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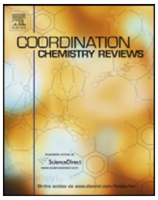

Review

Recent developments in the synthesis and isolation of p-block centered polycations

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Contents

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ABSTRACT

The rapidly expanding area of main group atom centered polycations is reviewed. For groups 13, 14, 15 and low-oxidation state group 16 dications, the critical feature is the use of neutral ligands to complete the coordination sphere of the otherwise highly electron deficient polycations. The focus of this review is on compounds where the polycationic charge can be localized onto a central p-block element, and materials that can be isolated in the condensed phase and structurally characterized, rather than on fleeting species that may be observed in the gas phase.

1. Introduction

Recent years have seen many significant advances in fundamental main group chemistry. These include the development of the frustrated Lewis pair by Stephan [1], p-block molecular allotropy led by the groups of Bertrand and coworkers [2–4], Kira and coworkers [5], Robinson and coworkers [6,7], and Jones and coworkers [8], the use of weakly coordinating anions to isolate highly reactive cations (Krossing and coworker [9] and Reed [10]), an on-going interest in low-oxidation state compounds and complexes featuring multiple bonds between heavy p-block elements [11–16]. The driving force for these investigations is the development of new structure, bonding and reactivity, which ideally allows for the discovery of previously unknown transformations and/or materials. Of special interest is the activation of simple, relatively unreactive substrates such as H_2 and CO_2 using inexpensive, transition metal free compounds. The reversible addition of H_2 to a frustrated Lewis pair is a representative example, with implications in hydrogen storage technology and metal-free catalytic hydrogenation, which are considered to be important problems [17]. Another area within main group chemistry that has seen a recent expansion of interest is the synthesis and isolation of polycationic p-block compounds, with a charge of +2 or greater that can be localized onto a central atom, the chemistry of which will be reviewed here.

2. p-Block polycations

The overriding principle one must consider when working in p-block chemistry is the preference of a closed shell configuration for the valence orbitals for all of the atoms in a molecule. For the p-block, this totals eight electrons (s^2p^6), and is known as

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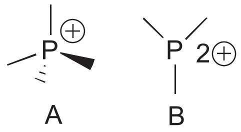


Fig. 1. A generic phosphonium cation (A) and hypothetical phosphorus(V) dication (B).

the octet rule. Elements from the 3rd row and below can accommodate more electrons (hypervalency) owing to the availability of d-orbitals, however, eight is considered the minimum number. The electrons can be in the form of "bonding pairs", shared by adjacent atoms or "lone pairs", localized on a single atom. Many exceptions to the octet rule have been identified, but these species are generally highly reactive (*e.g.* $InMe_3$), radical, or require electronic (*e.g.* BF_3, $[Ar_3Si]^+$) and/or steric (*e.g.* $Ar_2Ge:$) stabilization to render them isolable. Often atom centers represented as lacking an octet do actually attain eight electrons in their valence shells, for example the *tert*-butyl cation is stabilized by electron donation into the empty p-orbital on the central from the σ bonds on the neighboring C–H bonds (hyperconjugation) [18]. Violations of the octet rule are prevalent as reactive intermediates (*e.g.* carbocations), and an area of great interest is isolating these intermediates as relatively stable species to allow for more systematic studies of their reactivity.

p-Block compounds carrying a polycationic charge are more rare than monocationic compounds as they are intrinsically more electron deficient, and therefore will be less able to attain a closed shell s^2p^6 electron configuration for all of their atoms. A representative example is shown in Fig. 1, depicting a general P(V) cation with eight valence electrons (A) and a P(V) dication carrying six valence electrons (B). The former case is the extremely common family of phosphonium cations, however, not a single isolated example of a six-electron P(V) dication is known. The as yet unrealized potential for high reactivity in compounds carrying a dicationic or greater charge gives motivation for the study of these compounds.

3. Neutral ligands in the stabilization of polycationic p-block species

The method of choice to isolate p-block polycations is the use of neutral ligands to coordinate the central element, filling the valence shell and delocalizing the positive charge to peripheral atoms. Compounds of this type may be viewed from two different extremes in their bonding models, here defined as the "covalent" or "dative" model. In the covalent model strict Lewis rules are applied, with all bonds drawn as a line representing the sharing of two electrons between atoms, and formal charges inserted as required. In the dative model a neutral ligand (Lewis base) uses its lone pair of electrons to form a bond with an electron deficient central atom containing a vacant orbital (Lewis acid). This donation of electrons is represented by an arrow from the Lewis base to the Lewis acid. Fig. 2 illustrates a general group 14 dication (+2 oxidation state) in both extreme representations.

While these are simply different ways of representing compounds on paper, dative bonds often carry real physical differences when compared with normal covalent bonds. Generally, dative bonds are weaker than standard covalent bonds, and susceptible to ligand exchange reactions if a stronger Lewis base is introduced. The key difference is the minimum energy pathway for bond cleavage; for a covalent bond the cleavage is homolytic, with both fragments taking one electron, giving a pair of radical species, a high-energy process as radicals in these type of examples are considered unstable. Conversely, for a dative bond the bond rupture is heterolytic, with the Lewis base taking both electrons. These concepts are discussed in a detailed review by Haaland [19] but are most concisely stated in the definition of a "dative" or "coordinative covalent" bond accepted by IUPAC: [20].

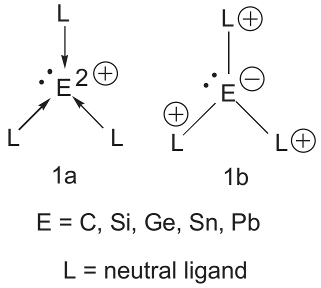


Fig. 2. Extremes in bonding representations for generic group 14 dication 1. Representation 1a is the "dative" model, and 1b is a standard Lewis model.

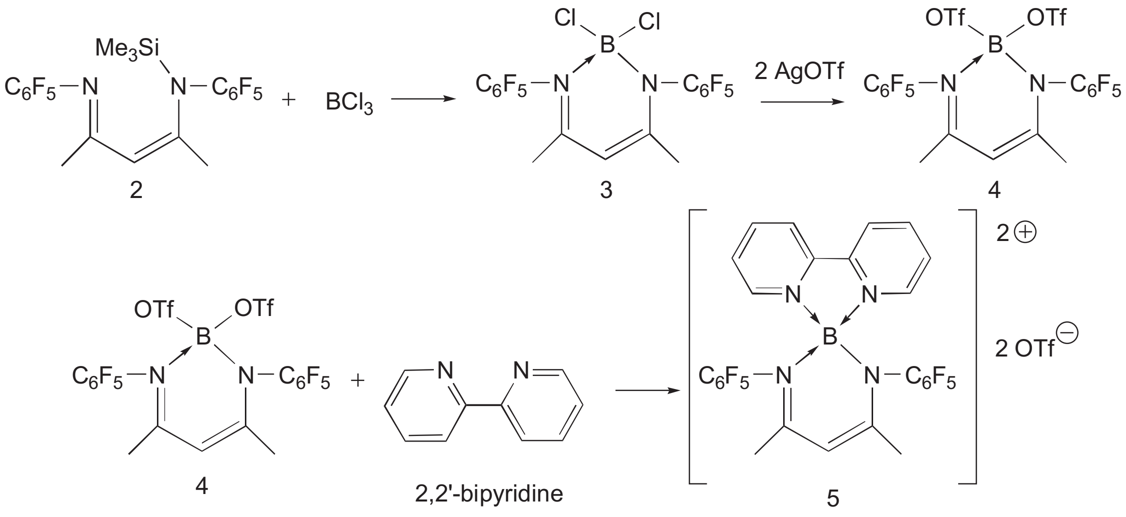
"The coordination bond formed upon interaction between molecular species, one of which serves as a donor and the other as an acceptor of the electron pair to be shared in the complex formed, *e.g.* the NB bond in H_3NBH_3. In spite of the analogy of dative bonds with covalent bonds, in that both types imply sharing a common electron pair between two vicinal atoms, the former are distinguished by their significant polarity, lesser strength, and greater length. The distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or in inert solvent follows the heterolytic bond cleavage path."

In most cases the real bonding description is somewhere in between the two extremes, with the charge delocalized over the entire molecule in line with molecular orbital theory. Calculations of residual charge for these systems typically find the charge evenly shared between the central Lewis acidic element, and the Lewis basic atoms of the ligands. In this review the dative bonding model will be used primarily, but it is important to bear in mind the complexities of chemical bonding, and a complete bonding description nearly always requires quantum chemical studies.

4. Group 13 di- and trications

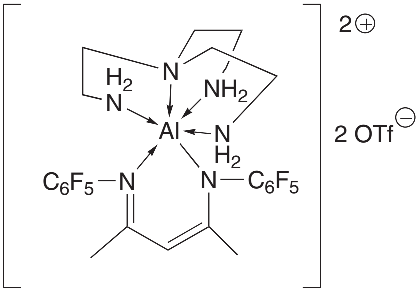
Boron polycations are of interest due to the well-established Lewis acidic chemistry of boranes (R_3B). Cationic derivatives of borane, where one of the anionic R groups has been removed, or replaced by a neutral ligand enhanced Lewis acidity on the boron center [21]. Despite being a clear target, with easily accessible starting materials (*i.e.* $RBCl_2$, BCl_3) the first structurally characterized boron dication was not reported until 2007 by Cowley and coworkers, utilizing a highly versatile β-diketiminate ligand [22]. The synthesis (Scheme 1) relied on a trimethylsilyl derivative of the ligand (**2**) as a mild methathesis reagent for the introduction of the boron center (**3**). This was followed by halide abstraction using AgOTf to generate a bistriflate boron species (**4**). The B–O bonds were found to be slightly longer than typical B–O single bonds, and dissolution in polar solvents such as MeCN resulted in the displacement of a single triflate, and the generation of a boron monocation. Addition of the bidentante 2,2′-bipyridine (bipy) ligand resulted in displacement of both triflates, giving boron centered dication **5**. The charge on the boron atom was calculated to be +1.3, with the remainder of the positive charge dispersed onto the bipyridine. Calculations on the structure of the dication without the supporting bipy ligand showed that an F atom from the flanking $-C_6F_5$ groups on the β-diketiminate would enter into a bridging conformation with the boron center.

A similar strategy was used to synthesize a β-diketiminate supported aluminum dication (**6**), with the exception that tetradentate tris(2-aminoethyl)amine ligand was used to displace the triflates [23]. Attempted use of bipy in this case gave an octahedral aluminum complex with the triflate anions remaining bound, due to



Scheme 1. Synthetic route to boron centered dication 5.

aluminum's ability to accommodate six bonds, in contrast with the lighter element boron, which can only accommodate a maximum of four substituents.



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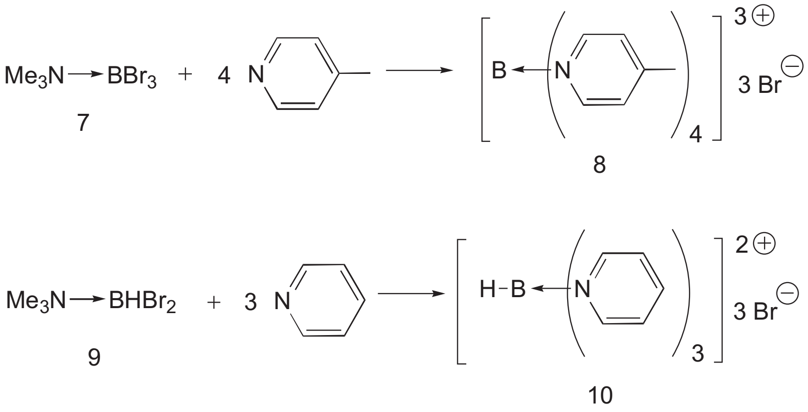
Vargas-baca and Cowley structurally characterized a series of boron centered di- and trications which had been synthesized in the 1960s and 1970s [24]. Either four pyridines (trications) or three neutral pyridine ligands and 1 hydride (dications) bind to the boron in a tetrahedral arrangement. The synthesis of the trications involves the reaction of an excess of 4-methylpyridine with an amine-BBr_3 complex (**7**), with displacement of the amine and all three bromides giving **8** (Schemes 2 and 3). The displacement of the bromine atoms relies on the well-known phenomenon of heavy halide displacement from boron; heavier halides form much weaker bonds to boron than fluorine, and are easily replaced by certain ligands [25]. The starting material for the dication **10** is an amine–$BHBr_2$ complex (**9**), the strongly Lewis basic hydride is not displaced by the pyridine ligands. The corresponding $(Me_3P)_3$–BH dication is also known, generated from $BHBr_2{\cdot}SMe_2$ and an excess of Me_3P [26]. This family of compounds is stable under an ambient atmosphere, and can be crystallized in the presence of H_2O.

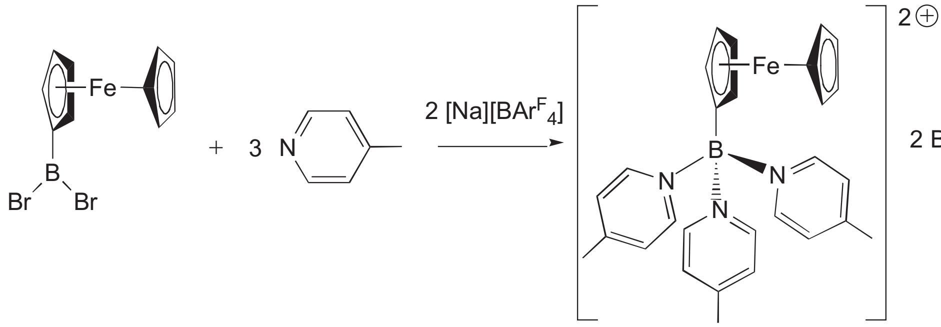
Braunschweig et al. also used heavy halide displacement from boron to generate boron dications appended to a ferrocene moiety, in this case the presence of metathesis reagent $[Na][BAr^F]$ gave the dication paired with the weakly coordinating $[BAr^F]^-$ anion [27]. The dicationic charge was found to increase the oxidation potential of the ferrocene fragment, as compared with monocationic and neutral derivatives.

5. Group 14 dications

The recent study of polycations from group 14 has focused on Ge(II). The reaction of $GeCl_2$·dioxane with the N-heterocyclic carbene (NHC) $^iPr_2IM$ gives coordination complex **12** (Scheme 4). Metathesis of the chlorine atoms with TMS-I to introduce the more labile iodine (**13**), followed by addition of an excess of $^iPr_2IM$ resulted in displacement of the iodine atoms to give germanium(II) centered dication **14** [28]. The charge on the germanium atom was calculated using three different methods, which gave results between +0.05 and +1.02, all significantly lower than the +2 formal charge in the dative representation, with the NHC ligands bearing the remainder of the charge. The use of three different methods



Scheme 2. Halide displacement from bromoboranes giving boron centered di- and trications.



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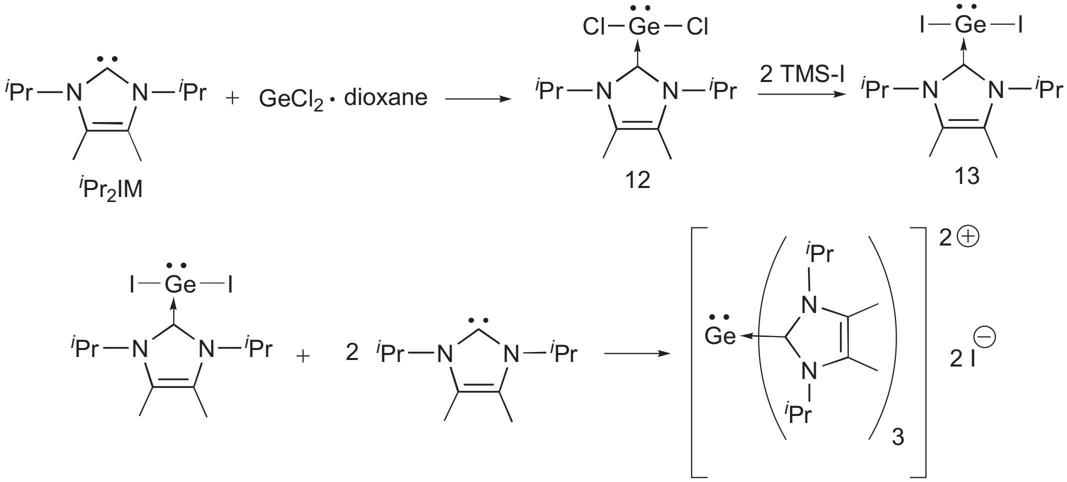
Scheme 3. Synthesis of ferrocene appended boron dication 11.



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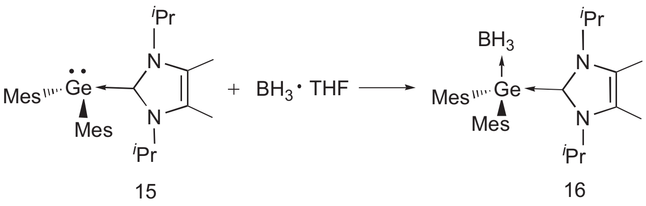
Scheme 4. Synthetic route to an N-heterocyclic carbene stabilized Ge(II) dication 14.

giving quite different values is an important consideration; often the results from only one theoretical method is presented by the authors of a given study, which may skew any conclusions drawn.

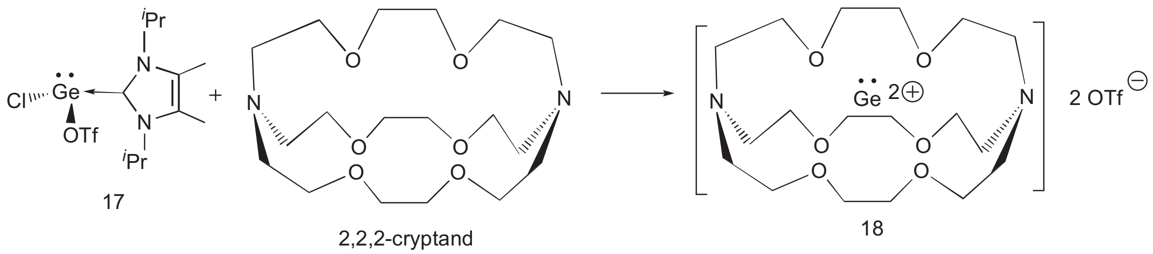
Computational analysis demonstrated the HOMO of the dication to be the lone pair of electrons on the germanium center, thus $[R_3Ge:]^{2+}$ can be considered a dicationic group 14 analogue of a phosphine ($R_3P:$). A related neutral Ge(II) species (**15**) was demonstrated to act as a Lewis base towards BH_3 using the lone pair of electrons about the germanium atom forming adduct **16** (Scheme 5) [29].

The addition of the macrocycle 2,2,2-cryptand to the NHC supported electrophilic Ge(II) reagent **17** resulted in complete liberation of all the substituents about germanium (Scheme 6) [30]. This "naked" Ge(II) dication encased within the cryptand (**18**) is a novel type of p-block compound reminiscent of macrocyclic enclosed metal cations obtained in s-block chemistry. Compound **18** is of particular interest because there are no two-center-two-electron bonds between the cryptand ligand and the germanium atom; the Ge–O and Ge–N Wiberg bond orders were found to be 0.10 and 0.11, respectively. The residual charge on the germanium atom was calculated to be remarkably high (+1.38), indicating minimal charge transfer to the cryptand, therefore **18** is best described as a Ge^{2+} ion, protected by residing in the cryptand. The driving force for the formation of **18**, involving cleavage of the bond between germanium and a strongly Lewis basic NHC was proposed to be the high lattice energy of the dication, which was completely insoluble to the reaction solvent (THF), although the lattice energy was not quantified. The encased germanium atom was found to be chemically accessible, as addition of anionic fragments (*i.e.* $[O^tBu]^-$) to **18** resulted in liberation of the dicationic germanium, giving known Ge(II) complexes.

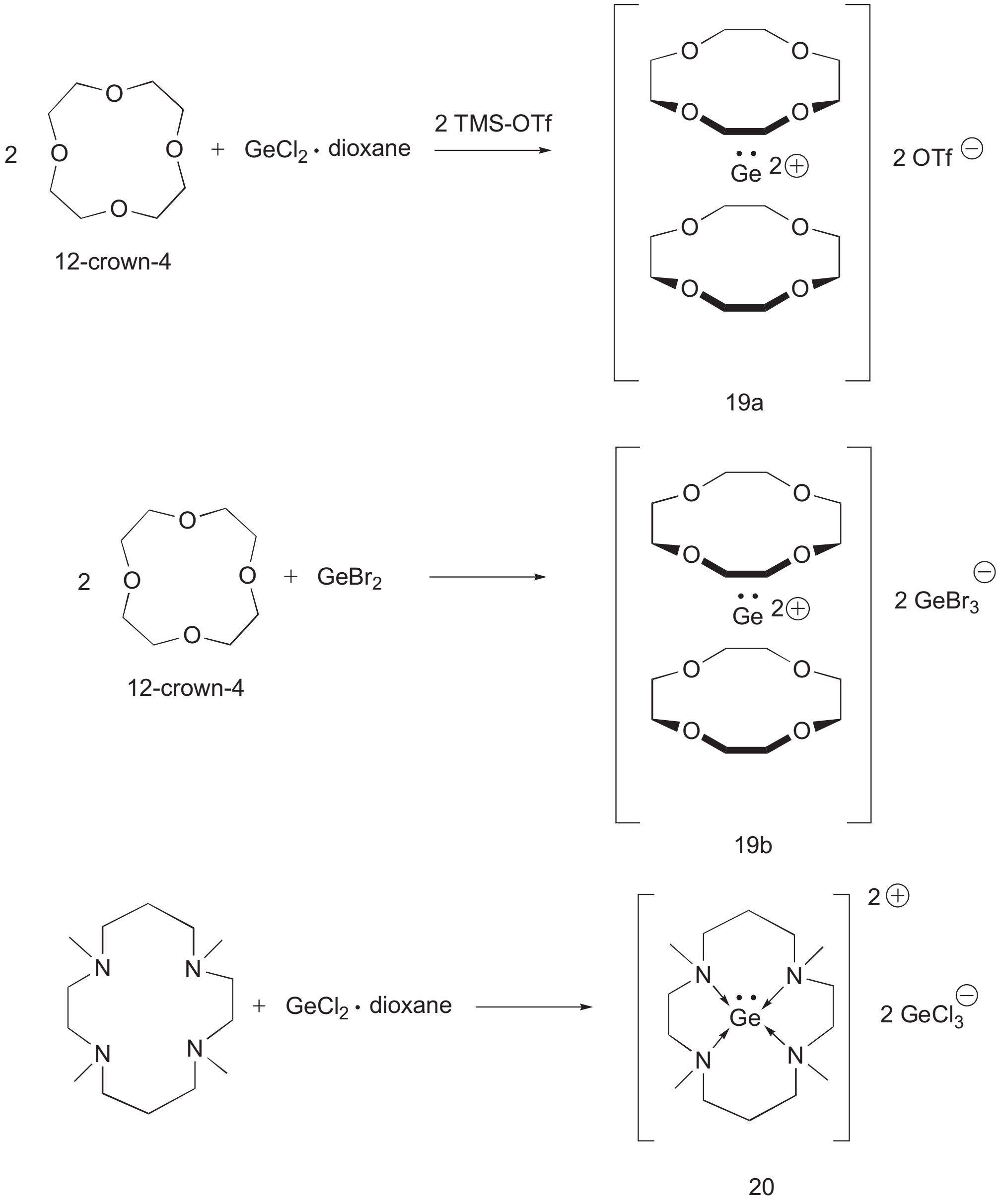


Scheme 5. Coordination of BH_3 by germanium phosphine analogue 15.

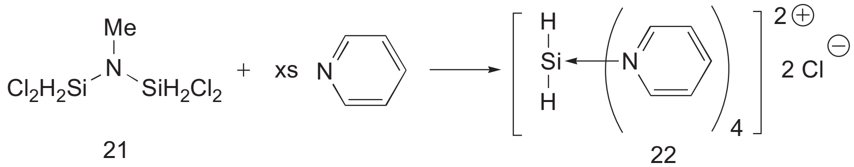
Subsequently it was reported that the addition of the macrocyclic ether 12-crown-4 to $GeCl_2$·dioxane in the presence of a halide abstraction reagent (TMS–OTf) gave a Ge(II) dication sandwiched between two crown ether ligands (**19a**, Scheme 7) [31]. Simultaneously, Reid and coworkers reported that the reaction of 12-crown-4 with $GeBr_2$ gave the same cation as a $[GeBr_3]^-$ salt (**19b**) without the need for an additional halide abstraction reagent [32]. Macrocyclic amines were also found to sequester Ge(II) dications *via* simple reaction with $GeCl_2$·dioxane (**20**). In all cases the macrocycle completes the coordination sphere of the germanium, although in the absence of any discrete two-center-two-electron bonds for the 12-crown-4 complexes. The analogous chemistry for tin has also been reported, in this case the dications were synthesized by the direct reaction of $Sn(OTf)_2$ with the crown ethers 12-crown-4 and 15-crown-5 [33].



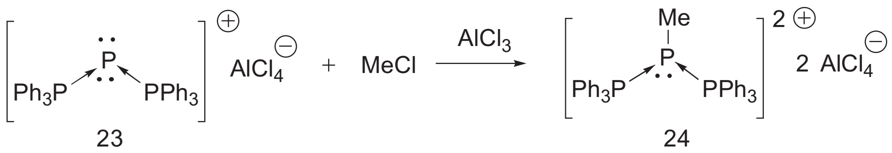
Scheme 6. Encapsulation of Ge(II) dication in the macrocycle 2,2,2-cryptand.



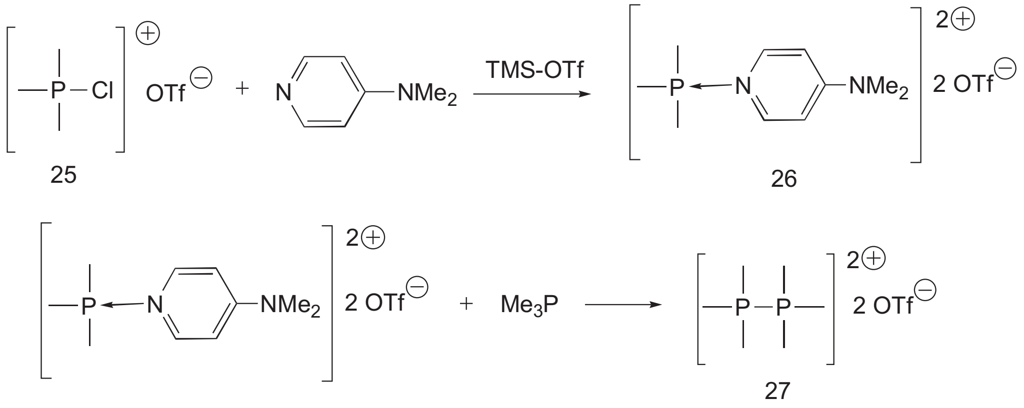
Scheme 7. Formation of Ge(II) centered dications using macrocyclic donors.



Scheme 8. Generation of Si(IV) dication 22 *via* coordination of pyridine.



Scheme 9. Alkylation of triphosphenium cation giving base stabilized Me-P: dication 24.



Scheme 10. Halide abstraction and coordination reaction giving dication 26, and subsequent ligand exchange reaction with trimethylphosphine giving P-P dication 27.

The study of dicationic silicon compounds is far less developed than germanium. One Si(IV) dication has been reported in an octahedral complex featuring two axial hydrides and four equatorial pyridine ligands synthesized by addition of excess pyridine to silyl amine **21** (Scheme 8). Compound **22** was isolated as a few crystals, and only characterized by single crystal X-ray crystallography [34].

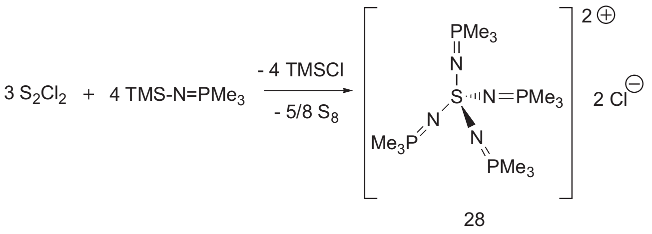
6. Group 15 dications

There are few reports of ligand stabilized group 15 dications. Schmidpeter et al. used an alkylation reaction in the presence of a Lewis acid ($AlCl_3$) to generate a P(III) centered dication (**24**) from the base stabilized P(I) triphosphenium cation **23**, and the analogous chemistry using arsine groups has also been performed (Scheme 9) [35]. Several more derivatives were later synthesized and crystallographically characterized by Dillon et al. using direct alkyl- and arylation reactions using organotriflate reagents as well as protonation reactions [36–38].

The lone P(V) example of a phosphorus centered polycation is made through the reaction of trimethylchlorophosphonium triflate (**25**) with TMS–OTf in the presence of 4-DMAP (4-dimethylaminopyridine), resulting in halide abstraction of chloride from phosphorus with concomitant coordination by 4-DMAP (Scheme 10) [39]. The $[R_3P]^{2+}$ fragment in compound **25** can be considered as a highly Lewis acidic dicationic analogue of a trialkyl borane or allane, with 4-DMAP acting as a stabilizing Lewis base. The coordinative nature of the DMAP-phosphorus interaction was demonstrated *via* a ligand exchange reaction with the stronger donor PMe_3, resulting in displacement of the 4-DMAP and P–P bond formation giving compound **26**. In **26**, the two phosphorus atoms are indistinguishable spectroscopically, and therefore the complex should not be represented as an adduct.

7. Group 16 dications

Discrete group 16 dications without supporting ligands can be isolated due to the availability of higher oxidation states (+4, +6) for the group 16 elements. Group 16 atoms are therefore able to accommodate a dicationic charge while still retaining an octet of electrons, mitigating the requirement for additional ligands. The first such example was reported by Dehnicke and coworkers in 1995 *via* the disproportionation of S_2Cl_2 in the presence of a phophorane iminato ligand (introduced bound to $–SiMe_3$ (TMS)) giving an S(VI) centered dication (**28**) [40].

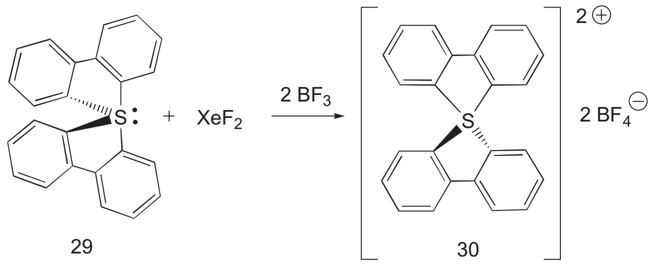


Scheme 11. Disproportion of S_2Cl_2 in the presence of phosphorane iminato ligand giving S(VI) centered dication 28.

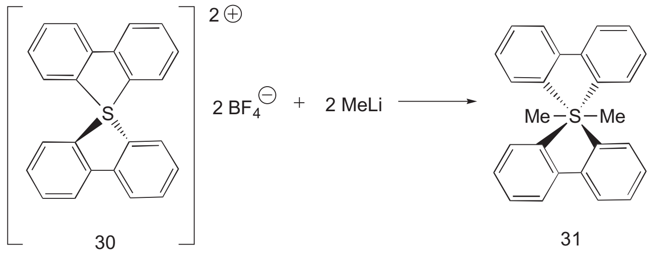
Furukawa and coworkers found that the oxidation of bis(2,2′-biphenylene)sulfurane **29** with XeF_2 in the presence of the halide abstraction reagent $BF_3{\cdot}Et_2O$ gave the stable (impervious to atmospheric air/moisture) dication **30** [41] (Scheme 11).

The authors of this study described **30** as an organosulfur(IV) dication, however, given the synthesis involves the oxidation of a sulfur(IV) compound using the F_2 synthon XeF_2, the formal oxidation number of the central sulfur is best described as +6. This is in line with the oxidation state assignment protocols outlined by Macdonald and coworker for the group 15 elements, which relies on the number of lone pairs of electrons about the central element [12]. In group 16 (with the exception of oxygen) zero lone pairs of electrons implies the +6 oxidation state, one lone pair +4, and two lone pairs +2. For compound **30** the assignment of the +6 oxidation state is also congruent with analogy to the isovalent $R_4Si(IV)$ silane and $[R_4P(V)]^+$ phosphonium species. The formalisms described by Macdonald for the determination of oxidation states gives the oxidation number a more physical meaning (# of non-bonding pairs of electrons about the central element). Compound **30** could be alkylated using MeLi giving **31**, the first example of a neutral sulfur(VI) compound bearing six organic groups [42] (Schemes 12 and 13).

The selenium and tellurium analogues of **30** were also synthesized, although the selenium compound was unstable at ambient temperatures, and the tellurium complex **32** formed an octahedral,

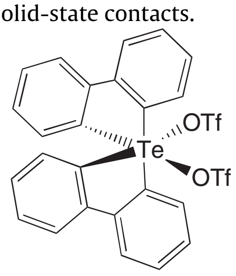


Scheme 12. Oxidation of sulfurane 29 followed by halide abstraction giving S(VI) dication 30.



Scheme 13. Alkylation of 30 giving S(VI) persulfurane 31.

overall neutral species incorporating the triflate counter-anions [43]. The Te–O contacts were found to be 2.425 Å, greatly elongated from a standard Te–O single bond distance (~2.0 Å) and were described as simply solid-state contacts.



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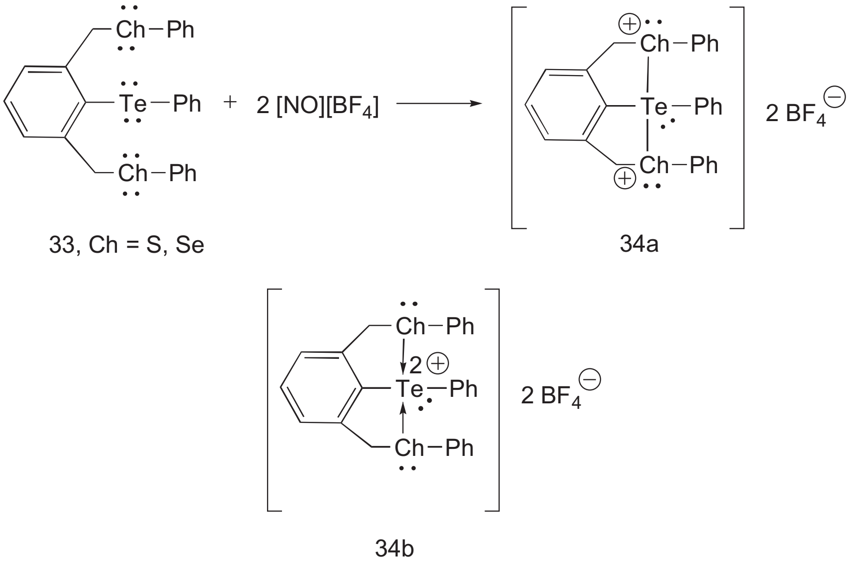
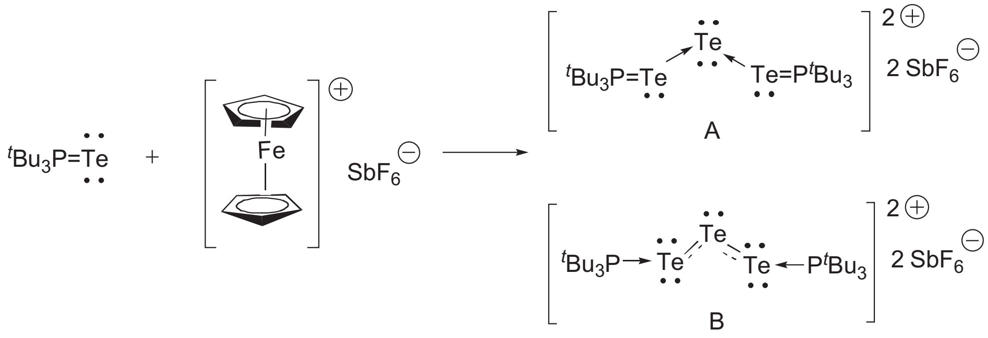
The same group has also reported the synthesis of transannular tellurium(IV) dications *via* the oxidation of **33** with [NO][BF$_4$] (Scheme 14) [44]. The compounds were primarily represented as **34a**, with two cationic charges located on the flanking E atoms. However, *ab initio* calculations indicated that the bulk of the charge (+1.4 to +1.6) was carried by the central element. Therefore the bonding could be described as a Te(IV) dication, stabilized by intramolecular dative bonds from neighboring sulfur or selenium donors (**34b**).

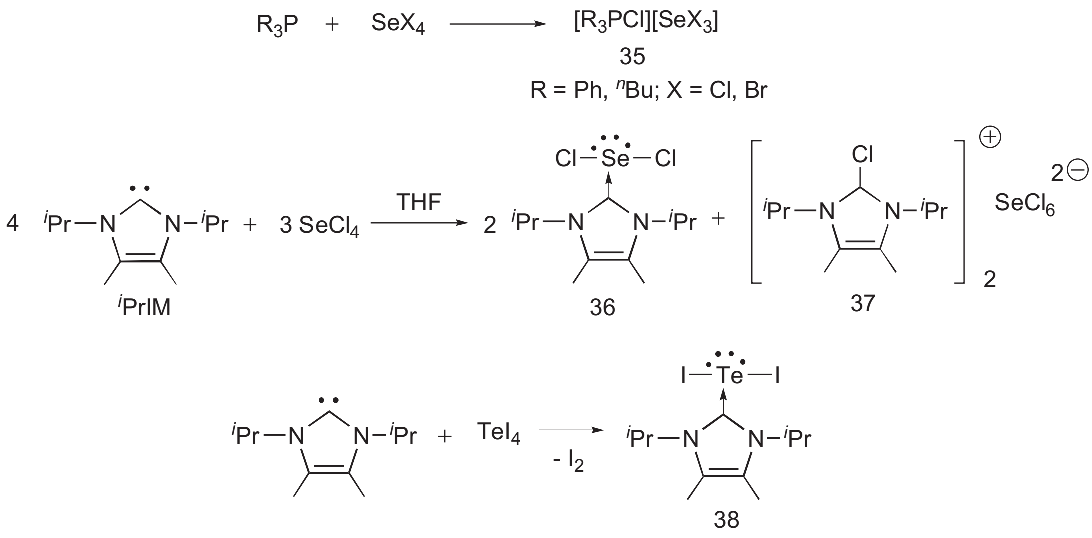
Until recently there were few examples of mononuclear group 16 dications stabilized by neutral two-electron ligands. Foss et al. have reported a series of base stabilized square planer tellurium dications, from the reactions of TeO$_2$ with HX in the presence of excess thiourea ligand, however, the synthetic pathway is restricted to this specific family [45]. Kuhn reported a compound that could be considered a base stabilized tellurium dication, from



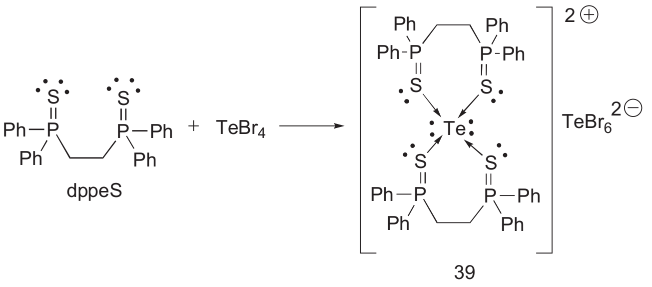
Scheme 14. Oxidation of 33 giving transannular tellurium centered dication 34.



Scheme 15. Generation of phosphine stabilized [Te$_3$]$^{2+}$ species.



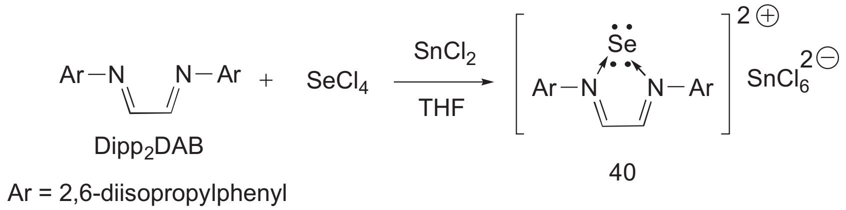
Scheme 16. Redox reactions between chalcogen tetrahalides and phosphine and NHC ligands.



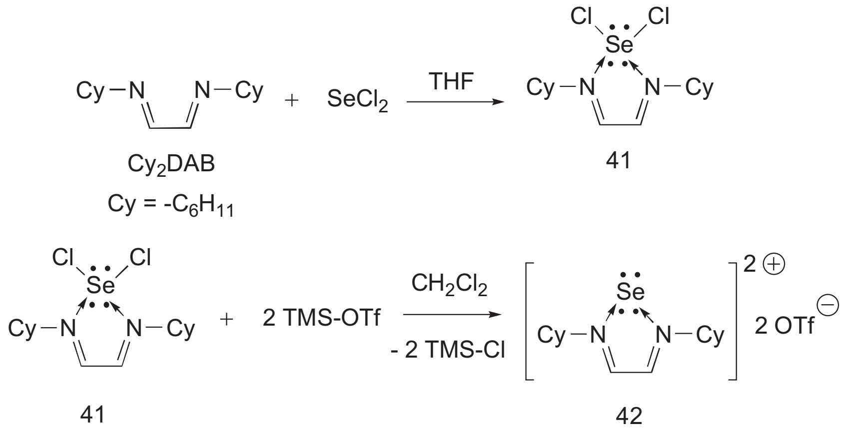
Scheme 17. Synthesis of Te(II) dication 39 *via* spontaneous reduction of $TeBr_4$ in the presence of neutral ligand dppeS.

the oxidation of phosphine telluriudes with ferrocenium salts. The complex was represented with the canonical forms A and B (Scheme 15), as either a phosphine telluride stabililzed tellurium dication, or a phosphine stabilized $[Te_3]^{2+}$ complex, respectively [46]. However, based on the long Te–P bond lengths (2.5 Å) and intermediate between single and double Te–Te bonds (2.71 Å), the authors concluded that representation B best described the complex.

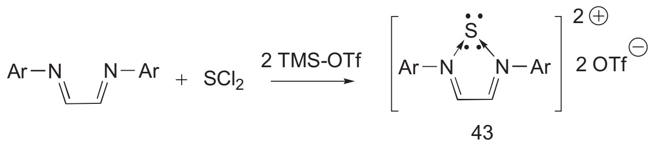
The paucity of examples for group 16 dications is surprising given that the tetrahalides of selenium and tellurium are available commercially as easily handled solids, and would seem to be ideal starting materials for the generation of highly charged species. The group 16 halides have a propensity to undergo reduction in the presence of neutral ligands particularly with the common triorganophosphine and N-heterocyclic carbene ligands (*e.g.* gen-



Scheme 18. Synthesis of diimine supported Se(II) dication 40 *via* the controlled reduction of $SeCl_4$ by $SnCl_2$.



Scheme 19. Synthesis of DAB sequestered Se^{2+} paired with triflate anions.

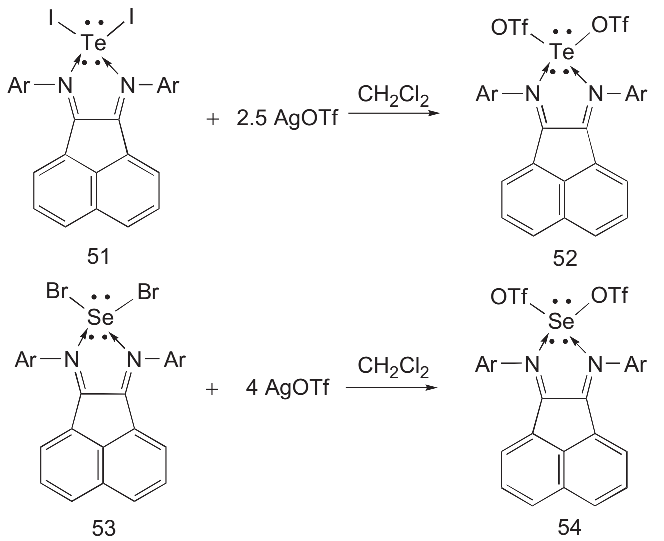


Scheme 20. Synthesis of DAB sequestered S^{2+}.

eration of compounds **35**, **36** and **38**) [47,48] (Scheme 16). The oxidation by-product in reactions resulting in ligand–chalcogen bond formation is often X_2 (X = Cl, Br), a highly reactive species, resulting in the generation of undesirable by-products (*e.g.* chloroimidazolium salt **37**) and lowered yields [49,50].

The commercially available tetrahalides of selenium and tellurium are particularly susceptible to this type of reactivity. There is only one report of the tetrahalides being used as a direct precursor for a dication, the reaction of dppeS (bisdiphenylphosphinoethanesulfide) with $TeBr_4$, which resulted in reduction at tellurium (Te(IV)–Te(II)), and the isolation of a square planar Te(II) dication with a $[TeBr_6]^{2-}$ counterion (**39**) [51] (Scheme 17). The incorporation of hexahalochalcogenate anions is a common result when using ChX_4, as the tetrahalides are effective halide abstraction reagents, which can be problematic as the $[ChX_6]^{2-}$ dianions carry much of the reactivity of ChX_4, and can also act as a halide source [52].

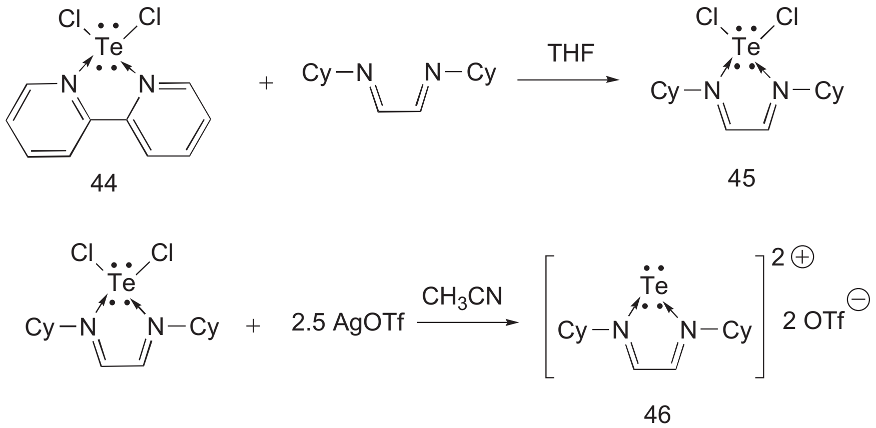
The binary halides are less prone to reduction, however, SCl_2 and SeX_2 are unstable compounds, and $TeCl_2$ is only known as a transient species in the gas phase [53–56]. Coordination of a Lewis base has been shown to stabilize ChX_2 by several groups over the past decades [51,57–65], but only recently were these coordination complexes considered as a source of ChX_2 [66,67]. Additionally, the *trans* influence from the ligands weakens the Ch–X bonds, rendering the complexes susceptible to halide abstraction for the generation of dications. The first transformation of this type involved the *in situ* reduction of $SeCl_4$ with $SnCl_2$, in the presence of the α-dimine ligand $Dipp_2DAB$ (Dipp = Ar = 2,6-diispropylphenyl, DAB = diazabutadiene). Coordination of $SeCl_2$ by $Dipp_2DAB$ occurred concomitant with halide abstraction by the oxidation by-product $SnCl_4$ giving dication **40** as a $[SnCl_6]^{2-}$ salt [68] (Scheme 18).



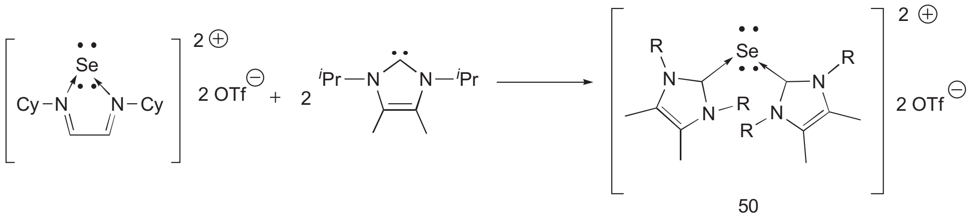
Scheme 23. Synthesis of $Ch(OTf)_2$ reagents *via* halide abstraction.

Unfortunately, the $[SnCl_6]^{2-}$ dianion carries the same issues as the hexahalochalcogenate dianions, acting as a source of chloride, and an electrophilic tin center. Diazabutadiene ligands can also sequester ChX_2 as stable complexes, that can act as precursors for dications. For example, Cy_2DAB (Cy = cyclohexyl) forms a complex with $SeCl_2$ (**41**), and a subsequent reaction with two stoichiometric equivalents of TMS–OTf gave dication **42**, in this case paired with inert triflate anions [69] (Scheme 19).

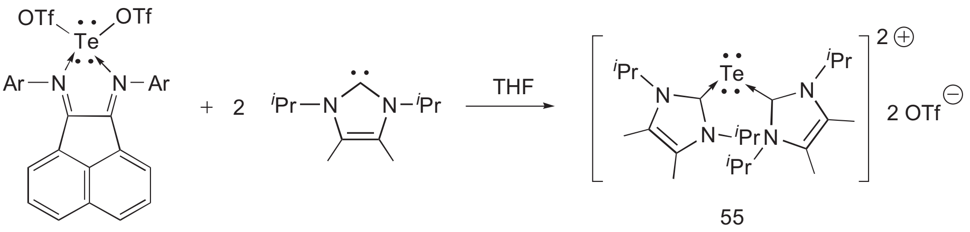
A 2:1 stoichiometric ratio of TMS–OTf and SCl_2 was found to act as an effective S^{2+} synthon for the generation of sulfur centered dications supported by a variety of different α-dimine ligands [70,71] (Scheme 20).



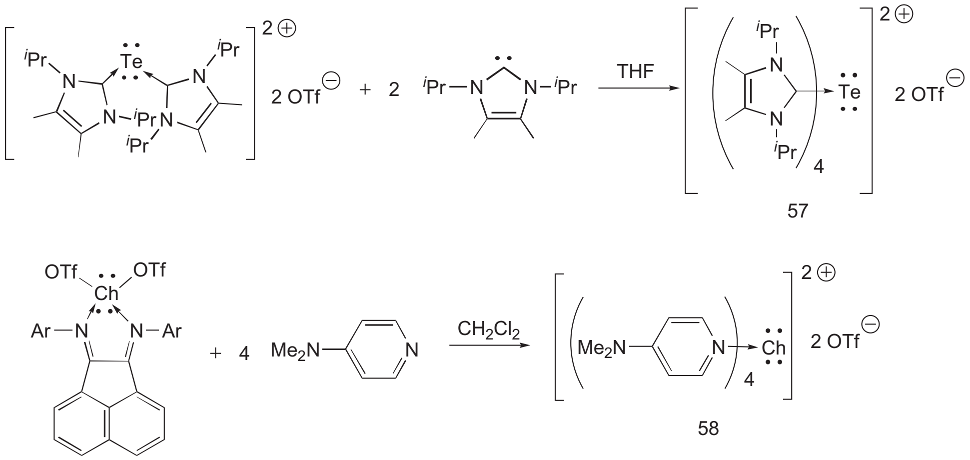
Scheme 21. Synthesis of DAB sequestered Te^{2+}.



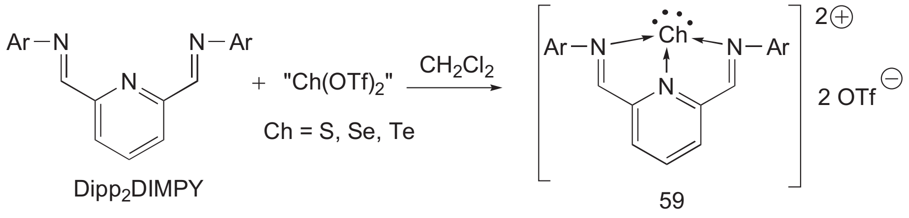
Scheme 22. Ligand exchange reaction transferring Se^{2+} from DAB to NHC.



Scheme 24.



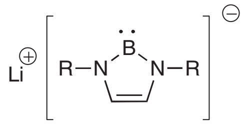
Scheme 25. Synthesis of "pinwheel" Ch^{2+} complexes.



Scheme 26. Synthesis of DIMPY sequestered Ch^{2+} dications.

Due to the transient nature of $TeCl_2$, the tellurium congener **46** was synthesized using ligand exchange from a 2,2-bipyridine stabilized form of $TeCl_2$ by Cy_2DAB, followed by halide abstraction with an excess of AgOTf (Scheme 21).

This family of compounds represent dicationic structural analogues of the ubiquitous N-heterocyclic carbene ligand; N-heterocyclic carbene analogues are also known for groups 13 (negatively charged, Lewis basic, *e.g.* **47**), group 14 (neutral, Lewis basic, *e.g.* **48**) and group 15 (positively charged, Lewis amphiphilic, *e.g.* **49**), and have shown a rich chemistry complementary to, and divergent from the parent NHCs.



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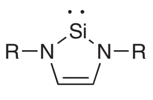
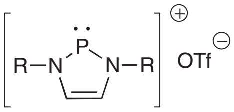


48



49

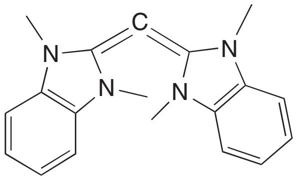
Despite the similar appearance, the dicationic group 16 NHC analogues have a highly different electronic structure, having a diimine bonding motif, rather than the N–C and C═C bond functionalities observed for NHCs and the group 13–15 analogues. This difference was predicted with theoretical calculations for both the dication, and the neutral dichloride species; for the neutral compound the diimine framework was 58 kJ/mol lower in energy [65,72]. Additionally, the central chalcogen atoms carry two lone pairs of electrons, rather than the expected one lone pair. Given the significantly different electronic structure of the group 16 NHC analogues, unique reactivity would be anticipated as compared with the other groups, therefore we envisioned using these compounds as synthetic equivalents of "$Ch(II)^{2+}$". For example, it was found that careful addition of the NHC $^iPr_2IM$ to **42** resulted in ligand exchange, and the generation of bis-NHC supported dication **50** [69] (Scheme 22).

However, a siginificant amount of protonated NHC was also generated, and attempted ligand exhange by the reaction of 4-DMAP with **42** gave protonated 4-DMAP as the isolated product. The "backbone" protons on **42** were implicated as the source of the protons, therefore a modified ligand set was used, the BIAN class of α-dimine ligands.

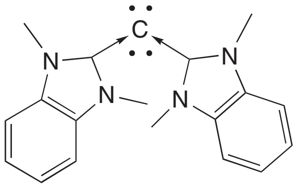
A TeI_2–$Dipp_2BIAN$ complex (**51**, BIAN = bis(aryl)iminoacenapthene) was reported by Cowley and coworkers and was found to be susceptible to halide abstraction as addition of an excess of AgOTf gives **52** [73,74] (Scheme 23). The triflate anions formed weak covalent bonds to tellurium, therefore **52** could be described as a *pseudo* binary halide of tellurium. A similar complex was synthesized for selenium (**54**) from stable $SeBr_2$ source **53**, but has not been structurally characterized. This family of compounds has been demonstrated to act as an effective source of Ch^{2+} in ligand exchange reactions to generate chalcogen centered dications bearing a variety of neutral two-electron ligands (Schemes 24 and 25).

The addition of two equivalents of $^{i}Pr_2IM$ to **52** gives the dication **55**, similar to the selenium compound **50**.

These two complexes can be considered dicationic, heavy atom analogues of the "bent allene" or "carbodicarbene" (**56**) recently reported by Bertrand and coworkers [4]. The C–C–C bond angle in the carbodicarbene was 134°, in **50** and **55** the C–Ch–C angles are 96.3(1) and 91.5(1), respectively. This angle represents the use of unhybridized orthogonal p-orbitals to form the C–Ch bonds, therefore **50** and **55** should not be represented as having multiple-bond character, and are analogues of **56b**. This is in line with the C–Ch bond distances, which display no shortening indicative of multiple bonding. The monocationic phosphorus centered analogue is known, and displays a P–P–P bond angle of 97°, which may indicate some degree of multiple bonding character [75].



56a



56b

Two additional equivalents of $^{i}Pr_2IM$ were added to **55** giving a square planar tellurium centered dication with a "paddlewheel" bonding motif. This compound is highly unstable owing to the extremely weak Te–C bonds (range 2.34–2.52 Å).

The reaction of **52** and **54** with four stoichiometric equivalents of 4-DMAP resulted in facile ligand exchange, and the synthesis of square planar "pinwheel" dications bearing nearly perfect D_{4h} symmetry, with no evidence for protonated 4-DMAP as a by-product.

The first group 16 complexes of the diiminopyridine (DIMPY) family of ligands with the Ch^{2+} dication found in the N,N,N chelate were also synthesized using these pseudo-halide starting materials (**59**) [76] (Scheme 26). The sulfur analogue (the first example of a non-metal complexed by a DIMPY ligand) was generated by the addition of $Dipp_2DIMPY$ to a 2:1 mixture of TMS–OTf and SCl_2 in CH_2Cl_2. These dications are remarkable, because of their stability, most of the group 16 dications described above are very sensitive compounds, decomposing if held in solution for a few hours at room temperature, and immediately decomposing upon exposure to ambient atmosphere. Not only are the DIMPY based dications stable in solution under an N_2 atmosphere, they are even resilient to the open environment of the laboratory.

8. Summary

Recent developments in the synthesis of ligand stabilized p-block polycations has been reviewed. It is clear, both from the increasing number and quality of publications that this is an area of growing importance. These materials have great promise for use as "E^{2+}" synthons, as evidenced by successful ligand exchange/liberation reactions for some of the examples. However, yet to be demonstrated is the practical use of these dications, either in ongoing synthetic transformations/activations, or incorporation into functional materials, which are the next challenges in this field.

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