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Uncovering New Bonding Motifs: The Synthesis of Chalcogen and Phosphorus Complexes Supported by Nitrogen Based Ligands

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry

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Abstract

The chemistry of the main group elements with nitrogen based ligands has been an area that has received little attention in comparison to transition metals. The preliminary investigations have focused on groups 13 and 14 revealing new bonding motifs and interesting reactivity. This has motivated us to synthesize group 15 and 16 derivatives in new bonding arrangements capable of activating small molecules.

In pursuit of isolating such species, the reactivity of sulfur dichloride and "$S(OTf)_2$" with a series of diazabutadiene (DAB) ligands was explored. The substitution on the ligand was extremely influential on the outcome of the reaction. Alkyl groups on the nitrogen atom resulted in the production of 1,2,5-thiadiazolium heterocycles by loss of an alkyl group whereas methyl groups on the backbone carbon atom led to reaction with the eneamine tautomer of the ligand to give *N,C*-bound heterocycles. This could be avoided with aryl groups or hydrogen atoms on the backbone carbons and aryl groups on the nitrogen centres. The latter reactions produced dicationic analogues of the N-Heterocyclic carbene, the first examples for sulfur.

The chemistry of the chalcogen halides and bistriflate synthons with the diiminopyridine (DIMPY) ligand showed similar trends. Methyl groups on the backbone carbon resulted in bonding through a methyl carbon whereas phenyl groups or hydrogen atoms in the same position produced *N,N',N''*-chelated cations or dications. The dicationic triflate salts are stable in the open atmosphere, a remarkable feature for highly charged cations. The chemistry was also extended to phosphorus. Collectively these species represent the first DIMPY complexes for phosphorus, sulfur, selenium and tellurium.

Sulfur(II) dications with amine donors, namely pentamethyldiethylenetriamine could also be prepared. The complex was highly unstable indicating imine and pyridine groups offer greater stabilization. In addition to the chelate complexes, monodentate pyridine ligands coordinate to a dicationic sulfur centre. The monodentate species displayed reactivity with a variety of unsaturated organic substrates. Altering the group on the *para* position of the pyridine proved to have a significant effect on the reactivity indicating potential tuneability for the system.

Keywords

Chalcogen • cation • carbene analogue • sulfur • selenium • tellurium • phosphorus • nitrogen ligands • pyridine • diazabutadiene • diiminopyridine • polycation

Co-Authorship Statement

This thesis includes material from five previously published or manuscripts presented in Chapters 2, 3 and 4. Chapter 5 has been recently accepted for publication. The initial communication presented in Chapter 2 was co-authored by Caleb D. Martin, Michael J. Ferguson, Michael C. Jennings and Paul J. Ragogna. (*Angew. Chem. Int. Ed.* **2009**, *48*, 2210-2213.). All of the experimental work was performed by C. D. Martin. X-ray diffraction data were solved by M. C. Jennings, M. J. Ferguson and C. D. Martin. C. D. Martin and P. J. Ragogna assembled the manuscript collaboratively for publication. A portion of the manuscript co-authored by Jason L. Dutton, Caleb D. Martin, Michael J. Sgro, Nathan D. Jones and Paul J. Ragogna (*Inorg. Chem*, **2009**, *48*, 3239) was included in Chapter 2. Only the data on compounds **2.1SCl** and **2.2SCla** were presented. C. D. Martin performed all of the experimental work for these two compounds. J. L. Dutton and P. J. Ragogna composed the original manuscript and the information was rewritten by C. D. Martin to fit into this body of work. A third manuscript also appeared in Chapter 2; by C. D. Martin and P. J. Ragogna. (*Inorg. Chem.* **2010**, *49*, 4324). All experimental work was performed and the manuscript composed by C. D. Martin and edited by P. J. Ragogna.

A portion of the work in Chapter 3 was published in the manuscript co-authored by C. D. Martin, C. M. Le, and P. J. Ragogna (*J. Am. Chem. Soc.* **2010**, *131*, 15126). Experimental work concerning **3.1SeOTf**, **3.1TeOTf** and **3.1aTeOTf** was done by C. M. Le and the remainder by C. D. Martin. C. D. Martin was responsible for writing the manuscript for publication and P. J. Ragogna for edits.

The manuscript presented in Chapter 4 was co-authored by C. D. Martin and P. J. Ragogna (*Inorg. Chem.* **2010**, *49*, 8164). C. D. Martin performed all of the experimental work in addition to the composition of the manuscript. P. J. Ragogna is credited with edits.

Chapter 5 was recently accepted for publication (*Dalton Trans.*, **2011**). All experiments were conducted and the manuscript composed by C. D. Martin. P. J. Ragogna edited the manuscript.

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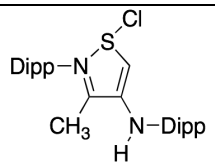
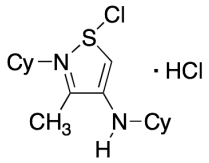
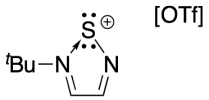
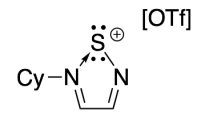
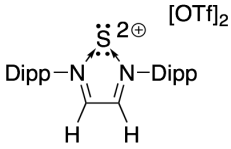
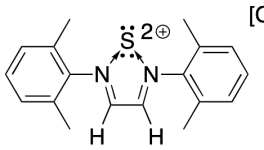
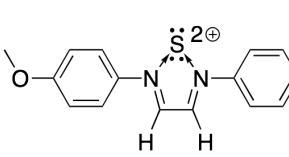
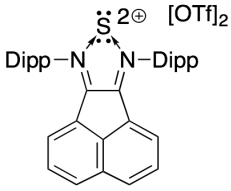
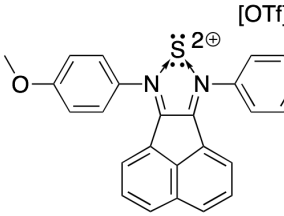
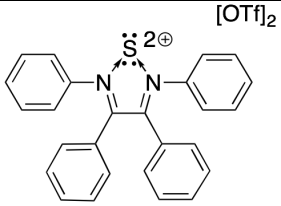
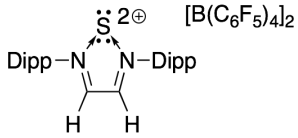
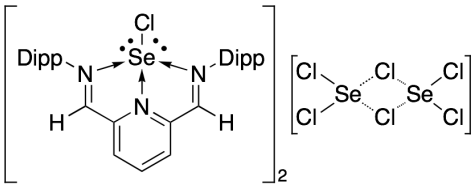
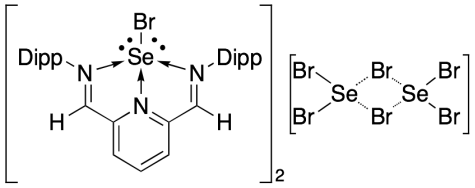
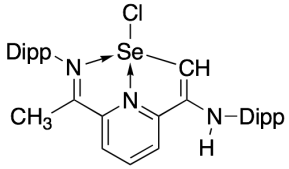
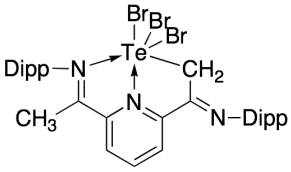
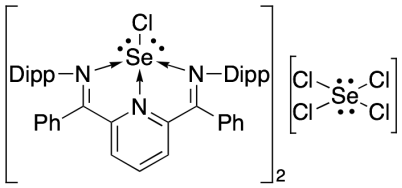
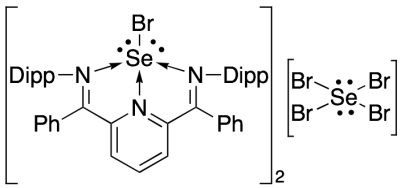
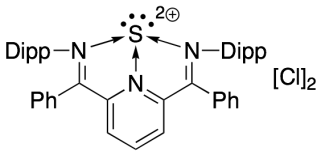
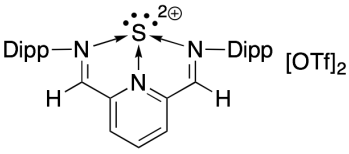
2.1SCl		42
2.2SCla		43
2.3S[OTf]		44
2.4S[OTf]		44
2.5S[OTf]		45
2.6S[OTf]		45
2.7S[OTf]		46
2.8S[OTf]		46
2.9S[OTf]		47

2.10S[OTf]		48
2.5S[B(C_6F_5)$_4$]		48
3.1SeCl		75
3.1SeBr		75
3.2SeCl		76
3.2TeBr		76
3.3SeCl		77
3.3SeBr		78
3.3S[Cl]		79
3.1S[OTf]		79

List of Abbreviations

δ	chemical shift
Δδ	change in chemical shift
Σv.d.w.	sum of van der Waals radii
°C	degree Celcius
{^{1}H}	proton decoupled
Å	Angstrom
Anal	analysis
atm	atmosphere
avg.	average
BIAN	bisiminoacenaphthene
br	broad
Calcd	calculated
c.f.	*confer* (compare)
Ch	chalcogen
cm	centimetre
CV	cyclic voltammetry
Cy	cyclohexyl
CYCLAM	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
d	doublet
DAB	diazabutadiene
D_c	calculated density
dd	doublet of doublets
DIC	diisopropylcarbodiimide
DIMPY	diiminopyridine
Dipp	2,6-diisopropylphenyl
Dmp	2,6-dimethylphenyl
d.p.	decomposition point
dt	doublet of triplets
EA	elemental analysis
e.g.	*exempli gratia* (for example)
et al.	*et alii* (and others)
Et_2O	diethylether
ESI-MS	electrospray ionization – mass spectrometry
FLP	Frustrated Lewis Pair
FT-IR	fourier transform infrared
FW	formula weight
g	gram
g/mol	gram/mole
GOF	goodness of fit
h	hour
HOMO	highest occupied molecular orbital
Hz	hertz
i.e.	*id est* (that is)
in situ	in its original place
in vacuo	in a vacuum

^{i}Pr	isopropyl
J	couling constant
K	kelvin
LUMO	lowest unoccupied molecular orbital
M	molar
m	multiplet
Me	methyl
MeO	methoxy
Mes	mesityl, 1,3,5-trimethylphenyl
mL	millilitre
mmol	millimole
MP	melting point
m/z	mass to charge ratio
n	integer number
NHC	N-Heterocylic carbene
NHP	N-Heterocylic phosphenium
NHSi	N-Heterocylic silylene
NMR	nuclear magnetic resonance
OTf	trifluoromethanesulfonate; triflate; $[CF_3SO_3]^-$
p	*para*
Ph	phenyl
PMDETA	N,N',N',N'',N''-pentamethyldiethylenetriamine
ppm	part per million
psi	pounds per square inch
pyr	pyridine
Oct	octyl
q	quartet
R	organic substituents
R	rectus
ROP	ring opening polymerization
RT	room temperature
s	singlet
S	sinister
sept	septet
t	triplet
TACN	1,4,7-trimethyl-1,4,7-triazacyclononane
^{t}Bu	tertiary-butyl
TMEDA	*N*,*N*,*N*′,*N*′-tetramethyl-ethane-1,2-diamine
THF	tetrahydrofuran
TMS	trimethylsilyl
UV-Vis	ultraviolet-visible
UWO	*The* University *of* Western Ontario
vs	versus

Chapter 1

Advancing the Frontiers of Main Group Chemistry

1.1 Recent Developments in Main Group Chemistry

The past six years have seen a renaissance in main group chemistry.[1,2] Previously, the objectives of main group chemists were primarily focused around the generation of functional materials and isolating new bonding motifs.[3] Although those themes still exist, recently, the realization has occurred that the p-block elements can perform tasks that were previously restricted to transition metals. These include the activation of small molecules, catalysis, and sequestering highly reactive molecular entities.

The general evolution of this new p-block chemistry has typically been to synthesize or discover a very reactive species, then to develop its utility in small molecule activations or catalytic transformations. Some great examples of species that have followed this trend include carbenes,[2] the frustrated Lewis pair,[4] the p-block carbene analogues[5] and the heavy analogues of alkenes and alkynes.[1]

The group 15 and 16 elements in unusual coordination geometries and electronic environments should also have promise in the field of small molecule activation. The approach to isolating such species can be through the coordination of donor ligands to the main group centre. As the nitrogen based ligands have stabilized several reactive group 13 and 14 derivatives such as the carbene analogues, this approach should readily translate to the later groups. This dissertation will focus on the synthesis of reactive cationic pnictogen and chalcogen centres sequestered using nitrogen based ligands, and subsequently examine the reactivity of these species.

1.2 Carbenes and Carbene Analogues

Main group complexes including carbenes and their p-block analogues have been shown to be reactive towards a variety of molecules. Carbenes have a neutral two coordinate

carbon centre, with a lone pair and an unoccupied p-orbital forming a sextet within its valence shell.[2] For many years these species were proposed as reaction intermediates, but were not isolated in a laboratory as a stable species until 1988.[9] Although the first carbene had little use, this molecule served as a stepping stone to a succeeding report by Arduengo in 1991, known as the classic N-Heterocyclic carbene (NHC; **1.1**; Figure 1.1).[10] These molecules proved to be excellent ligands for transition metals and their metal complexes proved to be very fruitful in catalytic reactions.[11] The initial NHC was a five-membered C_3N_2 ring with two nitrogen centres adjacent to carbon and a carbon-carbon double bond in the framework. A proper Lewis structure of the NHC is an ylide with lone pairs on the nitrogen atoms delocalizing electron density into the empty p-orbital on carbon and satisfying its octet (**1.1a** and **1.1b**). Although the first example had a carbon-carbon double bond within the five membered heterocycle providing a 6 π-electron aromatic system for further stabilization, it was not essential as the saturated analogue (**1.2**) has been isolated.[12] The incorporation of the NHC has been an important discovery in transition metal chemistry, ultimately resulting in a catalyst that won a share of the 2005 Nobel Prize.

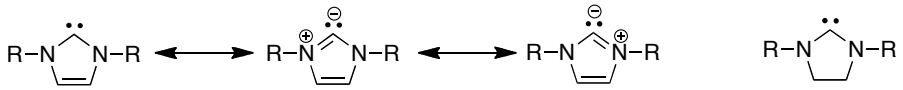


Figure 1.1: Structural representations of the classic NHC (**1.1**) indicating the ylidic nature of the molecule and the saturated analogue (**1.2**).

The area of carbene research has since blossomed with the quest of isolating new carbenes by different methods to stabilize the reactive carbon atom (Figure 1.2 contains a small selection).[13] The carbenes can be in both cyclic or acyclic systems. They can have a variety of heteroatoms such as P, Si, S or O adjacent to the central carbon atom but typically the neighbouring atoms have a lone pair to stabilize the empty p-orbital on carbon (**1.3**-**1.7**).[9,14-16] A recent report of the cyclopropenylidene (**1.8**) proved that heteroatoms next to carbon were not required to isolate the carbene centre.[17] The bond angles, donor ability and chemistry of all of these derivatives have been shown to have

significant differences and give the potential to tune the electronics for specific σ-donor properties.[13]

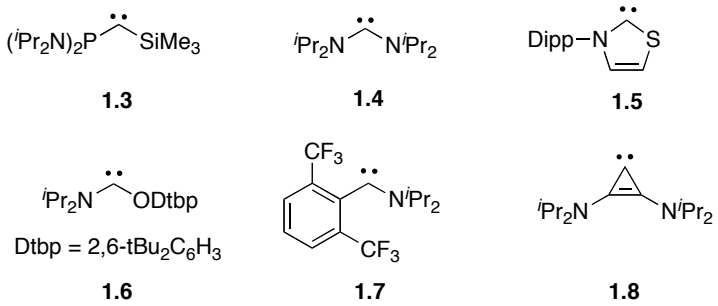


Figure 1.2: A selection of carbenes with various atoms adjacent to the carbene centre.

The number of carbenes available is vast; the most effective derivatives in small molecule activation have both high degrees of nucleophilicity and electrophilicity (small singlet-triplet or HOMO-LUMO gap; Figure 1.3).[2] The ferrocene bridged carbene (**1.9**),[18] acyclic alkyl amino carbene (**1.10**),[19] cyclic alkyl amino carbene (**1.11**),[19] and amido carbene (**1.12**)[20] are all species that have the desired small HOMO-LUMO gap. These molecules readily activate dihydrogen, ammonia, carbon monoxide, nitriles, Si-H and P-H bonds.[2]

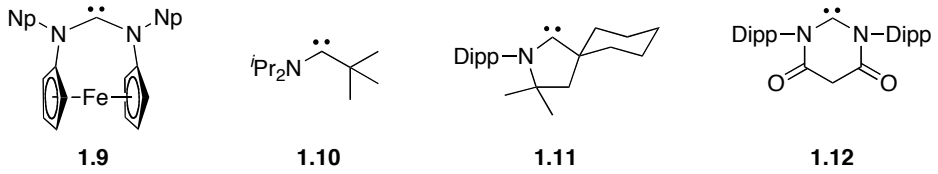


Figure 1.3: A selection of carbenes effective in the activation of small molecules.

The heavier congener of the NHC, the five membered N-heterocyclic silylene (NHSi; **1.13**; Figure 1.4), has also proven to be extremely active in this realm of chemistry.[21] The five membered NHSi has activated O-H bonds, alkyl/aryl halides, silyl halides, azides, olefins, alkynes, ketones, imines, nitriles and elemental chalcogens among others.

An analogous six membered ring system, supported by the *β*-diketiminate ligand (**1.14**; Figure 1.4) was prepared in 2006 and has even greater reactivity than its five membered counterpart.[5] This particular molecule has three reactive sites: the exocyclic alkene, the lone pair and the empty p-orbital on silicon, giving the potential for versatile reactivity. In

addition to being effective in the activation of the majority of the substrates described above with the five membered NHSi, the six membered system also reacts with the pnictines (NH_3, PH_3 and AsH_3).[22] Ammonia and phosphine react at the silicon centre to form a phosphide and amide (**1.15**) with a silicon hydride. Arsine produces the analogous molecule (**1.16**) but it lies in equilibrium with a donor stabilized arsa-silene (**1.16a**) by transfer of a hydrogen to a carbon on the ligand framework indicating the reactivity of the alkene and giving insight to the versatility of this reagent.

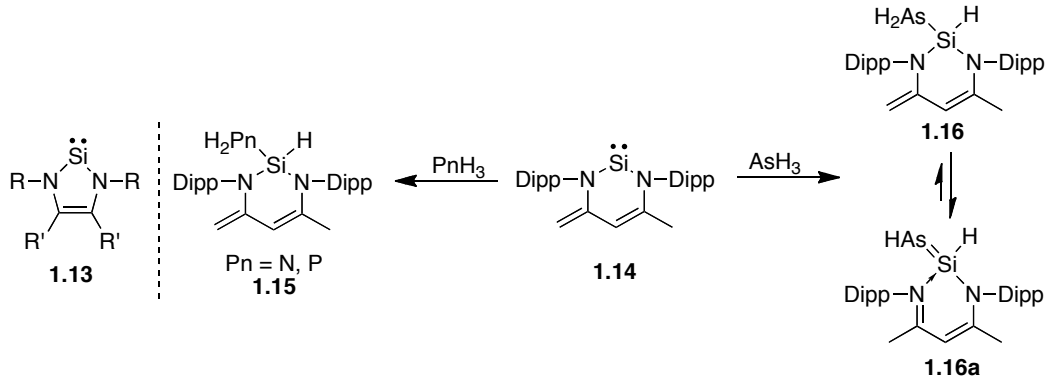
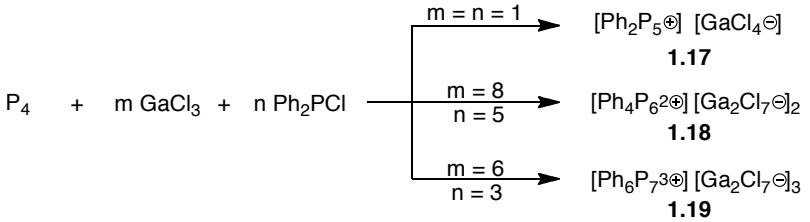


Figure 1.4: Structure of five membered NHSi (**1.13**) and the activation of the pnictines (PnH_3) with the six membered NHSi (**1.14**).

The phosphorus analogues of the carbene, the phosphenium cations, have also been a contributor in the field of small molecule activation.[23] A nice example is observed from the mixture of a diorganohalophosphine in the presence of gallium trichloride to generate a phosphenium cation *in situ* that can then stoichiometrically insert into one, two or three P-P bonds of the tetrahedron of white phosphorus (Scheme 1.1; **1.17**-**1.19**).[24] Other reactivity studies show they undergo cycloadditions with unsaturated hydrocarbons.[25]

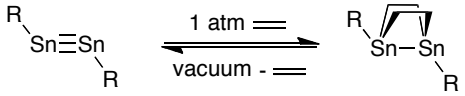


Scheme 1.1: Reactivity of a phosphenium cation with P_4.

As silicon and phosphorus are useful in transformations with small molecules, the group 16 third row element, sulfur, should also possess such desirable reactivity if the proper bonding motif can be achieved. A report in 1979 has reported the isolation of such species, formally a sulfenium dication.[26] This species would be isoelectronic to both the silylene and phosphenium cation. The molecule bears a charge of 2+ on the sulfur centre, hence greater reactivity can be anticipated in comparison to the neutral (Si) or monocationic (P) row three derivatives and its chemistry should be explored.

1.3 Heavy Analogues of Alkenes and Alkynes

Heavy analogues of alkenes and alkynes have also proven to be capable in the activation of several small molecules.[1] These heavy unsaturated systems are very reactive and need extraordinarily bulky groups to stabilize the main group centres. An example of their reactivity is the distannyne (**1.20**; Scheme 1.2) displaying reversible reactivity with ethylene.[27] Compound **1.20** binds two equivalents of ethylene by cycloaddition (**1.21**) and in a vacuum the ethylene is easily removed from the tin atoms. In addition to olefins, these species can activate many other molecules including dihydrogen.[28]



1.20 **1.21**

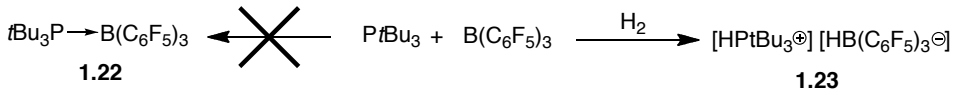
Scheme 1.2: Demonstration of the reversible binding of a distannyne (**1.20**) with ethylene.

1.4 Frustrated Lewis Pairs

The seminal paper by Stephan *et al.* on frustrated Lewis pairs (FLPs) has burgeoned a whole new area of research.[4,29] The concept of an FLP is having the combination of a sterically congested Lewis acid and Lewis base preventing the formation of the classical adduct (**1.22**; Scheme 1.3). This quenched reactivity permits the two species to act on substrates synergistically. The first reaction reported was the cleavage of dihydrogen (**1.23**).[30] The bifurcation of H_2 is difficult as the bond is strong (436 kJ/mol) and has no polarization. The only prior example of a non-metal species carrying out such chemistry

was a digermyne reacting with H_2 to produce a mixture of germanes and the corresponding germene.[28] This chemistry has been developing rapidly. Some FLPs have proven to be effective in the delivery of H_2, and are now capable of catalytically hydrogenating numerous organic substrates.[31,32]

The Lewis bases proficient in FLP chemistry have been extended beyond phosphines to include pyridines, imines, amines and carbenes among others.[4] The Lewis acids however have been limited; the most prominent being $B(C_6F_5)_3$ and other fluorinated aryl boranes. There have only been sparse reports of aluminum trihalides and an electron deficient allene acting as the Lewis acceptor.[33,34] The bond activations have been useful to many small molecules including N_2O, CO_2, ethers, alkenes, alkynes, in addition to S-S and O-H bonds.[33-37]



Scheme 1.3: An example of the reactivity of "frustrated Lewis pairs" with H_2.

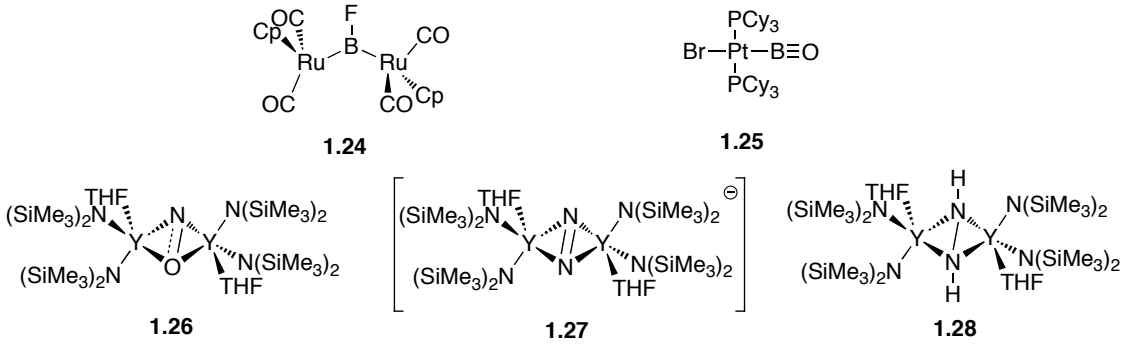
1.5 Isolating Reactive Molecular Units

In terms of developing novel complexes capable of activating small molecules, reactive molecular units are good targets. In addition to carbenes, many other unstable element centres and molecular units exist. These species include highly reactive radicals and units that are extremely electron rich or electron deficient. Elaborate methods have been utilized in the past by many talented chemists to generate these derivatives. Significant discoveries have been made by spectroscopically observing very reactive species under cryogenic and photolytic conditions in noble gas matrices or by observing such species in the gas phase.[38-40] Although this research is very important in understanding the fundamental structure and bonding of molecules, the practicality of utilizing species that require heroic efforts to generate in a flask is not feasible.

These low temperature and gas-phase investigations have spawned numerous studies into developing methods of isolating reagents stable in a laboratory under an inert atmosphere and at ambient temperature. The two most common means to stabilize these reactive units have been to incorporate the species within the coordination sphere of metals, or to

provide supporting substituents to electronically stabilize and/or sterically protect such fleeting molecules.

Utilizing metals to sequester molecular units has proven to be effective with the recent examples of BF, BO^-, NO_2^-, N_3^- and $N_2H_2^{2-}$ (**1.24-1.28**; Figure 1.5).[6,41-47] The metals stabilize the electron deficient or electron rich units primarily through π-backbonding interactions. The BF molecule is isoelectronic to CO, a stable gas abundant in the atmosphere. As boron and fluorine have very different electronegativites, the relative orbital energies prevent significant mixing between the electronegative fluorine with the electropositive boron centre, rendering the molecule extremely reactive. The BF species was able to be isolated by binding two ruthenium metal centres to the boron atom, stabilizing it by π-backbonding interactions (**1.24**).[6] The early transition metals (*e.g.* yttrium) are very good at stabilizing electron rich units as they have high energy d-orbitals which can π-backbond with the higher energy antibonding orbitals and has proven to be effective in isolating NO_2^-, N_3^- and $N_2H_2^{2-}$ (**1.26-1.28**, respectively) among others.[43-47] This is in contrast to the late metals that have d-orbitals lower in energy to interact with electron deficient centres such as BF and BO^- (**1.24** and **1.25**).[6,42]



1.24 **1.25** **1.26** **1.27** **1.28**

Figure 1.5: Structures of transition metal stabilized reactive intermediates.

In addition to metals utilizing d-orbitals for π-backbonding stabilization, strong donor ligands such as phosphines, pyridines and carbenes can also be used to isolate reactive species. This approach has been known for many years with an example being the carbodiphosphorane, a carbon(0) complex first generated in 1961 (**1.29**; Figure 1.6).[48] This derivative can be drawn as a carbon(0) centre with two coordinating phosphines

(**1.29**); a dianionic carbon centre with two covalent bonds (**1.29a**); or by the representation with two carbon-phosphorus double bonds (**1.29b**).

The recent synthesis of the carbodicarbene (**1.30**) has generated a renewed interest in this carbon(0) chemistry.[7] The carbodicarbene is similar to the carbodiphosphorane, simply exchanging the phosphines for carbenes. A resonance structure can be drawn as an allene (**1.30a**).[49,50] At the time of publication, this species represented the allene with the highest degree of bending known. Reports have shown that bent allenes are very strong σ-donors and can even act as four electron donors.[51,52] Carbodiphosphoranes display the ability to act as Lewis bases in FLP chemistry, proving that these molecules are not only anomalies in the traditional bonding of carbon.[53]

This carbon(0) chemistry has inspired research on making p-block analogues of the carbodicarbene. Examples include the nitrogen(I) and phosphorus(I) cations (**1.31**), as well as the selenium(II) and tellurium(II) dicationic analogues (**1.32**).[54-57] The tellurium centre can accommodate an additional two carbenes to form a square planar complex (**1.33**).[55] The best bonding description for the latter species are donor-acceptor complexes.

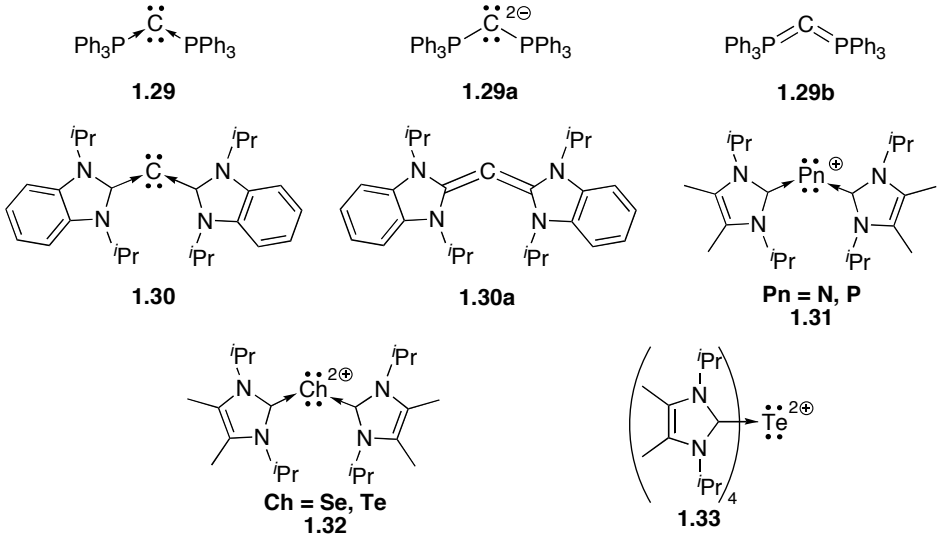


Figure 1.6: Structural representations of the carbodiphosphorane (**1.29)**, carbodicarbene (**1.30**), the pnictogen(I) (**1.31**) and chalcogen(II) analogues (**1.32**) and the four coordinate tellurium species (**1.33**).

Donor ligands have shown the ability to stabilize many other low coordinate reactive main group molecules. This has been accomplished with the B_2H_2, Si_2, P_2 and As_2 molecules in recent years (**1.34**-**1.36**; Figure 1.7).[58-61] The B_2H_2 molecule (**1.34**) features the first boron-boron double bond, with each boron atom having a hydride and a carbene to satisfy its octet.[59] The bonding of the Si_2 molecule (**1.35**) can be described as a based stabilized disilene with a lone pair on each silicon centre.[58] The group 15 species, diarsenic and diphosphorus (**1.36**),[60,61] do not have multiple bonding like the other examples, simply a single bond. The Si_2, P_2 and As_2 examples can be viewed as new allotropes of silicon, phosphorus and arsenic. These examples differ from typical allotropes as the organic groups on the main group centres make them soluble in many organic solvents.[62]

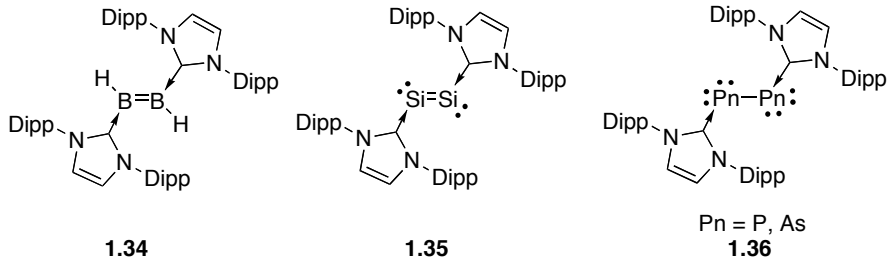


Figure 1.7: Carbene stabilized homoatomic main group molecules.

Germanium dihydride was recently stabilized by a similar concept.[63] The strategy involved having a carbene donate electron density into the empty p-orbital on germanium and the lone pair on germanium coordinate to the Lewis acid BH_3 (**1.37**; Figure 1.8). This is an interesting example of a molecule stabilized by both a Lewis acid and a Lewis base. In order to isolate the tin analogue, a transition metal Lewis acid was needed (**1.38**).[64] Thus proving that in some cases transition metals are better ligands than non-metals at stabilizing main group centres.

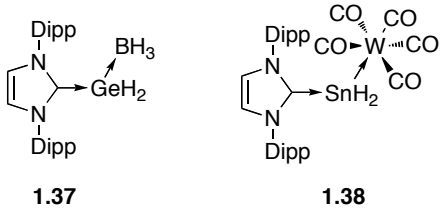


Figure 1.8: Examples of stabilizing main group centres using a Lewis acid and Lewis

base.

1.6 Main Group Polycations

Recent years have shown an interest in isolating main group polycations (*e.g.* **1.32** and **1.33**; Figure 1.10).[8] Polycations are molecules of which a formal charge of 2+ or greater can be assigned to the central element of interest. These species are predicted to be highly unstable, hence have the ability to activate small molecules. This instability makes them challenging synthetic targets as the molecules in this bonding arrangement are typically electron deficient, often lacking the quintessential octet. To satisfy this deficiency, an approach has been to bind Lewis bases to the central element and occupy the empty coordination sites as performed with the other reactive molecular units (*e.g.* **1.29**-**1.38**).

The known group 13 polycations are restricted to boron and aluminum (Figure 1.9). The addition of pyridine to BBr_3 displaces two or all three halides to access boron di- and tri-cations depending on the stoichiometry (**1.40**, **1.41**).[65,66] The first structurally characterized species for this group was a boron dication featuring a β-diketiminate ligand to stabilize the boron centre in conjunction with bipyridine (**1.42**).[67] A similar approach has been followed with aluminum, in this case a tetraamine coordinated to the dicationic aluminum (**1.43**).[68] The tetraamine was necessary as aluminum accommodates larger coordination numbers.

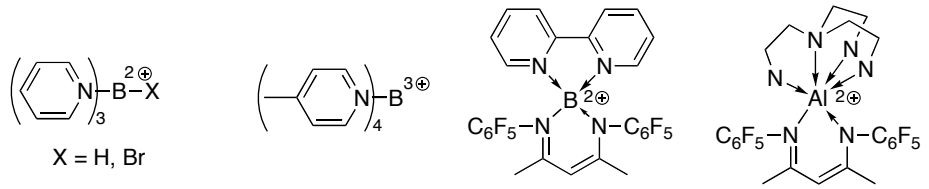


Figure 1.9: Structural representations of the known group 13 dications.

Group 14 dications have been prepared for silicon, germanium and tin (Figure 1.10). A silicon(IV) centre with two hydrides and four pyridine donors in the coordination sphere was the primary example of this group (**1.44**) and the only example in the 4+ oxidation state.[69] The remaining representatives are in the 2+ oxidation state. Three carbenes can be bound to a Ge(II) centre with a lone pair to satisfy its octet (**1.45**).[70] Interestingly, this

species acts as a Lewis base and can be viewed as a dicationic analogue of a phosphine. The approach to prepare the majority of the germanium and tin dications has been to utilize macrocycles to complex the main group centre with multiple weak contacts. The cryptand ligand forms a stable cavity to completely encapsulate the germanium(II) ion (**1.46**).[71] Crown ethers, depending on cavity size, can sequester dicationic complexes of Ge and Sn.[72-74] Small cavities (with respect to the ionic radius of the main group element) form sandwich species or appropriately sized macrocycles can isolate Ge(II) or Sn(II) dicationic centres within the cyclic ring (**1.47**-**1.49**). The crown ethers can also be substituted for nitrogen based macrocycles such as cyclic amines (**1.50**).[73] The weak dative interactions in the macrocyclic species should allow for the release of Ge^{2+} and Sn^{2+} for various reactions.

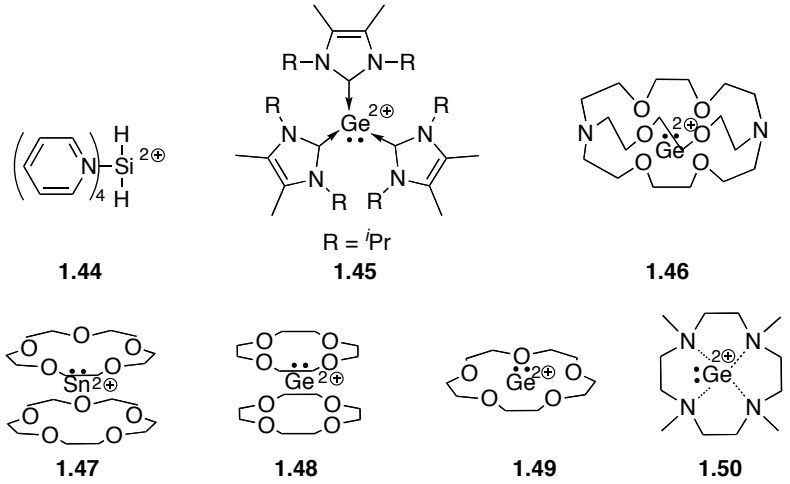


Figure 1.10: Structural representations of the known group 14 dications.

With respect to group 15, polycationic chemistry has been restricted to phosphorus and a singular arsenic example (Figure 1.11). A phosphorus(V) dication with three methyl groups was isolated by the coordination of a DMAP donor to occupy the empty p-orbital (**1.51**).[75] Phosphorus(III) mono- and di- and tri-cations can be prepared by the 1:1 or 2:1 stoichiometric metathesis reactions of a NHC-TMS complex with PCl_3 (**1.52**).[76] A similar phosphorus(III) dication can be synthesized with two phosphine donors to coordinate to the phosphorus atom with a lone pair and methyl substituent (**1.53**).[77] In terms of arsenic, a guanidinate ligand and bipyridine have been shown to bind to a dicationic arsenic(III)

centre and occupy the vacant coordination sites rendering the pnictogen centre stable (**1.54**).[78]

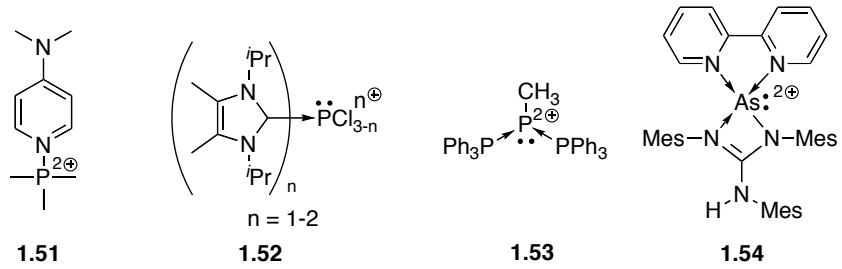


Figure 1.11: Structural representations of the known group 15 dications.

The group 16 elements are interesting synthetic targets as they are more electronegative than the former three groups. Two examples have been mentioned for group 16 with carbene donors stabilizing chalcogen(II) dicationic centres (**1.32** and **1.33**; Figure 1.6).[54,55] The pioneering work in this area was done by Furukawa *el al.* in the development of trans-annulated chalcogen(IV) dications featuring proximal chelating thioethers to stabilize the dicationic centre (**1.55**, **1.56**; Figure 1.12).[79-83] Two sulfur(VI) dications are known with carbon (**1.57**) and phosphorane iminato ligands (**1.58**).[84,85] The sulfur(IV) species are formally dicationic analogues of the ubiquitous hydrocarbon methane. These species are all four coordinate and highly stable. Since these all have high coordination numbers, it is anticipated that these molecules would be inert for bond activation reactions. It is not surprising that these species are air and moisture stable. Telluro and thio-urea stabilized dications have also been prepared for tellurium(II) centres typically through redox routes (*e.g.* **1.59**).[86-88]

The most interesting example in the literature is reported by Cowley *et al.*, they explained their synthesis of a two coordinate sulfur(IV) dication with two amides and a lone pair at sulfur (**1.60**).[26] The molecule would be classified as a sulfenium dication, isovalent to the carbene. This species has however only been characterized by multinuclear NMR and vibrational spectroscopy. Solid-state structures have been reported for the majority of the other examples and the current standard for comprehensive characterization of new bonding motifs involves obtaining a structure from X-ray diffraction studies. Attention should be devoted to this derivative.

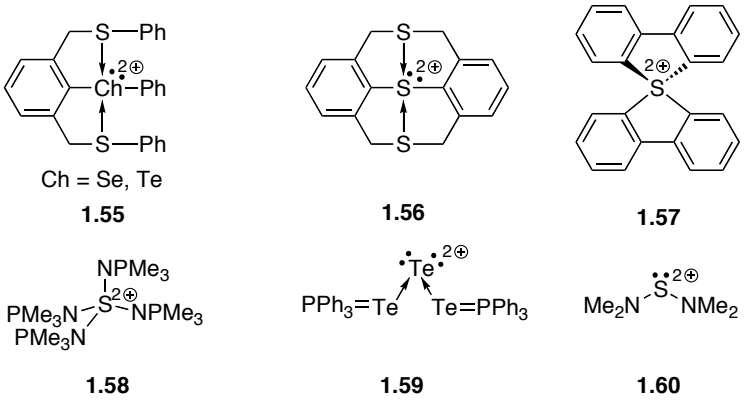


Figure 1.12: Structural representations of the known group 16 dications.

1.7 Nitrogen Based Ligands

The use of nitrogen based ligands whether they be monodentate, multidenate, neutral or anionic has been a critical component to many facets of inorganic chemistry research. This has been highlighted not only in the main group polycations but also in the carbene analogues.[89] Although these p-block examples have been prepared, the target element centres sequestered have typically been transition metals.[90] The metal complexes have been useful in several areas of catalysis, which in turn has opened their applications to numerous areas of organic synthesis.[91] The types of available nitrogen based ligands are vast with prominent examples being amides, amines, imines, pyridines and nitriles (**1.61**-**1.65**, respectively; Figure 1.13). The latter four species are neutral, hence form dative bonds to the metal whereas amides have a covalent linkage to the metal. Even though several of the mentioned ligands form dative bonds (**1.62**-**1.65**), the donor properties of each are significantly different and can have a great effect on chemistry at the metal centre.

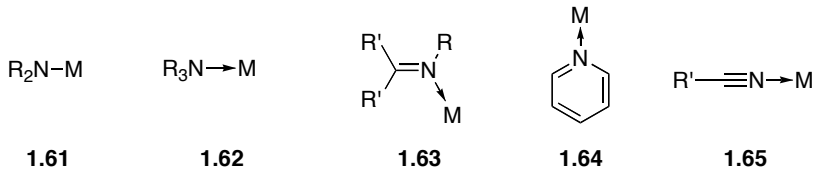


Figure 1.13: Monodentate nitrogen ligands binding to metal centres.

From the ligands listed above, it can be envisioned that numerous combinations of either the same, or different units can be incorporated into a single ligand. Derivatives with symmetric chelates include diamides (**1.66**), macrocyclic amines (**1.67**), diazabutadiene (**1.68**) and 2,2'-bipyidine (**1.69**; Figure 1.14). Common species with more than one type of nitrogen donor are the anionic β-diketiminate (**1.70**), amidinate (**1.71**), 2-amidopyridine (**1.72**), as well as the neutral diiminopyridine ligands (**1.73**). The chelate effect of these ligands offers additional stability to the metal centre. The combination of anionic and neutral moieties can be easily altered to have multidentate ligands with various anionic charges. The number of spacer atoms between the donors can also be changed to adjust the cavity to accommodate the metal centre. In many cases the ligand has various sites available to incorporate electron withdrawing, electron donating or bulky groups that offers the potential to easily fine-tune the electronics and sterics. The combination of all of these features justifies their wide utility in current chemistry.

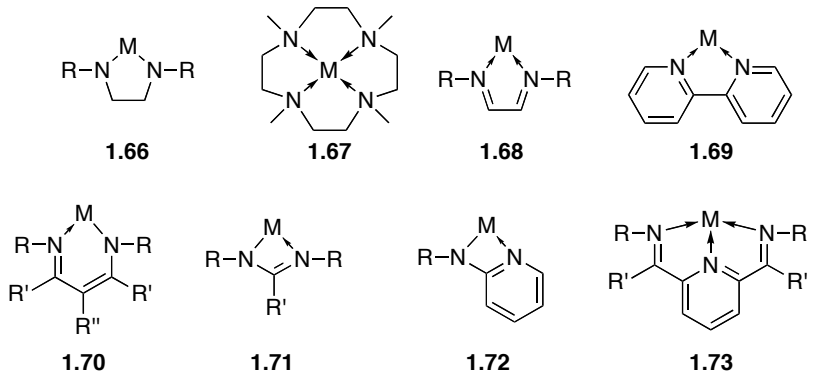
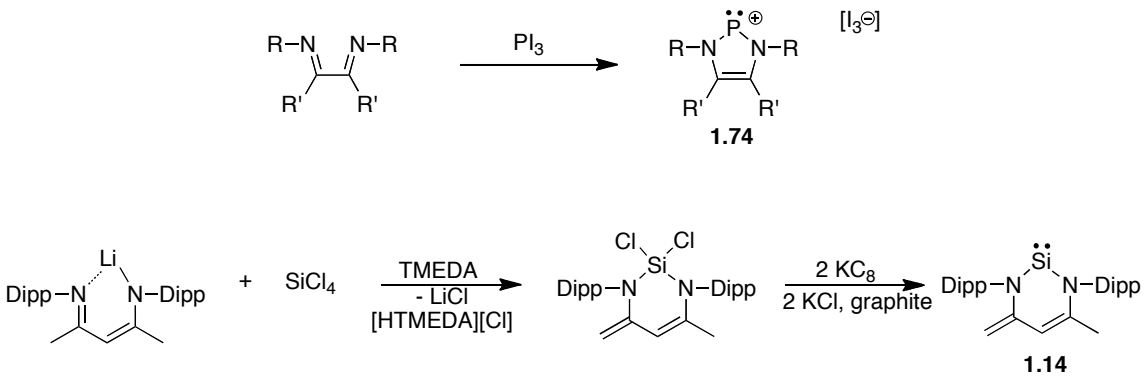


Figure 1.14: Schematic diagram of metal complexes supported by multidentate nitrogen based ligands.

The chemistries of the transition metals with the aforementioned ligands have been widely explored and studies with main group elements are more scarce. Some nitrogen based ligands have been used in p-block chemistry, as the diazabutadiene ligand (**1.68**) is the precursor to make up the framework for the NHC and the five membered main group analogues (*e.g.* **1.74**, NHP, Scheme 1.4).[92,93] The β-diketiminate ligand has shown the ability to isolate reactive centres, an excellent example being the six membered NHSi (**1.14**).[94] The group 13 and group 14 chemistries of these ligands have been explored in

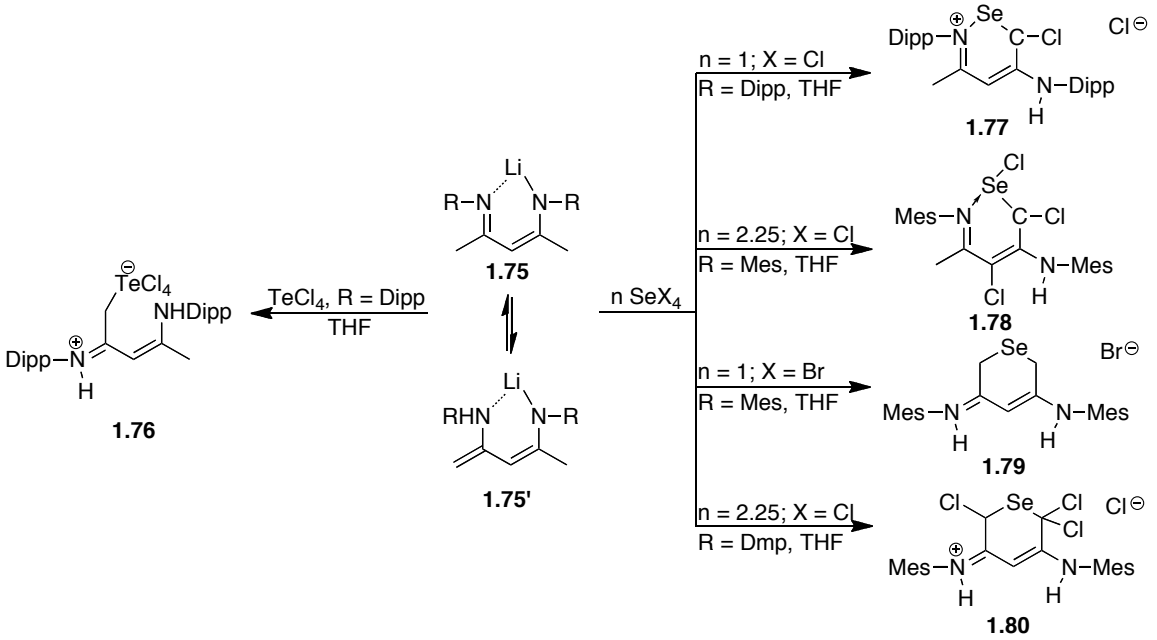
some detail whereas minimal reports exist for groups 15 and 16.[95]



Scheme 1.4: The synthesis of the NHP (**1.74**) from DAB and PI_3 (top) and the synthesis of the six membered NHSi (**1.14**; bottom).

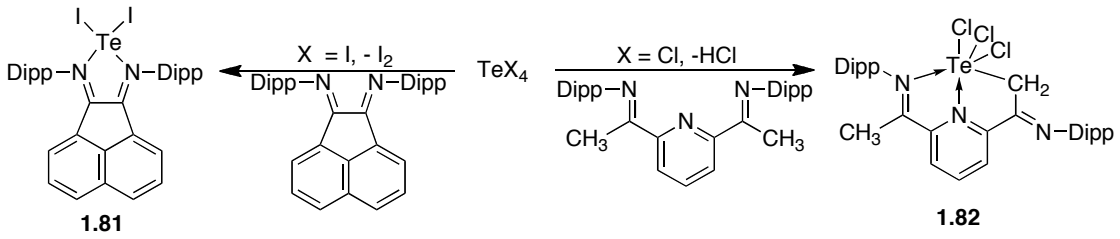
1.8 Chalcogen Chemistry with Multidentate Nitrogen Based Ligands

The Richards group has performed some studies on the chemistry of the β-diketiminate ligand with the chalcogen tetrahalides.[96,97] The experiments show that rather than the expected reactivity occurring through the two nitrogen atoms, the carbon on the ligand framework forms a bond to the chalcogen. This is postulated to occur through reaction with the eneamine tautomer (**1.75'**, Scheme 1.5). The outcome of the reactions was highly variable being dependent on the chalcogen, halide, solvent, stoichiometry and the groups on the nitrogen atoms. The yields also ranged from small batches of single crystals to 60%. When tellurium(IV) chloride was used, a carbon bound $TeCl_4$ moiety is obtained (**1.76**). In the case with $SeCl_4$, a selenium(II) product is produced in all cases but four different products were observed in changing the previously mentioned variables (**1.77**-**1.80**). The latter observation indicates that the chalcogen(IV) halides are susceptible to releasing dihalide that in many cases halogenates the ligand. The chemistry with the chalcogen(II) halides with nitrogen based ligands should be easier to control and be more viable targets. Furthermore, the bonding through a methyl group indicates that reactivity through the eneamine tautomer is favourable.



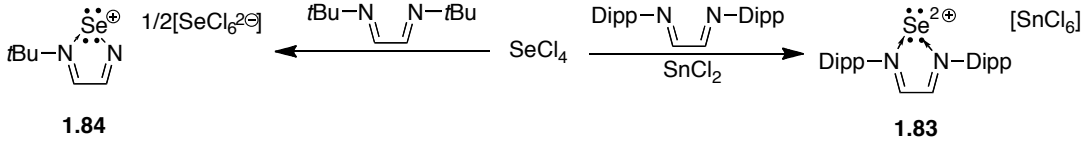
Scheme 1.5: Reaction products of ChX_4 reagents with β-diketiminate ligands featuring methyl groups on the α-carbon.

Alan Cowley *et al.* have reported some more controllable chemistry with multidentate neutral nitrogen based ligands. Tellurium(IV) iodide reacts with BIAN by the elimination of I_2 to produce a base sequestered TeI_2 species (Scheme 1.6; **1.81**).[98] In examination of a methyl substituted DIMPY ligand, bonding through the methyl group occurs to produce an *N,N'C*-bound tellurium heterocycle (**1.82**) as observed with the chemistry with the methyl substituted β-diketiminate ligand.



Scheme 1.6: Reactions of neutral DIMPY and BIAN ligands with tellurium(IV) halides.

Early reports from our group have shown that these imine based systems are capable of isolating highly reactive centres much like TeI_2. A good example is the selenium polycation, Se^{2+} (**1.83**; Scheme 1.7).[99] This was accomplished by the reaction of $SeCl_4$, $SnCl_2$ and an aryl substituted diazabutadiene featuring hydrogen atoms on the backbone carbon atom to yield the *N,N'*-chelated dicationic selenium centre. This species represented the first dicationic chalcogen analogue of the NHC. The reaction of $SeCl_4$ with a DAB ligand with tertiary butyl groups on nitrogen and hydrogen atoms on the carbon atoms produced a 1,2,5-selenadiazolium salt with an $SeCl_6^{2-}$ counteranion in addition to the byproduct 2-chloro-2-methylpropane.[100] This research has yet to be extended to sulfur. The chemistry of sulfur with these ligands should also provide interesting outcomes.



Scheme 1.7: Reactions of $SeCl_4$ with DAB ligands.

1.9 Scope of the Thesis

The current project involves examining the reactivity of neutral nitrogen based donors with phosphorus, selenium, tellurium and in the most detail with sulfur. The chemistry of the chalcogens with the common nitrogen based ligands is in its infancy. Although more widely studied, phosphorus also lacks some complexes with nitrogen based ligands. The particular ligands in this study are the diazabutadiene (DAB), diiminopyridine (DIMPY), *N,N,N',N'',N''*-pentamethyldiethylenetriamine and pyridine derivatives. The reactivity of

the ligands with a series of main group halides will be explored determining that the substitution on the ligand framework in many cases has a significant impact on the chemistry. As previous groups have observed with nitrogen based ligands, bonding through carbon atoms on the ligand framework is problematic. Studies both controlling and avoiding this reactivity will be of focus. All of the ligands have been widely used in transition metal chemistry and learning more about their reactivity will undoubtedly be helpful for the rest of the periodic table.

The synthetic targets will ultimately be intrinsically interesting molecules. These include the dicationic sulfur carbene analogue, the first *N,N',N''*-chelated chalcogen and phosphorus DIMPY complexes, as well as multidentate amine and pyridine sequestered sulfur(II) dications. Following the synthesis, the molecules will be tested as reagents for small molecule activations. From the conclusions of these studies, steps towards a greater understanding of the group 15 and 16 elements with nitrogen based ligands will be made and the information should be transferrable to the rest of the p-block and the d-block. This report by no means closes the door on a chapter of main group chemistry but rather opens it to a series of opportunities with new molecules and their subsequent chemistries.

1.10 References

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Chapter 2

Reactions of Diazabutadiene and Bisiminoacenaphthene Ligands with the In Situ Generated "$S(OTf)_2$" Synthon and SCl_2[ϕ]

2.1 Introduction

The reactivity of α-diimine ligands (*e.g.* 1,4-diazabutadiene, DAB; 1,2-bisiminoacenaphthene, BIAN; Figure 1) with the majority of the elements on the periodic table has been widely explored. The bulk of these studies have been conducted on metals, whereas non-metallic elements have, for the most part, been ignored.[1] Exceptions lie with carbon, boron and phosphorus, which have been extensively studied with Schiff-base ligand systems and revealed highly novel outcomes.[2]

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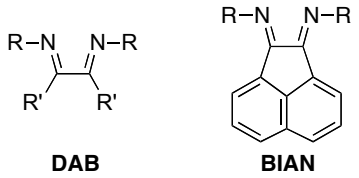

Figure 2.1: The structures of the diazabutadiene (DAB) and bisiminoacenaphthene (BIAN) ligands.

With respect to the common main group starting materials, reagents for such chemistry are the electrophilic main group halides. Boron trichloride reacts in a 1:1 stoichiometry with aryl BIAN derivatives with the displacement of a halide resulting in the diimine sequestered boron cation with a chloride anion (Figure 2.2; **A**). If the same reaction is conducted with a second equivalent of BCl_3 or 2 equivalents of BBr_3, the halide binds to

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ϕ A version of this work has been published in a) Martin, C. D.; Jennings, M. C.; Ferguson, M. J.; Ragogna, P. J. *Angew. Chem. Int. Ed.*, **2009**, 2210. b) Martin, C. D.; P. J. Ragogna *Inorg. Chem.* **2010**, *49*, 4324. And c) Dutton, J. L.; Martin, C. D.; Sgro, M. J.; Jones, N. D.; Ragogna, P. J. *Inorg. Chem.* **2009**, *48,* 3239. This work has been reproduced with permission.

the second BX_3 molecule resulting in a BX_4^- anion.[3,4] Similarly, an alkyl DAB ligand reacts stoichiometrically with BBr_3 producing an analogous cationic diimine BBr_2 complex with a Br^- counterion (**B**).[5] The reaction of an aryl DAB with BCl_3 in a 1:1 stoichiometry in hexanes gives rise to covalent N-B bonds with a loss of the diimine framework giving a neutral diazaborolidine with double-halogenation of the backbone carbon atoms (**C**).[6,7] Switching the solvent to CH_2Cl_2 produces a different outcome as the elimination of HCl occurs generating a carbon-carbon double bond in the ligand framework (**D**).[7]

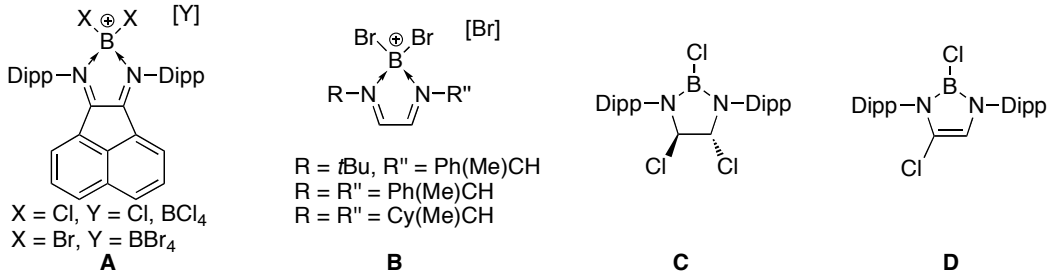


Figure 2.2: Reaction products of DAB and BIAN ligands with boron trihalides.

Reactions of DAB or BIAN ligands with PBr_3 proceed cleanly in the presence of a halide trap (*e.g.* cyclohexene) and undergo a charge-transfer giving the corresponding bromo-phosphines (Figure 2.3; **E**, **F**).[8] The reaction proceeds by generating a P(I) intermediate which is then oxidized to P(III) by the ligand in a subsequent step by a charge-transfer process. These halophosphorus compounds are precursors to N-heterocyclic phosphenium cations (**G**, **H**) via halide abstraction. The phosphenium cations can also be made directly with a 1:1 mixture of $SnCl_2$ and PCl_3 or PI_3 alone with either DAB or BIAN ligands.[9-11] The reactivity proved consistent in all cases regardless of the substitution on the backbone carbon.

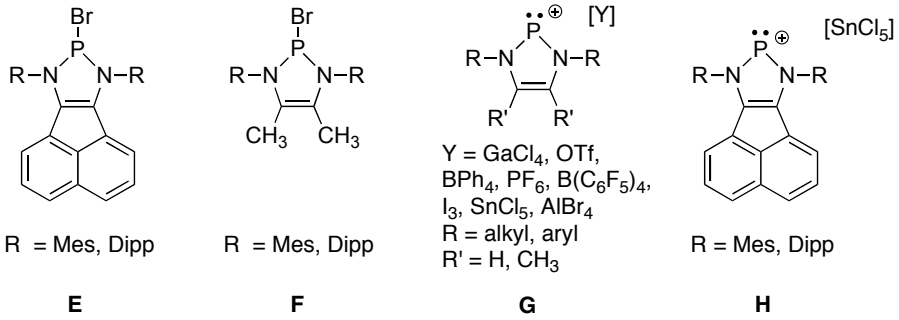


Figure 2.3: Bromophosphines and phosphenium cations derived from DAB and BIAN ligands.

Research in our group has been focused on the interactions of these ligands with the chalcogens, mainly focused on selenium.[12-21] Selenium dichloride and dibromide react with BIAN or DAB ligands with aryl groups on N produce a "trapped" SeX_2 unit (Figure 2.4; **I**, **J**).[16] If *tert*-butyl groups are present on nitrogen, $SeCl_4$ and $SeCl_2$ both produce 1,2,5-selenadiazolium ring system (**K**, **L**).[12,14] The reaction of an aryl DAB with $SeCl_4$ in the presence of $SnCl_2$ which acts as both a reductant and halide abstracting agent yields the dicationic N-Heterocyclic carbene analogue (**M**).[13] This discovery was significant as it is a rare chalcogen(II) dication and represented the first example of an NHC analogue to the right of group 15 on the periodic table as all of the 2nd to 5th row elements for groups 13-15 had been reported, with the exception of indium. A dicationic sulfur centre would be an appealing addition to this series as the electronegativity is greater than selenium, its isolation is anticipated to be more challenging.

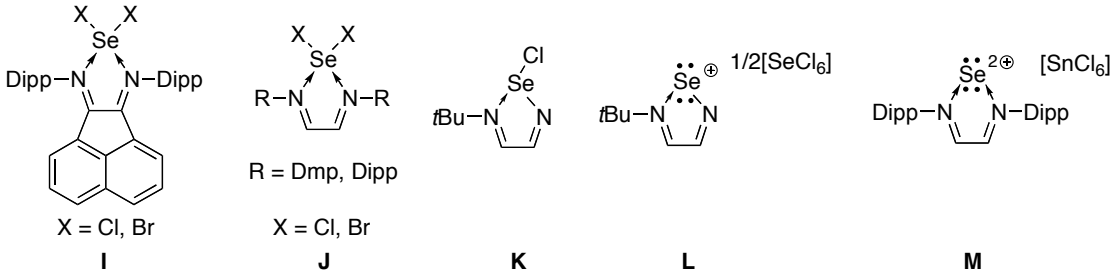


Figure 2.4: Reaction products of selenium halides with BIAN and DAB ligands.

The DAB ligands represent the direct precursor to the carbene analog. In the literature no reactions of sulfur reagents with α-diimine ligands have been reported. In this context,

we have conducted a comprehensive study on the reactivity of α-diimine ligands (Figure 2.5; **2.1**-**2.10**) with SCl_2 and an SCl_2 mixture with two stoichiometric equivalents of TMSOTf (TMS = trimethylsilyl; OTf = trifluoromethanesulfonate/triflate) with the ultimate target being the dicationic sulfur NHC analog. Interestingly, the substitution at nitrogen and the groups on the backbone carbon play a critical role in the outcome of the reaction. Through these studies we have isolated a series of new sulfur-nitrogen heterocycles, among them the NHC analog.

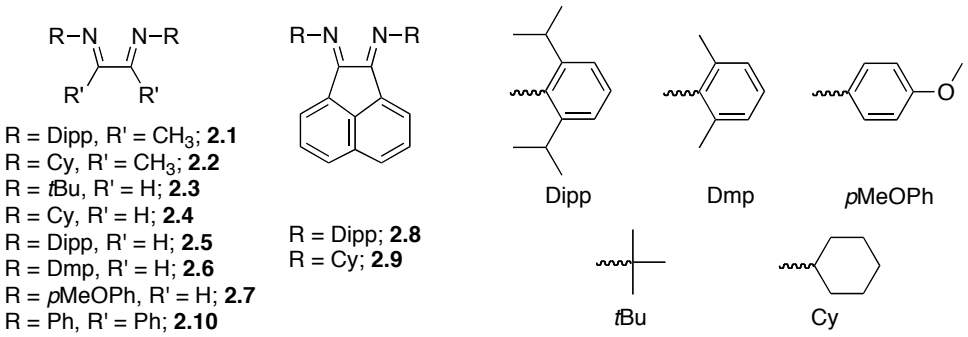


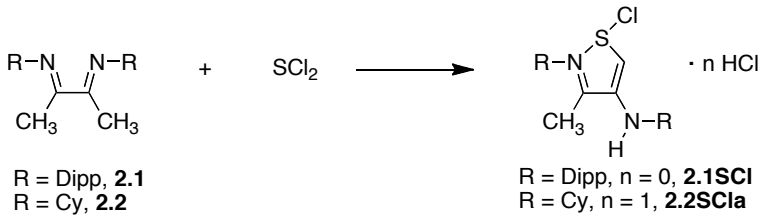
Figure 2.5: The DAB and BIAN ligands reacted with sulfur reagents in this study.

2.2 Results and Discussion

2.2.1 Synthesis

The 1:1 stoichiometric reaction of SCl_2 with **2.1** in THF immediately produced a deep red solution. Normal pentane was added to the mixture resulting in the precipitation of an orange powder. Washing the powder with Et_2O and obtaining an ^1H NMR spectrum of the redissolved solids in $CDCl_3$ revealed two separate resonances for the methine protons on the diisopropylphenyl groups (δ = 3.14 ppm and 2.20 ppm) bound to the nitrogen atoms with equivalent integrations indicating asymmetry in the ligand framework. The integration on the backbone methyl group was reduced from six to three and two new singlets were observed each integrating to one (δ = 8.32 ppm and 6.10 ppm). Although the proton NMR spectrum was indicative of a single product, the assignment could not be made solely on these data. Crystals were grown from a CH_2Cl_2 solution and a solid-state structure obtained that revealed an unusual N,C-bound five-membered SNC_3 heterocycle contrary to the expected *N,N'*-bound species observed in group 13-15 chemistry (**2.1SCl**; Scheme 2.1). The NMR spectroscopic data support the solid-state structure as the two

singlets can be rationalized from the olefinic C-H proton originating from the former methyl group and an N-H on the exocyclic nitrogen.



Scheme 2.1: Reaction of **2.1** and **2.2** with SCl_2 to produce the SNC_3 heterocycles.

A similar ^1H NMR spectrum was obtained from the reaction of **2.2** with SCl_2, indicating two inequivalent cyclohexyl groups. The sparingly soluble pale beige powder isolated was believed to be **2.2SCl**, however combustion analysis of the product was consistent with the hydrochloride salt **2.2SCla**. Attempts at removing the HCl with base were unsuccessful or led to decomposition of the heterocycle. Unfortunately, despite numerous attempts, X-ray quality crystals could not be grown but by analogy to the Dipp derivative, the structure could be assigned. The difference of **2.2SCla** being a hydrochloride salt versus the free base as in **2.1SCl**, is attributed to the increase in basicity that the cyclohexyl group provides in comparison to the diisopropylphenyl group.

A proposed mechanism for the reaction is outlined in Figure 2.6. The methyl substituted ligands can undergo tautomerization to the corresponding eneamine which is believed to be the active species reacting with SCl_2 through the alkene. This is followed by the imine coordinating to sulfur to form the five membered ring and eliminating HCl (in the case of **2.2**, the hydrochloride adduct is isolated). This reactivity has also been observed with the diiminopyridine and β-diketiminate ligands.[19,22,23]

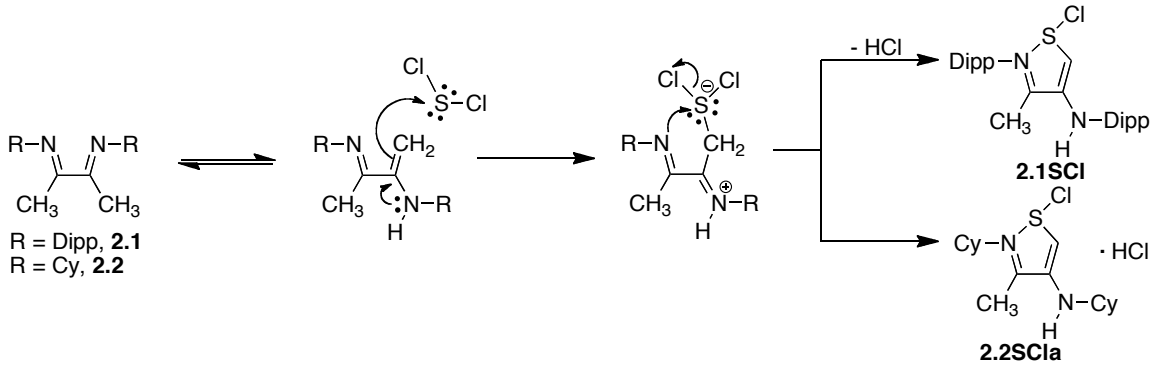
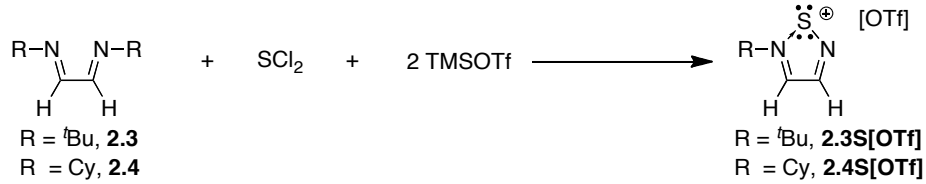


Figure 2.6: Proposed reaction pathway to generate the $S_1N_1C_3$ heterocycles.

Although interesting and unique to group 16, the reactivity of the methyl group was undesireable in regards to obtaining the *N,N'*-bound species. In this regard, our approach moved to DAB ligands lacking methyl groups on the backbone carbon atoms.

To examine the effect of alkyl substitution on the nitrogen atom, the reactions of "$S(OTf)_2$" with *tert*-butyl and cyclohexyl DAB ligands (**2.3** and **2.4**) in CH_2Cl_2 were carried out (Scheme 2.2).* The reaction of TMSOTf and SCl_2 in a 2:1 stoichiometry in CH_2Cl_2 at -78°C yielded a light orange solution. A solution of ligand was added to the "$S(OTf)_2$" mixture which produced pale beige slurries. The addition of *n*-pentane induced further precipitation, the supernatant was discarded and the solids dried *in vacuo*. The ^{1}H NMR spectrum of the redissolved solids revealed pure products with a break in symmetry of the two backbone protons observed in both cases (**2.3S[OTf]**, δ = 10.13, 9.03 ppm; **2.4S[OTf]**, δ = 10.09, 8.93 ppm). Also noteworthy, was a 50% reduction of the integration values of the *tert*-butyl or cyclohexyl protons suggesting the loss of an alkyl group on one of the nitrogen atoms. An *in situ* ^{1}H NMR spectroscopy experiment in $CDCl_3$ of the reaction of **2.3** with "$S(OTf)_2$" clearly indicated the formation of 2-chloro-2-methylpropane (δ = 1.62 ppm) as a reaction byproduct.

* In an attempt to characterize this "$S(OTf)_2$" species, the mixture was probed by $^{19}F\{^1H\}$ NMR spectroscopy. The $^{19}F\{^1H\}$ NMR spectrum at room temperature gave a singlet shifted to lower field, indicating a more ionic triflate. However, despite extensive attempts to identify a single, pure product, nothing definitive could be ascertained. Furthermore, if the chemistry (reported in this chapter) is carried out in the absence of OTf^-, only starting material and decomposition products are observed in the ^{1}H NMR spectra. Therefore we assign $S(OTf)_2$ as an *in situ* preparation.



Scheme 2.2: Reaction of N-alkyl DAB ligands with "$S(OTf)_2$".

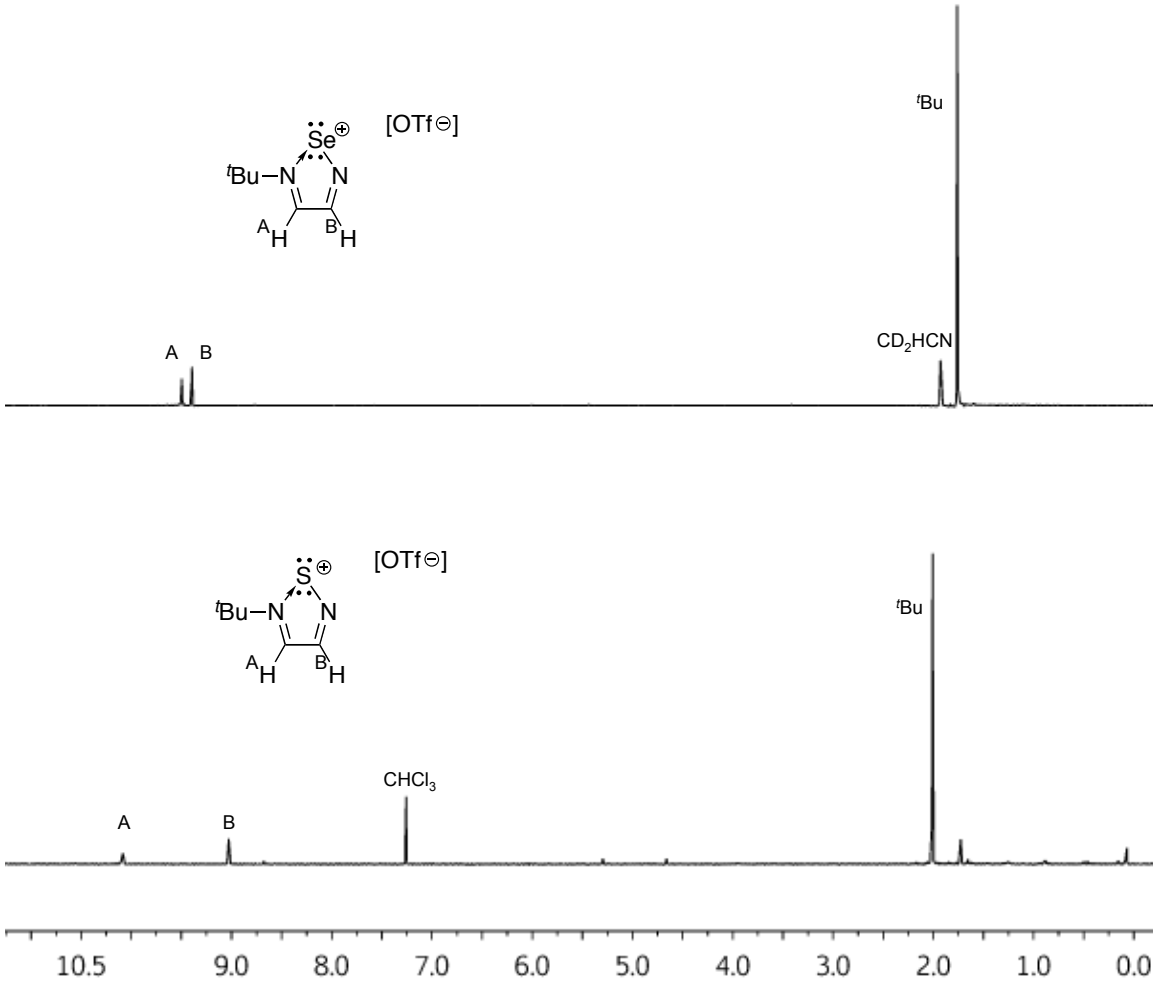
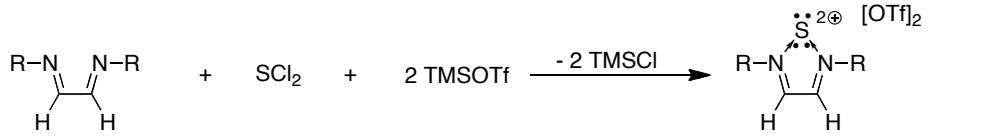


Figure 2.7: Stacked plot of ^{1}H NMR spectra of **2.3S[OTf]** in $CDCl_3$ (bottom) and the selenium congener in CD_3CN (top).

The ^{1}H NMR spectra were reminiscent of the related selenium system with **2.3** (δ = 9.49, 9.40 ppm) which also had a break in symmetry of the ligand framework (Figure 2.7).[14] The $^{19}F\{^{1}H\}$ NMR spectra displayed one signal diagnostic of ionic triflate (δ = -78.4 ppm

cf. $[NOct_4][OTf]$ δ = -78.5 ppm). Based on these data the compounds could be assigned the same connectivity as the selenium derivative, the thiadiazolium triflate salts **2.3S[OTf]** and **2.4S[OTf]**.[14,20] This 1,2,5-chalcadiazolium ring system is not unusual for the heavy chalcogens (S, Se, Te).[12,14,20,24-26] Unfortunately these compounds were highly unstable in solution with **2.4S[OTf]** decomposing within 10 minutes of being synthesized. Even as a powder at room temperature, decomposition was observed within 20 minutes. Given this instability, crystallization attempts were unsuccessful.

Based on the previous observations, alkyl substitution on nitrogen was to be avoided as well as methyl groups on the backbone carbon atom in order to produce *N,N*'-bound sulfur complexes. The natural evolution was to explore DAB ligands with aryl groups on N and protons on the backbone carbon atoms (aryl = Dipp, **2.5**; Dmp, **2.6**; *p*MeOPh, **2.7**; Scheme 2.3). Any attempts at reactions of SCl_2 with DAB ligands resulted in recovery of starting material, hence "$S(OTf)_2$" was utilized. To a solution of "$S(OTf)_2$" in CH_2Cl_2, one equivalent of a DAB ligand in CH_2Cl_2 was added dropwise generating crimson (**2.5**, **2.6**) or purple solutions (**2.7**). Removal of the volatiles *in vacuo* gave rise to red/orange or purple powders.



R = Dipp, **2.5**
R = Dmp, **2.6**
R = pMeOPh, **2.7**

R = Dipp, **2.5S[OTf]**
R = Dmp, **2.6S[OTf]**
R = pMeOPh, **2.7S[OTf]**

Scheme 2.3: Reactions of aryl DAB ligands with "$S(OTf)_2$".

Proton NMR spectroscopy of the redissolved crude powder in CD_3CN from the reactions revealed a major product (~70% purity) with a diagnostic downfield shift of the backbone protons on the DAB ligand (δ = 10.23-9.69 ppm *cf.* free ligand δ = 8.42-8.13 ppm).[27] The major products in the spectra consisted of one set of resonances indicative of a symmetric bonding environment as the signal for the backbone protons integrated to two with respect to the two aryl groups. Single resonances were observed in the $^{19}F\{^1H\}$ NMR spectrum consistent with ionic triflate in solution (δ = -78.6 to -78.7 ppm). Based on these data, the bonding was assigned as the *N,N'*-chelated dicationic chalcogen

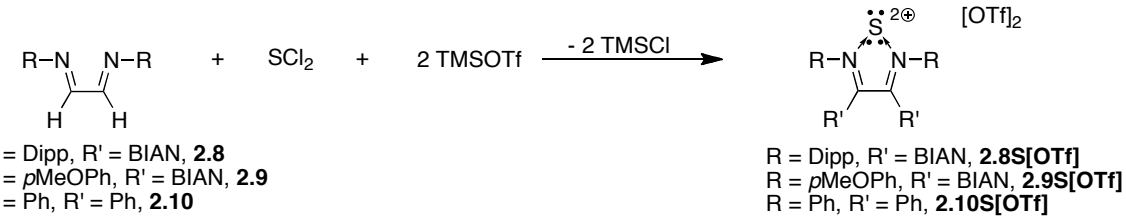
complexes (**2.5S[OTf]**, **2.6S[OTf]** and **2.7S[OTf]**) with two triflate counteranions. The solid-state structures obtained confirmed this but did display distant S···O contacts to the sulfur centre.

Upon increasing the stoichiometry of "$S(OTf)_2$" to 1.5 stoichiometric equivalents in all three reactions, the yield in the crude mixture increased to approximately 85%. We postulate that the imine nitrogen atoms are sufficiently basic to deprotonate the backbone protons on the dicationic heterocycle which are acidic upon the coordination of the ligand to the highly charged sulfur center. This ultimately results in decomposition of the desired product, as the protonated ligand became more prevalent in the crude ^{1}H NMR spectrum. Decreasing the amount of free ligand in solution hinders this process and allows the reaction to proceed more cleanly. Conveniently, the excess SCl_2 and TMSOTf can be easily removed by washing with *n*-pentane or *in vacuo*. A related observation has been made with the heterocyclic nitrenium cation (nitrogen analog of **G**; Figure 2.3) as the backbone proton on these systems can also be abstracted.[28]

Despite extensive efforts to develop a high yielding purification procedure, the highest isolated yield of a pure product for the *para*-methoxy derivative was on the order of 5%, despite the reaction going to 85% as indicated by ^{1}H NMR spectroscopy. The difficulties in purifying this material can be attributed to the high insolubility of **2.7S[OTf]** in organic solvents and adding to this problem, **2.7S[OTf]** also has very similar solubility to the impurities.

To examine an analogous ligand framework lacking the reactive backbone protons, the chemistry was extended to the closely related aryl BIAN ligand system (aryl = Dipp, **2.8**; *p*MeOPh, **2.9**; Scheme 2.4) and the DAB ligand featuring phenyl groups on both the nitrogen atoms and the backbone carbon atoms (**2.10**). We anticipated that incorporating large organic groups should improve the solubility and avoid the acidic backbone hydrogens. Crude powders from the reactions of "$S(OTf)_2$" with **2.8**-**2.10** displayed the desired enhanced solubilities in organic solvents making the isolation of larger quantities of pure material possible. The *para*-methoxyphenyl BIAN derivative (**2.9S[OTf]**) was isolated as deep red crystals in 51% yield by two subsequent recrystallizations from a 1:1 solvent mixture of CH_3CN and Et_2O of the bulk powder at -30°C as confirmed by ^{1}H NMR spectroscopy. Crystals suitable for X-ray crystallographic studies were grown by

vapour diffusion of Et_2O into acetonitrile confirming the structure of **2.9S[OTf]**. The diisopropylphenyl analog (**2.8S[OTf]**) and DAB derivative with phenyl groups on both carbon and nitrogen (**2.10S[OTf]**) were purified by recrystallization of the bulk powder from a saturated solution of CH_2Cl_2 and pentane stored at -30°C overnight, which generated orange X-ray quality crystals of both compounds in good yield (73% and 60%, respectively). In all cases ^{1}H NMR spectroscopy revealed a symmetric bonding environment regarding the ligand framework. The ^{1}H NMR spectra displayed downfield shifts of the BIAN (**2.8S[OTf]** and **2.9S[OTf]**) and phenyl protons (**2.10S[OTf]**) on the backbone carbon atoms in the products consistent with the coordination of the ligand to a highly charged center.[29,30] Single resonances in the ^{19}F{^{1}H} NMR spectra were indicative of ionic triflate (**2.8S[OTf]** δ = -78.6 ppm; **2.9S[OTf]** δ = -78.3 ppm; **2.10S[OTf]** δ = -78.4 ppm). These data supported the synthesis of dicationic SC_2N_2 heterocycles.

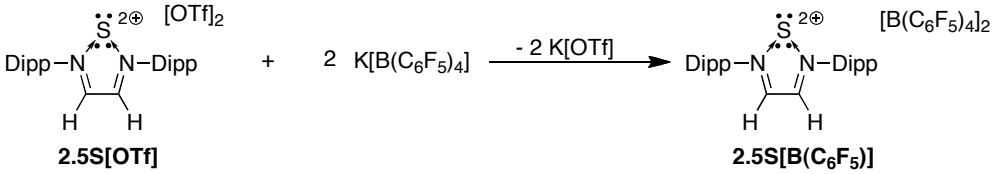


Scheme 2.4: Reactions of α-diimine ligands containing aryl groups on the backbone carbon atoms with "$S(OTf)_2$".

The connectivity of the heterocycles with aryl groups on the backbone carbon atoms was analogous to the DAB complexes with H-substitution on the backbone carbon confirming that the acenaphthene or the phenyl groups do not change the outcome of the reaction but improves the solubility of the products allowing the isolation of the *para*-methoxy derivative.

As triflates are known to covalently bind to electropositive centers in many circumstances, an anion exchange reaction was carried out by stirring **2.5[OTf]** with $K[B(C_6F_5)_4]$ in CH_2Cl_2 to produce the dication with the more weakly coordinating anion in order to confirm the ionic nature of the sulfur complexes (Scheme 2.5). After recrystallization, the ^{1}H NMR spectrum of the redissolved crystals matched that of **2.5S[OTf]**. The ^{19}F{^{1}H} NMR spectrum indicated the absence of triflate and the presence

of $[B(C_6F_5)_4]$, confirming the composition as (**2.5S[B(C_6F_5)$_4$]**). The solid-state structure had the same dicationic SN_2C_2 heterocycle present.



2.5S[OTf] **2.5S[B(C_6F_5)]**

Scheme 2.5: Anion exchange reaction of **2.5S[OTf]** with $K[B(C_6F_5)_4]$ to produce **2.5S[B(C_6F_5)$_4$]**.

The dicationic salts (**2.5S[X]-2.10S[X]**) all were unstable in solution at room temperature for periods greater than 2 hours but solid samples could be stored for weeks in an inert atmosphere at room temperature. The compounds all represent the first dicationic structural mimics of the N-Heterocyclic carbene.

2.2.2 X-ray Crystallography

Examination of the solid-state structure of **2.1SCl** reveals an N-C bound AX_3E_2 sulfur center in a distorted T-shaped geometry (Figure 2.8). Chlorine and nitrogen atoms each occupy an axial position and the carbon atom resides in the equatorial site. The result of a proton transfer (eneamine tautaumer) is confirmed by the C(1)-C(2) bond length of 1.373(6) Å and the C(2)-N(2) bond at 1.380(6) Å, which are contracted and extended, respectively in comparison to the uncoordinated ligand. The sulfur-chlorine bond shows significant elongation [2.849(2) Å], this metrical parameter indicates ionic character to the complex. However, the distance is well within the sum of the van der Waals radii (Σv.d.w. S-N 3.65 Å)[31] and despite this elongation, the chlorine atom still defines a T-shaped geometry about sulfur. This elongation of the S-Cl bond may be a function of hydrogen bonding in the solid state to the proton bound to N(2) of an adjacent molecule (Cl···H 2.50 Å) in addition to the nitrogen atom donating strongly into the same p-orbital on sulfur.

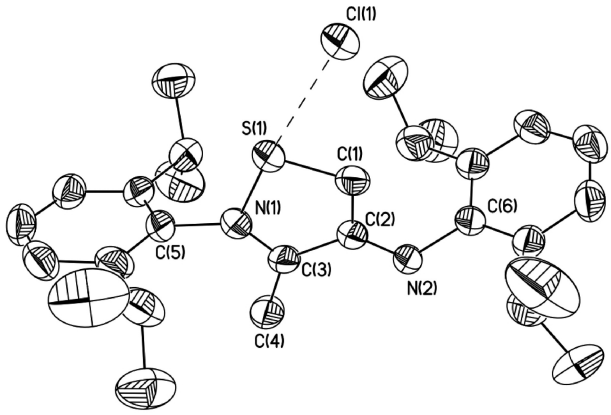


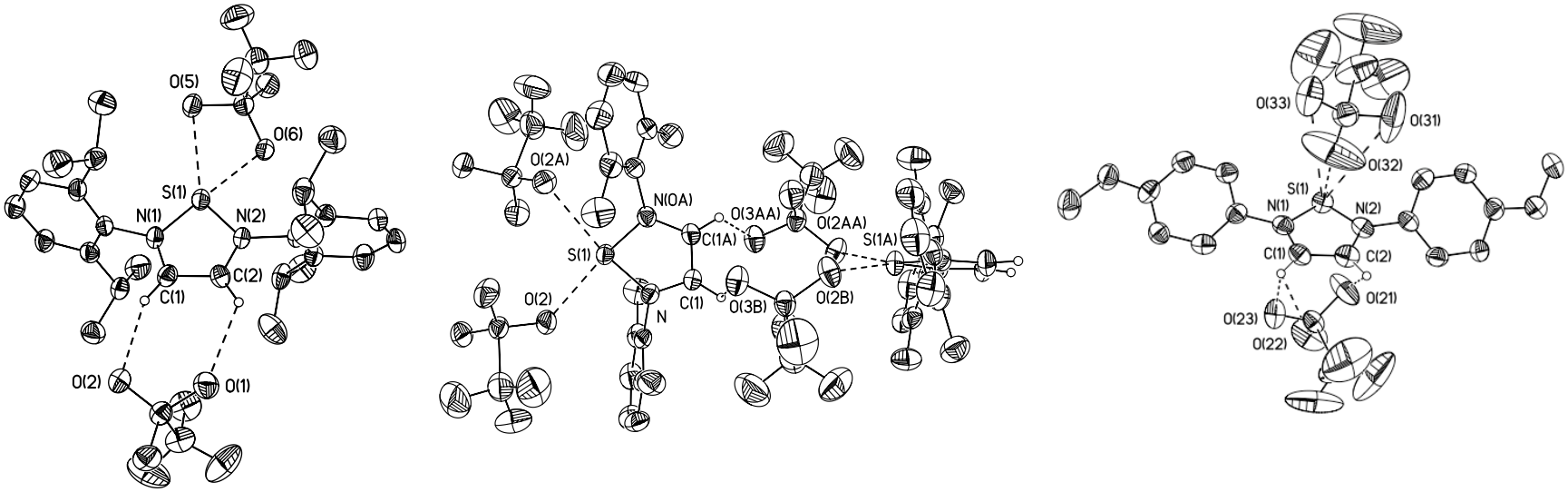
Figure 2.8: Solid-state structure of **2.1SCl**. Thermal ellipsoids are drawn to the 50% probability level, CH_2Cl_2 solvate and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): S(1)-N(1) 1.710(3), S(1)-C(1) 1.686(4), C(1)-C(2) 1.374(6), C(2)-C(3) 1.422(6), C(2)-N(2) 1.377(5), C(3)-N(1) 1.322(6).

In all of the crystal structures of **2.5S[OTf]**-**2.7S[OTf]** the bonding motif is a planar 5-membered SC_2N_2 ring [Figure 2.9; Tables 2.1 and 2.2; largest deviation from planarity 0.020(9)Å]. The color of compound **2.7S[OTf]** in the solid state and in solution is deep purple, contrary to **2.5S[OTf]** and **2.6S[OTf]**, which are orange. This high coloration is likely a result of the oxygen atoms *para* to the DAB ligand donating into the DAB π-system extending the conjugation. The metrical parameters indicate that the interplanar aryl/ SC_2N_2 ring angles are significantly smaller than those of **2.5S[OTf]** and **2.6S[OTf]**. The angles are on the order of 30° whereas in **2.5S[OTf]** and **2.6S[OTf]**, the aryl rings are much closer to being orthogonal to the sulfur heterocycle (**2.7S[OTf]**: 26.8°, 37.9° *cf.* **2.5S[OTf]**: 80.7°, 97.2°; **2.6S[OTf]** 76.1°). This phenomenon also could be present as **2.7S[OTf]** does not present bulky substituents on the *ortho* positions of the aryl ring, permitting the ring to orient itself with the SC_2N_2 plane.

The BIAN and all phenyl DAB complexes are essentially isostructural to the DAB derivatives bearing protons on the backbone carbons (**2.5S[OTf]**-**2.7S[OTf]**; Figure 2.10). The bulkier BIAN and phenyl substituted backbone orient the aryl rings more out of the plane than the hydrogen substituted DAB ligands. With respect to the BIAN complexes, **2.9S[OTf]** is highly colored like the *para*-methoxy substituted DAB complex

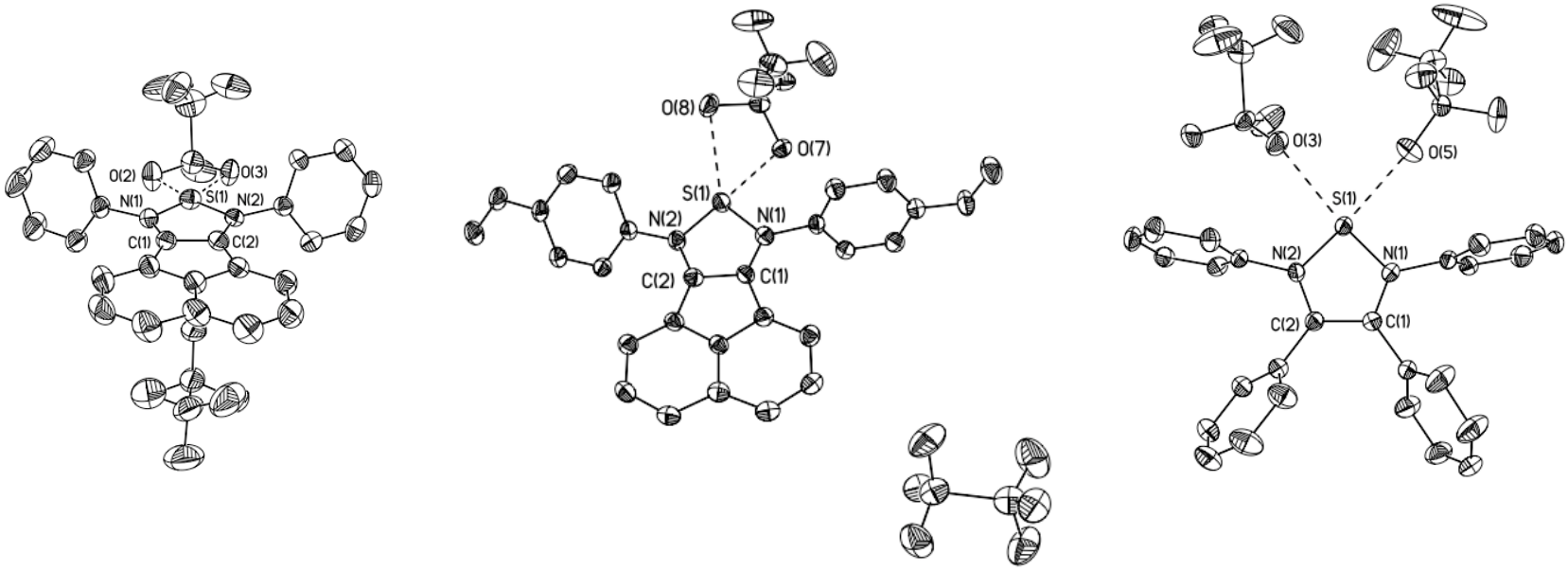
2.7S[OTf] and orients the aryl rings more in plane than the bulkier Dipp derivative, **2.8S[OTf]** (interplanar angles: **2.9S[OTf]** = 46.3, 80.5 *cf.* **2.8S[OTf]**= 76.2°, 81.3°).

The endocyclic bonds in all six dicationic complexes within the SC_2N_2 ring [C-N 1.293(9)-1.339(6); C-C 1.379(8)-1.439(5) Å] support the retention of two C=N double bonds and a C-C single bond, consistent with the free ligand. Sulfur-nitrogen bonds slightly shorter than typical sulfur-nitrogen single bonds [1.655(3)-1.708(3) Å *cf.* 1.74 Å] are observed, which can be rationalized by the binding of the ligand to the electron deficient sulfur(II) center. These endocyclic bond lengths are in close agreement with computational results (C-C 1.389, C-N 1.331, S-N 1.705 Å). Although a Lewis representation properly delocalizes the dicationic charge on the peripheral nitrogen atoms, given the previously published computational data and solid-state structural features, the bonding in these compounds can be best described by a *N*,*N*'-chelated sulfur center bearing two lone pairs with a formal charge of +2. This dative model is further underscored by the relative ease with which the sulfur atom can be displaced from the chelate ring by the addition of strong Lewis bases such as phosphines.



2.5[OTf] **2.6[OTf]** **2.7[OTf]**

Figure 2.9: Solid-state structures of **2.5S[OTf]-2.7S[OTf]**. Ellipsoids are drawn to 50% probability, all hydrogen atoms excluding hydrogen atoms interacting with the anion and solvates are omitted for clarity.



2.8S[OTf] **2.9S[OTf]** **2.10S[OTf]**

Figure 2.10: Solid-state structures of **2.8S[OTf]**-**2.10S[OTf]**. From left to right, top to bottom: Ellipsoids are drawn to 50% probability, all hydrogen atoms excluding hydrogen atoms interacting with the anion and solvates are omitted for clarity Isopropyl groups are omitted for clarity in **2.8S[OTf]**.

Table 2.1. Selected metrical parameters for **2.5S[OTf]**-**2.10S[OTf]** and **2.5S[B(C_6F_5)$_4$]**. Bond lengths are in angstroms (Å) and angles in degrees (°).

	2.5S[OTf]	**2.6S[OTf]**	**2.7S[OTf]**	**2.8S[OTf]**	**2.9S[OTf]**	**2.10S[OTf]**	**2.5S[B(C_6F_5)$_4$]**	[b]Calculated[32]
[a]S-N	1.696(6)	1.695(3)	1.658(5)	1.697(3)	1.705(3)	1.676(2)	1.655(3)	1.705
	1.699(6)		1.682(4)	1.708(3)	1.704(3)	1.679(2)		
[a]N-C	1.293(9)	1.305(5)	1.323(7)	1.312(5)	1.323(4)	1.325(3)	1.313(4)	1.331
	1.324(9)		1.339(6)	1.316(5)	1.325(4)	1.329(3)		
[a]C-C	1.407(10)	1.390(8)	1.379(8)	1.439(5)	1.412(4)	1.421(4)	1.396(7)	1.389
O···S	2.313(5)	2.615(3)	2.997(6)	2.654(4)	2.454(2)	2.638(2)	--	--
O···H	2.265	2.309	2.290	--	--	--	--	--
N-S-N	87.8(3)	88.0(2)	90.3(2)	90.38(15)	90.15(12)	88.80(11)	90.9(2)	90.3
[a]SC_2N_2 deviation from planarity	0.011(10)	0.005(8)	0.020(9)	0.019(5)	0.005(4)	0.004(5)	0.001(7)	--
Aryl/SC_2N_2 angle	80.7, 82.8	76.1	26.8, 37.9	76.2, 81.3	46.3, 80.5	86.2, 89.5	76.6	--

[a]All metrical parameters refer to endocyclic E-E bonds. [b]Calculated optimized geometries are for the *N*-Ph substituted derivatives featuring protons on the backbone carbon atoms.

Table 2.2. X-ray details of **2.1SCl**, **2.5S[OTf]**-**2.10S[OTf]** and **2.5S[B(C_6F_5)$_4$]**.

Compound	**2.1SCl**	**2.5S[OTf]**	**2.6S[OTf]**	**2.7S[OTf]**	**2.8S[OTf]**	**2.9S[OTf]**	**2.10S[OTf]**	**2.5S[B(C_6F_5)$_4$]**
Empirical formula	$C_{29}H_{41}Cl_3N_2S_1$	$C_{28}H_{36}F_6N_2O_6S_3$	$C_{24}H_{30}F_6N_2O_7S_3$	$C_{20}H_{19}F_6N_3O_8S_3$	$C_{38.5}H_{40}Cl_1F_6N_2O_6S_3$	$C_{28}H_{20}F_6N_2\ O_8S_3$	$C_{28}H_{20}F_6N_2O_6S_3$	$C_{76}H_{40}B_2Cl_4F_{40}N_2S$
FW (g/mol)	556.05	706.77	668.68	639.56	872.36	722.64	690.64	1936.58
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	*P*21/*c*	P-1	I*bca*	P*na*2(1)	P2(1)/*c*	P*bca*	P-1	P*bcn*
a (Å)	10.887(2)	10.488(2)	16.0424(14)	7.2453(9)	20.459(4)	18.324(4)	10.446(2)	18.958(4)
b (Å)	19.883(4)	10.941(2)	16.6859(15)	16.174(2)	12.219(2)	13.677(3)	11.972(2)	12.585(3)
c (Å)	14.898(3)	15.231(3)	22.960(2)	22.279(3)	17.293(4)	23.463(5)	13.970(3)	32.661(7)
α (deg)	90	77.92(3)	90	90	90	90	113.30(3)	90
β (deg)	92.75(3)	82.44(3)	90	90	110.96(3)	90	94.40(3)	90
γ (deg)	90	73.50(3)	90	90	90	90	108.73(3)	90
V (Å^3)	3221(1)	1633.8(6)	6146.1(10)	2610.8(6)	4036.8(14)	5880(2)	1477.4(5)	7792(3)
Z	4	2	8	4	2	8	2	4
D_c (mg m^{-3})	1.147	1.437	1.445	1.627	1.435	1.633	1.553	1.651
radiation, λ(Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	193(2)	150(2)	193(2)	193(2)	150(2)	150(2)	150(2)	150(2)
$R1[I>2\sigma I]^a$	0.0795	0.0856	0.0674	0.0597	0.0717	0.0601	0.0481	0.0645
$wR2(F^2)^a$	0.2628	0.2095	0.2042	0.1476	0.1982	0.1749	0.1377	0.1824
GOF (S)^a	1.045	1.167	1.036	1.055	1.0200	1.017	1.089	1.051

^{a} $R1(F[\mathrm{I} > 2(\mathrm{I})]) = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; $wR2(F^2\ [\text{all data}]) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

Sulfur-oxygen contacts between the cations and anions in all species within the sum of the van der Waals radii (Σv.d.w. S-O = 3.25 Å) are observed.[31] However, there is no distortion of the corresponding sulfur-oxygen bond in the triflate ions, contrary to what is observed in covalently bound substituents. In these covalent species, the corresponding S-O bond length for the coordinated oxygen atom is significantly elongated with respect to the other two S-O bonds within the triflate.[17] In the compounds with H-substitution on the imine carbon, the closest cation-anion interactions lie between the oxygen atom and the acidic backbone proton. The contacts are well within the sum of the van der Waals radii (shortest contact 2.290 Å *cf.* 2.60 Å).[31] In spite of the oxygen contacts with the dicationic sulfur center, these species are distinct dication-anion pairs. Spectroscopic solution data and the metrical parameters are consistent of a dicationic species as they are in agreement with the computational results.[32]

Compound **2.5S[B(C_6F_5)$_4$]** also displays detectable cation–anion contacts in the solid state (Figure 2.11). The closest contact occurs between the backbone proton of the ligand and a fluorine atom from a C_6F_5 ring, which lies within the sum of the van der Waals radii (2.080 *cf.* 2.60 Å).[31] One long S···F contact on the very edge of the sum of the van der Waals radii [3.077(3) *cf.* 3.20 Å] is also found.[31] However, the corresponding C-F bond in the anion displays no tendency towards elongation as observed in other main-group compounds [1.351(4) *cf.* 1.414(6) Å].[33] The two anions are symmetry related, and an AX_4E_2 electron-pair configuration might be expected about sulfur, which would exhibit a clear square-planar geometry common to 12-electron chalcogen centers. However, the angle between the N-S-N and F···S···F planes is not consistent with a square-planar geometry (deviation from planarity is 20.4°). These combined observations lead to the conclusion that no substantial S···F cation-anion interactions are present. The virtually identical bonding arrangements between the triflate and the [B(C_6F_5)$_4$] derivatives indicate that both are true dicationic heterocycles.

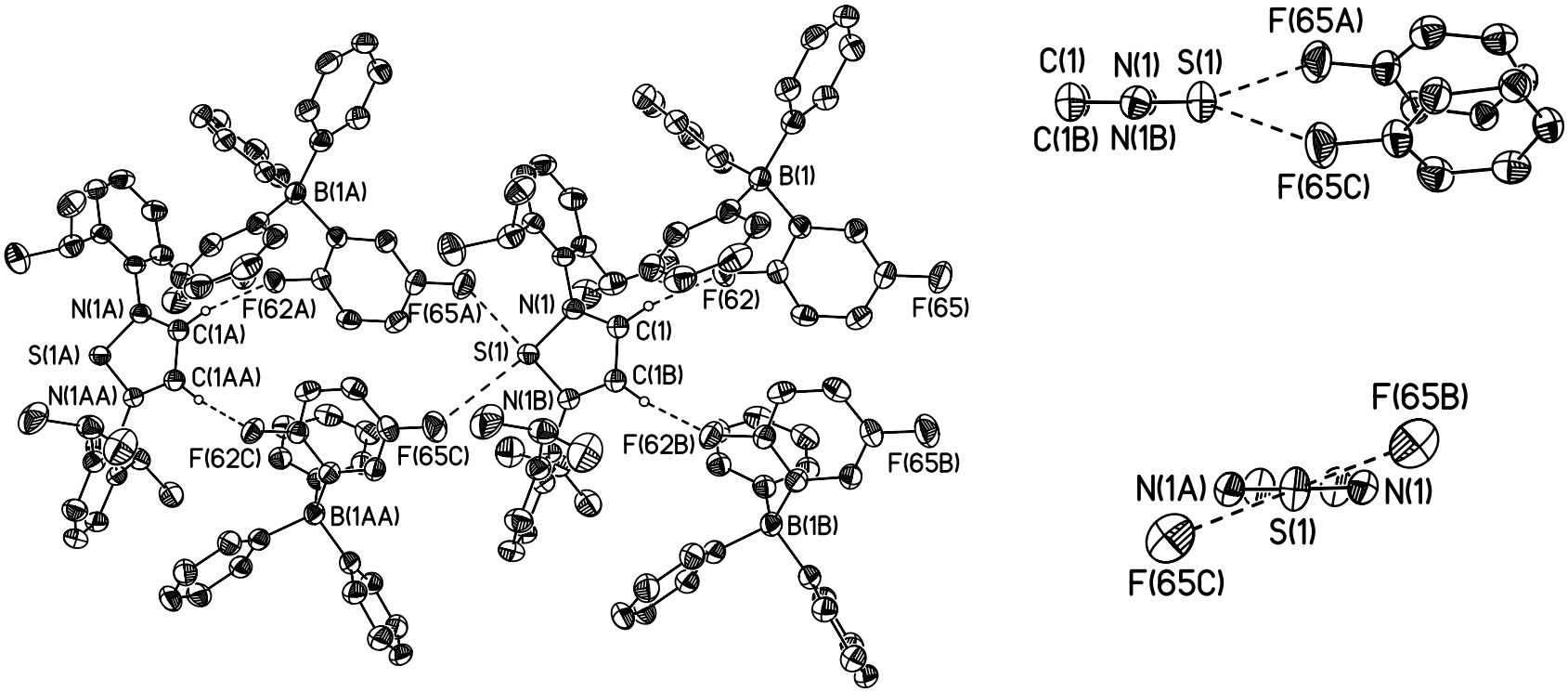


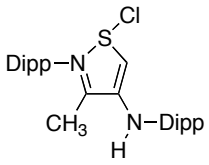
Figure 2.11: Solid-state structure of **2.5S[B(C_6F_5)$_4$]** (left) with views of the fluorine contacts about the sulfur centre (right). Ellipsoids are drawn to 50% probability, all hydrogen atoms not in the backbone, solvate molecules and fluorine atoms excluding those interacting with the anion are omitted for clarity. Selected anion cation contacts (Å): F(65A)···S(1) 3.079(3), F(62)···H(1A) 2.084.

2.3 Conclusion

The reactivity of DAB and BIAN ligands with SCl_2 and "$S(OTf)_2$" is highly dependent on both the substitution on the α-carbon and the nitrogen atoms, which was very different from the reported chemistry with the other non-metals. Methyl groups on the backbone carbon atoms led to *N,C*-bound sulfur heterocycles. If alkyl groups were present on N and hydrogen atoms on the backbone carbon, 1,2,5-thiadiazolium rings were produced. In cases where H, BIAN or phenyl groups were bound to the α-carbon and aryl groups on nitrogen the *N,N'*-sequestered sulfur(II) dicationic triflate salts were synthesized and structurally characterized. Although contacts between the cation and anion were present in the solid-state, an anion exchange reaction to produce the $B(C_6F_5)_4$ salt confirmed these compounds as dicationic species. These derivatives represent the first sulfur structural mimics of N-heterocyclic carbene.

2.4 Experimental Section

2.1SCl



A solution of **2.1SCl** (0.100 g, 0.248 mmol; THF 5 mL) was added to a solution of SCl_2 (0.0255 g, 0.248 mmol; THF 5 mL) immediately giving an orange slurry, which was allowed to stir for 10 min. The product was precipitated by the addition of Et_2O (5 mL). The supernatant was decanted and the precipitate was washed with Et_2O (2 × 5 mL) and dried *in vacuo* giving **2.1SCl** as a pale yellow powder.

Yield: 0.080 g, 69%; d.p. 230-233 °C;

^{1}H NMR ($CDCl_3$, δ ppm) 8.32 (s, 1H), 7.57 (t, 1H, ^3J = 8.0 Hz), 7.33 (d, 2H, ^3J = 8.0 Hz), 7.29 (m, 1H), 7.21 (d, 2H), 6.10 (s, 1H), 3.14 (sept, 2H, ^3J = 7.2 Hz), 2.32 (s, 3H), 2.20 (sept, 2H, ^3J = 6.8 Hz), 1.15 (m, 24H);

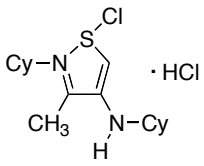
$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ ppm) 158.2, 146.5, 145.9, 142.4, 135.0, 132.1, 131.0, 130.4, 127.8, 124.1, 28.5, 24.9, 24.0, 23.6, 15.7;

FT-Raman (cm^{-1}(ranked intensity)): 112(12), 142(4), 304(14), 455(3), 515(1), 551(10), 888(8), 1045(13), 1252(5), 1450(7), 1372(9), 1588(6), 2868(15), 2910(2), 2964(11);

FT-IR (cm^{-1}(ranked intensity)): 773(4), 809(1), 850(11), 937(12), 1058(9), 1216(14), 1256(10), 1327(15), 1371(5), 1399(8), 1473(3), 1518(7), 1555(6), 2968(2), 3127(13).

Elemental analysis (%), Found (Calcd): 71.08(71.38), 8.58(8.35), 5.88(5.95);
ESI-MS (*m*/*z*): 435 $[M - Cl]^+$

2.2SCla



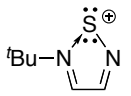
A solution of **2.2** (0.100 g, 0.406 mmol; 5 mL THF) was added to a solution of SCl_2 (0.0414 g, 0.406 mmol; THF 5 mL) immediately giving a pale beige precipitate, and the reaction mixture was allowed to stir for 10 min. The supernatant was decanted, and the precipitate was washed with THF (5 × 8 mL) and dried in vacuo giving **2.2Sa**.

Yield: 0.069 g, 49%; d.p. 195-197 °C;
^{1}H NMR (CD_3CN; δ ppm) 7.86 (s, 1H), 4.61 (m, 1H), 3.21 (m, 1H), 2.55 (s, 3H), 2.19-1.12 (m, 22H);
$^{13}C\{^1H\}$ NMR (C_5D_5N, δ ppm) 157.4, 142.2, 134.5, 68.2, 62.0, 34.2, 32.9, 26.3, 25.7, 25.6, 25.0, 14.8;
FT-Raman (cm^{-1}(ranked intensity)): 116(6), 164(12), 231(15), 351(20), 465(7), 482(4), 589(2), 700(11), 789(16), 802(10), 848(19), 885(18), 975(17), 1028(8), 1058(14), 1266(13), 1445(9), 2858(3), 2898(5), 2946(1);
FT-IR (cm^{-1}(ranked intensity)): 482(3), 568(11), 685(7), 851(16), 941(19), 976(17), 1026(6), 1153(9), 1191(20), 1263(13), 1379(12), 1456(2), 1491(14), 1541(18), 1560(8), 2516(15), 2630(4), 2860(5), 2938(1) 3106(10).
Elemental analysis for $SCl_2C_{16}H_{28}$, Found (Calcd): C 53.98(54.68), H 7.39(8.04), N 7.66(7.98);
ESI-MS (*m*/*z*): 279 $[M - HCl_2]^+$

General Synthesis of 2.3[OTf]-2.10[OTf]

Trimethylsilyltrifluoromethane sulfonate in CH_2Cl_2 (1.5 mL) was added dropwise to a solution of SCl_2 in CH_2Cl_2 (10 mL) at -78 °C and stirred for 15 min. A solution of DAB or BIAN in CH_2Cl_2 (8 mL) was added dropwise to the mixture yielding beige slurries (**2.3**, **2.4**) or orange/red solutions (**2.5**, **2.6**, **2.8**) or purple (**2.7, 2.9**) solutions. Amounts and workup are listed individually below.

2.3S[OTf]



TMSOTf (0.264 g, 1.19 mmol), SCl_2 (0.058 g, 0.595 mmol), **2.3** (0.100 g, 0.595 mmol). Normal pentane was added to the reaction mixture, resulting in the formation of more white precipitate. The supernatant was decanted, and the solid dried *in vacuo* giving a white powder. The material was found to be unstable in solution for periods greater than 15 min and as a solid for periods greater than 30 min; therefore, ^{13}C NMR data and elemental analysis could not be obtained.

Yield: 0.136 g, 88%; d.p. 95−101 °C;

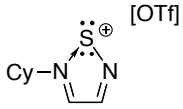
^{1}H NMR ($CDCl_3$, δ) 10.13 (s, 1H), 9.03 (s, 1H), 2.01 (s, 9H);

$^{19}F\{^{1}H\}$ NMR (CH_3CN, δ) -78.4;

FT-IR (cm^{-1} (ranked intensity)); 518(6), 553(14), 574(11), 638(4), 846(7), 1001(13), 1027(3), 1169(5), 1248(1), 1278(2), 1382(10), 1418(9), 1480(15), 3073(8), 3089(12);

FT-Raman (cm^{-1}(ranked intensity)) 314(5), 349(3), 575(12), 706(2), 758(8), 783(11), 846(6), 1030(1), 1151(14), 1226(13), 1448(15), 2920(10), 2997(4), 3088(9).

2.4S[OTf]



TMSOTf (0.202 g, 0.907 mmol), SCl_2 (0.047 g, 0.454 mmol), **2.4** (0.100 g, 0.454 mmol). Normal pentane was added to the reaction mixture, resulting in the formation of a beige precipitate. The supernatant was decanted, and the solid dried *in vacuo* giving a beige powder. The material was found to be unstable in solution for periods longer than 10 min and as a solid for periods greater than 20 min; therefore, ^{13}C NMR data and elemental analysis could not be obtained.

Yield: 0.099 g, 69%; d.p. 48 °C;

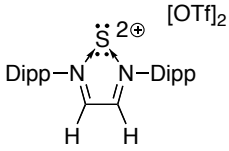
^{1}H NMR ($CDCl_3$, δ 10.09 (s, 1H), 8.93 (s, 1H), 5.33 (m, 1H), 2.39-1.28 (m, 10H);

$^{19}F\{^{1}H\}$ NMR (CH_3CN, δ) -78.4;

FT-IR (cm^{-1}(ranked intensity)) 517(12), 556(4), 575(9), 731(6), 760(5), 812(1), 841(3), 897(2), 1029(15), 1168(13), 1251(14), 1459(11), 2866(8), 2943(10), 3064(7);

FT-Raman (cm^{-1} (ranked intensity)) 121(8), 316(7), 349(6), 575(12), 626(15), 760(3), 805(11), 1034(1), 1147(9), 1247(13), 1273(10), 1354(14) 1451(3), 2866(4), 2949(2).

2.5S[OTf]



TMSOTf (0.266 g, 1.20 mmol), SCl_2 (0.062 g, 0.60 mmol), **2.5** (0.150 g, 0.399 mmol). The solids were washed with Et_2O (4×5 mL) giving a light orange powder.

Yield: 0.185 g, 78 %; d.p. 147-149 °C;

^{1}H NMR (CD_3CN, δ) 10.23 (s, 2 H), 7.81 (t, 2 H, ^3J = 7.6 Hz), 7.60 (d, 4 H, ^3J = 7.6 Hz), 2.45 (sept, 4 H, ^3J = 6.8 Hz), 1.33 (d, 12 H, ^3J = 6.4 Hz), 1.30 ppm (d, 12 H, ^3J = 6.8 Hz);

$^{13}C\{^1H\}$ NMR (CH_3CN, δ) 163.0, 145.9, 135.9, 131.5, 126.9, 30.4, 24.6, 24.4;

$^{19}F\{^1H\}$ NMR (CH_3CN, δ) -78.7;

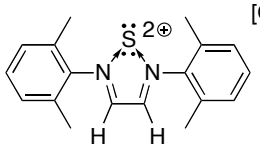
FT-IR (cm^{-1}(relative intensity)) 519(8), 577(12), 638(3), 762(13), 810(10), 1007(5), 1028(1), 1170(6), 1201(4), 1230(7), 1270(2), 1317(14), 1371(15), 1468(9), 2975(11);

FT-Raman (cm^{-1}(relative intensity)) 126(4), 316(15), 673(2), 762(7), 1007(13), 1028(6), 1047(8), 1068(14), 1244(5), 1351(3), 1445(1), 1583(12), 2914(9), 2942(10), 2982(11);

Elemental analysis (%) calcd for $C_{28}H_{36}F_6N_2O_6S_3$: C 47.58, H 5.14, N 3.97; found C 47.24, H 5.52, N 3.94.

ESI-MS: *m*/*z* 408 ($[M]^+$, $[C_{26}H_{36}N_2S]^+$).

2.6S[OTf]



TMSOTf (0.378 g, 1.70 mmol), SCl_2 (0.088 g, 0.851 mmol), **2.6** (0.150 g, 0.567 mmol). The solids were redissolved in CH_3CN (6 mL), and the product was selectively precipitated with Et_2O (6 mL) to yield a light orange powder.

Yield: 0.277 g, 82 %; d.p. 148-151 °C;

^{1}H NMR (CD_3CN, *δ*) 10.17 (s, 2 H), 7.66 (t, 2 H, ^3J = 5.6 Hz), 7.47 (d, 4 H, ^3J = 5.2 Hz), 2.32 (s, 12 H);

$^{13}C\{^1H\}$ NMR (CH_3CN, *δ*) 162.2, 136.0, 135.7, 135.4, 131.2, 18.3;

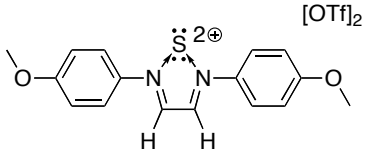
$^{19}F\{^1H\}$ NMR (CD_3CN, *δ*) -78.6 ppm.

FT-IR (cm^{-1}(relative intensity)) 518(5), 578(8), 638(3), 762(13), 784(6), 1030(2), 1095(12), 1169(4), 1231(11), 1276(1), 1393(15), 1479(7), 1523(9), 1604(10), 3113(14);

FT-Raman (cm^{-1}(relative intensity)) 123(1), 318(14), 349(15), 505(6), 552(13), 681(8),

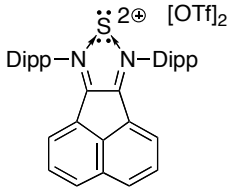
761(12), 1028(9), 1068(4), 1156(7), 1258(11), 1336(2), 1406(10), 1436(3), 1583(5);
Elemental analysis (%) calcd for $C_{20}H_{20}F_6N_2O_6S_3$: C 40.40, H 3.39, N 4.71; found C 40.59, H 3.51, N 4.78.

2.7S[OTf]



TMSOTf (0.372 g, 1.68 mmol), SCl_2 (0.086 g, 0.84 mmol), **2.7** (0.150 g, 0.558 mmol). Despite numerous efforts **2.7S[OTf]** could only be isolated in small quantities (less than 10 mg) by vapour diffusion of Et_2O into CH_3CN.
d.p. 185-187 °C;
^{1}H NMR (CD_3CN, δ) 9.69 (s, 2H), 7.86 (d, 4H, ^3J = 6.0 Hz), 7.32 (d, 4H, ^3J = 4.8 Hz), 3.99 (s, 6H);
$^{19}F\{^1H\}$ NMR (CH_3CN, δ) -78.7;
FT-IR (cm^{-1}(ranked intensity)) 518(11), 575(14), 639(8), 760(12), 833(7), 977(15), 1033(3), 1161(2), 1272(1), 1438(9), 1465(6), 1509(5), 1577(13), 1591(4), 3076(10);
FT-Raman (cm^{-1}(ranked intensity)) 415(14), 702(11), 795(13), 1005(9), 1091(5), 1146(7), 1171(8), 1300(1), 1341(2), 1434(3), 1451(4), 1505(10), 1563(12), 1596(6), 1650(15);
Elemental Analysis (%) calcd for $S_3O_6F_6C_{18}H_{16}N_2$: C 36.12, H 2.69, N 4.65; found C 36.12, H 3.12, N 4.65.

2.8S[OTf]



TMSOTf (0.167 g, 0.600 mmol), SCl_2 (0.031 g, 0.300 mmol), **2.8** (0.150 g, 0.300 mmol). The volatiles were removed *in vacuo*, the powder was redissolved in CH_2Cl_2 (4 mL), and *n*-pentane was added (6 mL); the solution was stored at -30 °C overnight giving a red crystalline material. The crystals were collected, and *n*-pentane (2 mL) was added to the mother liquor yielding a second crop of crystals;
Yield: 0.171 g, 73%; d.p. 154-156 °C;
^{1}H NMR (CD_3CN, δ) 8.56 (d, 2H, ^3J = 8.0 Hz), 7.91 (t, 2H, ^3J = 8.0 Hz), 7.84 (t, 2H, ^3J = 8.0 Hz), 7.60 (d, 4H, ^3J = 8.0 Hz), 7.47 (d, 2H, ^3J = 7.2 Hz), 2.94 (sept, 4H, ^3J = 6.8 Hz),

1.40 (d, 12 H, ^{3}J = 6.8 Hz), 1.15 (d, 12H, ^{3}J = 6.4 Hz);

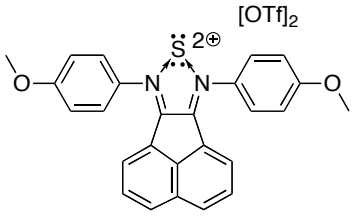
$^{13}C\{^{1}H\}$ NMR (CH_3CN, δ) 165.5, 146.0, 140.5, 136.0, 132.2, 132.1, 131.9, 130.6, 129.8, 127.6, 120.7, 30.2, 24.4, 24.3;

$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, δ) -78.3;

FT-IR (cm^{-1}(ranked intensity)) 353(15), 474(9), 524(6), 577(10), 637(2), 771(5), 810(12), 832(13), 1031(3), 1165(10), 1230(11), 1275(1), 1511(14), 1611(8), 2968(7);

FT-Raman (cm^{-1}(ranked intensity)) 85(5), 136(12), 352(6), 474(3), 562(4), 977(7), 1020(10), 1030(8), 1102(15), 1217(9), 1249(8), 1368(14), 1506(1), 1586(13), 1603(2).

2.9S[OTf]



TMSOTf (0.169 g, 0.76 mmol), SCl_2 (0.039 g, 0.38 mmol), **2.9** (0.150 g, 0.38 mmol). The volatiles were removed *in vacuo* and the powder was redissolved in CH_3CN (4 mL) and Et_2O was added (4 mL), the solution was stored at -30ºC for two hours giving a deep red microcrystalline material. This was recrystallized from a 1:1 CH_3CN:Et_2O mixture yielding pure material;

Yield: 0.140 g, 51%; d.p. 160-161ºC;

^{1}H NMR (CD_3CN, δ) 8.73 (d, 2H, ^{3}J = 8.4 Hz), 8.12 (d, 2H, ^{3}J = 7.2 Hz), 8.08-8.02 (m, 6H), 7.42 (d, 2H, ^{3}J = 8.8 Hz), 4.03 (s, 6H);

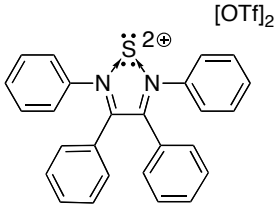
$^{13}C\{^{1}H\}$ NMR (CH_3CN, δ) 165.7, 162.1, 148.5, 139.3, 131.6, 131.4, 128.6, 125.4, 120.2, 117.6, 57.3;

$^{19}F\{^{1}H\}$ NMR (CH_3CN, δ) -78.6;

FT-IR (cm^{-1}(ranked intensity)) 472(10), 521(7), 571(12), 637(2), 778(9), 837(4), 1030(3), 1154(8), 1218(13), 1276(1), 1374(15), 1419(14), 1445(11), 1507(5), 1601(6);

FT-Raman (cm^{-1}(ranked intensity)) 358(13), 432(5), 472(11), 792(14), 977(15), 1158(3), 1184(7), 1210(4), 1261(8), 1334(6), 1372(10), 1441(9), 1508(1), 1569(12), 1598(2).

2.10S[OTf]



TMSOTf (0.195 g, 0.878 mmol), SCl_2 (0.045 g, 0.439 mmol), **2.10** (0.160 g, 0.439 mmol). The volatiles were removed *in vacuo*, and the powder was redissolved in CH_2Cl_2 (4 mL). Normal pentane was added (4 mL), the solution was then stored at -30 °C overnight giving an orange powder. The supernatant was decanted, and the solids were washed with *n*-pentane (3 × 5 mL) and dried *in vacuo*.

Yield: 0.184 g, 60%; d.p. 111-113 °C;

^{1}H NMR ($CDCl_3$, δ) 8.08 (d, 4 H, ^3J = 8.4 Hz), 7.73 (t, 2H, ^3J = 7.6 Hz), 7.67-7.55 (m, 10H), 7.37 (t, 4H, ^3J = 8.0 Hz);

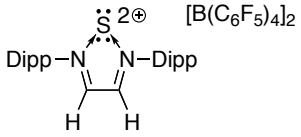
^{13}C{^{1}H} NMR (CH_3CN, δ) 165.9, 135.5, 132.8, 132.1, 131.6, 130.4, 128.1, 124.0;

^{19}F{^{1}H} NMR (CH_3CN, δ) -78.4;

FT-IR (cm^{-1} (ranked intensity)) 1596(9), 1485(10), 1457(14), 1433(8), 1296(13), 1250(1), 1162(5), 1025(2), 788(15), 758(4), 729(11), 694(6), 637(3), 574(12), 519(7);

FT-Raman (cm^{-1} (ranked intensity)) 3074(11), 1596(2), 1505(8), 1484(15), 1433(6), 1365(1), 1318(13), 1117(4), 1026(7), 1002(3), 627(14), 464(9), 404(10), 356(12), 102(5).

2.5[B(C_6F_5)$_4$]



A CH_2Cl_2 solution of K[B(C_6F_5)$_4$] (0.204 g, 0.284 mmol; 5 mL) was combined with **2.5SOTf** (0.100 g, 0.142 mmol) in CH_2Cl_2 (5 mL) at room temperature and stirred for 15 min. The mixture was filtered, and *n*-pentane (8 mL) was added to the supernatant resulting in the precipitation of a deep red powder. The powder was dried *in vacuo*.

Yield: 0.208 g, 83 %; d.p. 124-126 °C;

^{1}H NMR (CD_3CN, *δ*) 10.21 (s, 2 H), 7.83 (t, 2 H, ^{3}J = 7.8 Hz), 7.61 (d, 4 H, ^{3}J = 8.4 Hz), 2.42 (sept, 4 H, ^3J = 7.2 Hz), 1.33 (d, 12 H, ^3J = 7.8 Hz), 1.29 ppm (d, 12 H, ^{3}J = 6.0 Hz);

^{13}C{^{1}H} NMR (CH_3CN, *δ*) 163.5, 149.5 (d, ^{1}J = 244.7 Hz), 146.1, 139.7 (d, ^{1}J = 246.5 Hz), 137.7 (d, ^{1}J = 247.0 Hz), 136.5, 131.7, 127.2, 125.8, 30.7, 24.7, 24.5;

^{19}F{^{1}H} NMR (CD_3CN, *δ*) -133.1, -163.3, -167.8;

FT-IR (cm^{-1}(relative intensity)) 575(14), 637(12), 663(6), 685(7), 757(5), 776(8), 805(15), 981(2), 1093(3), 1206(11), 1279(10), 1375(13), 1465(1), 1517(4), 1646(9);
FT-Raman (cm^{-1}(relative intensity) 144(1), 394(11), 422(12), 449(7), 476(9), 492(6), 587(8), 693(10), 1044(4), 1056(5), 1238(13), 1313(2), 1415(3), 1337(14), 1580(15);
Elemental analysis (%) calcd for $C_{74}H_{36}B_2F_{40}N_2S$: C 50.28, H 2.05, N 1.81; found C 50.27, H 1.83, N 1.60.

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Chapter 3

Reactions of Chalcogen Halides and Pseudohalides with Unsaturated and Saturated Tridentate Nitrogen Ligands[ϕ]

3.1 Introduction

3.1.1 Chemistry of Unsaturated Tridentate Nitrogen Ligands

The diiminopyridine ligand (DIMPY; **3.1**-**3.3**; Figure 3.1) has become an omnipresent ligand in transition-metal chemistry as it can stabilize metal centres that have shown great utility in catalysis.[1] Analogous neutral or monocationic p-block derivatives from groups 13-15 have been reported, although often with only a few or singular representatives, except in the cases of tin and lead, where a plethora of compounds have been identified.[2-11] Nonmetal as well as dicationic congeners have remained elusive. These highly charged species are of interest, as they possess atom centres that are potentially powerful reagents for a variety of stoichiometric or catalytic reactions.[12]

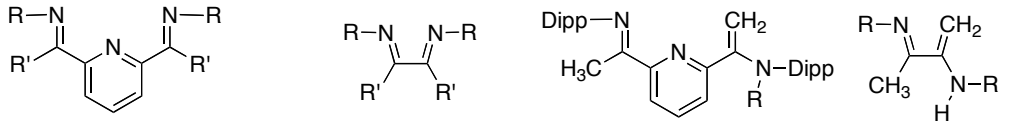


Figure 3.1: The diiminopyridine (DIMPY), the methyl substituted diazabutadiene (DAB) ligands and the corresponding eneamine tautomers.

The traditional bonding motif for these Schiff bases has typically been *via* chelation through the nitrogen centres in the multifunctional ligands. In reports with the 1,4-

ϕ A portion of this work has been published in Martin, C. D.; Le, C. M.; P. J. Ragogna *J. Am. Chem. Soc.* **2010**, *131*, 15126. and has been reproduced with permission.

diazabutadiene ligands (DAB; *e.g.* **2.1**, **2.2**), reactions with group 13-15 halides showed virtually the same reactivity with the ligand to produce *N,N'*-bound species regardless of the substitution on the backbone carbon atom (R').[13-20] For the chalcogens it has been determined that the substitution on the backbone carbon atom gives different products.[21-25] Hydrogen atoms, phenyl groups or an acenaphthene group led to the formation of *N,N'*-chelate chalcogen complexes of $TeCl_2$, $TeBr_4$, $SeCl_2$, $SeBr_2$ and Ch^{2+} (Ch = S, Se, Te; Figure 3.2; **A**-**D**) whereas a methyl group on the α-carbon resulted in *N,C*-bound heterocycles (**2.1ChX** and **2.2ChX**). The latter result is postulated to occur by reaction with the eneamine tautomer of the ligand (**2.1'** and **2.2'**).[21] The tellurium(IV) halides formed heterocycles featuring an exocyclic imine (**2.1TeX** and **2.2TeX**) in contrast to sulfur and selenium(II) halides that had an exocyclic amine (**2.1SCl**, **2.2SCl**, **2.1SeX** and **2.2SeX**).

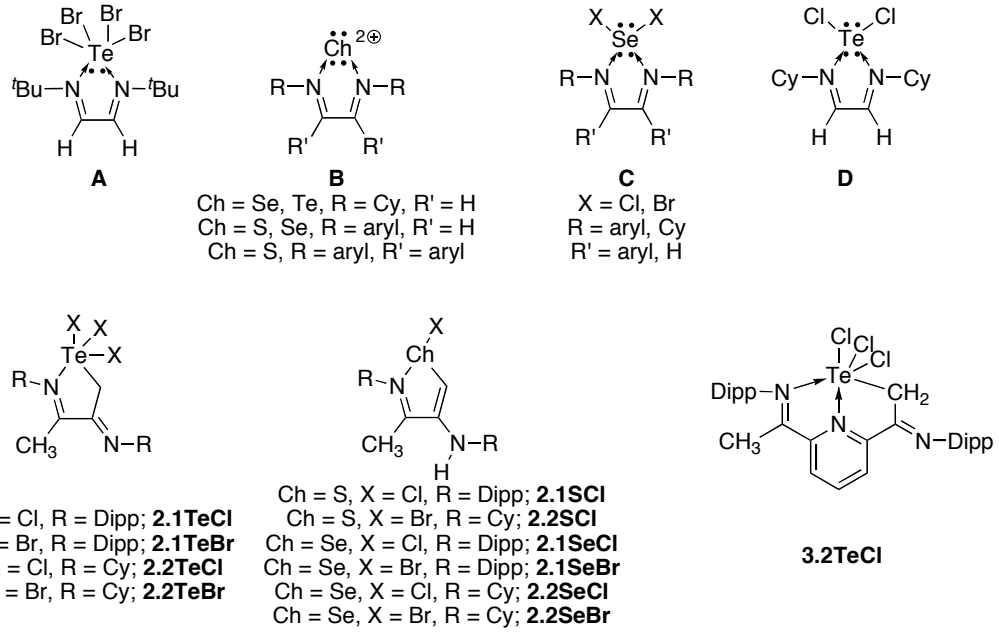


Figure 3.2: Reaction products of chalcogen halides with DAB and DIMPY ligands.

Recent discoveries have shown the ability of DIMPY ligands to stabilize low oxidation state main group complexes [*e.g.* In(I), As(I)].[4,7] There has been only one report of a reaction of this class of ligands with the chalcogen halides by Cowley *et al*. in 2006.[24] The reaction of $TeCl_4$ with a methyl substituted DIMPY ligand (**3.2**) resulted in an

N,N',C-bound tellurium complex (**3.2TeCl**), rather than the expected *N,N',N''*-bound species. As with the DAB chemistry it is believed that reaction is occurring with the eneamine tautomer (**3.2**'). This chapter reports a synthetic study of the DIMPY ligand with the chalcogen halides and chalcogen bis(triflate) synthons with different substitution at the α-carbon while keeping the groups on N constant with diisopropylphenyl groups (Dipp). The difference of a hydrogen, methyl or phenyl group greatly influenced the reaction giving neutral, monocationic or dicationic chalcogen(II) centres. These molecules represent the first *N,N',N''*-DIMPY coordination complexes for the chalcogens in addition to the first DIMPY main group dications.

3.1.2 Non-Metal Chemistry with Saturated Nitrogen Ligands

From the observations that imine ligands can sequester sulfur centres,[25,26] it can be envisioned that the chemistry of chalcogen dications can be extended to saturated nitrogen systems. A survey of the literature reveals only a few multidentate amine donor complexes with the non-metal elements exist, aside from boron.[27-31] From these sparse reports, it is apparent that the amine ligands have the ability to stabilize highly reactive centres (Figure 3.3) such as main group cations and polycations.[28,31]

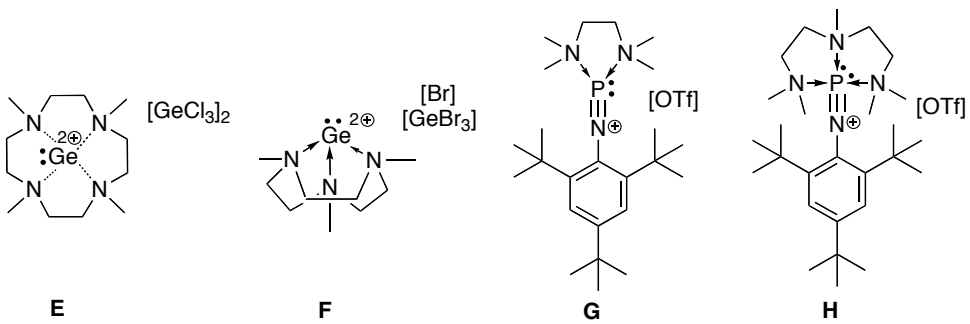


Figure 3.3: Structures of the amine sequestered non-metal complexes (**E-H**).

Germanium(II) dications can be sequestered within the cavity of the macrocyclic amines Me_4-CYCLAM (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and Me_3-TACN (1,4,7-trimethyl-1,4,7-triazacyclononane) by the nitrogen atoms stabilizing the electron deficient germanium centre (**E**, **F**).[31] The acyclic multidentate ligands, TMEDA (*N,N,N',N'*-tetramethylethylenediamine) and PMDETA (*N,N,N',N'',N''*-

pentamethyldiethylenetriamine; **3.4**) form complexes with the phosphadiazonium cation rendering the reactive phosphorus centre stable (**G**, **H**).[28]

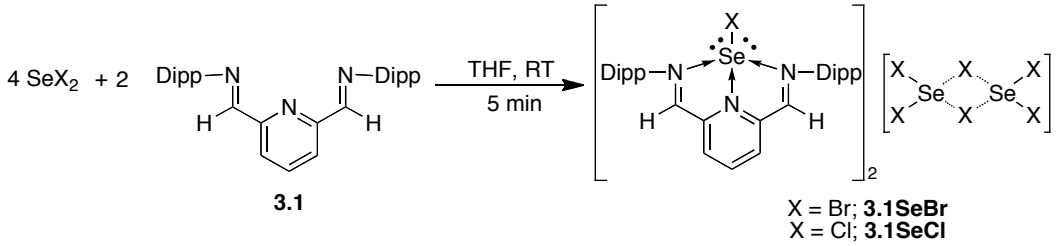
There are no structurally characterized homoleptic amine chalcogen complexes known. Some reports examine the ionic nature of amines with the chalcogen tetrahalides in solution but ultimately these studies offer no solid-state structural information.[32] This study reports the first isolated and structurally characterized sulfur amine complex, accomplished utilizing the PMDETA ligand.

3.2 Results and Discussion

3.2.1 Synthesis of the Diiminopyridine Chalcogen Complexes

The 1:1 stoichiometric reaction of a selenium dihalide (SeX_2, X = Cl, Br) with the hydrogen substituted DIMPY ligand (**3.1**) in THF immediately gave orange (X = Cl) or red (X = Br) slurries. The products could be precipitated from solution by the addition of *n*-pentane yielding fine red and orange powders, respectively. The supernatant was decanted and the solids dried *in vacuo*. Redissolving the powders in CD_3CN and obtaining a ^1H NMR spectrum revealed virtually identical spectra for both the $SeCl_2$ and $SeBr_2$ reactions as highly pure products with a symmetric ligand framework. Downfield shifts were observed for the two protons on the α-carbon atoms with respect to the free ligand consistent with the coordination to selenium (X = Cl, δ = 9.78 ppm; X = Br, δ = 9.74 ppm *cf*. δ = 8.44 ppm).[33] Crystals suitable for X-ray diffraction studies revealed a SeX^+ monocation sequestered by the DIMPY ligand paired with an SeX_3^- anion (dimerizes in the solid state to give $Se_2X_6^{2-}$; Scheme 3.1). Removing the solvent from the supernatant *in vacuo* and obtaining a ^1H NMR spectrum of the redissolved powder indicated an appreciable amount of unreacted ligand. Given the 1:1 stoichiometric reaction only producing ~45% yield, and the product containing a ratio of one ligand to two SeX_2 moieties, the stoichiometry of SeX_2 was increased to two, which improved yields to over 85%. These data prove the production of **3.1SeX** regardless of the stoichiometry. The reactivity was contrary to the SeX_2 DAB complexes (**C**) as the DAB ligands do not displace a halide. The difference in reactivity between the two ligands is rationalized by the additional donor on the DIMPY ligand requiring a halide to vacate a

coordination site to form the preferential square planar bonding arrangement about selenium.



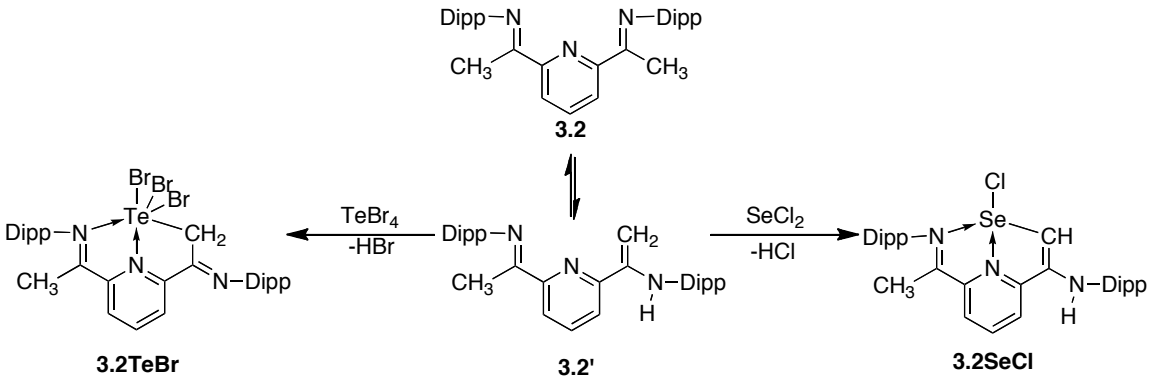
Scheme 3.1: Reaction of selenium dihalides with **3.1** to produce **3.1SeBr** and **3.1SeCl**.

Stirring a CH_2Cl_2 solution of **3.1** with a solution of SCl_2 in the same solvent and obtaining a ^{1}H NMR spectrum revealed only the presence of free ligand indicative of no reaction. Reactions of the same ligand with the chalcogen tetrahalides $SeCl_4$, $SeBr_4$, $TeBr_4$ and $TeCl_4$ all resulted in mixtures as indicated by ^{1}H NMR spectroscopy. It is known that the chalcogen halides are susceptible to releasing X_2 that would degrade the product or halogenate the ligand.[34-36] This has also been observed in DAB phosphorus and boron chemistry.[15,37]

The analogous reactions were performed with the methyl-substituted ligand (**3.2**). Stirring $TeBr_4$ with **3.2** in THF produced an orange suspension over four hours (Scheme 3.2). Filtering the solids and removing the solvent from the supernatant gave an orange powder that was washed with Et_2O. Redissolving the powder in $CDCl_3$ and obtaining an ^{1}H NMR spectrum revealed a single product with a break in symmetry of the ligand framework with two separate isopropyl resonances. Further evidence was a peak at δ = 4.57 ppm integrating to two protons consistent with a methylene resonance and a peak at δ = 2.37 ppm integrating to three protons that accounts for the methyl group; both are shifted downfield with respect to the free ligand (δ = 2.28 ppm).[38] The FT-IR spectrum lacked an N-H stretch supporting the presence of an exocyclic imine. It was also apparent that one of the methyl groups on an α-carbon was absent, indicating that the *N,N',C*-bound $TeBr_3$ unit, analogous to the reported **3.2TeCl** complex was the isolated product.[24] Thus the reaction was again occurring through the eneamine tautomer (**3.2'**). Crystals suitable for

X-ray diffraction studies were grown from vapour diffusion of *n*-pentane into THF confirming the identity of **3.2TeBr**, the DIMPY analogue of **2.1TeBr**.

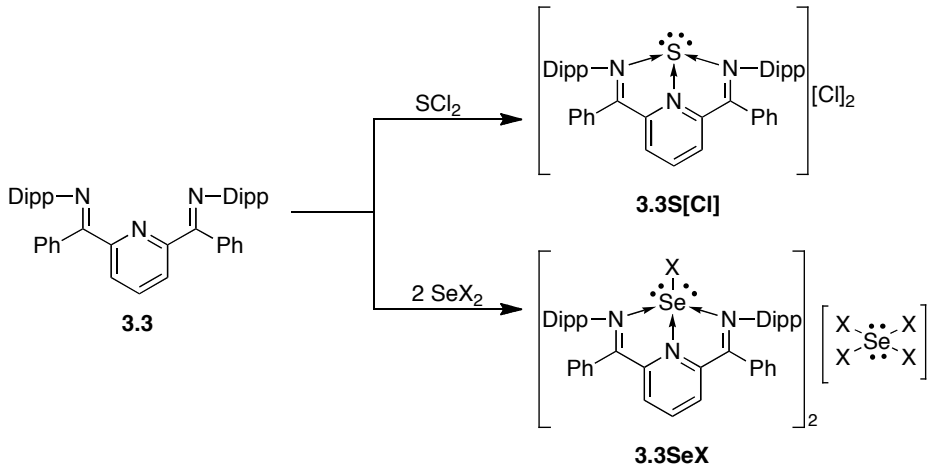
The reaction of $SeCl_2$ with **3.2** in THF produced a dark red solution. Normal pentane was added producing a red precipitate. The solids were collected by filtration and washed with Et_2O to yield a red powder after drying *in vacuo*. The ^1H NMR spectrum of the redissolved material in $CDCl_3$ displayed a break in symmetry of the ligand framework once again in addition to a reduction of the integration of the methyl group to three, consistent of binding through one of the methyl groups on an α-carbon atom. A new peak with respect to the free ligand was observed at δ = 8.16 ppm integrating to one suggesting a single C-H. The FT-IR spectrum of a KBr pellet of the powder displayed a diagnostic N-H stretch (broad peak at 3425 cm^{-1}) supporting the presence of an exocyclic amino group, not observable in the ^1H NMR spectrum. Although crystals of suitable quality for X-ray diffraction studies could not be grown, the identity of the compound could be assigned as **3.2SeCl** based on these data and by analogy to the DAB chemistry (**2.1SeCl**).[21] As observed in the corresponding DAB chemistry, tellurium forms a complex with an exocyclic imine whereas selenium produces an exocyclic amine.



Scheme 3.2: Reactions of $TeBr_4$ and $SeCl_2$ with **3.2**.

The reactions of $SeCl_4$, $SeBr_4$, $SeBr_2$ and SCl_2 with **3.2** all produced indiscernible complex mixtures based on ^1H NMR spectroscopy. It is unpredictable if the reactivity with the eneamine tautomer is controllable and unfortunately this was not the case for $SeBr_2$ and SCl_2 as mixtures were produced of which the desired products could not be isolated or observed from the crude ^1H NMR spectra.

In order to examine the effect of an aryl group on the α-carbon, the reaction of SCl_2 with **3.3** (phenyl substitution at nitrogen) in CH_2Cl_2 was carried out resulting in the generation of an orange solution (Scheme 3.3). Addition of *n*-pentane to the solution and storing the reaction vial at -35 °C produced a large crop of yellow crystals. Obtaining a ^{1}H NMR spectrum of the dried crystals redissolved in $CDCl_3$ revealed a single product with a symmetric ligand framework. The protons on the 3 and 5 positions of the pyridine ring were shifted downfield with respect to free ligand ($\Delta\delta$ = 1.90 ppm).[2] A solid-state structure from X-ray diffraction studies on crystals grown by vapour diffusion of *n*-pentane into chloroform revealed a *N,N',N''*-bound sulfur(II) dication with two chloride counteranions (**3.3S[Cl]**). In general this confirms the higher reactivity of DIMPY ligands in comparison to their DAB counterparts as the corresponding reaction of a DAB ligand with phenyl groups on the α-carbon atoms showed no reaction with SCl_2 in the absence of TMSOTf.



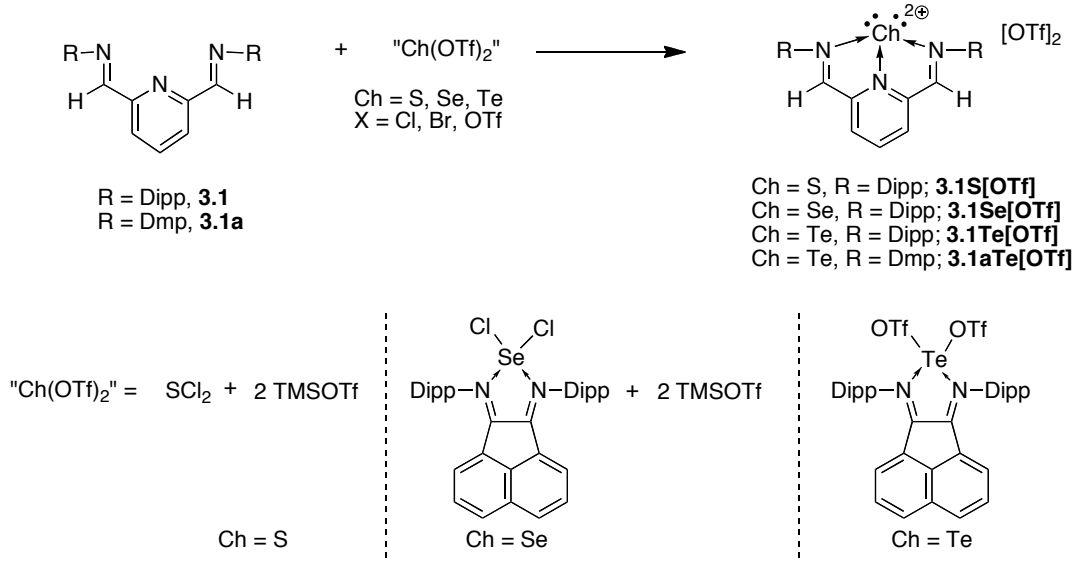
Scheme 3.3: Reactions of SCl_2 and SeX_2 with **3.3**.

The 1:2 stoichiometric reaction of the phenyl substituted DIMPY ligand (**3.3**) with the SeX_2 reagents were carried out as **3.1** reacted in this stoichiometry. The reactions produced brown (X = Br) and purple (X = Cl) solutions. Adding *n*-pentane to the mixture resulted in the precipitation of orange (X = Cl) and brown (X = Br) powders. Redissolving the powders in $CDCl_3$ and obtaining an ^{1}H NMR spectrum revealed diagnostic downfield shifts of the pyridine protons on the ligand similar to SCl_2. X-ray

quality crystals were grown by vapour diffusion of *n*-pentane into a saturated CH_2Cl_2 solution of **3.3SeCl** indicating the identity as two *N,N',N''*-chelated $SeCl^+$ monocations paired with an $SeCl_4^{2-}$ dianion. This would arise from a 2:3 stoichiometry of the ligand to $SeCl_2$. It is suspected that a mixture of complex counter anions is present with various combinations of selenium and chlorine. From the analogous ^1H NMR spectrum it is ascertained that the reaction product is a $SeBr^+$ cation, although the exact nature of the anion is not certain. Unfortunately crystals suitable for diffraction experiments could not be grown to confirm this. The difference of a hydrogen and a phenyl group on the α-carbon proved not to be significant in the case of selenium as both derivatives formed monocationic complexes.

Further evidence that complexation of **3.3** has occurred are sharp resonances in the proton NMR spectra. The free ligand undergoes restricted rotation on the NMR time scale due to the presence of the bulky phenyl groups that results in severe broadening of all signals except at elevated temperatures (115 °C in dimethyl sulfoxide-d_6).[2] However, the complexes formed with SeX_2 and SCl_2 do not display hindered dynamics at ambient temperature on the NMR timescale. This phenomenon has also been observed in other complexes with phenyl substituted DIMPY ligands in the literature.[2-4] Examination of the corresponding reactions of $SeCl_4$, $SeBr_4$, $TeCl_4$ and $TeBr_4$ with **3.3** all resulted in complex mixtures or decomposition.

The reactivity of the chalcogen bis(triflate) synthons with **3.1** was explored in hopes of generating the homologous series of chalcogen(II) dications similar to **3.3S[Cl]** with triflate anions.[22,25,39] The 1:1 stoichiometric reaction of a $Ch(OTf)_2$ (Ch = S, Se, Te) synthon with **3.1** at room temperature or -78 °C (**3.1S[OTf]**) resulted in the precipitation of solid material (Scheme 3.4). The supernatant was decanted from **3.1Se[OTf]** and **3.1Te[OTf]**, and the powders were washed with Et_2O. The resulting solids were dried *in vacuo* to give yellow and amber powders, respectively. For compound **3.1S[OTf]**, the solvent was removed *in vacuo*, and the solids were recrystallized from a 1:1 acetonitrile/Et_2O solution.



Scheme 3.4: Reactions of "$Ch(OTf)_2$" with **3.1** and **3.1a** to produce the dicationic triflate salts.

The solids isolated were redissolved in acetonitrile-d_3 and obtaining the ^1H NMR spectra displayed resonances for the protons on the α-carbon atoms shifted further downfield than the monocationic compounds (**3.1SeCl** and **3.1SeBr**) diagnostic for a dicationic complex (**3.1Ch[OTf]**, δ = 10.53 to 10.35 ppm; *cf.* **3.1SeX**, δ = 9.78 to 9.74 ppm). All of the spectra indicated a single product with a symmetric environment for the DIMPY ligand. The $^{19}F\{^1H\}$ NMR spectra were indicative of ionic triflate in solution for all of the complexes, signifying negligible cation-anion association in solution (**3.1Ch[OTf]**, δ = -78.5 to -78.6 ppm; *cf.* ionic $[NOct_4][OTf]$, δ = -78.5 ppm; covalent CH_3OTf, δ = -75.4 ppm).[40] Crystals of **3.1S[OTf]** and **3.1Se[OTf]** suitable for X-ray diffraction studies were grown by vapour diffusion of Et_2O into acetonitrile solutions of the redissolved bulk powders. In both cases, the diffraction experiments revealed dicationic complexes of sulfur and selenium, where the salts were isolated in high yields (**3.1S[OTf]**, 82%; **3.1Se[OTf]**, 87%) analogous to **3.3S[Cl]**. Despite valiant efforts, suitable crystals of **3.1Te[OTf]** could not be obtained, however the material was comprehensively characterized, and all of the data were consistent with the proposed formulation (isolated in 99% yield). The same reaction was carried out with virtually the same DIMPY ligand substituting 2,6-dimethylphenyl groups on N (**3.1a**) rather than 2,6-diisopropylphenyl

groups to slightly change the crystallization properties but keep similar electronics and sterics at the nitrogen atom. The spectroscopic data were consistent with the **3.1Ch[OTf]** complexes and to our delight, X-ray diffraction quality crystals were able to be grown by vapour diffusion of diethyl ether into an acetonitrile solution confirming the identity of **3.1a[TeOTf]** obtained in 90% yield.

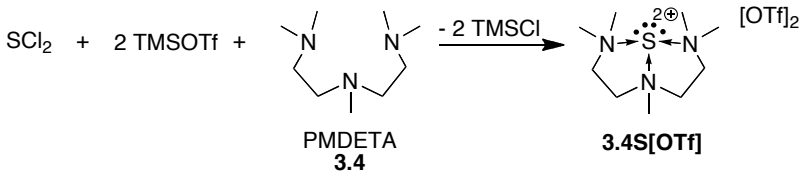
Surprisingly, storing samples of the dications under open air led to no signs of decomposition for a period of three weeks for **3.1Se[OTf]** and 2 months for **3.1S[OTf]** and **3.1Te[OTf]**. This is in stark contrast to the highly unstable bidentate dicationic derivatives.[25,26] Even after the addition of water to **3.1S[OTf]**, no decomposition was observed over 1 h, a remarkable feature for main group polycationic species. However, compounds **3.1Se[OTf]** and **3.1Te[OTf]** decomposed immediately upon the addition of water.

3.2.2 Synthesis of a Dicationic Sulfur(II) Amine Complex

A solution of PMDETA (**3.4**) in CH_2Cl_2 was added to a freshly prepared CH_2Cl_2 solution of SCl_2 and TMSOTf in a 1:1:2 stoichiometry generating a copious amount of white precipitate (Scheme 3.5). The supernatant was decanted and the solids were dried *in vacuo*. Redissolving the bulk material in CD_3CN and obtaining an ^{1}H NMR spectrum revealed what appeared to be a single product but with the terminal methyl resonances split into two peaks and second order coupling observed for the ethylene bridges. As the ^{1}H NMR spectrum was complex, X-ray diffraction studies on crystals grown by liquid diffusion of Et_2O into CH_3CN. The solid-state structure revealed an *N,N',N''*-chelated sulfur(II) dication.

The ^{1}H NMR spectrum could be rationalized as the ligand bound to the chalcogen centre is in a locked configuration. Two resonances are observed for the terminal methyl groups as the methyl groups become inequivalent in a locked system. The methyl resonances are also shifted downfield from free PMDETA (δ = 3.03, 2.87 ppm *cf.* δ = 2.23 ppm) consistent with the binding to an electron deficient centre. Further evidence of a locked ligand framework in solution were the four resonances with integral values of two and having second order coupling for the bridging ethylene groups. In the free ligand the ethylene groups are simplified as two triplets integrating to four. Proton decoupled

fluorine NMR spectroscopy confirmed ionic triflate in solution (δ = -78.5 ppm). All of these data are consistent with the formulation of an *N,N'N''*-chelated sulfur(II) dication supported by the PMDETA ligand isolated in 91% yield (**3.4S[OTf]**).



Scheme 3.5: The synthetic route to **3.4S[OTf]**.

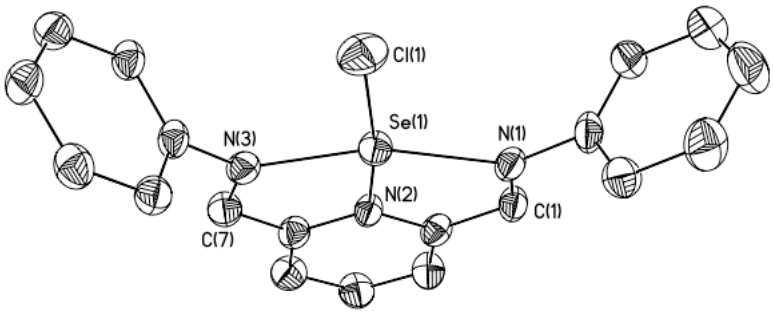
3.2.3 X-Ray Crystallography of the Chalcogen DIMPY Complexes

The solid-state structures of **3.1SeCl** and **3.1SeBr** both revealed a selenium halide monocation sequestered in the DIMPY chelate (Figure 3.4; See Table 3.1 for X-ray details and Table 3.2 for selected bond lengths and angles). The cationic selenium centre is in a distorted square planar geometry consistent with an AX_4E_2 electron pair configuration. The Se-N bond lengths are slightly longer for the imine nitrogens than the pyridine nitrogen atoms. The selenium halide bonds are long [X = Cl, 2.6498(14) Å; X = Br, 2.845(2) Å] which is attributed to the strong donation of the pyridine nitrogen into the same p-orbital. The imine within the ligand framework is retained [C-N = 1.278(15)-1.298(6)]. The counter anion is a SeX_6^{2-} dianion (SeX_3^- dimer) shared over two asymmetric units.

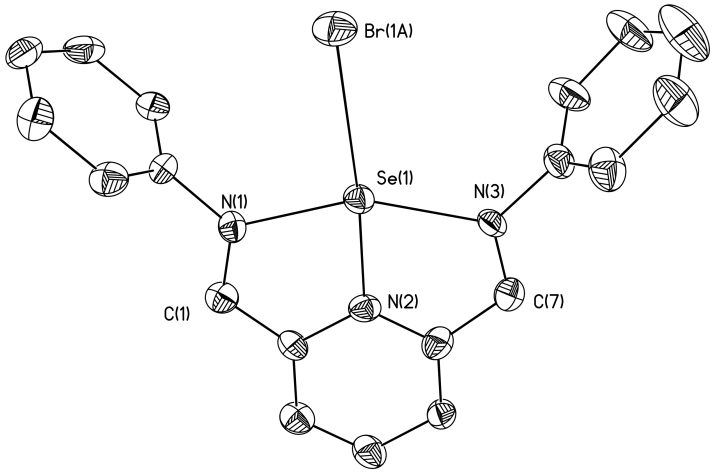
Examining the solid-state structure of **3.2TeBr**, reveals the tellurium centre in a distorted octahedron with a stereochemically inactive lone pair (Figure 3.5). Occupying the six coordination sites are three bromines, a carbon, the pyridine and a distant imine contact to complete the octahedron. The tellurium-bromine bond lengths are very similar to the methyl-DAB reaction products [Range 2.6323(7) - 2.6774(7) *cf.* 2.634(1) - 2.680(1) Å]. The N-Te bond distance for the pyridine nitrogen is markedly shorter than that of the imine [2.359(3) *cf.* 2.793(3) Å] which retains its N-C double bond [1.268(5) Å]. The exocyclic carbon-nitrogen bond is also characteristic of an imine moiety [1.269(5) Å]. The carbon-tellurium bond of 2.133(4) Å is consistent with a typical Te-C single bond. In

general, these metrical parameters are in close agreement to the previously published **3.2TeCl**.[24]

The solid-state structure of **3.3SeCl** reveals a $SeCl^+$ monocationic DIMPY complex as observed in **3.1SeCl**. The bond lengths within the cation are very similar, almost within statistical error with the other. The main difference in the structure lies in the counter anion, a $SeCl_4^{2-}$ dianion rather than $Se_2Cl_6^{2-}$ in **3.1SeCl**. This particular anion is rare, as only two other solid-state structures have been reported in the CSD.[41,42] The metrical parameters of the anion are consistent with the literature precedent featuring a square planar geometry about selenium.

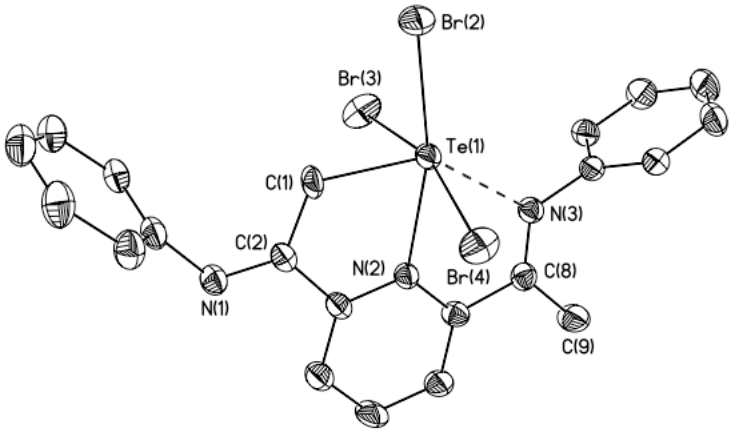


3.1SeCl

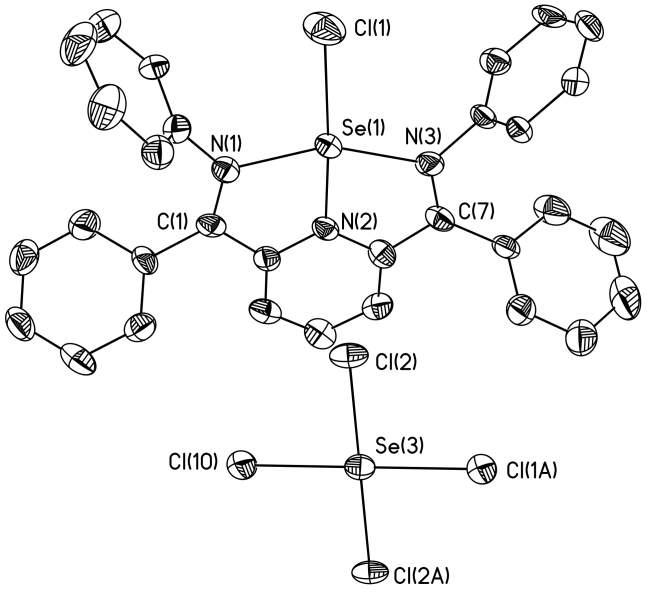


3.1SeBr

Figure 3.4: Solid-state structures of **3.1SeCl** and **3.1SeBr**. Ellipsoids are drawn to 50% probability, hydrogen atoms, anions, solvates and isopropyl groups are omitted for clarity.



3.2TeBr



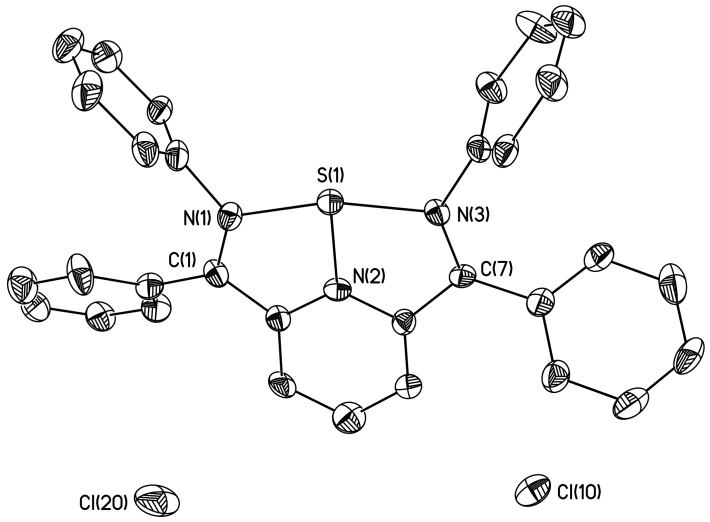
3.3SeCl

Figure 3.5: Solid-state structures of **3.2TeBr** and **3.3SeCl**. Ellipsoids are drawn to 50% probability, hydrogen atoms, anions, solvates and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (º) for **3.2TeBr** (**3.3SeCl** reported in Table 3.1): Te(1)-C(1) 2.133(4), Te(1)-N(2) 2.359(3), Te(1)-Br(2) 2.6323(7), Te(1)-Br(3) 2.6562(8), Te(1)-Br(4) 2.6774(7), Te(1)-N(3) 2.793(3), N(3)-C(8) 1.268(5), N(1)-C(2) 1.269(5), C(2)-C(1) 1.508(6).

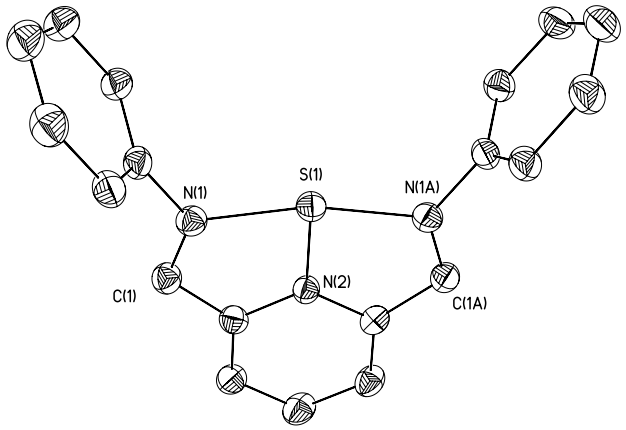
Compounds **3.3[Cl]**, **3.1S[OTf]**, **3.1Se[OTf]**, and **3.1aTe[OTf]** all exhibit a T-shaped geometry about the chalcogen centre, consistent with an AX_3E_2 electron pair configuration (Figures 3.6 and 3.7). Both of the imine nitrogen atoms occupy axial positions within the trigonal bipyramid, and the pyridine nitrogen and the two lone pairs occupy the equatorial positions. A positive correlation is observed between increasing size of the central atom and increasing Ch-N bond lengths for **3.3S[Cl]**, **3.1S[OTf]**, **3.1Se[OTf]**, and **3.1bTe[OTf]**. In all of the compounds, the axial Ch-N bonds are longer than the equatorial Ch-N bonds which is attributed to the two imine nitrogens donating into the same p-orbital. For **3.1S[OTf]**, the N(2)-S(1) bond is slightly shorter than typical N-S single bonds [1.719(3) Å (*cf.* 1.76 Å)] and slightly longer than in the only other known sulfur(II) dicationic systems [1.655(3)-1.699(6) Å], which can be attributed to the increase in coordination number from two to three.[25,26,43]

There are no detectable cation-anion contacts within the sum of the van der Waals radii between the triflate or chloride anion and the chalcogen centre in **3.1S[OTf]**, **3.3S[Cl]** or in **3.1Se[OTf]**. Compound **3.1bTe[OTf]** displays distant Te···O contacts within the sum of the van der Waals radii [closest contact 2.776(4) Å *cf.* 3.58 Å].[43] Upon close inspection of the tellurium structure, the corresponding sulfur oxygen bond lengths within the anion show no asymmetry, consistent with the absence of a covalent interaction between the dicationic chalcogen centre and the anion.

In all of the *N,N',N''*-chelated chalcogen dications and monocations, the dative bonding model has been drawn (Schemes 3.1, 3.3 and 3.4), but in view of the metrical parameters, the charge is likely delocalized throughout the dication, resulting in a hybrid structure best represented as the pyridinium/iminium salts.

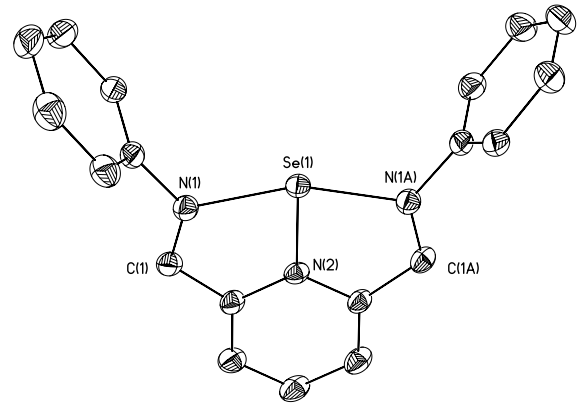


3.3S[Cl]

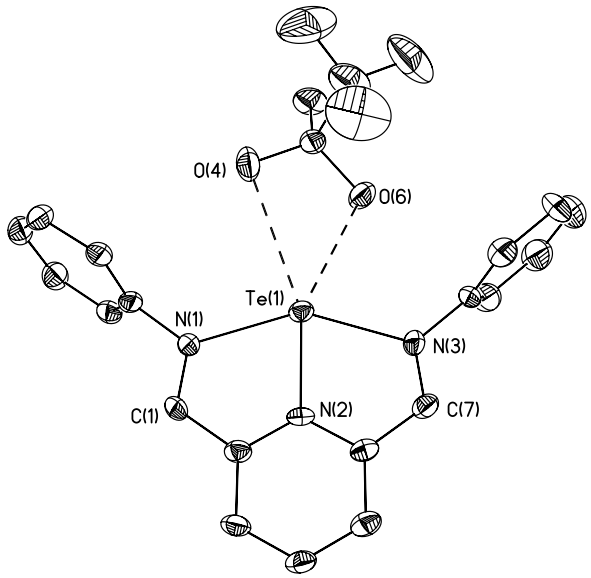


3.1S[OTf]

Figure 3.6: Solid-state structures of the dications **3.3S[Cl]**, and **3.1S[OTf]**. Ellipsoids are drawn to the 50% probability level. Hydrogen atoms, isopropyl or methyl groups, solvates, and anions not interacting with the chalcogen centre have been omitted for clarity.



3.1Se[OTf]



3.1aTe[OTf]

Figure 3.7: Solid-state structures of the dications **3.1Se[OTf]**, and **3.1aTe[OTf]**. Ellipsoids are drawn to the 50% probability level. Hydrogen atoms, isopropyl or methyl groups, solvates, and anions not interacting with the chalcogen centre have been omitted for clarity.

Table 3.1: X-ray details for **3.1SeCl**, **3.1SeBr**, **3.2TeBr**, **3.3S[Cl]**, **3.3SeCl**, **3.1S[OTf]**, **3.1Se[OTf]** and **3.1aTe[OTf]**.

Compound	**3.1SeCl**	**3.1SeBr**	**3.2TeBr**	**3.3S[Cl]**	**3.3SeCl**	**3.1S[OTf]**	**3.1Se[OTf]**	**3.1aTe[OTf]**
Empirical formula	$C_{37}H_{45}F_6Cl_4N_6Se_2$	$C_{37}H_{39}F_6Br_4N_3Se_2$	$C_{37}H_{42}Br_3N_3OTe$	$C_{45}H_{49}Cl_8N_3S$	$C_{86}H_{94}Cl_6N_6Se_3$	$C_{37}H_{49}F_6N_3O_7S_3$	$C_{37}H_{49}F_6N_3O_7S_2Se$	$C_{27}H_{26}F_6N_4O_6S_2Te$
FW (g/mol)	873.51	1045.30	912.07	947.53	1661.25	857.97	904.87	808.24
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	P-1	$P2_1/c$	$C2/c$	$C2/c$	$P2_1$
a (Å)	11.413(2)	11.950(2)	10.592(2)	12.5843(19)	12.7211	19.380(4)	19.3723(11)	11.995(2)
b (Å)	14.309(3)	14.476(3)	14.103(3)	13.324(2)	20.3795	15.591(3)	15.4754(9)	8.2243(16)
c (Å)	26.438(5)	26.043(8)	26.190(5)	16.054(2)	17.9128	14.358(3)	14.5351(7)	16.523(3)
α (deg)	90	90	90	71.556(3)	90	90	90	90
β (deg)	101.87(3)	103.39(3)	98.63(3)	72.774(3)	95.894	92.26(3)	91.768(2)	100.76(3)
γ (deg)	90	90	90	80.973(4)	90	90	90	90
V (Å^3)	4225.6(15)	4382.7(18)	3868.1(13)	2433.1(6)	4619.3(8)	4335.1(15)	4355.5(4)	1601.4(5)
Z	4	4	4	2	2	4	4	2
D_c (mg m^{-3})	1.373	1.584	1.566	1.293	1.194	1.315	1.380	1.676
radiation, λ (Å)	.71073	.71073	.71073	.71073	.71073	.71073	.71073	.71073
temp (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
$R1[I>2\sigma I]^a$	0.0604	0.0930	0.0438	0.0775	0.0652	0.0496	0.0434	0.0362
$wR2(F^2)^a$	0.1825	0.3007	0.1339	0.2031	0.1769	0.1297	0.1149	0.0988
GOF (S)^a	0.966	1.279	1.055	1.045	0.950	1.034	1.037	1.101

[a] $R1(F[\mathrm{I} > 2(\mathrm{I})]) = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; $wR2(F^2\ [\text{all data}]) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

Table 3.2: Selected bond lengths (Å) and angles (°) for the *N,N',N''*-DIMPY complexes **3.1SeCl**, **3.1SeBr**, **3.3S[Cl]**, **3.3SeCl**, **3.1S[OTf]**, **3.1Se[OTf]** and **3.1aTe[OTf]**.

Bond Length	**3.1SeCl**	**3.1SeBr**	**3.3S[Cl]**	**3.3SeCl**	**3.1S[OTf]**	**3.1Se[OTf]**	**3.1aTe[OTf]**
Ch(1)-N(1)	2.209(4)	2.086(9)	1.883(4)	2.107(4)	1.9068(17)	2.025(2)	2.243(4)
Ch(1)-N(3/1A[a])	2.056(4)	2.137(9)	1.923(4)	2.078(4)	1.9068(17)[a]	2.025(2)[a]	2.241(4)
Ch(1)-N(2)	1.931(4)	1.932(9)	1.727(4)	1.928(4)	1.719(3)	1.872(3)	2.098(3)
C(1)-N(1/1A[a])	1.278(6)	1.278(15)	1.295(6)	1.275(7)	1.280(3)	1.275(3)	1.284(6)
C(7/1A[a])-N(3/1A[a])	1.298(6)	1.292(15)	1.279(5)	1.286(7)	1.280(3)[a]	1.275(3)[a]	1.284(7)
Ch(1)-X(1)	2.6498(14)	2.845(2)	--	2.6948(18)	--	--	--
Bond Angle							
N(1)-Ch(1)-N(2)	76.01(16)	78.1(4)	82.37(18)	78.03(19)	82.39(6)	78.79(6)	72.77(15)
N(2)-Ch(1)-N(3/1A[a])	78.55(15)	76.7(4)	82.68(17)	76.84(18)	82.39(6)[a]	78.79(6)[a]	73.35(16)
N(1)-Ch(1)-X(1)	111.23(11)	96.7(3)	--	97.93(14)	--	--	--
N(3/1A[a])-Ch(1)-X(1)	94.17(11)	107.6(3)	--	106.95(14)	--	--	--

[a] The cations in **3.1S[OTf]** and **3.1Se[OTf]** lie on a site of symmetry with N(1) and N(3) being symmetry related.

3.2.4 X-Ray Crystallography of the Dicationic Sulfur(II) Amine Complex

X-Ray crystallographic studies confirmed the proposed structure of **3.4S[OTf]** from the solution spectroscopic data (Figure 3.8; See Table 3.4 for X-ray Data). The asymmetric unit consisted of two dications, four triflate anions and five acetonitrile molecules. The closest sulfur-oxygen contact between a cation and an anion [3.158(4) Å] lies on the edge of the sum of the van der Waals radii of the two atoms (3.25 Å) however there is no elongation of the corresponding S-O bond in the anion.[43] The lack of an elongated S-O bond length in the triflate anion confirms negligible cation-anion interactions.

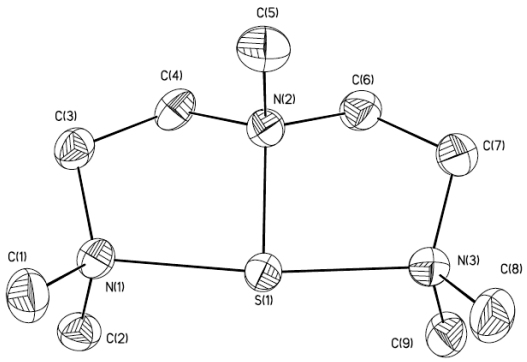


Figure 3.8: Solid-state structure of **3.4S[OTf]**. Only one dication from the asymmetric unit is shown. Ellipsoids are drawn to 50% probability. Hydrogen atoms, acetonitrile solvates, anions and the other dication are omitted for clarity. Selected bond lengths (Å) and angles (°); metrical parameters for other cation in the asymmetric unit are in brackets: S(1)-N(1) 2.071(4) [2.028(4)], S(1)-N(2) 1.821(4) [1.826(4)], S(1)-N(3) 2.043(4) [2.049(4)]; N(1)-S(1)-N(2) 85.94(17) [86.78(18)], N(2)-S(1)-N(3) 86.74(17) [86.15(17)], N(1)-S(1)-N(3) 171.38(18) [172.56(18)].

The electron configuration in **3.4S[OTf]** can be described as AX_3E_2 with two nitrogen atoms occupying the axial positions while the third nitrogen atom and the two lone pairs reside in equatorial sites, leading to a T-shaped geometry. A comparison of the metrical parameters with **3.1S[OTf]**, the other T-shaped chalcogen dication with triflate counterions can be found in Table 3.4. The axial equatorial N-S-N bond angles are close to 90° [range 85.94(17)° to 86.78(18)°] and bond angles between the two axial nitrogen

atoms are close to 180° [171.38(18)° and 172.56(18)°] consistent with a distorted T-shaped geometry. These angles are larger than the related diiminopyridine complex (**3.1S[OTf]**) as the PMDETA ligand is more flexible than the rigid DIMPY framework. As observed in **3.1S[OTf]**, the more proximal bond length of the equatorial nitrogen [1.821(4) Å and 1.826(4) Å] and distal bond lengths of the axial nitrogen atoms [range 2.028(4) Å - 2.071(4) Å] are rationalized by the donation of the two axial amines into the same p-orbital. The nitrogen sulfur bond lengths of **3.4S[OTf]** are significantly longer than **3.1S[OTf]** indicating the lesser stabilization that the PMDETA ligand offers in comparison to the DIMPY ligand. This is also reflected in the relative stabilities of the two compounds as **3.1S[OTf]** is stable in the open atmosphere for weeks and **3.4S[OTf]** decomposes instantly upon exposure to air.

Table 3.3: Bond lengths (Å) and angles (°) of **3.1S[OTf]** and **3.4S[OTf]** (avg).

Bond Length	**3.1S[OTf]**	**3.4S[OTf]**
S(1)-N(1)	2.050(4)	1.9068(17)
S(1)-N(3/1A)[a]	2.046(4)	1.9068(17)[a]
S(1)-N(2)	1.824(4)	1.719(3)
Bond Angle		
N(1)-Ch(1)-N(2)	86.36(18)	82.39(6)
N(2)-Ch(1)-N(3/1A)[a]	86.21(17)	82.39(6)[a]
N(1)-S(1)-N(3/1A)[a]	172.47(18)	164.78(12)

[a] The dication resides on a site of symmetry.

Table 3.4: X-ray details of **3.4S[OTf]**.

Compound	**3.4S[OTf]**
Empirical formula	$C_{64}H_{122}F_{24}N_{22}O_{24}S_{12}$
FW (g/mol)	2424.56
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	17.482(4)
b (Å)	13.711(3)
c (Å)	22.602(5)
α (deg)	90
β (deg)	92.79(3)
γ (deg)	90
V (Å^3)	5411.3(19)
Z	2
D_c (mg m^{-3})	1.488
radiation, λ (Å)	0.71073
temp (K)	150(2)
$R1[I>2\sigma I]^a$	0.0783
$wR2(F^2)^a$	0.2627
GOF (S)^a	1.063

^{a} $R1(F[\mathrm{I} > 2(\mathrm{I})]) = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; $wR2(F^2$ [all data]$) = [w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) $= [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

3.3 Conclusion

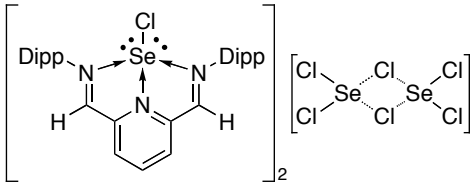
By the reactions of chalcogen halides with diiminopyridine ligands featuring -H, -Ph or -CH_3 substitution on the α-carbon, new sulfur, selenium and tellurium complexes were isolated including the first *N,N',N''*-chelated complexes with this ubiquitous ligand. The methyl DIMPY derivative (**3.2**) reacted through one of the methyl groups to give *N,N',C*-bound complexes with an exocyclic imine (Ch = Te) or an exocyclic amine moiety (Ch = Se). The reaction is believed to go through the eneamine tautomer and expel hydrohalide in the process much like the DAB chemistry. The hydrogen DIMPY ligand (**3.1**) reacted with the selenium dihalides in a 1:2 stoichiometry to afford the *N,N',N''*-chelated SeX^+ monocationic complexes, differing from the neutral DAB SeX_2 complexes. The phenyl substituted DIMPY (**3.3**) proved to be more reactive than the H substituted derivative to produce a dicationic sulfur complex with two chloride counteranions. In the case for selenium, a four coordinate monocationic complex centre with a rare SeX_4^{2-} anion was isolated. Selenium binds weakly to a halide as it can accommodate higher coordination numbers making a square planar geometry in contrast to sulfur. In many cases with chalcogen halide starting materials in the +4 oxidation state undesirable halogenation occurred.

The reaction of "$S(OTf)_2$" with the saturated amine PMDETA also produced an *N,N',N''* sequestered sulfur(II) dication. This compound represents the first homoleptic amine-sulfur complex. The structure is resilient in solution confirmed by the second order coupling of the protons on the ethylene linkers. Solid-state structural analysis indicates that the sulfur nitrogen bonds are significantly longer than the known pyridine or imine sulfur bonds suggesting a weak interaction between the ligand and the sulfur centre.

The diiminopyridine dicationic derivatives proved to be air stable, an unexpected observation given the high instability of the corresponding dicationic diazabutadiene complexes. This is a remarkable feature given that a dicationic charge is centralized on the chalcogen atom and should deem them highly unstable. The PMDETA complex was highly unstable but this weak bonding indicates the species should be a good reagent for the release of S^{2+}.

3.4 Experimental Section

3.1SeCl



A solution of **3.1** (0.077 g, 0.170 mmol in 3 mL THF) was added to a freshly prepared solution of $SeCl_2$ (0.341 mmol in 6 mL THF) and stirred for 5 minutes resulting in a red slurry. Normal pentane (6 mL) was added resulting in the formation of more solids. The supernatant was decanted and the resulting solids washed with Et_2O. The red powder was dried *in vacuo*.

Yield: 0.110 g, 86 %; d.p. 180-182 °C;

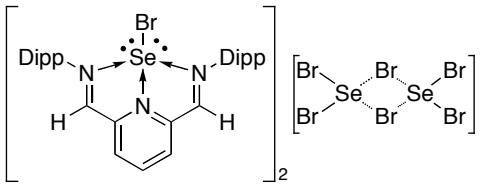
^{1}H NMR (CD_3CN, δ) 9.78 (s, 2H), 9.05 (br, 2H), 8.95 (br, 1H), 7.45 (t, 2H, ^3J = 7.6 Hz), 7.37 (d, 4H, ^3J = 7.6 Hz), 2.68 (br, 4H), 1.19 (d, 24H, ^3J = 6.4 Hz);

FT-Raman (cm^{-1}, ranked intensity): 2966(15), 1611(2), 1585(9), 1569(1), 1542(6), 1411(11), 1245(3), 1171(4), 1024(10), 563(14), 335(7), 302(5), 174(13), 132(12), 105(8);

FT-IR (cm^{-1}, ranked intensity): 2965(1), 2856(7), 1541(13), 1460(3), 1385(14), 1365(10), 1167(8), 1097(12), 1061(2), 1023(6), 949(15), 925(11), 806(5), 791(4), 752(9);

ESI-MS *m/z* 567 [M$^+$] M = $C_{31}H_{39}N_3SeCl$.

3.1SeBr



A solution of **3.1** (0.115 g, 0.253 mmol in 3 mL THF) was added to a freshly prepared solution of $SeBr_2$ (0.507 mmol in 6 mL THF) and stirred for 5 minutes resulting in a deep red slurry. Normal pentane (6 mL) was added resulting in the formation of more solids. The red powder was dried *in vacuo*.

Yield: 0.196 g, 84 %; d.p. 130-132 °C;

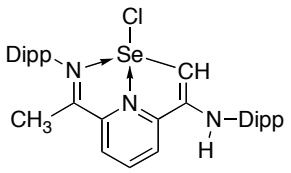
^{1}H NMR (CD_3CN, δ) 9.74 (s, 2H), 9.09 (br, 2H), 8.99 (br, 1H), 7.45 (br, 2H), 7.37 (d, 4H, ^{3}J = 7.2 Hz), 2.66 (br, 4H), 1.20 (m, 24H);

FT-Raman (cm^{-1}, ranked intensity): 2937(14), 1609(4), 1568(3), 1541(9), 1441(15), 1409(7), 1291(13), 1240(5), 1168(6), 1023(8), 562(12), 309(10), 232(2), 208(1), 147(11).

FT-IR(cm^{-1}, ranked intensity): 2963(2), 1539(10), 1459(3), 1385(11), 1364(7), 1164(5), 1097(14), 1060(1), 1022(6), 922(8), 805(4), 790(12), 750(9), 719(13), 561(15).

ESI-MS *m/z* 612 [M^+], M = $C_{31}H_{39}N_3SeBr$.

3.2SeCl



A solution of **3.2** (0.164 g, 0.342 mmol in 4 mL THF) was added to a freshly prepared solution of $SeCl_2$ (0.341 mmol in 4 mL THF) and stirred for 5 minutes generating a red solution. Normal pentane (8 mL) was added to the mixture resulting in a red precipitate. The supernatant was removed and the solids washed with Et_2O (5 X 5 mL) and the red solids dried.

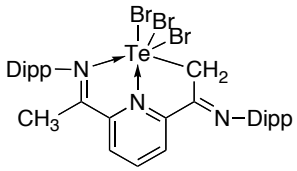
Yield: 0.129 g, 58 %; d.p. 188-190 °C;

^{1}H NMR ($CDCl_3$, δ) 8.35-8.25 (m, 2H), 8.16 (s, 1H), 8.02 (d, 1H, ^3J = 7.8 Hz), 7.30-7.16 (m, 6H), 4.44 (s, 1H), 3.11 (sept, 2H, ^3J = 7.2 Hz), 2.69 (sept, 2H, ^3J = 7.2 Hz), 2.37 (s, 3H), 1.22 (d, 24H, ^3J = 7.2 Hz);

FT-Raman (cm^{-1}, ranked intensity): 2964(14), 2927(11), 1632(3), 1588(4), 1572(1), 1516(8), 1444(13), 1295(7), 1246(9), 1005(10), 886(15), 331(12), 252(6), 144(5), 85(2);

FT-IR(cm^{-1}, ranked intensity): 3425(5, broad), 3299(4), 2961(1), 2865(14), 1633(15), 1602(8), 1534(9), 1515(11), 1463(2), 1386(6), 1365(7), 1207(13), 818(10), 798(12), 765(3).

3.2TeBr



A solution of **3.2** (0.100 g, 0.208 mmol in 3 mL THF) was added to a solution of $TeBr_4$ (0.093g, 0.208 mmol in 3 mL THF) and stirred for 4 hours resulting in an orange solution. The mixture was centrifuged and the solvent removed from the supernatant producing an orange powder.

Yield: 0.109 g, 62 %; d.p. 171-173°C;

^{1}H NMR ($CDCl_3$, δ) 8.79 (d, 1H, ^3J = 7.8 Hz), 8.45 (t, 1H, ^3J = 7.8 Hz), 8.25 (d, 1H, ^3J = 7.8 Hz), 7.25-7.17 (m, 6H), 4.57 (s, 2H), 2.96 (sept, 2H, ^3J = 7.2 Hz), 2.78 (sept, 2H, ^3J =

7.2 Hz), 2.37 (s, 3H), 1.26 (overlapping doublets, 12H), 1.13 (overlapping doublets, 12H);

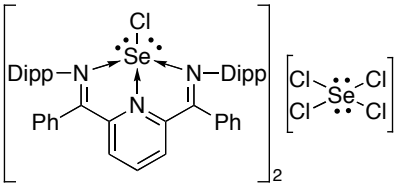
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ) 160.8, 146.2, 142.5, 141.4, 133.8, 133.6, 132.1, 131.6, 129.6, 127.2, 125.1, 28.4, 26.5, 23.4;

$^{125}Te\{^{1}H\}$ NMR (CD_2Cl_2, δ) 1290;

FT-Raman (cm^{-1}, ranked intensity): 3063(13), 2964(8), 2930(9), 1629(4), 1589(3), 1568(7), 1463(11), 1316(6), 1243(5), 1011(14), 648(12), 365(15), 178(1), 166(2), 105(10).

FT-IR (cm^{-1}, ranked intensity): 2964(2), 1628(5), 1587(12), 1462(3), 1364(10), 1315(11), 1241(9), 1172(8), 1093(15), 1010(7), 911(4), 822(14), 789(6), 758(13), 731(1).

3.3SeCl



A solution of **3.3** (0.075 g, 0.124 mmol in 2 mL THF) was added to a freshly prepared solution of $SeCl_2$ (3.72 mmol in 6 mL THF) generating a red solution. Normal pentane (10 mL) was added to the solution precipitating orange material. The mixture was stored at -35°C for 30 minutes and centrifuged. The supernatant was decanted and the solids washed with Et_2O (2 × 6 mL). The solids were dried *in vacuo* giving an orange powder.

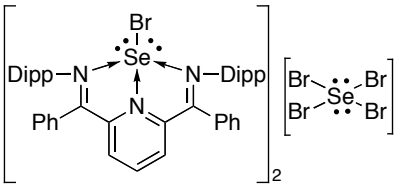
Yield: 0.090 g, 66 %; d.p. 174-177°C.;

^{1}H NMR (CD_3CN, δ) 8.87-8.75 (m, 3H), 7.68-7.23 (m, 16H), 2.71 (sept, 4H, ^{3}J = 6.4 Hz), 1.27 (d, 12H, ^{3}J = 6.4 Hz), 0.98 (d, 12H, ^{3}J = 6.4 Hz);

FT-Raman (cm^{-1}, ranked intensity): 3060(9), 1597(3), 1560(4), 1403(6), 1350(15), 1302(12), 1247(10), 1152(5), 1100(11), 1044(13), 1023(8), 1000(7), 575(14), 241(2), 132(1);

FT-IR (cm^{-1}, ranked intensity): 2966(9), 1560(11), 1458(5), 1444(10), 1386(14), 1340(12), 1265(13), 1055(8), 935(15), 806(4), 784(3), 763(7), 727(2), 693(1), 656(6).

3.3SeBr



A solution of **3.3** (0.075 g, 0.124 mmol in 2 mL THF) was added to a freshly prepared solution of $SeBr_2$ (3.72 mmol in 6 mL THF) resulting in a dark red solution. A red precipitate was generated after adding *n*-pentane (10 mL) to the mixture. The supernatant was removed and the remaining solids were washed with Et_2O (2 × 6 mL).

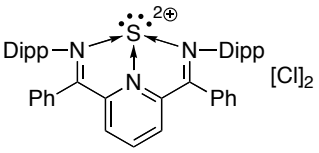
Yield: 68 %, 0.125; d.p. 182-184°C;

^{1}H NMR (CD_3CN, δ) 9.07-8.92 (m, 3H), 7.73-7.29 (m, 16H), 2.73 (sept, 4H, ^3J = 6.8 Hz), 1.26 (overlapping doublets, 12H), 0.94 (overlapping doublets, 12H).

FT-Raman(cm^{-1}(ranked intensity)) 3063(13), 1596(6), 1567(5), 1400(8), 1356(10), 1216(15), 1151(9), 1100(14), 1042(11), 1000(12), 241(2), 190(3), 143(4), 109(1), 86(7).

FT-IR(cm^{-1}(ranked intensity)) 2963(2), 2927(8), 2867(13), 1578(4), 1462(10), 1446(7), 1347(5), 1150(15), 1100(9), 1056(12), 1026(11), 787(3), 767(6), 693(1), 660(14).

3.3S[Cl]



A solution of **3.3** (0.150 g, 0.247 mmol in 4 mL CH_2Cl_2) was added to a solution of SCl_2 (0.025 g, 0.247 mmol in 4 mL CH_2Cl_2) immediately generating a yellow solution. The addition of *n*-pentane and storing the solution at -35°C overnight resulted in the formation of a large crop of yellow crystals. The supernatant was decanted and the crystals dried *in vacuo*.

Yield: 95 %; d.p. 124-127°C;

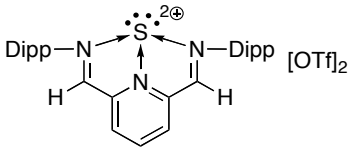
^{1}H NMR (CD_3CN, δ) 9.43 (d, 2H, ^3J = 8.4 Hz), 9.27 (t, 1H, ^3J = 7.8 Hz), 7.82-7.38 (m, 16H), 2.91 (sept, 4H, ^3J = 6.8 Hz), 1.11 (d, 12H, ^3J = 6.8 Hz), 0.78 (d, 12H, ^3J = 6.8 Hz);

^{13}C{^{1}H} NMR ($CDCl_3$, δ) 160.8, 146.2, 142.5, 141.4, 133.8, 133.6, 132.1, 131.6, 129.6, 127.2, 125.1, 28.4, 26.5, 23.4;

FT-Raman (cm^{-1}(ranked intensity)) 3064(9), 1598(1), 1580(2), 1537(15), 1400(4), 1332(14), 1246(13), 1222(7), 1154(5), 1099(12), 1054(8), 1000(6), 498(11), 401(10), 101(3).

FT-IR (cm^{-1}(ranked intensity)) 2963(2), 2927(8), 2867(13), 1578(4), 1462(10), 1446(7), 1347(5), 1150(15), 1100(9), 1056(12), 1026(11), 787(3), 767(6), 693(1), 660(14).

3.1S[OTf]



Sulfur dichloride (0.348 g, 3.38 mmol) was added neat to a solution of TMSOTf (1.500 g, 6.75 mmol) in CH_2Cl_2 (40 mL) at -78°C and stirred for 15 min. A solution of **3.1** (1.532 g, 3.38 mmol) in CH_2Cl_2 (15 mL) was added dropwise to the mixture yielding a yellow/orange solution. The volatiles were removed *in vacuo* and the resulting powder was redissolved in CH_3CN (10 mL). Diethyl ether (10mL) was added, and the solution stored at -30°C resulting in the formation of a large crop of yellow crystals. The crystals were washed with Et_2O (3 × 10 mL) and dried *in vacuo*.

Yield: 2.65 g, 82 %; d.p. 240-265°C;

^1H NMR (CD_3CN, δ) 10.36 (s, 2H), 9.70 (d, 2H, ^3J = 8.0 Hz), 9.36 (t, 1H, ^3J = 7.6 Hz), 7.61 (t, 2H, ^3J = 8.0 Hz), 7.45 (d, 4H, ^3J = 7.6 Hz), 2.56 (septet, 4H, ^3J = 6.4), 1.14 (overlapping doublets, 24H);

$^{13}C\{^1H\}$ NMR (CD_3CN, δ) 156.7, 145.0, 144.4, 141.4, 137.2, 133.2, 130.9, 125.4, 29.3, 24.8, 24.2;

$^{19}F\{^1H\}$ NMR (CD_3CN, δ) -78.5;

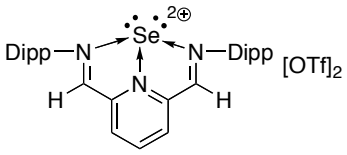
FT-IR (cm^{-1}(ranked intensity)) 429(3), 574(15), 723(2), 759(14), 935(5), 1061(13), 1085(10), 1109(12), 1335(8), 1389(6), 1508(4), 1553(1), 1598(7), 2874(9), 3073(11);

FT-Raman (cm^{-1}(ranked intensity)) 98(4), 138(3), 350(11), 758(10), 1032(7), 1045(6), 1108(12), 1168(8), 1248(5), 1445(14), 1552(1), 1587(2), 1626(9), 2870(15), 2941(13).

ESI-MS: *m/z* 484 ($[M - H]^+$), 634 ($[M + OTf]^+$).

Anal. Calcd for $C_{33}H_{39}F_6N_3O_6S_3$: C 50.56, H 5.02, N 5.36; Found: C 50.93, H 4.89, N 5.40.

3.1Se[OTf]



To a solution of $SeCl_2$BIAN in THF (0.200 g, 0.31 mmol; 4 mL), neat TMSOTf (0.1396 g, 0.63 mmol) was added giving a crimson solution. A solution of **1** (0.1426 g, 0.31 mmol) in THF (4 mL) was added to the mixture resulting in the formation of a red slurry. Normal pentane (6 mL) was added generating more precipitate. The supernatent was decanted and the resulting solids washed with Et_2O (3 × 6 mL) and dried *in vacuo* giving a yellow powder.

Yield: 0.2260 g, 87%, d.p. 217-221°C;

^{1}H NMR (CD_3CN, δ) 10.35 (s, 2H), 9.56 (d, 2H, ^3J = 8 Hz), 9.30 (t, 1H, ^3J = 8 Hz), 7.59 (t, 2H, ^3J = 8 Hz), 7.46 (d, 4H, ^3J = 7.6 Hz), 2.63 (septet, 4H, ^3J = 6.8 Hz), 1.19 (d, 12H, ^3J = 6.8 Hz), 1.15 (d, 12H. ^3J = 6.8 Hz);

^{13}C{^{1}H} NMR (CD_3CN, δ) 158.7, 144.4, 143.4, 137.5, 133.7, 132.2, 125.2, 28.9, 24.0, 23.9;

^{19}F{^{1}H} NMR (CD_3CN, δ) -78.5;

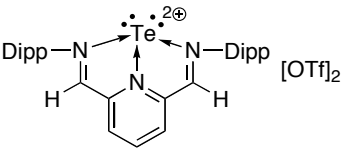
FT-IR (cm^{-1}(ranked intensity)) 431(12), 472(14), 548(15), 870(10), 905(11), 977(9), 1552(13), 1735(5), 1913(6), 1954(8), 2300(7), 2384(2), 2479(3), 2606(1), 2737(4);

FT-Raman (cm^{-1}(ranked intensity)) 102(7), 143(4), 347(9), 575(10), 889(14), 1033(6), 1172(8), 1444(15), 1619(3), 1248(5), 1550(2), 1587(1), 2871(13), 2939(12), 2972(11).

ESI-MS: *m/z* 532 ($[M - H]_+$), 682 ($[M + OTf]^+$).

Anal. Calcd for $C_{33}H_{39}F_6N_3O_6Se$: C 47.70, H 4.73, N 5.06; Found: C 48.30, H 4.16, N 5.12.

3.1Te[OTf]



A solution of **3.1** in CH_2Cl_2 (3 mL) was added to a solution of Te(OTf)2BIAN in CH_2Cl_2 (4 mL). The mixture was stirred for 5 min, yielding a dark red/brown solution. Normal pentane (5 mL) was added until a yellow precipitate was generated. The supernatant was decanted and the powder washed with Et_2O (3 × 6 mL) and solids dried *in vacuo* giving an amber powder;

Yield: 0.0902 g, 99%; d.p. 232-236°C;

^{1}H NMR (CD_3CN, δ) 10.53 (s, 2H), 9.43 (d, 2H, ^{3}J = 8.4 Hz), 9.14 (t, 1H, ^{3}J = 8 Hz), 7.57 (t, 2H, 8 Hz), 7.45 (d, 4H, ^{3}J = 8 Hz), 2.67 (septet, 4H, 6.4 Hz), 1.19 (overlapping doublets, 24 H);

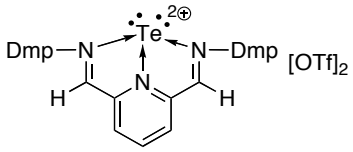
^{13}C{^{1}H} NMR (CD_3CN, δ) 163.3, 146.3, 143.9, 143.0, 138.4, 137.4, 131.8, 125.4, 29.4, 24.7, 24.0;

^{19}F{$_{1}$H} NMR (CD_3CN, δ) -78.6;

^{125}Te{^{1}H} NMR (CD_3CN, δ) 2190;

FT-IR (cm^{-1}(ranked intensity)) 487(6), 699(4), 728(7), 861(5), 935(8), 1390(12), 1417(3), 1483(15), 1541(11), 1571(9), 1594(10), 1717(1), 1955(2), 2873(14), 3064(13).

3.1aTe[OTf]



The identical synthesis was used as for **3.1Te[OTf]** substituting **3.1a** for **3.1**. **3.1a** (0.0508 g, 0.13 mmol), $Te(OTf)_2$BIAN (0.1164 g, 0.13 mmol).

Yield: 0.0881 g, 90%; d.p. 221-277°C;

^{1}H NMR (CD_3CN, δ) 10.47 (s, 2H), 9.34 (d, 2H, ^{3}J = 7.6 Hz), 9.08 (t, 1H, ^{3}J = 8 Hz), 7.38 (t, 2H, ^{3}J = 7.2 Hz), 7.32 (d, 4H, ^{3}J = 7.2), 2.20 (s, 12H);

^{13}C{^{1}H} NMR (CD_3CN δ) 163.9, 146.8, 143.5, 141.5, 138.2, 132.3, 131.0, 129.9, 18.42;

^{19}F{^{1}H} NMR (CD_3CN, δ) -78.7 ppm;

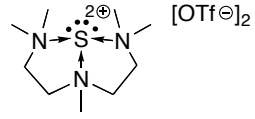
FT-IR (cm^{-1}(ranked intensity)) 411(12), 446(7), 707(11), 1370(15), 1671(6), 1745(8), 1795(2), 1877(5), 1921(10), 1956(9), 2022(3), 2295(4), 2750(1), 3500(13), 3616(14);

FT-Raman (cm^{-1}(ranked intensity)) 124(1), 503(10), 520(13), 538(9), 574(4), 599(7), 648(12), 1031(3), 1091(14), 1173(5), 1260(11), 1418(8), 1573(2), 1617(6), 2818(15).

ESI-MS: *m/z* 469 ([M – H]$^{+}$), 618 ([M + OTf]$^{+}$).

Anal. Calcd for $C_{25}H_{23}F_6N_3O_6S_2$: C 39.13, H 3.02, N 5.48 Found: C 39.34, H 3.06, N 5.26.

3.4S[OTf]



Neat TMSOTf (0.426 g, 1.916 mmol) was added to a solution of SCl_2 (0.099 g, 0.96 mmol) in CH_2Cl_2 (10 mL). To this solution, a solution of **3.4** (0.166 g, 0.958 mmol) in CH_2Cl_2 (5 mL) was added

yielding a white precipitate. The supernatant was removed and the solids washed with Et_2O (3 X 10 mL). The white powder was dried *in vacuo*.

Yield: 0.443 g, 91%; d.p. 128-130ºC;

^{1}H NMR (CD_3CN, δ); 4.37 (dd, 2H ^2J = 12.8 Hz, ^3J = 4.8 Hz), 4.06 (td, 2H, ^{2}J = 13.2 Hz, ^{3}J = 5.6 Hz), 3.67(dd, 2H, ^{2}J = 14.4 Hz, ^{3}J = 5.2 Hz), 3.59 (s, 3H), 3.57 (td, 2H, ^{2}J = 14.4 Hz, ^{3}J = 4.8 Hz), 3.03 (s, 6H), 2.87 (s, 6H);

^{13}C{^{1}H} NMR (CH_3CN, δ) 67.8, 56.2, 53.2, 51.2, 49.8;

^{19}F{^{1}H} NMR (CD_3CN, δ) -78.5;

FT-IR (cm^{-1}(ranked intensity)) 420(7), 489(2), 519(10), 575(9), 640(14), 768(8), 920(6), 972(5), 1036(15), 1111(1), 1161(13), 1228(12), 1474(11), 1654(3), 2820(4);

FT-Raman (cm^{-1}(ranked intensity)) 85(1), 121(15), 154(6), 169(3), 221(8), 276(9), 315(10), 349(11), 433(14), 480(7), 575(5), 599(13), 758(4), 802(12), 1036(2).

3.5 References

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Chapter 4

The Synthesis and Reactivity of Sulfur(II) Dications Stabilized By Monodentate Ligands[ϕ]

4.1 Introduction

It has been anticipated that species bearing a high charge localized on a central element such as main group polycations should have reactivity garnered towards the activation of small molecules. There have been many of these types of molecules prepared in recent years but no examples have demonstrated the ability to activate small molecules.[1-25] This is a vital area in the fields of organic and inorganic chemistry especially for the transformation of abundant chemical feedstocks into more complex molecules or for targeted synthesis.[26] In the past, transition metal catalysts have been the dominant players in this field but recently, nonmetal reagents have shown utility in this area, spurring further developments within the p-block. Most noteworthy has been the development of the "Frustrated Lewis Pair" by the Stephan and Erker groups. The Frustrated Lewis Pair is derived from the combination of a sterically encumbered Lewis acid and Lewis base that the formation of a classical adduct permitting them to react with a substrate.[27,28] Certain carbenes, specifically the cyclic alkyl amino and diamido derivatives, have also shown the ability to transform several unreactive substrates and have proven useful in the activation of a variety of molecules, such as dihydrogen, alkynes, alkenes, carbon dioxide, ammonia, and nitrous oxide.[29-38] Aside from these reagents, other nonmetal examples for performing such tasks are minimal.[39-45]

Main group complexes have shown a rich chemistry in addition reactions across the double bond in unsaturated organic substrates. Notable examples include hydroborations and, in the presence of a catalyst, hydrostannation and hydrosilylation reactions.[46,47] With respect to the reactivity of sulfur compounds with alkenes, sulfur homopolyatomic

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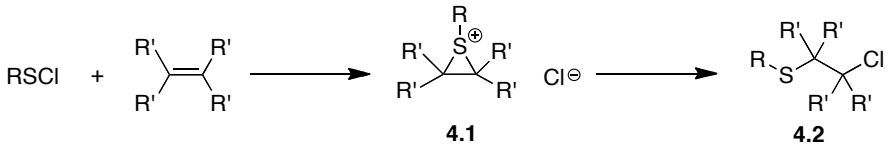
cations form novel heterocycles with nitriles through cycloaddition reactions and sulfur chlorides have been shown to undergo additions with olefins.[48,49] A particular reaction of interest early in the 20th century was in the production of sulfur mustard.[50] This chemical warfare agent was first synthesized in 1822 by Despretz, which was accomplished by the direct reaction of SCl_2 with ethylene to produce the toxin.[51] The reaction has been studied extensively since that time, and the proposed mechanism involves the formation of a cationic thiiranium intermediate (**4.1**), followed by attack of the halide to a carbon atom in the three-membered ring to yield the desired thioether (**4.2**, Scheme 4.1).[52] Although these reactions have been known for a number of years, developments are still being made today, and most noteworthy is the work by Denmark.[53,54] The thioether preparation has been very useful in organic synthesis but toxicity is a concern and an alternative pathway avoiding this issue is desired.



Scheme 4.1: The reaction of sulfur chlorides with olefins in thioether synthesis.

In this context, we have tested the dicationic sulfur molecules featuring bi- and tridentate (**2.5S-2.10S**; **3.1S** and **3.4S**) ligands about the sulfur atom in small molecule activations (Figure 4.1).[4-6] Preliminary reactivity studies have thus far been unsuccessful as the tridentate derivatives are too stable, and the bidentate species react uncontrollably. Herein we synthesize the first monodentate sequestered sulfur(II) dications featuring monodentate pyridine ligands (**4.3**). These species readily undergo addition with carbon-carbon and carbon-nitrogen double bonds into the sulfur-nitrogen dative bond displaying new reactivity for main group polycations. Pyridine ligands are of interest as the substitution on the pyridine ring has a distinct influence on the donor properties at the nitrogen atom, and this provides a means of tuning the electronic properties of the dication. The synthesis, characterization, and reactivity of these new sulfur(II) dications,

with electron donating, neutral, and withdrawing substituents at the *para* position of the ligand is examined.

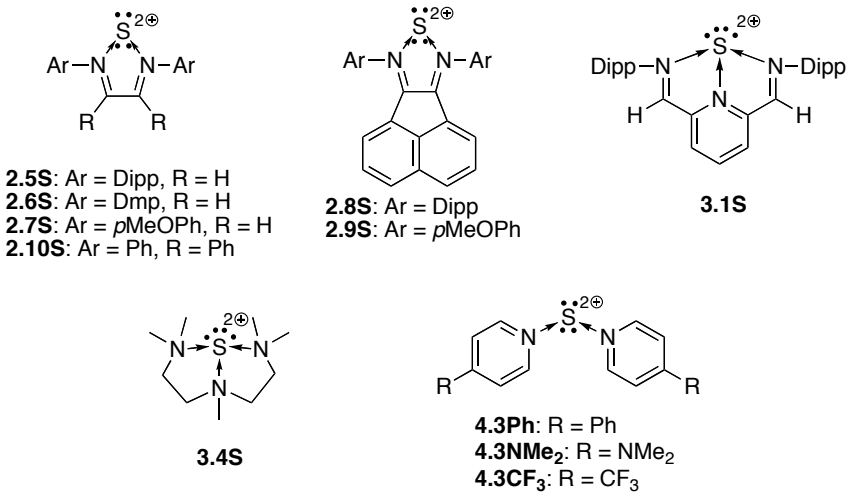


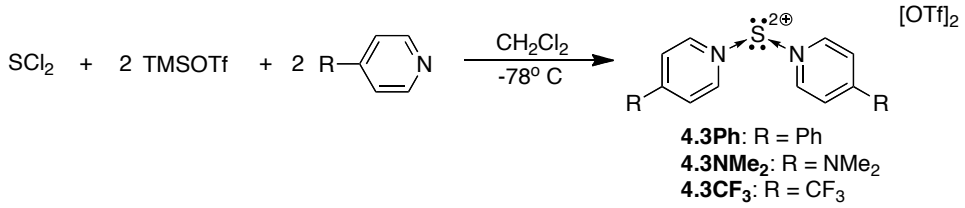
Figure 4.1: Bi- and tridentate supported sulfur(II) dications (**2.5S**-**2.10S, 3.1S** and **3.4S**) and the new monodentate derivatives (**4.3**); Dipp = 2,6-diisopropylphenyl, *p*MeOPh = *para*-methoxyphenyl, Dmp = 2,6-dimethylphenyl.

4.2 Results and Discussion

4.2.1 Synthesis

The addition of two stoichiometric equivalents of TMSOTf to SCl_2 in CH_2Cl_2 at -78 °C generated an orange solution, to which a *para*-substituted pyridine (**4.3Ph**, R = Ph; **4.3NMe$_2$**, R = NMe_2; **4.3CF$_3$**, R = CF_3) in CH_2Cl_2 was added resulting in the immediate generation of a copious amount of white precipitate (Scheme 4.2). The supernatant was removed by decantation or filtration and the white solids were dried *in vacuo*. Proton NMR spectroscopy of the bulk materials in CD_3CN displayed a single set of signals consistent with only one pyridine species present for all three derivatives. Diagnostic features were downfield shifts of the pyridine signals with respect to the free ligands, which is consistent with the bidentate and tridentate derivatives and is indicative of binding to an electron deficient centre. The $^{19}F\{^1H\}$ NMR spectra of **4.3Ph**, **4.3NMe$_2$**, and **4.3CF$_3$** revealed signals for ionic triflate in solution (δ = -78.6 ppm *cf.* $[NOct_4][OTf]$ δ = -78.5 ppm) and **4.3CF$_3$** contained a second signal at -68.5 ppm for the trifluoromethyl group, also shifted downfield with respect to the free pyridine. X-ray diffraction

experiments of **4.3Ph** and **4.3NMe$_2$** confirmed the identity of the compounds, two pyridine ligands coordinating to a dicationic sulfur centre, consistent with the multinuclear NMR spectroscopic data. All three compounds were prepared in high yields (**4.3Ph**: 89%; **4.3NMe$_2$**: 93%; **4.3CF$_3$**: 87%) and were all extremely air/moisture sensitive, decomposing rapidly upon exposure to the open atmosphere.

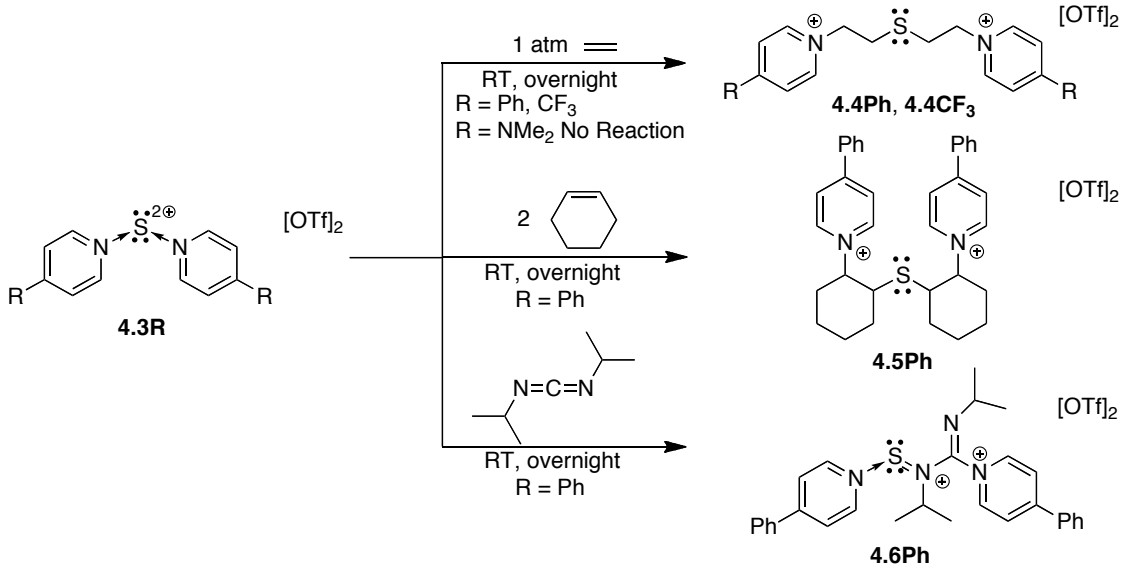


Scheme 4.2: Synthetic route to pyridine stabilized sulfur(II) dications (**4.3Ph**, **4.3NMe$_2$**, and **4.3CF$_3$**).

Benchmark reactions of these new complexes were then carried out using a series of organic substrates (Scheme 4.3). The reaction of **4.3Ph** with the simplest olefin, ethylene, was monitored by ^{1}H NMR spectroscopy and after 15 min elapsed, the reaction mixture began turning light brown. The ^{1}H NMR spectrum showed the emergence of a signal at δ = 5.41 ppm for free ethylene, two overlapping triplets as well as four sets of triplets ranging between 2.9 and 5 ppm (Figure 4.2). After allowing the reaction to proceed for 2.5 h, there was a predominant set of resonances indicating the reaction was proceeding to a single product. It is also noteworthy that throughout the course of the reaction the $\{^1H\}^{19}F$ NMR spectrum displayed a peak characteristic of covalent triflate (δ = -75.0 ppm). The reaction was left to stir overnight, allowing for complete conversion.

Single crystals of sufficient quality for X-ray diffraction experiments were grown from the bulk powder by vapor diffusion of Et_2O into a saturated acetone solution in the open atmosphere. The redissolved crystals in acetonitrile-d_6 gave two triplets at 4.73 and 3.19 ppm, which each integrated to four with respect to the ligand indicative of an equal number of pyridine ligands to ethylene groups in the product. These signals were shifted upfield from ethylene consistent with a change in hybridization from sp^2 to sp^3 at the carbon centre. On the basis of these data the structure was assigned as **4.4Ph**, with the ethylene moiety inserted into the sulfur-nitrogen dative bond, which was confirmed by X-

ray diffraction studies.



Scheme 4.3: Reactivity of the dicationic systems with organic substrates.

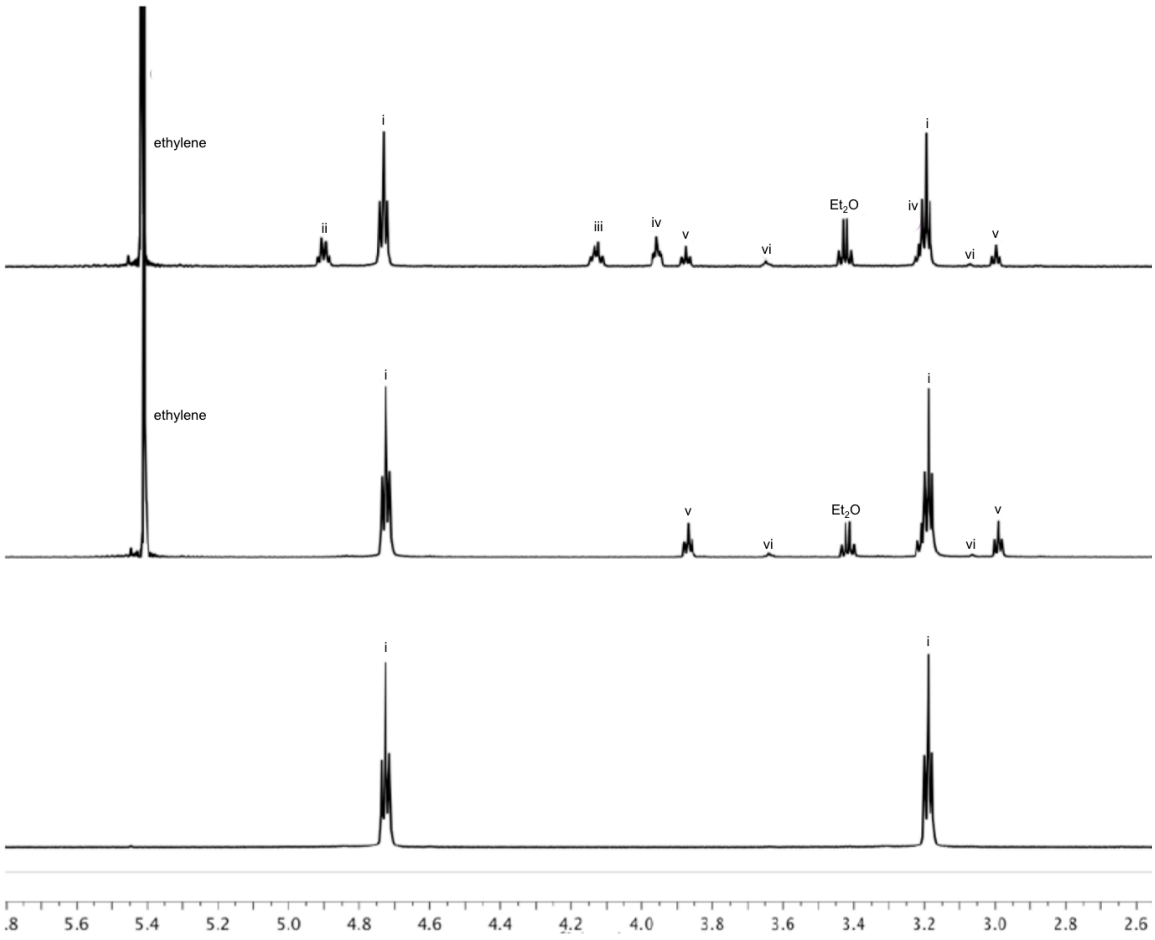


Figure 4.2: Stacked ^{1}H NMR plot of the reaction progress of **4.3Ph** with ethylene in CD_3CN zoomed in on the ethylene region; Top: spectrum 15 min after the solution was exposed to ethylene; Middle: spectrum after 2.5 h; Bottom: spectrum of purified **4.4Ph**. ii and iii denote thiiranium intermediates; iv, v, and vi denote other intermediates; i denotes product.

A proposed mechanism for this insertion is outlined in Figure 4.3. The first step likely involves dissociation of one of the pyridine ligands from **4.3R** giving **A**, which undergoes a cyclization with ethylene to produce the thiiranium ring **B**. Although a weak nucleophile, a triflate counterion ring opens to give **C**, where free pyridine in solution easily displaces the triflate (**D**). Although it is more intuitive to have the free pyridine act as the nucleophile in this step, covalent triflate signals are clearly present in the $^{19}F\{^{1}H\}$

NMR spectra (consistent with **C** and **G**), which subsequently disappear as the reaction proceeds.[55] This process then occurs a second time (through **E**, **F**, and **G**) to yield the final product **4.4R**. In total 10 sets of triplets are expected; however, only six are clearly observed; the intermediates **A** and **E** are likely consumed very quickly, thus not observable on the NMR time scale and the overlapping signals are assigned to species **B** and **F** as they resemble peaks reminiscent of protons within a thiiranium ring.[53] Intermediates **C**, **D**, and **F** would each produce an additional two sets of signals and the asymmetric **G** two more set of triplets, to produce five pairs of triplets (total of 10). This mechanism is only a hypothesis, an in-depth kinetic study would be necessary to clearly elucidate the definitive steps.

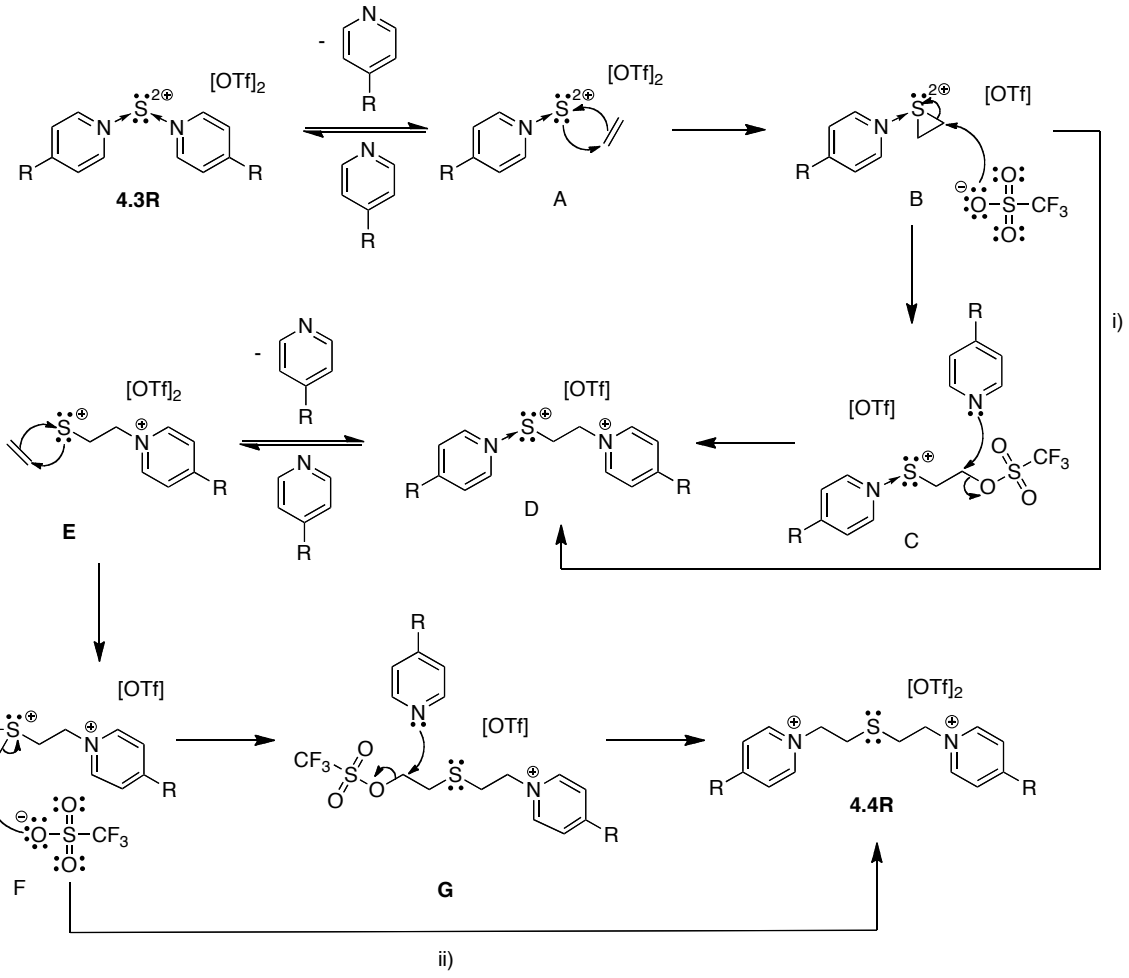


Figure 4.3: Proposed mechanism of the conversion of **4.3R** to **4.4R**. In steps (i) and (ii) pyridine could also ring open the thiiranium intermediate.

The analogous reactions were carried out with **4.3NMe$_2$** and **4.3CF$_3$**, examining a more electron donating group (NMe_2) at the *para* position as well as a more electron withdrawing group (CF_3) with respect to the phenyl substituted species to determine the effect of varying the donor strength of the ligand. The dimethylamino substituted dication did not react at all with ethylene even at elevated pressures and temperatures (200 psi, 90°C), whereas a faster reaction was observed for **4.3CF$_3$**. The proton NMR spectrum of the redissolved solids revealed similar resonances for the ethylene moiety, reminiscent of **4.4Ph**, consistent with the formation of the ethylene inserted product **4.4CF$_3$**. This indicates the potential for tuning the system by taking advantage of the variability at the *para* position.

To see if the reactivity could be extended to other olefins, neat cyclohexene was added to an acetonitrile solution of **4.3Ph**. The solution slowly transformed to a light brown colour. After stirring overnight, the volatiles were removed *in vacuo* giving a brown paste. Proton NMR spectroscopy of the unpurified material indicated the presence of primarily one cyclohexene containing product. Two successive recrystallizations of the material by vapor diffusion of Et_2O into acetone gave colourless crystals. The integrations in the ^{1}H NMR spectrum of the redissolved crystals in acetone-d_6 indicated the presence of an equivalent number of cyclohexyl and pyridine groups. The two signals of the alkene protons were shifted to higher field with respect to cyclohexene. By analogy to the ethylene reaction, the product was assigned as **4.5Ph**, the product resulting from the addition of two cyclohexyl units into the S-N bonds. It is noteworthy that the product contains four chiral centres giving the possibility of several enantiomers. However, only a single diastereomer was observed by proton NMR spectroscopy.

To investigate the reactivity of these complexes with heteroatomic olefins, carbon-nitrogen bonds were studied using *N*,*N*′-diisopropylcarbodiimide (DIC). One equivalent of DIC was added to a solution of **4.3Ph** in CH_3CN, and the solution was stirred for 10 h resulting in a light brown colour. The volatiles were removed *in vacuo* leaving a brown paste. The paste was redissolved in acetonitrile and diethylether was added. Upon storing the solution at -35°C, a white precipitate was obtained. Redissolving the solids in CD_3CN and obtaining a ^{1}H NMR spectrum, a loss of symmetry in the DIC moiety was apparent. Two sets of resonances for the pyridine protons indicated two chemically inequivalent

pyridines were present, and in total, integrated in a 2:1 ratio with respect to the DIC molecule, indicative of the incorporation of a single diimide into the product. The $^{19}F\{^{1}H\}$ NMR spectrum displayed a single peak consistent with ionic triflate in solution (δ = -78.5 ppm). On the basis of these data, the product was tentatively assigned as the addition product of the sulfur dication into one of the C═N bonds in DIC (**4.6Ph**) with the formation of a new S-N bond and a new N-C bond with the diimide. X-ray diffraction experiments confirmed the identity of this reaction product.

4.2.2 X-ray Crystallography

Compounds **4.3Ph** and **4.3NMe$_2$** were crystallized by vapor diffusion of Et_2O into acetonitrile yielding colourless crystals. The two compounds are isostructural, and are both in the *C*2/*c* space group with the molecule lying on a centre of symmetry (Figures 4.4 and 4.5). Both pyridine ligands are bound to the dicationic sulfur centre with bond lengths slightly shorter than typical nitrogen-sulfur single bonds, which is attributed to their attraction to the electropositive centre (1.737(3), **4.3Ph** and 1.717(3), **4.3NMe$_2$** *cf.* 1.76 Å).[56] The difference in these bond lengths is subtle but surprisingly; this has a large influence in the reactivity. The N-S-N bond angles are 101.1(2)° and 100.3(2)°, consistent with two ligands and two lone pairs or an AX_2E_2 electron pair configuration. The oxygen atoms of the triflate anions do lie within the sum of the van der Waals radii for O and S (closest contact S···O 2.829(3), **4.3Ph**; S···O 2.888(3), **4.3NMe$_2$**; *cf.* 3.25 Å); however, they do not complete a square planar geometry about the sulfur centre (Figure 4.6) which would be consistent with covalently bound triflate to a chalcogen centre.[56,57] In fact, the interplanar bond angles show a significant deviation from an ideal square planar geometry (25.5° for **4.3Ph**, 26.4° for **4.3NMe$_2$** *cf.* 0°). Furthermore, there is no elongation in the corresponding sulfur-oxygen bond length with respect to the other sulfur-oxygen bonds in the triflate anions, which would be observed if a covalent interaction were present [**4.3Ph**: S(2)-O(1) 1.430(3), *cf.* 1.424(3) and 1.434(3) Å; **4.3NMe$_2$**: S(2)-O(1) 1.435(3) *cf.* 1.430(3) and 1.442(3) Å].[7] On the basis of these data, the molecules were assigned the structures of a dicationic sulfur(II) centre stabilized by two pyridine ligands with two triflate counterions. Despite numerous attempts, we were unable to grow crystals of suitable quality for X-ray diffraction experiments for **4.3CF$_3$**.

However, on the basis of the analogous spectroscopic data, the structure was assigned to **4.3CF$_3$**.

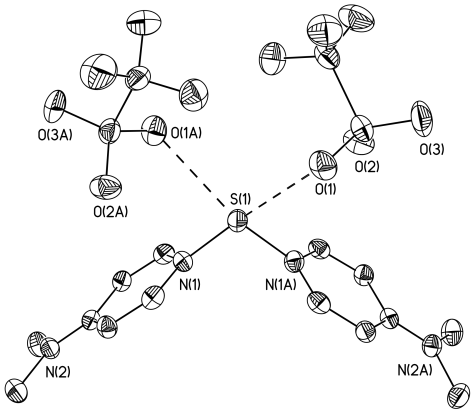


Figure 4.4: Solid-state structure of **4.3NMe$_2$**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)-N(1) 1.717(3), S(1)···O(3) 2.888(3), N(1)-S(1)-N(1A) 101.1(2).

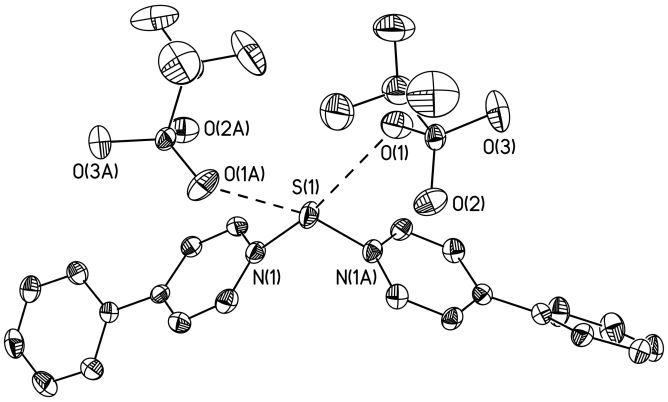


Figure 4.5: Solid-state structure of **4.3Ph**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)-N(1) 1.737(3), S(1)···O(1) 2.829(3), N(1)-S(1)-N(1A) 100.3(2).

Figure 4.6: View of the dicationic sulfur centre in (a) **4.3NMe$_2$** and (b) **4.3Ph**, interplanar O-S-O and N-S-N angles: **4.3Ph**: 25.5° and **4.3NMe$_2$**: 26.4°.

Upon the examination of the solid-state structure of the reaction product with ethylene, **4.3Ph** ethyl groups were found to be inserted in between the pyridine nitrogen and the formerly dicationic sulfur centre from **4.3Ph**, generating new N-C bonds with the pyridine ligand and S-C bonds with the dicationic centre (Figure 4.7). The carbon-carbon bond length has elongated significantly from that of ethylene [1.33 *cf.* 1.518(3) Å] consistent with the conversion from a double to a single bond. The newly formed N-C and S-C bonds are also consistent with single bonds confirming the structure as **4.4Ph**.

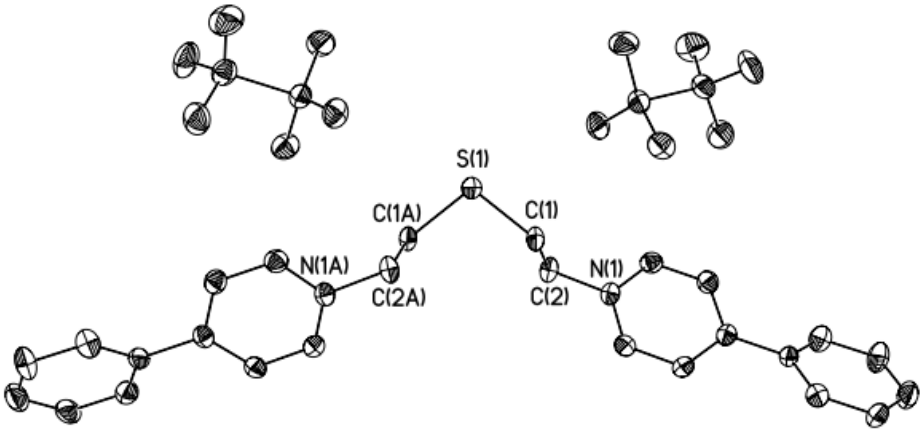


Figure 4.7: Solid-state structure of **4.4Ph**. Ellipsoids are drawn to 50% probability, and all hydrogen atoms and solvates are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)-C(1) 1.805(2), N(1)-C(2) 1.487(3), C(1)-C(2) 1.518(3), C(1)-S(1)-C(1A) 103.28(16).

The addition reaction product with cyclohexene showed a related solid-state structure to **4.4Ph** (Figure 4.8). However, the fact that the carbon atoms bear an additional group in comparison to ethylene gives the potential for multiple products, as there are four chiral centres in the molecule. On the basis of the ^{1}H NMR data, only one species was observed. Compound **4.5Ph** crystallized in the triclinic space group *P*-1, with two molecules lying within the unit cell related to one another by a centre of symmetry. The asymmetric unit revealed a molecule in the *R*,*R*,*R*,*R* - configuration; however, given the centrosymmetric space group, the other molecule in the unit cell is its mirror image (*S*,*S*,*S*,*S* - configuration). This means the crystal is a 50:50 racemic mixture of the two enantiomers, consistent with the ^{1}H NMR spectroscopic data as both species would produce identical

spectra. It can be concluded that the pyridine and sulfur in all cases are positioned *anti* to one another, which is reasonable as this arrangement imposes more favourable steric interactions.

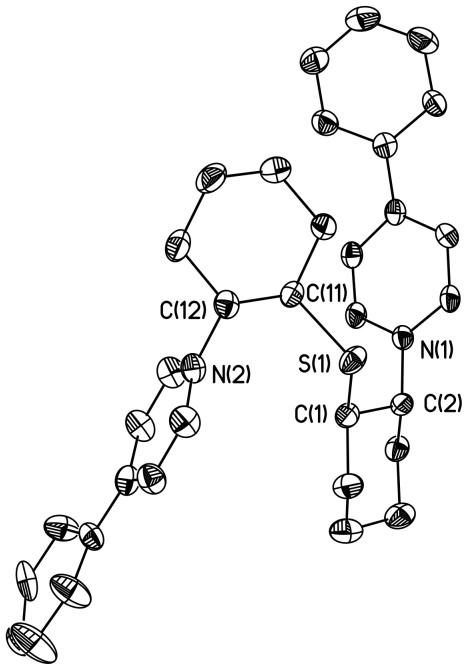


Figure 4.8: Solid-state structure of **4.5Ph** displaying the molecule in the *R*,*R*,*R*,*R* - configuration within the unit cell; only one position of the disordered phenyl group is shown. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)-C(1) 1.824(4), S(1)-C(11) 1.824(4), C(1)-C(2) 1.530(5), C(11)-C(12) 1.519(5), C(2)-N(1) 1.490(5), C(12)-N(2) 1.496(5), C(1)-S(1)-C(11) 106.92(18).

Examination of the solid-state structure of **4.6Ph** (Figure 4.9) further demonstrates the ability of **4.3Ph** to undergo addition reactions. In this case, one pyridine group remains bound to the sulfur centre, and the other has migrated to the central carbon atom in the diimide unit. The sulfur is now bound to a nitrogen atom from the DIC species. The sulfur-nitrogen bond lengths are 1.664(4) and 1.801(4) Å for the newly formed bond to the diimide and for the pyridine ligand, respectively. The latter is longer than that in the dication, which could be attributed to the reduced cationic character at sulfur. The newly formed S-N bond is shorter than a single bond, indicating a strong interaction with the

DIC moiety. The nitrogen-carbon bond lengths from the DIC unit are 1.379(5) and 1.254(5) Å, consistent with the retention of one double bond and the elongation of the other to a single bond. The geometry about the nitrogen atom is trigonal planar [sum of angles about N(11) = 360.0°]. The most accurate structural representation would have the positive charge on the nitrogen atom from the DIC moiety and a double bond to the sulfur centre. The elongated pyridine sulfur interaction from the dication is a result of the pyridine being bound to a neutral sulfur atom (Table 4.1).

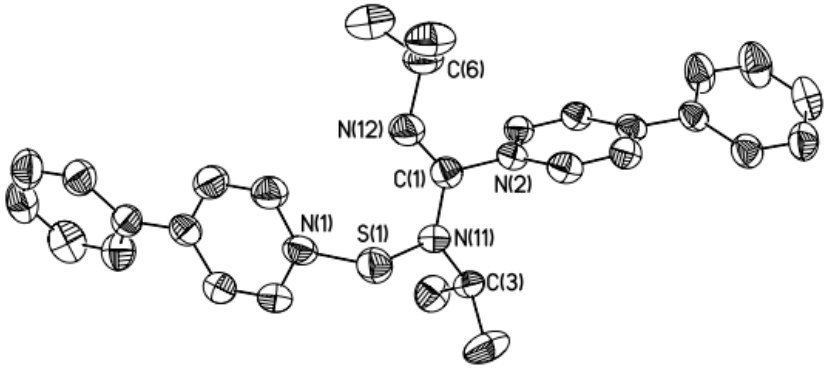


Figure 4.9: Solid-state structure of **4.6Ph**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)-N(11) 1.664(4), S(1)-N(1) 1.801(4), N(11)-C(1) 1.379(5), C(1)-N(12) 1.254(5), N(2)-C(1) 1.477(5), N(1)-S(1)-N(11) 105.37(17), S(1)-N(11)-C(3) 121.4(3), C(1)-N(11)-C(3) 122.8(3), S(1)-N(11)-C(1) 115.8(3).

Table 4.1: X-ray details for **4.3Ph**, **4.3NMe$_2$**, **4.4Ph**, **4.5Ph** and **4.6Ph**.

Compound	**4.3Ph**	**4.3NMe$_2$**	**4.4Ph**	**4.5Ph**	**4.6Ph**
Empirical formula	$C_{24}H_{18}F_6N_2O_6S_3$	$C_{16}H_{20}F_6N_4O_6S_3$	$C_{31}H_{32}F_6N_2O_7S_3$	$C_{36}H_{38}F_6N_2O_6S_3$	$C_{31}H_{32}F_6N_4O_6\ S_3$
FW (g/mol)	640.58	574.54	754.77	804.86	766.79
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*P*-1	*P*-1
a (Å)	25.234(3)	20.142(4)	30.303(6)	11.287(2)	8.3050(5)
b (Å)	9.8706(13)	10.009(2)	10.033(2)	12.121(2)	15.0203(10)
c (Å)	11.2571(15)	11.392(2)	11.027(2)	14.544(3)	15.1251(10)
α (deg)	90	90	90	83.80(3)	107.243(4)
β (deg)	104.2900(10)	90.17(3)	92.44(3)	89.35(3)	95.421(4)
γ (deg)	90	90	90	72.99(3)	98.949(3)
V (Å^3)	2717.1(6)	2296.5(8)	3349.4(12)	1891.1(7)	1760.2(2)
Z	4	4	4	2	2
D_c (mg m^{-3})	1.566	1.662	1.497	1.413	1.447
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	173(2)	150(2)	150(2)	150(2)	150(2)
$R1[I>2\sigma I]^a$	0.0596	0.0583	0.0505	0.0664	0.0759
$wR2(F^2)^a$	0.1657	0.1323	0.1375	0.1914	0.2325
GOF $(S)^a$	1.283	1.065	1.042	1.013	1.043

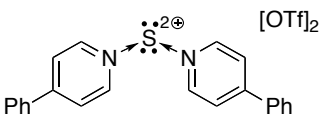
[a] $R1(F[\mathrm{I} > 2(\mathrm{I})]) = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; $wR2(F^2\ [\text{all data}]) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

4.3 Conclusion

Through these studies, a new series of sulfur(II) dications were synthesized by utilizing monodentate pyridine ligands to stabilize the sulfur centre. These compounds may be described as pyridinium salts, but based on the lability of the sulfur-nitrogen bond in the chemistry of the molecules, the dative model is more accurate, and these species represent the first monodentate stabilized sulfur(II) dications. The substitution at the *para* position on the pyridine ring could be altered, which was influential on the reactivity at the sulfur centre and proved to be useful in reacting the dications with olefins. It was determined that the strong donor ligand, dimethylaminopyridine, prevented any reaction from occurring, while the phenyl and trifluoromethyl substituted pyridine readily reacted inserting the olefin into the sulfur-nitrogen bond. The reaction is very similar to that of sulfur dichloride with ethylene in the production of sulfur mustard. The reaction products possess a carbon atom bound to a pyridinium centre, which represents an excellent leaving group and should be useful in the onward synthesis of new organic molecules. The system was extended from ethylene to cyclohexene showing the analogous reactivity producing only products with substituents *anti* to one another. Moreover, the addition chemistry was also transferable to carbon-nitrogen bonds. The 1:1 stoichiometric reaction with *N*,*N*′-diisopropylcarbodiimide resulted in the pyridine bonding to the central carbon in the diimide and a covalent sulfur nitrogen bond. The versatility of this system is interesting and the scope should be explored.

4.4 Experimental Section

4.3Ph



A solution of SCl_2 (0.032 g, 0.315 mmol) and TMSOTf (0.140 g, 0.629 mmol) in CH_2Cl_2 (5 mL) was prepared at -78 °C. To this mixture 4-phenylpyridine (0.098 g, 6.29 mmol) in CH_2Cl_2 (5 mL) was added immediately generating a white precipitate. The supernatant was decanted and the solids were dried *in vacuo*.

Yield: 0.180 g, 89%; d.p. 170-172 °C;

^{1}H NMR (CD_3CN, δ) 9.33 (d, 4H, ^3J = 6.6 Hz), 8.45 (d, 4H, ^3J = 6.6 Hz), 8.01 (d, 4H, ^3J = 8.4 Hz), 7.74 (t, 2H, ^3J = 7.8 Hz), 7.68−7.65 (m, 4H);

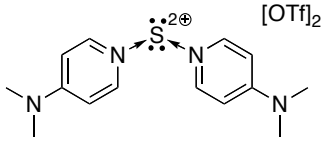
^{13}C NMR (CH_3CN, δ) 155.2, 152.0, 136.6, 136.4, 133.1, 131.8, 128.8;

^{19}F{^{1}H} NMR (CH_3CN, δ) -78.6;

FT-IR (cm^{-1}(ranked intensity)) 3110(11), 1619(5), 1518(15), 1487(14), 1236(1), 1167(8), 1028(3), 833(12), 770(4), 729(10), 694(7), 574(9), 639(2), 518(6), 385(13);

FT-Raman (cm^{-1}(ranked intensity)) 3072(14), 1621(5), 1596(1), 1511(8), 1301(2), 1226(4), 1081(6), 1058(12), 1034(3), 1000(7), 780(11), 616(13), 403(10), 315(15), 113(9).

4.3NMe$_2$



[OTf]$_2$

The analogous procedure for **4.3Ph** was utilized with the same quantities substituting DMAP (0.077 g, 0.629 mmol) for 4-phenylpyridine.

Yield: 0.168 g, 93%; d.p. 136-138 °C;

^{1}H NMR (CD_3CN, δ) 8.34 (d, 4H, ^{3}J = 8.0 Hz), 6.90 (d, 4H, ^{3}J = 8.4 Hz), 3.24 (s, 12H);

^{13}C NMR (CH_3CN, δ) 158.1, 147.1, 110.0, 41.4;

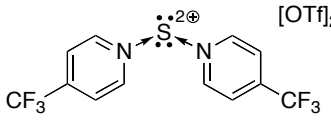
^{19}F{^{1}H} NMR (CH_3CN, δ) -78.6;

FT-IR (cm^{-1}(ranked intensity)) 519(8), 574(12), 636(4), 804(11), 833(9), 1030(1), 1082(13), 1149(6), 1220(5), 1270(2), 1403(10), 1446(14), 1575(7), 1630(3), 3064(15);

FT-Raman (cm^{-1}(ranked intensity)) 112(10), 246(13), 314(6), 350(7), 575(12), 649(9), 769(1), 941(5), 1032(2), 1226(14), 1405(15), 1577(3), 1640(4), 2948(8), 3100(11).

Elemental analysis: Calc for $C_{16}H_{20}F_6N_4O_6S_3$ C 33.45, H 3.51, N 9.76; found C 33.45, H 3.22, N, 9.56.

4.3CF$_3$



[OTf]$_2$

A solution of SCl_2 (0.032 g, 0.315 mmol) and TMSOTf (0.140 g, 0.629 mmol) in CH_2Cl_2 (5 mL) was prepared at -78 °C. To this mixture 4-trifluoromethylpyridine (0.093 g, 0.629 mmol) in CH_2Cl_2 (5 mL) was added generating a white precipitate. Normal pentane (5 mL) was added resulting in more solids precipitating from solution. The supernatant was decanted and the solids were dried *in vacuo*.

Yield: 0.171 g, 87%; d.p. 179-181 °C;

^{1}H NMR (CD_3CN, δ) 9.65 (d, 4H, ^{3}J = 6.4 Hz), 8.50 (d, 4H, ^{3}J = 6.4 Hz);

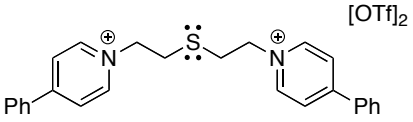
^{13}C NMR (CH_3CN, δ) 153.8, 127.8, 123.1;

^{19}F{^{1}H} NMR (CH_3CN, δ) -65.5 (s, 6F), -78.6 (s, 6F);

FT-IR(cm^{-1}(ranked intensity)) 1613(11), 1519(10), 1329(5), 1257(1), 1229(14), 1149(3), 1085(8), 1036(2), 803(7), 735(12), 703(13), 654(4), 597(15), 575(9), 518(6);

FT-Raman (cm^{-1}(ranked intensity)) 3101(10), 1639(15), 1326(14), 1067(3), 1031(2), 800(1), 762(4), 653(11), 576(13), 484(12), 353(5), 318(7), 285(9), 231(8), 129(6).

4.4Ph



A solution of **4.3Ph** (0.150 g, 0.234 mmol) in CH_3CN (10 mL) was prepared in a Schlenk round bottomed flask in a dinitrogen atmosphere. The flask was immersed in a liquid nitrogen bath and the solution was frozen. The nitrogen was removed *in vacuo* and the flask was warmed to room temperature allowing the solvent to thaw. The flask was filled with one atmosphere of ethylene and stirred overnight. The solvent was removed *in vacuo* resulting in a yellow paste. The desired material was crystallized in the open atmosphere by vapor diffusion of ether into acetone.

Yield: 0.112 g, 69%; m.p. 138-141 °C;

^{1}H NMR (CD_3CN, δ) 8.75 (d, 4H, ^{3}J = 7.2 Hz), 8.29 (d, 4H, ^{3}J = 6.6 Hz), 7.95-7.93 (m, 4 H), 7.69-7.62 (m, 6H), 4.73 (t, 6.6 Hz, 4H), 3.19 (t, 6.6 Hz, 4H);

^{13}C NMR ($(CD_3)_2CO$, δ): 157.3, 146.2, 134.8, 133.1, 130.7, 129.0, 125.7, 60.4, 32.4;

^{19}F{^{1}H} NMR (CH_3CN, δ) -78.6;

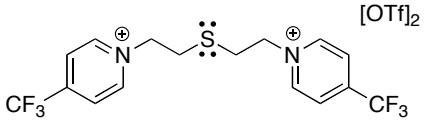
FT-IR (cm^{-1}(ranked intensity)) 1641(4), 1561(11), 1525(15), 1492(14), 1440(9), 1275(1), 1223(12), 1143(5), 1029(3), 867(13), 766(6), 691(8), 637(2), 572(10), 517(7);

FT-Raman (cm^{-1}(ranked intensity)) 3109(10), 1655(9), 1329(15), 1228(14), 1177(11), 1083(8), 1034(1), 839(3), 759(7), 665(4), 575(12), 350(6), 316(5), 109(13), 85(2).

Elemental Analysis: Calc for $C_{31}H_{32}F_6N_2O_7S_3$ C 48.27, H 3.76, N 4.02; Found C 48.79, H 3.65, N, 3.84;

ESI-MS *m*/*z* 547 [M^{2+}][OTf^-].

4.4CF$_3$



The analogous procedure for **4.4Ph** was used substituting **4.3CF$_3$** (0.200 g, 3.21 mmol) in place of **4.3Ph**. The resulting yellow paste was dissolved in THF (3 mL) and pentane (3 mL) was added in the open atmosphere. The solution was stored at -30 °C overnight generating a white solid. The supernatant was decanted and the solids were dried *in vacuo*.

Yield: 0.089 g, 41%; m.p. 146-148 °C;

^{1}H NMR ((CD$_3$)$_2$CO, δ) 9.61 (d, 4H, ^{3}J = 6.4 Hz), 8.67 (d, 4H, ^{3}J = 6.4 Hz), 5.26 (t, 4H, ^{3}J = 7.2 Hz), 3.56 (t, 4H, ^{3}J = 6.8 Hz);

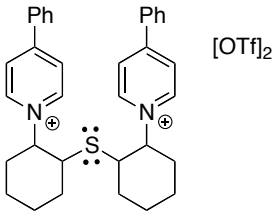
^{13}C NMR ((CD$_3$)$_2$CO, δ): 148.8, 126.1, 126.0, 62.2, 32.4;

^{19}F{^{1}H} NMR ((CD$_3$)$_2$CO, δ) -65.0 (6F), -78.2 (6F);

FT-IR (cm^{-1}(ranked intensity)) 3068(10), 1654(15), 1474(8), 1326(12), 1262(7), 1147(1), 1080(4), 1032(3), 864(6), 836(13), 747(9), 640(2), 600(14), 574(11), 518(5);

FT-Raman (cm^{-1}(ranked intensity)) 3105(11), 1654(9), 1431(15), 1331(14), 1228(13), 1171(6), 1083(5), 1035(1), 835(2), 757(7), 666(4), 575(12), 349(3), 314(8), 107(10).

4.5Ph



To a solution of **4.3Ph** (0.200 g, 0.313 mmol) in acetonitrile (5 mL), neat cyclohexene (0.039 g, 0.625 mmol) was added and the reaction was stirred overnight resulting in a light brown solution. The volatiles were removed *in vacuo* giving a brown paste. The material was purified by two recrystallizations by vapor diffusion of Et$_2$O into a concentrated acetone solution in the open atmosphere.

Yield: 0.106 g, 42%; m.p. 249-251 °C;

^{1}H NMR ((CD$_3$)$_2$CO, δ): 9.28 (d, 4H, ^{3}J = 5.6 Hz), 8.63 (d, 4H, ^{3}J = 6.4 Hz), 8.13−8.11 (m, 4H), 7.73−7.67 (m, 6H), 4.59 (td, ^{3}J = 8.0 Hz, ^{3}J = 4.0 Hz, 2H), 3.28 (td, ^{3}J = 7.6 Hz, ^{3}J = 4.0 Hz, 2H), 2.42-2.39 (m, 2H), 2.21-1.15 (m, 16H);

^{13}C NMR ((CD$_3$)$_2$CO, δ): 157.9, 134.8, 133.3, 130.8, 129.1, 128.8, 126.0, 76.1, 51.4, 36.0, 34.1, 25.9, 25.3;

$^{19}F\{^{1}H\}$ NMR ($(CD_3)_2CO$, δ) -78.0;

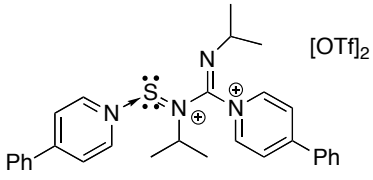
FT-IR (cm^{-1}(ranked intensity)) 3055(12), 1635(2), 1524(15), 1491(14), 1441(10), 1260(1), 1154(5), 1031(3), 868(13), 770(6), 727(9), 688(11), 638(4), 573(8), 517(7);

FT-Raman (cm^{-1}(ranked intensity)) 2866(14), 1635(2), 1560(1), 1520(7), 1227(15), 1163(3), 1034(5), 1001(4), 795(12), 756(8), 574(11), 408(9), 348(13), 263(10), 109(6);

Elemental analysis: Calc for $C_{36}H_{38}F_6N_2O_6S_3$ C 53.72, H 4.76, N 3.48; Found C 53.53, H 4.59, N, 3.73;

ESI-MS *m/z* 655 $[M^{2+}][OTf^-]$.

4.6Ph



A solution of **4.3Ph** (0.100 g, 0.156 mmol) in acetonitrile (4 mL) was prepared in a vial and neat DIC (0.020 g, 0.156 mmol) was added. The solution was stirred for 10 h and acquired a light brown colour. The volatiles were removed *in vacuo* producing a brown oil. The oil was dissolved in a minimal amount of acetonitrile (1 mL) and diethylether (2 mL) was added dropwise. The vial was stored at -35 °C for 1 h which caused the precipitation of a white powder. The supernatant was removed and the solids were dried *in vacuo*.

Yield: 0.49 g, 41%; d.p. 155-157 °C;

^{1}H NMR (CD_3CN, δ) 9.10 (br, 2H), 8.85 (br, 2H), 8.56 (d, 2H, ^{3}J = 5.4 Hz), 8.34 (dd, 2H, ^{3}J = 7.2 Hz, ^{4}J = 1.8 Hz), 8.07 (d, 2H, ^{3}J = 7.8 Hz), 7.99 (d, 2H, ^{3}J = 7.8 Hz), 7.76 (t, 1H, ^{3}J = 7.2 Hz), 7.73-7.65 (m, 5H), 3.99 (br, 1H), 3.19 (br, 1H), 1.35 (br, 6H), 1.27, (d, 6H, ^{3}J = 6.0 Hz).

^{13}C NMR (CD_3CN, δ): 161.1, 158.9, 143.4, 134.7, 133.4, 134.3, 133.7, 133.5, 130.8, 130.7, 129.8, 129.2, 127.3, 127.2, 126.0, 59.5, 53.4, 23.7, 21.8;

$^{19}F\{^{1}H\}$ NMR (CH_3CN, δ) −78.6;

FT-IR (cm^{-1}(ranked intensity)) 3080(15), 1638(6), 1524(13), 1489(11), 1294(4), 1232(5), 1151(7), 1029(2), 834(9), 763(3), 720(14), 685(12), 639(1), 575(10), 518(8);

FT-Raman (cm^{-1}(ranked intensity)) 1629(3), 1616(9), 1597(1), 1297(2), 1220(4), 1517(8), 1088(10), 1036(5), 1005(6), 771(15), 754(12), 402(11), 348(13), 312(14), 110(7);

ESI-MS *m/z* 766 $[M^{3+}][OTf^-]$.

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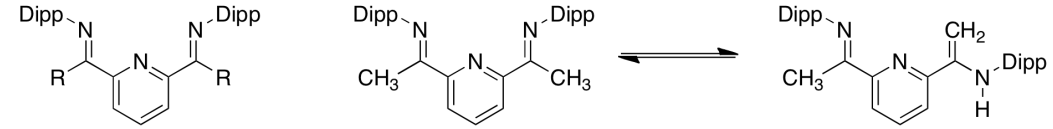
Chapter 5

The Reactivity of Phosphorus Halides with Diiminopyridine Ligands[ϕ]

5.1 Introduction

Recent years have witnessed a surge of interest in probing the reactivity of α-diimine ligands with the main group elements. The 1,4-diaza-1,3-butadiene (DAB) system has been widely explored, while studies with the diiminopyridine ligand (DIMPY, Figure 5.1; R = group on N; **5.1**: R = H; **5.2**: R = CH_3; **5.3**: R = C_6H_5)[θ] have been mostly restricted to the heavy group 13-15 elements (n ≥ 3), which preferentially form complexes with the p-block centres in low oxidation states.[1-8] For example, the redox reaction of AsI_3 with **5.2** yields an As(I) species, in contrast to the analogous transformation with DAB, which produces an As(III) cation.[4] The previous chapters provide good evidence that for DAB, DIMPY and also the related β-diketiminate ligands, the substitution on both the α-carbon and imine nitrogen atoms can be highly influential in the outcome of the reaction. Hydrogen atoms on the α-carbon are often found to be acidic and prone to halogenation[9-11] whereas the methyl substituted derivative can react as the eneamine tautomer (*e.g.* for DIMPY **5.2'**).[12-16]



DIMPY
Dipp = 2,6-diisopropylphenyl
R = H(**5.1**), CH_3(**5.2**), Ph(**5.3**)

5.2 **5.2'**

Figure 5.1: The DIMPY ligands (left; **5.1**-**5.3**), and tautomerization of **5.2** to the

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ϕ A version of this work has been accepted for publication Martin, C. D.; Ragogna, P. J. *Dalton Trans.* DOI: 10.1039/c1dt11111f.

θ The ligands **3.1**, **3.2** and **3.3** are represented in this chapter for simplicity by **5.1**, **5.2** and **5.3**, respectively.

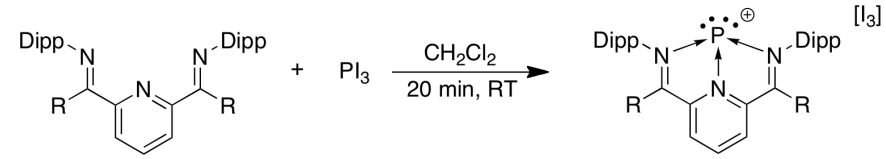
eneamine **5.2'** (right).

Despite the vast amounts of P-N chemistry in the literature, phosphorus surprisingly lacks a DIMPY complex. Although not observed with arsenic, we surmised that the related eneamine chemistry could proceed with phosphorus. This reactivity is unable to occur with the less common -H and -C_6H_5 ligands (**5.1** and **5.3**) and should provide a P(I) species via redox reaction.* In this context, we exploit the reactions of DIMPY ligands with varying substitution on the α-carbon (**5.1**-**5.3**) with the phosphorus trihalides (PCl_3, PBr_3 and PI_3) with the goal of synthesizing the first phosphorus diiminopyridine complex.

5.1 Results and Discussion

5.1.1 Synthesis

A solution of **5.2** in CH_2Cl_2 was added to PI_3 in the same solvent and stirred for 20 minutes at room temperature resulting in a colour change from yellow to red. A $^{31}P\{^1H\}$ NMR spectrum of an aliquot of the reaction mixture revealed a complex mixture of phosphorus containing products (Figure 5.2). The analogous transformations were performed with **5.1** and **5.3**, also generating red solutions (Scheme 5.1).



Scheme 5.1: Synthetic route to the P(I) DIMPY complexes **5.1P[I_3]** and **5.3P[I_3]**.

The *in situ* $^{31}P\{^1H\}$ NMR spectra obtained for the latter two reactions displayed a dominant resonance, shifted to high field relative to PI_3 (**5.1**: δ = 169 ppm; **5.3**: δ = 154 ppm *cf.* PI_3 δ = 174 ppm). Red solids were precipitated from the reaction mixture by

* Scifinder search results indicate that **5.2** is the most widely used: **5.2**: 331 references; **5.1**: 30 references; **5.3**: 14 references. (all examples have 2,6-diisopropylphenyl substitution at N)

adding *n*-pentane, washed with Et_2O and dried *in vacuo*. The corresponding ^1H NMR spectra of the redissolved solids indicated the presence of a single DIMPY containing product. The spectrum obtained from the reaction with **5.1** (Figure 5.3) had the resonance for the protons on the α-carbon atom split into a doublet with coupling consistent with typical $^3J_{H\text{-}P}$ values and the peak was shifted downfield suggesting the successful incorporation of phosphorus into the ligand framework ($\Delta\delta$ = 0.90 ppm, $^3J_{H\text{-}P}$ = 5.6 Hz).[17,18] Diagnostic features in both spectra were downfield shifts of the protons at the 3 and 5 positions on the pyridine rings (**5.1**: $\Delta\delta$ = 0.71 ppm; **5.3**: $\Delta\delta$ = 1.12 ppm)[17,19] consistent with the coordination of the ligand to a cationic centre.

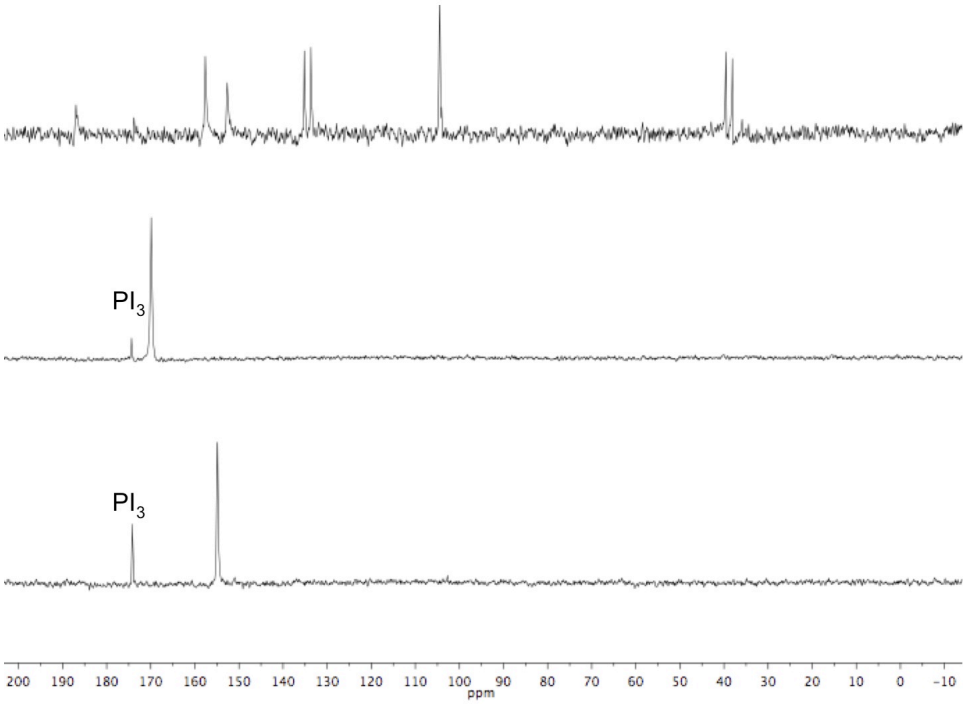


Figure 5.2: Stacked *in situ* $^{31}P\{^1H\}$ NMR spectra of reactions of PI_3 with the DIMPY ligands. From top to bottom: **5.2**, **5.1** and **5.3**.

X-ray diffraction analyses of single crystals of both compounds grown by vapour diffusion of *n*-pentane into $CHCl_3$ confirmed the identity of the redox products **5.1P[I_3]** and **5.3P[I_3]** isolated in 81% and 77% yields, respectively (Figure 5.4). Given the plethora of unidentifiable products in the ^{31}P NMR spectrum for the attempted synthesis

of **5.2P[I$_3$]** the reaction was not pursued. It is speculated that this is due to uncontrollable reactivity with the eneamine tautomer (**5.2'**).†

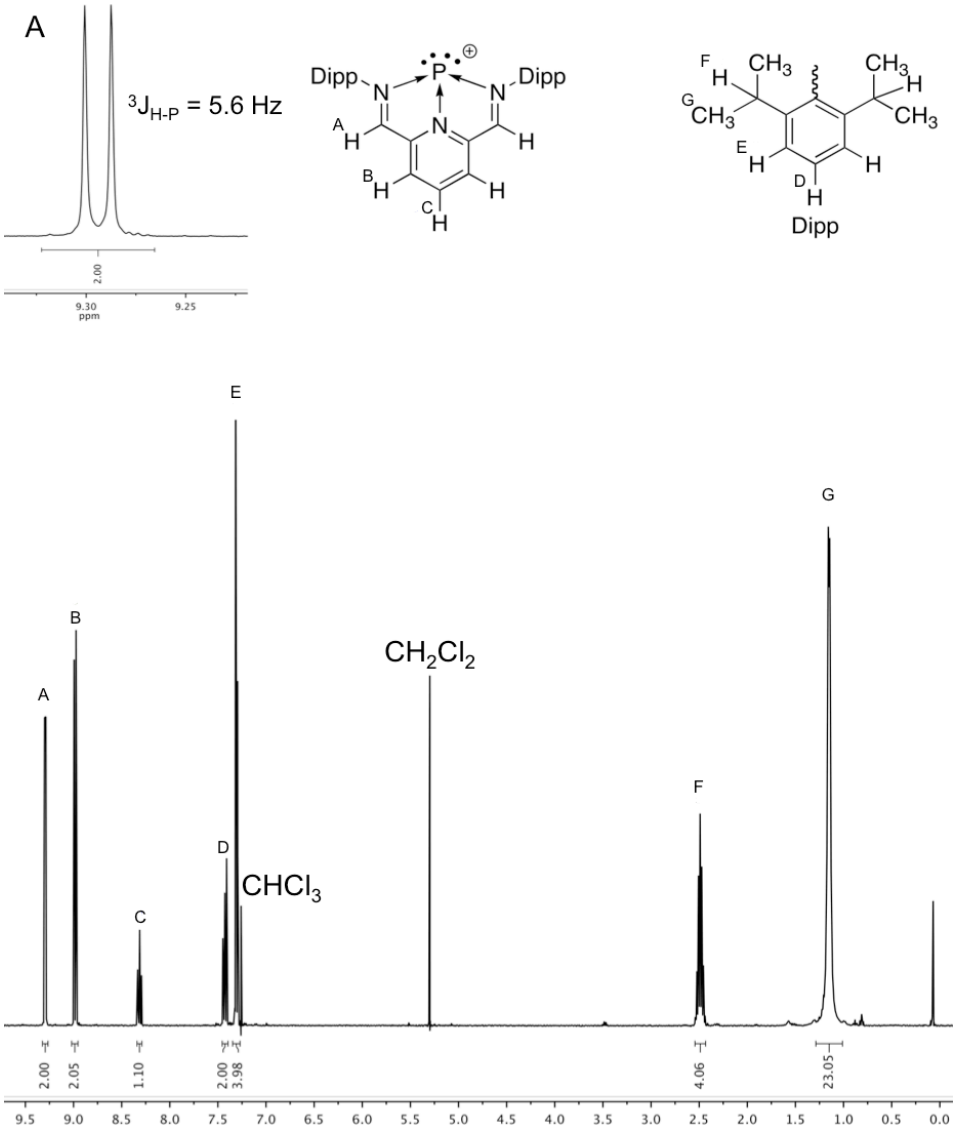
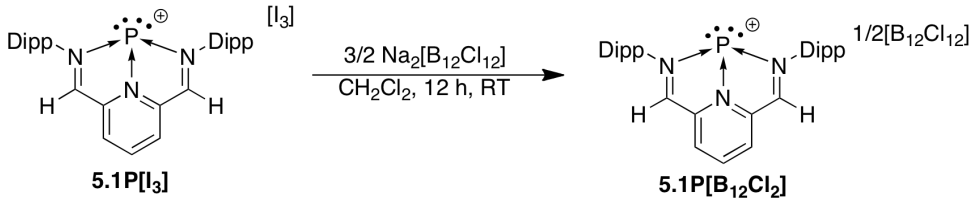


Figure 5.3: Proton NMR spectrum of **5.1P[I$_3$]** in $CDCl_3$ (bottom: full sweep window; top left: doublet for the backbone protons.

Complex **5.1P[I$_3$]** was reacted with 1.5 stoichiometric equivalents of $Na_2[B_{12}Cl_2]$ at room

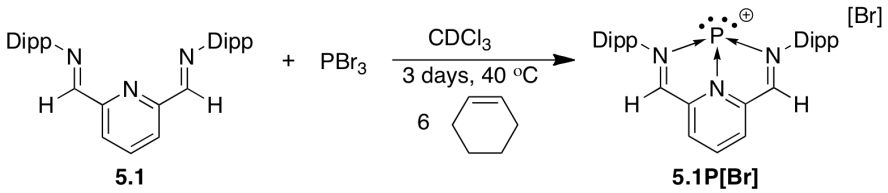
† Although this chemistry could be harnessed for other main group examples in previous studies,[12-14] this was not the case for this system.

temperature for 12 hours to yield the anion exchange product with the more robust $B_{12}Cl_{12}$ dianion. Centrifuging the reaction mixture, precipitating the orange product with *n*-pentane from the supernatant and drying *in vacuo* gave the salt in 65% yield. The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra were similar to **5.1P[I$_3$]** and a single peak in the $^{11}B\{^{1}H\}$ NMR spectrum (δ = -12.7 ppm) confirmed the presence of $B_{12}Cl_{12}^{2-}$. X-ray diffraction experiments on orange crystals grown by vapour diffusion of Et_2O into CH_2Cl_2 confirmed the identity of **5.1P[B$_{12}$Cl$_{12}$]** as the cationic phosphorus DIMPY complex in a 2:1 ratio with a $B_{12}Cl_{12}^{2-}$ counteranion.



Scheme 5.2: Metathesis reaction of **5.1P[I$_3$]** with $Na_2[B_{12}Cl_{12}]$ to produce **5.1P[B$_{12}$Cl$_{12}$]**.

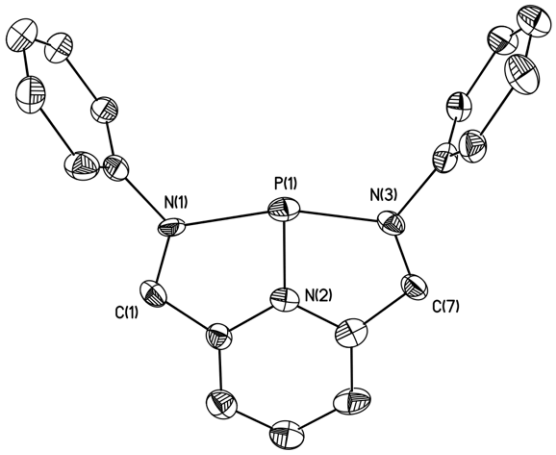
Examining the analogous chemistry of PCl_3 with **5.1** or **5.3** in the presence of the halide trap cyclohexene[20,21] to aid the redox reaction in targeting the P(I) complex did not result in any reaction based on *in situ* $^{31}P\{^{1}H\}$ NMR spectroscopy, even at reflux temperatures in toluene. A new phosphorus signal (δ = 166 ppm) slowly appeared in the reaction of phosphorus tribromide with **5.1** and 6 stoichiometric equivalents of cyclohexene at room temperature. Conversion to one peak was observed upon reaction at 40°C for 3 days (Scheme 5.3). Heating the sample above 40°C led to decomposition. The compound could be isolated as orange crystals in 28% yield which were subjected to X-ray diffraction analysis revealing a P(I) cation within the HDIMPY framework and a bromide counteranion (**5.1P[Br]**). In all cases, the attempted transformation with PBr_3, cyclohexene and **5.3** resulted in no reaction even when refluxing in toluene. Reactions of PBr_3 or PCl_3 with **5.3** and cyclohexene produced mixtures by $^{31}P\{^{1}H\}$ NMR spectroscopic analysis with no indication of clean formation of a P(I) salt.



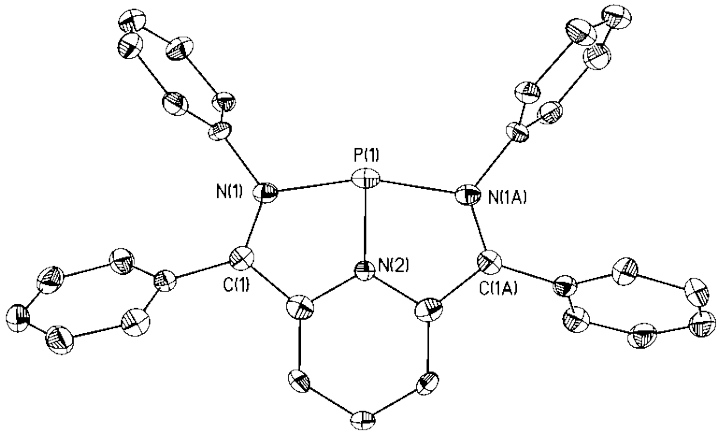
Scheme 5.3: Reaction of **5.1** with PBr_3 to produce **5.1P[Br]**.

5.2.2 X-ray Crystallography

The solid-state structures of **5.1P[I_3]**, **5.1P[$B_{12}Cl_{12}$]**, **5.1P[Br]** and **5.3P[I_3]** reveal a T-shaped phosphorus(I) cation consistent with two lone pairs and three bound nitrogen centres (AX_3E_2 electron pair configuration; Figure 5.4 and 5.5). The pyridine nitrogen occupies an equatorial site while the two imine nitrogen atoms reside in axial positions. For all four compounds, the anions are distant from the cationic P(I) centres. The N_{pyr}-P bond in **5.3P[I_3]** lies on a site of symmetry while in all the complexes of **5.1**, the two imine groups are asymmetrical. Previously reported computational data on the prosphorus diiminopyridine compound bearing hydrogen atoms on the α-carbon atom and nitrogen atoms indicate that the assymetrical structure is the minimum on the potential energy surface.[22] These observations are likely a phenomenon observed in the solid-state and gas-phase as in solution NMR spectroscopic studies, only one peak is observed for the diagnostic protons on the α-carbon indicating an equilibrium position.

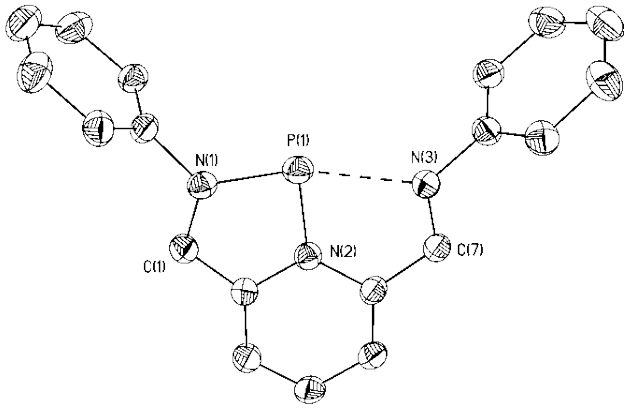


5.1P[I_3]

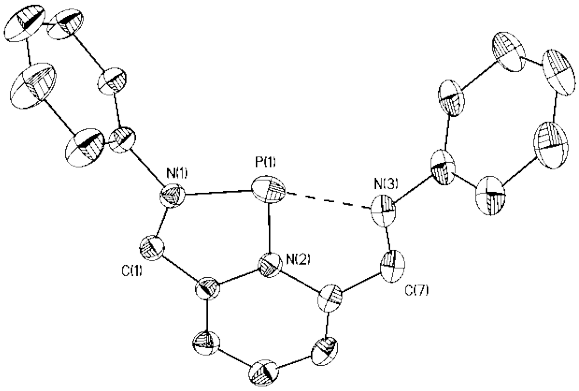


5.3P[I_3]

Figure 5.4: Solid-state structure of the cation in **5.1P[I_3]** and **5.3P[I_3]**. Thermal ellipsoids are drawn to the 50% probability level. Anion, hydrogen atoms, solvates and isopropyl groups are removed for clarity. For **5.3P[I_3]** only one assymetric unit is shown.



5.1P[$B_{12}Cl_{12}$]



5.1P[Br]

Figure 5.5: Solid-state structure of the cation in **5.1P[$B_{12}Cl_{12}$]** and **5.1P[Br]**. Thermal ellipsoids are drawn to the 50% probability level. Anion, hydrogen atoms, solvates and isopropyl groups are removed for clarity.

Table 5.1: Selected bond lengths (Å) for **5.1P[I_3]**, **5.3P[I_3]**, **5.1P[$B_{12}Cl_{12}$]** and **5.1P[Br]**.

	5.1P[I_3]	**5.3P[I_3]**	**5.1P[$B_{12}Cl_{12}$]**	**5.1P[Br]**
P(1)-N(1)	1.877(7)	1.934(6), 1.936(6)	1.808(2)	1.755(3)
P(1)-N(3)	1.975(8)	[a]	2.177(2)	2.318(3)
P(1)-N(2)	1.722(6)	1.722(8), 1.714(9)	1.730(2)	1.722(3)
C(1)-N(1)	1.303(11)	1.311(9), 1.333(10)	1.320(3)	1.327(5)
C(7)-N(3)	1.316(11)	[a]	1.284(3)	1.285(4)

[a] The cation lies on a site of symmetry with N(1) and C(1) being related to N(3) and C(7) by symmetry making the corresponding bond lengths equal.

Table 5.2: X-ray details of **5.1P[I_3]**, **5.3P[I_3]**, **5.1P[$B_{12}Cl_{12}$]** and **5.1P[Br]**.

Compound	**5.1P[I_3]**	**5.3P[I_3]**	**5.1P[$B_{12}Cl_{12}$]**	**5.1P[Br]**
Empirical formula	$C_{32}H_{40}Cl_3I_3N_3P$	$C_{43}H_{47}B_2I_3N_3P$	$C_{31}H_{39}B_6Cl_6N_3P$	$C_{32}H_{39}BrCl_2N_3P$
FW (g/mol)	984.69	1017.51	762.18	647.44
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2/c$	$C2/c$	$P2_1/c$
a (Å)	11.690(2)	24.522(2)	18.3065(6)	17.049(3)
b (Å)	12.287(2)	8.6258(8)	17.4020(6)	13.120(3)
c (Å)	13.601(2)	21.669(2)	25.0012(9)	17.259(4)
α (deg)	90	90	90	90
β (deg)	93.493(4)	113.291(2)	92.7560(10)	119.39(3)
γ (deg)	90	90	90	90
V (Å^3)	1950.0(5)	4210.0(7)	7955.4(5)	3363.6(12)
Z	2	4	8	4
D_c (mg m^{-3})	1.677	1.605	1.273	1.278
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073
temp (K)	150(2)	150(2)	150(2)	150(2)
$R1[I>2\sigma I]^a$	0.0500	0.0707	0.0416	0.0606
$wR2(F^2)^a$	0.1399	0.1703	0.0936	0.2018
GOF (S)^a	1.056	1.149	1.051	1.070

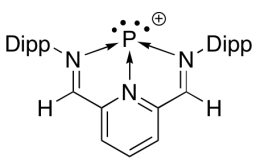
^{a} $R1(F[\mathrm{I} > 2(\mathrm{I})]) = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; $wR2(F^2$ [all data]) $= [w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) $= [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

5.3 Conclusion

In summary, **5.1P[I_3]**, **5.1P[$B_{12}Cl_{12}$]**, **5.1P[Br]** and **5.3P[I_3]** represent examples of uncommon P(I) salts.[23-25] The DIMPY complexes differ from the analogous 1,4-diza-1,3-butadiene (DAB) species as they do not undergo a charge transfer process with the ligand to produce P(III) heterocycles. These compounds represent the first isolated phosphorus DIMPY complexes, only the second example for a non-metal, made possible by utilizing the less common hydrogen and phenyl substituted ligands rather than the methyl derivative.

5.4 Experimental Section

5.1P[I_3]



[I_3]

A solution of **5.1** (0.150 g, 0.331 mmol) in CH_2Cl_2 (4 mL) was added to a solution of PI_3 (0.136 g, 0.331 mmol) in the same solvent (4 mL) in the dark. The solution was stirred for 20 minutes resulting a deep red solution. Normal pentane (8 mL) was added to precipitate red powder. The supernatant was discarded and the solids washed with Et_2O (3 X 5 mL) and dried *in vacuo*.

Yield: 0.231 g, 81%; d.p. 254-256 ^oC;

^1H NMR ($CDCl_3$, δ (ppm)) 9.34 (d, 2H, $^3J_{H-P}$ = 5.6 Hz), 9.01 (d, 2H, ^3J = 8.0 Hz), 8.30 (t, 1H, ^3J = 8.0 Hz), 7.43 (t, 2H, ^3J = 7.6 Hz), 7.30 (d, 4H, ^3J = 7.6 Hz), 2.49 (septet, 4H, ^3J = 6.8), 1.15 (overlapping doublets, 24H);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ (ppm)) 146.3, 142.4, 136.9 (d, $^2J_{C-P}$ = 10 Hz), 135.6, 131.1, 129.6, 128.2, 124.0, 28.9, 24.9;

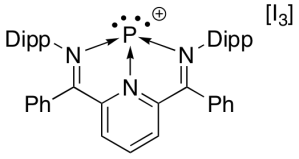
$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ (ppm)) 169;

FT-IR (cm^{-1} (ranked intensity)) 469(8), 736(5), 756(6), 778(12), 798(1), 1071(3), 1055(11), 1102(14), 1167(10), 1260(7), 1351(9), 1381(13), 1455(4), 2957(2), 2962(15);

FT-Raman (cm^{-1} (ranked intensity)) 87(10), 118(1), 479(13), 586(14), 710(8), 888(12), 1044(6), 1247(5), 1355(15), 1387(11), 1590(4), 2865(7), 2933(3), 2962(2), 3068(9);

ESI-MS: *m/z* 484 ([**5.1P**]$^+$).

5.3P[I_3]



A solution of **5.3** (0.150 g, 0.248 mmol) in CH_2Cl_2 (4 mL) was added to a solution of PI_3 (0.102 g, 0.248 mmol) in the same solvent (4 mL) in the dark. The solution was stirred for 20 minutes resulting a deep red solution. Normal pentane (8 mL) was added to precipitate a red powder. The supernatant was discarded and the solids washed with Et_2O (3 X 5 mL) and dried *in vacuo*.

Yield: 0.195 g, 77%; d.p. 323-324 ^oC;

^1H NMR ($CDCl_3$, δ (ppm)) 8.65 (d, 2H, ^3J = 8.0 Hz), 8.21 (t, 1H, ^3J = 8.0 Hz), 7.53-7.47 (mult, 10H), 7.17 (t, 2H, ^3J = 7.6 Hz), 2.55 (septet, 4H, ^3J = 6.8), 1.10 (d, 12H, ^3J = 6.4 Hz), 0.89 (d, 12H, ^3J = 6.8 Hz);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ (ppm)) 155.6, 143.2, 136.9 (d, $^2J_{C-P}$ = 9 Hz), 133.1, 131.4, 131.3, 131.0, 129.4, 129.3, 128.2, 124.1 28.9, 26.9, 23.1;

$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ (ppm)) 154;

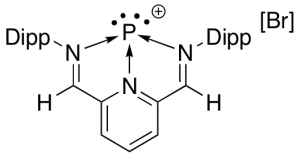
FT-IR (cm^{-1}(ranked intensity)) 700(5), 732(7), 766(9), 804(4), 1023(11), 1056(6), 1226(12), 1253(15), 1303(13), 1321(2), 1362(10), 1384(8), 1444(14), 1460(3), 2964(1);

FT-Raman (cm^{-1}(ranked intensity)) 117(1), 244(14), 402(13), 496(12), 1000(4), 1043(11), 1156(5), 1248(9), 1350(15), 1482(7), 1518(3), 1598(2), 2930(8), 2969(10), 3052(6);

ESI-MS: *m/z* 636 ([**5.3P**]$^+$).

Elemental analysis: Calc. for $C_{43}H_{47}N_3PI_3$ C 50.73, H 4.66, N 4.13; Found C 50.70, H 4.75, N, 4.06.

5.1P[Br]



In an NMR tube, neat PBr_3 (0.21 mL, 0.221 mmol) was added to a $CDCl_3$ (1 mL) solution of **5.1** (0.100 g, 0.221 mmol) and cyclohexene (0.134 mL, 1.33 mmol). The NMR tube was agitated and placed in an oil bath at 40°C for 3 days resulting in a deep red solution. To the mixture, CH_2Cl_2 (1 mL) and *n*-pentane (3 mL) were added sequentially and the solution stored at -30°C for an hour to produce orange crystals of **5.1P[Br]**.

Yield: 0.035g, 28%; d.p. 141-143 ^oC;

^{1}H NMR ($CDCl_3$, δ (ppm)) 9.87 (d, 2H, $^{3}J_{H-P}$ = 5.2 Hz), 9.57 (d, 2H, ^{3}J = 7.6 Hz), 8.27 (t, 1H, ^{3}J = 7.6 Hz), 7.41 (t, 2H, ^{3}J = 7.6 Hz), 7.28 (d, 4H, ^{3}J = 7.6 Hz), 2.36 (septet, 4H, ^{3}J = 6.8), 1.13 (br, 24H);

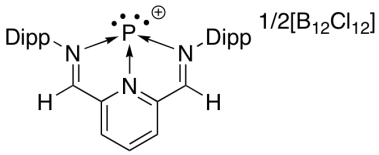
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ (ppm)) 147.8, 142.2, 136.9 (d, $^{2}J_{C-P}$ = 10 Hz), 135.5, 132.1, 129.4, 127.7, 123.8, 28.8, 24.6;

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ (ppm)) 166;

FT-IR (cm^{-1} (ranked intensity)) 471(15), 639(12), 723(2), 758(10), 804(6), 922(4), 1072(7), 1100(14), 1177(8), 1324(5), 1364(9), 1459(3), 1587(11), 2189(13), 2962(1).

ESI-MS: *m/z* 484 ([**5.1P**]$^{+}$).

5.1P[$B_{12}Cl_{12}$]



A slurry of $Na_2[B_{12}Cl_{12}]$ (0.213 g, 0.349 mmol) in CH_2Cl_2 (5 mL) was added to a solution of **5.1P[I_3]** (0.200 g, 0.231 mmol) in CH_2Cl_2 (5 mL) and stirred for 12 hours. The resulting slurry was centrifuged and *n*-pentane (8 mL) was added to the supernatant and the solution stored at -30°C over night. The supernatant was decanted and the resulting orange solids dried *in vacuo*.

Yield: 0.111 g, 65%; d.p. 196-197 ^{o}C;

^{1}H NMR (CD_2Cl_2, δ (ppm)) 9.29 (d, 2H, $^{3}J_{H-P}$ = 5.2 Hz), 9.40 (d, 2H, ^{3}J = 8.0 Hz), 8.30 (t, 1H, ^{3}J = 8.0 Hz), 7.45 (t, 2H, ^{3}J = 8.0 Hz), 7.33 (d, 4H, ^{3}J = 8.4 Hz), 2.41 (septet, 4H, ^{3}J = 6.8), 1.13 (overlapping doublets, 24H);

$^{11}B\{^{1}H\}$ (CD_2Cl_2, δ (ppm)) -12.7;

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, δ (ppm)) 149.6, 145.7, 140.1 (d, $^{2}J_{C-P}$ = 10 Hz), 138.7, 134.0, 132.9, 131.5, 127.2, 32.1, 27.8;

$^{31}P\{^{1}H\}$ (CD_2Cl_2, δ (ppm)) 169 ppm;

FT-IR (cm^{-1} (ranked intensity)); 534(2), 714(10), 757(7), 802(6), 1031(1), 1168(9), 1256(13), 1324(5), 1364(8), 1460(4), 1499(14), 1604(11), 2868(15), 2962(3), 3067(13);

FT-Raman (cm^{-1} (ranked intensity)) 112(3), 141(2), 163(1)*, 299(4), 472(8), 1044(13), 1177(14), 1244(7), 1323(15), 1442(10), 1636(12), 1505(6), 1589(5), 2932(9), 2965(11).

*Peak at 163(1) corresponds to I_2 impurity.

ESI-MS: *m/z* 484 ([**5.1P**]$^{+}$), 1038(**5.1P[$B_{12}Cl_{12}$]** – H).

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Chapter 6

Conclusions and Future Directions

6.1 Conclusions

This thesis described numerous reactions of chalcogen halides, chalcogen pseudohalides and phosphorus halides with a series of neutral nitrogen based donors. The donors utilized were the diazabutadiene (DAB), diiminopyridine (DIMPY), bisiminoacenaphthene (BIAN), pentamethyldiethylenetriamine (PMDETA) and pyridine ligands. The main group complexes isolated varied from neutral to cationic and dicationic.

6.1.1 Reactions of Nitrogen Based Ligands with Chalcogen Halides and Pseudohalides

The reactions of SCl_2 and an "$S(OTf)_2$" synthon with α-diimine ligands (BIAN, DAB), varying the substitution on the nitrogen and α-carbon atoms revealed that the groups on both positions are highly influential on the outcome of the reaction. The reaction of "$S(OTf)_2$" with a DAB ligand bearing alkyl groups on the nitrogen atoms and hydrogen atoms on the α-carbon atoms resulted in the loss of one of the alkyl groups on a nitrogen atom to produce 1,2,5-thiadiazolium salts. If alkyl or aryl groups were present on N and methyl groups on the α-carbon, the reaction with SCl_2 proceeded through the eneamine tautomer of the ligand yielding *N,C*-bound neutral SNC_3 heterocycles by the elimination of HCl. The reaction between "$S(OTf)_2$" and a ligand featuring aryl substituents on nitrogen and hydrogen atoms, phenyl groups or acenaphthene on the backbone carbon atoms produced a series of *N,N'*-chelated sulfur(II) dications. The dicationic species represent the first dicationic structural mimics of the ubiquitous N-Heterocyclic carbene for sulfur and the first sulfur(II) dications. In general, the reactivity of SCl_2 and $S(OTf)_2$ with DAB and BIAN ligands proved to be different than that of the other non-metallic elements.

The reactions of chalcogen halides with the diiminopyridine ligands were also examined in detail. The substitution on nitrogen was constant with diisopropylphenyl groups in all cases and variable at the α-carbon with hydrogen, methyl or phenyl groups. The DIMPY ligands differ from the DAB and BIAN ligands as they have a pyridine moiety between the two imine groups and form tridentate chelates. The reaction of a methyl substituted DIMPY ligand and $TeBr_4$ formed an *N,N',C*-bound $TeBr_3$ complex which agreed with the literature report of the analogous transformation with $TeCl_4$. The corresponding reaction with $SeCl_2$ also produced an *N,N'C*-bound chalcogen centre but the bonding differed as an exocyclic amine was produced in contrast to the Te species having an exocyclic imine. The selenium dihalides reacted with -H and -Ph substituted DIMPY derivatives to produce square planar SeX^+ cations sequestered within the DIMPY cavity. The anions were shown to vary, but in all cases produced complex selenium halide dianions. Stirring SCl_2 with the phenyl substituted ligand produced an *N,N',N''*-chelated sulfur(II) dication with two chloride anions whereas no reaction occurred between SCl_2 and the hydrogen derivative. In many cases, indiscernible mixtures were obtained presumably from the release of halide.

Reactions of "$Ch(OTf)_2$" synthons with the hydrogen substituted DIMPY ligand produced the homologous series of *N,N',N''*-chelated chalcogen(II) dications. These species displayed remarkable stability, a surprising feature for donor stabilized main group polycations. A comparison of these results with the DAB chemistry indicate that the DIMPY ligands are stronger donors given the stability of the dications, and the ability to displace a halide in reactions involving the selenium dihalides. Collectively these species represent the first *N,N',N''*-chelated chalcogen DIMPY complexes, a ligand that has extensive chemistry reported for the transition metal elements.

The isolation of sulfur(II) dications was not restricted to chelating imine ligands and was extended to a multidentate amine ligand. Pentamethyldiethylenetriamine (PMDETA) was shown to form a tridentate chelated sulfur(II) dication in a reaction with "$S(OTf)_2$". The geometry and electron configuration of the molecule was analogous to the DIMPY derivatives. A striking difference was significantly lengthened sulfur nitrogen bond lengths for the PMDETA derivative indicating a weaker interaction between the ligand

and the dicationic centre. These weak interactions indicate that this species should be a good reagent for the delivery of S^{2+}.

After synthesizing these new molecules that feature novel bonding motifs, the goal was to utilize such species in small molecule activation reactions. In the past, these types of transformations have been restricted to transition metals. Unfortunately, the DAB, BIAN, DIMPY and PMDETA complexes did not display reactivity with substrates. Sulfur(II) dications stabilized by monodentate pyridine ligands were prepared and reacted with carbon-carbon and carbon-nitrogen double bonds *via* insertion into the sulfur pyridine bond. The substitution on the *para* position of the pyridine ligand could be altered with electron donating (NMe_2), electron withdrawing (CF_3) or neutral (Ph) groups which proved to be very influential on the reactivity. The stronger donating pyridine (NMe_2) prevented reaction from occurring while the weaker donor ligand (CF_3) decreased the reaction time in comparison with the phenyl substituted derivative. This result indicating the reactivity can be tuned. These transformations represent the first examples of small molecule activation by main group polycations.

6.1.2 Reactions of Diiminopyridine Ligands with Phosphorus Halides

Despite several reports of phosphorus DAB chemistry, a phosphorus DIMPY complex was absent in the literature. Examining reactions of PI_3 with hydrogen, methyl and phenyl substituted DIMPY ligands it was revealed that only the hydrogen and phenyl derivatives yielded phosphorus DIMPY complexes while the more popular methyl derivative produced multiple products. Extrapolating the results from the chalcogen chemistry rationalize that uncontrollable reactivity occurs with the eneamine tautomer that is easily avoided with the -H and -Ph ligands. The complexes are rare reports of P(I) complexes and the first of such featuring a tridentate ligand.

6.1.3 Summary

Collectively the observations of the diazabutadiene, bisiminoacenaphthene and diiminopyridine chemistry with phosphorus and the group 16 elements draws conclusions that the reactivity of these ligands is not always as predicted through nitrogen chelation. Methyl groups on the α-carbon have a tendency to react through the eneamine tautomer

which in some cases can be controlled to give *N,C*-bound heterocycles. Alkyl groups on nitrogen are susceptible to being lost in the course of the transformation while aryl groups on nitrogen proved to be innocent. The presence of hydrogen and phenyl groups on the backbone carbon atom and aryl groups on N allowed the synthesis of the desirable chelated main group centres. Preliminary studies indicate amines can also chelate dicationic chalcogen centres. Although these observations are all derived from results of the p-block elements, they will undoubtedly give insight to the reactivity with transition metals complexes that are very important in an array of catalytic reactions.

6.2 Future Directions

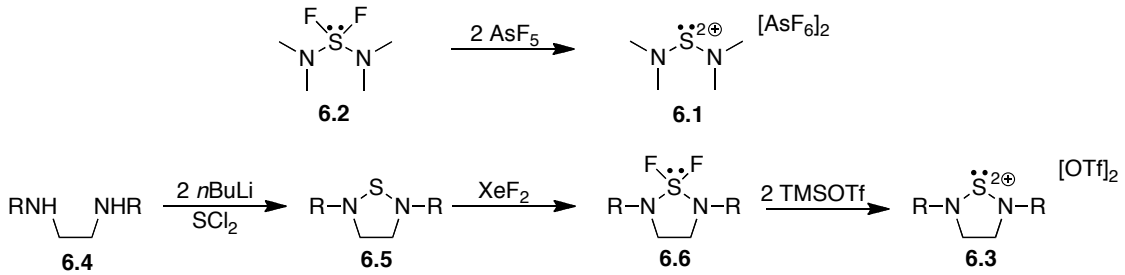
6.2.1 Group 16 amide complexes

Although significant progress was made in the area of phosphorus and chalcogen chemistry with nitrogen based ligands, there remains a great deal of unknown chemistry in this realm. All of the reported examples were with neutral donors. The dative linkages between the main group element and ligand may not be the best approach towards accessing derivatives capable of small molecule activation as the main group centre can be easily displaced from the ligand. Efforts toward synthesizing chalcogen reagents with covalent linkages to the ligand deserve attention given the fact that the NHC, NHSi and NHP, all of which possess covalent bonds to the ligand have proven to be effective in this regard.[1-3]

Cowley *et al.* reported the isolation of a sulfenium dication (**6.1**) in 1979 but a solid-state structure was not reported and the molecule was not fully characterized.[4] This species would have an empty p-orbital and a lone pair on sulfur meaning it would be isolelectronic to the NHSi and NHP. The synthesis outlined in the communication is feasible (Scheme 6.1); the compound is prepared by a halide abstraction from the neutral sulfur difluoride starting material (**6.2**) with arsenic pentafluoride. Other fluoride abstracting agents such as TMSOTf and BF_3 could be used to simplify the preparation. This molecule should be structurally characterized and its chemistry examined in detail.

In addition to the acyclic derivative (**6.1**), the cyclic species (**6.3**) would also be of interest as the molecules would have different properties and reactivities. An expedient synthesis consists of synthesizing the neutral SN_2C_2 heterocyclic precursor (**6.5**) by

deprotonation of a saturated DAB ligand (**6.4**) and reaction of the dilithiated salt with SCl_2. Fluorination of the sulfur centre with xenon difluoride would produce the sulfur(IV) species (**6.6**) and subsequent halide abstraction with TMSOTf to yield the cyclic sulfenium dication.



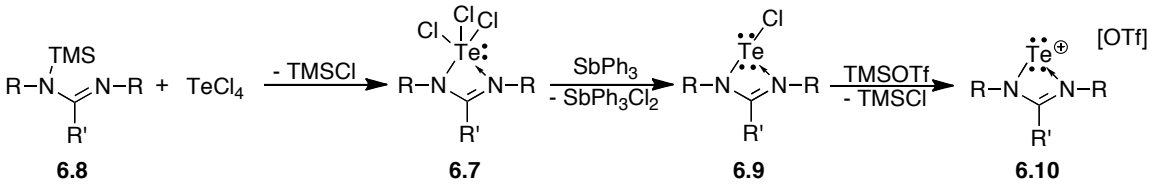
Scheme 6.1: Proposed synthesis of the acyclic (**6.2**) and cyclic sulfenium dications (**6.6**).

Monoanionic chelating ligands have also shown the ability to sequester reactive element centres, however there are minimal reports in the literature for group 15 and 16.[5,6] Richards *et al.* reported the reactions of chalcogen tetrahalides with *β*-diketiminate ligands featuring methyl groups on the framework which ultimately led to uncontrollable reactions with the eneamine tautomer.[7,8] From the observations with DAB and DIMPY ligands, methyl groups should be avoided for such chemistry.[9,10]

The *β*-diketiminate chalcogen complexes should be attainable by making the appropriate modifications to the ligand but more interesting derivatives would be the amidinate group 16 species (**6.7**). The four membered ring would impose strain on the system rendering the molecules more reactive than the six membered species derived from the *β*-diketiminate ligands. A singular example in the literature has been reported with regards to group 16 amidinate chemistry.[11] The reaction of $TeCl_4$ with a TMS-amidinate (**6.8**) ligand eliminated TMSCl to produce the chelated tellurium(IV) complex (**6.7**; Scheme 6.2). No further studies have been performed on this complex.

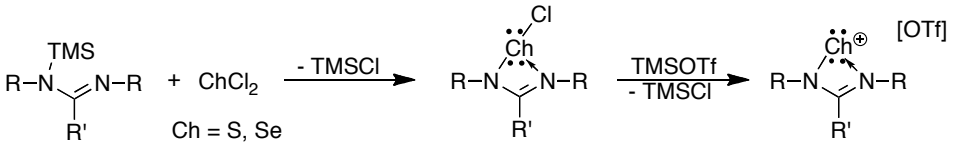
As indicated in the other reports of group 16 chemistry with nitrogen based ligands, the chalcogen(IV) halides are prone to releasing dihalogen usually interfering in future reactions.[7,12] Keeping this in mind, the chalcogen(II) reagents do not have such susceptibility and would be better targets for this chemistry. The tellurium(II) derivative (**6.9**) could be prepared by the facile reduction of the known Te(IV) complex (**6.7**) with

$SbPh_3$. The synthesis of the sulfur(II) and selenium(II) systems (**6.11**) could be achieved by the same synthetic route as the Te(IV) complex simply utilizing $SeCl_2$ and SCl_2 as the chalcogen sources (Scheme 6.3). The corresponding cationic species (**6.10**, **6.12**) could be prepared by halide abstraction. Through the synthesis of these covalently bound chalcogen cations, the achievement of obtaining reagents capable of activating numerous small molecules is certainly possible.



6.8 **6.7** **6.9** **6.10**

Scheme 6.2: Synthesis of the known Te(IV) amidinate complex (**6.7**) and the proposed synthetic route to the Te(II) cationic species (**6.10**).

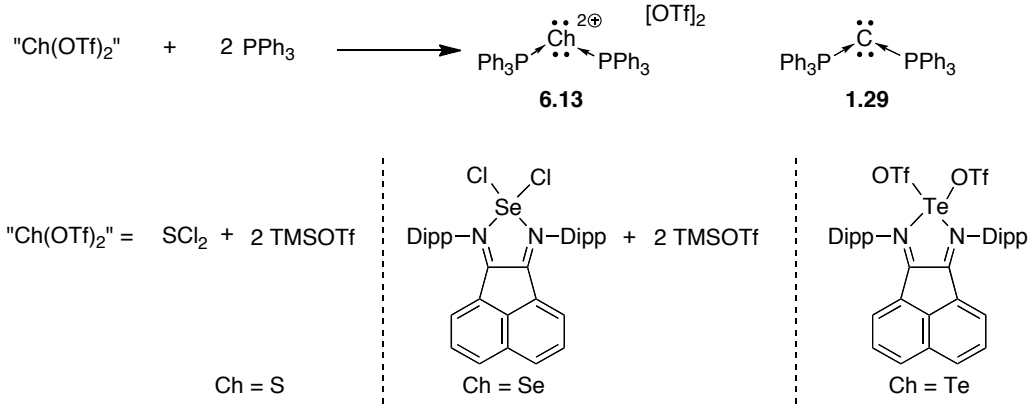


6.8 **6.11** **6.12**

Scheme 6.3: Proposed synthesis of the sulfur and selenium amidinate complexes.

6.2.2 Utilizing "$ChOTf_2$" Synthons to Generate New Bonding Arrangements

We have demonstrated the ability to utilize a series of "$ChOTf_2$" synthons to deliver chalcogen(II) centres to ligand frameworks.[13-17] These reagents should be useful in a number of other transformations to access new chalcogen based molecules which otherwise could not be synthesized. Sources of chalcogens, as the elemental form or the halides have the propensity to react with phosphines to oxidize the phosphorus atom giving the thermodynamically favourable phosphine chalcogenides (R_3PCh).[12] Previous attempts to synthesize phosphine sequestered chalcogen dications have led to decomposition products primarily consisting of the oxidized phosphorus product. However, with the "$ChOTf_2$" synthons, the phosphine sequestered dications (**6.13**) will be accessible (Scheme 6.4). These complexes are of interest as they are analogues to the carbodiphosphorane (**1.29**); a molecule that has been known for five decades.[18,19]



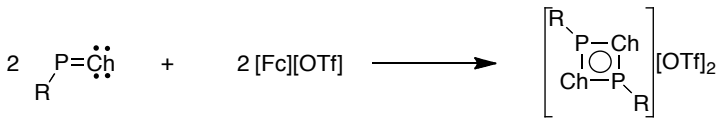
Scheme 6.4: The synthesis of the phosphine sequestered chalcogen dications utilizing "$Ch(OTf)_2$" synthons.

Another series of molecules that have proven to be difficult to isolate have been the chalcogenophosphanes (**6.14**; Ch = S, Se, Te). The sulfur derivative (thiophosphane) has long been sought but only isolated by incorporating donating substituents to form ylide structures or by incorporating the moiety into the coordination sphere of transition metal centres.[20-23] Reports have shown that the tri-*tert*-butylphenyl thiophosphane can be prepared, but trimerizes and disproportionates.[24] To kinetically stabilize the species, extremely bulky groups are needed such as the terphenyl group (terphenyl = 2,6-bis[(2,6-diisopropyl)phenyl]phenyl).[25] By utilizing Ch^{2+} synthons, a direct reaction with the dilithiated terphenyl phosphine (**6.15**) should yield a series of monomeric chalcogenophosphanes. The nature of the bonding and reactivity of these molecules should be very interesting.

Scheme 6.5: Proposed synthesis of the chalcogenophosphanes utilizing "$Ch(OTf)_2$" reagents; R = terphenyl = 2,6-bis[(2,6-diisopropyl)phenyl]phenyl).

An interesting molecule derived from the chalcogenophosphanes would be the one-electron oxidation product with ferrocenium triflate (Scheme 6.6). This could lead to a

radical species that would undergo dimerization to form dicationic heteroatom analogues of cyclobutadienide (**6.16**).



6.14 [Fc] = ferrocenium **6.16**

Scheme 6.6: Oxidation of the chalcogenophosphanes (**6.14**) to yield the heterocycle (**6.16**).

6.3 Final Remarks

In summary, the molecules prepared in this dissertation have expanded on the understanding of the chemistry of nitrogen based ligands with the pnictogens and chalcogens. These discoveries should be applicable to many other elements spanning the periodic table. Preliminary reports show the monodentate pyridine sequestered sulfur(II) dications are reactive towards unsaturated organic substrates. An in depth study of the scope of this reaction would be beneficial to explore its utility in organic synthesis. In addition the proposed molecules in this chapter should also have promise in such studies. The results from the project will without a doubt branch into many new journeys in main group chemistry. By continuing these studies, phosphorus and chalcogen reagents having the capabilities of transition metals should be attainable.

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Appendix 1
General Experimental Details

All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Labmaster dp glove box or using standard Schlenk techniques.

Sulfur dichloride,[1] $SeCl_2$BIAN,[2] $Te(OTf)_2$BIAN,[3] DAB,[4-6] BIAN[7,8] and DIMPY[9-11] were synthesized using literature procedures. The DAB ligand **2.10** was made by the method described by Gibson substituting aniline as the amine.[12] Selenium dichloride and $SeBr_2$ were prepared as THF solutions following the literature procedures and used within minutes of preparation.[13,14] Trimethylsilyltrifluoromethanesulfonate, 4-dimethylaminopyridine, 4-trifluoromethylpyridine, *N,N'*-diisopropylcarbodiimide, $SeCl_4$, $SeBr_4$, $TeCl_4$ and $TeBr_4$ were purchased from Alfa Aesar and used as received. Phosphorus triiodide was obtained from Sigma Aldrich and used as obtained. The reagents PCl_3, PBr_3 and PMDETA were purchased from Alfa Aesar and distilled prior to use. Ethylene was obtained from PRAXAIR Specialty Gases and Equipment and 4-phenylpyridine from Fisher Scientific. Dichloromethane, CH_3CN, *n*-pentane, *n*-hexane, THF and Et_2O were obtained from Caledon Laboratories and dried using an MBraun Controlled Atmospheres Solvent Purification System. Acetone and THF were used as received from Caledon. The dried solvents were stored in Strauss flasks under an N_2 atmosphere, or over 4 Å molecular sieves in the glove box. Solvents used for ^{1}H NMR spectroscopy [CD_2Cl_2, $CDCl_3$, CD_3CN and $(CD_3)_2CO$] were purchased from Sigma-Aldrich, and dried by storing in the glove box over 4 Å molecular sieves.

Multinuclear NMR data are listed in ppm, relative to Me_4Si (^{13}C and ^{1}H) and $CFCl_3$ (^{19}F), coupling constants are in Hertz and all NMR spectra were recorded on an INOVA 400 MHz (^{1}H = 399.76 MHz, ^{13}C = 100.52 MHz, ^{19}F = 376.15 MHz, ^{125}Te = 126.12 MHz) spectrometer or INOVA 600 MHz spectrometer. All ^{31}P chemical shifts were externally referenced to 85% H_3PO_4 (δ = 0.00 ppm) and ^{19}F NMR spectra were referenced to $CFCl_3$ (δ = 0.00 ppm) using neat $CF_3(C_6H_5)$ (δ = -63.9 ppm) as an external reference standard. Boron-11 experiments were referenced externally to BF_3-Et_2O (δ = 0.00 ppm). The ^{125}Te{^{1}H} spectra were externally referenced to $TeMe_2$ (δ = 0.00 ppm using H_6TeO_6 δ = 712 ppm). Single crystal X-ray diffraction data were collected on a Nonius Kappa-CCD

area detector or a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under N-paratone oil, mounted on nylon loops or MiTeGen micromounts then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL.

Samples for FT-Raman spectroscopy were packed in capillary tubes and flame-sealed. Data were collected using a Bruker RFS 100/S spectrometer, with a resolution of 4 cm^{-1}. FT-IR spectra were collected on samples as KBr pellets using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm^{-1}. Decomposition points were recorded in flame-sealed capillary tubes using a Gallenkamp Variable Heater. Elemental analyses were performed by Columbia Analytical Services in Tucson, AZ; Laboratoire d'analyse élémentaire at Université de Montréal or Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

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