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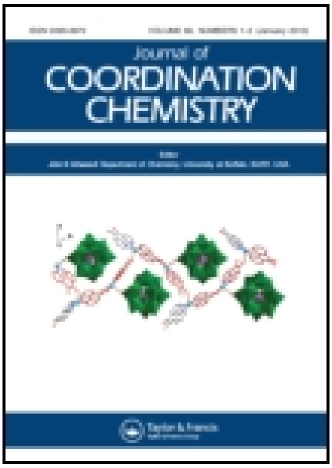

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# Review: Structurally characterized α-diimine complexes of s- and p-block elements

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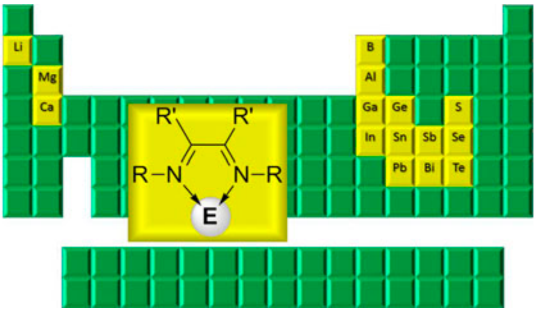

This review provides an account on the structurally characterized s- and p-block element complexes of neutral α-diimine ligands and their chemical properties. These ligands provide the opportunity to control the coordination sphere around the main group element center and electronic properties of the complexes by varying the substituents present in them. In many instances, α-diimine main group element complexes themselves undergo reactivity via redox and free radical mechanisms.

*Keywords*: α-Diimines; Main group elements; Radical anion; Redox reactions

## 1. Introduction

α-Diimines are bidentate nitrogen donor ligands and are among the widely used ancillary ligands in coordination chemistry. The versatility of this class of ligands has given rise to diverse applications in the fields of organic and organometallic synthesis [1–8] and catalysis [9–12]. α-Diimines can be prepared easily by condensation of α-diketones and primary amines under acidic conditions (scheme 1a) [13]. This gives systems such as alkyl and aryl-substituted 1,3-diazabutadiene (**I**), bis(iminoacenaphthene) (**II**), tetrakis(imino)pyracene (**III**), aminotroponimine (**IV**), 2,2′-bipyridine (**V**), and 1,10-phenanthroline (**VI**) (figure 1).

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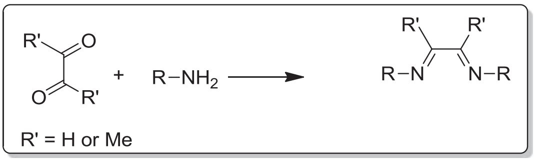


Scheme 1a.

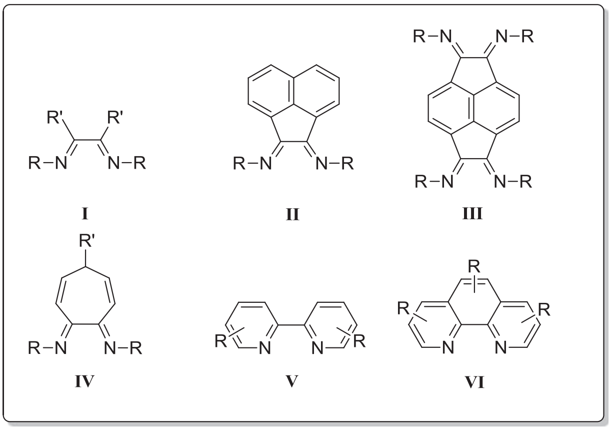


Figure 1. General structure of α-diimines.

α-Diimines have been extensively utilized in transition metal coordination chemistry and usually coordinate to the metal centers resulting in the formation of five-membered chelated rings (**VII**). There are cases where the diimines have been reduced, either singly (**VIII**) or doubly (**IX**) (figure 2).

Electronic and structural properties of metal complexes can easily be tuned by having appropriate substituents on the nitrogens as well as on the backbone carbons constituting the diimine framework. A detailed review on the chemistry of α-diimine complexes is lacking. In 1982, Van Koten and Vrieze provided a review on diimine complexes summarizing the unusual coordination modes and reactivity of some transition metal complexes [14]. To the best of our knowledge, there have been no reviews published in this area, except one on bis(imino)acenaphthenes (II, figure 1) by Cowley and co-workers [15]. This review covers all the structurally characterized α-diimine complexes of s- and p-block elements based on a search carried out in Cambridge Structural Database in December 2013. Work on neutral α-diimine complexes of s- and p-block elements has gathered increasing momentum since

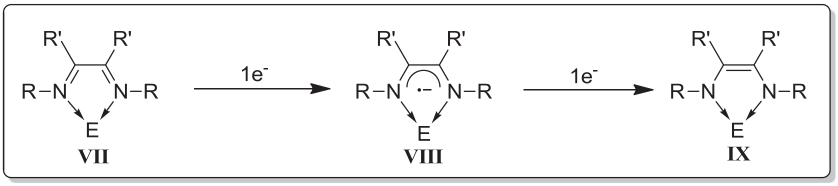
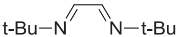
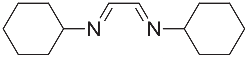
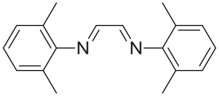
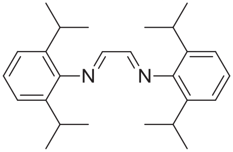
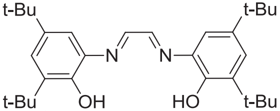
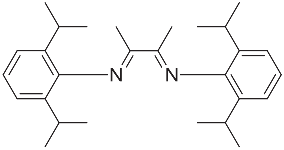
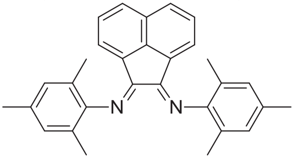
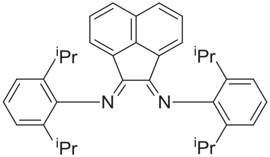
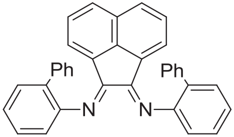
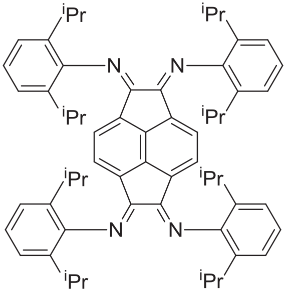
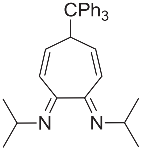


Figure 2. Neutral and reduced α-diimine complexes – general structure.

Table 1. List of structures, names, abbreviations, and references for synthetic procedures.

| Structure | Name | Abbr. | Refs. |
|---|---|---|---|
|  | 1,4-di-*tert*-butyl-1,3-diazabutadiene | $^{t}\mathrm{Bu}_2$**DAB** | [13, 14, 16, 17] |
|  | 1,4-dicyclohexyl-1,3-diazabutadiene | $\mathrm{Cy}_2$**DAB** | [13, 17, 18] |
|  | 1,4-bis(2,6-dimethylphenyl)-1,3-diazabutadiene | $\mathrm{dmp}_2$**DAB** | [7, 13, 18–20] |
|  | 1,4-bis(2,6-diisopropyl)-1,3-diazabutadiene | $\mathrm{dipp}_2$**DAB** | [2–5, 7, 13, 19–24] |
|  | 1,4-bis(2-hydroxy-3,5-di-tert-butylphenyl)-1,3-diazabutadiene | $(\mathrm{H}_2\mathrm{hbp})_2$**DAB** | [25] |
|  | 1,4-bis(2,6-diisopropyl)-1,3-diaza-2,3-dimethylbutadiene | $\mathrm{dipp}_2\mathrm{Me}_2$**DAB** | [14, 19, 20, 26, 27] |
|  | Bis(2,4,6-trimethylphenyl-imino)-acenaphthene | mes-**BIAN** | [6, 28–32] |
|  | Bis(2,6-diisopropylphenylimino)-acenaphthene | dipp-**BIAN** | [20, 21, 28, 31, 33–38] |
|  | Bis(2-phenylphenylimino)-acenaphthene | dph-**BIAN** | [39, 40] |
|  | Tetrakis(2,6-diispropropylphenyl-imino)-pyracene | dipp-**TIP** | [41] |
|  | N-isopropyl-2-(isopropylamino)-troponimine | H[$^{i}$Pr-**ATI**] | [42–45] |

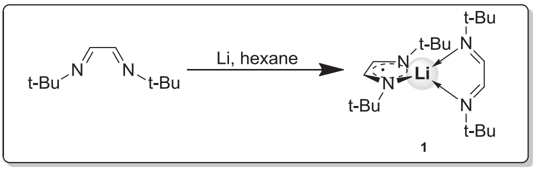
the 1990s. Table 1 gives a complete list of those α-diimine ligands pertaining to this review, along with their structures, abbreviations used, and references where their respective synthetic methodologies have been elucidated and detailed discussions on structure, electronic behavior, and stability are provided. Henceforth, C–C and C–N bond lengths will refer to those corresponding to the α-diimine backbone N=C–C=N, unless stated otherwise. In this review, we have focused on ligands of the types **I**–**IV**. We have excluded those ligands in which the nitrogens of the α-diimine ligand are part of an aromatic system.

## 2. s-Block complexes

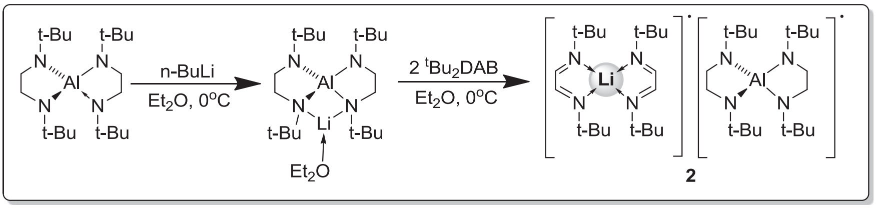
### 2.1. *Group 1 complexes*

Alkali metals readily react with DAB ligands by reducing them. The first work on alkali metals was carried out by Hanson and co-workers in 1994 [46]. Lithium was reacted with a hexane solution of $^{t}Bu_2DAB$ at room temperature, resulting in the formation of $[Li(^{t}Bu_2DAB)_2]$ (**1**) as shown in scheme 1b. This complex has one neutral moiety and one reduced radical anion of $^{t}Bu_2DAB$ bound to the Li. Single crystal XRD study indicates that there are marked differences in the C–C and C–N bond distances involved in the chelation. (Reduced radical anion; Li–N(mean) = 1.994 Å and $C_{ring}$–N(mean) = 1.317 Å and C–C = 1.399 Å and on the other ligand simply acting as a neutral bidentate, Li–N(mean) = 2.141 Å, $C_{ring}$–N(mean) = 1.242**,** C–C = 1.488 Å.) In the same work, complex **1** was used to synthesize the doubly reduced Mg and Zn derivatives from their respective metal halide salts.

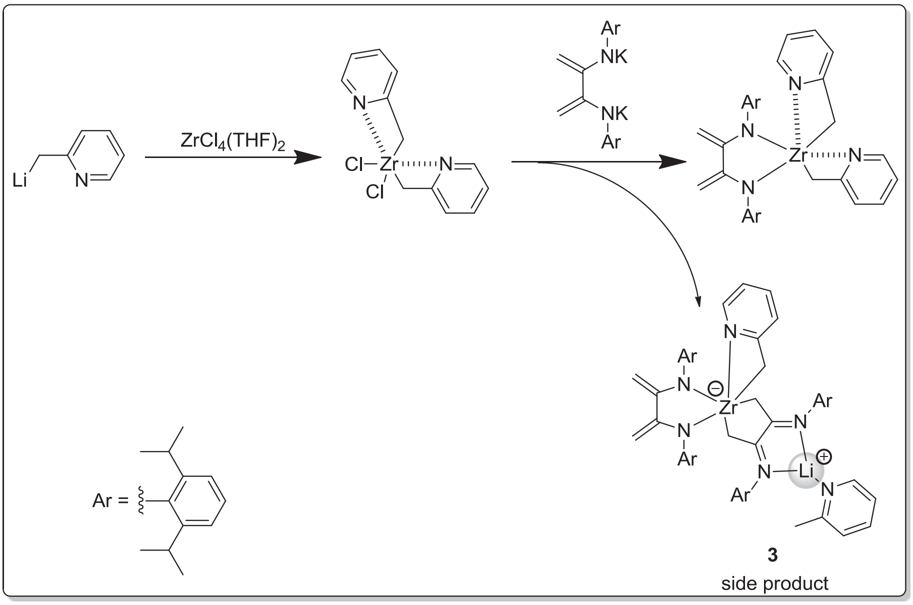
In 1997, Raston and co-workers synthesized EPR-active $[Li(^{t}Bu_2DAB)_2][Al\{[N(^{t}Bu)CH_2]_2\}_2]$ (2) according to scheme 2 [47]. Crystal structure determined through single crystal XRD experiment is indicative of an ionic formulation with both $^{t}Bu_2DAB$ ligands bound to Li being neutral chelates (N–C(mean) = 1.255 Å and C–C(mean) = 1.475 Å). EPR studies in solution showed a combination of signals from **1** and a paramagnetic Al center. It is noteworthy that the geometry of the Li center in **2** is somewhat comparable to that of **1** (Li–N (mean) = 2.081 Å).



Scheme 1b.



Scheme 2.



Scheme 3.

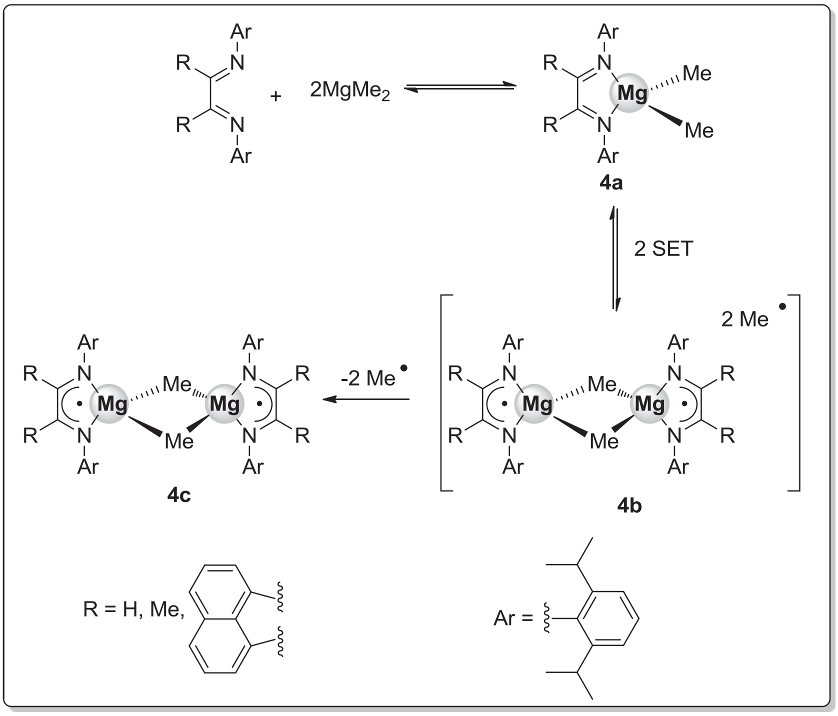
Lee *et al.* in 2003, isolated and characterized a crystalline lithium complex **3** as a side product of a reaction targeted at synthesizing enamido Zr complexes for application in ethylene polymerization (scheme 3) [48]. C–N (mean) and C–C bond lengths for the diimine moiety bound to the Li were 1.302 and 1.520 Å, respectively, and they emphasize the neutrality of the diimine framework.

### 2.2. *Group 2 complexes*

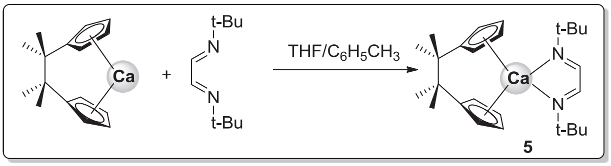
Paramagnetic diimine complexes (**4b** and **4c**) of Mg were isolated by Bailey and co-workers in 2006 [49]. A speculated mechanism for this reaction is shown in scheme 4. A short-lived neutral diimine species of the form $LMgMe_2$ (**4a**) (L = diimine ligand) is thought to be the intermediate in a single electron transfer mechanism, which eventually results in the formation of a dimer facilitated by elimination of methyl radicals which are still present in the solvent cage (**4b**). The methyl radicals are thought to get eliminated from the solvent cage at room temperature to provide the structurally characterized biradical species **4c** as shown in scheme 4.

This sort of electron transfer that results in reduction of the α-diimine moieties explains why many neutral ligand complexes of alkaline earth metals haven't been structurally characterized.

The first X-ray characterized ansa-metallocene complex of calcium (**5**) was synthesized by Edelman and co-workers [50]. Synthesis of **5** was carried out by treating dianionicbis (6,6–dimethylfulvenyl) calcium with α-diimines (scheme 5). The diimine was able to coordinate as a neutral ligand without being reduced either singly or doubly, unlike in most other alkaline earth metal systems [46, 51–55].



Scheme 4.



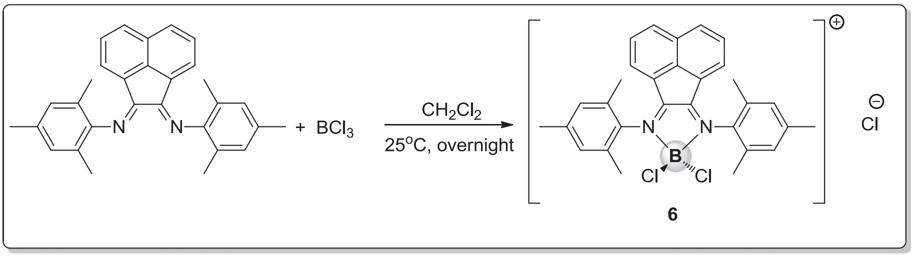
Scheme 5.

## 3. p-Block complexes

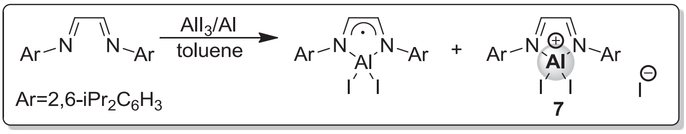
### 3.1. *Group 13 complexes*

In 2006, Cowley and co-workers synthesized **6** from reaction of $BCl_3$ with mes-BIAN, in which one of the B–Cl bonds is broken by the ligand to yield the product with a cationic boron complex and chloride (scheme 6) [56]. The geometry about boron is tetrahedral. C–C and C–N bond distances (on an average) of 1.494 and 1.281 Å reflect the neutrality of the BIAN ligand chelated to boron.

In 2002, Jones and co-workers obtained an Al(III) cationic complex $[I_2Al(Ar_2DAB)]I$ (**7**) ($Ar = 2,6\text{–}^iPr_2C_6H_3$) as a trace product of the reaction depicted in scheme 7 [57]. $Ar_2DAB$ was reacted with a 1 : 2 mixture of $AlI_3$ and Al powder. In about 12 h, a paramagnetic Al (III) complex and a trace by-product **7** was formed.



Scheme 6.



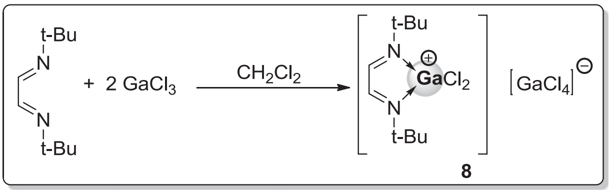
Scheme 7.

It is proposed that the Al powder reduces the initially formed **7** to the paramagnetic Al (II) complex. Hence it was taken out of the equation, and **7**, which can be formulated as an $Ar_2DAB$ adduct of $[AlI_2]^+$, was synthesized by reacting 1 equivalent of $Ar_2DAB$. C–C bond length is 1.442 Å; although significantly smaller than other neutral DAB ligands where the corresponding bond length has been greater than 1.45 Å [58, 59], and the N–C bond length (avg) is 1.30 Å. This suggests a neutral DAB-Al(III) donor–acceptor linkage with minimal delocalization of charge over the ligand π system.

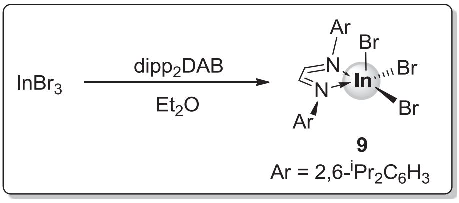
Cowley and co-workers obtained a cationic DAB-Ga complex $[{}^tBu_2DABGaCl_2][GaCl_4]$ (**8**) via scheme 8, where the diimine moiety is clearly neutral [59]. This situation is in contrast with those found in the aluminum case where the DAB systems are reduced. The C–C and C–N bond lengths (average: 1.478 and 1.253 Å, respectively) are indicative of a neutral diimine framework.

In 2002, Jones and co-workers carried out the reaction of $dipp_2DAB$ with $InBr_3$ in $Et_2O$ in 1 : 1 M ratio to synthesize $dipp_2DABInBr_3$ (**9**), the first DAB-$MX_3$ (M = group 13 element) adduct to be structurally characterized [58]. In the solid state, C–C bond length was 1.57 Å and C–N bond lengths were 1.24 and 1.27 Å. A $^1H$ NMR spectra revealed that all the methyl groups in **9** were equivalent in solution. The compound is fluxional in solution at all temperatures and there exists an equilibrium between the reactants and the product (scheme 9).

Although the $[{}^iPr\text{-}ATI]^-$ ligand is not neutral, the diimine framework that forms the backbone of this ligand can be modified to make it structurally similar to a neutral diimine ligand. $[\{1,2\text{-}(N^iPr)_{2\text{–}5}\text{-}CPh_3\text{-cyclohepta-3,6-diene}\}InMe_2][B(C_6F_5)_4]$ (**10**) was prepared in



Scheme 8.

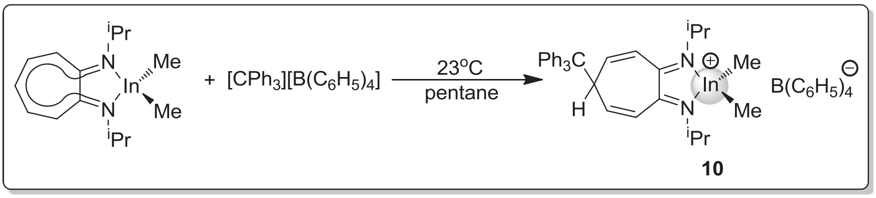


Scheme 9.

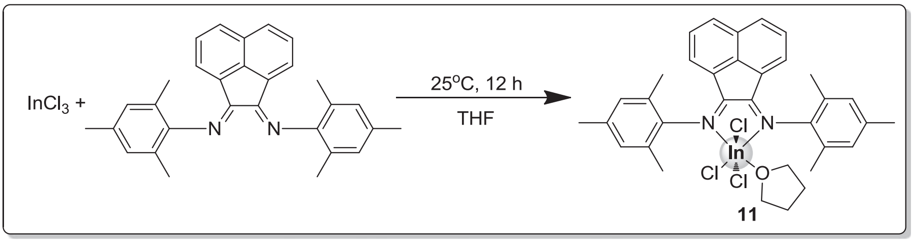
such a fashion via scheme 10 by Jordan and co-workers [43]. Addition of $[Ph_3C][B(C_6F_5)_4]$ to ($^i$Pr-ATI)($InMe_2$) serves as a tool to break down the charge delocalization within the ligand system and transforms it into a diimine-like moiety. The C–C and C–N bonds observed in **10** correspond to that of single and double bonds, respectively.

Cowley and co-workers in 2006 synthesized and characterized a series of aryl-BIAN complexes of In and Tl [60]. (mes-BIAN)$InCl_3$(THF) (**11**) and [(mes–BIAN)$_2$Tl][$PF_6$] (**12**) were synthesized using $InCl_3$ and $TlPF_6$, respectively, as per schemes 11 and 12. C–C bond length of 1.525 Å in **11** and 1.523 Å in **12** along with average C–N bond lengths of 1.280 Å in **11** and 1.270 Å in **12** are indicative of the neutrality of the aryl-BIAN moiety. Compound **11** has an indium with a distorted octahedral geometry, while **12** has an interesting structure where Tl is surrounded by four nitrogens in a tetragonal space group. Tl is positioned above the equatorial plane constituting the nitrogens. A bite angle of 59.83° is observed, smaller than 70° for the group 13 complexes encountered so far. It is the first crystallographically characterized compound of Tl(I) chelated by a neutral α-diimine ligand.

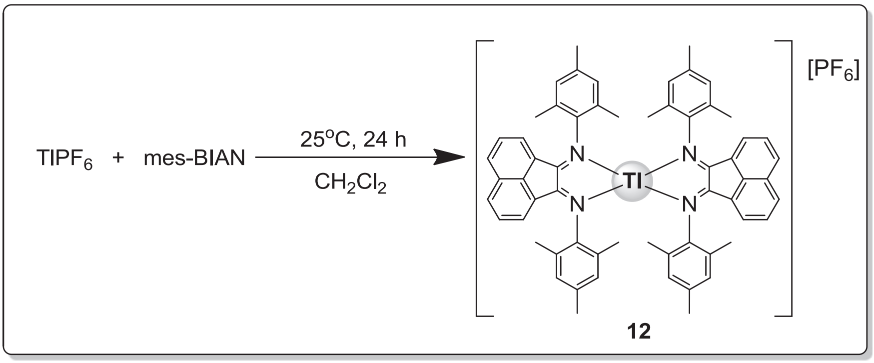
Indium trihalide complexes supported by a TIP ligand, [$(InCl_3)_2$(dipp-TIP)] (**13**), [$(InBr_3)_2$(dipp-TIP)] (**14**), and [$(InI_3)_2$(dipp-TIP)] (**15**), were prepared and structurally characterized by Vasudevan and Cowley in 2011 [61] (scheme 13). Average C–C bond lengths of 1.510–1.550 Å and C–N bond lengths of 1.260–1.285 Å for **13**–**15** are exemplary of the neutrality of the TIP ligand motif and hence of the +3 oxidation state of In in each case.



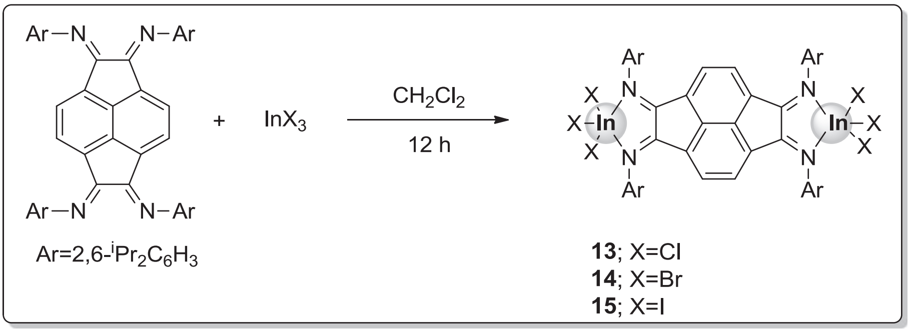
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

Whereas, in the In-BIAN complexes, the geometry around indium was distorted octahedral, with the binuclear In-TIP complexes, it is trigonal bipyramidal.

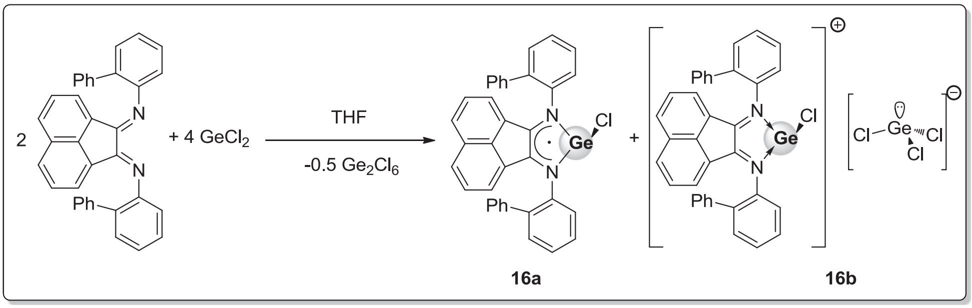
### 3.2. *Group 14 complexes*

Fedushkin and co-workers, in 2006, treated dph–BIAN with $GeCl_2$ to obtain two compounds dph–BIANGeCl (**16a**) and [dph–BIANGeCl][$GeCl_3$] (**16b**) (scheme 14) [62]. The former is a neutral molecule with an electron localized over the ligand, whereas the latter consists of an anionic $[GeCl_3]^-$ and a cationic $[(dph\text{–}BIAN)GeCl]^+$ moiety. Crystallographic data on the cation of **16b** revealed C–C bond length of 1.487 Å and C–N bond length of 1.291 Å (average), evidence to the neutrality of BIAN.

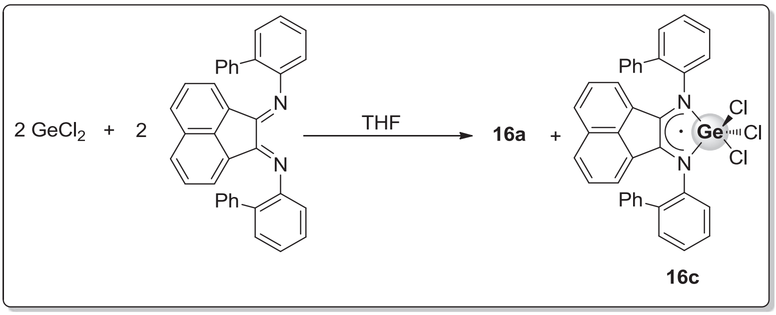
An ESR spectrum of a toluene solution of **16a** and **16b** shows signal broadening, which is observed due to the following equilibrium situation in solution:

$$\mathbf{16b} \rightleftharpoons \mathbf{16a} + 0.5\,Ge_2Cl_6$$

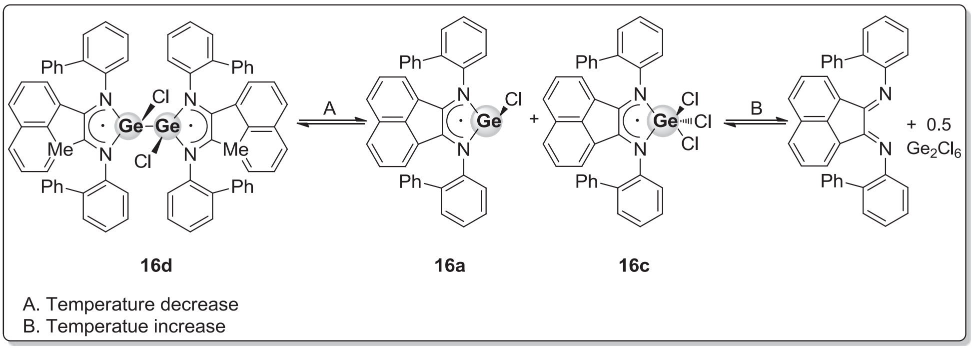
ESR study of the reaction mixture of dph-BIAN and $GeCl_2$ in THF shows dependence on temperature indicating the existence of (dph-BIAN)$GeCl_3$ (**16c**) at low temperatures and (dph–BIAN)GeCl at higher temperatures. Schemes 15 and 16 are derivative of these data.



Scheme 14.



Scheme 15.



A. Temperature decrease
B. Temperatue increase

Scheme 16.

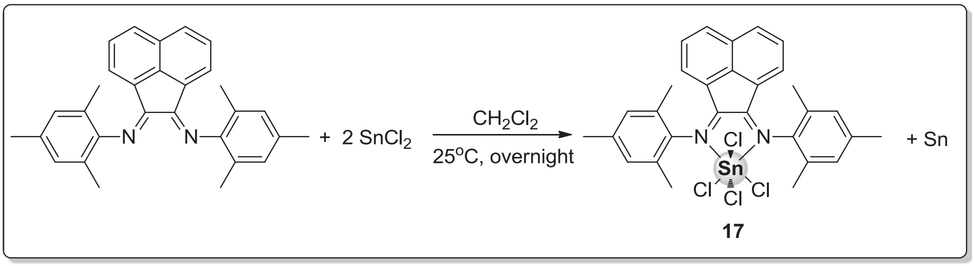
It is to be noted that the second product of scheme 14, **16b**, is obtained due to the following process:

$$\mathbf{16a} + \mathbf{16c} \overset{\text{THF}}{\rightleftharpoons} \mathbf{16b} + \text{dph} - \text{BIAN}$$

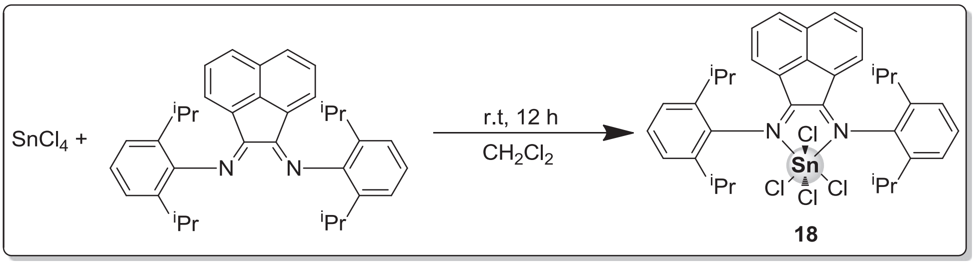
Cowley and co-workers reported the synthesis and characterization of the first BIAN complex of Sn(IV), [(mes-BIAN)$SnCl_4$] (**17**) [56]. Complex **17** is obtained via a disproportionation reaction of $SnCl_2$ into elemental Sn and **17** upon the addition of mes-BIAN (scheme 17). C–C bond length of 1.450 Å and C–N bond lengths of 1.291 Å suggest a neutral diimine framework in a distorted octahedral arrangement around Sn.

A complex with the formula [(dipp-BIAN)$SnCl_4$] (**18**) was synthesized by Cowley and co-workers (scheme 18) [60], and analyzed using XRD studies. The geometry around Sn is a distorted octahedron; C–C bond length of 1.527 Å and C–N bond length of 1.288 Å are indicative of a neutral ligand coordinated to the Sn(IV) metal center. The structure is very similar to that of **17**.

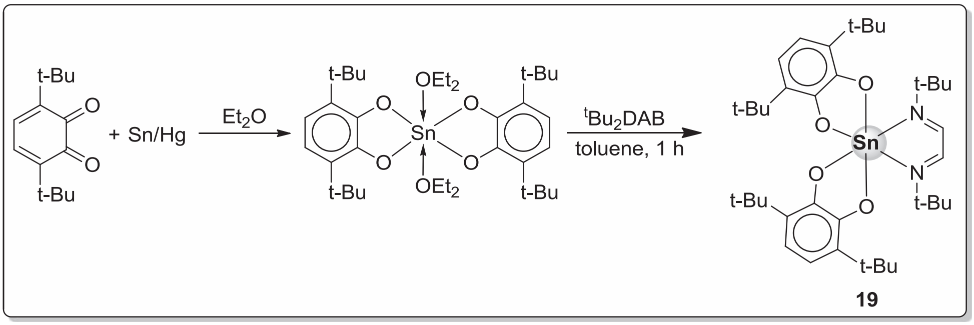
In 2006, in a study involving tin catecholate complexes, $Cat_2SnL_n$, where Cat = dianion of 3,6-di-tert-butylcatechol, L = donor ligands, and $n = 1, 2$ [63], a distorted octahedral complex $Cat_2Sn^tBu_2DAB$ **19** was synthesized as outlined in scheme 19.



Scheme 17.



Scheme 18.

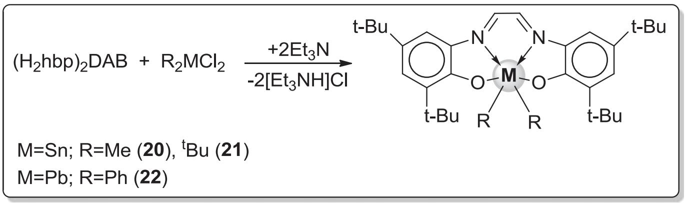


Scheme 19.

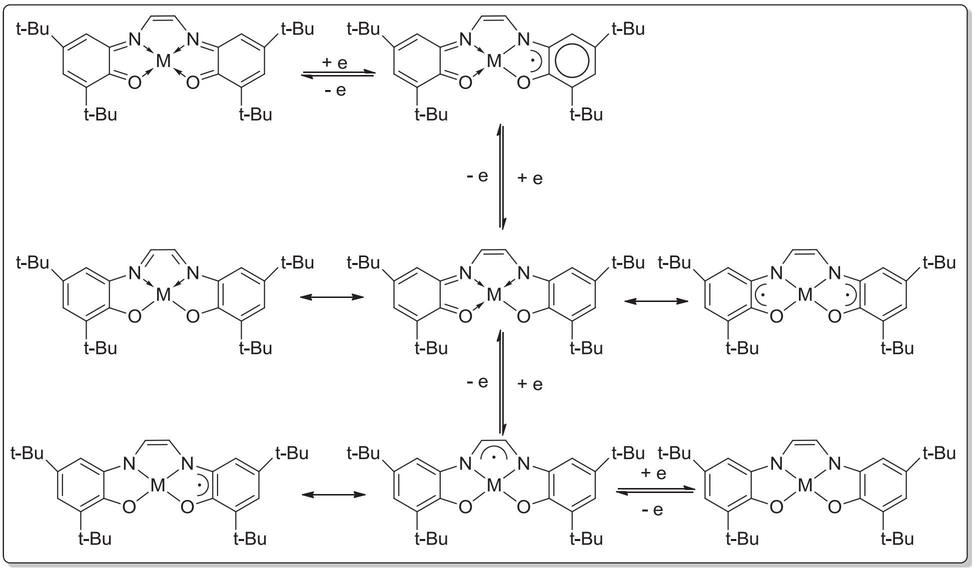
Sn-O bond lengths that were symmetrical in $Cat_2Sn(Et_2O)_2$ become significantly unsymmetrical once the DAB ligand is inserted, due to the sterically crowded $^tBu$ moieties on the DAB framework. C–C bond length of 1.469 Å and average C–N bond length of 1.264 Å are as expected for a neutral diimine.

Piskunov *et al.* studied Sn(IV) and Pb(IV) complexes of $[(hbp)_2DAB]^{2-}$, which is redox active and behaves as a tetradentate ligand with the aforementioned elements [64]. $Me_2Sn[(hbp)_2DAB]$ (**20**), $^tBu_2Sn[(hbp)_2DAB]$ (**21**), and $Ph_2Pb[(hbp)_2DAB]$ (**22**) were synthesized (scheme 20a). Sn and Pb have distorted octahedral geometry around them with the ligand ONNO constituting the equatorial plane and the R-groups located in the apical positions.

Although the diimine moiety is preserved even after chelation, there appears to be some elongation of C=N bond which is indicated by IR spectroscopy (1561–1585 $cm^{-1}$). The corresponding stretching frequency for free DAB ligands appears at 1600 $cm^{-1}$. DFT studies also reflect the same, along with distortion of other C–C and C–O bonds within the arene system, which strongly suggests that electronics of the ligand plays a major role in the existence of redox equilibria (scheme 20b).



Scheme 20a.

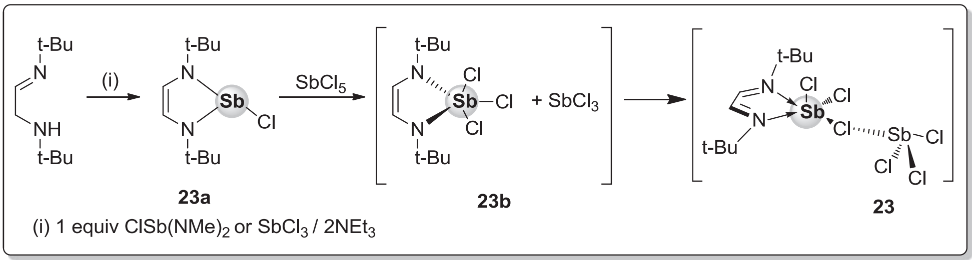


Scheme 20b. Redox states and resonance structures of $[hbp_2DAB]^{2-}$.

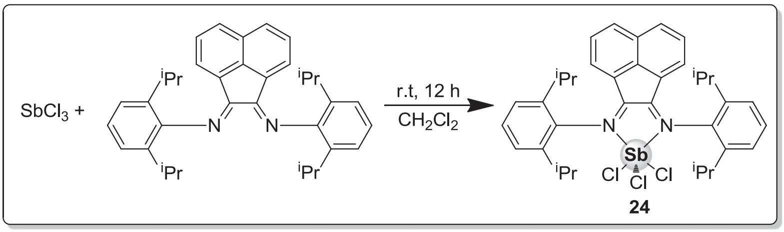
### 3.3. *Group 15 complexes*

Gudat and co-workers in 2004, synthesized and crystallographically characterized $^{t}Bu_2DAB.(SbCl_3)_2$ (**23**) [65]. The synthesis of **23**, an adduct of $SbCl_3$ and $^{t}Bu_2DAB$, is achieved via scheme 21. It is hypothesized that **23b** forms via oxidative chlorination of **23a** which subsequently decays to **23**. Though stable enough to be characterized by single crystal XRD studies, **23** dissociated in solution. The solid-state structure contains two pyramidal $SbCl_3$ units and the neutral $^{t}Bu_2DAB$ ligand is coordinated to one Sb. The C–C and C=N bond lengths are 1.472 and 1.277 Å (average), respectively.

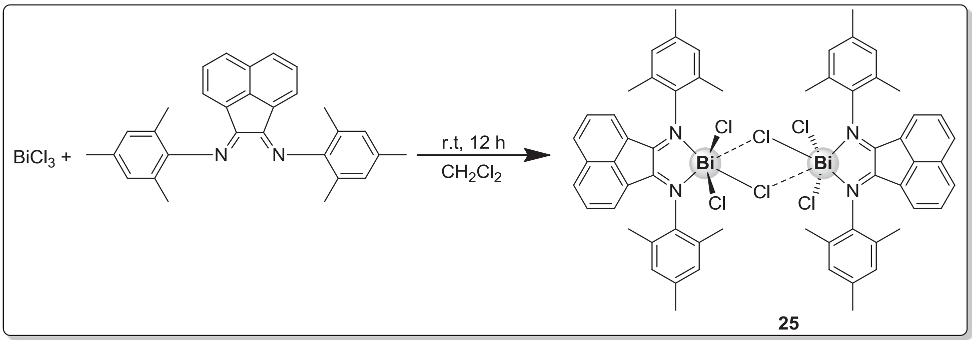
Cowley and co-workers in 2006, reported the synthesis and characterization of [(dipp-BIAN)$SbCl_3$] (**24**) and [(mes-BIAN)$BiCl_3$] (**25**) via schemes 22 and 23, respectively [60]. Arsenic, on the other hand, forms neither a dipp-BIAN nor a mes-BIAN complex. Complex **24** is monomeric, with Sb having distorted square pyramidal geometry around it



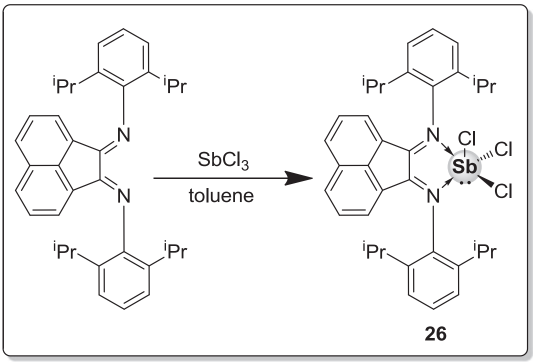
Scheme 21.



Scheme 22.



Scheme 23.



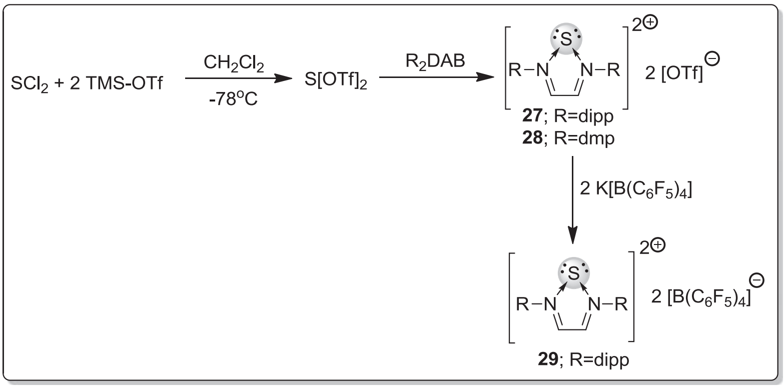
Scheme 24.

and the lone pair on Sb occupying one of the equatorial positions. In contrast, **25** forms a binuclear Bi complex in the solid state, the geometry around each Bi being best described as distorted octahedral. The bridged chlorides bound to Bi exhibit varying distances of 2.6976 and 3.0488 Å. The shorter distance is indicative of a covalent bond and the longer one is that of a coordinate bond. C–C bond lengths of 1.527 and 1.515 Å and C–N bond lengths of (1.266, 1.300 Å) and (2.606, 2.708 Å) in **24** and **25**, respectively, are evidence to the neutrality of the ligand moiety.

Fedushkin and co-workers reported the characterization of a dipp-BIAN complex of antimony, (dipp-BIAN)$SbCl_3$ (**26**) synthesized via scheme 24 [62]. With a C–C bond length of 1.524 Å and C–N bond lengths of 1.277 and 1.288 Å, it is clear that the ligand is neutral. The Sb has a distorted octahedral geometry around it, where the apical positions are taken by one $Cl^-$ and a lone pair. It is proposed that the large size of antimony and the bulky and rigid nature of the ligand framework give unprecedentedly small bite angle of 63°.

### 3.4. *Group 16 complexes*

In 2009, Ragogna and co-workers synthesized and characterized a series of sulfur-containing neutral diimine-chelated compounds [($dipp_2$DAB)S][OTf]$_2$ (**27**), [($dmp_2$DAB)S][OTf]$_2$ (**28**), and [($dipp_2$DAB)S][$B(C_6F_5)_4$] (**29**), according to scheme 25 [66].



Scheme 25.

As described in the above scheme, **27** and **28** were prepared starting from $SCl_2$ and via a subsequent anion-exchange reaction with $K[B(C_6F_5)_4]$, **29** was obtained. C–C and C–N bond lengths of **27** and **28** (average: 1.398 and 1.309 Å) are indicative of retention of the C–C single and C=N double bond characters of the bonds. As far as the central sulfur is concerned, there appears to be some interaction with the triflate through S–O(triflate) contacts in **27** and **28**. Complex **29**, on the other hand, shows no such significant interactions. The structures of the dications are pretty much the same. For all practical purposes, they can all be visualized as planar $C_2N_2S$ heterocycles.

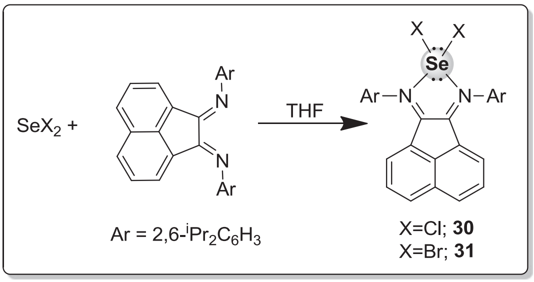
Dutton *et al.* in 2009 used the dipp-BIAN ligand to synthesize and characterize two $SeX_2$ complexes – dipp-BIANSeCl$_2$ (**30**) and dipp-BIANSeBr$_2$ (**31**) [67]. X-ray quality crystals could not be obtained for the corresponding dipp$_2$DAB analogs (scheme 26).

Structurally, **30** revealed a square planar geometry around Se(II); **31** was isostructural with **30**. Complexes **30** and **31**, exhibit C–C and C–N bond lengths (on an average) of 1.493 and 1.288 Å, clearly indicative of a neutral diimine backbone.

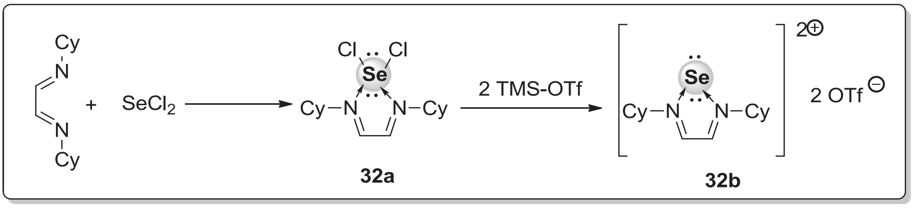
Dutton, Ragogna, and co-workers in 2010 obtained selenium complexes [(Cy$_2$DAB)SeCl$_2$] (**32a**) and [(Cy$_2$DAB)Se][OTf]$_2$ (**32b**) similar to the dicationic sulfur complex **27** [68]. Two diimine complexes (**32a** and **32b**) were synthesized and characterized according to scheme 27, of which only one (**32b**) was characterizable through single-crystal XRD studies.

Similar to **27** and **28**, there definitely exists cation–anion interaction via Se–O contacts of lengths 2.57 and 2.711 Å. C–N and C–C bond lengths of 1.30 and 1.42 Å, respectively, reflect the retention of the neutral diimine backbone.

Ragogna and co-workers have also used $^tBu_2DAB$ as the ligand in their investigations of complexes of Se and Te [69]. When DAB was reacted with $SeX_4$, a two-electron reduction



Scheme 26.



Scheme 27.

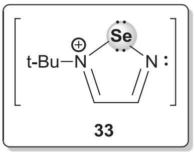


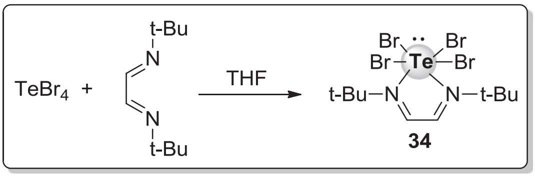
Figure 3.

along with elimination of ${}^tBuCl$ ensued. This gave a series of ionic compounds with **33** as the cation (see figure 3). Clearly, one Se–N bond is covalent while the other is dative.

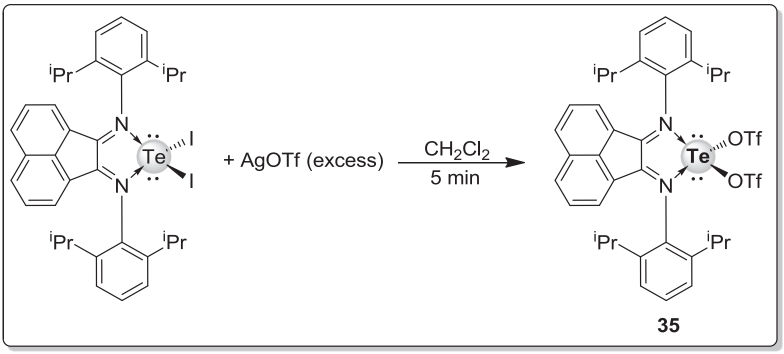
On the contrary, the reaction with $TeX_4$ proceeded without any such redox process. With $TeBr_4$, the DAB was intact, and formed an adduct, namely $TeBr_4 \cdot {}^tBu_2DAB$ (**34**) (see scheme 28**)**. The reaction with $TeCl_4$ was not productive, the adduct being unstable. However, when the reaction was carried out at −30 °C and the product immediately filtered, it was stable over a period of 24 h. A similar reaction with $TeI_4$ did not occur. The solid-state structure of **34** has a distorted octahedral geometry around Te with C–C and C–N(average) bond lengths of 1.442 and 1.277 Å, respectively, conforming to the neutrality and innocence of the diimine ligand.

In 2009, Ragogna and co-workers synthesized and characterized another tellurium diimine complex, chelated by dipp-BIAN, (dippBIAN)Te(OTf)$_2$ (**35**) [70]. Cowley and Reeske had previously reported the isolation and characterization of a similar complex, (dipp-BIAN)TeI$_2$ [71]. Using this as a template, **35** was obtained when (dipp-BIAN)TeI$_2$ was reacted with an excess of AgOTf (scheme 29).

The geometry of **35** can be described as a square planar arrangement of tellurium at the center, surrounded by oxygens (from triflate) and nitrogens (from BIAN). The average C–C



Scheme 28.



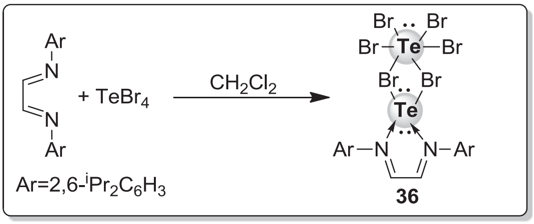
Scheme 29.

and C–N bond lengths in the BIAN moiety are 1.444 and 1.301 Å, respectively. As compared to the Te–N bonds in (dipp-BIAN)$TeI_2$, those in **35** are much shorter, This is in agreement with the stronger σ–donor ability of $I^-$ in comparison with $OTf^-$. Complex **35** readily reacts with four equivalents of 4-DMAP (4-dimethylaminopyridine) to replace all the dipp-BIAN.

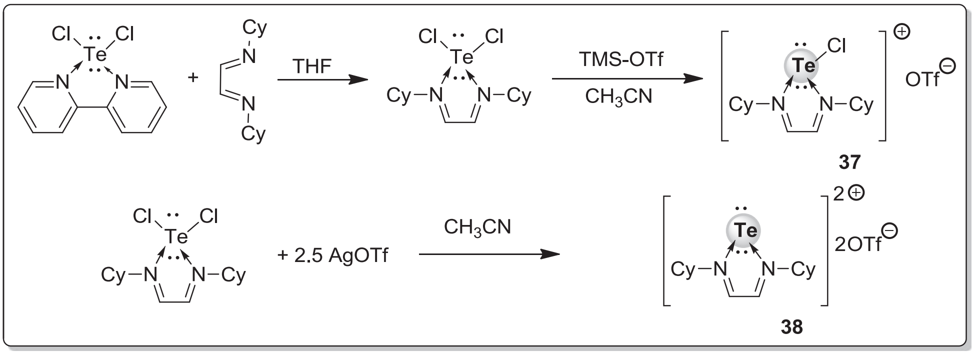
Ragogna and Dutton in 2010 reported the synthesis and characterization of three tellurium analogs of previously discussed group 16 complexes – ($dipp_2DAB$)$Te_2Br_6$ (**36**), [($Cy_2DAB$)TeCl][OTf] (**37**), and [($Cy_2DAB$)Te]$[OTf]_2$ (**38**) (refer schemes 30 and 31) [72]. Complex **36** contains a hexahalochalcogenide $[TeBr_6]^{2-}$ which is a ready source of halides, and to avoid this, another route was investigated via the use of a more stable and possible source of $TeCl_2$, namely bipy$TeCl_2$. The change from dipp to Cy was made in **37** and **38** because there was no reaction when $dipp_2DAB$ was used in this modification. Once ($Cy_2DAB$)$TeCl_2$ (a compound very similar to **32a**) was formed, halide abstraction reagents TMS-OTf (weaker) and AgOTf (stronger) were used to generate triflate complexes **37** (monohalo) and **38** (all halogens abstracted). These complexes were used further to synthesize Te(IV) carbene analogs.

Structurally, **36** has a square planar arrangement around Te. Te–N distances indicate a weaker interaction between the two atoms. The [(DAB)$TeBr_2$] acts as a Lewis base to bind to $TeBr_4$.

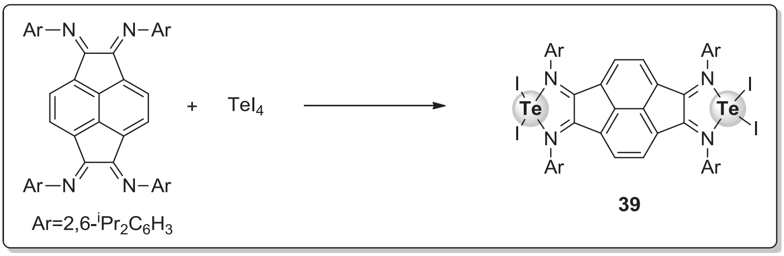
Complex **37** has a T-shaped orientation around Te. This complex has one Cl bonded to Te, the Te–N bond trans to which is longer (2.152 Å) than the other (2.090 Å). Unlike **37**, **38** exhibits short Te–O contacts to the triflate anion (average 2.57 Å), longer than normal



Scheme 30.



Scheme 31.



Scheme 32.

Te–O single bonds (1.95 Å). Complexes **36**, **37**, and **38** all exhibit C–C bond length (average) of 1.434 Å and C–N bond length (average) of 1.288 Å, consistent with neutrality of the diimine ligand when coordinated to group 16 elements.

The reaction of $TeI_4$ with dipp-TIP ligand leads to the formation of $[(TeI_2)_2$(dipp-TIP)] (**39**) [73]. The C–C and C–N bond lengths of 1.51 and 1.28 Å are indicative of single and double bonds, respectively. This reaction presents an interesting case where the main group element, tellurium, gets reduced and the diimine ligand retains its electronic character after the reaction (scheme 32).

## 4. Conclusion

α-Diimine ligands bind to the s- and p-block elements leading to a variety of reactivity patterns. Diimine ligands, in certain cases, get readily reduced in s- and p-block chemistry. Fluxionality of neutral diimine complexes has been observed in solution. A switch between a paramagnetic and a diamagnetic species has been observed in the case of germanium compounds with variation in temperature [62]. Main group analogs of N-heterocyclic carbenes, N-heterocyclic silylenes, and phosphenium cations have been synthesized [57, 58, 65, 66, 70, 72], and there is scope for progress in these fields in the near future. α-Diimine complexes also have played a significant role in catalysis, especially of polymerization reactions [74]. Future work can be directed toward exploiting the redox properties of diimine complexes in organic transformations.

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