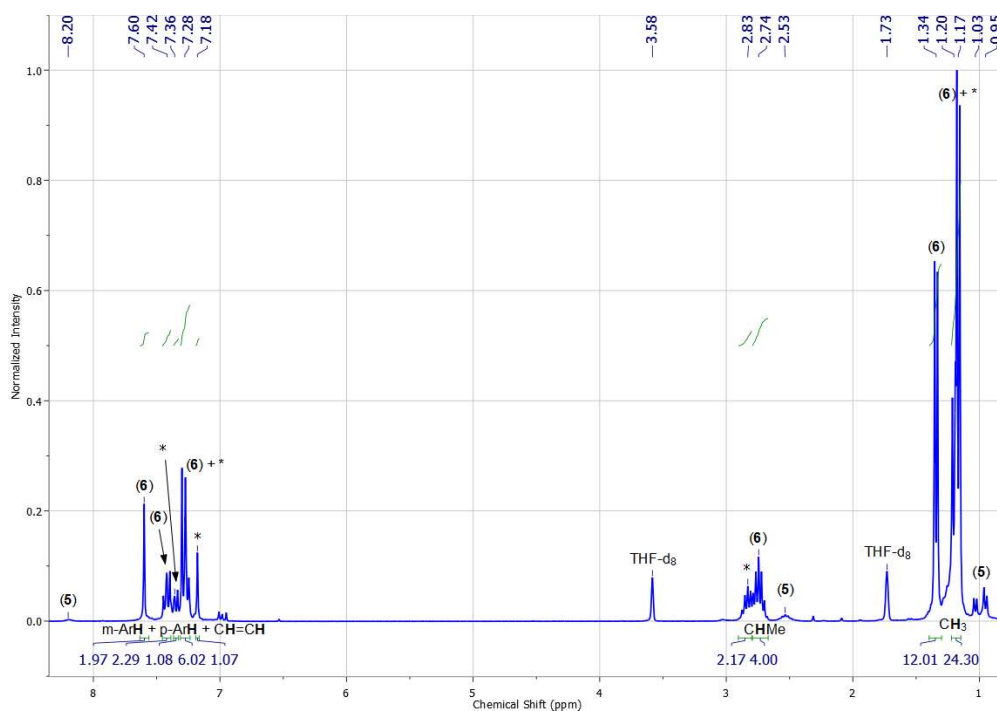


Figure A76: ^1H NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with one equivalent of NHC^{Dipp} in THF-d_8 , showing the bonded and non-bonded NHC^{Dipp} and imidazolium $[(\text{NHC}^{\text{Dipp}})\text{H}]^+$ cation present due to the partial decomposition of NHC^{Dipp} reagent. Figure is based on the reference [324].

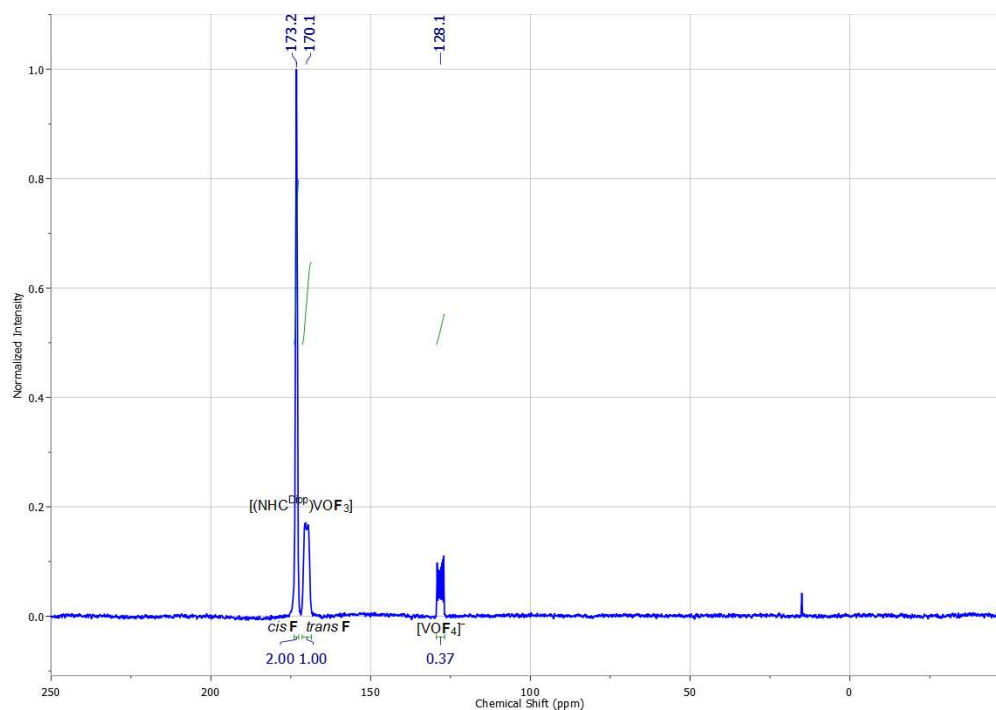


Figure A77: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with one equivalent of NHC^{Dipp} in THF-d_8 , showing neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex and $[\text{VOF}_4]^-$ anion present due to the partial decomposition of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

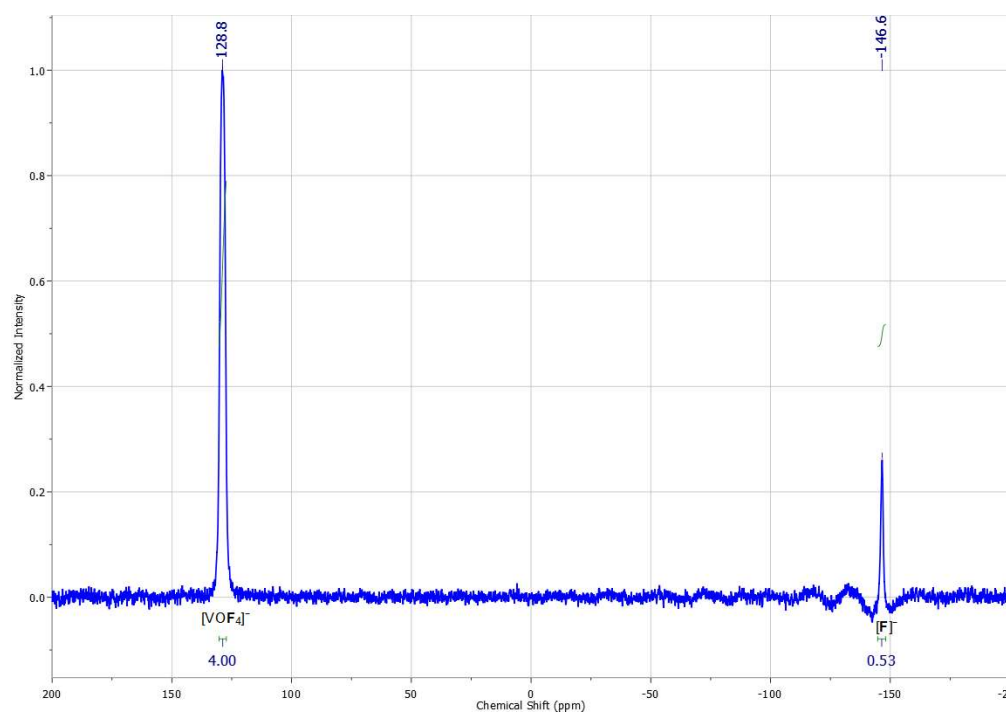


Figure A78: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) with one equivalent of $[\text{NHC}^{\text{Dipp}}][\text{F}]$ in CD_3CN , showing $[\text{VOF}_4]^-$ and $[\text{F}]^-$ anions. Figure is based on the reference [324].

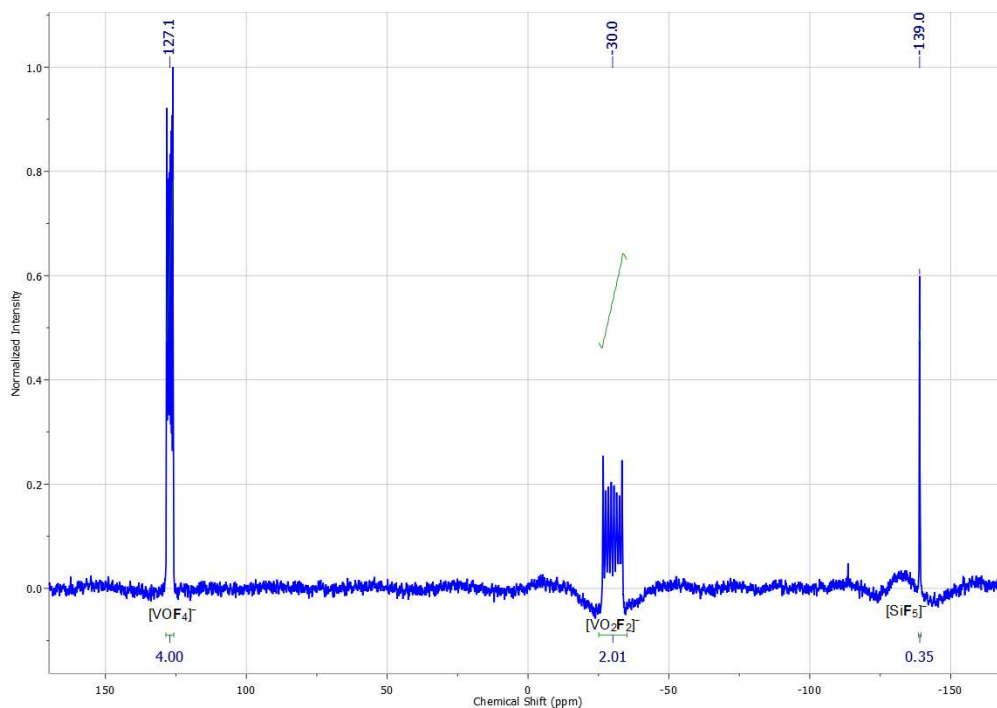


Figure A79: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with 0.5 equivalent of H_2O in THF-d_8 , showing $[\text{VOF}_4]^-$, $[\text{VO}_2\text{F}_2]^-$ and $[\text{SiF}_5]^-$ anions present due to the total hydrolysis of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

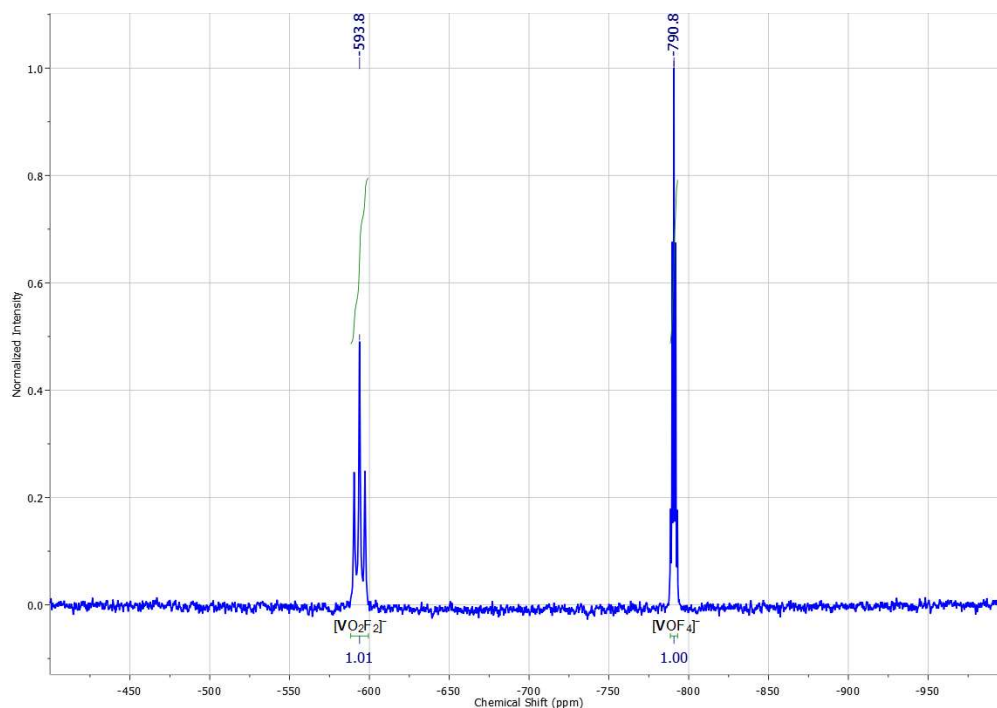


Figure A80: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) with 0.5 equivalent of H_2O in THF-d_8 , showing $[\text{VOF}_4]^-$ and $[\text{VO}_2\text{F}_2]^-$ anions present due to the total hydrolysis of neutral $[(\text{NHC}^{\text{Dipp}})\text{VOF}_3]$ (**5**) complex. Figure is based on the reference [324].

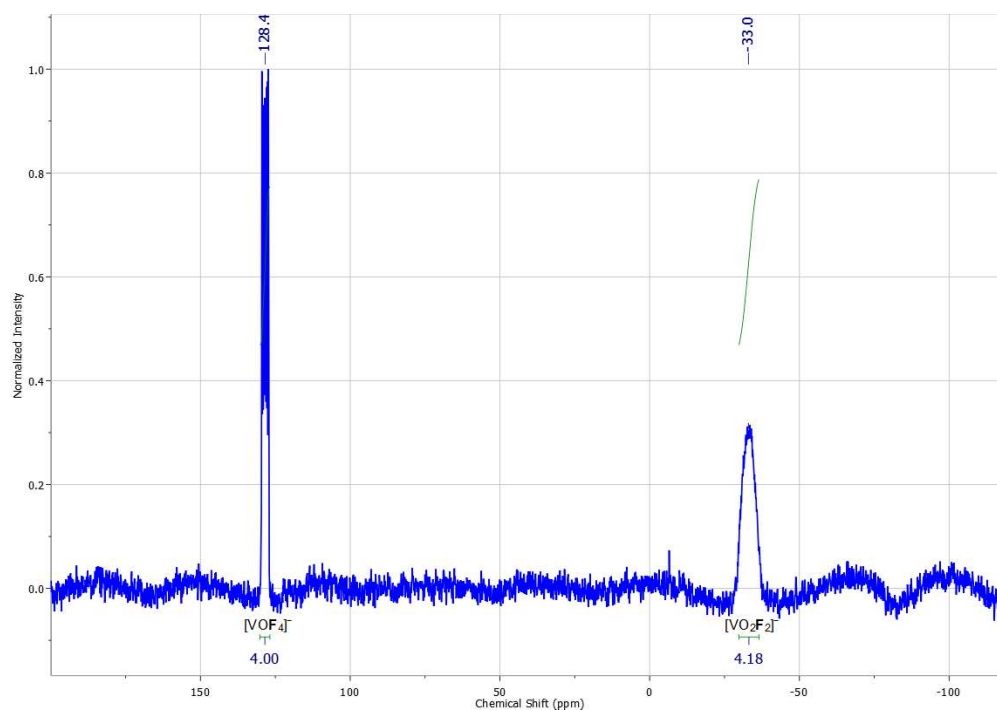


Figure A81: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) with 10 equivalents of H_2O in CD_3CN , showing partial decomposition of $[\text{VOF}_4]^-$ anion into $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

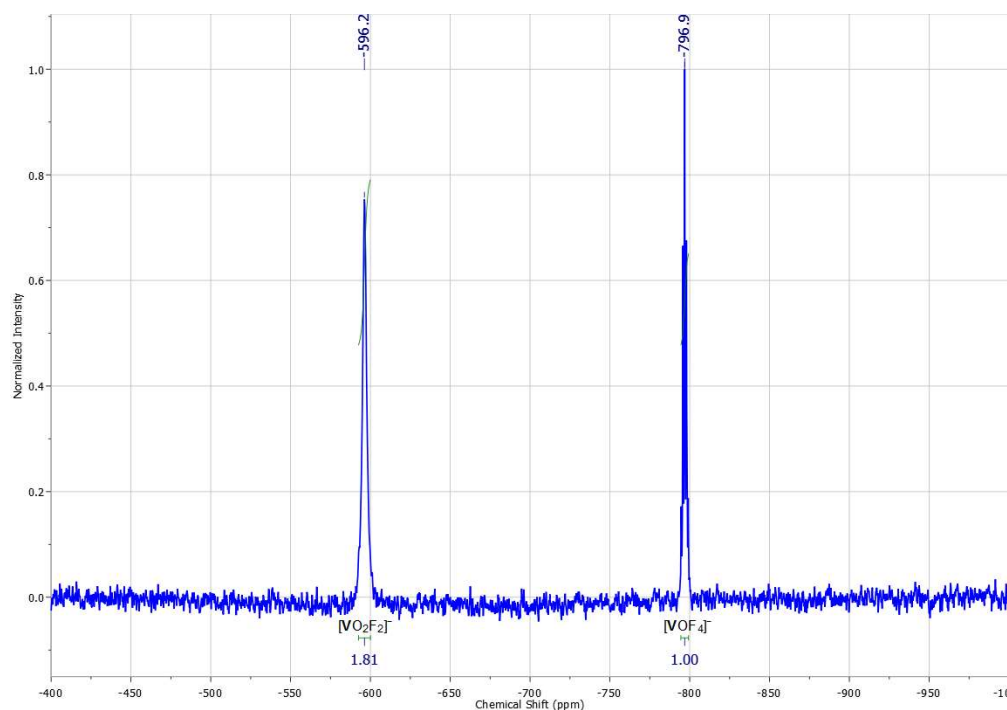


Figure A82: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) with 10 equivalents of H_2O in CD_3CN , showing partial decomposition of $[\text{VOF}_4]^-$ anion into $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

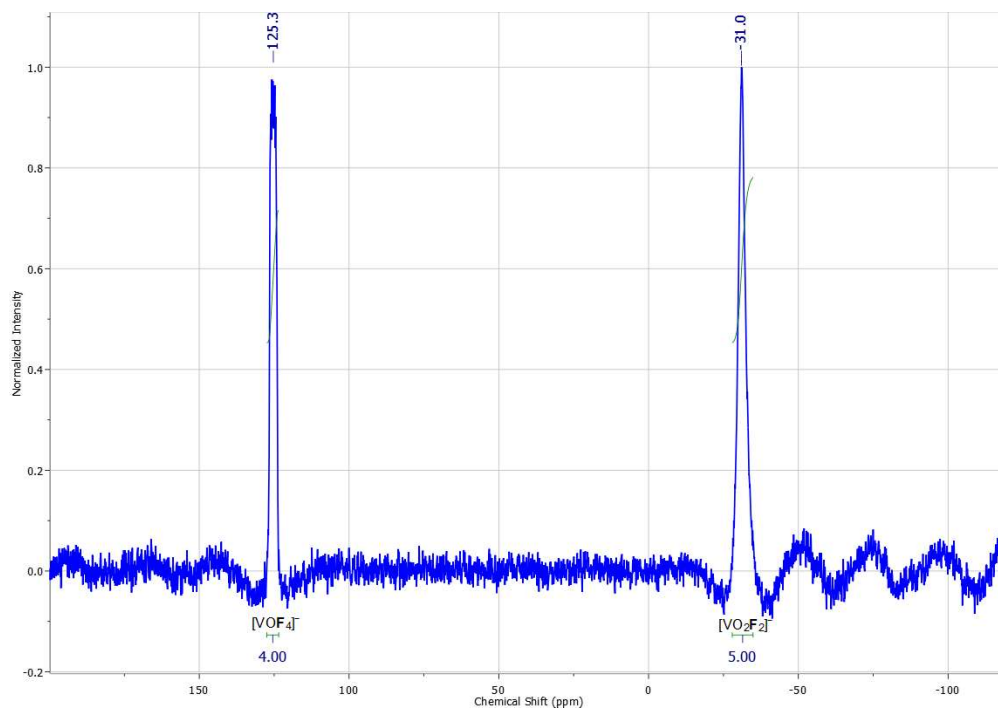


Figure A83: ^{19}F NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) with 30 equivalents of H_2O in CD_3CN , showing severe decomposition of $[\text{VOF}_4]^-$ anion into $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

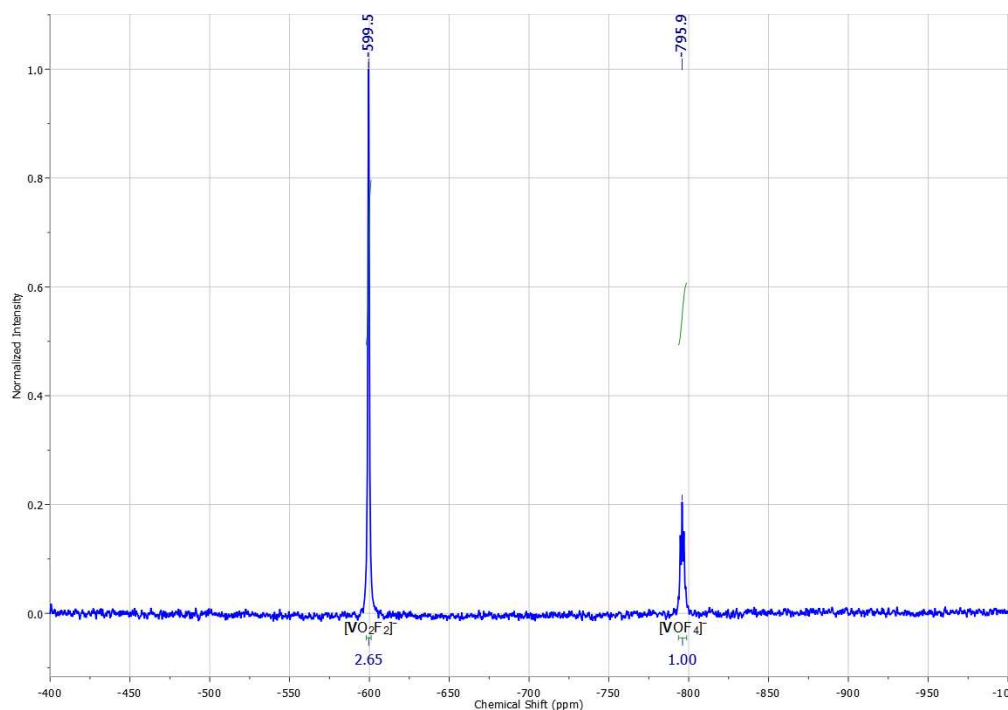


Figure A84: ^{51}V NMR spectrum of $[(\text{NHC}^{\text{Dipp}})\text{H}][\text{VOF}_4]$ (**6**) with 30 equivalents of H_2O in CD_3CN , showing severe decomposition of $[\text{VOF}_4]^-$ anion into $[\text{VO}_2\text{F}_2]^-$ anion. Figure is based on the reference [324].

References

- [1] D. Bourissou, O. Guerret, F. P. Gabbaï, and G. Bertrand, "Stable Carbenes," *Chem. Rev.*, vol. 100, no. 1, pp. 39–92, 2000.
- [2] F. E. Hahn and M. C. Jahnke, "Heterocyclic Carbenes: Synthesis and Coordination Chemistry," *Angew. Chemie Int. Ed.*, vol. 47, no. 17, pp. 3122–3172, 2008.
- [3] H. Jacobsen, A. Correa, A. Poater, C. Costabile, and L. Cavallo, "Understanding the M–(NHC) (NHC=N-heterocyclic carbene) bond," *Coord. Chem. Rev.*, vol. 253, no. 5–6, pp. 687–703, 2009.
- [4] H. Tomioka, T. Watanabe, K. Hirai, K. Furukawa, T. Takui, and K. Itoh, "2,2',4,4',6,6'-Hexabromodiphenylcarbene. The First Stable Triplet Carbene in Fluid Solution at Low Temperature and in the Crystal State at Room Temperature," *J. Am. Chem. Soc.*, vol. 117, no. 23, pp. 6376–6377, 1995.
- [5] W. Kirmse, "Persistent Triplet Carbenes," *Angew. Chemie Int. Ed.*, vol. 42, no. 19, pp. 2117–2119, 2003.
- [6] K. Hirai, T. Itoh, and H. Tomioka, "Persistent Triplet Carbenes," *Chem. Rev.*, vol. 109, no. 8, pp. 3275–3332, 2009.
- [7] W. A. Herrmann and C. Köcher, "N-Heterocyclic Carbenes," *Angew. Chemie Int. Ed.*, vol. 36, no. 20, pp. 2162–2187, 1997.
- [8] M. N. Hopkinson, C. Richter, M. Schedler, and F. Glorius, "An overview of N-heterocyclic carbenes," *Nature*, vol. 510, no. 7506, pp. 485–496, 2014.
- [9] R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, "The Electronic Structure of Methylenes," *J. Am. Chem. Soc.*, vol. 90, no. 6, pp. 1485–1499, 1968.
- [10] R. Gleiter and R. Hoffmann, "On Stabilizing a Singlet Methylene," *J. Am. Chem. Soc.*, vol. 90, no. 20, pp. 5457–5460, 1968.
- [11] D. A. Dixon and A. J. Arduengo III, "Electronic Structure of a Stable Nucleophilic Carbene," *J. Phys. Chem.*, vol. 95, no. 11, pp. 4180–4182, 1991.
- [12] C. Heinemann and W. Thiel, "Ab initio study on the stability of diaminocarbenes," *Chem. Phys. Lett.*, vol. 217, no. 1–2, pp. 11–16, 1994.
- [13] A. Igau, H. Grutzmacher, A. Baceiredo, and G. Bertrand, "Analogous α,α' -Bis-Carbenoid Triply Bonded Species: Synthesis of a Stable λ^3 -Phosphinocarbene- λ^5 -Phosphaacetylene," *J. Am. Chem. Soc.*, vol. 110, no. 19, pp. 6463–6466, 1988.
- [14] A. J. Arduengo III, R. L. Harlow, and M. Kline, "A Stable Crystalline Carbene," *J. Am. Chem. Soc.*, vol. 113, no. 1, pp. 361–363, 1991.
- [15] H. W. Wanzlick and E. Schikora, "Ein neuer Zugang zur Carben-Chemie," *Angew. Chemie*, vol. 72, no. 14, p. 494, 1960.
- [16] H. W. Wanzlick, "Aspects of Nucleophilic Carbene Chemistry," *Angew. Chemie Int. Ed.*, vol. 1, no. 2, pp. 75–80, 1962.

- [17] A. J. Arduengo III, H. V. R. Dias, D. A. Dixon, R. L. Harlow, W. T. Klooster, and T. F. Koetzle, "Electron Distribution in a Stable Carbene," *J. Am. Chem. Soc.*, vol. 116, no. 15, pp. 6812–6822, 1994.
- [18] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, and M. Kline, "Electronic Stabilization of Nucleophilic Carbenes," *J. Am. Chem. Soc.*, vol. 114, no. 14, pp. 5530–5534, 1992.
- [19] A. J. Arduengo III, "Looking for Stable Carbenes: The Difficulty in Starting Anew," *Acc. Chem. Res.*, vol. 32, no. 11, pp. 913–921, 1999.
- [20] D. M. Lemal, R. A. Lovald, and K. I. Kawano, "Tetraaminoethylenes. The Question of Dissociation," *J. Am. Chem. Soc.*, vol. 86, no. 12, pp. 2518–2519, 1964.
- [21] H.-W. Wanzlick, B. Lachmann, and E. Schikora, "Chemie nucleophiler Carbene, VIII. Zur Bildung und Reaktivität des Bis-[1.3-diphenyl-imidazolidinylidens-(2)]," *Chem. Ber.*, vol. 98, no. 10, pp. 3170–3177, 1965.
- [22] M. K. Denk, K. Hatano, and M. Ma, "Nucleophilic Carbenes and the Wanzlick Equilibrium: A Reinvestigation," *Tetrahedron Lett.*, vol. 40, no. 11, pp. 2057–2060, 1999.
- [23] Y. Liu and D. M. Lemal, "Concerning the 'Wanzlick equilibrium,'" *Tetrahedron Lett.*, vol. 41, no. 5, pp. 599–602, 2000.
- [24] V. P. W. Böhm and W. A. Herrmann, "The 'Wanzlick Equilibrium,'" *Angew. Chemie Int. Ed.*, vol. 39, no. 22, pp. 4036–4038, 2000.
- [25] M.-J. Cheng, C.-L. Lai, and C.-H. Hu, "Theoretical study of the Wanzlick equilibrium," *Mol. Phys.*, vol. 102, no. 23–24, pp. 2617–2621, 2004.
- [26] R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini, and J. Schütz, "When and How Do Diaminocarbenes Dimerize?," *Angew. Chemie Int. Ed.*, vol. 43, no. 44, pp. 5896–5911, 2004.
- [27] W. Kirmse, "The Beginnings of N-Heterocyclic Carbenes," *Angew. Chemie Int. Ed.*, vol. 49, no. 47, pp. 8798–8801, 2010.
- [28] Y. Liu, P. E. Lindner, and D. M. Lemal, "Thermodynamics of a Diaminocarbene–Tetraaminoethylene Equilibrium," *J. Am. Chem. Soc.*, vol. 121, no. 45, pp. 10626–10627, 1999.
- [29] F. E. Hahn, L. Wittenbecher, D. Le Van, and R. Fröhlich, "Evidence for an Equilibrium between an N-heterocyclic Carbene and Its Dimer in Solution," *Angew. Chemie Int. Ed.*, vol. 39, no. 3, pp. 541–544, 2000.
- [30] C. M. Weinstein, C. D. Martin, L. Liu, and G. Bertrand, "Cross-Coupling Reactions between Stable Carbenes," *Angew. Chemie Int. Ed.*, vol. 53, no. 25, pp. 6550–6553, 2014.
- [31] C. Heinemann, T. Müller, Y. Apeloig, and H. Schwarz, "On the Question of Stability, Conjugation, and 'Aromaticity' in Imidazol-2-ylidenes and Their Silicon Analogs," *J. Am. Chem. Soc.*, vol. 118, no. 8, pp. 2023–2038, 1996.
- [32] E. Despagne-Ayoub and R. H. Grubbs, "A Stable Four-Membered N-Heterocyclic Carbene," *J. Am. Chem. Soc.*, vol. 126, no. 33, pp. 10198–10199, 2004.
- [33] R. W. Alder *et al.*, "Complexation of stable carbenes with alkali metals," *Chem. Commun.*, no. 3, pp. 241–242, 1999.
- [34] D. Enders *et al.*, "Preparation, Structure, and Reactivity of 1,3,4-Triphenyl-4,5-

- dihydro-1H-1,2,4-triazol-5-ylidene, a New Stable Carbene,” *Angew. Chemie Int. Ed.*, vol. 34, no. 9, pp. 1021–1023, 1995.
- [35] A. J. Arduengo III, J. R. Goerlich, and W. J. Marshall, “A Stable Diaminocarbene,” *J. Am. Chem. Soc.*, vol. 117, no. 44, pp. 11027–11028, 1995.
- [36] A. J. Arduengo III *et al.*, “Imidazolyliidenes, Imidazolinylidenes and Imidazolidines,” *Tetrahedron*, vol. 55, no. 51, pp. 14523–14534, 1999.
- [37] A. J. Arduengo III *et al.*, “An Air Stable Carbene and Mixed Carbene ‘Dimers,’” *J. Am. Chem. Soc.*, vol. 119, no. 52, pp. 12742–12749, 1997.
- [38] R. W. Alder, P. R. Allen, and S. J. Williams, “Stable Carbenes as Strong Bases,” *Chem. Commun.*, no. 12, pp. 1267–1268, 1995.
- [39] A. M. Magill, K. J. Cavell, and B. F. Yates, “Basicity of Nucleophilic Carbenes in Aqueous and Nonaqueous Solvents—Theoretical Predictions,” *J. Am. Chem. Soc.*, vol. 126, no. 28, pp. 8717–8724, 2004.
- [40] Y. Chu, H. Deng, and J.-P. Cheng, “An Acidity Scale of 1,3-Dialkylimidazolium Salts in Dimethyl Sulfoxide Solution,” *J. Org. Chem.*, vol. 72, no. 20, pp. 7790–7793, 2007.
- [41] J. Cheng, L. Wang, P. Wang, and L. Deng, “High-Oxidation-State 3d Metal (Ti–Cu) Complexes with N -Heterocyclic Carbene Ligation,” *Chem. Rev.*, vol. 118, no. 19, pp. 9930–9987, 2018.
- [42] V. Nair, S. Bindu, and V. Sreekumar, “N-Heterocyclic Carbenes: Reagents, Not Just Ligands!,” *Angew. Chemie Int. Ed.*, vol. 43, no. 39, pp. 5130–5135, 2004.
- [43] D. Enders, O. Niemeier, and A. Henseler, “Organocatalysis by N-Heterocyclic Carbenes,” *Chem. Rev.*, vol. 107, no. 12, pp. 5606–5655, 2007.
- [44] A. Grossmann and D. Enders, “N-Heterocyclic Carbene Catalyzed Domino Reactions,” *Angew. Chemie Int. Ed.*, vol. 51, no. 2, pp. 314–325, 2012.
- [45] L. Tschugajeff, M. Skanawy-Grigorjewa, and A. Posnjak, “Über die Hydrazin-Carbylamin-Komplexe des Platins,” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 148, no. 1, pp. 37–42, 1925.
- [46] P. de Frémont, N. Marion, and S. P. Nolan, “Carbenes: Synthesis, properties, and organometallic chemistry,” *Coord. Chem. Rev.*, vol. 253, no. 7–8, pp. 862–892, 2009.
- [47] E. O. Fischer and A. Maasböl, “On the Existence of a Tungsten Carbonyl Carbene Complex,” *Angew. Chemie Int. Ed.*, vol. 3, no. 8, pp. 580–581, 1964.
- [48] F. Zaragoza Dörwald, *Metal Carbenes in Organic Synthesis*. Darmstadt, Germany: Wiley-VCH, GmbH, 1998.
- [49] G. Frenking, M. Solà, and S. F. Vyboishchikov, “Chemical bonding in transition metal carbene complexes,” *J. Organomet. Chem.*, vol. 690, no. 24–25, pp. 6178–6204, 2005.
- [50] C. D. Montgomery, “Fischer and Schrock Carbene Complexes: A Molecular Modeling Exercise,” *J. Chem. Educ.*, vol. 92, no. 10, pp. 1653–1660, 2015.
- [51] R. R. Schrock, “An ‘Alkylcarbene’ Complex of Tantalum by Intramolecular α -Hydrogen Abstraction,” *J. Am. Chem. Soc.*, vol. 96, no. 21, pp. 6796–6797, 1974.
- [52] K. H. Dötz, *Metal Carbenes in Organic Synthesis*. Heidelberg, Germany: Springer, 2004.
- [53] K. Öfele, “1,3-DIMETHYL-4-IMIDAZOLINYLLIDEN-(2)-

- PENTACARBONYLCHROM EIN NEUER ÜBERGANGSMETALL–CARBEN-KOMPLEX,” *J. Organomet. Chem.*, vol. 12, no. 3, pp. P42–P43, 1968.
- [54] H. W. Wanzlick and H. J. Schönherr, “Direct Synthesis of a Mercury Salt-Carbene Complex,” *Angew. Chemie Int. Ed.*, vol. 7, no. 2, pp. 141–142, 1968.
- [55] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, and G. Bertrand, “Stable Cyclic (Alkyl)(Amino)Carbenes as Rigid or Flexible, Bulky, Electron-Rich Ligands for Transition-Metal Catalysts: A Quaternary Carbon Atom Makes the Difference,” *Angew. Chemie Int. Ed.*, vol. 44, no. 35, pp. 5705–5709, 2005.
- [56] H. V. Huynh, “Electronic Properties of N-Heterocyclic Carbenes and Their Experimental Determination,” *Chem. Rev.*, vol. 118, no. 19, pp. 9457–9492, 2018.
- [57] N. M. Scott and S. P. Nolan, “Stabilization of Organometallic Species Achieved by the Use of N-Heterocyclic Carbene (NHC) Ligands,” *Eur. J. Inorg. Chem.*, vol. 2005, no. 10, pp. 1815–1828, 2005.
- [58] R. A. Kelly III *et al.*, “Determination of N-Heterocyclic Carbene (NHC) Steric and Electronic Parameters using the [(NHC)Ir(CO)2Cl] System,” *Organometallics*, vol. 27, no. 2, pp. 202–210, 2008.
- [59] M. Scholl, S. Ding, C. W. Lee, and R. H. Grubbs, “Synthesis and Activity of a New Generation of Ruthenium-Based Olefin Metathesis Catalysts Coordinated with 1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene Ligands,” *Org. Lett.*, vol. 1, no. 6, pp. 953–956, 1999.
- [60] A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, and S. P. Nolan, “A Combined Experimental and Theoretical Study Examining the Binding of N-Heterocyclic Carbenes (NHC) to the Cp*RuCl (Cp* = η^5 -C5Me5) Moiety: Insight into Stereoelectronic Differences between Unsaturated and Saturated NHC Ligands,” *Organometallics*, vol. 22, no. 21, pp. 4322–4326, 2003.
- [61] H. Clavier and S. P. Nolan, “Percent buried volume for phosphine and N-heterocyclic carbene ligands: steric properties in organometallic chemistry,” *Chem. Commun.*, vol. 46, no. 6, pp. 841–861, 2010.
- [62] S. Díez-González, N. Marion, and S. P. Nolan, “N-Heterocyclic Carbenes in Late Transition Metal Catalysis,” *Chem. Rev.*, vol. 109, no. 8, pp. 3612–3676, 2009.
- [63] E. Peris, “Smart N-Heterocyclic Carbene Ligands in Catalysis,” *Chem. Rev.*, vol. 118, no. 19, pp. 9988–10031, 2018.
- [64] L. Mercs and M. Albrecht, “Beyond catalysis: N-heterocyclic carbene complexes as components for medicinal, luminescent, and functional materials applications,” *Chem. Soc. Rev.*, vol. 39, no. 6, pp. 1903–1912, 2010.
- [65] K. M. Hindi, M. J. Panzner, C. A. Tessier, C. L. Cannon, and W. J. Youngs, “The Medicinal Applications of Imidazolium Carbene–Metal Complexes,” *Chem. Rev.*, vol. 109, no. 8, pp. 3859–3884, 2009.
- [66] W. Liu and R. Gust, “Metal N-heterocyclic carbene complexes as potential antitumor metallodrugs,” *Chem. Soc. Rev.*, vol. 42, no. 2, pp. 755–773, 2013.
- [67] W. Liu and R. Gust, “Update on metal N-heterocyclic carbene complexes as potential anti-tumor metallodrugs,” *Coord. Chem. Rev.*, vol. 329, pp. 191–213, 2016.
- [68] R. Visbal and M. C. Gimeno, “N-heterocyclic carbene metal complexes: photoluminescence and applications,” *Chem. Soc. Rev.*, vol. 43, no. 10, pp. 3551–

- 3574, 2014.
- [69] C. I. Ezugwu, N. A. Kabir, M. Yusubov, and F. Verpoort, "Metal-organic frameworks containing N-heterocyclic carbenes and their precursors," *Coord. Chem. Rev.*, vol. 307, no. 2, pp. 188–210, 2016.
 - [70] C. A. Smith *et al.*, "N-Heterocyclic Carbenes in Materials Chemistry," *Chem. Rev.*, vol. 119, no. 8, pp. 4986–5056, 2019.
 - [71] C. M. Crudden and D. P. Allen, "Stability and reactivity of N-heterocyclic carbene complexes," *Coord. Chem. Rev.*, vol. 248, no. 21–24, pp. 2247–2273, 2004.
 - [72] N. Kuhn and A. Al-Sheikh, "2,3-Dihydroimidazol-2-ylidenes and their main group element chemistry," *Coord. Chem. Rev.*, vol. 249, no. 7–8, pp. 829–857, 2005.
 - [73] J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, and I. J. B. Lin, "Coinage Metal–N-Heterocyclic Carbene Complexes," *Chem. Rev.*, vol. 109, no. 8, pp. 3561–3598, 2009.
 - [74] P. L. Arnold and I. J. Casely, "F-Block N-Heterocyclic Carbene Complexes," *Chem. Rev.*, vol. 109, no. 8, pp. 3599–3611, 2009.
 - [75] A. Doddi, M. Peters, and M. Tamm, "N-Heterocyclic Carbene Adducts of Main Group Elements and Their Use as Ligands in Transition Metal Chemistry," *Chem. Rev.*, vol. 119, no. 12, pp. 6994–7112, 2019.
 - [76] S. Bellemin-Laponnaz and S. Dagorne, "Group 1 and 2 and Early Transition Metal Complexes Bearing N-Heterocyclic Carbene Ligands: Coordination Chemistry, Reactivity, and Applications," *Chem. Rev.*, vol. 114, no. 18, pp. 8747–8774, 2014.
 - [77] K. P. Kepp, "A Quantitative Scale of Oxophilicity and Thiophilicity," *Inorg. Chem.*, vol. 55, no. 18, pp. 9461–9470, 2016.
 - [78] M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni, and S. Zacchini, "A crystallographic and DFT study on a NHC complex of niobium oxide trifluoride," *J. Coord. Chem.*, vol. 69, no. 18, pp. 2766–2774, 2016.
 - [79] S. P. Downing and A. A. Danopoulos, "Indenyl- and Fluorenyl-Functionalized N-Heterocyclic Carbene Complexes of Titanium and Vanadium," *Organometallics*, vol. 25, no. 6, pp. 1337–1340, 2006.
 - [80] S. P. Downing *et al.*, "Indenyl- and Fluorenyl-Functionalized N-Heterocyclic Carbene Complexes of Titanium, Zirconium, Vanadium, Chromium, and Yttrium," *Organometallics*, vol. 26, no. 15, pp. 3762–3770, 2007.
 - [81] R. Srivastava *et al.*, "Early/Late Heterobimetallic Tantalum/Rhodium Species Assembled Through a Novel Bifunctional NHC-OH Ligand," *Chem. - A Eur. J.*, vol. 24, no. 17, pp. 4361–4370, 2018.
 - [82] S. Bellemin-Laponnaz, R. Welter, L. Brelot, and S. Dagorne, "Synthesis and structure of V(V) and Mn(III) NHC complexes supported by a tridentate bis-aryloxide-N-heterocyclic carbene ligand," *J. Organomet. Chem.*, vol. 694, no. 5, pp. 604–606, 2009.
 - [83] L. P. Spencer, C. Beddie, M. B. Hall, and M. D. Fryzuk, "Synthesis, Reactivity, and DFT Studies of Tantalum Complexes Incorporating Diamido-N-heterocyclic Carbene Ligands. Facile Endocyclic C–H Bond Activation," *J. Am. Chem. Soc.*, vol. 128, no. 38, pp. 12531–12543, 2006.
 - [84] D. Pugh, J. A. Wright, S. Freeman, and A. A. Danopoulos, "'Pincer' dicarbene

- complexes of some early transition metals and uranium,” *Dalt. Trans.*, no. 6, pp. 775–782, 2006.
- [85] T. R. Helgert, T. K. Hollis, A. G. Oliver, H. U. Valle, Y. Wu, and C. E. Webster, “Synthesis, Characterization, and X-ray Molecular Structure of Tantalum CCC-N-Heterocyclic Carbene (CCC-NHC) Pincer Complexes with Imidazole- and Triazole-Based Ligands,” *Organometallics*, vol. 33, no. 4, pp. 952–958, 2014.
- [86] T. R. Helgert *et al.*, “Extreme π -Loading as a Design Element for Accessing Imido Ligand Reactivity. A CCC-NHC Pincer Tantalum Bis(imido) Complex: Synthesis, Characterization, and Catalytic Oxidative Amination of Alkenes,” *Organometallics*, vol. 35, no. 20, pp. 3452–3460, 2016.
- [87] T. R. Helgert, C. E. Webster, T. K. Hollis, H. U. Valle, P. Hillesheim, and A. G. Oliver, “Free methylidyne? CCC-NHC tantalum bis(imido) reactivity: protonation, rearrangement to a mixed unsymmetrical CCC-N-heterocyclic carbene/N-heterocyclic dicarbene (CCC-NHC/NHDC) pincer tantalum bis(imido) complex,” *Inorganica Chim. Acta*, vol. 469, pp. 164–172, 2018.
- [88] J. A. Ziegler, C. Prange, T. D. Lohrey, R. G. Bergman, and J. Arnold, “Hydroboration Reactivity of Niobium Bis(N-heterocyclic carbene)borate Complexes,” *Inorg. Chem.*, vol. 57, no. 9, pp. 5213–5224, 2018.
- [89] D. S. McGuinness, V. C. Gibson, and J. W. Steed, “Bis(carbene)pyridine Complexes of the Early to Middle Transition Metals: Survey of Ethylene Oligomerization and Polymerization Capability,” *Organometallics*, vol. 23, no. 26, pp. 6288–6292, 2004.
- [90] G. Liang, T. K. Hollis, and C. E. Webster, “Computational Analysis of the Intramolecular Oxidative Amination of an Alkene Catalyzed by the Extreme π -Loading N-Heterocyclic Carbene Pincer Tantalum(V) Bis(imido) Complex,” *Organometallics*, vol. 37, no. 11, pp. 1671–1681, 2018.
- [91] W. A. Herrmann, K. Öfele, M. Elison, F. E. Kühn, and P. W. Roesky, “Nucleophilic cyclocarbenes as ligands in metal halides and metal oxides,” *J. Organomet. Chem.*, vol. 480, no. 1–2, pp. C7–C9, 1994.
- [92] A. Wacker *et al.*, “Metal complexes of anionic 3-borane-1-alkylimidazol-2-ylidene derivatives,” *J. Organomet. Chem.*, vol. 641, no. 1–2, pp. 195–202, 2002.
- [93] C. D. Abernethy, G. M. Codd, M. D. Spicer, and M. K. Taylor, “A Highly Stable N-Heterocyclic Carbene Complex of Trichloro-oxo-vanadium(V) Displaying Novel Cl–Ccarbene Bonding Interactions,” *J. Am. Chem. Soc.*, vol. 125, no. 5, pp. 1128–1129, 2003.
- [94] J. C. Daran, Y. Jeannin, G. Constant, and R. Moranco, “Etude Cristallographique du Monoacétonitriletrichloromonooxovanadium(V),” *Acta Crystallogr. Sect. B*, vol. 31, no. 7, pp. 1833–1837, 1975.
- [95] J.-C. Daran, A. Gourdon, and Y. Jeannin, “Etude Cristallographique du Bis(benzonitrile)trichlorooxovanadium(V),” *Acta Crystallogr. Sect. B*, vol. 36, no. 2, pp. 309–312, 1980.
- [96] G. Frenzen, W. Massa, T. Ernst, and K. Dehnicke, “Synthese und Kristallstruktur von $[\text{VCl}_2(15\text{-Krone-5})]+[\text{VOCl}_4]^-$,” *Zeitschrift für Naturforsch. B*, vol. 45, no. 10, pp. 1393–1397, 1990.
- [97] T. A. Kabanos, A. D. Keramidas, A. Papaioannou, and A. Terzis, “Model

- Investigations for Vanadium-Protein Interactions: Synthesis and X-ray Structures of mer-[VOCl₃(Hpycan)] and [VOCl₂(CH₃CN)(Hpycan)] {Hpycan = N-(2-Nitrophenyl)pyridine-2-carboxamide},” *Inorg. Chem.*, vol. 33, no. 5, pp. 845–846, 1994.
- [98] A. Noll, S. Rabe, and U. Müller, “Die Oxochlorovanadate PPh₄[VOCl₃OH], PPh₄[VOCl₄], (PPh₄)₂[VOCl₄] · 2CH₃CN und (PPh₄)₂[VOCl₄] · CH₃CN mit auffälligen Abweichungen von der quadratisch-pyramidalen Anionenstruktur,” *Zeitschrift für Naturforsch. B*, vol. 54, no. 5, pp. 591–596, 1999.
- [99] S. Zhang, W.-C. Zhang, D.-D. Shang, Z.-Q. Zhang, and Y.-X. Wu, “Ethylene/propylene copolymerization catalyzed by vanadium complexes containing N-heterocyclic carbenes,” *Dalt. Trans.*, vol. 44, no. 34, pp. 15264–15270, 2015.
- [100] S. Zhang, W.-C. Zhang, D.-D. Shang, and Y.-X. Wu, “Synthesis of Ultra-High-Molecular-Weight Ethylene-Propylene Copolymer via Quasi-Living Copolymerization with N-Heterocyclic Carbene Ligated Vanadium Complexes,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 57, no. 4, pp. 553–561, 2019.
- [101] W. Zhang and K. Nomura, “Facile Synthesis of (Imido)vanadium(V)–Alkyl, Alkylidene Complexes Containing an N-Heterocyclic Carbene Ligand from Their Trialkyl Analogues,” *Organometallics*, vol. 27, no. 24, pp. 6400–6402, 2008.
- [102] C. Lorber and L. Vendier, “Synthesis and structure of early transition metal NHC complexes,” *Dalt. Trans.*, no. 35, pp. 6972–6984, 2009.
- [103] A. Igarashi, E. L. Kolychev, M. Tamm, and K. Nomura, “Synthesis of (Imido)Vanadium(V) Dichloride Complexes Containing Anionic N-Heterocyclic Carbenes That Contain a Weakly Coordinating Borate Moiety: New MAO-Free Ethylene Polymerization Catalysts,” *Organometallics*, vol. 35, no. 11, pp. 1778–1784, 2016.
- [104] G. Nagai *et al.*, “Effect of Al Cocatalyst in Ethylene and Ethylene/Norbornene (Co)polymerization by (Imido)vanadium Dichloride Complexes Containing Anionic N-Heterocyclic Carbenes Having Weakly Coordinating Borate Moiety,” *J. Japan Pet. Inst.*, vol. 60, no. 5, pp. 256–262, 2017.
- [105] K. Nomura *et al.*, “Solution XAS Analysis of Various (Imido)vanadium(V) Dichloride Complexes Containing Monodentate Anionic Ancillary Donor Ligands: Effect of Aluminium Cocatalyst in Ethylene/Norbornene (Co)polymerization,” *J. Japan Pet. Inst.*, vol. 61, no. 5, pp. 282–287, 2018.
- [106] M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni, and S. Zacchini, “A structurally-characterized NbCl₅–NHC adduct,” *Chem. Commun.*, vol. 50, no. 34, pp. 4472–4474, 2014.
- [107] G. Ciancaleoni, L. Belpassi, and F. Marchetti, “Back-Donation in High-Valent d0 Metal Complexes: Does It Exist? The Case of NbV,” *Inorg. Chem.*, vol. 56, no. 18, pp. 11266–11274, 2017.
- [108] M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni, and S. Zacchini, “Coordination complexes of niobium and tantalum pentahalides with a bulky NHC ligand,” *Dalt. Trans.*, vol. 45, no. 16, pp. 6939–6948, 2016.
- [109] Z. Wei, W. Zhang, G. Luo, F. Xu, Y. Mei, and H. Cai, “Mono- and bis-N-heterocyclic carbene complexes of tantalum and niobium with high oxidation

- states,” *New J. Chem.*, vol. 40, no. 7, pp. 6270–6275, 2016.
- [110] M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni, C. Pinzino, and S. Zacchini, “Coordination Compounds of Niobium(IV) Oxide Dihalides Including the Synthesis and the Crystallographic Characterization of NHC Complexes,” *Inorg. Chem.*, vol. 55, no. 9, pp. 4173–4182, 2016.
- [111] P. A. Petrov, T. S. Sukhikh, and M. N. Sokolov, “NHC adducts of tantalum amidohalides: the first example of NHC abnormally coordinated to an early transition metal,” *Dalt. Trans.*, vol. 46, no. 15, pp. 4902–4906, 2017.
- [112] F. Pintchovski, S. Soled, and A. Wold, “Preparation, Crystal Structure, and Properties of $\text{NH}_4\text{V}_3\text{O}_6\text{F}$,” *Inorg. Chem.*, vol. 15, no. 2, pp. 330–334, 1976.
- [113] H. Rieskamp and R. Mattes, “Dioxofluoro-oxalato-vanadat: ein fünffach koordiniertes, monomeres Komplexion des Vanadins(V),” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 419, no. 3, pp. 193–199, 1976.
- [114] M. I. Khan, Q. Chen, H. Höpe, S. Parkin, C. J. O’Connor, and J. Zubieta, “Hydrothermal Synthesis and Characterization of Hexavanadium Polyoxo Alkoxide Anion Clusters: Crystal Structures of the Vanadium(IV) Species $\text{Ba}[\text{V}_6\text{O}_7(\text{OH})_3\{(\text{OCH}_2)_3\text{CCH}_3\}_3] \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2[\text{V}_6\text{O}_7\{(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3\}_4]$, of the Mixed-Valence Complex (Me₃NH) EDIT,” *Inorg. Chem.*, vol. 32, no. 13, pp. 2929–2937, 1993.
- [115] A. Müller, J. Meyer, H. Bögge, A. Stämmeler, and A. Botar, “Trinuclear Fragments as Nucleation Centres: New Polyoxoalkoxyvanadates by (Induced) Self-Assembly,” *Chem. - A Eur. J.*, vol. 4, no. 8, pp. 1388–1397, 1998.
- [116] C. Ninclaus, D. Riou, and G. Férey, “Hydrothermal synthesis and structural determinations of some new polyoxofluorovanadates $[\text{V}_{14}\text{O}_{36}\text{F}_4]_8$ — interleaved by water molecules and organic cations $\text{NH}_3(\text{CH}_2)_n\text{NH}_3$ ($n = 4$ –6),” *Chem. Commun.*, no. 9, pp. 851–852, 1997.
- [117] I. Omri, M. Graia, and T. Mhiri, “Synthesis, Crystal Structure, Vibrational and Optical Properties of $(\text{Hdea})_4(\text{V}_7\text{O}_{19}\text{F}) \cdot 0.42\text{H}_2\text{O}$, an Original $(\text{V}_7\text{O}_{19}\text{F})_4$ — Cluster Oxyfluoride,” *J. Clust. Sci.*, vol. 26, no. 3, pp. 815–825, 2015.
- [118] Y.-P. Tong, X.-D. Zheng, J.-J. Li, Y.-W. Lin, and G.-T. Luo, “A Tetradecanuclear Polyoxofluorovanadate Cluster Compound with 1-Methylimidazole Possessing Ring-like $[\text{V}_{10}\text{O}_{20}]$ Ladder Core and Unusual Electronic Configuration: Synthesis, Structure and Theoretical Calculation,” *Chinese J. Inorg. Chem.*, vol. 35, no. 6, pp. 1093–1100, 2019.
- [119] L. Krivosudský, P. Schwendt, R. Gyepes, and J. Filo, “ $[\text{V}_{12}\text{O}_{30}\text{F}_4(\text{H}_2\text{O})_2]_4$ —: One-pot synthesis and characterization of a novel fluorinated dodecavanadate,” *Inorg. Chem. Commun.*, vol. 49, pp. 48–51, 2014.
- [120] M. Gómez, A. Pastor, E. Álvarez, J. L. Olloqui-Sariego, and A. Galindo, “Halide encapsulation by dicarboxylate oxido-vanadium cage complexes,” *Dalt. Trans.*, vol. 47, no. 7, pp. 2183–2191, 2018.
- [121] J. Spandl, I. Brüdgam, and H. Hartl, “Von kleinen Bausteinen zu neuen Poly-alkoxo-oxometallat-Derivaten: Synthese und Strukturaufklärung von $\text{K}_4[\text{VIV}_{12}\text{O}_{12}(\text{OCH}_3)_{16}(\text{C}_4\text{O}_4)_6]$, $\text{Cs}_{10}[\text{VIV}_{24}\text{O}_{24}(\text{OCH}_3)_{32}(\text{C}_4\text{O}_4)_{12}][\text{VIV}_8\text{O}_8(\text{OCH}_3)_{16}(\text{C}_2\text{O}_4)]$ und

- M2[VIV8O8(OCH3)16(VIVOF4)] (M=[N(nBu)4] bzw. [NEt4]),” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 629, no. 3, pp. 539–544, 2003.
- [122] K. Y. Monakhov *et al.*, “Supramolecular Recognition Influences Magnetism in [X@HVIV8VV14O54]6– Self-Assemblies with Symmetry-Breaking Guest Anions,” *Chem. - A Eur. J.*, vol. 21, no. 6, pp. 2387–2397, 2015.
- [123] M. Nicolaou *et al.*, “Design and Assembly of Covalently Functionalised Polyoxofluorovanadate Molecular Hybrids,” *Chem. - A Eur. J.*, vol. 24, no. 15, pp. 3836–3845, 2018.
- [124] M. Nicolaou, C. Drouza, and A. D. Keramidis, “Controlled one pot synthesis of polyoxofluorovanadate molecular hybrids exhibiting peroxidase like activity,” *New J. Chem.*, vol. 43, no. 45, pp. 17595–17602, 2019.
- [125] Y. Kikukawa, T. Yokoyama, S. Kashio, and Y. Hayashi, “Synthesis and characterization of fluoride-incorporated polyoxovanadates,” *J. Inorg. Biochem.*, vol. 147, pp. 221–226, 2015.
- [126] M. F. Davis, W. Levason, J. Paterson, G. Reid, and M. Webster, “Complexes of Vanadium(V) Oxide Trifluoride with Nitrogen and Oxygen Donor Ligands: Coordination Chemistry and Some Fluorination Reactions,” *Eur. J. Inorg. Chem.*, vol. 2008, no. 5, pp. 802–811, 2008.
- [127] K. Okaya, T. Kobayashi, Y. Koyama, Y. Hayashi, and K. Isobe, “Formation of VV Lacunary Polyoxovanadates and Interconversion Reactions of Dodecavanadate Species,” *Eur. J. Inorg. Chem.*, vol. 2009, no. 34, pp. 5156–5163, 2009.
- [128] S. A. Fairhurst, D. L. Hughes, G. J. Leigh, J. R. Sanders, and J. Weisner, “Novel binuclear vanadium(V)–Schiff base cations containing single fluorine bridges and the structure of difluorodioxovanadate(1–),” *Dalt. Trans.*, vol. 0, no. 18, pp. 2591–2598, 1994.
- [129] N. F. Choudhary, P. B. Hitchcock, and G. J. Leigh, “Six-coordinate vanadyl tetradentate Schiff base complexes with methanol, methoxide, water or fluoride as the sixth ligand,” *Inorganica Chim. Acta*, vol. 310, no. 1, pp. 10–20, 2000.
- [130] K. Oyaizu and E. Tsuchida, “The First Oxovanadium Ring in [{O=V(salen)}2(μ-F)][VO(salen)][BF4] · (CH2Cl2)x Crystals,” *J. Am. Chem. Soc.*, vol. 125, no. 19, pp. 5630–5631, 2003.
- [131] S. S. Passadis *et al.*, “Synthesis, Bonding, and Reactivity of Vanadium(IV) Oxido–Fluorido Compounds with Neutral Chelate Ligands of the General Formula cis-[VIV(=O)(F)(LN–N)2]+,” *Inorg. Chem.*, vol. 55, no. 4, pp. 1364–1366, 2016.
- [132] H. Rieskamp and R. Mattes, “Oxotetrafluoro-vanadate(V): Die Kristallstruktur von [enH2][VOF4(H2O)]2,” *Zeitschrift für Naturforsch. B*, vol. 31, no. 5, pp. 541–543, 1976.
- [133] R. Stomberg, “The Crystal Structure of Ammonium Difluorooxidiperoxovanadate(V), (NH4)3[VF2O(O2)2],” *Acta Chem. Scand.*, vol. 38A, pp. 541–545, 1984.
- [134] M. Leimkühler and R. Mattes, “The Structure of the VO2F43– Ion: Crystal Structure of (NH4)3VO2F4,” *J. Solid State Chem.*, vol. 65, no. 2, pp. 260–264, 1986.
- [135] J. Chrappová, P. Schwendt, and J. Marek, “NMR study of the [VO(O2)2F]2– ion in solution: Synthesis, vibrational spectra and crystal structure of

- [NH₃CH₂CH₂NH₃][VO(O₂)₂F],” *J. Fluor. Chem.*, vol. 126, no. 9–10, pp. 1297–1302, 2005.
- [136] N. Buchholz, M. Leimkuehler, L. Kiriazis, and R. Mattes, “A Series of Tris(μ -fluoro)divanadates(III, IV, V) Containing the Biocahedral [V₂(O,F)₉]^{3–} unit. Synthesis, Characterization, and Structures of (NMe₄)₃V₂F₉, (NMe₄)₃V₂O₂F₇, (NMe₄)₃V₂O₄F₅, and (NMe₄)₂KV₂O₄F₅ · H₂O,” *Inorg. Chem.*, vol. 27, no. 12, pp. 2035–2039, 1988.
- [137] M. Hilbers, M. Leimkühler, and R. Mattes, “Zwei- und dreikernige Fluorooxoanionen des Vanadins. Kristallstrukturen von Cs(NMe₄)[V₂O₂F₈(H₂O)] und (Na,K)(NMe₄)₂[V₃O₃F₁₂],” *Zeitschrift für Naturforsch. B*, vol. 44, no. 4, pp. 383–388, 1989.
- [138] P. Bukovec and L. Golič, “Ammonium Tetrafluorooxovanadate(IV),” *Acta Crystallogr. Sect. B*, vol. 36, no. 8, pp. 1925–1927, 1980.
- [139] R. Stomberg and S. Olson, “The Crystal Structure of Ammonium Fluorooxidiperoxovanadate(2–), (NH₄)₂[VFO(O₂)₂],” *Acta Chem. Scand.*, vol. 38A, pp. 801–806, 1984.
- [140] S. L. Benjamin, W. Levason, and G. Reid, “Medium and high oxidation state metal/non-metal fluoride and oxide–fluoride complexes with neutral donor ligands,” *Chem. Soc. Rev.*, vol. 42, no. 4, pp. 1460–1499, 2013.
- [141] E. Ahlborn, E. Diemann, and A. Müller, “Darstellung, IR-Spektren und röntgenographische Untersuchungen von Dioxodifluor- und Dioxodichlorovanadaten(V),” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 394, no. 1–2, pp. 1–7, 1972.
- [142] R. Mattes and H. Rieskamp, “Die Kristallstruktur von Ammonium-dioxodifluorovanadat,” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 399, no. 2, pp. 205–210, 1973.
- [143] H. Rieskamp and R. Mattes, “Oxofluoro-oxalato-vanadate des vierwertigen Vanadins: Schwingungsspektrum und Struktur von Na₃[VOF(C₂O₄)₂] · 6H₂O,” *Zeitschrift für Naturforsch. B*, vol. 31, no. 5, pp. 537–540, 1976.
- [144] T. Kanatani, K. Matsumoto, and R. Hagiwara, “Syntheses and Physicochemical Properties of Low-Melting Salts Based on VOF₄[–] and MoOF₅[–], and the Molecular Geometries of the Dimeric (VOF₄[–])₂ and Mo₂O₄F₆^{2–} Anions,” *Eur. J. Inorg. Chem.*, vol. 2010, no. 7, pp. 1049–1055, 2010.
- [145] M. Lozinšek, “Hydroxylammonium Tetrafluoridooxidovanadate(V) – (NH₃OH)[VOF₄],” *Acta Chim. Slov.*, vol. 62, no. 2, pp. 378–384, 2015.
- [146] M. Hilbers, M. Meiwald, and R. Mattes, “Mehrkernige Oxo-Vanadium- und Oxo-Molybdän-Komplexe mit dem Dianion der Quadratsäure als Brückenligand. Strukturen von [C(NH₂)₃]₄[V₂O₂F₄(C₄O₄)₂] · 4H₂O, [nBu₄N]₄[V₃O₃F₄(C₄O₄)₃] · 2H₂O, [Et₄N]₃[Mo₃O₈F(C₄O₄)₂], [Et₄N]₄[Mo₄O₁₀F₆(C₄O₄)] und EDIT,” *Zeitschrift für Naturforsch. B*, vol. 51, no. 1, pp. 57–67, 1996.
- [147] A. Stasch, M. Schormann, J. Prust, H. W. Roesky, H.-G. Schmidt, and M. Noltemeyer, “Acetylacetonatodifluorooxometalates of vanadium and molybdenum: syntheses and crystal structures,” *Dalt. Trans.*, no. 13, pp. 1945–1947, 2001.

- [148] P. Bukovec, S. Milićev, A. Demšar, and L. Golič, "Crystal Structure and Infrared and Raman Spectra of Tetramethylammonium Di- μ -fluoro-bis[aquadifluoro-oxovanadate(IV)]," *Dalt. Trans.*, no. 9, pp. 1802–1806, 1981.
- [149] A. Demšar and P. Bukovec, "Synthesis and Crystal Structure of Tetraethylammonium Di- μ -fluoro-bis[aquadifluoro-oxovanadate(IV)]," *Croat. Chem. Acta*, vol. 57, no. 4, pp. 673–677, 1984.
- [150] J. Darriet, Q. Xu, and A. Tressaud, "Structure of $[N(CH_3)_4][VOF_3(H_2O)]$," *Acta Crystallogr. Sect. C*, vol. 43, no. 2, pp. 224–226, 1987.
- [151] A. Demšar, I. Leban, and G. Giester, "SYNTHESIS AND CRYSTAL STRUCTURE OF LUTIDINIUM AQUAFLUOROOXOVANADATE(IV)," *Acta Chim. Slov.*, vol. 49, no. 2, pp. 259–265, 2002.
- [152] N. F. Stephens, M. Buck, and P. Lightfoot, "Polar ordering of polar octahedra in $[C_2N_2H_{10}][VOF_4(H_2O)]$," *J. Mater. Chem.*, vol. 15, no. 40, pp. 4298–4300, 2005.
- [153] D. W. Aldous, R. J. Goff, P. J. Attfield, and P. Lightfoot, "Novel Vanadium(IV) Oxyfluorides with 'Spin-Ladder'-Like Structures, and Their Relationship to $(VO)_2P_2O_7$," *Inorg. Chem.*, vol. 46, no. 4, pp. 1277–1282, 2007.
- [154] D. W. Aldous, N. F. Stephens, and P. Lightfoot, "Hydrothermal chemistry of oligomeric vanadium oxyfluorides," *Dalt. Trans.*, no. 22, pp. 2271–2282, 2007.
- [155] D. W. Aldous, N. F. Stephens, and P. Lightfoot, "The role of temperature in the solvothermal synthesis of hybrid vanadium oxyfluorides," *Dalt. Trans.*, vol. 0, no. 37, pp. 4207–4213, 2007.
- [156] P. DeBurgomaster, W. Ouellette, H. Liu, C. J. O'Connor, G. T. Yee, and J. Zubietta, "Solvatothermal chemistry of organically-templated vanadium fluorides and oxyfluorides," *Inorganica Chim. Acta*, vol. 363, no. 6, pp. 1102–1113, 2010.
- [157] F. Himeur, P. K. Allan, S. J. Teat, R. J. Goff, R. E. Morris, and P. Lightfoot, "Increasing the dimensionality of hybrid vanadium oxyfluorides using ionothermal synthesis," *Dalt. Trans.*, vol. 39, no. 26, pp. 6018–6020, 2010.
- [158] D. W. Aldous, A. M. Z. Slawin, and P. Lightfoot, "A new chain structure: catena-poly-[4,4'-(ethane-1,2-diyl)dipyridinium bis[aquadifluoridooxidovanadate]- μ -fluorido]," *Acta Crystallogr. Sect. C*, vol. 66, no. 5, pp. m130–m132, 2010.
- [159] F. H. Aidoudi, P. J. Byrne, P. K. Allan, S. J. Teat, P. Lightfoot, and R. E. Morris, "Ionic liquids and deep eutectic mixtures as new solvents for the synthesis of vanadium fluorides and oxyfluorides," *Dalt. Trans.*, vol. 40, no. 16, pp. 4324–4331, 2011.
- [160] R. Gautier, R. Gautier, K. B. Chang, and K. R. Poeppelmeier, "On the Origin of the Differences in Structure Directing Properties of Polar Metal Oxyfluoride $[MO_xF_{6-x}]_2^-$ ($x = 1, 2$) Building Units," *Inorg. Chem.*, vol. 54, no. 4, pp. 1712–1719, 2015.
- [161] F. H. Aidoudi *et al.*, "An ionothermally prepared $S = 1/2$ vanadium oxyfluoride kagome lattice," *Nat. Chem.*, vol. 3, no. 10, pp. 801–806, 2011.
- [162] F. H. Aidoudi, C. Black, K. S. A. Arachchige, A. M. Z. Slawin, R. E. Morris, and P. Lightfoot, "Structural diversity in hybrid vanadium(IV) oxyfluorides based on a common building block," *Dalt. Trans.*, vol. 43, no. 2, pp. 568–575, 2014.
- [163] L. Clark *et al.*, "Extending the Family of $V_4^+ S=1/2$ Kagome Antiferromagnets,"

- Angew. Chemie Int. Ed.*, vol. 54, no. 51, pp. 15457–15461, 2015.
- [164] Y.-P. Chang, L. Furness, W. Levason, G. Reid, and W. Zhang, “Complexes of vanadium(IV) oxide difluoride with neutral N- and O-donor ligands,” *J. Fluor. Chem.*, vol. 191, pp. 149–160, 2016.
- [165] H. Lu, R. Gautier, Z.-X. Li, W. Jie, Z. Liu, and K. R. Poeppelmeier, “The dimeric $[\text{V}_2\text{O}_2\text{F}_8]^{4-}$ anion: Structural characterization of a magnetic basic-building-unit,” *J. Solid State Chem.*, vol. 200, pp. 105–109, 2013.
- [166] C. Black and P. Lightfoot, “ $\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$: a new V^{4+} layer structure related to VOF_3 ,” *Acta Crystallogr. Sect. C*, vol. 72, no. 1, pp. 80–83, 2016.
- [167] P. DeBurgomaster and J. Zubietta, “A binuclear vanadium oxyfluoride: di- μ -oxido-bis[(2,2'-bipyridyl)fluoridooxidovanadium(V)],” *Acta Crystallogr. Sect. E*, vol. 66, no. 9, pp. m1091–m1091, 2010.
- [168] P. DeBurgomaster and J. Zubietta, “A binuclear vanadium oxyfluoride: di- μ -oxido-bis[fluoridooxido(1,10-phenanthroline)vanadium(V)],” *Acta Crystallogr. Sect. E*, vol. 66, no. 10, pp. m1303–m1303, 2010.
- [169] A. Demšar and P. Bukovec, “SYNTHESIS AND THE MOLECULAR AND CRYSTAL STRUCTURE OF AQUADIFLUOROOXO(1,10-PHENANTHROLINO)VANADIUM(IV), $[\text{VOF}_2(\text{H}_2\text{O})(1,10\text{-PHENANTHROLINE})]$,” *J. Fluor. Chem.*, vol. 24, no. 3, pp. 369–375, 1984.
- [170] A. J. Edwards, D. R. Slim, J. E. Guerchais, and J. Sala-Pala, “Fluoride Crystal Structures. Part 30. 2,2'-Bipyridylfluorodioxovanadium(V),” *Dalt. Trans.*, no. 10, pp. 984–986, 1977.
- [171] M. F. Davis *et al.*, “Synthesis, chemistry and structures of complexes of the dioxovanadium(v) halides VO_2F and VO_2Cl ,” *Dalt. Trans.*, vol. 0, no. 44, pp. 6265–6273, 2008.
- [172] J. C. Pérez-Flores *et al.*, “ VO_2F : a new transition metal oxyfluoride with high specific capacity for Li ion batteries,” *J. Mater. Chem. A*, vol. 3, no. 41, pp. 20508–20515, 2015.
- [173] M. A. Cambaz *et al.*, “Vanadium Oxyfluoride/Few-Layer Graphene Composite as a High-Performance Cathode Material for Lithium Batteries,” *Inorg. Chem.*, vol. 55, no. 8, pp. 3789–3796, 2016.
- [174] J. Supeł, U. Abram, A. Hagenbach, and K. Seppelt, “Technetium Fluoride Trioxide, TcO_3F , Preparation and Properties,” *Inorg. Chem.*, vol. 46, no. 14, pp. 5591–5595, 2007.
- [175] H. W. Roesky, I. Leichtweis, and M. Noltemeyer, “Oxo Fluorides of Titanium and Vanadium. Preparation and Crystal Structures of $[\text{Cp}^*\text{TiF}(\mu\text{-O})]_4$ and $\text{OVF}_2\text{N}=\text{PPh}_3$,” *Inorg. Chem.*, vol. 32, no. 23, pp. 5102–5104, 1993.
- [176] J. Kohl and D. Wiedemann, “(OC-6-13)-Difluoridooxidobis(propan-2-ol)(propan-2-olato)vanadium(V),” *Acta Crystallogr. Sect. C*, vol. 69, no. 12, pp. 1482–1484, 2013.
- [177] G. Pausewang and W. Rüdorff, “Über Alkali-oxofluorometallate der Übergangsmetalle. $\text{A}_3\text{ImeOxF}_6-x$ -Verbindungen mit $x = 1, 2, 3$,” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 364, no. 1–2, pp. 69–87, 1969.
- [178] A. Le Bail, A.-M. Mercier, and I. Dix, “ $\text{Sr}_5(\text{VIVOF}_5)_3\text{F}(\text{H}_2\text{O})_3$ refined from a non-merohedrally twinned crystal,” *Acta Crystallogr. Sect. E*, vol. 65, no. 6, pp. i46–i47,

- 2009.
- [179] M. E. Welk, C. L. Stern, K. R. Poeppelmeier, and A. J. Norquist, "Effects of Reaction Gel Dehydration on the Synthesis of $\text{Cu}(\text{NC}_5\text{H}_5)_4\text{VOF}_4$ and $[\text{Cu}(\text{NC}_5\text{H}_5)_4\text{VOF}_4][\text{Cu}(\text{NC}_5\text{H}_5)_4(\text{H}_2\text{O})\text{VOF}_4] \cdot \text{H}_2\text{O}$," *Cryst. Growth Des.*, vol. 7, no. 5, pp. 956–961, 2007.
 - [180] K. Waltersson, "Neutron and X-Ray Diffraction Structure Determination of $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$, a Compound Previously Assigned Cs_2VF_6 Composition," *J. Solid State Chem.*, vol. 29, no. 2, pp. 195–204, 1979.
 - [181] R. Mattes and H. Foerster, "The Crystal Structure of 'Green' $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$ and Its Relationship to 'Blue' $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$," *J. Solid State Chem.*, vol. 45, no. 1, pp. 154–157, 1982.
 - [182] M. Schabert, G. Pausewang, and W. Massa, "Kristallstruktur und spektroskopische Daten von $\text{Rb}_2[\text{VOF}_4(\text{H}_2\text{O})]$," *Zeitschrift für Anorg. und Allg. Chemie*, vol. 506, no. 11, pp. 169–177, 1983.
 - [183] M. D. Donakowski *et al.*, "The Role of Polar, Lambda (Λ)-Shaped Building Units in Noncentrosymmetric Inorganic Structures," *J. Am. Chem. Soc.*, vol. 134, no. 18, pp. 7679–7689, 2012.
 - [184] H. Rieskamp and R. Mattes, "Fluorreiche Oxofluorovanadate(V): Die Kristallstruktur von $[\text{enH}_2][\text{VOF}_5]$," *Zeitschrift für Naturforsch. B*, vol. 31, no. 11, pp. 1453–1455, 1976.
 - [185] R. Stomberg, "Crystal Structure of Sodium Pentafluorooxovanadate(V), $\text{Na}_2[\text{VF}_5\text{O}]$, and Potassium catena- μ -Fluoro-difluorodioxovanadate(V), $\text{K}_2\text{n}[(\text{VF}_3\text{O}_2)_\text{n}]$, Two Decomposition Products in the System $\text{V}_2\text{O}_5/(\text{MF}, \text{HF})/\text{H}_2\text{O}_2/\text{H}_2\text{O}$," *Acta Chem. Scand.*, vol. 40A, pp. 325–330, 1986.
 - [186] M. E. Welk, A. J. Norquist, C. L. Stern, and K. R. Poeppelmeier, "The Structure-Directing Properties of $[\text{VOF}_5]^{2-}$," *Inorg. Chem.*, vol. 39, no. 18, pp. 3946–3947, 2000.
 - [187] M. D. Donakowski *et al.*, "Syntheses of Two Vanadium Oxide–Fluoride Materials That Differ in Phase Matchability," *Inorg. Chem.*, vol. 54, no. 3, pp. 765–772, 2015.
 - [188] R. Stomberg, "The Crystal Structure of Potassium Fluorooxidiperoxovanadate(V), $\text{K}_2[\text{VFO}(\text{O}_2)_2]$," *Acta Chem. Scand.*, vol. 38A, pp. 223–228, 1984.
 - [189] R. Stomberg and S. Olson, "The Disordered Structure of Cesium Fluorooxidiperoxovanadate(2–), $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$," *Acta Chem. Scand.*, vol. 38A, pp. 821–823, 1984.
 - [190] G. A. Senchyk, A. B. Lysenko, E. B. Rusanov, and K. V. Domasevitch, "Crystal structure of tetrakis[μ -3-carboxy-1-(1,2,4-triazol-4-yl)adamantane- κ 2N1:N2]tetrafluoridodi- μ 2-oxido-dioxidodisilver(I)divanadium(V) tetrahydrate," *Acta Crystallogr. Sect. E*, vol. 75, no. 6, pp. 808–811, 2019.
 - [191] H. Yu, M. L. Nisbet, and K. R. Poeppelmeier, "Assisting the Effective Design of Polar Iodates with Early Transition-Metal Oxide Fluoride Anions," *J. Am. Chem. Soc.*, vol. 140, no. 28, pp. 8868–8876, 2018.
 - [192] D. W. Aldous and P. Lightfoot, "Crystallisation of some mixed Na/V and K/V fluorides by solvothermal methods," *Solid State Sci.*, vol. 11, no. 2, pp. 315–319, 2009.

- [193] R. Mattes and H. Förster, "STRUCTURAL AND SPECTROSCOPIC STUDIES OF Cs₃V₂O₄F₅ AND OF ISOSTRUCTURAL PHASES IN THE Cs₃Mo₂O₆F₃–Cs₃V₂O₂F₇ AND Cs₃Mo₂O₆F₃–Cs₃V₂O₄F₅ SYSTEMS," *J. Less Common Met.*, vol. 87, no. 2, pp. 237–247, 1982.
- [194] M. Holland *et al.*, "Polar Alignment of Λ-Shaped Basic Building Units within Transition Metal Oxide Fluoride Materials," *Inorg. Chem.*, vol. 53, no. 1, pp. 221–228, 2014.
- [195] A. E. Lapshin, Y. I. Smolin, Y. F. Shepelev, P. Schwendt, and D. Gyepesova, "Structure of tripotassium μ-fluoro-μ-peroxo-bis(fluorooxoperoxovanadate)(3–) hydrogen fluoride dihydrate," *Acta Crystallogr. Sect. C*, vol. 46, no. 10, pp. 1753–1755, 1990.
- [196] J. Chrappová, P. Schwendt, M. Sivák, M. Repiský, V. G. Malkin, and J. Marek, "Dinuclear fluoro-peroxovanadium(v) complexes with symmetric and asymmetric peroxo bridges: syntheses, structures and DFT studies," *Dalt. Trans.*, no. 3, pp. 465–473, 2009.
- [197] M.-L. Liang, Y.-X. Ma, C.-L. Hu, F. Kong, and J.-G. Mao, "A(VO₂F)(SeO₃) (A = Sr, Ba) and Ba(MOF₂)(TeO₄) (M = Mo, W): first examples of alkali-earth selenites/tellurites with a fluorinated d⁰-TM octahedron," *Dalt. Trans.*, vol. 47, no. 5, pp. 1513–1519, 2018.
- [198] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, and G. C. Verschoor, "Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen–Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate," *Dalt. Trans.*, no. 7, pp. 1349–1356, 1984.
- [199] J. V. Hatton, Y. Saito, and W. G. Schneider, "NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS OF SOME GROUP V METAL FLUORIDES AND OXYIONS," *Can. J. Chem.*, vol. 43, no. 1, pp. 47–56, 1965.
- [200] J. A. S. Howell and K. C. Moss, "Nuclear Magnetic Resonance Studies on Fluorine-containing Compounds. Part III. The Tetrafluoro-oxovandate(V) Ion," *J. Chem. Soc. A*, no. 0, pp. 270–272, 1971.
- [201] G. W. Bushnell and K. C. Moss, "The Crystal Structure of Caesium Oxotetrafluorovanadate(V)," *Can. J. Chem.*, vol. 50, no. 22, pp. 3700–3705, 1972.
- [202] H. Rieskamp and R. Mattes, "Darstellung, Schwingungsspektren und Struktur von Oxotetrafluorovanadaten MIVOF₄ (MI = Na, K, Rb, Cs, Tl, (CH₃)₄N)," *Zeitschrift für Anorg. und Allg. Chemie*, vol. 401, no. 2, pp. 158–164, 1973.
- [203] M. Lozinšek, E. Goresnik, and B. Žemva, "Silver(I) Tetrafluoridooxidovanadate(V) – Ag[VOF₄]," *Acta Chim. Slov.*, vol. 61, no. 3, pp. 542–547, 2014.
- [204] M. K. Chaudhuri, H. S. Dasgupta, S. K. Ghosh, and D. T. Khathing, "SYNTHESIS OF ALKALI OXYTETRAFLUOROVANADATES(V)," *Synth. React. Inorg. Met. Chem.*, vol. 12, no. 1, pp. 63–69, 1982.
- [205] R. J. Gillespie and U. R. K. Rao, "51V and 19F N.M.R. Study of VO₂F₄3– in Solution," *Chem. Commun.*, no. 8, pp. 422–423, 1983.
- [206] R. C. Hibbert, "A 51V and 19F N.M.R. Study of Vanadium(v) Oxide Fluoride Complexes Displaying Vanadium–Fluorine Coupling," *Chem. Commun.*, no. 6, pp.

- 317–318, 1985.
- [207] W. Priebsch and D. Rehder, “Preparation and ^{51}V NMR Characteristics of Oxovanadium(V) Compounds. Relation between Metal Shielding and Ligand Electronegativity,” *Inorg. Chem.*, vol. 24, no. 19, pp. 3058–3062, 1985.
 - [208] R. C. Hibbert, “Vanadium(v) Fluoride Complexes in Organic Solvents. A Vanadium-51 and Fluorine-19 Nuclear Magnetic Resonance Study,” *Dalt. Trans.*, no. 4, pp. 751–753, 1986.
 - [209] M. Lozinšek, E. Goreschnik, and B. Žemva, “Lead Fluoridooxidovanadates(V), $\text{Pb}(\text{V}_2\text{O}_2\text{F}_8)$, $\text{Pb}(\text{VOF}_5)$, and Mixed Valent Fluoridooxidovanadate(IV,V), $\text{Pb}_3\text{F}(\text{V}_4\text{O}_3\text{F}_{18})$,” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 638, no. 12–13, pp. 2123–2128, 2012.
 - [210] N. G. Furmanova, I. A. Verin, A. N. Zozulin, and E. G. Il'in, “кристаллическая структура $[\text{NEt}_3\text{H}][\text{NbOF}_4(\text{H}_2\text{O})]$,” *Kristallografiya*, vol. 37, no. 1, pp. 136–140, 1992.
 - [211] L. Arnaudet *et al.*, “Preparation, Characterization, and Crystal Structure of the Adducts $\text{WOF}_4 \cdot n\text{C}_5\text{H}_5\text{N}$ ($n = 1, 2$),” *Inorg. Chem.*, vol. 28, no. 2, pp. 257–262, 1989.
 - [212] L. Arnaudet, R. Bougon, B. Buu, M. Lance, M. Nierlich, and J. Vigner, “Preparation, Characterization, and Crystal Structure of the Adducts $\text{WF}_6 \cdot \text{F-py}$ and $\text{WOF}_4 \cdot \text{F-py}$ ($\text{F-py} = 2\text{-Fluoropyridine}$),” *Inorg. Chem.*, vol. 32, no. 7, pp. 1142–1146, 1993.
 - [213] D. Turnbull, S. D. Wetmore, and M. Gerken, “Synthesis, Characterization, and Lewis Acid Behavior of $[\text{W}(\text{NC}_6\text{F}_5)\text{F}_4]_x$ and Computational Study of $\text{W}(\text{NR})\text{F}_4$ ($\text{R} = \text{H}, \text{F}, \text{CH}_3, \text{CF}_3, \text{C}_6\text{H}_5, \text{C}_6\text{F}_5$), $\text{W}(\text{NC}_6\text{F}_5)\text{F}_4(\text{NCCH}_3)$, and $\text{W}(\text{NC}_6\text{F}_5)\text{F}_4(\text{NC}_5\text{H}_5)_n$ ($n = 1, 2$),” *Inorg. Chem.*, vol. 58, no. 9, pp. 6363–6375, 2019.
 - [214] W. Levason, G. Reid, and W. Zhang, “Coordination complexes of the tungsten(VI) oxide fluorides WOF_4 and WO_2F_2 with neutral oxygen- and nitrogen-donor ligands,” *J. Fluor. Chem.*, vol. 184, pp. 50–57, 2016.
 - [215] W. Levason, F. M. Monzittu, G. Reid, W. Zhang, and E. G. Hope, “Complexes of molybdenum(VI) oxide tetrafluoride and molybdenum(VI) dioxide difluoride with neutral N- and O-donor ligands,” *J. Fluor. Chem.*, vol. 200, pp. 190–197, 2017.
 - [216] P. A. Tucker, P. A. Taylor, J. H. Holloway, and D. R. Russell, “The Adduct $\text{XeF}_2 \cdot \text{WOF}_4$,” *Acta Crystallogr. Sect. B*, vol. 31, no. 3, pp. 906–908, 1975.
 - [217] M. Kunz and I. D. Brown, “Out-of-Center Distortions around Octahedrally Coordinated d_0 Transition Metals,” *J. Solid State Chem.*, vol. 115, no. 2, pp. 395–406, 1995.
 - [218] M. E. Welk, A. J. Norquist, F. P. Arnold, C. L. Stern, and K. R. Poeppelmeier, “Out-of-Center Distortions in d_0 Transition Metal Oxide Fluoride Anions,” *Inorg. Chem.*, vol. 41, no. 20, pp. 5119–5125, 2002.
 - [219] H. K. Izumi, J. E. Kirsch, C. L. Stern, and K. R. Poeppelmeier, “Examining the Out-of-Center Distortion in the $[\text{NbOF}_5]^{2-}$ Anion,” *Inorg. Chem.*, vol. 44, no. 4, pp. 884–895, 2005.
 - [220] K. C. Moss, “Nuclear Magnetic Resonance Studies on Fluorine-containing

- Compounds. Part II. Reactions of Niobium Pentafluoride with Organic Donor Molecules," *J. Chem. Soc. A*, no. 0, pp. 1224–1226, 1970.
- [221] J. A. S. Howell and K. C. Moss, "Nuclear Magnetic Resonance Studies on Fluorine-containing Compounds. Part V. Reactions of Tantalum Pentafluoride with Organic Donor Molecules," *J. Chem. Soc. A*, no. 0, pp. 2483–2487, 1971.
- [222] J. C. Fuggle, D. W. A. Sharp, and J. M. Winfield, "NIOBIUM, TANTALUM AND MOLYBDENUM PENTAFLUORIDE COMPLEXES WITH ORGANIC LIGANDS," *J. Fluor. Chem.*, vol. 1, no. 4, pp. 427–431, 1972.
- [223] "Our unpublished study on adducts of MF₅ (M = As, Sb, Nb, Ta) with nitrile ligands." .
- [224] E. L. Muetterties and W. D. Phillips, "Structure and Exchange Processes in Some Inorganic Fluorides by Nuclear Magnetic Resonance," *J. Am. Chem. Soc.*, vol. 81, no. 5, pp. 1084–1088, 1959.
- [225] T. K. Davies and K. C. Moss, "Nuclear Magnetic Resonance Studies on Fluorine-containing Compounds. Part I. Antimony Pentafluoride and its Reactions with Antimony Trifluoride, Arsenic Trifluoride, and Niobium Pentafluoride," *J. Chem. Soc. A*, no. 0, pp. 1054–1058, 1970.
- [226] T. Nakajima, B. Žemva, and A. Tressaud, *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications*, First. Lausanne, Switzerland: Elsevier Science, S.A., 2000.
- [227] I. C. Tornieporth-Oetting, T. M. Klapötke, T. S. Cameron, J. Valkonen, P. Rademacher, and K. Kowski, "Reactivity of Lewis Acids towards Nitriles; Crystal Structure and Electron Deformation Density of C₂N₂ · SbF₅ and Photoelectron Spectrum of AsF₅," *Dalt. Trans.*, no. 4, pp. 537–543, 1992.
- [228] T. Saal, K. O. Christe, and R. Haiges, "Lewis adduct formation of hydrogen cyanide and nitriles with arsenic and antimony pentafluoride," *Dalt. Trans.*, vol. 48, no. 1, pp. 99–106, 2019.
- [229] R. Haiges *et al.*, "Protonation of nitriles: isolation and characterization of alkyl- and aryltrilium ions," *Dalt. Trans.*, vol. 45, no. 20, pp. 8494–8499, 2016.
- [230] N. C. Deno, R. W. Gaugler, and M. J. Wisotsky, "The Base Strengths and Chemical Behavior of Nitriles in Sulfuric Acid and Oleum Systems," *J. Org. Chem.*, vol. 31, no. 6, pp. 1967–1968, 1966.
- [231] G. A. Olah and T. E. Kiovsky, "Stable Carbonium Ions. LXV. Protonation of Hydrogen Cyanide and Alkyl nitriles in FSO₃H–SbF₅–SO₂ Solution. Comparative Study of Meerwein's N-Alkyltrilium Ions," *J. Am. Chem. Soc.*, vol. 90, no. 17, pp. 4666–4672, 1968.
- [232] T. van Dijk, J. C. Slootweg, and K. Lammertsma, "Nitrilium ions – synthesis and applications," *Org. Biomol. Chem.*, vol. 15, no. 48, pp. 10134–10144, 2017.
- [233] K. Hoesch, "Eine neue Synthese aromatischer Ketone. I. Darstellung einiger Phenolketone," *Berichte der Dtsch. Chem. Gesellschaft*, vol. 48, no. 1, pp. 1122–1133, 1915.
- [234] J. Houben, "Über die Kern-Kondensation von Phenolen und Phenol-äthern mit Nitrilen zu Phenol- und Phenol-äther-Ketimiden und -Ketonen," *Berichte der Dtsch. Chem. Gesellschaft*, vol. 59, no. 11, pp. 2878–2891, 1926.
- [235] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, "Über tertiäre

- Oxoniumsalze," *J. für Prakt. Chemie*, vol. 147, no. 10–12, pp. 257–285, 1937.
- [236] I. Stahl and D. G. Seapy, "Trimethyloxonium Tetrafluoroborate," in *Encyclopedia of Reagents for Organic Synthesis*, Second., Chichester, UK: John Wiley & Sons, Ltd., 2009.
- [237] H. Perst and D. G. Seapy, "Triethyloxonium Tetrafluoroborate," in *Encyclopedia of Reagents for Organic Synthesis*, Second., Chichester, UK: John Wiley & Sons, Ltd., 2009.
- [238] F. Klages and W. Grill, "Untersuchungen in der Reihe der Nitrilium-Salze 5. Mitteilung über Oniumsalze," *Justus Liebigs Ann. Chem.*, vol. 594, no. 1, pp. 21–32, 1955.
- [239] H. Meerwein, P. Laasch, R. Mersch, and J. Spille, "Über Nitriliumsalze, I. Mitteil," *Chem. Ber.*, vol. 89, no. 2, pp. 209–224, 1956.
- [240] R. Keese, F. Berdat, and P. Macchi, "Stereoselectivity of Additions to N-Methyl Acetonitrilium Fluorosulfonate," *J. Org. Chem.*, vol. 78, no. 5, pp. 1965–1970, 2013.
- [241] T. van Dijk *et al.*, "Facile Synthesis of Phosphaamidines and Phosphaamidines using Nitrilium Ions as an Imine Synthon," *Angew. Chemie Int. Ed.*, vol. 53, no. 34, pp. 9068–9071, 2014.
- [242] T. van Dijk, M. S. Bakker, F. Holtrop, M. Nieger, J. C. Slootweg, and K. Lammertsma, "Base-Stabilized Nitrilium Ions as Convenient Imine Synthons," *Org. Lett.*, vol. 17, no. 6, pp. 1461–1464, 2015.
- [243] R. G. Giles, H. Heaney, and M. J. Plater, "Reactions of nitrilium salts with indole and pyrrole and their derivatives in the synthesis of imines, ketones and secondary amines," *Tetrahedron*, vol. 71, no. 39, pp. 7367–7385, 2015.
- [244] K. O. Christe, C. J. Schack, and R. D. Wilson, "Novel Onium Salts. Synthesis and Characterization of $\text{OH}_3^+\text{SbF}_6^-$ and $\text{OH}_3^+\text{AsF}_6^-$," *Inorg. Chem.*, vol. 14, no. 9, pp. 2224–2230, 1975.
- [245] E. M. Larson, K. D. Abney, A. C. Larson, and P. G. Eller, "Structure of Oxonium Hexafluoroantimonate(V)," *Acta Crystallogr. Sect. B*, vol. 47, no. 2, pp. 206–209, 1991.
- [246] D. Mootz and K. Bartmann, "The Fluoronium Ions H_2F^+ and H_3F_2^+ : Characterization by Crystal Structure Analysis," *Angew. Chemie Int. Ed.*, vol. 27, no. 3, pp. 391–392, 1988.
- [247] R. J. Gillespie and K. C. Moss, "The Hydrogen Fluoride Solvent System. Part I. Solutions of Antimony Pentafluoride and Antimony Tetrafluoride Monofluorosulphate," *J. Chem. Soc. A*, vol. 0, no. 0, pp. 1170–1175, 1966.
- [248] P. M. Esteves, A. Ramírez-Solís, and C. J. A. Mota, "The Nature of Superacid Electrophilic Species in HF/SbF_5 : A Density Functional Theory Study," *J. Am. Chem. Soc.*, vol. 124, no. 11, pp. 2672–2677, 2002.
- [249] G. A. Olah, K. Leeli, Q. Wang, and G. K. S. Prakash, *Onium Ions*. New York, New York, USA: John Wiley & Sons, Inc., 1998.
- [250] B. L. Booth, K. O. Jibodu, and M. F. J. R. P. Proença, "The Chemistry of Nitrilium Salts. Part 2. The Preparation of Nitrilium Trifluoromethanesulphonate Salts and Their Reactions with Some Oxygen and Sulphur Nucleophiles," *Perkin Trans. 1*, no. 0, pp. 1067–1073, 1983.

- [251] M. I. Amer, B. L. Booth, G. F. M. Noori, and M. F. J. R. P. Proença, "The Chemistry of Nitrilium Salts. Part 3. The Importance of Triazinium Salts in Houben–Hoesch Reactions Catalyzed by Trifluoromethanesulphonic Acid," *Perkin Trans. 1*, no. 0, pp. 1075–1082, 1983.
- [252] P. Puthiaraj, Y.-R. Lee, S. Zhang, and W.-S. Ahn, "Triazine-based covalent organic polymers: design, synthesis and applications in heterogeneous catalysis," *J. Mater. Chem. A*, vol. 4, no. 42, pp. 16288–16311, 2016.
- [253] H. Wang *et al.*, "Covalent triazine frameworks for carbon dioxide capture," *J. Mater. Chem. A*, vol. 7, no. 40, pp. 22848–22870, 2019.
- [254] Y. Zhang and S. Jin, "Recent Advancements in the Synthesis of Covalent Triazine Frameworks for Energy and Environmental Applications," *Polymers (Basel)*, vol. 11, no. 1, p. 31, 2019.
- [255] N. Tahir, C. Krishnaraj, K. Leus, and P. Van Der Voort, "Development of Covalent Triazine Frameworks as Heterogeneous Catalytic Supports," *Polymers (Basel)*, vol. 11, no. 8, p. 1326, 2019.
- [256] M. Liu, L. Guo, S. Jin, and B. Tan, "Covalent triazine frameworks: synthesis and applications," *J. Mater. Chem. A*, vol. 7, no. 10, pp. 5153–5172, 2019.
- [257] C. Krishnaraj, H. S. Jena, K. Leus, and P. Van Der Voort, "Covalent triazine frameworks – a sustainable perspective," *Green Chem.*, vol. 22, no. 4, pp. 1038–1071, 2020.
- [258] S. Biswas and S. Batra, "One-Step Synthesis of 2-Amino-5H-pyrimido[5,4-b]indoles, Substituted 2-(1,3,5-triazin-2-yl)-1H-indoles, and 1,3,5-Triazines from Aldehydes," *European J. Org. Chem.*, vol. 2012, no. 18, pp. 3492–3499, 2012.
- [259] Q. You *et al.*, "Synthesis of 1,3,5-triazines via Cu(OAc)₂-catalyzed aerobic oxidative coupling of alcohols and amidine hydrochlorides," *Org. Biomol. Chem.*, vol. 13, no. 24, pp. 6723–6727, 2015.
- [260] A. R. Tiwari, A. T., and B. M. Bhanage, "NIS-catalyzed oxidative cyclization of alcohols with amidines: a simple and efficient transition-metal free method for the synthesis of 1,3,5-triazines," *Org. Biomol. Chem.*, vol. 13, no. 45, pp. 10973–10976, 2015.
- [261] F. C. Schaefer and G. A. Peters, "Synthesis of the s-Triazine System. III. Trimerization of Imidates," *J. Org. Chem.*, vol. 26, no. 8, pp. 2778–2784, 1961.
- [262] D. Janietz and M. Bauer, "A New Facile Synthesis of 2-Substituted 4,6-Diphenyl-1,3,5-triazines," *Synthesis (Stuttg.)*, vol. 1993, no. 1, pp. 33–34, 1993.
- [263] H. Zhong *et al.*, "New Optoelectronic Materials Based on Bitriazines: Synthesis and Properties," *Org. Lett.*, vol. 10, no. 5, pp. 709–712, 2008.
- [264] L. Hintermann, L. Xiao, and A. Labonne, "A General and Selective Copper-Catalyzed Cross-Coupling of Tertiary Grignard Reagents with Azacyclic Electrophiles," *Angew. Chemie Int. Ed.*, vol. 47, no. 43, pp. 8246–8250, 2008.
- [265] T. L. Cairns, A. W. Larchar, and B. C. McKusick, "The Trimerization of Nitriles at High Pressures," *J. Am. Chem. Soc.*, vol. 74, no. 22, pp. 5633–5636, 1952.
- [266] I. S. Bengelsdorf, "High Pressure-High Temperature Reactions. I. The Trimerization of Aromatic Nitriles," *J. Am. Chem. Soc.*, vol. 80, no. 6, pp. 1442–1444, 1958.
- [267] W. Jarre, D. Bieniek, and F. Korte, "SYNTHESE UND REAKTIONEN VON

- SYMMETRISCH SUBSTITUIERTEN S-TRIAZINEN UNTER HOHEM DRUCK," *Tetrahedron*, vol. 31, no. 6, pp. 619–623, 1975.
- [268] J. H. Forsberg *et al.*, "Use of Lanthanide(III) Ions as Catalysts for the Reactions of Amines with Nitriles," *J. Org. Chem.*, vol. 52, no. 6, pp. 1017–1021, 1987.
- [269] J. H. Forsberg, V. T. Spaziano, S. P. Klump, and K. M. Sanders, "Lanthanide(III) Ion Catalyzed Reaction of Ammonia and Nitriles: Synthesis of 2,4,6-Trisubstituted-s-triazines," *J. Heterocycl. Chem.*, vol. 25, no. 3, pp. 767–770, 1988.
- [270] A. M. Garcia, D. M. Bassani, J.-M. Lehn, G. Baum, and D. Fenske, "Self-Assembly of Multicomponent Multimetallic Lead(II) Complexes of Cylindrical Architecture," *Chem. - A Eur. J.*, vol. 5, no. 4, pp. 1234–1238, 1999.
- [271] A. de la Hoz, A. Díaz-Ortiz, J. Elguero, L. J. Martínez, A. Moreno, and A. Sánchez-Migallón, "Solvent-free preparation of tris-pyrazolyl-1,3,5-triazines," *Tetrahedron*, vol. 57, no. 20, pp. 4397–4403, 2001.
- [272] F. Xu, J.-H. Sun, H.-B. Yan, and Q. Shen, "CYCLOTRIMERIZATION OF NITRILES CATALYZED BY SmI₂/AMINES: SYNTHESIS OF 2,4,6-TRISUBSTITUTED-S-TRIAZINES," *Synth. Commun.*, vol. 30, no. 6, pp. 1017–1022, 2000.
- [273] F. Xu, X.-H. Zhu, Q. Shen, J. Lu, and J.-Q. Li, "Catalytic Cyclotrimerization of Arylnitriles Using the Novel Samarium(II) Complexes as Catalysts," *Chinese J. Chem.*, vol. 20, no. 11, pp. 1334–1339, 2002.
- [274] H. L. Anderson, S. Anderson, and J. K. M. Sanders, "Ligand binding by butadiyne-linked porphyrin dimers, trimers and tetramers," *Perkin Trans. 1*, no. 18, pp. 2231–2245, 1995.
- [275] T. Murase and M. Fujita, "Highly Blue Luminescent Triazine–Amine Conjugated Oligomers," *J. Org. Chem.*, vol. 70, no. 23, pp. 9269–9278, 2005.
- [276] G. Thiele, B. Wagner, and S. Dehnen, "Solvothermal Reactions in and with Nitriles," *Eur. J. Inorg. Chem.*, vol. 2015, no. 32, pp. 5329–5334, 2015.
- [277] F. W. Swamer, G. A. Reynolds, and C. R. Hauser, "ACTION OF BASIC REAGENTS ON BENZONITRILE TO FORM TRIAZINES," *J. Org. Chem.*, vol. 16, no. 1, pp. 43–46, 1951.
- [278] J. J. Ritter and R. D. Anderson, "Trimerization of Benzonitrile with Sodium," *J. Org. Chem.*, vol. 24, no. 2, pp. 208–210, 1959.
- [279] F. H. Case and E. Koft, "The Synthesis of Certain Substituted 1,3,5-Triazines Containing the Ferriin Group," *J. Am. Chem. Soc.*, vol. 81, no. 4, pp. 905–906, 1959.
- [280] W. Zhang, S. Liao, Y. Xu, and Y. Zhang, "APPLICATION OF ALKALI METAL HYDRIDES OF NANOMETRIC SIZE IN REDUCTION, CYCLOTRIMERIZATION AND METALATION," *Synth. Commun.*, vol. 27, no. 22, pp. 3977–3983, 1997.
- [281] S. Hayami and K. Inoue, "Structure and Magnetic Property of the Organic Triradical with Triazine Skeleton; 2,4,6-Tris{p-(N-oxy-N-tert-butylamino)phenyl}triazine," *Chem. Lett.*, vol. 28, no. 7, pp. 545–546, 1999.
- [282] A. Herrera, R. Martínez-Alvarez, P. Ramiro, M. Chioua, and R. Chioua, "A Practical and Easy Synthesis of 2,4,6-Trisubstituted-s-triazines," *Synthesis (Stuttg.)*,

- no. 4, pp. 503–505, 2004.
- [283] G. E. Salnikov, A. M. Genaev, V. G. Vasiliev, and V. G. Shubin, “Interaction of acetonitrile with trifluoromethanesulfonic acid: unexpected formation of a wide variety of structures,” *Org. Biomol. Chem.*, vol. 10, no. 11, pp. 2282–2288, 2012.
- [284] K. Wakabayashi, M. Tsunoda, and Y. Suzuki, “Studies on s-Triazines. I. Cotrimerization of Trichloroacetonitrile with Other Nitriles,” *Bull. Chem. Soc. Jpn.*, vol. 42, no. 10, pp. 2924–2930, 1969.
- [285] S. Yanagida, M. Yokoe, I. Katagiri, M. Ohoka, and S. Komori, “Studies on Nitrile Salts. IV. Trimerization of Nitriles to 1,3,5-Triazines by the Combined Catalyst $\text{PCl}_5\text{--HCl}$,” *Bull. Chem. Soc. Jpn.*, vol. 46, no. 1, pp. 306–310, 1973.
- [286] T. J. Podesta and A. G. Orpen, “Tris(Pyridinium)Triazine in Crystal Synthesis of 3-Fold Symmetric Structures,” *Cryst. Growth Des.*, vol. 5, no. 2, pp. 681–693, 2005.
- [287] D. Cui, M. Nishiura, and Z. Hou, “Lanthanide-Imido Complexes and Their Reactions with Benzonitrile,” *Angew. Chemie Int. Ed.*, vol. 44, no. 6, pp. 959–962, 2005.
- [288] A. Díaz-Ortiz, A. de la Hoz, A. Moreno, A. Sánchez-Migallón, and G. Valiente, “Synthesis of 1,3,5-triazines in solvent-free conditions catalysed by silica-supported lewis acids,” *Green Chem.*, vol. 4, no. 4, pp. 339–343, 2002.
- [289] Z. Deng, W. Qiu, W. Li, and Y. Li, “Cyclotrimerization of nitriles catalyzed by Li_3N ,” *Chinese Sci. Bull.*, vol. 49, no. 2, p. 127, 2004.
- [290] P. Kuhn, M. Antonietti, and A. Thomas, “Porous, Covalent Triazine-Based Frameworks Prepared by Ionothermal Synthesis,” *Angew. Chemie Int. Ed.*, vol. 47, no. 18, pp. 3450–3453, 2008.
- [291] P. Kuhn, A. Forget, D. Su, A. Thomas, and M. Antonietti, “From Microporous Regular Frameworks to Mesoporous Materials with Ultrahigh Surface Area: Dynamic Reorganization of Porous Polymer Networks,” *J. Am. Chem. Soc.*, vol. 130, no. 40, pp. 13333–13337, 2008.
- [292] S. Ren *et al.*, “Porous, Fluorescent, Covalent Triazine-Based Frameworks Via Room-Temperature and Microwave-Assisted Synthesis,” *Adv. Mater.*, vol. 24, no. 17, pp. 2357–2361, 2012.
- [293] D. B. G. Williams and M. Lawton, “Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants,” *J. Org. Chem.*, vol. 75, no. 24, pp. 8351–8354, 2010.
- [294] L. Hintermann, “Expedient syntheses of the N-heterocyclic carbene precursor imidazolium salts $\text{IPr} \cdot \text{HCl}$, $\text{IMes} \cdot \text{HCl}$ and $\text{IXy} \cdot \text{HCl}$,” *Beilstein J. Org. Chem.*, vol. 3, no. 1, p. 22, 2007.
- [295] B. Alič and G. Tavčar, “Reaction of N-heterocyclic carbene (NHC) with different HF sources and ratios – A free fluoride reagent based on imidazolium fluoride,” *J. Fluor. Chem.*, vol. 192, no. Part A, pp. 141–146, 2016.
- [296] G. A. Kolta, D. W. A. Sharp, and J. M. Winfield, “SUBSTITUTION AND REDOX REACTIONS INVOLVING VANADIUM OXOTRIFLUORIDE,” *J. Fluor. Chem.*, vol. 14, no. 2, pp. 153–162, 1979.
- [297] HORIBA Jobin Yvon, *LabSpec 5*, 5.78.24. Villeneuve d’Ascq, France: HORIBA Jobin Yvon Molecular & Microanalysis Division, 2010.

- [298] Mestrelab Research, *MestReNova 11 EDIT*, 11.0.3-186. Santiago de Compostela, Spain: Mestrelab Research, 2017.
- [299] Rigaku Corporation, *CrysAlisPro Software System*, 171.39.46. Oxford, UK: Rigaku Oxford Diffraction, 2013.
- [300] R. C. Clark and J. S. Reid, “The Analytical Calculation of Absorption in Multifaceted Crystals,” *Acta Crystallogr. Sect. A*, vol. 51, no. 6, pp. 887–897, 1995.
- [301] G. M. Sheldrick, “SHELXT – Integrated space-group and crystal-structure determination,” *Acta Crystallogr. Sect. A*, vol. 71, no. 1, pp. 3–8, 2015.
- [302] G. M. Sheldrick, “Crystal structure refinement with SHELXL,” *Acta Crystallogr. Sect. C*, vol. 71, no. 1, pp. 3–8, 2015.
- [303] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, “OLEX2: a complete structure solution, refinement and analysis program,” *J. Appl. Crystallogr.*, vol. 42, no. 2, pp. 339–341, 2009.
- [304] K. Brandenburg, *Diamond - Crystal and Molecular Structure Visualization*, 4.5.3. Bonn, Germany: Crystal Impact, 2018.
- [305] M. J. Frisch *et al.*, *Gaussian 16*, Rev. B.01. Wallingford, Connecticut, USA: Gaussian, 2016.
- [306] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized Gradient Approximation Made Simple,” *Phys. Rev. Lett.*, vol. 77, no. 18, pp. 3865–3868, 1996.
- [307] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, “A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu,” *J. Chem. Phys.*, vol. 132, no. 15, p. 154104, 2010.
- [308] S. Grimme, S. Ehrlich, and L. Goerigk, “Effect of the Damping Function in Dispersion Corrected Density Functional Theory,” *J. Comput. Chem.*, vol. 32, no. 7, pp. 1456–1465, 2011.
- [309] F. Weigend and R. Ahlrichs, “Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy,” *Phys. Chem. Chem. Phys.*, vol. 7, no. 18, pp. 3297–3305, 2005.
- [310] F. Weigend, “Accurate Coulomb-fitting basis sets for H to Rn,” *Phys. Chem. Chem. Phys.*, vol. 8, no. 9, pp. 1057–1065, 2006.
- [311] D. Vanderbilt, “Soft self-consistent pseudopotentials in a generalized eigenvalue formalism,” *Phys. Rev. B*, vol. 41, no. 11, pp. 7892–7895, 1990.
- [312] P. Giannozzi *et al.*, “Advanced capabilities for materials modelling with Quantum ESPRESSO,” *J. Phys. Condens. Matter*, vol. 29, no. 46, p. 465901, 2017.
- [313] S. Grimme, “Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction,” *J. Comput. Chem.*, vol. 27, no. 15, pp. 1787–1799, 2006.
- [314] V. Barone, M. Casarin, D. Forrer, M. Pavone, M. Sambi, and A. Vittadini, “Role and Effective Treatment of Dispersive Forces in Materials: Polyethylene and Graphite Crystals as Test Cases,” *J. Comput. Chem.*, vol. 30, no. 6, pp. 934–939, 2009.
- [315] W. Tang, E. Sanville, and G. Henkelman, “A grid-based Bader analysis algorithm without lattice bias,” *J. Phys. Condens. Matter*, vol. 21, no. 8, p. 084204, 2009.
- [316] A. Arnaldsson, W. Tang, S. Chill, W. Chai, and G. Henkelman, *Computer Program*

- for *Bader Charge Analysis*, 1.03. Austin, Texas, USA, 2017.
- [317] P. E. Blöchl, “Projector augmented-wave method,” *Phys. Rev. B*, vol. 50, no. 24, pp. 17953–17979, 1994.
- [318] A. Kokalj, “XCrySDen—a new program for displaying crystalline structures and electron densities,” *J. Mol. Graph. Model.*, vol. 17, no. 3–4, pp. 176–179, 1999.
- [319] T. H. Dunning, “Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen,” *J. Chem. Phys.*, vol. 90, no. 2, pp. 1007–1023, 1989.
- [320] R. A. Kendall, T. H. Dunning, and R. J. Harrison, “Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions,” *J. Chem. Phys.*, vol. 96, no. 9, pp. 6796–6806, 1992.
- [321] D. E. Woon and T. H. Dunning, Jr., “Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon,” *J. Chem. Phys.*, vol. 98, no. 2, pp. 1358–1371, 1993.
- [322] A. K. Wilson, D. E. Woon, K. A. Peterson, and T. H. Dunning, Jr., “Gaussian basis sets for use in correlated molecular calculations. IX. The atoms gallium through krypton,” *J. Chem. Phys.*, vol. 110, no. 16, pp. 7667–7676, 1999.
- [323] Ž. Zupanek, M. Tramšek, A. Kokalj, and G. Tavčar, “The peculiar case of conformations in coordination compounds of group V pentahalides with N-heterocyclic carbene and synthesis of their imidazolium salts,” *J. Fluor. Chem.*, vol. 227, p. 109373, 2019.
- [324] Ž. Zupanek, M. Tramšek, A. Kokalj, and G. Tavčar, “Reactivity of VOF₃ with N-Heterocyclic Carbene and Imidazolium Fluoride: Analysis of Ligand–VOF₃ Bonding with Evidence of a Minute π Back-Donation of Fluoride,” *Inorg. Chem.*, vol. 57, no. 21, pp. 13866–13879, 2018.
- [325] F. Marchetti and G. Pampaloni, “Interaction of niobium and tantalum pentahalides with O-donors: coordination chemistry and activation reactions,” *Chem. Commun.*, vol. 48, no. 5, pp. 635–653, 2012.
- [326] W. Levason, F. M. Monzittu, and G. Reid, “Coordination chemistry and applications of medium/high oxidation state metal and non-metal fluoride and oxide-fluoride complexes with neutral donor ligands,” *Coord. Chem. Rev.*, vol. 391, pp. 90–130, 2019.
- [327] A. J. Arduengo III, F. Davidson, R. Krafczyk, W. J. Marshall, and R. Schmutzler, “Carbene Complexes of Pnictogen Pentafluorides and Boron Trifluoride,” *Monatshefte für Chemie*, vol. 131, no. 3, pp. 251–265, 2000.
- [328] T. Böttcher, O. Shyshkov, M. Bremer, B. S. Bassil, and G.-V. Röschenthaler, “Carbene Complexes of Phosphorus(V) Fluorides by Oxidative Addition of 2,2-Difluorobis(dialkylamines) to Phosphorus(III) Halides,” *Organometallics*, vol. 31, no. 4, pp. 1278–1280, 2012.
- [329] C. Tian, W. Nie, M. V. Borzov, and P. Su, “High-Yield Thermolytic Conversion of Imidazolium Salts into Arduengo Carbene Adducts with BF₃ and PF₅,” *Organometallics*, vol. 31, no. 5, pp. 1751–1760, 2012.
- [330] C. Tian, W. Nie, Q. Chen, G. Sun, J. Hu, and M. V. Borzov, “C- and N-Adducts of N-alkenyl substituted Arduengo carbene and N-alkyl substituted imidazole with

- PF5: synthesis and structural investigation,” *Russ. Chem. Bull.*, vol. 63, no. 12, pp. 2668–2674, 2014.
- [331] A. Doddi, C. Gemel, R. W. Seidel, M. Winter, and R. A. Fischer, “Coordination complexes of TiX_4 ($X=F, Cl$) with a bulky N-heterocyclic carbene: Syntheses, characterization and molecular structures,” *Polyhedron*, vol. 52, pp. 1103–1108, 2013.
- [332] G. B. Nikiforov, H. W. Roesky, P. G. Jones, J. Magull, A. Ringe, and R. B. Oswald, “Preparation of Ti(IV) Fluoride N-Heterocyclic Carbene Complexes,” *Inorg. Chem.*, vol. 47, no. 6, pp. 2171–2179, 2008.
- [333] R. D. Shannon, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides,” *Acta Crystallogr. Sect. A*, vol. 32, no. 5, pp. 751–767, 1976.
- [334] H. D. B. Jenkins, H. K. Roobottom, J. Passmore, and L. Glasser, “Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii,” *Inorg. Chem.*, vol. 38, no. 16, pp. 3609–3620, 1999.
- [335] G. A. Olah, G. K. S. Prakash, Á. Molnár, and J. Sommer, *Superacid Chemistry*, Second. Hoboken, New Jersey, USA: John Wiley & Sons, Inc., 2009.
- [336] O. I. Guzyr *et al.*, “Conversion of Alkyltantalum Chlorides to Fluorides Using Trimethyltin Fluoride as a Fluorinating Agent. Crystal Structures of $(p\text{-MeC}_6\text{H}_4\text{CH}_2)_3\text{TaF}_2$, $(\text{Me}_3\text{SnCl} \cdot \text{Me}_3\text{SnF} \cdot \text{TaF}_5)_n$, $(\text{Me}_3\text{Si})_2\text{CHTaCl}_4$, $\{(\text{Me}_3\text{Si})_2\text{CHTaCl}_4 \cdot [(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ta}_2\text{Cl}_6(\mu_2\text{-O})\}$, and $(\text{Me}_3\text{Si})_2\text{CHTaF}_4$,” *Organometallics*, vol. 18, no. 5, pp. 832–836, 1999.
- [337] D. Nuszhar, F. Weller, K. Dehnicke, and W. Hiller, “Synthesen und Kristallstrukturen von $[\text{Na}(15\text{-Krone-5})]\text{-}[\text{NbF}_5(\text{NPPH}_3)]$, $(\text{PPh}_3\text{NH}_2)[\text{NbF}_5(\text{NPPH}_3)]$ und $[\text{Cs}(15\text{-Krone-5})_2](\text{WOF}_5)$,” *J. Alloys Compd.*, vol. 183, pp. 30–44, 1992.
- [338] M. Bortoluzzi, F. Marchetti, G. Pampaloni, M. Pucino, and S. Zacchini, “Coordination complexes of NbX_5 ($X = F, Cl$) with (N,O)- and (O,O)-donor ligands and the first X-ray characterization of a neutral NbF_5 adduct,” *Dalt. Trans.*, vol. 42, no. 36, pp. 13054–13064, 2013.
- [339] S. Alvarez, “A cartography of the van der Waals territories,” *Dalt. Trans.*, vol. 42, no. 24, pp. 8617–8636, 2013.
- [340] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry*, Sixth. Hoboken, New Jersey, USA: John Wiley & Sons, Inc., 2008.
- [341] B. Alič, A. Štefančič, and G. Tavčar, “Small molecule activation: SbF_3 auto-ionization supported by transfer and mesoionic NHC rearrangement,” *Dalt. Trans.*, vol. 46, no. 10, pp. 3338–3346, 2017.
- [342] R. Schowner, W. Frey, and M. R. Buchmeiser, “Cationic Tungsten-Oxo-Alkylidene-N-Heterocyclic Carbene Complexes: Highly Active Olefin Metathesis Catalysts,” *J. Am. Chem. Soc.*, vol. 137, no. 19, pp. 6188–6191, 2015.
- [343] M. Pucino, V. Mougél, R. Schowner, A. Fedorov, M. R. Buchmeiser, and C. Copéret, “Cationic Silica-Supported N-Heterocyclic Carbene Tungsten Oxo Alkylidene Sites: Highly Active and Stable Catalysts for Olefin Metathesis,” *Angew. Chemie Int. Ed.*,

- vol. 55, no. 13, pp. 4300–4302, 2016.
- [344] M. A. Ellwanger *et al.*, “Tuning the Lewis acidity of difluorido gold(III) complexes: the synthesis of $[\text{AuClF}_2(\text{SIMes})]$ and $[\text{AuF}_2(\text{OTeF}_5)(\text{SIMes})]$,” *Chem. Commun.*, vol. 54, no. 67, pp. 9301–9304, 2018.
- [345] K. Radan, E. Goresnik, and B. Žemva, “Xenon(II) Polyfluoridotitanates(IV): Synthesis and Structural Characterization of $[\text{Xe}_2\text{F}_3]^+$ and $[\text{XeF}]^+$ Salts,” *Angew. Chemie Int. Ed.*, vol. 53, no. 50, pp. 13715–13719, 2014.
- [346] B. Alič, M. Tramšek, A. Kokalj, and G. Tavčar, “Discrete GeF_5^- Anion Structurally Characterized with a Readily Synthesized Imidazolium Based Naked Fluoride Reagent,” *Inorg. Chem.*, vol. 56, no. 16, pp. 10070–10077, 2017.
- [347] M. D. Donakowski, A. Görne, J. T. Vaughey, and K. R. Poeppelmeier, “ $\text{AgNa}(\text{VO}_2\text{F}_2)_2$: A Trioxovanadium Fluoride with Unconventional Electrochemical Properties,” *J. Am. Chem. Soc.*, vol. 135, no. 26, pp. 9898–9906, 2013.
- [348] R. J. Baker, A. J. Davies, C. Jones, and M. Kloth, “Structural and spectroscopic studies of carbene and N-donor ligand complexes of Group 13 hydrides and halides,” *J. Organomet. Chem.*, vol. 656, no. 1–2, pp. 203–210, 2002.
- [349] R. W. Simms, M. J. Drewitt, and M. C. Baird, “Equilibration between a Phosphine-Cobalt Complex and an Analogous Complex Containing an N-Heterocyclic Carbene: The Thermodynamics of a Phosphine-Carbene Exchange Reaction,” *Organometallics*, vol. 21, no. 14, pp. 2958–2963, 2002.
- [350] N. P. Mankad, T. G. Gray, D. S. Laitar, and J. P. Sadighi, “Synthesis, Structure, and CO_2 Reactivity of a Two-Coordinate (Carbene)copper(I) Methyl Complex,” *Organometallics*, vol. 23, no. 6, pp. 1191–1193, 2004.
- [351] S. Rostamzadehmansor, G. Ebrahimzadehrajai, S. Ghammamy, K. Mehrani, and L. Saghatforoush, “Synthesis and characterization of three new fluorovanadate complexes: $\text{N}(\text{C}_2\text{H}_5)_4^+[\text{VOF}_4]^-$, $\text{N}(\text{CH}_3)_4^+[\text{VOF}_3\text{Cl}]^-$, $\text{N}(\text{C}_4\text{H}_9)_4^+[\text{VOF}_3\text{Br}]^-$ and theoretical calculations of VOF_4^- , VOF_3Cl^- and VOF_3Br^- ions,” *J. Fluor. Chem.*, vol. 129, no. 8, pp. 674–679, 2008.
- [352] H. H. Brintzinger, “MECHANISMS OF DIHYDROGEN ACTIVATION BY ZIRCONOCENE ALKYL AND HYDRIDE DERIVATIVES,” *J. Organomet. Chem.*, vol. 171, no. 3, pp. 337–344, 1979.
- [353] J. A. Marsella, C. J. Curtis, J. E. Bercaw, and K. G. Caulton, “Low-Temperature Infrared Study of d_0 Carbonyl Complexes,” *J. Am. Chem. Soc.*, vol. 102, no. 24, pp. 7244–7246, 1980.
- [354] H. S. La Pierre, J. Arnold, R. G. Bergman, and D. F. Toste, “Carbon Monoxide, Isocyanide, and Nitrile Complexes of Cationic, d_0 Vanadium Bisimides: π -Back Bonding Derived from the π Symmetry, Bonding Metal Bisimido Ligand Orbitals,” *Inorg. Chem.*, vol. 51, no. 24, pp. 13334–13344, 2012.
- [355] J. B. Lambert, J. J. Papay, S. A. Khan, K. A. Kappauf, and E. S. Magyar, “Conformational Analysis of Five-Membered Rings,” *J. Am. Chem. Soc.*, vol. 96, no. 19, pp. 6112–6118, 1974.
- [356] P. L. Bayless, “Empirical pK_b and pK_a for Nonmetal Hydrides from Periodic Table Position,” *J. Chem. Educ.*, vol. 60, no. 7, pp. 546–547, 1983.

- [357] R. Starkey, J. Norman, and M. Hintze, "Who Knows the K_a Values of Water and the Hydronium Ion?," *J. Chem. Educ.*, vol. 63, no. 6, pp. 473–474, 1986.
- [358] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, "Über tertiäre Oxoniumsalze, II," *J. für Prakt. Chemie*, vol. 154, no. 3–5, pp. 83–156, 1939.
- [359] J. E. Gordon and G. C. Turrell, "Observations on N-Methylacetoneitrilium and N-Phenylbenzonitrilium Hexachloroantimonates," *J. Org. Chem.*, vol. 24, no. 2, pp. 269–271, 1959.
- [360] J. Hvoslef, M. L. Tracy, and C. P. Nash, "Interatomic Distances and Angles in Four Planar Systems with Adjacent C–O and C–N Bonds: Structures of Pivalamide (I), Dipivalamide (II), N-Pivaloylpivalamidinium Pyrosulfate (III) and N-Pivaloylpivalamidine (IV)," *Acta Crystallogr. Sect. C*, vol. 42, no. 3, pp. 353–360, 1986.
- [361] S. Dolci, F. Marchetti, G. Pampaloni, and S. Zacchini, "A crystallographic and spectroscopic study on the reactions of WCl_6 with carbonyl compounds," *Dalt. Trans.*, vol. 42, no. 16, pp. 5635–5648, 2013.
- [362] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, "Tables of Bond Lengths Determined by X-Ray and Neutron Diffraction. Part 1. Bond Lengths in Organic Compounds," *Perkin Trans. 2*, no. 12, p. S1, 1987.
- [363] S. Yanagida, T. Fujita, M. Ohoka, I. Katagiri, and S. Komori, "Studies on Nitrile Salts. I. Dimerization of Nitriles Having α -Hydrogen in the Presence of Hydrogen Chloride," *Bull. Chem. Soc. Jpn.*, vol. 46, no. 1, pp. 292–299, 1973.
- [364] S. J. Daunt, H. F. Shurvell, and L. Pazdernik, "THE SOLID VIBRATIONAL SPECTRA OF s-TRIAZINE AND s-TRIAZINE- d_3 AND THE MONOCLINIC TO RHOMBOHEDRAL PHASE TRANSITION," *J. Raman Spectrosc.*, vol. 4, no. 2, pp. 205–223, 1975.
- [365] P. J. Larkin, M. P. Makowski, and N. B. Colthup, "The form of the normal modes of s-triazine: infrared and Raman spectral analysis and ab initio force field calculations," *Spectrochim. Acta Part A*, vol. 55, no. 5, pp. 1011–1020, 1999.
- [366] G. A. Crowder, "Vibrational Spectra of tert-Butyl Cyanide," *J. Phys. Chem.*, vol. 75, no. 18, pp. 2806–2808, 1971.
- [367] A. Łapiński, J. Spanget-Larsen, M. Langgård, J. Waluk, and J. G. Radziszewski, "Raman Spectrum of the Phenyl Radical," *J. Phys. Chem. A*, vol. 105, no. 46, pp. 10520–10524, 2001.
- [368] J. E. Lancaster, R. F. Stamm, and N. B. Colthup, "The vibrational spectra of s-triazine and s-triazine- d_3 ," *Spectrochim. Acta*, vol. 17, no. 2, pp. 155–165, 1961.
- [369] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Third. Chichester, UK: John Wiley & Sons, Ltd., 2001.
- [370] Bio-Rad Laboratories, "2,4,6-triphenyl-1,3,5-triazine (Compound ID: Gx7ET2PFpui, SpectraBase Spectrum ID: 3hZryJkOyqB)," *SpectraBase*. [Online]. Available: http://spectrabase.com/spectrum/3hZryJkOyqB?a=SPECTRUM_3hZryJkOyqB. [Accessed: 31-Jan-2020].
- [371] P. DeBurgomaster and J. Zubietta, "Organic–inorganic hybrid materials: Ligand influences on the structural chemistry of copper-vanadates," *Inorganica Chim. Acta*,

- vol. 363, no. 12, pp. 2912–2919, 2010.
- [372] R. Gautier, M. D. Donakowski, and K. R. Poeppelmeier, “Orientational order of $[\text{VOF}_5]^{2-}$ and $[\text{NbOF}_5]^{2-}$ polar units in chains,” *J. Solid State Chem.*, vol. 195, pp. 132–139, 2012.
- [373] R. Gautier and K. R. Poeppelmeier, “Alignment of Acentric Units in Infinite Chains: A ‘Lock and Key’ Model,” *Cryst. Growth Des.*, vol. 13, no. 9, pp. 4084–4091, 2013.
- [374] J. M. Chamberlain, T. A. Albrecht, J. Lesage, F. Sauvage, C. L. Stern, and K. R. Poeppelmeier, “Crystal Growth of $\text{Ag}_3\text{MO}_x\text{F}_{6-x}$ ($\text{M} = \text{V}$, $x = 2$; $\text{M} = \text{Mo}$, $x = 3$),” *Cryst. Growth Des.*, vol. 10, no. 11, pp. 4868–4873, 2010.
- [375] B. Ahmed *et al.*, “Mixed Transition Metal (Oxy)fluoride Paramagnet Chains: Synthesis, Structure, and Characterization,” *Eur. J. Inorg. Chem.*, vol. 2019, no. 26, pp. 3112–3119, 2019.
- [376] G. A. Senchyk *et al.*, “AgI/VV Heterobimetallic Frameworks Generated from Novel-Type $\{\text{Ag}_2(\text{VO}_2\text{F}_2)_2(\text{triazole})_4\}$ Secondary Building Blocks: A New Aspect in the Design of SVOF Hybrids,” *Inorg. Chem.*, vol. 51, no. 15, pp. 8025–8033, 2012.
- [377] W. Ouellette and J. Zubietta, “Solid state coordination chemistry of the copper(II)/bisterpy/vanadate system: The structures of $[\text{Cu}_2(\text{bisterpy})\text{V}_4\text{O}_{12}] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{bisterpy})\text{V}_4\text{F}_2\text{O}_{11}]$ (bisterpy= $2,2':4',4'':2'',2'''$ -quarter-pyridyl, $6',6''$ -di-2-pyridine),” *Solid State Sci.*, vol. 9, no. 8, pp. 658–663, 2007.
- [378] B. Anke, M. Rohloff, M. G. Willinger, W. Hetaba, A. Fischer, and M. Lerch, “Improved photoelectrochemical performance of bismuth vanadate by partial O/F-substitution,” *Solid State Sci.*, vol. 63, pp. 1–8, 2017.
- [379] T. Mahenthirarajah, Y. Li, and P. Lightfoot, “Hydrothermal Synthesis of Vanadium Oxyfluoride Chains Incorporating Covalently Bound Copper Coordination Complexes,” *Inorg. Chem.*, vol. 47, no. 19, pp. 9097–9102, 2008.
- [380] R. Gautier *et al.*, “Spin Frustration from cis-Edge or -Corner Sharing Metal-Centered Octahedra,” *J. Am. Chem. Soc.*, vol. 135, no. 51, pp. 19268–19274, 2013.
- [381] X.-L. Cao, F. Kong, C.-L. Hu, X. Xu, and J.-G. Mao, “ $\text{Pb}_4\text{V}_6\text{O}_{16}(\text{SeO}_3)_3(\text{H}_2\text{O})$, $\text{Pb}_2\text{VO}_2(\text{SeO}_3)_2\text{Cl}$, and $\text{PbVO}_2(\text{SeO}_3)\text{F}$: New Lead(II)–Vanadium(V) Mixed-Metal Selenites Featuring Novel Anionic Skeletons,” *Inorg. Chem.*, vol. 53, no. 16, pp. 8816–8824, 2014.
- [382] M. D. Donakowski, A. I. Vinokur, and K. R. Poeppelmeier, “The Dimeric $[\text{V}_2\text{O}_4\text{F}_6]^{4-}$ Vanadium Oxide-Fluoride Anion in $\text{Na}_2(\text{M}(\text{H}_2\text{O})_2)(\text{V}_2\text{O}_4\text{F}_6)$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+} , and Cu^{2+}),” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 638, no. 12–13, pp. 1991–1995, 2012.
- [383] M. P. Crosnier-Lopez, H. Duroy, and J. L. Fourquet, “ $\text{Ba}_3\text{V}_2\text{O}_4\text{F}_8$: $[\text{V}_4(\text{O},\text{F})_{20}]^{8-}$ Tetrameric Groups of Octahedra Inserted in a Tridimensional Network of (FBa_4) Tetrahedra,” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 619, no. 9, pp. 1597–1602, 1993.
- [384] I. D. Brown and D. Altermatt, “Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database,” *Acta Crystallogr. Sect. B*, vol. 41, no. 4, pp. 244–247, 1985.
- [385] N. E. Brese and M. O’Keeffe, “Bond-Valence Parameters for Solids,” *Acta*

Crystallogr. Sect. B, vol. 47, no. 2, pp. 192–197, 1991.

Bibliography

Publications Related to the Thesis

Journal Articles

- Ž. Zupanek, M. Tramšek, A. Kokalj and G. Tavčar, "The peculiar case of conformations in coordination compounds of group V pentahalides with N-heterocyclic carbene and synthesis of their imidazolium salts," *Journal of fluorine chemistry*, **2019**, vol. 227, pp. 109373-1–109373-9. DOI: 10.1016/j.jfluchem.2019.109373
- Ž. Zupanek, M. Tramšek, A. Kokalj and G. Tavčar, "Reactivity of VOF_3 with N-heterocyclic carbene and imidazolium fluoride : analysis of ligand- VOF_3 bonding with evidence of a minute π back-donation of fluoride," *Inorganic chemistry*, **2018**, vol. 57, no. 21, pp. 13866–13879. DOI: 10.1021/acs.inorgchem.8b02377.

Conference Paper

- G. Tavčar, B. Alič, Ž. Zupanek, E. Gruden and M. Tramšek, "Imidazolium based fluoride donor as a reagent for the preparation of discrete anionic species," at *19th European Symposium on Fluorine Chemistry*, 25.-31. August 2019, Warsaw, Poland: University of Warsaw, **2019**.
- G. Tavčar, B. Alič, Ž. Zupanek, E. Gruden, A. Kokalj, J. Petrovčič, J. Iskra and M. Tramšek, "Novel bulky imidazolium fluorine reagents in inorganic and organic chemistry," at *International Conference on Fluorine Chemistry 2019 Himeji*, 22.-24. May 2019, Egret Himeji, Hyogo, Japan: Society for the Promotion of Science, **2019**.
- Ž. Zupanek, M. Tramšek and G. Tavčar, "Oxonium salts - useless or useful," at *22nd International Symposium on Fluorine Chemistry*, 22.-27. July 2018, Oxford, UK: Royal Society of Chemistry, **2018**.
- Ž. Zupanek and G. Tavčar, "Nove koordinacijske spojine fluoridooksidovanadatov," at *23rd Slovenian Chemical Days 2017*, 20.-22. September 2017, Portorož, Slovenia: Slovenian Chemical Society, **2017**.
- Ž. Zupanek and G. Tavčar, " $\text{H}_3\text{O}^+\text{SbF}_6^-$ as a reagent in cyclotrimerization of nitriles," at 9th Jožef Stefan International Postgraduate School Students' Conference and 11th Young researchers' Day, 19.-20. April 2017, Ljubljana, Slovenia: Jožef Stefan International Postgraduate School, Jožef Stefan Institute, **2017**.

- Ž. Zupanek and G. Tavčar, "Reaktivnost fluoridnih Lewisovih kislin z nitrili," at *22nd Slovenian Chemical Days 2016*, 28.-30. September 2016, Portorož, Slovenia: Slovenian Chemical Society, **2016**.
- Ž. Zupanek and G. Tavčar, "Synthesis of novel coordination compounds of tantalum(V) halides," at *10th Young researchers' day*, 31. March 2016, Ljubljana, Slovenia: Jožef Stefan Institute, **2016**.

Biography

The author of this thesis Žiga Zupanek was born on September 19, 1989, in Ljubljana, Slovenia. He finished primary education in 2004 at the Primary School Rodica and concluded secondary education in 2008 at the School Center of Rudolf Maister. He proceeded with his education at the university level and enrolled in the Chemistry study programme at the Faculty of Chemistry and Chemical Technology, University of Ljubljana. He obtained his Bachelor's Degree in 2014 for his work in analytical chemistry and thesis entitled "Optimization of extraction and chromatographic separation methods for determination of sedatives in various animal samples", which he prepared under the work supervision of Assoc. Prof. Dr. Ksenija Šinigoj Gačnik and academic supervision of Prof. Dr. Helena Prosen. He pursued further academic education and doctoral degree (PhD) by applying to the Jožef Stefan International Postgraduate School in the Ecotechnology study programme. With the funding from the Slovenian Research Agency, he received the position of a Young Researcher at the Jožef Stefan Institute under the supervision of Asst. Prof. Dr. Gašper Tavčar. He reached the stage of PhD candidate in his doctoral study in 2019.

