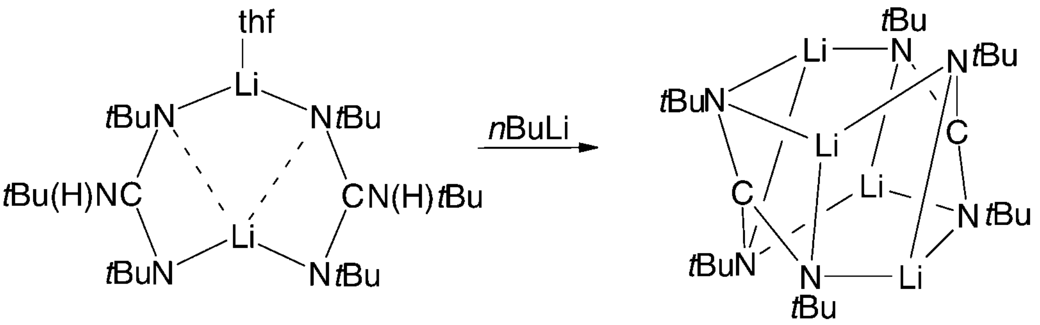
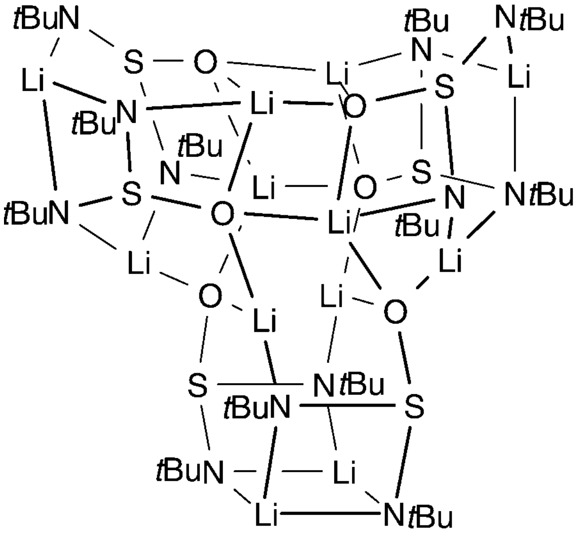
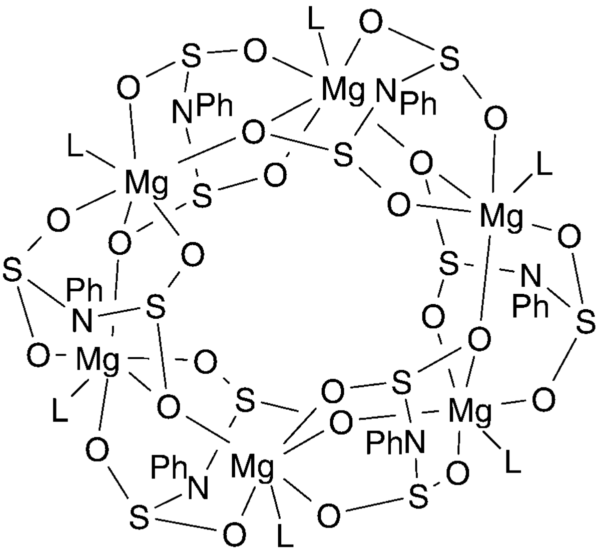
Imido Anions

Synthesis



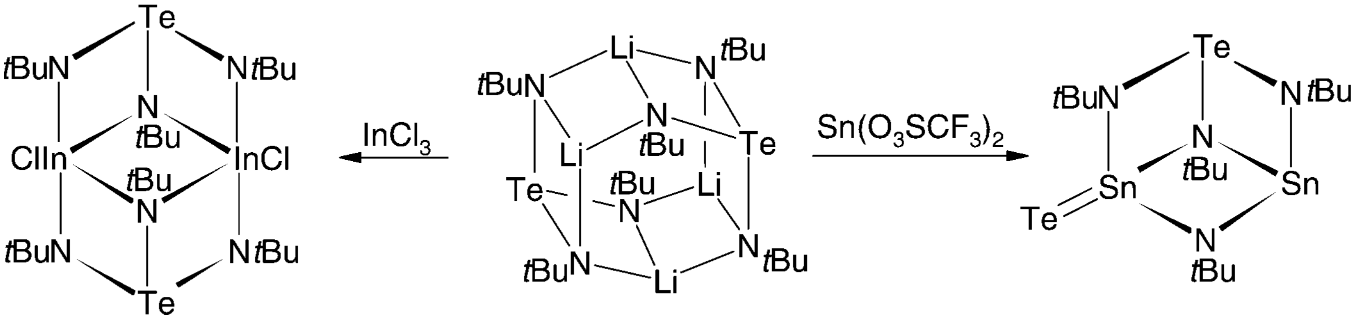
Structures





(L = thf)

Ligand Behavior



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Imido Analogues of Common Oxo Anions: A New Episode in the Chemistry of Cluster Compounds

Justin K. Brask and Tristram Chivers*

Oxo anions of p- and d-block elements, for example, SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, and CrO_4^{2-}, are commonly encountered species. The full or partial replacement of the oxo ligands by isoelectronic imido (NR) groups generates homoleptic polyimido anions of the type $[E(NR)_x]^{z-}$ or heteroleptic imidooxo anions with the general formula $[O_yE(NR)_{x-y}]^{z-}$ (where E = main group element or transition metal). The alkali metal derivatives of this new class of anions form ternary or quaternary cluster systems, respectively. The structures of these clusters can be rationalized in terms of the self-assembly of fundamental building blocks. An understanding of the factors that control this process may allow the design of functional materials with specific properties. In addition, these anions are attracting attention as multidentate ligands with unique electronic and stereochemical properties that may engender novel metal-centered chemistry.

Keywords: cluster compounds · coordination chemistry · isoelectronic analogues · main group elements · transition metals

1. Introduction

The “isoelectronic principle”, first espoused by Langmuir,[1] is a simple and useful concept, especially in inorganic chemistry. It is frequently invoked in the application of Valence Shell Electron Pair Repulsion Theory for the prediction of the shapes of molecules with a central p-block element. The polyhedral skeletal electron-pair counting (Wade’s) rules,[2] which are so successful in predicting the structures of electron-deficient main group element and transition metal clusters,[3] also rely on this idea. For the synthetic chemist the first preparation of an unknown compound has often been prompted by the existence of an isoelectronic analogue. Furthermore, many isoelectronic species undergo analogous reactions.

The NR (R = H, alkyl, aryl) group is isoelectronic with an oxo (O) ligand, but the organic substituent in the former gives rise to significant differences in the properties of isoelectronic analogues. For example, CO_2 and $C(NR)_2$ are both multiply bonded monomers, but carbon dioxide is a gas whereas *N*,*N*′-dialkyl carbodiimides are liquids. More dramatically, tellurium dioxide $(TeO_2)_\infty$ is a three-dimensional polymer[4] while the tellurium diimide $t\text{BuNTe}(\mu\text{-N}t\text{Bu})_2\text{TeN}t\text{Bu}$ is dimeric.[5] The imido ligand is a versatile cornerstone for the construction of cluster molecules as exemplified by the iminoalanes $(RAlNR')_n$ which may adopt cubane ($n = 4$), hexagonal prismatic ($n = 6$), or larger structures ($n = 7, 8$) depending on the steric requirements of the R and R′ groups.[6] Interestingly, the industrially important alkylalumoxanes $(RAlO)_n$, isoelectronic with iminoalanes, form larger clusters such as a nonamer (R = *t*Bu).[7a,b] Moreover, recent density functional theory (DFT) calculations indicate that a dodecamer (R = Me, $n = 12$), formed by the dimerization of two hexagonal prisms, is the most stable oligomer.[7c]

Oxo anions of the general formula $[EO_x]^{z-}$ (E = p- or d-block element) are frequently encountered species in all areas of chemistry and, indeed, in everyday life. The full or partial replacement of the oxo ligands by imido groups leads to a new class of anions, that is, polyimido anions of the type $[E(NR)_x]^{z-}$ or imidooxo anions with the general formula $[O_yE(NR)_{x-y}]^{z-}$. As a further extension, the oxo ligands in the heteroleptic systems can be replaced by S or Se substituents.

The first homoleptic polyimido anions of p- or d-block elements, $[S(NH)_4]^{2-}$ and $[Te(NH)_3]^{2-}$, were obtained as their dipotassium salts more than thirty years ago, but characterization was limited to elemental analyses.[8] More recently the lithium derivatives of $[P(NMes^*)_2]^-$[9] (Mes* = 1,3,5-

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$tBu_3C_6H_2$) and $[Si(NtBu)_3]^{2-}$[10] were reported by the groups of Lappert and Veith, respectively, but structural information was lacking. In 1989 Wilkinson et al. described the first structural determination for this novel class of cluster compounds.[11] The core of the dimeric d-block element complex $[Li_2\{W(NtBu)_4\}]_2$ was shown to consist of an $Li_4W_2N_6$ hexagonal prism.[11] In the last decade these ternary cluster systems, and the related quaternary systems formed by alkali metal derivatives of imidooxo anions of p-block elements, have been extensively investigated. Their structures can be understood in terms of the self-assembly of fundamental building blocks. In addition to this structural interest, the anions themselves are attracting attention as multidentate ligands with novel electronic and geometric properties. Curiously, although neutral imido transition metal complexes have been widely studied,[12] the polyimido anions of p-block elements have attracted more attention than their d-block counterparts, as illustrated by the examples given in Tables 1 and 2. This review begins with a discussion of synthetic approaches to these anionic species. Subsequently, the focus is on the structural principles involved in cluster formation and the behavior of the anions as coordinating ligands. Selected aspects of the chemistry of polyimido anions of Group 15 and 16 elements have been reviewed previously.[13, 14]

2. Synthetic Strategies

A variety of methodologies have been employed for the synthesis of polyimido and imidooxo systems. However, three general strategies have emerged as the most versatile: a) deprotonation of amido complexes, b) transamination reactions, and c) nucleophilic addition. Examples of the advantages and limitations of each of these approaches will be discussed in this section.

2.1. Metallation of Primary Amido Complexes

The metallation of compounds with primary amido groups, NHR (R = alkyl or aryl), is perhaps the most obvious route to polyimido anions of p- or d-block elements. Indeed the monolithiation of Mes*N=P(NHMes*) with *n*BuLi represents the first preparation of a well-defined complex containing a polyimido anion [Eq. (a), Mes* = 1,3,5-$tBu_3C_6H_2$].[9] The related complexes $[(L)Li\{P(NR)(NR')\}]_n$ (R = Mes*, R′ = CPh_3, L = Et_2O, $n = 1$;[19] R = Mes*, R′ = *t*Bu or 1-adamantyl

$$n\text{BuLi} + \text{Mes*N=P(NHMes*)} \longrightarrow \text{LiP(NMes*)}_2 + n\text{BuH} \qquad \text{(a)}$$

(1-Ad), $n = 2$;[19] R = R′ = *t*Bu, L = thf, $n = 2$[20]) and $[(thf)_2Mg\{P(NtBu)_2\}_2]$ (generated by magnesiation with $MgBu_2$),[20] which also contain examples of bisimidophosphorus(III) monoanions, were subsequently prepared in a similar manner. Interestingly the order of addition of the reagents sometimes affects the outcome of these lithiation reactions. Thus the addition of the amidoimido compound $tBuNHP(\mu\text{-}NtBu)_2PNHtBu$ to the alkyllithium reagent produces the unsolvated tetramer $[Li\{P(NtBu)_2\}]_4$ whereas the reverse addition yields the adduct $[Li\{P(NtBu)_2\}]_4 \cdot 0.25\,P_4(NtBu)_6$.[21]

Polyimido analogues of the metaphosphate ion, PO_3^-, have also been prepared from the corresponding amido compounds. Thus lithiation of $(Mes^*N)_2P(NHMes^*)$ with *n*BuLi in THF produces the ion pair $[(thf)_4Li][P(NMes^*)_3]$, which

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Justin Kirkegaard Brask was born in Aarhus, Denmark in 1973 and moved to Banff, Canada in 1977. He graduated with first class honours in Chemistry (with a minor in Pure Mathematics) from the University of Calgary, Canada, in 1996. He obtained his Ph.D. from the same university in 2000 under the supervision of Professor T. Chivers in the area of main group element chemistry. Dr. Brask is currently an NSERC (Canada) post-doctoral fellow at the Massachusetts Institute of Technology, Cambridge, USA, in the group of Professor C. C. Cummins working with highly reactive early transition metal complexes.

Table 1. Polyimido and imido/oxo(chalcogenido) anions of p-block elements.

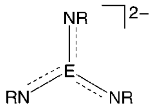
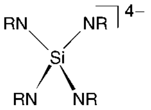
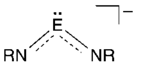
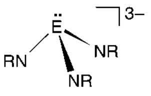
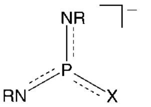
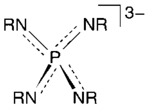
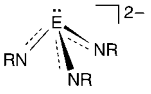
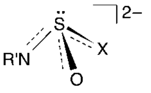
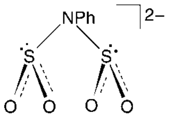
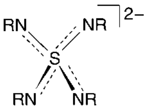
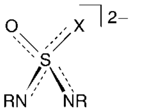
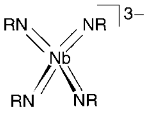
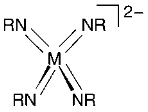
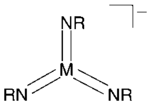
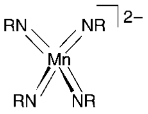
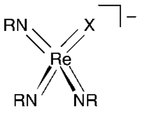
Periodic group	Polyimido or imido/ oxo(chalcogenido) ion	Related oxo anion	E or X
14		carbonate, CO_3^{2-} metasilicate, SiO_3^{2-}	C[15, 16] Si[10]
14		orthosilicate, SiO_4^{4-}	[17]
15		nitrite series, EO_2^-	N[18] P[9, 19–21] As[22, 23] Sb[24, 25] Bi[25]
15		arsenite, AsO_3^{3-} stibinite, SbO_3^{3-}	As[26] Sb[27]
15		metaphosphate, PO_3^-	NR[28] S[29] Se[29]
15		phosphate, PO_4^{3-}	[30]
16		sulfite, SO_3^{2-} selenite, SeO_3^{2-} tellurite, TeO_3^{2-}	S[31] Se[32] Te[33]
16		sulfite, SO_3^{2-}	NR[34, 35] O[36]
16		disulfite, $S_2O_5^{2-}$	[35]
16		sulfate, SO_4^{2-}	[37]
16		sulfate, SO_4^{2-}	NR[38] O[39]

Table 2. Polyimido and imidooxo anions of d-block elements.

Periodic group	Transition metal polyimido anion	Related oxo anion	M or X
5		niobate, NbO_4^{3-}	[40]
6		chromate, CrO_4^{2-} molybdate, MoO_4^{2-} tungstate, WO_4^{2-}	Cr[41] Mo[42] W[11, 42]
7		unknown	Tc[43] Re[44]
7		manganate, MnO_4^{2-}	[45]
7		perrhenate, ReO_4^-	NR[11, 46] O[44]

contains the homoleptic ion $[P(NMes^*)_3]^-$.[28] Similarly, the isoelectronic imidothio and imidoselena ions $[SP(NtBu)_2]^-$ and $[SeP(NtBu)_2]^-$, respectively, are generated as the dimers $[(thf)_2Na\{EP(NtBu)_2\}]_2$ and polymers $[(thf)_xK\{EP(NtBu)_2\}]_\infty$ ($E = S$, $x = 1$; $E = Se$, $x = 1.5$) by metallation of $(tBuNH)(E)P(\mu\text{-}NtBu)_2P(E)(NHtBu)$ ($E = S$, Se) with two equivalents of $MN(SiMe_3)_2$ ($M = Na$ or K).[29]

Lithiation is also effective for the preparation of polyimido anions of Group 14 elements. The trisimidocarbonate and trisimidometasilicate complexes $[(thf)_3Li_2\{C(NPh)_3\}]_2$[15] and $[Li_2\{Si(NtBu)_3\}]_n$[10] are formed by treatment of $PhN{=}C(NHPh)_2$ or $(tBuNH)_2Si(\mu\text{-}NtBu)_2Si(NHtBu)_2$, respectively, with *n*-butyl- or methyllithium in the appropriate molar ratios. The resulting dianions $[E(NR)_3]^{2-}$ ($E = C$, Si) are isoelectronic with the common oxo anions CO_3^{2-} and SiO_3^{2-}, respectively.

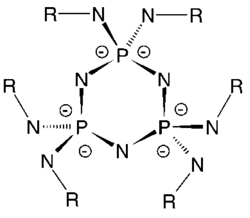
Most of the known polyimido anions of d-block elements (Table 2) have been obtained by the lithiation method. The dilithium derivatives of the homologous series of tetrahedral Group 6 ions $[M(NtBu)_4]^{2-}$ ($M = Cr$, Mo, W) are produced by lithiation of $(tBuN)_2M(NHtBu)_2$ [Eq. (b)].[11, 41, 42] The isoelectronic tetrakisimidoperrhenate ion is similarly prepared as the complex $[(tmeda)Li\{Re(NtBu)_4\}]$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethyl 1,2-ethanediamine) from $(tBuN)_3Re(NHtBu)$.[11, 46] Treatment of the monoamido species $[(thf)_2Li]_2[Nb(NMes)_3(NHMes)]$ with one equivalent of *t*BuLi generates the trilithium complex $[(thf)_4Li_3\{Nb(NMes)_4\}]$.[40]

$$4\,MeLi + 2\,(tBuN)_2M(NHtBu)_2 \longrightarrow [Li_2\{M(NtBu)_4\}]_2 + 4\,CH_4 \tag{b}$$

The strategy of deprotonating amido complexes has also proven fruitful for studies of imidooxo systems. In particular, the sulfamides $O_2S(NHR)_2$ ($R = i$Pr, *t*Bu) have been utilized as precursors to bisimidosulfate ions, for example, the complexes $[Li_2\{O_2S(NiPr)_2\}]_n$ and $[(thf)Li_2\{O_2S(NtBu)_2\}]_n$ are prepared by dilithiation reactions with *n*-butyllithium.[39b] On the other hand, magnesiation of $O_2S(NHtBu)_2$ with one equivalent of dibutylmagnesium is incomplete, yielding the amidoimidosulfate complex $[(tmeda)Mg\{O_2S(NtBu)(NHtBu)\}_2]$. The mixed-metal species $[(thf)_4Li_4Mg\{O_2S(NtBu)_2\}_3]_2$ is obtained upon further deprotonation of this complex with *n*BuLi in THF [Eq. (c)].[39a]

$$\begin{aligned} &8\,nBuLi + 4\,[(tmeda)Mg\{O_2S(NtBu)(NHtBu)\}_2] \longrightarrow \\ &\underbrace{[(thf)_4Li_4Mg\{O_2S(NtBu)_2\}_3]_2}_{\mathbf{35}} + {}^{2}\!/_{n}[Mg\{O_2S(NtBu)_2\}]_n + 8\,nBuH + 4\,TMEDA \end{aligned} \tag{c}$$

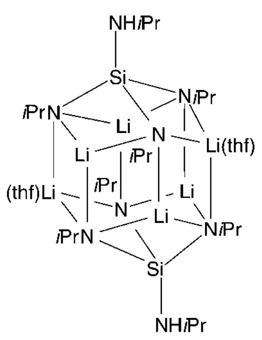
Polylithiation is successful for generating the hexakisimido-*c*-triphosphazene hexaanion $[NP(NCy)_2]_3^{6-}$ (**1**), by treatment of the corresponding amido derivative $[NP(NHCy)_2]_3$ with six



1 (R = Cy)

equivalents of *n*BuLi in TMEDA/toluene.[47] The dimeric complex $[(\mathrm{thf})_2\mathrm{Li}_6\{\mathrm{NP(NCy)_2}\}_3]_2$ is obtained upon recrystallization from THF/hexane.[47] However, the putative intermediate trianion $[\mathrm{NP(NCy)(NHCy)}]_3{}^{3-}$ can only be isolated by treatment of $[\mathrm{Li}_6\{\mathrm{NP(NCy)_2}\}_3]_2$ with three equivalents of *n*BuOH and not by trilithiation of $[\mathrm{NP\{NHCy\}_2}]_3$ with *n*BuLi.[48]

In many cases, however, polylithiation of amido compounds is incomplete. For example, the reaction of Si(NH*i*Pr)$_4$ with an excess of *n*BuLi yields the dimeric trilithiated complex [(thf)Li$_3$\{Si(N*i*Pr)$_3$(NH*i*Pr)\}]$_2$ (**2**).[17] For amido derivatives of Group 13 elements incomplete lithiation is accompanied by fascinating, unanticipated consequences. For example, the attempted trilithiation of the trisaminoborane B(NH*t*Bu)$_3$ with alkyllithium reagents yields dilithium boraamidinates **3** [Eq. (d)] rather than the trisimidoorthoborate ion [B(N*t*Bu)$_3$]$^{3-}$.[49] In effect the organolithium reagent behaves



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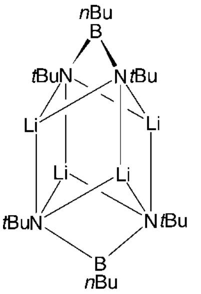
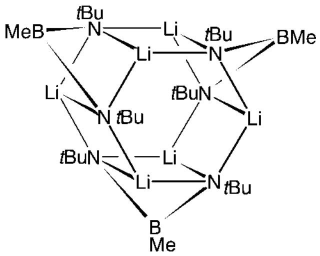


3a



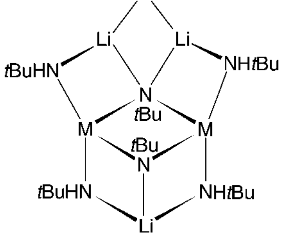
3b

$$3\,\mathrm{LiR} + \mathrm{B(NH}t\mathrm{Bu)_3} \longrightarrow \underset{\mathbf{3}}{\frac{1}{n}[\mathrm{Li_2\{RB(N}t\mathrm{Bu)_2\}}]_n} + \mathrm{LiNH}t\mathrm{Bu} + 2\,\mathrm{HR} \tag{d}$$

as a nucleophile, displacing a *tert*-butylamino group from boron, as well as a deprotonating agent. Similar behavior has been reported for an amido–niobium system [Eq. (e) Mes = 2,4,6-trimethylphenyl].[50] Alkyl or aryl boraamidinates have previously been prepared by the dilithiation of diaminoboranes RB(NHR′)$_2$,[51] but the new route to these boron analogues of amidinates avoids the need to prepare alkylboron dihalides.

$$n\mathrm{BuLi} + [\{(\mathrm{thf})_2\mathrm{Li}\}_2\{\mathrm{Nb(NMes)_3(NHMes)}\}] \longrightarrow [\{(\mathrm{thf})_2\mathrm{Li}\}_2\{(n\mathrm{Bu})\mathrm{Nb(NMes)_3}\}] + \mathrm{LiNHMes} \tag{e}$$

The trisalkylamido complexes of heavier Group 13 elements [M(NH*t*Bu)$_3$]$_2$ (M = Al, Ga) are dimeric. For these cases, partially lithiated complexes act as a template for the entrapment of monomeric or dimeric alkyllithium or lithium alkylamide fragments.[52] Thus treatment of [Al(NH*t*Bu)$_3$]$_2$ with an excess of *n*-butyl-, *tert*-butyl-, or methyllithium results in formation of the adducts [Li$_3$\{Al$_2$(N*t*Bu)$_3$(NH*t*Bu)$_3$\}] · (*n*BuLi)$_2$,[52a] [Li\{Al(N*t*Bu)(NH*t*Bu)$_2$\}]$_2$ · *t*BuLi (**4**), or [Li\{Al(N*t*Bu)(NH*t*Bu)$_2$\}]$_2$ · LiNH*t*Bu (**5**),[52b] respectively. The related gallium complex [Li\{Ga(N*t*Bu)(NH*t*Bu)$_2$\}]$_2$ · LiNH*t*Bu (**6**), generated by reaction of [Ga(NH*t*Bu)$_3$]$_2$ with three equivalents of *t*BuLi, has also been prepared.[52b] The unsolvated forms of *n*BuLi and lithium *tert*-butylamide are hexameric and octameric, respectively, in the solid state.[53, 54]



4, M = Al, R = *t*Bu
5, M = Al, R = NH*t*Bu
6, M = Ga, R = NH*t*Bu

2.2. Transamination Reactions

Wright and co-workers have demonstrated the versatility of transamination reactions for preparing homoleptic polyimido anions of Group 15 elements.[22–25, 26a, 27] This approach employs the reagents E(NMe$_2$)$_3$ (E = As, Sb, Bi) in reactions with primary amines and/or s-block metal amides.

Unsolvated complexes containing trisimido analogues of arsenite and stibinite, that is, [E(N*t*Bu)$_3$]$^{3-}$ (E = As or Sb, respectively), are produced in good yields in hexane as shown in Equation (f).[26a, 27b] The solvated dimers [(thf)Li$_3$\{Sb(NR)$_3$\}]$_2$ (R = CH$_2$CH$_2$Ph or 2,4-(MeO)$_2$C$_6$H$_3$) are obtained if THF is used as the reaction solvent.[27] Interestingly, in the complex [(Me$_2$NH)Li$_3$\{Sb(NCy)$_3$\}]$_2$ (Cy = cyclohexyl) two of the ligands are HNMe$_2$ molecules generated by transamination.[27b] By contrast, treatment of E(NMe$_2$)$_3$ with a 1:1 mixture of cyclohexylamine and MNHCy (M = Li, Na) gives s-block metal derivatives of the ions [E(NCy)$_2$]$^-$ (E = As, Sb) [Eq. (g)],[22–24] isoelectronic with oxo anions from the

$$2\,\mathrm{E(NMe_2)_3} + 6\,\mathrm{LiNH}t\mathrm{Bu} \longrightarrow [\mathrm{Li_3\{E(N}t\mathrm{Bu)_3\}}]_2 + 6\,\mathrm{HNMe_2} \tag{f}$$

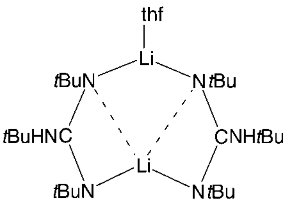
nitrite series (Table 1). The heavier congener $[Bi(NtBu)_2]^-$, prepared in a similar manner, is obtained as the THF-solvated dimer $[(thf)Li\{Bi(NtBu)_2\}]_2$.[25]

$$4\,E(NMe_2)_3 + 4\,H_2NCy + 4\,MNHCy \longrightarrow [M\{E(NCy)_2\}]_4 + 12\,HNMe_2 \tag{g}$$

2.3. Nucleophilic Addition

Nucleophilic addition of primary amidolithium reagents to heteroallenes (or their Group 16 analogues), followed by deprotonation, represents a versatile route to homoleptic polyimido and heteroleptic imidooxo anions of Group 14 and Group 16 elements. For example, the trisimidotellurite complex $[Li_2\{Te(NtBu)_3\}]_2$ is prepared by reaction of the dimeric tellurium(IV) diimide $tBuNTe(\mu\text{-}NtBu)_2TeNtBu$ and four equivalents of LiNH*t*Bu, a reaction in which the lithium reagent behaves both as a nucleophile and as a base [Eq. (h)].[33a] The lighter congeners, $[E(NtBu)_3]^{2-}$ (E = S, Se), can be obtained analogously from the corresponding monomeric diimides $E(NtBu)_2$.[31, 32] This method may also be used for the preparation of the tetrakisimidosulfate ion $[S(NtBu)_4]^{2-}$ by reaction of the sulfur(VI) triimide $S(NtBu)_3$ with two equivalents of LiNH*t*Bu.[37] The analogous reaction of *N,N'*-di-*tert*-butylcarbodiimide with LiNH*t*Bu yields the amidoimido complex $[(thf)Li_2\{C(NtBu)_2(NHtBu)\}_2]$ (**7**). In this case, the stronger base *n*BuLi is necessary for the deprotonation step to give the trisimidocarbonate ion [Eq. (i)].[16]

$$4\,LiNHtBu + tBuNTe(\mu\text{-}NtBu)_2TeNtBu \longrightarrow [Li_2\{Te(NtBu)_3\}]_2 + 2\,H_2NtBu \tag{h}$$



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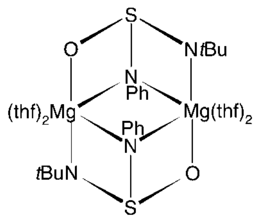
$$2\,nBuLi + \underset{\mathbf{7}}{[(thf)Li_2\{C(NtBu)_2(NHtBu)\}_2]} \longrightarrow [Li_2\{C(NtBu)_3\}]_2 + 2\,nBuH + THF \tag{i}$$

This method is readily applicable to the preparation of heteroleptic imidooxo anions. For example, treatment of the sulfinylimines RNSO (R = *t*Bu, Me_3Si) or sulfur dioxide with two equivalents of LiNH*t*Bu leads to lithium complexes of the imidooxo sulfite ions $[OS(NtBu)(NR)]^{2-[34]}$ or $[O_2S(NtBu)]^{2-}$,[36] respectively [Eq. (j), $x = 1$: R = *t*Bu, $SiMe_3$, $n = 6$; $x = 2$: n is not known].

$$2\,LiNHtBu + O_xS(NR)_{2-x} \longrightarrow \frac{1}{n}[Li_2\{O_xS(NtBu)(NR)_{2-x}\}]_n + H_2NtBu \tag{j}$$

The reagent $[(thf)Mg(NPh)]_6$[55] has also been employed as an imide-transfer agent in nucleophilic addition reactions. The deck-chair cluster $[(thf)_2Mg\{OS(NtBu)(NPh)\}]_2$ (**8**) is prepared by treating $[(thf)Mg(NPh)]_6$ with *t*BuNSO in THF.[35] In a notable application of this approach the Mg^{2+} derivative of the novel imidodisulfite ion $[PhN(SO_2)_2]^{2-}$ is generated by reaction of $[(thf)Mg(NPh)]_6$ with SO_2 [Eq. (k)], which provides the first example of the double insertion of sulfur dioxide into a single functional group.[35]



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$$[(thf)Mg(NPh)]_6 + 12\,SO_2 \longrightarrow [(thf)Mg\{O_2S(\mu\text{-}NPh)SO_2\}]_6 \tag{k}$$

2.4. Miscellaneous Methods

The synthetic approaches outlined in Sections 2.1 – 2.3 account for the preparation of the majority of known polyimido or imidooxo anions of p-block elements and transition metals. However, several important species have been generated in other ways.

The dilithium imide $Li_2(Nnaph)$ (naph = α-naphthyl)[56] can be utilized as a source of the $[(Et_2O)Li(Nnaph)]^-$ ion to provide the tetralithium derivative of a tetrakisimidoorthosilicate ion $[Si(Nnaph)_4]^{4-}$ [Eq. (l)].[17] The isoelectronic $[P(Nnaph)_4]^{3-}$ ion is obtained as the ion-pair complex $[(thf)_4Li][(thf)_4Li_2\{P(Nnaph)_4\}]$ by the curious reaction of P_2I_4 with α-naphthylamine in THF/NEt_3, followed by the addition of *n*-BuLi.[30] The complex $[Li_2PH(NR)_3]_2$ (R = 2-C_6H_4OMe), which contains an imido analogue of the phosphite ion $[HPO_3]^{2-}$, is formed from the reaction of PCl_3 with three equivalents of 2-$MeOC_6H_4NH_2$ and subsequent treatment with *n*-BuLi.[57]

$$4\,Li_2(Nnaph) + SiCl_4 + 4\,Et_2O \longrightarrow [(Et_2O)Li]_4[Si(Nnaph)_4] + 4\,LiCl \tag{l}$$

Polyimido anions of Group 7 metals have been prepared by reduction of trisimido metal(VII) halides. The tetrahedral Mn^{VI} ion $[Mn(NtBu)_4]^{2-}$ is obtained by treatment of $(tBuN)_3MnCl$ with five equivalents of LiNH*t*Bu in DME.[45] The trisimido M^V monoanions $[M(NDipp)_3]^-$ (M = Tc, Re, Dipp = 2,6-diisopropylphenyl) are generated by reduction of such halide complexes with sodium metal or sodium amalgam, [Eq. (m)].[43, 44] Treatment of $[(thf)_2Na\{Re(NDipp)_3\}]_n$, obtained in this way, with an equimolar amount of Me_3NO in the presence of Et_4NCl yields the ion-pair complex $(Et_4N)[ORe(NDipp)_3]$.[44] The trisimidoperrhenate ion $[ORe(NDipp)_3]^-$ is a rare example of a transition metal centered imido oxo anion.

$$[(DippN)_3ReCl] + 2\,Na/Hg + 2\,THF \longrightarrow \frac{1}{n}[(thf)_2Na\{Re(NDipp)_3\}]_n + NaCl + 2\,Hg \tag{m}$$

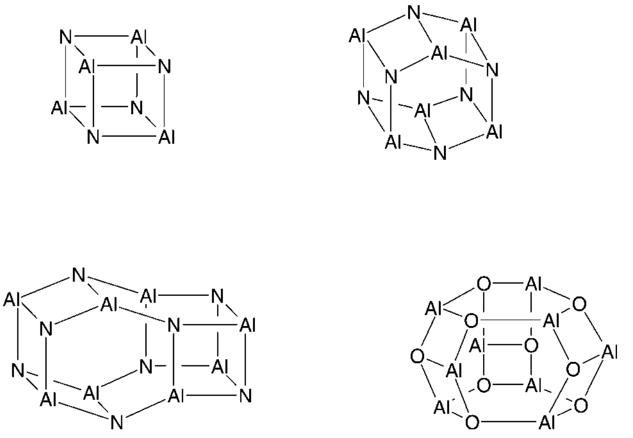
A potentially more versatile route to heteroleptic systems involves the direct replacement of an oxo ligand in an oxo anion by an imido (NR) group. An elegant example of this methodology, the reaction of the polyoxometallate $[NBu_4]_2[Mo_6O_{19}]$ with organic isocyanates RNCO to generate anions of the type $[Mo_6O_{19-x}(NR)_x]^{2-}$ ($x = 1-5$), was reported recently.[58a] An interesting development of this approach involves the incorporation of the styrylimido ligand into a polyoxometallate by the reaction of $(NBu_4)_2[Mo_6O_{19}]$ with $Ph_3P{=}NC_6H_4CH{=}CH_2$.[58b] The complex $(NBu_4)_2[Mo_6O_{18}(NC_6H_4CH{=}CH_2)]$ was copolymerized with 4-methyl-styrene.[58b] The formation of imido derivatives of polyoxometallates from the reaction of $[Mo_6O_{19}]^{2-}$ with aromatic amines is generally facilitated by dicyclohexylcarbodiimide.[58c]

3. Solid-State Structures

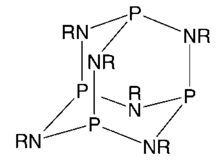
The determination of the solid-state structures of many organolithium and lithium amide reagents by X-ray crystallography has given rise to a rationalization of cluster formation in terms of a so-called laddering principle.[59, 60] A conspicuous feature of such compounds is their tendency to form oligomeric units in the solid state. Ring laddering and, hence, cluster formation is facilitated by incorporation of the Li^+ ions, which leads to the aggregation of *contact* ion pairs (ladder rungs). Although the Li–C bond is essentially ionic in character, multicenter (electron-deficient) bonding occurs in organolithium compounds as a result of the strongly polarizing nature of the Li^+ ion.[61] The formation and subsequent aggregation of Li–N (for example, lithium amides) and Li–O units can be attributed to this phenomenon as well. Although coordination of Li^+ ions by donor solvents usually inhibits aggregation, a recent investigation of lithium thioamidates shows that solvation of lithium may actually promote polymer formation.[62] The steric requirements of the alkyl or aryl substituents on the nitrogen atoms also play a significant role in dictating the cluster structure.[59] These concepts are also applicable to the cluster structures adopted by alkali metal derivatives of polyimido and imidooxo anions of p- and d-block elements.

3.1 Cluster Structures of Imido Derivatives of p-Block Elements

The versatility of the imido ligand as a component of cluster compounds is exemplified by the variety of iminoalanes, $(R'AlNR)_n$, which may adopt cubic, hexagonal prismatic, or larger arrangements depending on the steric requirements of the R and R′ substituents (Scheme 1).[6] The isoelectronic oxoalanes $(RAlO)_n$ may also adopt larger cluster structures, for example, the 18-atom cluster $(t\mathrm{Bu}AlO)_9$ (Scheme 1).[7] The RN^{2-} ligand is also a well-established feature of Group 14 and 15 element clusters. Complexes of the type $(MNt\mathrm{Bu})_4$ (M = Ge, Sn, Pb) form cubanes,[63] while two isomers of the polycyclic P^{III} imides $P_4(NR)_6$ are known: an adamantane-type cluster (**9a**, R = Me, Et, *i*Pr)[64] and a tetracycle (**9b**, R = *i*Pr, *t*Bu),[21, 65] which contains two four-membered P_2N_2 rings doubly bridged by NR groups. The 24-membered arylimido metallacycles $Sb_{12}(NAr)_{18}$ (**10**, Ar = 2-OMe C_6H_4,[66a] Ph[66b]) represent a particularly fascinating example of the adaptability of the imido ligand.



Scheme 1. Fundamental building blocks of imino- and oxoalanes, $(RAlNR')_n$ and $(RAlO)_n$. The R groups attached to Al and N are omitted for clarity.



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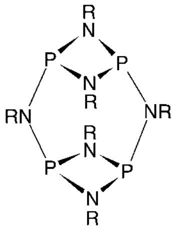

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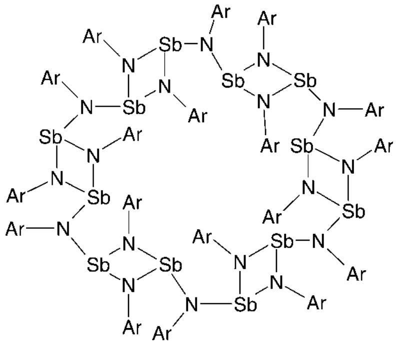

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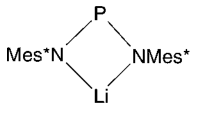
3.2. s-Block Metal Complexes of Polyimido Anions

Like the imido complexes of alkali and alkaline earth metals, for example, $[(thf)Mg(NR)]_6$ (R = Ph, naph)[55] and $[(Et_2O)_3Li_{10}(Nnaph)_5]_2$,[56] the s-block metal derivatives of homoleptic polyimido anions tend to form oligomers in the solid state. Such arrangements maximize electrostatic interactions between the polar $RN^- - M^+$ units. The influence of solvation and the nature of the nitrogen R group on the formation of cluster structures by ternary and quaternary systems involving alkali metal derivatives of polyimido or imidooxo anions of p- or d-block elements is considered in the following sections.

3.2.1. *Fundamental Building Blocks*

The effect of the steric bulk of the NR group is illustrated dramatically by the structures of P^{III} systems of the type

$[Li\{P(NR)(NR')\}]_n$. The monomeric structure **11** is found for R = R′ = Mes*.[21] Replacement of one of the Mes* groups by a *t*Bu or 1-Ad group results in dimerization to give the eight-membered rings **12**.[19] When R = R′ = *t*Bu the unsolvated



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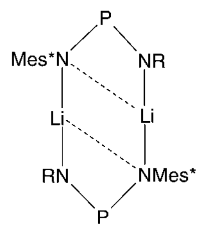
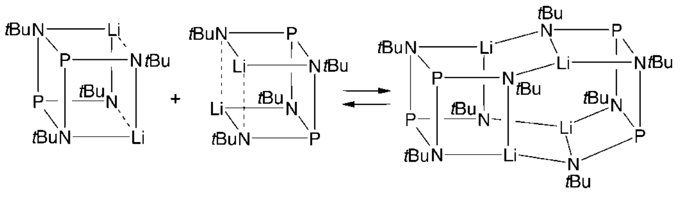


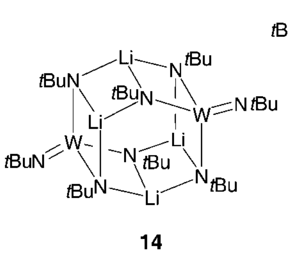
12, R = *t*Bu, 1-Ad

tetramer $[Li\{P(NtBu)_2\}]_4$ (**13**) [Eq. (n)], which is similar to the iminoalane $(RAlNR')_8$ (Scheme 1), is formed as a result of the face-to-face dimerization of two cubes.[21] The related complexes $[M\{E(NCy)_2\}]_4$ (M = Li, Na; E = As, Sb)[22–25] are isostructural with **13**.



13

The binary 12-atom (A_6X_6) hexagonal prism, which may also be viewed as a six-runged cyclic ladder, is a common structural motif for main group element cluster compounds, for example, the iminoalanes and *tert*-butylalumoxanes (see Scheme 1). Lithium derivatives of homoleptic polyimido anions of p- or d-block elements represent the only ternary analogues of this fundamental building block. For example, the tetrakisimidotungstate complex $[Li_2\{W(NtBu)_4\}]_2$ (**14**) contains a C_{2h}-symmetric $Li_4W_2N_6$ hexagonal-prismatic core.[11, 42b] The dilithium trisimidochalcogenite dimers $[Li_2\{E(NtBu)_3\}]_2$ (**15a–c**) also share this motif in forming $Li_4E_2N_6$-based clusters.[31–33]



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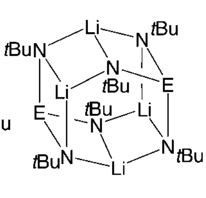
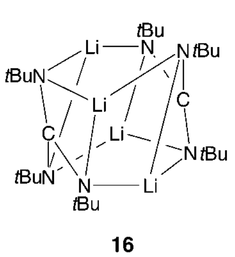


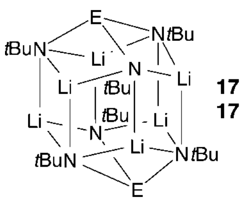
15a, E = S
15b, E = Se
15c, E = Te



16

The near tetrahedral or trigonal-pyramidal geometries at the Group 6 or 16 centers in **14** and **15**, respectively, allow for the formation of relatively undistorted hexagonal prismatic structures, especially in the case of **15c** for which the Li–N and Te–N rungs of the cyclic ladder are almost equal in length (ca. 2.0 Å).[33] On the other hand, the structure of the trisimidocarbonate complex $[Li_2\{C(NtBu)_3\}]_2$ (**16**), which contains a $Li_4C_2N_6$ core, is based on a severely distorted hexagonal prism.[16] This distortion arises from the requirement of planarity at the carbon centers and the disparity between C–N and Li–N bond lengths.

A more complex fundamental building block for unsolvated homoleptic polyimido anions is the 14-atom $(Li_6E_2N_6)$ bicapped hexagonal prism, which provides a framework for the dimeric trisimidopnicogenite clusters $[Li_3\{E(NtBu)_3\}]_2$ (**17**).[26a, 27b] These structures are best described as containing



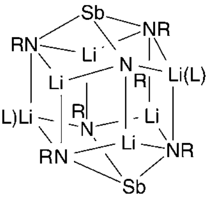
17a, E = As
17b, E = Sb

a cyclic Li_6N_6 ladder, the six-membered Li_3N_3 rings of which are capped by As or Sb atoms. The Li_6N_6 ladder adopts a puckered conformation to accommodate the rigid nature of the trianions (Group 15 elements).[13a]

3.2.2. *Effects of Solvation*

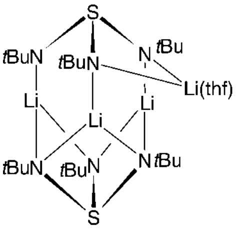
The addition of Lewis-basic solvents has proven successful for aiding the characterization of several anionic polyimido systems; however, the specific effect of the added donor solvent on the resulting structures can vary significantly. Structural changes may include a) minor distortion of cluster structure, b) major disruption of cluster structure, or c) stabilization of smaller aggregates.

Occasionally solvation has no significant structural effect. The structures of $[(L)Li_3\{Sb(NR)_3\}]_2$ (**18**; 2,4-dmp = 2,4-$(MeO)_2C_6H_3$) are similar to those of the unsolvated cluster



18a, R = CH_2CH_2Ph, L = thf
18b, R = Cy, L = $HNMe_2$
18c, R = 2,4-dmp, L = thf

17b[27] with the exception of subtle consequences arising from the presence of two 4-coordinate Li^+ ions. This observation is consistent with the concept of "structural direction by the dominant metal", in the form of $[Sb(NR)_3]^{3-}$, as advocated by Wright and co-workers.[13a] An example of a minor disruption of cluster structure is provided by the monosolvated derivative $[(thf)Li_4\{S(NtBu)_3\}_2]$ (**19**).[31] One of the Li^+ ions in **15a** is pulled away from the $Li_4S_2N_6$ core, which results in the partially opened framework of **19**. A more dramatic structural change caused by solvation is observed for the hexakis THF-solvated dimer $[(thf)_3Li_2\{C(NPh)_3\}]_2$ (**20**),[15] when compared to the unsolvated analogue **16**. The primary cause of the different structures of **16** and **20** is clearly the solvation of the Li^+ centers in **20** (rather than the change in the NR group).[16]



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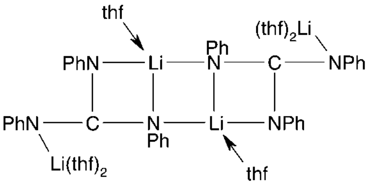

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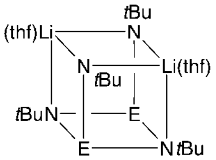
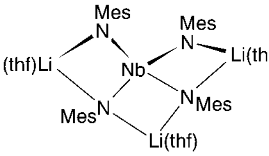


21a, E = P
21b, E = Bi

An unraveling process conceptually relates the dimeric dilithium trisimidocarbonate complexes **16** and **20**.[16] In effect, the initial coordination of THF molecules to the lithium ions of one Li_2N_2 face in the hexagonal-prismatic core of **16** leads, by Li–N bond-breaking, to the step-shaped ladder structure **20**.

The stabilization of smaller oligomers by solvation of the s-block metal cations is exemplified by the $Li_2E_2N_4$ cubane clusters of the THF-solvated Group 15 dimers $[(thf)Li\{E(N\textit{t}Bu)_2\}]_2$ (**21**).[20, 25] Significantly, the isolation of **21a** gives credence to the suggestion that the tetramer **13** is formed from two $Li_2P_2N_4$ cubes [see Eq. (n)][21] Solvation of the Li^+ ions hinders, in the case of **21**, dimerization of these cubes at their Li_2N_2 faces, effectively trapping the cubane building blocks.

There are also several examples of complexes in which chelation or extensive solvation of Li^+ ions by Lewis bases prevents the aggregation of monomeric units, for example, $[(thf)_4Li_3\{Nb(NMes)_4\}]$ (**22**),[40] $[(dme)Li]_2[Mn(N\textit{t}Bu)_4]$ (**23**),[45] $[(tmeda)Li\{Re(N\textit{t}Bu)_4\}]$ (**24**),[11] and $[(thf)_4Li_2\{S(N\textit{t}Bu)_4\}]$ (**25**).[37]



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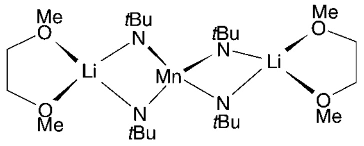

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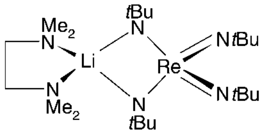

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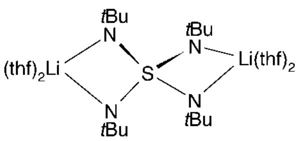

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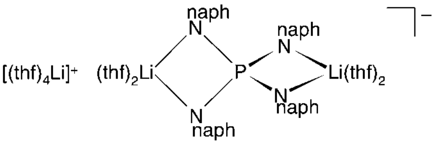
3.2.3. *Solvent-Separated Ion Pairs*

The structures of complexes **11**–**25** involve contact ion pairs. By contrast, the two known examples of homoleptic polyimido anions containing Group 15 element centers in the oxidation state V, that is, $[(thf)_4Li][(thf)_4Li_2\{P(Nnaph)_4\}]$ (**26**)[30] and $[(thf)_4Li][P(NMes^*)_3]$ (**27**),[28] consist of solvent-separated ion pairs. The cation in these P^V complexes is a sequestered Li^+ ion coordinated by four THF molecules. The anion in **26**, $[(thf)_4Li_2\{P(Nnaph)_4\}]^-$, is both isoelectronic and isostructural with the neutral sulfur(VI) complex **25**. By contrast, the trigonal planar ion $[P(NMes^*)_3]^-$ in **27** does not incorporate Li^+ ions. Significantly, complex **27** and the ionic Re^V complex $[N(PPh_3)_2][Re(NDipp)_3]$ (**28**)[44b] are the only structurally characterized examples of free polyimido anions of p-block elements or transition metals.



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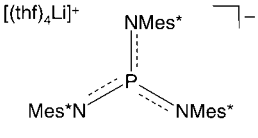

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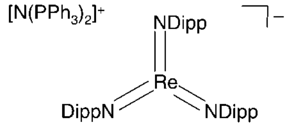

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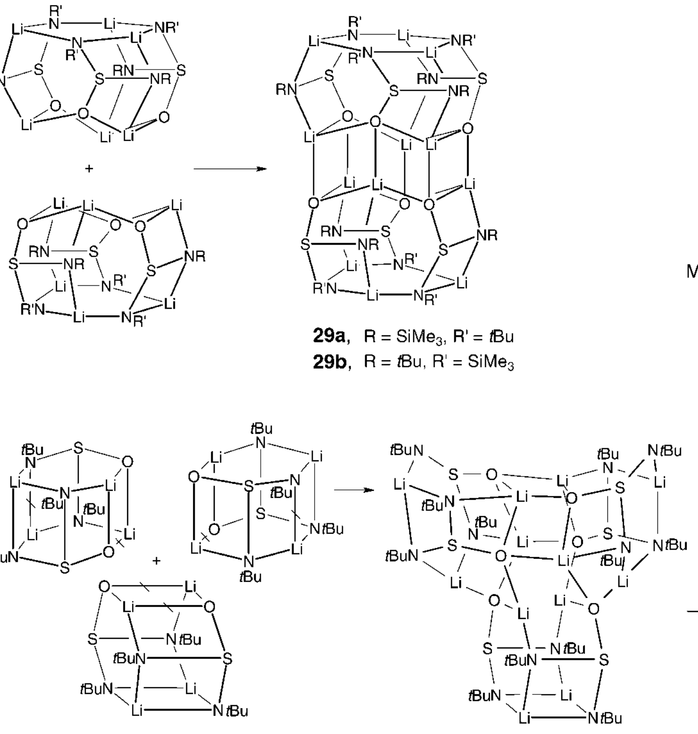
3.3. s-Block Metal Complexes of Imidooxo Anions of p-Block Elements

The replacement of one or more of the imido (RN^{2-}) groups attached to the central p-block element in homoleptic polyimido anions by an isoelectronic oxo (O^{2-}) ligand allows for further aggregation of fundamental building blocks by interactions involving highly polar, sterically unencumbered $(Li{-}O)_x$ ($x = 1$-3) units. Some examples of the novel structural architectures produced by this self-assembly process are presented below.

3.3.1. *Bisimidosulfite and Imidosulfite Ions*

The hexameric dilithium bisimidosulfite complexes $[Li_2\{OS(N\textit{t}Bu)(NSiMe_3)\}]_6$ (**29**) and $[Li_2\{OS(N\textit{t}Bu)_2\}]_6$ (**30**) both contain 36-atom ($Li_{12}S_6N_{12}O_6$) cluster structures.[34] It is clear, however, that these cluster cores result from the assembly of different fundamental building blocks. As depicted in Scheme 2, the centrosymmetric clusters **29** can be viewed as dimers in which two quaternary 18-atom ($Li_6S_3N_6O_3$) clusters are joined by their Li_3O_3 faces. A structurally similar Al_9O_9 unit is observed for the nonamer $(\textit{t}BuAlO)_9$ (see Scheme 1).[7a,b]

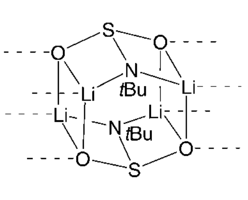
In a related, but more complex, process the 36-atom cluster in **30** can be envisaged to result from the trimerization of quaternary ($Li_4S_2N_4O_2$) hexagonal prisms by their Li_2O_2 faces (Scheme 2). Importantly, the isomer that involves the juxtaposition of Li–O linkages is favored among the possible isomers for these fundamental building blocks. To date, **30** is the only representative of a discrete cluster derived from the self-assembly of hexagonal prisms, although the formation of



Scheme 2. Proposed formation of the cluster structures **29** and **30**. In the formation of **30** the designation –/– indicates a bond broken in this process.

dimeric or tetrameric $Li_4S_2N_4O_2$ aggregates can readily be envisaged. The subtle effects that may result from changing the R group attached to nitrogen are illustrated strikingly by the different structures of the quaternary clusters **29** and **30**.

Quaternary complexes involving lithium and $[O_2S(NR)]^{2-}$ ions are likely to form extended structures, since the fundamental building blocks now contain two Li_xO_x ($x = 2$, 3) faces (**31** or **32**). Consistently, the complex $[Li_2\{O_2S(N\mathit{t}\text{-}Bu)\}]_n$ exhibits low solubility in organic solvents and a tendency towards gel formation.[36]



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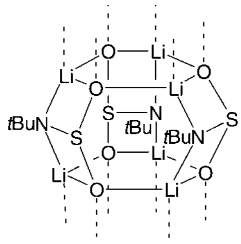
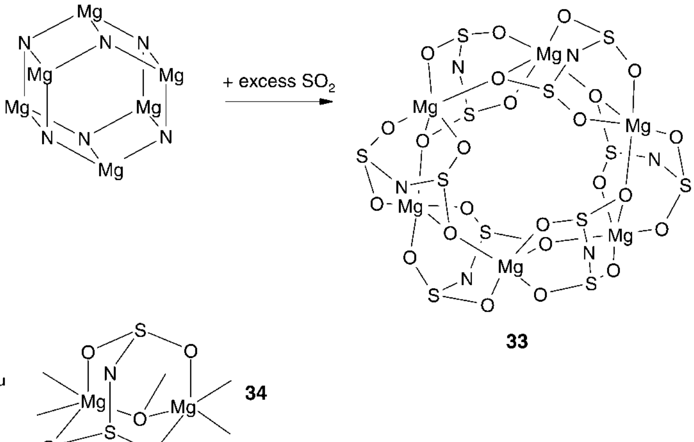


32

3.3.2. *The Imidodisulfite Ion*

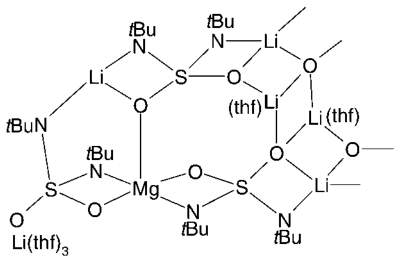
Complexes **29** and **30** (Scheme 2) are constructed from discernible fundamental building blocks that can conceivably exist independently. The following example involves building blocks that are not independent, but rather form as a result of edge-sharing, that is, the fusion of the basic units. The formation of the hexameric imidodisulfite complex $[(thf)Mg\{O_2S(\mu\text{-}NPh)SO_2\}]_6$ (**33**) involves the insertion of $12\,SO_2$ molecules into the Mg–NPh bonds of $[(thf)Mg(NPh)]_6$ (Scheme 3).[35] Complex **33** consists of a quaternary 48-atom ($Mg_6S_{12}N_6O_{24}$) cluster structure with S_6 molecular symmetry. Each of the $[O_2S(\mu\text{-}NPh)SO_2]^{2-}$ ions bischelates two Mg^{2+} ions, and one oxygen atom further exhibits monodentate coordination to a third Mg^{2+} ion. Thus the fundamental building block for **33** is a $Mg_2S_2NO_5$ adamantyl unit (**34**; Scheme 3). Each of these units is fused to two neighboring units by shared Mg–O edges.



Scheme 3. Synthesis of **33** and the basic structural building block **34**. For clarity, the Ph substituents on the nitrogen atoms and the THF molecules coordinated to the Mg^{2+} ions are omitted.

3.3.3. *Bisimidosulfate Ions*

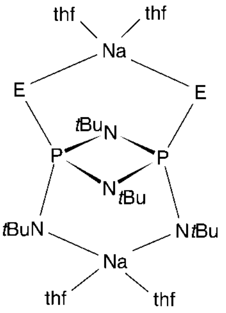
In contrast to the highly solvated tetrakisimidosulfate monomer **25**, the bisimidosulfate complexes $[Li_2\{O_2S(N\mathit{i}Pr)_2\}]_n$ and $[(thf)Li_2\{O_2S(N\mathit{t}Bu)_2\}]_n$ are amorphous in the solid state.[39b] Consequently, a heterobimetallic strategy involving the combination of magnesiation followed by lithiation was used to prepare $[(thf)_4Li_4Mg\{O_2S(N\mathit{t}Bu)_2\}_3]_2$ (**35**) [Eq. (c)].[39a] The central framework for **35** consists of a quinary 36-atom ($Li_6Mg_2S_6N_{12}O_{10}$) cluster core and two terminal O–Li(thf)$_3$ units. Each half of this centrosymmetric dimer contains one $[Li_2\{O_2S(N\mathit{t}Bu)_2\}]$ molecule and one $[\{(thf)_4Li_2Mg\}\{O_2S(N\mathit{t}Bu)_2\}_2]$ molecule. A central step-shaped Li_4O_4 ladder connects the two halves of **35**. The outer rungs of this ladder are formed by one Li–O bond from each $[Li_2\{O_2S(N\mathit{t}Bu)_2\}]$ molecule, while the inner rungs involve



35 (half of dimer + Li_4O_4 ladder) the O–Li(thf) bonds from the $[\{(thf)_4Li_2Mg\}\{O_2S(NtBu)_2\}_2]$ molecules. Undoubtedly, solvation of the terminal Li^+ ions by THF molecules obviates formation of a more extended structure, which could otherwise occur by assembly through Li–O edges.

3.4. s-Block Metal Complexes of Imidochalcogenido Anions of p-Block Elements

By analogy with the structurally informative investigations of alkali metal derivatives of imidooxo anions of p-block elements, the corresponding imidochalcogenido anions are a potentially intriguing class of species. To date, the imidothio- and imidoselenametaphosphate ions $[EP(NtBu)_2]^-$ [E = S or Se] are the only reported examples.[29] The sodium derivatives of these monoanions form *cis* isomers of the dimers $[(thf)_2Na\{EP(NtBu)_2\}]_2$ (**36**), which involve E,E′- and N,N′-chelation of the Na^+ ions, whereas the corresponding Li^+ salts adopt 'side-on' bis-N,E-chelation.[29b] Replacement of the Na^+ ions in **36** with K^+ results in formation of the extended structures $[(thf)_xK\{EP(NtBu)_2\}]_\infty$ (E = S, $x = 1$; E = Se, $x = 1.5$), which involve weak K⋯E interactions.[29]

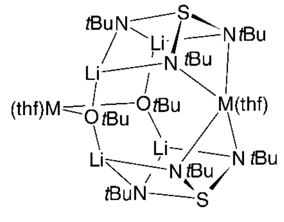


36a, E = S
36b, E = Se

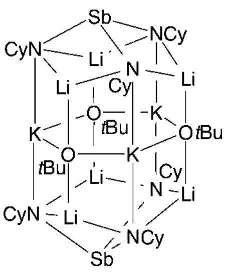
4. Cluster Expansion and Contraction

The incorporation of alkali metal alkoxides into ternary polyimido clusters leads to cage expansion. Addition of alkali metal *tert*-butoxides to the dimeric clusters $[Li_2\{S(NtBu)_3\}]_2$ (**15a**) and $[Li_3\{Sb(NCy)_3\}]_2$ (unsolvated **18b**) produces the mixed-metal complexes $[Li_2\{(thf)M\}\{S(NtBu)_3\}(OtBu)]_2$ (**37**)[67] and $[Li_3\{Sb(NCy)_3\}]_2 \cdot (KOtBu)_3$ (**38**), respectively.[68] The formation of **38** involves expansion of the 14-atom cluster core of **18b** to accommodate a six-membered $K_3(OtBu)_3$ ring between two intact $[Li_3\{Sb(NCy)_3\}]$ units.[68]

By contrast to the behavior of alkali metal alkoxides the interaction of ternary or quaternary polyimido cluster systems with lithium halides results in disaggregation.[14] The distorted cubane complexes $[\{(thf)Li\}_2\{S(NtBu)_3\}\{(thf)LiX\}]$ (**39a–c**) are obtained by the reaction of the dimer $[Li_2\{S(NtBu)_3\}]_2$ (**15a**) with in situ generated lithium halides[38] or lithium azide.[69a] The tellurium analogue **39d** is formed by direct addition of LiI to a THF solution of **15c**.[70] Recently a monomeric LiMe fragment has been trapped by $Li_2[S(NtBu)_3]$ to give the complex **39e**.[69b] A similar complex **39f** containing $LiOCH{=}CH_2$ derived from cleavage of THF by LitBu has been reported.[69c]



37a, M = Na
37b, M = K



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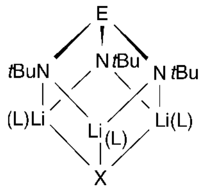
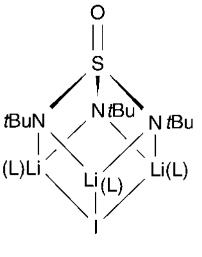


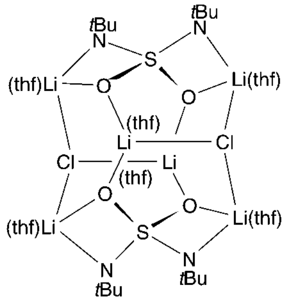
L = thf

39a, E = S, X = Br
39b, E = S, X = I
39c, E = S, X = N_3
39d, E = Te, X = I
39e, E = S, X = Me
39f, E = S, X = $OCHCH_2$

The trisimidosulfate complex **40** was obtained by the oxidation of **15a** with I_2 in the presence of O_2. Dilithium bisimidosulfates $[Li_2\{O_2S(NR)_2\}]_n$ (R = *i*Pr, *t*Bu) are insoluble, amorphous solids presumably with extended structures.[39b] However, crystalline derivatives are formed by the incorporation of lithium halides. Thus the dimer $[\{(thf)Li\}_2\{O_2S(NtBu)_2\}\{(thf)LiCl\}]_2$ (**41**) was obtained and structurally characterized.[39b] The assembly of extended structures through the Li–O edges in $[\{(thf)Li\}_2\{O_2S(NtBu)_2\}]$ is inhibited by interactions of these edges with the polar LiCl molecules.



40, L = thf

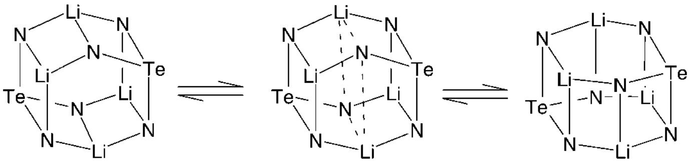


41

5. Solution Behavior: NMR Studies/Fluxional Processes

An important consideration for the characterization of aggregated complexes is that the solid-state structure may not reflect solution behavior and vice versa. In general, one of two phenomena can account for this dichotomy: a) intramolecular fluxional processes or b) dissociation of the complex into smaller oligomers.

As an example of the former behavior the hexagonal prism $[Li_2\{Te(NtBu)_3\}]_2$ (**15c**) exhibits a single resonance for NtBu groups in the ^1H NMR spectrum ([D$_8$]toluene) throughout the temperature range 185–298 K rather than the two resonances (2:1 ratio) expected on the basis of C_{2h} symmetry.[33] A fluxional process (fast on the NMR time scale) involving the concerted stretching and contraction of transannular Li–N interactions across the six-membered rings of the hexagonal prism has been proposed to account for this observation (Scheme 4).[33b]

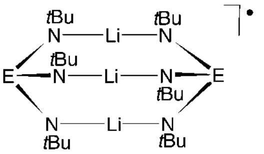


Scheme 4. Fluxional behavior of **15c**. For clarity, the *t*Bu groups are omitted.

A different type of solution behavior is indicated by NMR spectroscopic studies of tetramers of the type [Li{E(NR)$_2$}]$_4$ (E = Group 15 element). Variable-concentration cryoscopic molecular-mass measurements in benzene together with variable-temperature/concentration ^{7}Li NMR spectra of [Li{Sb(NCy)$_2$}]$_4$ in [D$_8$]toluene revealed a dissociative equilibrium in which dimeric units are produced (cf. Eq. (n)).[25]

6. EPR Investigations of Radical Anions

An intriguing and well-established characteristic of many chalcogen–nitrogen compounds is their ability to form deeply colored, long-lived radicals.[71, 72] This phenomenon is vividly apparent when solutions of **15a** are exposed to traces of air. The air-oxidation of hexane or toluene solutions of **15a** produces a dark blue radical.[31, 36, 38] The EPR spectrum of this radical comprises a septet (1:3:6:7:6:3:1) of decets, attributed to coupling of the unpaired electron with three equivalent ^{14}N nuclei and further interaction with three equivalent ^{7}Li nuclei.[36, 38] The oxidation of **15a** appears to involve the removal of one electron and one Li$^+$ ion from the 12-atom (Li$_4$S$_2$N$_6$) cluster to give a neutral 11-atom radical **42a** in which the radical anion [S(N*t*Bu)$_3$]$^{•-}$ is linked to the dianion [S(N*t*Bu)$_3$]$^{2-}$ by three Li$^+$ ions.[36, 38] On the basis of the EPR spectrum, which also consists of a septet of decets, a similar neutral radical cluster has been proposed for the Se congener **42b**.[36] The oxidation of **15a** by bromine provides an improved route to the sulfur(VI) triimide S(N*t*Bu)$_3$.[38] The chemistry of sulfur triimides S(NR)$_3$ (R = *t*Bu, SiMe$_3$) and related cations has been reviewed by Mews et al.[73]



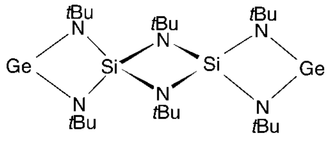
42a, E = S
42b, E = Se

7. Ligand Chemistry

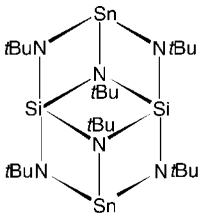
An important incentive for the study of polyimido and imidochalcogenido anions of p- and d-block elements involves their potential as multidentate ligands. The most common approach to coordination complexes utilizes the s-block metal derivatives of these ions as ligand-transfer agents in metathesis reactions, although transamination routes are also feasible. The majority of known coordination complexes exhibit ligation through the imido groups, but a few exceptions involving the central element have been reported. The reaction chemistry of the polyimido ions [Sb(NR)$_3$]$^{3-}$, [S(N*t*Bu)$_3$]$^{2-}$, and [S(N*t*Bu)$_4$]$^{2-}$ has been reviewed,[13, 14] and will therefore not be discussed here.

7.1. p-Block Element Centered Anions

The first report to hint at the utility of polyimido anions as a source of novel ligands involved the reaction of [Li$_2${Si(N*t*Bu)$_3$}]$_n$, generated in situ, with the divalent Group 14 halides MCl$_2$ (M = Ge, Sn) [Eq. (o)].[10] Two distinct arrangements are observed for the resulting complexes [M{Si(N*t*Bu)$_3$}]$_2$ (**43**, M = Ge; **44**, M = Sn). A spirocyclic structure forms the backbone for **43**, while **44** has a 10-atom (Sn$_2$Si$_2$N$_6$) deckchair core.



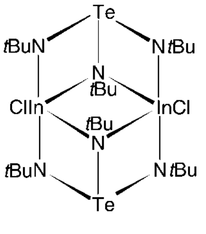
43



44

$$\frac{2}{n}[\mathrm{Li_2\{Si(N}t\mathrm{Bu)_3\}}]_n + 2\,\mathrm{MCl_2} \longrightarrow [\mathrm{M\{Si(N}t\mathrm{Bu)_3\}}]_2 + 4\,\mathrm{LiCl} \qquad \text{(o)}$$
$$\mathbf{43}\text{: M = Ge, }\mathbf{44}\text{: M = Sn}$$

The complex [Li$_2${Te(N*t*Bu)$_3$}]$_2$ (**15c**) is less susceptible to redox reactions than the sulfur analogue **15a**.[74] The [Te(N*t*Bu)$_3$]$^{2-}$ ion acts as an N,N'-chelating ligand in the boron complex [PhB(μ-N*t*Bu)$_2$TeN*t*Bu][33a] or as a tridentate ligand in combination with In (**45**) or heavy Group 15 element



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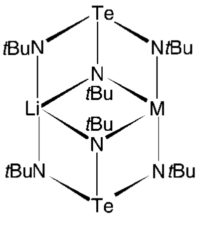
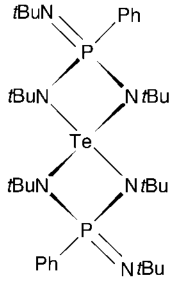


46a, E = Sb
46b, E = Bi

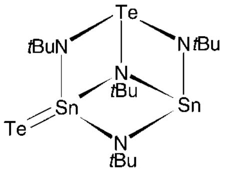


47

centers (**46**).[75a, 76] Redox behavior is observed, however, in the reaction of **15c** with $PhPCl_2$ to give the spirocyclic tellurium(IV) complex **47**. This process involves the oxidation of two P^{III} centers to P^{V} with the concomitant formation of elemental tellurium [Eq. (p)].[33a]

$$\underset{\mathbf{15c}}{[Li_2\{Te(NtBu)_3\}]_2} + 2\,PhPCl_2 \longrightarrow \underset{\mathbf{47}}{[Ph(tBuN)P(\mu\text{-}NtBu)_2Te(\mu\text{-}NtBu)_2P(NtBu)Ph]} + 4\,LiCl + Te \qquad (p)$$

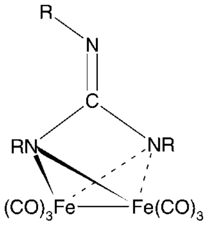
The redox process has an especially interesting outcome in the reaction of **15c** with $Sn(SO_3CF_3)_2$ which produces **48**, the first stannatellurone with four-coordinate tin [Eq. (q)].[75b] In complex **48** which contains Sn^{II}, Sn^{IV}, Te^{IV}, and Te^{-II} centers, one equivalent of $[Te(NtBu)_3]^{2-}$ effectively acts as a bridging, tridentate ligand (as in **45**) while the second equivalent serves as the source of tellurium for the SnTe unit and provides a μ-N*t*Bu group.



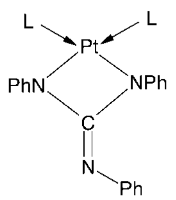
48

$$\underset{\mathbf{15c}}{[Li_2\{Te(NtBu)_3\}]_2} + 2\,Sn(O_3SCF_3) \longrightarrow \underset{\mathbf{48}}{(tBuN)_4Sn_2Te_2} + tBuN{=}NtBu + 4\,Li(O_3SCF_3) \qquad (q)$$

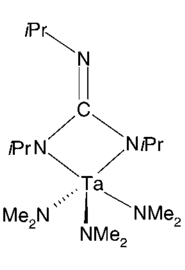
It is instructive to compare the ligand behavior of planar trialkyl(aryl)guanidinate ions $[C(NR)_3]^{2-}$ with that of the pyramidal $[Te(NtBu)_3]^{2-}$ ion. A variety of synthetic methods have been used to prepare dianionic guanidinate complexes of p- and d-block elements. The reaction of $[Fe(CO)_5]$ with carbodiimides RN=C=NR (R = *i*Pr, Cy) yields the complexes $[\mu^2\text{-}(RN)_3C][Fe(CO)_3]_2$ (**49**) in which two of the imido groups bridge the two iron centers.[77] N,N′-chelation is observed for the complexes $[(cod)Pt\{(\mu\text{-}PhN)_2CNPh\}]$ (**50**),[78] $[Ta(NMe_2)_3\{(\mu\text{-}iPrN)_2CNiPr\}]$ (**51**),[79] and $[Sb\{(iPrN)_2CNHiPr\}\{(iPrN)_2CNHiPr\}]$ (**52**).[80] Complexes of the type **51** (and the antimony complex **52**) are prepared by transamination routes [Eq. (r) M = Nb, Ta; R = *i*Pr, Cy].[79, 80]



49a, R = *i*Pr
49b, R = Cy



50, L_2 = cod



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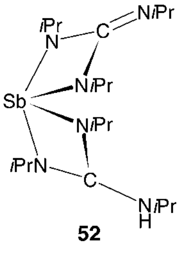
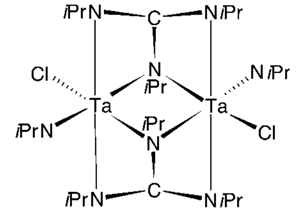


52

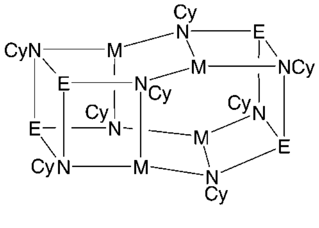
$$M(NMe_2)_5 + (RNH)_2CNR \longrightarrow [M(NMe_2)_3\{(RN)_2CNR\}] + 2\,Me_2NH \qquad (r)$$

The dinuclear complex $[(\mu\text{-}\eta^2{:}\eta^2(iPrN)_3C)Ta(NiPr)Cl]_2$ (**53**)[81] is the only example of the chelating bridging mode for the $[C(NiPr)_3]^{2-}$ ion (cf. **45**). In **53** the geometry at the central C atom is planar whereas that at Te in **45** is pyramidal. Another bridging dianionic ligand $[\{(iPrN)_2C\}_2NiPr]^{2-}$ for which no oxo analogue exists, has been generated from guanidinato–iron complexes.[82] Finally, the $[C(NPh)_3]^{2-}$ ligand behaves as an N-monodentate ligand towards Cd in the adduct $[\{(Me_3Si)_2N\}_2Cd\{(PhN)_3C\}Li(thf)_3]$.[83]

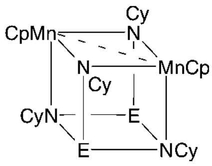


53

The robust nature of the ions $[E(NCy)_2]^-$ (E = As, Sb) was demonstrated by the generation of the d^{10} complexes $[M^I\{E(NCy)_2\}]_4$ (**54**) by reaction of the alkali metal salts $[M'\{E(NCy)_2\}]_4$ (M′ = Li, Na) with the appropriate copper or silver reagent.[23, 84, 85] This application was recently extended to include $[CpMn\{E(NCy)_2\}]_2$ (**55**) [Eq. (s)], the first complexes to incorporate a paramagnetic metal ion into a p-block ligand framework.[86]



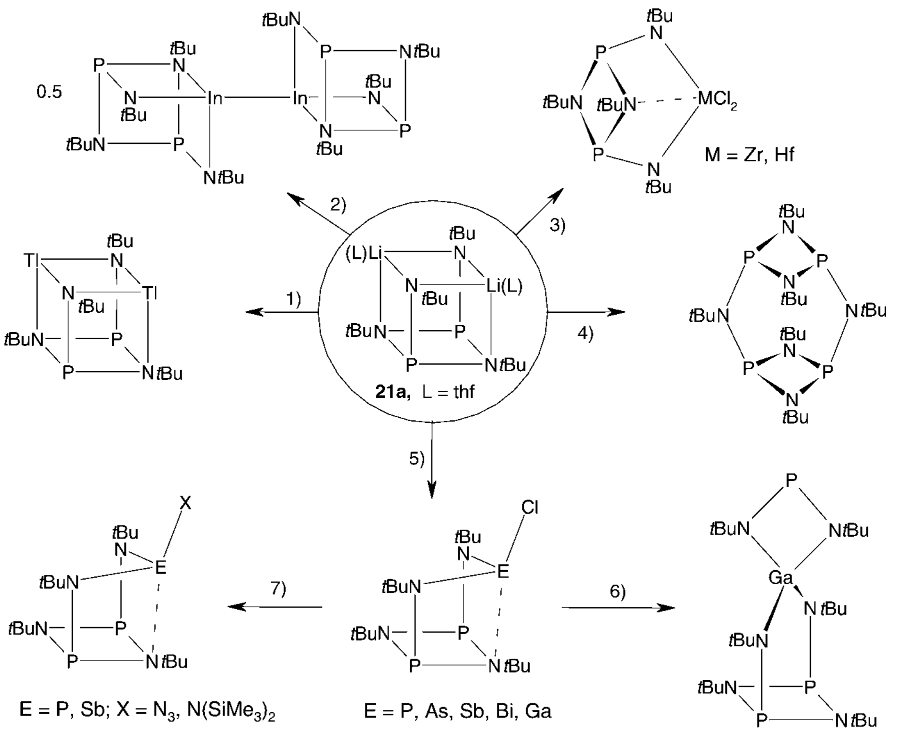
54a, E = As, M = Cu
54b, E = Sb, M = Cu
54c, E = Sb, M = Ag



55a, E = As
55b, E = Sb

$$[M'\{E(NCy)_2\}]_4 + 4\,Cp_2Mn \longrightarrow 2\,[CpMn\{E(NCy)_2\}]_2 + 4\,M'Cp \qquad (s)$$

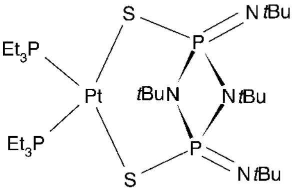
The ligating ability of the polyimido complex $[(thf)Li\{P(NtBu)_2\}]_2$ (**21a**), the phosphorus analogue of $[M'\{E(NCy)_2\}]_4$, has also been investigated extensively, as illustrated in Scheme 5. A noteworthy feature of the ligand behavior of this dimeric chelating ligand is the propensity to engage in intramolecular interactions involving one of the bridging N*t*Bu groups. This type of base stabilization is observed for complexes of the metals Zr, Hf,[88] and Ga, In,[87, 90] and the heavier Group 15 elements (Sb, Bi).[89] Another interesting observation is the formation of a monomeric 1,3-diaza-2-phosphaallyl ligand (cf. **11**) from the cyclo-



Scheme 5. Reactons of **21a**. 1) 2TlCl, −2LiCl;[87] 2) 2InCl, −2 LiCl, −In;[87] 3) MCl$_4$, −2LiCl;[88] 4) ClP(*m*-N*t*Bu)$_2$PCl, −2LiCl;[21] 5) ECl$_3$, −2LiCl;[89–91] 6) ½[(thf)Li{P(N*t*Bu)$_2$}]$_2$, −LiCl;[90] 7) NaN$_3$ or LiN(SiMe$_3$)$_2$, −(Na, Li)Cl.[89, 91] (The intramolecular E···N interaction is not observed for the small Group 15 elements E = P and As).[91]

reversion (ring opening) of **21a** in the formation of a spirocyclic Ga complex (see (6) in Scheme 5).[90] A comprehensive review by Stahl of the coordination chemistry of **21a** has appeared recently.[92]

The bis(imido)chalcogenido anions [EP(N*t*Bu)$_2$]$^-$ (E = S, Se) form dimeric units (see **36**) with a *cis*-arrangement of the chalcogens. This framework conceivably allows for three different modes of ligation: N,N′-chelation (end-on), E,E′-chelation (end-on), or N,E-chelation (side-on). Although these dianions have yet to be exploited extensively, a preliminary investigation revealed that the square-planar platinum(II) complex [(Et$_3$P)$_2$Pt{SP(N*t*Bu)$_2$}$_2$] (**56**) displays S,S′-coordination of the metal center by the [SP(N*t*Bu)$_2$]$_2^{2-}$ ion[93] in contrast to the N,N′-chelation observed for [Me$_2$Sn{SP(N*t*Bu)$_2$}]$_2$[94] and the N,E-ligation found for the bis(dimethylaluminum) complexes [(Me$_2$Al)$_2${EP(N*t*Bu)$_2$}$_2$] (E = O, S, Se).[95]



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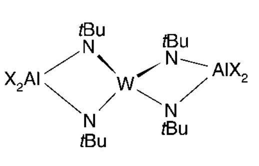
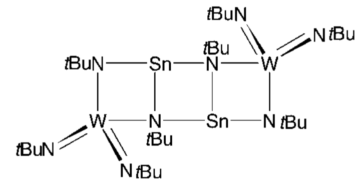
7.2. d-Block Element Centered Anions

The Group 6 complex **14** is a useful source of the ligand [W(N*t*Bu)$_4$]$^{2-}$ by metathesis. For example, reaction of **14** with AlX$_3$ (X = Me, Cl) leads to tetrakisimidotungstate complexes **57** [Eq. (t)],[42b] while a dimeric complex **58** was recently prepared by the treatment of **14** with two equivalents of SnCl$_2$.[96]



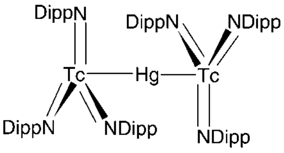
57a, X = Me
57b, X = Cl



58

$$\underset{\mathbf{14}}{[\mathrm{Li_2\{W(N}t\mathrm{Bu)_4\}]_2}} + 4\,\mathrm{AlX_3} \longrightarrow \underset{\mathbf{57}}{2[\mathrm{X_2Al}(\mu\text{-N}t\mathrm{Bu})_2\mathrm{W}(\mu\text{-N}t\mathrm{Bu})_2\mathrm{AlX_2}]} + 4\,\mathrm{LiX} \qquad (t)$$

The anion of the Group 7 complex [Na{Tc(NDipp)$_3$}]$_n$ coordinates to various functional groups through the Tc^{V} center rather than the imido groups. Treatment of this d^2 complex with HgBr$_2$ generates the linear trimetallic species **59** [Eq. (u)].[43] The rhenium analogue of **59** has also been reported.[44] Similarly, the 1:1 reaction of [Na{Tc(NDipp)$_3$}]$_n$ with ClAuPPh$_3$ gives the complex [(DippN)$_3$TcAu(PPh$_3$)] (**60**).[43]



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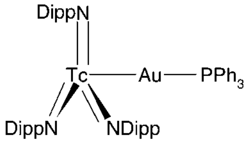


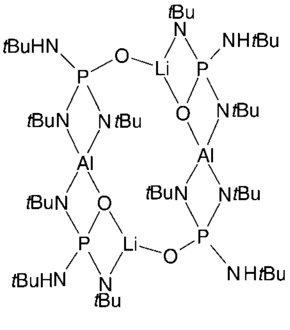
60

$$\frac{2}{n}[\mathrm{Na\{Tc(NDipp)_3\}}]_n + \mathrm{HgBr_2} \longrightarrow \underset{\mathbf{59}}{[(\mu\text{-Hg})\{\mathrm{Tc(NDipp)_3}\}_2]} + 2\,\mathrm{NaBr} \qquad (u)$$

8. Summary and Outlook

Alkali metal derivatives of homoleptic polyimido anions of the type $[E(NR)_x]^{z-}$ (E = d- or p-block element, R = alkyl or aryl) and their heteroleptic imidooxo analogues, $[O_yE(NR)_{x-y}]^{z-}$, form cluster structures comprised of fundamental building blocks or an assembly of these units. An underlying objective for structural studies of these cluster systems is to develop an understanding of, and possibly the ability to control, the aggregation process. The preliminary findings suggest several principles for the rationalization and prediction of cluster structures: a) the cluster geometry of the homoleptic polyimido system is indicative of the fundamental building block for the corresponding imidooxo analogue, b) the isomer of the fundamental building block that involves the juxtaposition of Li−O linkages is favored for the heteroleptic systems, c) the aggregation of these fundamental building blocks takes place through the highly polar, sterically unencumbered Li_xO_x units ($x = 1$: edges, $x = 2$ or 3: faces), and d) the replacement of one imido ligand in a homoleptic polyimido anion by an oxo ligand leads to discrete oligomeric clusters, while replacement of two imido ligands gives extended (polymeric) structures. Further work on imidooxo analogues of other common oxo anions such as PO_4^{3-} and SiO_4^{4-} and an investigation of the influence of the size of the alkali metal counter ion are necessary to test the general applicability of these principles. Preliminary experiments indicate that novel chemistry will result from studies of imido analogues of thio or selinido anions owing to the lability of certain element–chalcogen bonds.[29b, 97] The recent reports of the characterization of $[Li_2\{H_2C{=}S(NtBu)_2\}]_2$ draw attention to another isoelectronic analogy, that between RN and R_2C groups, that is worthy of further investigation.[98]

An intriguing extension of the investigations of imido analogues of simple oxo anions involves the synthesis of imido analogues of complex oxo anions such as aluminosulfates,[99] aluminosilicates $[Al(SiO_4)]^-$, and aluminophosphates $[Al(PO_4)_2]^{3-}$. In a preliminary investigation the reaction of $LiAlH_4$ with $OP(NHtBu)_3$ yielded **61**, the first imido analogue of an aluminophosphate.[100] The variables in this new class of cluster system include a) the size of the R group, b) the nature of the counter cation, and c) the O/NR ratio. Investigation of the structural effects of these variables is likely to lead to the preparation of larger cluster units. In addition, the presence of reactive exocyclic NH*t*Bu groups in **61** provides the possibility of linking this and related clusters to generate extended structures with defined pore sizes.



61

The homoleptic polyimido anions of p- or d-block elements also behave as adaptable ligands towards main group element and transition metal centers. The ability of these anions to stabilize low-coordinate, highly Lewis-acidic metal centers warrants further investigation in the context of possible catalytic applications.

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