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Coordination complexes of bis(amido)cyclodiphosph(III/V and V/V)azane imides and chalcogenides

Glen G. Briand, Tristram Chivers *, Mark Krahn

Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4

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* Corresponding author. Tel.: +1-403-220-5741; fax: +1-403-289-9488.
E-mail address: chivers@ucalgary.ca (T. Chivers).

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Abstract

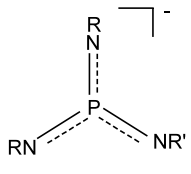
Metaphosphates with imido and chalcogenido substituents attached to a central phosphorus(V) center form ambidentate dimeric dianions that are potential components of metal-containing coordination polymers. This review summarizes the syntheses and structures of s-, p- and d-block metal complexes of these versatile ligands and their bis(amido)cyclodiphosph(V/V)azane precursors. The synthesis and structures of metal complexes of the corresponding cyclodiphosph(III/V)azane ligands are also discussed.

Keywords: Cyclodiphosph(III/V)azane; Cyclodiphosph(V/V)azane; Imidometaphosphates; Coordination compounds; Chalcogens; Ambidentate ligands

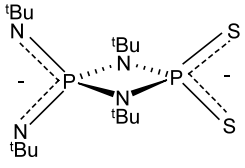
1. Introduction

Over the past decade, there has been a growing interest in homoleptic polyimido anions and heteroleptic imido/oxo(thio) anions of the p-block elements as their alkali-metal derivatives [1]. Early examples of this class of ligand include monomeric anions of the type $[P(NR)_2(NR')]^-$ (**1**), which are isoelectronic with the metaphosphate anion $[PO_3]^-$ [2]. More recently, our investigations of imido/oxo(thio) analogues $[P(E)(NR)_3]^{3-}$ (E = O, S) of the orthophosphate anion $[PO_4]^{3-}$ have led to the unexpected isolation and structural characterization of the dilithium salt of $[(^tBuN)_2P(\mu\text{-}N^tBu)_2PS_2]^{2-}$ (**2**), from the reaction of $SPCl_3$ with excess $LiN(H)^tBu$ [3]. This unsymmetrical dianion may be viewed as a cycloaddition product of the tris(imido)metaphosphate $[P(N^tBu)_3]^-$ (**1**, R = R′ = ^{t}Bu) and the hypothetical dithia(imido)metaphosphate $[S_2P(N^tBu)]^-$.

The discovery of this novel dianionic ligand, which has both 'hard' *N*,*N*′ and 'soft' *S*,*S*′ coordination sites, prompted our interest in other isomers of this system. The dianion $[(Me_3SiN)_2P(\mu\text{-}S)_2P(NSiMe_3)_2]^{2-}$ (**3**) has been reported [as the bis($AlCl_2^+$) complex], but the bridging function of the sulfur atoms limits coordination to the 'hard' nitrogen centers [4]. The third isomer, represented by **4a**, contains both 'hard' and 'soft' centres in terminal sites. This isomer, formally a dimer of the thiabis(imido)metaphosphate anion $[SP(N^tBu)_2]^-$, can be compared to phosphinates of the type $[R_2P(E)(NR')]^-$ (**5**) [5,6]. Other cognate anionic systems include the acetylacetonate analogues $[R_2P(E)NP(E)R_2]^-$ (**6**) [7] and the dianionic bis(imido)cyclodiphosph(III/III)azane ligands **7** [8].



1a, R = R' = Mes*
1b, R = Mes*, R' = ^{t}Bu



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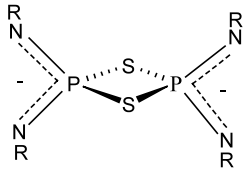
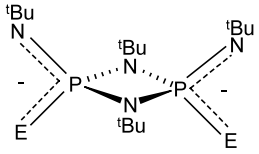
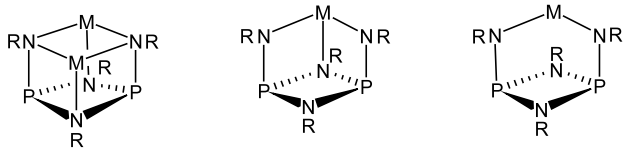


3 (R = $SiMe_3$)

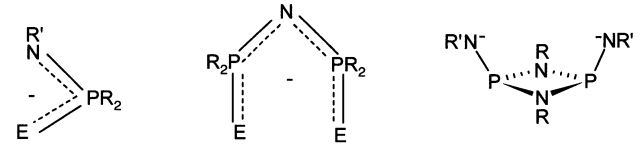


4a, E = S
4b, E = Se
4c, E = Te



I II III

Scheme 1.



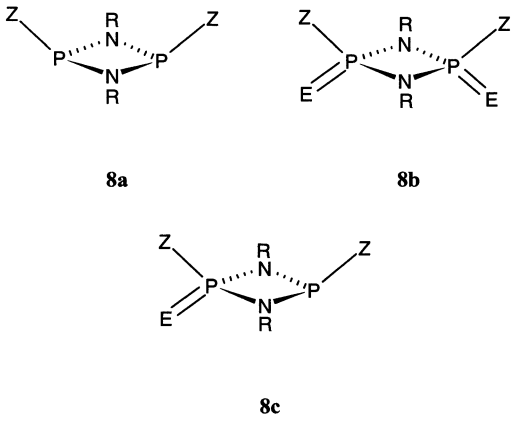
5, E = S, Se, Te **6**, E = O, S, Se **7**

Dianionic ligands of type **7** offer three possible coordination modes through terminal and bridging *N*-donor sites (**I**–**III** in Scheme 1), which allow the incorporation of s-, p-, or d-block metals that vary in size and oxidation state. By comparison with **5**–**7**, dianions of type **4** are potentially versatile ambidentate ligands. For example, two different modes of chelation involving the 'hard' (*N*) and 'soft' (*E*) centres are possible that may allow for the generation of coordination polymers containing different metals (Scheme 2).

2. General considerations

2.1. Scope

This account is intended to complement the recent review of the coordination chemistry of the dianions **7** by Stahl [8]. It will begin with a summary of the preparations, structures and spectroscopic properties of neutral compounds of the type **8b** and **8c**, which are precursors to anions of the type **4** and related P(III)/P(V) systems, respectively. Although, earlier investigations include complexes in which the exocyclic substituents were alkyls, aryls, halides and secondary amides (**8b**,**c**; Z = Me, ^{t}Bu, Ph, Cl, NMe_2) [9], this review is limited to derivatives in which Z is a primary amido substituent. The main body of the text is concerned with the coordination complexes of these anions with main-group and transition-metal centers, which will be discussed in the context of the related anionic ligands **5**–**7**.



8a **8b**

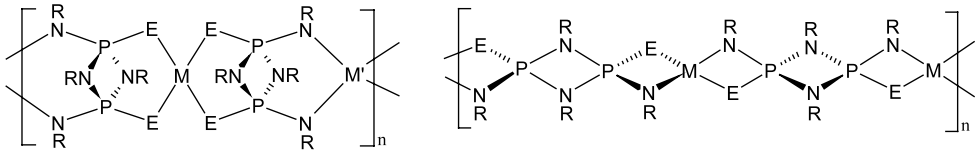
8c

Z = N(H)R'; R/R' = alkyl, aryl; E = NR, O, S, Se, Te

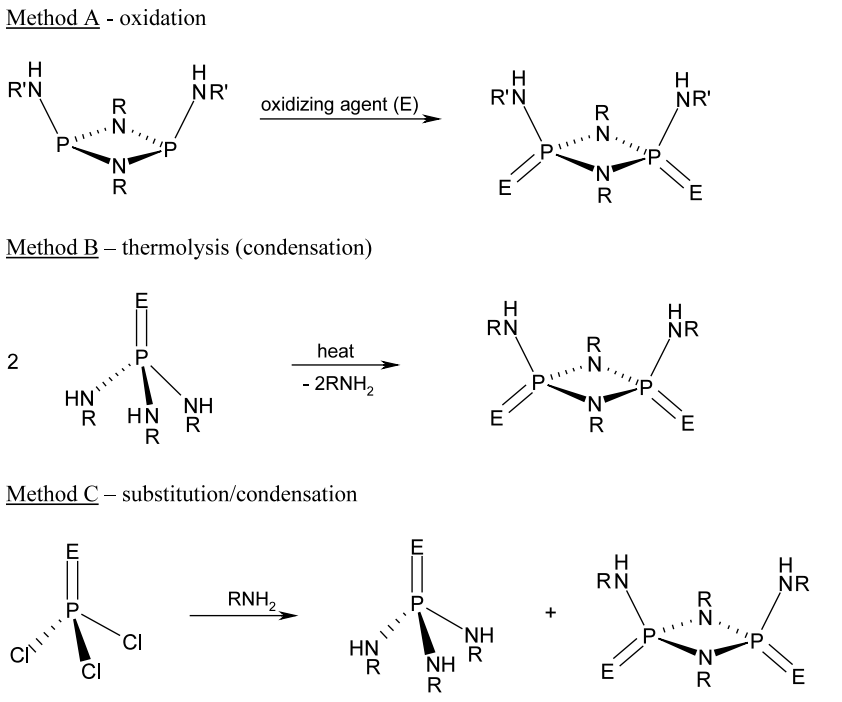
2.2. Nomenclature and structural representations

In keeping with the nomenclature adopted by Stahl [8], the name cyclodiphosph(X/Y)azane will be employed for compounds of the type **8a**–**c**, where X and Y specify the oxidation states at the two phosphorus centers. The terms symmetric and asymmetric are used to differentiate between cyclodiphosph(X/Y)azane systems in which R and R′ are either equivalent (i.e. R = R′) or different (i.e. R ≠ R′), respectively. The term dichalcogenide refers to complexes of the type **8b** (E = O, S, Se, Te); it does not imply a chalcogen–chalcogen bond. Similarly, monochalcogenide refers to **8c** (E = O, S, Se, Te). The term configurational isomer refers to the *cis* or *trans* arrangement of exocyclic substituents in **8b**, while the term conformational isomer is used for isomers that are distinguished by different arrangements (*endo* or *exo*) of the groups attached to the amido ligands [N(H)R′] in **8b** and **8c**.

Structural drawings are intended to represent coordination modes and connectivity of atoms, and are derived from X-ray crystallographic data. They are not indicative of formal bond orders.



Scheme 2.



Scheme 3.

3. Bis(amido)cyclodiphosphazanes

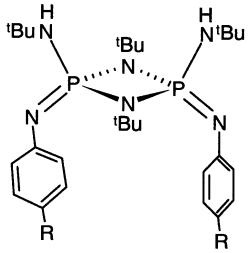
3.1. Syntheses and structures of bis(amido)cyclodiphosph(V/V)azanes

Several methods have been employed for the syntheses of bis(amido)cyclodiphosph(V/V)azanes. The most common general routes are given in Scheme 3, while specific details are given in the following subsections. A summary of the synthetic methods, yields, and ^{31}P-NMR data for all of the known cyclodiphosph(V/V)azanes is provided in Table 1.

Method A has been employed extensively and involves oxidation of the corresponding bis(amido)cyclodiphosph(III/III)azane, typically with an organic azide (E = NR), a hydroperoxide (E = O) or an elemental chalcogen (E = S, Se or Te). Methods B and C involve the direct or in situ condensation of a primary amine from $EP(NHR)_3$. As early as 1915, Michaelis showed that heating $SP(NHR)_3$ (R = Et, ^{n}Pr, ^{i}Bu) generates the corresponding primary amine and a material which he formulated as SP(NR)(NHR). It was not until 1966, however, that Bock and Wiegrabe assigned the correct dimeric structure based on molecular weight determinations [10]. Since then, the thermolysis of a variety of tris(amido)phosphates and tris(amido)thiophosphates has been investigated. In contrast to the direct condensation by thermolysis (Method B), which occurs for all R groups, the in situ route (Method C) gives a mixture of the tris(amido)thiophosphate and the corresponding cyclodiphosph(V/V)azane disulfide at lower temperatures for a select range of R groups.

3.1.1. Diimides

The well-established procedure for the oxidation of phosphorus(III) compounds with organic azides has recently been extended to bis(amido)cyclodiphosph(III/III)azanes [11]. The reaction of **8a** (R = R′ = ^{t}Bu) with aryl azides produced the *cis*-cyclodiphosph(V/V)azanes, **9a** and **9b**, in good yields (Method A). The analogous reaction with the less reactive trimethylsilyl azide gave only intractable mixtures; however, when the exocyclic substituent Z is Me or NMe_2, the oxidized products **8b** (Z = Me, NMe_2; E = $NSiMe_3$) are isolated [9b].



9a, R = H
9b, R = Me

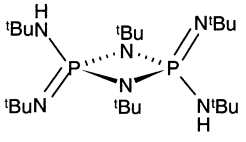
Other derivatives have been prepared by less obvious pathways. The symmetric *trans*-diimide **10** was isolated and structurally characterized, together with the dilithium derivative of **2**, from the reaction of $SPCl_3$ and an excess of $LiN(H)^tBu$ [12]. The asymmetric *trans*-

Table 1
Synthetic method, yield, and NMR data for bis(amido)cyclodiphosph(V/V)azanes [R′(H)N(E)P(μ-NR)$_2$P(E)N(H)R′] (**8b**) and cyclodiphosph(III/V)azanes [R′(H)N(E)P(μ-NR)$_2$PN(H)R′] (**8c**)

Compound	E	R	R′	Method [a]	Yield (%)	δ $^{31}P\{^1H\}$ (ppm)	$^1J(^{31}P-E)$ (Hz)	Solvent	Reference
Cyclodiphosph(V/V)azanes									
9a	NPh	^{t}Bu	^{t}Bu	A	74	−26.7(s)		C_6D_6	[11]
9b	NpTol	^{t}Bu	^{t}Bu	A	95	−29.2(s)		C_6D_6	[11]
10	N^{t}Bu	^{t}Bu	^{t}Bu	E	15	−42.9(s)		C_6D_6	[12]
12	O	^{t}Bu	^{t}Bu	A	97	−3.4(s)		C_6D_6	[14,15]
13a	O	^{i}Bu	^{i}Bu	B	21	NR			[10]
13b	O	^{i}Pr	^{i}Pr	B	30	NR			[10]
14a	S	Me	Me	A,B,C	39	58.2(s)		C_6D_6	[16]
14b	S	Et	Et	A,B,C	60	53.4(s)		C_6D_6	[16]
14c	S	^{i}Pr	^{i}Pr	A,B,C	45	46.8(s)		C_7D_8	[16]
14d	S	^{t}Bu	^{t}Bu	A,B,C	90	38.7(s)		C_7D_8	[16]
14e	S	^{n}Pr	^{n}Pr	B,C	91	NR			[17]
14f	S	^{n}Bu	^{n}Bu	B,C	8	NR			[17]
14g	S	^{i}Bu	^{i}Bu	B,C	21	59.9(s)		$CDCl_3$	[17]
14h	S	^{s}Bu	^{s}Bu	B,C	22	48.4(s)		$CDCl_3$	[17]
14I	S	Bz	Bz	B	19	55.7(s)		$CDCl_3$	[17]
14j	S	^{c}Pen	^{c}Pen	B	14	NR			[17]
14k	S	^{c}Hex	^{c}Hex	B	15	47.3(s)		$CDCl_3$	[17]
14l	S	Ph	Ph	A,B,C,E	9	−39.5(s)		C_6D_6	[20]
15	S	^{t}Bu	Ph	A	75	37.1(s)		C_6D_6	[14]
16	S	TMS	TMS	C	19	42.1(s)		C_6H_6	[19]
17a	S	CE [b]	CE [b]	A,E	66	44.9(s)		CD_2Cl_2	[21]
17b	S	CE [b]	CE [b]	A,E	7	47.5(s)		CD_2Cl_2	[21]
18	Se	^{t}Bu	^{t}Bu	A	87	23.0(s)	886	THF-d_8	[22]
19	Se	^{t}Bu	Ph	A	68	45.1(s)	886	C_6D_6	[14]
Cyclodiphosph(III/V)azanes									
21a	O	^{t}Bu	^{t}Bu	A	72	72.2(s), 3.9(s)		C_6D_6	[15]
21b	S	^{t}Bu	^{t}Bu	A	216	79.2(s), 40.0(s)		C_6D_6	[15]
21c	Se	^{t}Bu	^{t}Bu	D	97	80.9(s), 26.8(s)	817	THF-d_8	[15]
21d	Te	^{t}Bu	^{t}Bu	A	5	87.1(s), −39.7(s)	2024	C_7D_8	[23]

NR, not reported.
[a] Method: A, oxidation; B, thermolysis; C, substitution/condensation; D, disproportionation; E, miscellaneous.
[b] CE, macrocyclic crown ether substituent.

diimide **11** has also been structurally characterized, but the details of its synthesis have not been reported [13].



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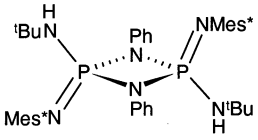
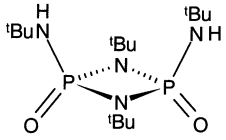


11

3.1.2. Dioxides

Oxidation employing cumene hydroperoxide [14] or *tert*-butyl hydroperoxide [15] provides the *cis*-dioxide **12** in high yields (Method A). Other derivatives have been prepared via thermolysis of tris(amido)phosphates (Method B). For example, heating tris(isobutylamido)phosphate [OP(NH^{i}Bu)$_3$] at 280–295 °C induces a condensation reaction to give **13a**, with elimination of isobutylamine. Similarly, the decomposition of OP(NH^{i}Pr)$_2$(NEt$_2$) above 250 °C generates the isopropyl analogue **13b** and diethylamine [10].



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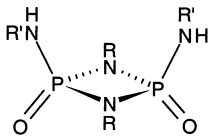


13a, R = R' = ^{i}Bu
13b, R = R' = ^{i}Pr

The neutral ligands **12**, **13a** or **13b** have not been structurally characterized, but the bis(*N*,*O*)-chelated dimethylaluminum complex of **12** adopts a *cis*-configuration (see Section 6.8.1).

3.1.3. Disulfides

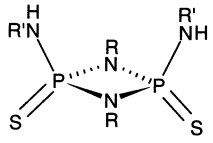
The disulfides represent the largest and most extensively studied category of cyclodiphosph(V/V)azanes. Several synthetic routes have been successfully employed in their preparation, and a relatively large

Table 2
Selected bond lengths [a] (Å) of bis(amido) cyclodiphosph(V/V)azanes [R′(H)N(E)P(μ-NR)$_2$P(E)N(H)R′] and cyclodiphosph(III/V)azanes [R′(H)N(E)P(μ-NR)$_2$PN(H)R′]

Compound	E	R	R′	Isomer	P–E	P–N (exo)	P–N (endo)	Reference
Cyclodiphosph(V/V)azanes								
9a	NPh	^{t}Bu	^{t}Bu	*cis*(*endo*,*endo*)	1.523(4)	1.621(5)	1.685(4)	[11]
9b	NpTol	^{t}Bu	^{t}Bu	*cis*(*endo*,*endo*)	1.529(2)	1.633(3)	1.690(2)	[11]
10	N^{t}Bu	^{t}Bu	^{t}Bu	*trans*(*endo*,*endo*)	1.522(3)	1.664(3)	1.708(3)	[12]
11	NMes*	Ph	^{t}Bu	*trans*(*exo*,*exo*)	1.527 [c]	1.644 [c]	1.708 [c]	[13]
14b	S	Et	Et	*trans*(*exo*,*exo*)	1.928(2)	1.616(4)	1.674(3)	[16]
14c	S	^{i}Pr	^{i}Pr	*trans*(*exo*,*exo*)	1.935 [c]	1.617 [c]	1.686 [c]	[18]
14d	S	^{t}Bu	^{t}Bu	*cis*(*endo*,*exo*)	1.925(1)	1.631(3)	1.685(3)	[16]
14l	S	Ph	Ph	*trans*(*exo*,*exo*)	1.909(3)	1.637(6)	1.698(5)	[20]
15	S	^{t}Bu	Ph	*cis*(*endo*,*exo*)	1.924(1)	1.648(3)	1.686(2)	[14]
16	S	TMS	TMS	*trans*(*endo*,*endo*)	1.930(1)	1.635(1)	1.690(1)	[19]
17a	S	CE [b]	CE [b]	*trans*(*exo*,*exo*)	1.914(1)	1.630(3)	1.695(3)	[21]
17b	S	CE [b]	CE [b]	*cis*(*endo*,*endo*)	1.926(2)	1.632(4)	1.694(4)	[21]
18	Se	^{t}Bu	^{t}Bu	*cis*(*endo*,*exo*))	2.078(2)	1.620(5)	1.682(5)	[28]
19	Se	^{t}Bu	Ph	*cis*(*endo*,*exo*)	2.082(1)	1.654(3)	1.689(2)	[14]
Cyclodiphosph(III/V)azanes								
21c	Se	^{t}Bu	^{t}Bu	*cis*(*endo*,*exo*)	2.1169(7)	1.646(2)	1.711(2)	[28]
21d	Te	^{t}Bu	^{t}Bu	*cis*(*endo*,*exo*)	2.370(1)	1.647(4)	1.717(4)	[23]

[a] Average values.
[b] CE, macrocyclic crown ether substituent.
[c] Esds not reported.

number of them have been structurally characterized (see Table 2). The derivatives **14a**–**d** are prepared in high yields via oxidation reactions (Method A) [16]. The asymmetric disulfide **15** is prepared similarly [14].

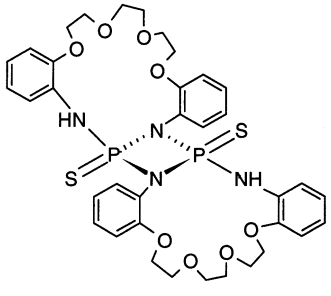


14a, R=R'=Me
14b, R=R'=Et
14c, R=R'=^{i}Pr
14d, R=R'=^{t}Bu
14e, R = R' = ^{n}Pr
14f, R = R' = ^{n}Bu
14g, R = R' = ^{i}Bu
14h, R = R' = ^{s}Bu
14i, R = R' = Bz
14j, R = R' = C_5H_9
14k, R = R' = C_6H_{11}
14l, R = R' = Ph
15, R = ^{t}Bu, R'= Ph
16, R = R' = TMS

The most extensively utilized synthetic method involves the thermolysis of tris(amido)thiophosphates (Method B), which has led to the isolation of the disulfides **14e**–**k**. Reactions occur at temperatures ranging from 190 to 240 °C with yields varying from 6 (R = ^{n}Bu) to 39% (R = Me) [17].

Method C has been used successfully for the preparation of **14c** and **14e**–**h** at ambient temperatures. Yields range from 5 to 22% and appear to be enhanced by the use of branched chain amines [17a,18]. Condensation reactions also occur in boiling acetonitrile to give **14a**, **14b**, **14d**, **14i** and **14k**, though yields were not reported [17c]. Similarly, the reaction of $SPCl_3$ with hexamethyldisilazane, $(Me_3Si)_2NH$, produces the dichloride, $(Me_3Si)NHP(S)Cl_2$ and the bis(amido)cyclodiphosph(V/V)azane disulfide, **16** [19]. The poorly understood reaction of α- or β-$P_4S_3I_2$ and aniline produces a moderate yield of **14l**, which has also been prepared by Methods A–C [17a,20].

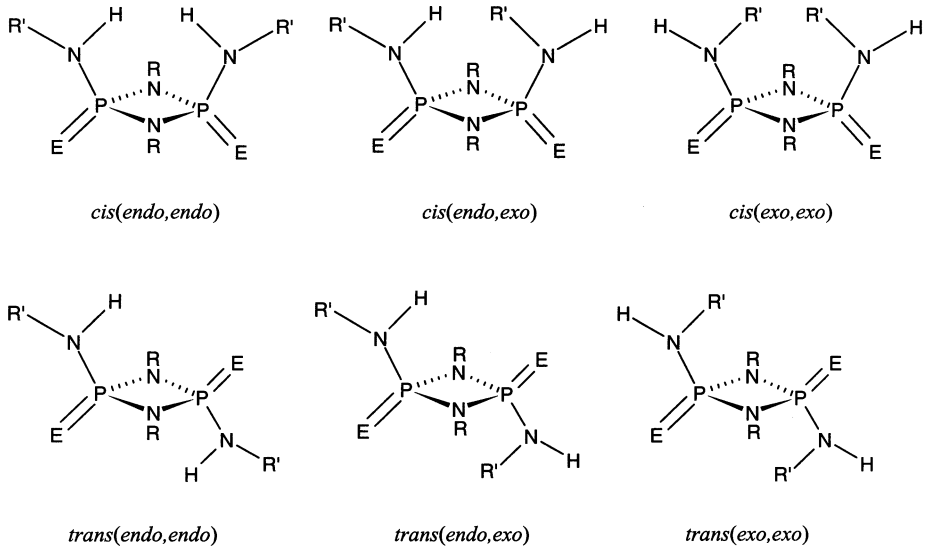
The bismacrocyclic crown ether complex **17** was formed from the reaction of triethylene glycol bis(2-aminophenyl)ether and hexamethylphosphorus triamide (HMPT) in boiling toluene, followed by in situ oxidation with sulfur. *Trans* and *cis* isomers, **17a** and **17b**, which are unique examples of primary amido cyclodiphosph(V/V)azane complexes linked by the *endo*- and *exo*-cyclic substituents, were obtained in a 9:1 molar ratio [21].



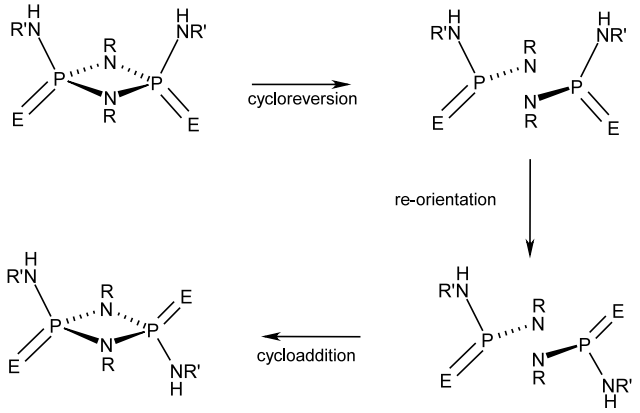
17a, *trans*
17b, *cis*

3.1.4. Diselenides

Both known examples of bis(amido)cyclodiphosph(V/V)azane diselenides, **18** and **19**, are formed in good

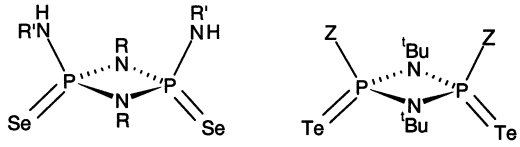


Scheme 4.



Scheme 5.

yields by oxidation of the corresponding P(III)/P(III) systems with elemental selenium (Method A) [14,22].



18, R = ^{t}Bu, R'= ^{t}Bu
19, R = ^{t}Bu, R' = Ph

20a, Z = NH^{t}Bu
20b, Z = Me
20c, Z = ^{t}Bu

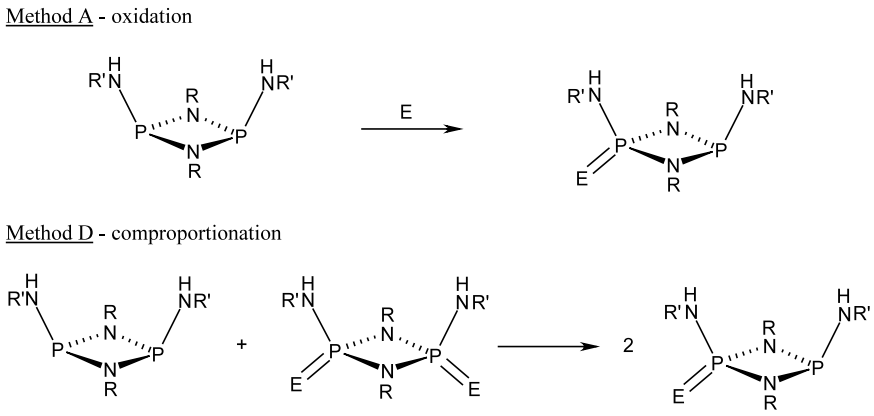
3.1.5. Ditellurides

The bis(amido)cyclodiphosph(V/V)azane ditelluride, **20a**, cannot be prepared by Method A; reaction of the corresponding P(III)/P(III) system with an excess of tellurium gives only the monotelluride (see Section 3.3.1) [23]. However, the related compounds with terminal alkyl substituents (**20b**,**c**) may be prepared by this method [24,25].

3.2. Isomerism in cyclodiphosph(V/V)azanes

Six isomers are possible for bis(amido)cyclodiphosph(V/V)azane systems (Scheme 4). For each of the two configurational isomers (*cis* or *trans*) there are three conformational isomers determined by the relative orientations of the substituents on the exocyclic nitrogen atoms. Structural data are summarized in Table 2. Since only four of the six possible arrangements have been observed, it is germane to consider the factors that may influence the formation of a particular isomer.

The *cis*/*trans* isomerization in these systems appears to be at least partially affected by steric effects, as illustrated by the diimides **9**–**11**. The sterically bulky ^{t}Bu and Mes* substituents in **10** and **11** prefer a *trans* arrangement, whereas the smaller aryl groups in **9a** and **9b** adopt a *cis* orientation. Since the cyclodiphosph(III/III)azane precursor to **10** is observed in a *cis*-configuration, it is possible that the isomerization to a *trans* isomer involves a ring-opening 'cycloreversion' process (Scheme 5), similar to that which occurs for cyclodiphosph(III/III)azanes with bulky R groups [8]. On the other hand steric considerations do not appear to exert an influence on isomer preference in the case of dichalcogenides **12**–**16** and **18**–**20** for which *cis* isomers are found for bulkier R groups and a *trans* geometry is adopted for smaller R groups. As in the P(III)/P(III) systems [8], the P_2N_2 ring is puckered in *cis* isomers, presumably to alleviate steric repulsions, and essentially planar in *trans* isomers. In summary, *cis*/*trans* isomerism in these P(V)–P(V) systems is not a well-understood phenomenon.



Scheme 6.

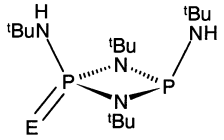
The *endo*/*exo* orientation of the primary amido substituents is another interesting structural property to consider. In nearly all cases, the amido substituents point along the P···P vector with the N–H group pointing toward (*endo*) or away from (*exo*) the center of the P_2N_2 ring. This structural feature is also poorly understood. The *cis*, diimides, **9a**,**b**, like their cyclodiphosph(III)azane precursor, maintain an *endo*/*endo* orientation. For the dichalcogenides, on the other hand, the *endo*/*exo* arrangement is typically adopted for bulkier R groups (*cis* isomers), while the *exo*/*exo* arrangement is observed for smaller R groups (*trans* isomers). Variable temperature NMR studies of disulfides indicate that adoption of the *endo*/*exo* conformation in *trans* isomers is temperature independent, with essentially no restriction of the amido group rotation. This suggests that the preference for *endo*,*endo* or *exo*,*exo* arrangements may be dictated by packing effects. Conversely, the orientations in *cis* isomers were found to be temperature dependent with a barrier to rotation in the 9.5–12.9 kcal mol^{-1} range [16].

3.3. Syntheses and structures of bis(amido)cyclodiphosph(III/V)azanes

Only two synthetic methods are useful for the preparation of cyclodiphosph(III/V)azanes. The first is the stoichiometric oxidation with the appropriate chalcogen, while the second involves comproportionation between the corresponding cyclodiphosph(III/III)azane and cyclodiphosph(V/V)azane dichalcogenide (Scheme 6). A summary of the synthetic methods, yields and ^{31}P-NMR data for cyclodiphosph(III/V)azanes is provided in Table 1. With one exception, the value of $^2J(^{31}P–^{31}P)$ is approximately zero for these P(III)–P(V) systems. Furthermore, the ^{31}P-NMR chemical shifts of the individual P(III) and P(V) centers are similar to those of the corresponding P(III)/P(III) and P(V)/P(V) systems, respectively. Consequently, identification of these compounds has relied heavily on the characteristic ^{1}H-NMR spectra for the alkyl groups attached to inequivalent nitrogen atoms. In the case of R = R′ = ^{t}Bu (**21a**–**d**) three characteristic resonances are observed in the N^{t}Bu region with relative intensities 2:1:1.

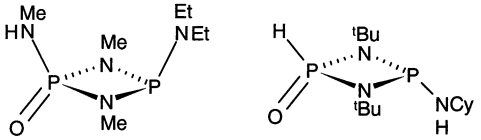
3.3.1. Monochalcogenides

The monoxide **21a** is prepared by controlled oxidation of **8a** (R = R′ = ^{t}Bu) with ^{t}BuOOH at −78 °C (Method A) [15]. A slight deficiency of ^{t}BuOOH is necessary to prevent the formation of the dioxide.



21a, E = O
21b, E = S
21c, E = Se
21d, E = Te

Although outside the scope of this review, two structurally characterized monoxides are worthy of note. First, the condensation reaction between the tris(methylamido)phosphate [OP(NHMe)$_3$] and tris(diethylamido)phosphine [P(NEt$_2$)$_3$] yields the asymmetric *cis*-monoxide **22a** [26]. Secondly, the hydride **22b** was formed unexpectedly from the reaction of [ClP(μ-N^{t}Bu)$_2$P(OAr)] with CyNH$_2$ [27]. In contrast to the *cis* orientation found in **22a**, the oxo ligand and the lone pair on the P(III) atom are *trans* in **22b**.



22a **22b**

The monosulfide **21b** is prepared by oxidation of **8a** (R = R′ = ^{t}Bu) with slightly less than one equivalent of elemental sulfur at low temperatures. At room tempera-

ture equal amounts of **8a** (R = R′ = ^{t}Bu) and disulfide **8b** (R = R′ = ^{t}Bu; E = S) are obtained [15].

Although attempts to prepare a monoselenide by stoichiometric oxidation of **8a** were not successful, the comproportionation reaction generates the monoselenide **21c** in quantitative yield at 75 °C in toluene (Method D, Scheme 6) [28]. The P=Se bond length of 2.1169(7) Å is in the typical range for phosphine selenides. Woollins et al. have reported the preparation of the monoselenide $Ph_2P(Se)NHPPh_2$ by reaction of equimolar quantities of $Ph_2P(Se)NH(Se)PPh_2$ and $Ph_2PNHPPh_2$ in chloroform at room temperature [29]. This approach is not effective for the preparation of the corresponding monosulfides because of the lower lability of P=S compared to P=Se bonds.

The monotelluride **21d** is prepared by oxidation of **8a** (R = R′ = ^{t}Bu) with elemental tellurium in boiling toluene [23]. The P=Te bond length of 2.370(1) Å is in the typical range for phosphine tellurides, while ^{31}P-NMR data for **21d** in d_8-THF are consistent with retention of the P=Te linkage in solution.

By analogy with the known chemistry of ligands of the type **6** [7], the monochalcogenides **21a–d** should be suitable precursors for multidentate ligands in which different chalcogens are connected to the two P(V) centres.

4. Coordination modes

As discussed in Section 1, dianions of the type **4a–c** and their monoprotonated derivatives are potentially versatile ambidentate ligands. In addition to the three known coordination modes for **7** (Scheme 1), several other modes of coordination, via 'hard' *N* and 'soft' *E* donor centres, are possible for anions derived from **8b** and **8c** as illustrated in Scheme 7.

5. Spectroscopic techniques

Solution NMR is the most valuable spectroscopic technique for elucidating the nature of coordination complexes derived from **8b** and **8c**. A ^{31}P-NMR chemical shift to lower frequency typically indicates the formation of an anion. Complexes of the monoanions or dianions are readily distinguished by the number of observed resonances. Metal complexes of the monoanion show two resonances, usually mutually coupled doublets, whereas coordination to the dianion gives rise to a singlet (see Tables 1 and 3). However, the ^{31}P-NMR spectra do not distinguish between the bis(*N*,*E*) and *N*,*N*′/*E*,*E*′ coordination modes for the dianion since both types of complexes have equivalent phosphorus environments.

^{77}Se (I = 1/2, 7.6%)- and ^{125}Te (I = 1/2, 7.0%)- NMR spectra can also aid in the identification of coordination complexes in solution. In particular, coupling constants are helpful in determining coordination of a metal to the chalcogen. For example, the value of $^1J(^{31}P–^{77}Se)$ decreases by ca. 200 Hz upon coordination as a result of the lower P–Se bond orders.

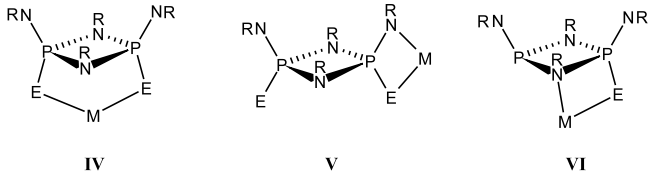
Infrared spectroscopy may be employed as a complimentary technique to NMR. The ν(P–E) stretching frequency shifts to lower frequencies upon coordination, as a result of the decrease in the P–E bond order. The observation of a ν(N–H) stretch is also indicative of an amido proton, which is not always detectable in ^{1}H-NMR spectra, and this signature can be used to identify complexes of the monoanions.

Although infrared and NMR spectroscopies provide valuable structural information, the only definitive method of determining coordination modes in the solid state is X-ray crystallography. Thus, nearly all of the coordination complexes discussed below have been structurally characterized.

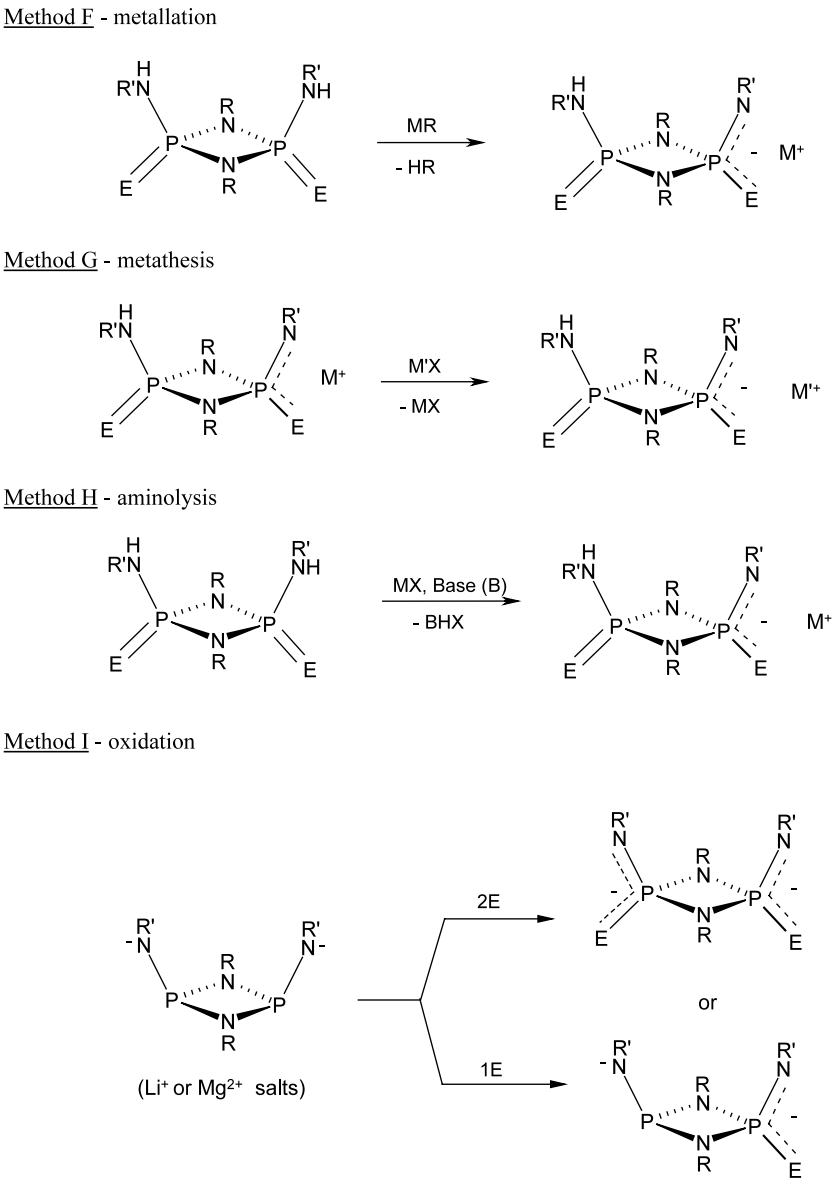
6. Syntheses and structures of coordination complexes

The first report of the deprotonation of the exocyclic amido substituent in these systems appeared 20 years ago [30]. Reaction of *trans*-[Ph(H)N(S)P(μ-NPh)$_2$P(S)N(H)Ph] (**14l**) with LiR (R = Me, ^{n}Bu) followed by treatment with MeX (X = Cl, Br) yielded the *N*-alkylated products *trans*-[Ph(Me)N(S)P(μ-NPh)$_2$P-(S)N(Me)Ph]. Since that time, other general methods have been developed as illustrated in Scheme 8. Specific details are given in the following subsections. NMR data for coordination complexes of cyclodiphosph(V/V)azane anions are provided in Table 3.

The most widely employed synthetic approach involves deprotonation of the ligand with a reactive organometallic, metal amide or metal alkoxide reagent. Although, this method is usually employed for the preparation of alkali-metal salts, it is also useful for zinc or aluminum derivatives (Method F). Transition-metal complexes are normally prepared via metathetical reactions between the anionic ligand, as an alkali-metal salt, and a metal halide (Method G). A third approach involves the direct reaction of the neutral ligand with a metal halide in the presence of a weak base (Method H). A less common synthesis, which is useful for generating



Scheme 7.



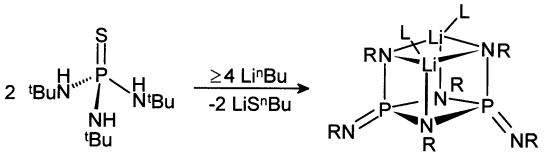
Scheme 8.

metal complexes of the tellurides, is the oxidation of a cyclodiphosph(III/III)azane metal complex with elemental chalcogen (Method I) (Table 4).

6.1. Group 1 elements

6.1.1. Lithium compounds

The dilithium salts of the cyclodiphosph(V/V)azane dianions derived from **8b** exhibit two different modes of ligand coordination. A cubane structure is observed for the tris(imido)metaphosphate dimer **23**, which was unexpectedly formed by sulfur extrusion in reaction of the tris(amido)thiophosphate, $[SP(NH^tBu)_3]$ with two or more equivalents of Li^nBu. Complex **23** is a dimer of the lithium salt of the trisimidometaphosphate (**1**, R = R′ = ^{t}Bu) [31]. Interestingly, hydrolysis of **23** generates the *trans* diimide **10** as shown by ^{31}P-NMR spectra [15].



23, R = ^{t}Bu, L = thf

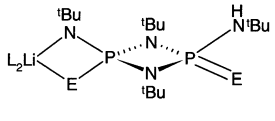
Related heteroleptic imido/chalcogenido metaphosphates are prepared by the reaction of $[^tBu(H)N(S)P(\mu\text{-}N^tBu)_2P(S)N(H)^tBu]$ (**14d**) with an organolithium reagent. Thus, treatment of **14d** with one equivalent of Li^nBu, in the presence of TMEDA,

Table 3
NMR data for coordination complexes of cyclodiphosph(V/V)azanes [R′(H)N(E)P(μ-NR)$_2$P(E)N(H)R′] (**8b**) and cyclodiphosph(III/V)azanes [R′(H)N(E)P(μ-NR)$_2$PN(H)R′] (**8c**)

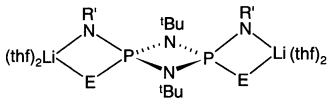
Compound	E	R	R′	M	δ ^{31}P{^{1}H} (ppm)	$^2J(^{31}P-^{31}P)$, $^1J(^{31}P-E)$ [Hz]	Solvent	Reference
Cyclodiphosph(V/V)azane monoanions								
35a	NPh	^{t}Bu	^{t}Bu	Ti	−1.4(d), −50.1(d)	48	C_6D_6	[11]
35b	NpTol	^{t}Bu	^{t}Bu	Ti	−3.0(d), −50.3(d)	47	C_6D_6	[11]
24	S	^{t}Bu	^{t}Bu	Li	36.3(d), 16.7(d)	21	C_6D_6	[32]
35c	S	^{t}Bu	^{t}Bu	Ti	36.2(d), 25.7(d)	26	C_6D_6	[11]
42	S	^{t}Bu	^{t}Bu	Cu	36.0(d), 24.8(d)	19	C_6D_6	[36]
38a	S	^{t}Bu	^{t}Bu	Ni	415.9(s, br), 104.3(s)		$CDCl_3$	[36]
38b	S	^{t}Bu	^{t}Bu	Pd	37.6(d), 26.9(d)	25	THF-d_8	[36]
39	S	^{t}Bu	^{t}Bu	Pd	33.5(d), 19.7(d)	22	THF-d_8	[36]
49a	S	^{t}Bu	^{t}Bu	Te	35.1(d), −9.0(s, br)	29	THF-H$_8$	[39]
25	Se	^{t}Bu	^{t}Bu	Li	23.6(d), −4.0(d)	8, 695	THF-d_8	[32]
35d	Se	^{t}Bu	^{t}Bu	Ti	22.5(d), 10.1(d)	14, NR	C_6D_6	[11]
43	Se	^{t}Bu	^{t}Bu	Zn	25.4(d), 15.9(d)	16, 625	THF-d_8	[15]
Cyclodiphosph(V/V)azane dianions								
36a	NTMS	TMS	TMS	Re	−1.9(s)		C_6D_6	[34]
36b	NTMS	TMS	TMS	Re	−8.3(s)		C_6D_6	[34]
23	N^{t}Bu	^{t}Bu	^{t}Bu	Li	−22.1(s)		C_6D_6	[31]
45a	NPh	^{t}Bu	^{t}Bu	Al	−16.2(s)		C_6D_6	[14]
45b	NpTol	^{t}Bu	^{t}Bu	Al	−16.2(s)		C_6D_6	[14]
45c	O	^{t}Bu	^{t}Bu	Al	1.8(s)		C_6D_6	[14]
26b	S	Ph	^{t}Bu	Li	24.8(s)		C_6D_6	[14]
45e	S	Ph	^{t}Bu	Al	22.8(s)		C_6D_6	[14]
45d	S	^{t}Bu	^{t}Bu	Al	22.3(s)		C_6D_6	[14]
47	S	^{t}Bu	^{t}Bu	Sn	50.9(s)		C_6D_6	[38]
26a	S	^{t}Bu	^{t}Bu	Li	15.6(s)		THF-d_8	[32]
29a	S	^{t}Bu	^{t}Bu	Na	29.4(s)		THF-d_8	[32]
30a	S	^{t}Bu	^{t}Bu	K	26.6(s)		THF-d_8	[22]
41	S	^{t}Bu	^{t}Bu	Pt	8.5(s)		THF-d_8	[36]
45f	Se	^{t}Bu	^{t}Bu	Al	3.9(s)	NR	C_6D_6	[14]
45g	Se	Ph	^{t}Bu	Al	21.3(s)	NR	C_6D_6	[14]
29b	Se	^{t}Bu	^{t}Bu	Na	3.9(s)	6, 677	THF-d_8	[22,32]
30b	Se	^{t}Bu	^{t}Bu	K	−0.03(s)	0, 686	THF-d_8	[22]
27	Te	^{t}Bu	^{t}Bu	Li	−50.0(s)	35, 1790	THF-d_8	[23]
Cyclodiphosph(III/V)azane monoanions								
37	NSiMe$_3$	SiMe$_3$	SiMe$_3$	Re	201.6(d), 29.0(d)	40	CD_2Cl_2	[35]
28	Se	^{t}Bu	^{t}Bu	Li	74.5(s), 3.1(s)	0, 622	THF-d_8	[32]
32	Se	^{t}Bu	^{t}Bu	K	75.6(s), 0.2(s)	0, 640	THF-d_8	[28]
40	Se	^{t}Bu	^{t}Bu	Ni	957.7(s, br), 22.2(s)	0, 0	$CDCl_3$	[28]
Cyclodiphosph(III/V)azane dianions								
46	S	^{t}Bu	^{t}Bu	Sn	64.5(d), 99.0(d)	15	C_6D_6	[38]
33	Se	^{t}Bu	^{t}Bu	K	104.3(d), 2.4(d)	29, 611	THF-d_8	[28]
34	Te	^{t}Bu	^{t}Bu	Mg	107.3(d), −26.2(d)	15, 1854	THF-d_8	[23]

NR, not reported.

produces the *N*,*S*-chelated complex **24**. The THF-solvated selenium analogue **25** is prepared in a similar way, but low temperatures are necessary to prevent P=Se bond cleavage (vide infra).



24 (E = S, L_2 = TMEDA)
25 (E = Se, L = thf)



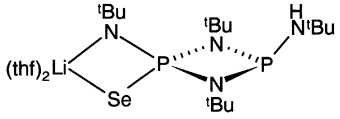
26a, E = S, R' = ^{t}Bu
26b, E = S, R' = Ph
27, E = Te, R' = ^{t}Bu

The dilithiated complex **26a** is prepared by metallation of **14d** with ^{t}BuLi in boiling THF [32], whereas ambient temperature and ^{n}BuLi are sufficient to yield **26b** from the more acidic arylamido disulfide **15** [14]. Compound **26a** also shows *N*,*S*-chelated lithium centers, while **26b** is assumed to have an analogous spirocyclic structure based on NMR data. The attempted synthesis of the diselenide analogue of **26a**, under similar reaction conditions results in cleavage of one of the P=Se bonds, with formation of LiSe^{t}Bu, to give the mixed oxidation state [P(III)/P(V)] *N*,*Se*-chelated complex **28** [32].

Table 4
Coordination mode and selected bond lengths [a] (Å) of bis(amido)cyclodiphosph(V/V)azanes (**8b**) and cyclodiphosph(III/V)azanes (**8c**)

Compound	E	R	R′	M	Coordination mode	P–E_M [b]	P–E [c]	M–E	M–N_{exo}	M–N_{endo}	Reference
Cyclodiphosph(V/V)azane monoanions											
35a	NPh	^{t}Bu	^{t}Bu	Ti	V	1.622(2)	NR	2.003(3)	2.014(2)		[11]
31	S	^{i}Pr	^{i}Pr	K	V	1.954(1)	1.939(1)	3.241(1)	2.786(3)		[15]
24	S	^{t}Bu	^{t}Bu	Li	V	1.978(2)	1.931(2)	2.46(1)	2.02(1)		[32]
35c	S	^{t}Bu	^{t}Bu	Ti	V	2.010(1)	1.921(2)	2.394(1)	2.037(4)		[11]
42	S	^{t}Bu	^{t}Bu	Cu	V	2.005(3)	1.939(3)	2.391(3)	1.961(7)		[36]
38a	S	^{t}Bu	^{t}Bu	Ni	V	2.003(1)	1.932(1)	2.3449(9)	1.971(2)		[36]
38b	S	^{t}Bu	^{t}Bu	Pd	V	2.006(2)	1.933(2)	2.338(2)	2.089(4)		[36]
49a	S	^{t}Bu	^{t}Bu	Te	V	2.034(2)		2.534(1)	2.535(4)		[39]
51	S	^{t}Bu	^{t}*B*u	Te	V	2.070(2)		2.426(2)	2.300(4)		[39]
35d	Se	^{t}Bu	^{t}Bu	Ti	V	2.1569(8)	2.065(1)	2.5058(8)	2.042(3)		[11]
49b	Se	^{t}Bu	^{t}Bu	Te	V	2.190(2)		2.628(1)	2.616(8)		[39]
Cyclodiphosph(V/V)azane dianions											
36a	NTMS	TMS	TMS	Re	V	1.576(6)		2.224(6)	2.224(6)		[34]
23	N^{t}Bu	^{t}Bu	^{t}Bu	Li	I		1.526(6)		2.112(9)	2.33(1)	[31]
45b	NpTol	^{t}Bu	^{t}Bu	Al	V	1.635(2)		1.950(2)	1.967(2)		[14]
45c	O	^{t}Bu	^{t}Bu	Al	V	1.529(1)		1.884(2)	1.939(2)		[14]
45d	S	^{t}Bu	^{t}Bu	Al	V	2.002(2)		2.354(2)	1.919(4)		[14]
47	S	^{t}Bu	^{t}Bu	Sn	III		NR		2.125(6)		[38]
26a	S	^{t}Bu	^{t}Bu	Li	V	2.003(2)		2.436(8)	1.999(9)		[32]
29a	S	^{t}Bu	^{t}Bu	Na	III, IV	1.993(3)		2.853(4)	2.442(7)	2.836(7)	[32]
30a	S	^{t}Bu	^{t}Bu	K	III, IV	2.00(1)		3.19(1)	2.76(3)	NR	[22]
41	S	^{t}Bu	^{t}Bu	Pt	IV	2.065(5)		2.371(4)			[36]
30b	Se	^{t}Bu	^{t}Bu	K	III, IV	2.167(4)		3.314(4)	2.79(1)	3.21(1)	[22]
Cyclodiphosph(III/V)azane monoanions											
37	NTMS	TMS	TMS	Re	II	1.542(7)		2.281(7)	2.160(7)	2.225(7)	[35]
28	Se	^{t}Bu	^{t}Bu	Li	V	2.163(2)		2.60(1)	1.96(1)		[32]
32	Se	^{t}Bu	^{t}Bu	K	V	2.1650(6)		3.3817(7)	2.918(2)		[28]
40	Se	^{t}Bu	^{t}Bu	Ni	V	2.170(2)		2.479(1)	1.954(2)		[28]
Cyclodiphosph(III/V)azane dianions											
48	S	^{t}Bu	^{t}Bu	Sn	II		1.872(3)		2.096(3)	2.539(3)	[8]
33	Se	^{t}Bu	^{t}Bu	K	II, VI	2.183(2)		2.932(5)	2.699(6)	3.166(5)	[28]
34	Te	^{t}Bu	^{t}Bu	Mg	II		2.385(2)		2.093(6)	2.423(6)	[23]

NR, not reported.
[a] Average value in Å.
[b] E_M, E substituent coordinated to metal center.
[c] E, E substituent not coordinated to metal center.



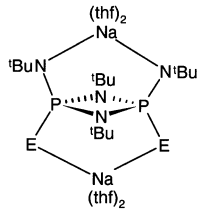
28

A different approach was necessary to prepare the thermally unstable tellurium analogue **27**. This involves oxidation of the dilithium salt of **7** (R = R′ = ^{t}Bu) with two equivalents of elemental tellurium in boiling THF. A preliminary X-ray analysis of the resulting, extremely moisture-sensitive, crystals confirmed the formation of **27** [23].

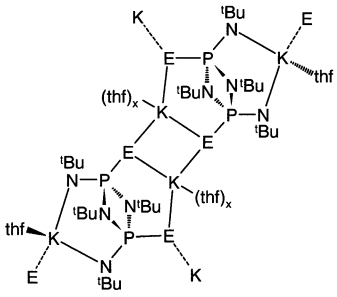
6.1.2. Sodium and potassium compounds

Metal complexes of cyclodiphosph(V/V)azane dianions with the larger sodium and potassium cations exhibit a different mode of coordination than that found for lithium. Metallation of **14d** or **18** with two equivalents of $MN(SiMe_3)_2$ (M = Na, K) under ambient conditions yields the disodium or dipotassium complexes **29a**,**b** or **30a**,**b**, respectively [22,32]. The larger sodium and potassium ions favor *N*,*N*′ and *E*,*E*′ chelation, forming six-membered rings. The sodium ions in **29a** and **29b** are solvated by two THF molecules, which apparently prevent further association. By contrast, the dipotassium complexes **30a** and **30b** dimerize through weak K–E interactions. The dimeric units further associate via weaker K–E interactions to give 20-membered rings that form an extended layered structure (Fig. 1).

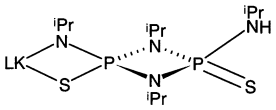
Metallation of **14d** or **18** with one equivalent of $MN(SiMe_3)_2$ (M = Na, K) generates a mixture of the dimetallated complexes (**29a/30a**, **29b/30b**) and unreacted **14d** or **18**. However, metallation of **14c** with one equivalent of KO^{t}Bu in the presence of 18-crown-6



29a, E=S
29b, E=Se



30a, E=S, x=1
30b, E=Se, x=2



31 (L = 18-crown-6)

yields the mono-metallated *N*,*S*-chelated complex **31** [15]. Although, **14c** is obtained as the *trans*-isomer [18], the monopotassium salt **31** adopts a *cis*-configuration.

Metallation of the P(III)/P(V) system **21c** with KO^tBu or $KN(SiMe_3)_2$, even at elevated temperatures, proceeds only to the formation of the monopotassium complex **32** [28]. The two potassium ions of the dimeric structure of **32** are each *N*,*Se*-chelated by two monoanionic ligands. Additionally, the potassium ions are solvated by one molecule of THF. The central $K_2N_2Se_2$ core of **32** forms a distorted octahedron.

By employing the stronger base benzylpotassium, KCH_2Ph, the dipotassium salt of the P(III)/P(V) monoselenide **33** can be prepared at room temperature [28]. Structural comparison with the corresponding P(V)/

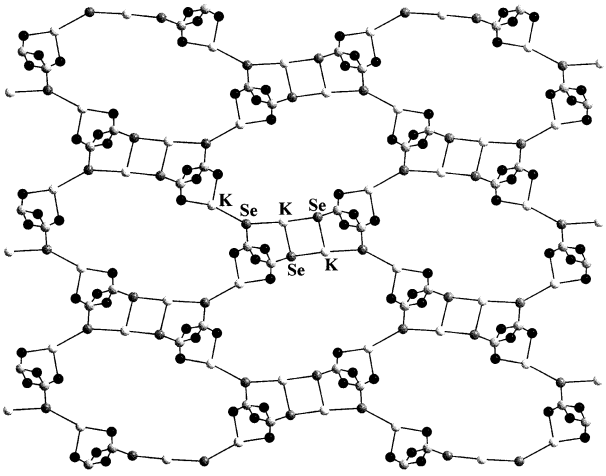


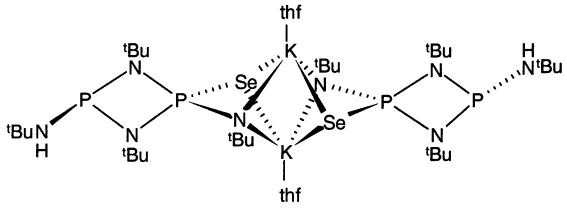
Fig. 1. The extended structure of **30b** showing the two types of K···Se interactions. For clarity ^{t}Bu groups on nitrogen and THF ligands coordinated to K^+ ions are omitted.

P(V) complex **30b** is informative. The absence of the second Se donor site in **33** precludes the formation of the extended structure observed for **30b** (Fig. 1), and results in a change of the coordination mode to the K^+ ions that form the central K_2Se_2 ring from *Se*,*Se′* to μ-*N*,*Se*. The second K^+ ion is *N*,*N′*,*N″* coordinated. Thus, both bridging N^{t}Bu groups of the P_2N_2 unit are involved in bonding to K^+ ions.

6.2. Group 2 elements

6.2.1. Magnesium compounds

In a similar approach to the preparation of **27c**, the reaction of the magnesium salt of **7** (R = R′ = ^{t}Bu) [33] with an excess of elemental tellurium yields the monotelluride **34** [23]. The X-ray structure of **34** shows a monomeric complex with retention of the seco-heterocubic arrangement with no significant change in the P=



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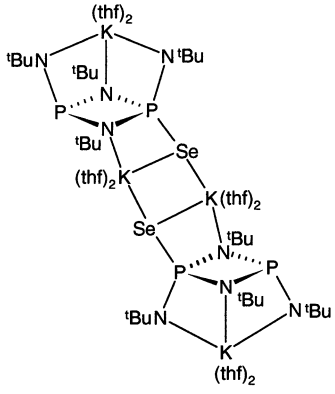
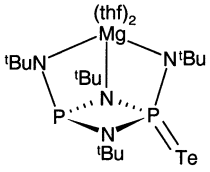


33

Te bond length compared to that in **21d**.



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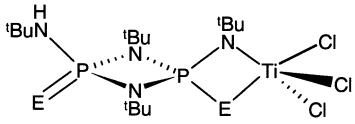
6.3. Group 4 elements

6.3.1. Titanium compounds

Titanium complexes can be prepared by aminolysis of titanium(IV) chloride in the presence of NEt_3 as an HCl-scavenger. Despite the use of an excess of $TiCl_4$, only monometallated compounds are obtained by this method [11]. Structural analysis shows that they are *N*,*E*-chelated $TiCl_3$ complexes **35a**–**d**.

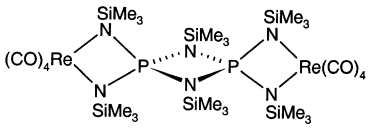


35a, E = NPh
35b, E = Nptol
35c, E = S
35d, E = Se

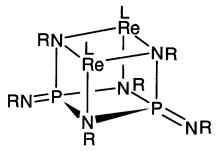
6.4. Group 7 elements

6.4.1. Rhenium compounds

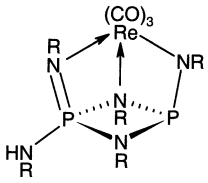
The co-thermolysis of $[(CO)_4Re(\mu\text{-}NSiMe_3)_2\text{-}PClN(SiMe_3)_2]$ and $(Me_3Si)_2NPNSiMe_3$ in toluene at 110 °C produces the *N*,*N*′-chelated spirocyclic complex **36a** and the cubane **36b** [34], both of which can be regarded as metal complexes of the dimeric trisimido-metaphosphate $[P(NSiMe_3)_3]_2^{2-}$. Apparently, the loss of a CO ligand on each rhenium atom causes the bis(*N*,*N*′)-chelated complex to rearrange to a cube. A similar structural relationship is apparent for spirocyclic dilithium derivatives of the type **26** and **27** and the cubane **23**, in which the departure of a THF ligand from each Li^+ cation is accompanied by formation of a cube. A third product of the co-thermolysis, complex **37**, provides a unique example of an *N*,*N*′,*N*″ bonding mode for a monoanionic P(III)/P(V) ligand system [35]. This coordination mode provides an interesting contrast to that found for monoanionic P(III)/P(V) chalcogen-containing ligands in **28** and **32**.



36a



36b, L=(CO)$_3$, R = SiMe$_3$



37 (R = SiMe$_3$)

6.5. Group 10 elements

6.5.1. Nickel and palladium compounds

The Ni(II) and Pd(II) complexes, **38a** and **38b**, are readily obtained by metathetical reactions between two equivalents of **24** and $NiCl_2(PEt_3)_2$ or $PdCl_2(PhCN)_2$, respectively [36]. The Ni^{2+} ion in this bis(*N*,*S*)-chelated complex is in a tetrahedral environment and exhibits paramagnetic properties, while the palladium analogue is a square planar, diamagnetic complex. On the basis of ^{31}P-NMR data, metathesis of two equivalents of **24** with $PdCl_2(PPh_3)_2$ produces the mono-chelated complex **39**, reflecting the stronger donation of PPh_3 (compared to PhCN) to palladium [36].

Interestingly, the reaction of **25** with $NiCl_2(PMe_3)_2$ results in cleavage of the non-coordinated P=Se bond by the displaced PMe_3 ligand to give **40**, a paramagnetic P(III)/P(V) complex of nickel(II), and $SePMe_3$ [28]. Complex **40** may also be prepared directly by the reaction of **32** with $NiCl_2(PMe_3)_2$.

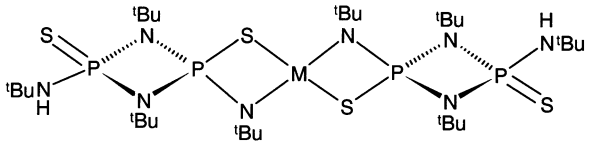
6.5.2. Platinum compounds

The metathetical reaction of two equivalents of **24** with $PtCl_2(PEt_3)_2$ generates the *S*,*S*′-chelated square-planar platinum(II) complex **41** [36]. The eliminated HCl reacts with the second equivalent of **24** to produce **14d** and LiCl. Alternatively, complex **41** is prepared by the reaction of $PtCl_2(PEt_3)_2$ with the dipotassium salt **30a**. As expected the platinum centre favors the soft sulfur donor sites over the hard nitrogen centres.

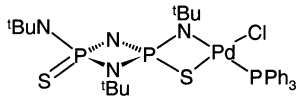
6.6. Group 11 elements

6.6.1. Copper compounds

The reaction of CuCl with **24** in the presence of PPh_3 produces the *N*,*S*-chelated three-coordinate copper(I) complex **42** [36].



38a, M=Ni (tetrahedral)
38b, M=Pd (square planar)



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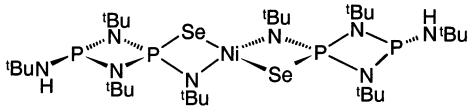

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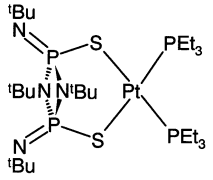

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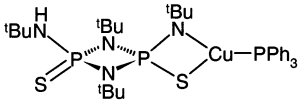

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6.7. Group 12 elements

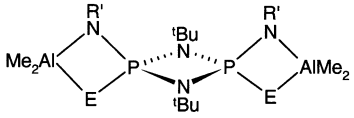
6.7.1. Zinc compounds

Zinc complexes of **14d** or **18** are prepared by metallation using dimethyl or diethyl zinc. The tetrahedral bis(*N*,*Se*)-chelated complex **43** is obtained by monodeprotonation of the diselenide **18** with $ZnMe_2$ [15]. By contrast, the reaction of **14d** or **18** with two equivalents of $ZnEt_2$ produces the monosubstituted complexes **44a** and **44b** [37].

6.8. Group 13 elements

6.8.1. Aluminum compounds

A variety of aluminum complexes **45a**–**g** have been obtained by metallation of bis(amido) ligands of the type **9**, **12**, **14**, **18** or **19** with two equivalents of trimethylaluminum [14]. In all cases, the dianionic ligand is bis(*N*,*E*)-chelated to aluminum.

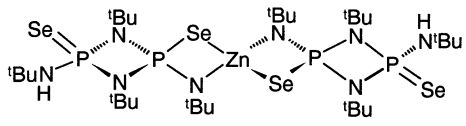


45a; E = NPh, R' = ^{t}Bu
45b; E = Nptol, R' = ^{t}Bu
45c; E = O, R' = ^{t}Bu
45d; E = S, R' = ^{t}Bu
45e; E = S, R' = Ph
45f; E = Se, R' = ^{t}Bu
45g; E = Se, R' = Ph

6.9. Group 14 elements

6.9.1. Tin compounds

The oxidation of the dimethyltin derivative of **7** (R = R′ = ^{t}Bu) with one or two equivalents of sulfur produces the monosulfide **46** and the disulfide **47**, respectively [38] (cf. synthesis of **34** and **27**). Significantly, oxidation by sulfur does not disrupt the *N*,*N*′ coordination mode of the ligand. The interesting dimer **48** is obtained by the



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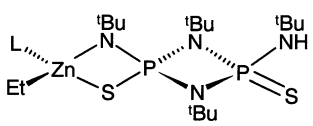
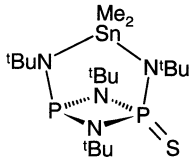


44a, E = S, L = thf
44b, E = Se, L = thf



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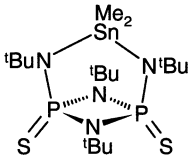

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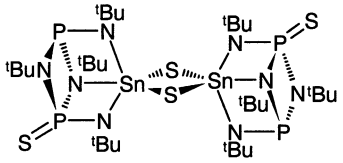


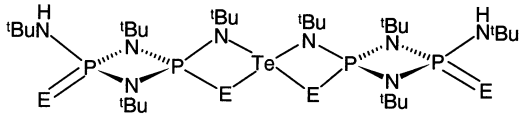
48

reaction of the tin(II) derivative of **7** ($R = R' = {}^tBu$) with two equivalents of sulfur [8]. In view of the facile generation of the disulfide **14d** in the preparation of the monosulfide **21b** (see Section 3.3.1), the preferential formation of **48** suggests that the Sn(II) centre is oxidized prior to oxidation of one of the P(III) centres.

6.10. Group 16 elements

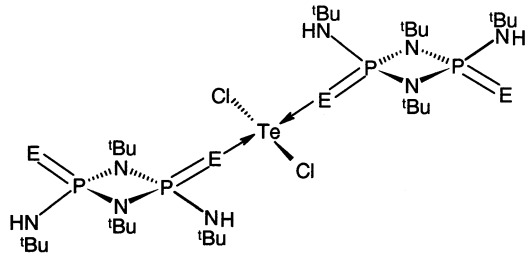
6.10.1. Tellurium compounds

The reaction of $TeCl_4$ with **24** (L = THF) or **25** in a 1:4 molar ratio in THF at low temperature results in redox processes and the isolation of the tellurium(II) complexes **49a** and **49b** in low yields [39]. The distorted square-planar complexes **49a** and **49b** are isostructural and show two monoanionic ligands chelating the tellurium center in an *N*,*E* manner. The Te–N bond lengths are ca. 0.5 Å longer than the single bond value of 2.05 Å indicating a weak interaction. These compounds are unstable in solution, decomposing to give elemental tellurium and the neutral dichalcogenide ligands **14d** and **18**.



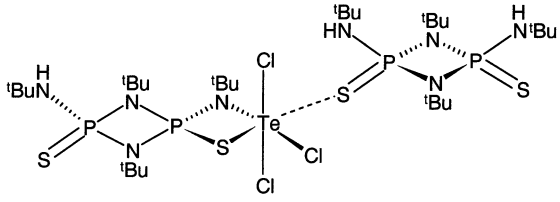
49a, E = S
49b, E = Se

A redox process also occurs when this reaction is carried out in a 1:2 molar ratio. With this stoichiometry, however, the square-planar tellurium(II) dichloride adducts **50a** and **50b** are isolated as the *trans*-isomers. Similar $TeCl_2$ adducts of thio- and seleno-ureas are well known [40]. Detailed ^{31}P-NMR and EPR studies of the reaction of **24** with $TeCl_4$ indicate that the formation of the neutral ligand **14d** and, presumably, **18** occurs via a radical process involving hydrogen abstraction from THF solvent [39].



50a, E = S
50b, E = Se

At shorter reaction times (3 h) the redox process is minimized in the 2:1 reaction and the tellurium(IV) complex **51** may be isolated. As in **49a**, the tellurium centre in **51** is chelated in an *N*,*S* manner to the monoanionic ligand. Additionally, the tellurium centre is weakly coordinated to one of the sulfur donor sites of a neutral disulfide ligand **14d** (cf. **50a**) [39].



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7. Summary and conclusions

A variety of methods has been developed for the preparation of coordination complexes of homoleptic and heteroleptic metaphosphates containing imido/chalcogenido ligands. The metallation approach using organometallic, metal alkoxide or metal amide reagents is effective for the most electropositive elements, i.e. Li, Na, K, as well as for Zn and Al. Arylimido derivatives of cyclodiphosph(V/V)azanes are significantly more readily metallated than their alkylimido analogues. The lability of the P=E bond is another important consideration in the metallation reactions. In selenium-containing systems (E = Se) cleavage of a P=Se bond

may occur to give mixed oxidation state [P(V)/P(III)] complexes. In the case of tellurium, the facile cleavage of P=Te bonds engendered a different approach to the preparation of complexes with electropositive metals that involves carrying out the metallation step prior to the oxidation with elemental chalcogen. Transition-metal complexes are readily obtained by metathetical reactions between transition-metal halides and the alkali-metal salts of mono- or dianions derived from bis(amido)cyclodiphosph(V/V)azanes. Studies of tellurium complexes revealed that the monoanions are susceptible to redox processes when the metal centre can exist in different oxidation states. This observation is likely to be significant in future studies of complexes of transition-metal ions that are susceptible to reduction.

The monoanions of P(V)/P(V) systems coordinate to metal centres exclusively by an 'end-on' (*N*,*E*)-chelation mode, presumably because the negative charge is delocalized on one side of these ambidentate ligands. The dianions adopt either bis(*N*,*E*)-chelation modes (for Li^+) or 'top and bottom' (*N*,*N*′ and *E*,*E*′) chelation in the case of Na^+ and K^+. In the former case, the smaller Li^+ ions can be accommodated in four-membered rings, whereas the larger Na^+/K^+ ions prefer a six-membered ring in order to reduce ring strain. Although, the data for metal centres with a 2+ charge are limited, the dianionic ligands have been shown to adopt either *S*,*S*′ [**41**, $M = Pt(PEt_3)_2^{2+}$] or *N*,*N*′ (**47**, $M = SnMe_2^{2+}$) chelation modes in such complexes. This selectivity, depending on the hard/soft properties of the metal centre, bodes well for the synthesis of coordination polymers containing different metals. Complexes of the type **38** are potential precursors of coordination polymers via metallation of the terminal ^{t}BuNH groups. The absence of the second chalcogen donor site in the P(III)/P(V) systems induces the involvement of the bridging nitrogen atoms in coordination to the metal centres. A novel bis(η^2-*P*,*N*) coordination mode has recently been described by Stahl et al. for a nickel complex of the dianionic P(III)/P(III) ligand **7** ($R = R' = {}^t$Bu) [41]. The coordination chemistry of cyclodiphosph(III/III)azanes as *P*-donor ligands has been extensively investigated [42]. In the light of those results, the interaction of P(III) centres in the P(III)/P(V) monochalcogenido complexes with transition metals provides another opportunity for generating coordination polymers.

Acknowledgements

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References

[1] For recent reviews, see: (a) J.K. Brask, T. Chivers, Angew. Chem. Int. Ed. Engl. 40 (2001) 3961;
(b) M.A. Beswick, M.E.G. Mosquera, D.S. Wright, J. Chem. Soc. Dalton Trans. (1998) 2437;
(c) M.A. Beswick, D.S. Wright, Coord. Chem. Rev. 176 (1998) 373;
(d) R. Fleischer, D. Stalke, Coord. Chem. Rev. 176 (1998) 431.
[2] E. Niecke, M. Frost, M. Nieger, V. von der Gönna, A. Ruban, W.W. Schoeller, Angew. Chem. Int. Ed. Engl. 33 (1994) 2111.
[3] J.K. Brask, T. Chivers, M. Krahn, G.P.A. Yap, unpublished results.
[4] N. Burford, P. Losier, S. Mason, P.K. Bakshi, T.S. Cameron, Inorg. Chem. 33 (1994) 5613.
[5] (a) T. Chivers, M. Parvez, M.A. Seay, Inorg. Chem. 33 (1994) 2147;
(b) T. Chivers, M. Parvez, M.A. Seay, Z. Anorg. Allg. Chem. (1995) 1813;
(c) T. Chivers, R.W. Hilts, Coord. Chem. Rev. 137 (1994) 201.
[6] (a) M. Bochmann, G.C. Bwembya, N. Whilton, X. Song, M.B. Hursthouse, S.J. Coles, A. Karaulov, J. Chem. Soc. Dalton Trans. (1995) 1887;
(b) M. Bochmann, G.C. Bwembya, M.B. Hursthouse, S.J. Coles, J. Chem. Soc. Dalton Trans. (1995) 2813 (and references cited).
[7] For recent reviews, see: (a) C. Silvestru, J. Drake, Coord. Chem. Rev. 223 (2001) 117;
(b) T.Q. Ly, J.D. Woollins, Coord. Chem. Rev. 176 (1998) 451;
(c) J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 2893;
(d) P. Bhattacharyya, J.D. Woollins, Polyhedron 14 (1995) 3367.
[8] For a recent reviews, see: L. Stahl, Coord. Chem Rev. 210 (2000) 203.
[9] (a) R. Keat, Top. Curr. Chem. 102 (1983) 89;
(b) R. Keat, The Chemistry of Inorganic Homo- and Heterocycles, vol. 2, Academic Press, London, 1987, p. 467;
(c) R.A. Shaw, Phosphorus Sulfur 4 (1978) 101.
[10] H. Bock, W. Wiegrabe, Chem. Ber. 99 (1966) 377.
[11] D.F. Moser, C.J. Carrow, L. Stahl, R.J. Staples, J. Chem. Soc. Dalton Trans. (2001) 1246.
[12] J.K. Brask, T. Chivers, M. Krahn, M. Parvez, unpublished results.
[13] M. Nieger, H. Hupfer, E. Niecke, R. Detsch, Cambridge Structural Database version 5.20, 1999.
[14] G.R. Lief, C.J. Carrow, L. Stahl, Organometallics 20 (2001) 1629.
[15] T. Chivers, M. Krahn, G. Schatte, unpublished results.
[16] T.G. Hill, R.C. Haltiwanger, M.L. Thompson, S.A. Katz, A.D. Norman, Inorg. Chem. 33 (1994) 1770.
[17] (a) J.D. Healy, R.A. Shaw, M. Woods, Phosphorus Sulfur 5 (1978) 239;
(b) M.B. Hursthouse, H.G. Parkes, L.S. Shaw (nee Gozen), R.A. Shaw, D.A. Watkins, Phosphorus Sulfur 28 (1986) 221.;
(c) M.B. Hursthouse, E.H. Ibrahim, H.G. Parkes, L.S. Shaw (nee Gozen), R.A. Shaw, D.A. Watkins, Phosphorus Sulfur 28 (1986) 261.
[18] R. Kempe, J. Sieler, Z. Kristallogr. 202 (1992) 157.
[19] (a) K. Dostal, J. Sikola, M. Meisel, H. Grunze, Z. Anorg. Allg. Chem. 543 (1986) 199;
(b) Z. Zak, T. Glowiak, Acta Crystallogr. Section C 47 (1991) 445.
[20] C.-C. Chang, R.C. Haltiwanger, M.L. Thompson, H.-J. Chen, A.D. Norman, Inorg. Chem. 18 (1979) 1899.
[21] J.-P. Dutasta, J.-P. Declercq, C. Esteban-Calderon, B. Tinant, J. Am. Chem. Soc. 111 (1989) 7136.
[22] T. Chivers, M. Krahn, M. Parvez, Chem. Commun. (2000) 463.
[23] G.G. Briand, T. Chivers, M. Parvez, G. Schatte, Abstract No. 475, 84th CSC Conference and Exhibition, Montreal, May 26–30, 2001.

[24] O.J. Scherer, G. Schnabl, Chem. Ber. 109 (1976) 2996.
[25] S. Pohl, Z. Naturforsch. 34b (1979) 256.
[26] S. Kleeman, E. Fluck, W. Schwarz, Phosphorus Sulfur 12 (1981) 19.
[27] M. Vijjulatha, K.C. Kumara Swamy, J.J. Vittal, L.L. Koh, Polyhedron 18 (1999) 2249.
[28] T. Chivers, M. Krahn, G. Schatte, Inorg. Chem., submitted for publication.
[29] P. Bhattacharyya, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1995) 3189.
[30] D.E. Coons, V.S. Allured, M.D. Noirot, R.C. Haltiwanger, A.D. Norman, Inorg. Chem. 21 (1982) 1947.
[31] T. Chivers, M. Krahn, M. Parvez, G. Schatte, Chem. Commun. (2001) 1922.
[32] T. Chivers, M. Krahn, M. Parvez, G. Schatte, Inorg. Chem. 40 (2001) 2547.
[33] I. Schranz, L. Stahl, R.J. Staples, Inorg. Chem. 37 (1998) 1493.
[34] O.J. Scherer, P. Quintus, J. Kaub, W.S. Sheldrick, Chem. Ber. 120 (1987) 1183.
[35] O.J. Scherer, P. Quintus, J. Kaub, W.S. Sheldrick, Chem. Ber. 120 (1987) 1463.
[36] T. Chivers, C. Fedorchuk, M. Krahn, M. Parvez, G. Schatte, Inorg. Chem. 40 (2001) 1936.
[37] L. Stahl, Private communication.
[38] G. Linti, H. Nöth, E. Schneider, W. Storch, Chem. Ber. 126 (1993) 611.
[39] G.G. Briand, T. Chivers, G. Schatte, Inorg. Chem. 41 (2002) in press.
[40] (a) S. Husebye, K.W. Törnroos, H. Zhu, Z. Anorg. Allg. Chem. 627 (2001) 1921;
(b) O. Foss, K. Maartmann-Moe, Acta Chem. Scand. A41 (1987) 121.
[41] G.R. Lief, C.J. Carrow, L. Stahl, R.J. Staples, Chem. Commun. (2001) 1562.
[42] M.S. Balakrishna, V.S. Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett St. Laurent, Coord. Chem. Rev. 129 (1994) 1.