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Titanium complexes of bis(1°-amido)cyclodiphosph(III)azanes and bis(1°-amido)cyclodiphosph(V)azanes: facial *versus* lateral coordination †

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Bis(1°-amino)cyclodiphosph(III)azanes and bis(1°-amino)cyclodiphosph(V)azanes show different coordination preferences with titanium(IV). The bis(*tert*-butylamino)cyclodiphosph(III)azane *cis*-[Bu^t(H)N(Bu^{t}NP)$_2$N(H)Bu^t] (**1**) reacts with $TiCl_4$ to afford {[(Bu^{t}NP)$_2$(NBu^t)$_2$]TiCl$_2$} (**2**), in which the ligand chelates the metal as a diamide, above the heterocycle. Oxidations of **1** with phenyl- or *p*-tolyl azide yield the cyclodiphosph(V)azanes *cis*-[Bu^t(H)N(ArN=PNBu^t)$_2$N(H)Bu^t] (Ar = phenyl (**3**), *p*-tolyl (**4**)). Single-crystal X-ray studies of **3** and **4** reveal structures similar to those of their parent cyclodiphosph(III)azanes, but with pendent arylimino groups attached to the phosphorus(V) atoms. When **3** and **4** are allowed to react with $TiCl_4$ the complexes {[Bu^t(H)N(ArN=PNBu^t)$_2$NBu^t]TiCl$_3$} (Ar = phenyl (**5**), *p*-tolyl (**6**)) are isolated. In these compounds the cyclodiphosph(V)azanes coordinate the metal laterally as monoanionic N–P–N ligands, similar to phosphoranates. An analogous side-on coordination is also found for the dichalcogeno complexes {[Bu^t(H)N(E=PNBu^t)$_2$NBu^t]TiCl$_3$} (E = S (**9**), Se (**10**)).

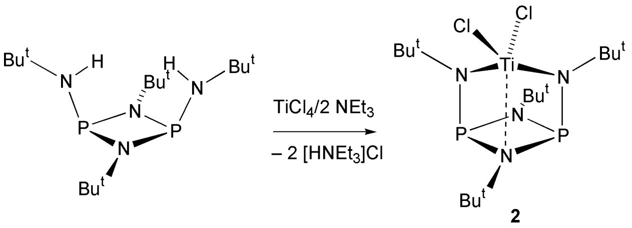
Introduction

Because of the importance of early-transition metal complexes in homogeneous polyolefin catalysis, there has been a resurgent interest in bis(amido) complexes of these metals.[1] We previously reported syntheses and structures of bis(*tert*-butylamido)cyclodiphosph(III)azane compounds of zirconium and hafnium, which, when activated with methylaluminoxane (MAO), polymerize ethylene.[2] Unlike their cyclodisilazane analogues,[3] however, these catalysts quickly deactivate during realistic polymerization conditions. The strongly Lewis-acidic catalyst, or the cocatalyst, presumably coordinates the lone-pair electrons of the phosphorus(III) atoms to initiate the destructive ring-opening of the ligand.

Cyclodiphosph(V)azanes are more robust than their phosphorus(III) counterparts, and many of the former are either known or easy to prepare from the latter by stereospecific chalcogen oxidations.[4] The phosphorus(III) heterocycles can also be oxidized with organic azides—a reaction that has not been reported previously. We had hoped that, just like chalcogen oxidation, the oxidation with organic azides would leave the bis(amido) moiety of the ligand essentially unchanged, while significantly increasing the kinetic and thermodynamic stabilities of these ligands to ring opening. Below we report syntheses and solid-state structures of bis(1°-amino)cyclodiphosph(V)azanes and their titanium complexes.

Results

Bis(amido)cyclodiphosph(III)azane complexes of zirconium and hafnium are readily prepared by the interaction of [(Bu^{t}NP)$_2$(NBu^{t}Li·THF)$_2$] with MCl_4 (M = Zr, Hf).[2] This procedure cannot be used for the synthesis of the corresponding titanium complex, because the dianion reduces the metal to the trivalent state.[5] The titanium–chloride bond of $TiCl_4$, however, is polar enough to react with neutral **1**,[6] Scheme 1, to yield the titanium compound **2** as an orange–red solid. The very simple ^1H, ^{13}C and ^{31}P NMR spectra of **2** suggested that, just like its zirconium and hafnium analogues, it was C_{2v}-symmetric in solution.



Scheme 1

A single-crystal X-ray analysis, Fig. 1, confirmed this spectroscopically assigned structure. Crystal data and selected bond parameters for **2** are listed in Tables 1 and 2, respectively. In the solid state, the molecule is a *seco*-heterocube of C_s symmetry, the titanium atom being the recipient of a donor bond from one of the ring-nitrogen atoms. All P–N bonds of the three-coordinate nitrogen atoms have essentially identical lengths (avg. 1.716(2) Å) while those of the four-coordinate nitrogen atom are expectedly longer, 1.779(2) Å. The titanium atom has idealized trigonal-bipyramidal coordination geometry and forms two normal, 1.925(2) Å, and one longer N–Ti bond, 2.267(2) Å, with the ligand. The slightly inequivalent titanium–chloride bonds of 2.2538(8) and 2.2780(7) Å have similar lengths as those in related compounds.[7,8]

Due to their instability, homogeneous titanium(IV) catalysts like **2**, are unsuitable for commercial olefin polymerization, but are useful model systems. For complex **2** the main mode of

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Table 1 Crystal data for compounds **2**–**5** and **9**–**10**

	2	**3**	**4**	**5**	**9**	**10**
Formula	$C_{16}H_{36}Cl_2N_4P_2Ti$	$C_{32}H_{56}N_6OP_2$	$C_{30}H_{52}N_6P_2$	$C_{31.5}H_{51}Cl_3N_6P_2Ti$	$C_{23}H_{45}Cl_3N_4P_2S_2Ti$	$C_{23}H_{45}Cl_3N_4P_2Se_2Ti$
M	465.23	602.77	558.72	729.91	657.94	750.93
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/m$ (no. 11)	$P2_1/m$ (no. 11)
T/K	213	293	293	213	293	213
a/Å	9.9454(1)	9.882(2)	12.144(3)	10.594(1)	9.130(1)	9.108(1)
b/Å	15.1386(1)	10.931(2)	20.535(2)	24.816(3)	13.450(1)	13.416(2)
c/Å	15.9841(1)	18.481(4)	13.454(1)	14.361(2)	14.142(1)	14.113(2)
α/°		89.14(3)				
β/°	93.614(1)	78.07(3)	90.84(1)	97.151(4)	94.488(9)	94.208(3)
γ/°		68.41(3)				
U/Å^3	2401.77(3)	1812.2(6)	3354.8(9)	3746.1(8)	1731.2(3)	1719.9(4)
Z	4	2	4	4	2	2
μ/mm^{-1}	0.720	0.152	0.157	0.557	0.700	2.710
Reflections collected	11105	10728	7190	23081	4142	11152
Independent reflections	4838 ($R_{int} = 0.0292$)	7478 ($R_{int} = 0.0393$)	5887 ($R_{int} = 0.0180$)	7630 ($R_{int} = 0.0778$)	3177 ($R_{int} = 0.0848$)	3895 ($R_{int} = 0.0275$)
$R(F)^a$ [$I > 2\sigma(I)$]	0.0404	0.1051	0.0501	0.0504	0.0480	0.0336
$wR2(F^2)^b$ [all data]	0.0886	0.2424	0.1526	0.1065	0.1390	0.0975

[a] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o^2 - F_c)^2]/[\Sigma w(F_o^2)^2]\}^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$.

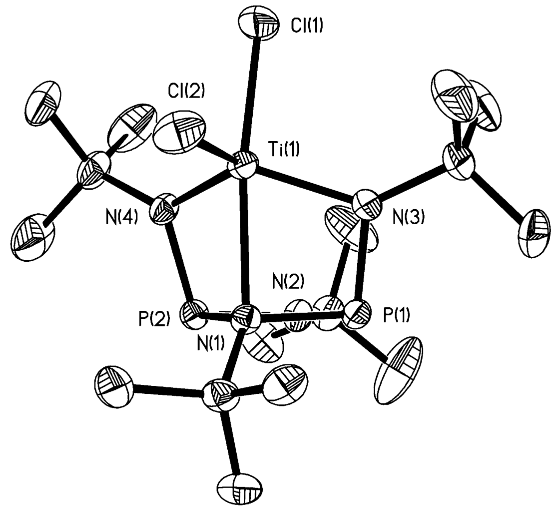


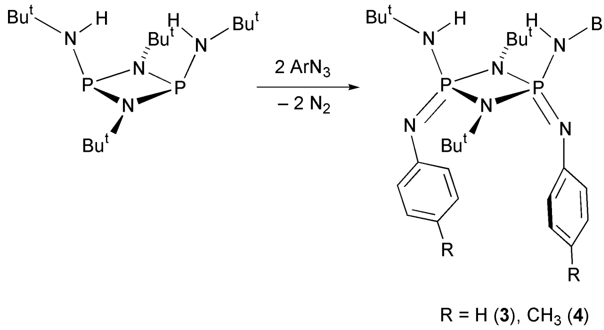
Fig. 1 Solid-state structure of **2**.

Table 2 Selected bond lengths (Å) and angles (°) for **2**

Ti–Cl(1)	2.2780(7)	P(1)–N(2)	1.718(2)
Ti–Cl(2)	2.2538(8)	P(1)–N(3)	1.711(2)
Ti–N(1)	2.267(2)	P(2)–N(1)	1.776(2)
Ti–N(3)	1.927(2)	P(2)–N(2)	1.716(2)
Ti–N(4)	1.923(2)	P(2)–N(4)	1.719(2)
P(1)–N(1)	1.781(2)		
Cl(1)–Ti–Cl(2)	99.20(3)	Cl(1)–Ti–N(4)	99.48(6)
N(3)–Ti–N(4)	116.35(8)	Cl(1)–Ti–N(1)	160.63(5)
Cl(1)–Ti–N(3)	99.41(6)	N(1)–P(1)–N(2)	81.33(9)
Cl(2)–Ti–N(3)	119.07(6)	P(1)–N(1)–P(2)	96.15(9)

deactivation appears to be the cycloreversion of the cyclodiphosph(III)azane, as suggested by the isolation of ligand recombination products from the reaction of asymmetrically substituted analogues of **2** with MAO.[9]

Because cyclodiphosph(V)azanes are thermodynamically more stable than their phosphorus(III) counterparts, we have begun using the phosphorus(V) molecules as ligands. Oxidations of phosphorus(III) compounds with organic azides (Staudinger reaction) are well known,[10] but these transformations have, to our knowledge, not been reported for cyclodiphosph(III)azanes. The treatment of **1** with aryl azides (Scheme 2) yielded the corresponding *cis*-2,4-bis(arylimino)cyclodiphosph(V)azanes **3** and **4** in very good yields. The attempted oxidations of cyclodiphosph(III)azanes with the less reactive trimethylsilyl azide, however, gave intractable mixtures.



Scheme 2

Compounds **3** and **4** are formal dimers of the aminobis(imino)phosphoranes [(Bu^{t}N=)(ArN=)PN(H)Bu^t] (Ar = phenyl, *p*-tolyl) respectively. The isolation of *trans*-{$(Me_3Si)_2N$-$[Me_3SiN{=}P(NSiMe_3)_2]_2N(SiMe_3)_2$}, the product of such a dimerization, had been communicated previously, but no structural details were given.[11]

The 2,4-bis(phenylimino)cyclodiphosph(V)azane was initially isolated as an oil, but on addition of tetrahydrofuran, it crystallized as a THF solvate, *viz.*, *cis*-{[Bu^t(H)N(PhN=PNBu^t)$_2$-N(H)Bu^t]·THF} (**3**). Even these crystals, however, were only of marginal quality, and we therefore also synthesized the 2,4-bis(*p*-tolylimino)cyclodiphosph(V)azane (**4**), which was free of solvent. This latter compound has the additional advantages of providing an NMR "handle" and having simpler NMR spectra. Both compounds were subjected to single-crystal X-ray studies. Selected crystal data and bond parameters of **3** and **4** appear in Tables 1 and 3, respectively. These bis(1°-amino)bis(imino)cyclodiphosph(V)azanes differ only in the presence of two methyl groups, and have thus virtually identical bond parameters. For this reason only the better-refined structure of **4** is discussed below.

The thermal-ellipsoid plot of **4**, Fig. 2, shows that azide oxidation is stereospecific, and that the top half of the molecule has retained its conformation, as we had hoped. All P–N bonds, however, are about 0.035(2) Å shorter than those in the parent molecule. The *tert*-butylimino groups are parallel with the perfectly planar heterocycle, but both the *tert*-butylamino and the *p*-tolylimino groups form obtuse angles with the ring, giving the molecule a letter "H" shape. As in **1** the N–H groups are endo, *i.e.*, they lie above the (P–N)$_2$ ring, while the aromatic rings are tucked below it. The exocyclic P–N(amino) and

Table 3 Selected bond lengths (Å) and angles (°) for **3** and **4**

	3	**4**
P(1)–N(1)	1.690(4)	1.689(2)
P(1)–N(2)	1.685(4)	1.693(2)
P(1)–N(3)	1.621(5)	1.630(2)
P(1)–N(5)	1.510(4)	1.515(2)
P(2)–N(1)	1.674(4)	1.688(2)
P(2)–N(2)	1.691(3)	1.689(2)
P(2)–N(4)	1.621(4)	1.636(3)
P(2)–N(6)	1.536(4)	1.542(2)
N(1)–P(1)–N(2)	82.5(2)	82.71(10)
N(3)–P(1)–N(5)	106.4(2)	106.41(13)
P(1)–N(1)–P(2)	97.6(2)	97.28(10)
P(1)–N(2)–P(2)	97.1(2)	97.09(10)
N(1)–P(2)–N(2)	82.8(2)	82.88(9)
N(4)–P(2)–N(6)	105.6(2)	105.81(13)

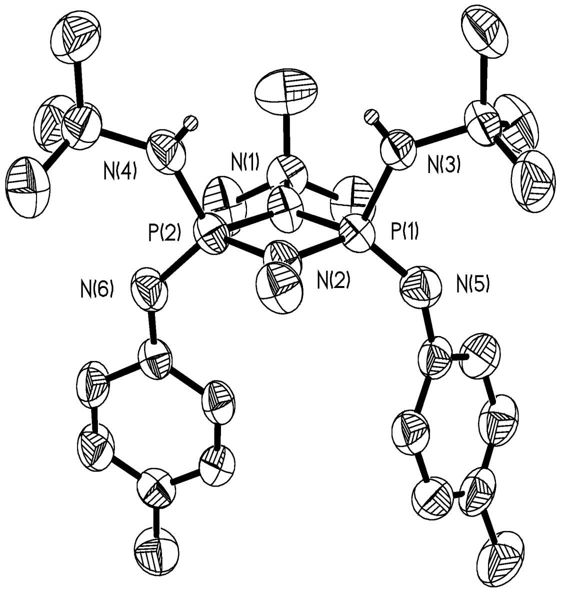


Fig. 2 Solid-state structure of **4**. The proximal *tert*-butyl group has been truncated to the quaternary carbon for clarity. Compound **3** has a similar structure.

P=N(imino) are decidedly nonequivalent (1.633(3) *vs.* 1.529(2) Å); the former being intermediate between single and double bonds, while the latter are true double bonds.[10]

Treatment of **3** or **4** with $TiCl_4$, Scheme 3, afforded red crystals, whose NMR spectra revealed much lower symmetries than required for *seco*-heterocubic molecules. The appearance of two signals in the ^{31}P NMR spectra provided convincing evidence that the cyclodiphosph(V)azanes coordinated one titanium atom laterally as monoanionic ligands. Spectroscopic and X-ray crystallographic data also showed that **5** was a hemi-toluene solvate, while **6** was solvent free.

A single-crystal X-ray study of **5** confirmed the preliminary structure assignment. The thermal-ellipsoid plot, Fig. 3, shows that the molecule consists of mutually perpendicular $(P–N)_2$ and (P–N–Ti–N) heterocycles, connected by a common atom (P1). Crystal data and bond parameters for **5** are collected in Tables 1 and 4, respectively. The cyclodiphosph(V)azane coordinates one titanium atom laterally as an aminoiminophosphoranate. Almost identical coordination geometries of the titanium atoms had been found in complexes of the type $[XYP(NSiMe_3)_2TiCl_3]$ [X = Cl, Y = $N(SiMe_3)_2$][7] (X = Cl, Y = CCl_3)[8] and $[Ph_2P(NSiMe_3)_2TiCl_3{\cdot}MeCN]$,[8] which have conventional phosphoranate ligands. The equidistant phosphorus–nitrogen (1.622(2) and 1.621(3) Å) and titanium–nitrogen bonds (2.003(3) and 2.014(2) Å) of **5** demonstrate the highly symmetrical metal chelation by the ligand. The titanium atom has a

Table 4 Selected bond lengths (Å) and angles (°) for **5**, **9** and **10**

	5	**9**	**10**
Ti–Cl(1)	2.2519(11)	2.2917(17)	2.2994(13)
Ti–Cl(2)	2.2205(11)	2.2068(11)	2.2133(9)
Ti–Cl(3)	2.2540(12)		
Ti–N(1)	2.003(3)	2.037(4)	2.042(3)
Ti–N(2)	2.014(2)		
Ti–S(Se)		2.3938(14)	2.5058(8)
P(1)–S(1)(Se1)		2.0097(13)	2.1569(8)
P(2)–S(2)(Se2)		1.9210(16)	2.0652(10)
P(1)–N(1)	1.622(2)	1.615(3)	1.613(3)
P(1)–N(2)	1.621(3)	1.664(2)	1.669(2)
P(1)–N(3)	1.652(2)		
P(1)–N(4)	1.655(2)		
Cl(1)–Ti–Cl(2)	112.68(4)	95.03(5)	94.64(4)
Cl(2)–Ti–Cl(2)#		117.08(8)	119.59(6)
Cl(1)–Ti–Cl(3)	92.77(5)		
Cl(2)–Ti–Cl(3)	96.23(5)		
N(1)–Ti–N(2)	71.90(10)		
Cl(1)–Ti–N(1)	88.29(8)	156.37(11)	156.45(12)
Cl(2)–Ti–N(1)	97.95(8)	97.23(6)	97.19(7)

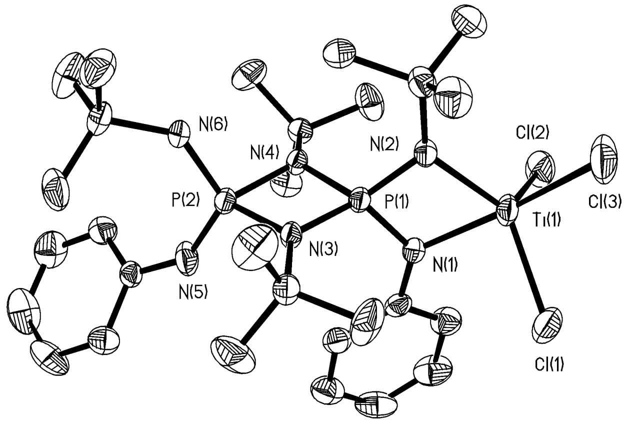
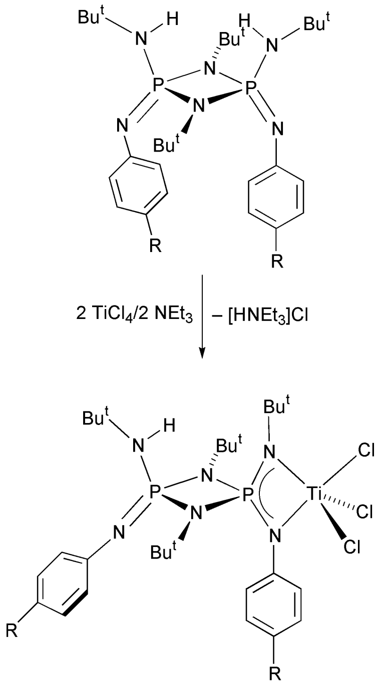


Fig. 3 Solid-state structure of **5**. The solvent molecule (toluene) is not shown.



R = H (**5**), CH_3 (**6**)

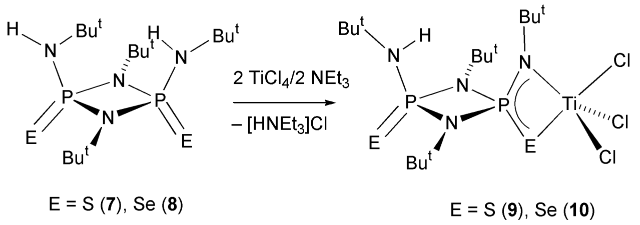
Scheme 3

more perfect trigonal-bipyramidal coordination environment than that in **2**. One nitrogen (N1) and one chlorine atom (Cl3) define the axial direction of the bipyramid, while the second nitrogen atom (N2) is equatorial. The nitrogen–titanium bonds are slightly longer than those in **2**, while the titanium–chloride bonds are slightly shorter (2.2205(11)–2.2540(12) Å).

The isolation of **5** and **6** showed, to our initial disappointment, that arylimino-substituted bis(amino)cyclodiphosph(V)-azanes chelate titanium as amino(imino)phosphoranates and not as diamides. Ligands like **3** and **4** are apparently predisposed to side-on coordination, due to the π-delocalization in the N–P–N moiety on chelation. This unwanted result caused us to investigate alternative phosphorus(V) ligands, namely 2,4-dichalcogenocyclodiphosph(V)azanes. These molecules, especially the selenium analogue, are less likely to exhibit π-delocalization through their N–P–E groups. Moreover, the softer chalcogen atoms are expected to bind the hard titanium(IV) less strongly than the nitrogen atoms, thereby encouraging the coordination of the bis(amino)cyclodiphosph(V)azanes as bis(amido) ligands.

Dithio-, and diseleno-cyclodiphosph(V)azanes are well known,[4] and structural studies on *cis*-$[\mathrm{Bu^t(H)N(S{=}PNBu^t)_2N(H)Bu^t}]$ (**7**),[12] for example, had shown that its *tert*-butylamino groups have a *cis* configuration, very similar to those in **3** and **4**. In contrast to the bis(arylimino)-substituted ligands, however, one of the NH groups of **7** has an *exo* orientation, while the second one is *endo*. The selenium analogue *cis*-$[\mathrm{Bu^t(H)N(Se{=}PNBu^t)_2N(H)Bu^t}]$ (**8**) can be readily prepared by refluxing **1** with grey selenium.[13]

When these 2,4-bis(1°-amino)-2,4-dichalcogenocyclodiphosph(V)azanes were allowed to react with $\mathrm{TiCl_4}$ (Scheme 4), under identical conditions as for the syntheses of **5** and **6**, similar orange–red solids were isolated. The NMR spectra immediately identified the products as structural analogues of **5** and **6**, rather than of **2**. Both complexes, **9** and **10**, crystallized as mono-toluene solvates of the formula $\{[\mathrm{Bu^t(H)N(E{=}PNBu^t)_2NBu^t]TiCl_3{\cdot}C_6H_5Me}\}$ (E = S (**9**), Se (**10**)).



Scheme 4

Crystal and bond parameters for the isostructural complexes **9** and **10** are collected in Tables 1 and 4, respectively. The thermal ellipsoid plot of **10**, Fig. 4, is representative for both compounds. Like **5** these molecules are spirocycles, but in contrast to **5**, they have crystallographic *m* symmetry. The mirror plane, which contains the (P–N–Ti–E) ring and both phosphorus atoms, bisects the cyclodiphosph(V)azane ring. The cyclodiphosph(V)azane and the three chloride ligands create a similar, albeit more distorted, trigonal-bipyramidal coordination geometry about titanium, N1 and Cl1 defining the axial direction. Due to the presence of the larger sulfur atom the Ti–N bond is slightly longer and the Ti–Cl bonds are more dissimilar. The titanium–sulfur bond in **9** 2.3938(14) Å, is shorter than in $[\mathrm{(MeC_5H_4)_2Ti(OS_5)}]$, Ti–S = 2.467 Å,[14] but this may be the result of the greater steric crowding in the organometallic compound. As expected, the P1–S1 bond (2.0097(13) Å) has lost some of its double-bond character and is longer than the free P2–S2 bond (1.9210(16) Å).

The only structural difference between **9** and **10** is the bonds to the chalcogen atoms, which are consistently *ca.* 0.1 Å longer for the selenium analogue. The Ti–Se bond (2.5058(8) Å) is slightly shorter than those in 1,4-$[\mathrm{(MeC_5H_4)_2Ti]_2Se_4}$ (2.542(1) and 2.563(1) Å).[15]

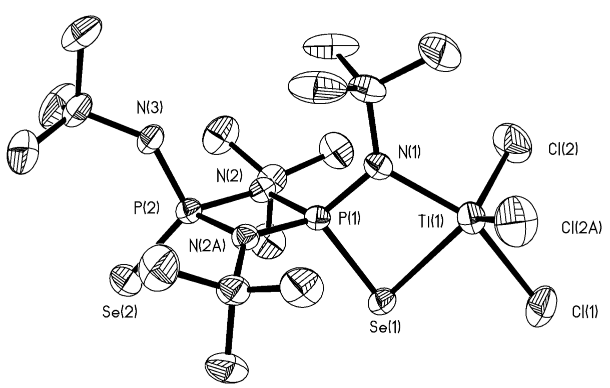


Fig. 4 Solid-state structure of **10**. The solvent molecule (toluene) is not shown. The disulfur complex (**9**) is isostructural.

Discussion

Cyclodiphosph(III)azanes are thermally stable, easy to synthesize heterocycles, whose central $\mathrm{(P{-}N)_2}$ moiety can be substituted with primary amines to yield chelating diamide ligands. Their $\mathrm{N{-}(P{-}N)_2{-}N}$ backbone encapsulates metals better than conventional diamides, and this obviates the need for large amino-nitrogen substituents to prevent dimerization of their complexes.

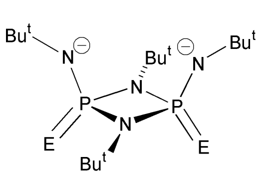
A typical example of such a bis(amido)cyclodiphosph(III)-azane complex is the titanium compound **2**, which is readily synthesized (Scheme 1) from neutral *cis*-$[\mathrm{Bu^t(H)N(Bu^tNP)_2N(H)Bu^t}]$ **1**, triethylamine and titanium tetrachloride. In this complex the P–N ligand chelates the titanium atom as a diamide, in a trihapto fashion, to form a *seco*-heterocubic complex. The coordination geometry of the metal atom in **2** is reminiscent of that of a corner position in α-$\mathrm{TiCl_3}$, which is still the most widely used polymerization catalyst for isotactic polypropylene.[16]

Like most trivalent phosphorus compounds, however, cyclodiphosph(III)azanes are both Lewis-basic and susceptible to oxidation—properties which render them and their complexes chemically reactive. Specifically, these ligands have a propensity to undergo cycloreversion in the presence of strong Lewis acids,[17] such as those present during olefin polymerization.

The oxidative instability of cyclodiphosph(III)azanes has previously been exploited for the rational synthesis of mono- and di-chalcogeno cyclodiphosph(V)azanes.[4] We have now used such P(V) cyclodiphosphazanes as chelating ligands in place of their P(III) analogues. By treating cyclodiphosph(III)azanes with azides or chalcogens the more robust cyclodiphosph(V)-azanes can be synthesized with minimal additional synthetic effort. Because ligand design in polyolefin catalysis requires an almost combinatorial approach, ease of conversion to cyclodiphosph(V)azanes was a consideration in this modification.

Oxidation removes the lone pairs as the most probable source of facile Lewis-acid attack. Perhaps even more important is the effect of the oxidation on the thermodynamic stability of the P(V) ligands. This is demonstrated by the P–N bond lengths of **3**, **4** and **7**, which are 0.027(2)–0.045(2) Å shorter than those of the P(III) species, indicative of stronger phosphorus–nitrogen bonds. Somewhat unexpectedly, equivalent P–N bonds in the P(V) molecules **3**, **4** and **7** are isometric, despite significant differences in the steric and electronic properties of their pendent groups. This suggests that the P–N bonds of these ligands are approaching their minimal values.

Contrary to our intentions bis(1°-amino)cyclodiphosph(V)-azanes do not function as simple chelating bis(amido) ligands, but are better considered dimeric aminobis(imino)phosphoranes. This discovery should have come as no surprise, of course, as a comparison of bis(1°-amino) cyclodiphosph(v)-azanes in their dianionic forms, **A** and **B**, shows. Because of π-electron delocalization **B** is the more stable of the two structures, and one may therefore expect these ligands to chelate metal atoms as heteroallyls.



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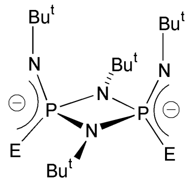
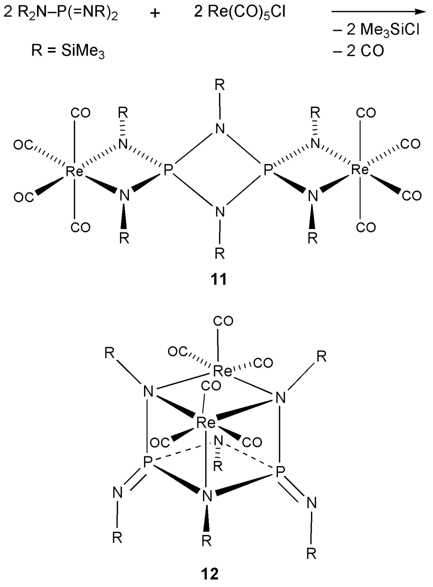


B

E = S, Se, N-Ar

Although such resonance arguments may explain the side-on binding of these ligands in complexes **5** and **6** and **9** and **10**, the true coordination behaviour of bis(amido)cyclodiphosph(v)-azanes is more complex. Scherer *et al.* had discovered that $Re(CO)_5Cl$ reacts with $[(Me_3Si)_2NP(=NSiMe_3)_2]$, Scheme 5, to yield three products, of which only two (**11** and **12**) are pertinent to our results.[18] In **11** the bis(amido)cyclodiphosph(v)azane chelates two $Re(CO)_4$ fragments as a bisphosphoranate to form a trispirocyclic complex, quite similar to **5** and **6**. Compound **12**, by contrast, is a heterocubic bimetallic bis(amido) complex, which is structurally related to **2**. It displays the coordination mode (albeit a dinuclear one) of the ligand we had hoped to see in **5** and **6** and **9** and **10**. Additional proof that bis(amino)cyclodiphosph(v)azanes have a diverse coordination behaviour, which is highly dependent upon the incorporated metal fragment, was recently provided by Chivers *et al.*[13] When they treated **7** or **8** with sodium or potassium bis(trimethylsilyl)amide a still different binding mode of these ligands was discovered. In these salts the ligand chelates one alkali metal with both amido-nitrogen atoms and the second one with both chalcogen atoms.



Scheme 5

Despite using 2 : 1 metal/ligand ratios (Schemes 3 and 4), we were unable to isolate dinuclear titanium complexes of **3**, **4**, **7** and **8**. We initially thought this to be due to thermodynamic factors (in bimetallic complexes the bulky *tert*-butyl groups would presumably be within van der Waals distances of each other). The recent isolations of trispirocyclic dinuclear main group derivatives of **3**, **4**, **7** and **8**,[19] which exhibit coordination modes analogous to **11**, however, show that this cannot be the reason. Our inability to detect dititanium complexes is thus likely due to kinetic factors (either the viscous reaction mixtures or the insolubility of the monotitanium complexes prevented proper mixing).

The title compounds, together with **11** and **12**, thus demonstrate the coordinative-flexibility of bis(1°-amido)cyclodiphosph(v)azanes. These heterocycles can chelate metals as bis(amido) (**12**), aminoiminophosphoranato (**11**), or as bis(amido)-bis(chalcogeno) ligands, depending on the size of the metal fragment and the degree of covalency of the bonds.

Chemically these ligands behave as aminoiminophosphoranates, irrespective if the phosphorus(v) atoms bear the relatively small and soft chalcogens sulfur and selenium, or the harder and sterically more encumbered arylimino groups. Despite their unexpected structures the title compounds may still be expected to have applications in olefin catalysis. Nickel complexes of aminoiminophosphoranates, for example, polymerize ethylene to short-chain branched polymers by an unusual 2,ω coupling process.[20] Catalytic tests on the titanium complexes are in progress.

Conclusion

Bis(1°-amino)cyclodiphosph(iii)azanes react with titanium tetrachloride to form *seco*-heterocubic bis(amido)complexes. Their oxidation products, the 2,4-dichalcogeno- and 2,4-diarylimino-substituted bis(1°-amino)cyclodiphosph(v)azanes, however, chelate the titanium atom as aminoimino- or amino-chalcogenophosphoranates. Given the extensive coordination chemistry of phosphoranates[21] (and of amidinates),[22] a similarly rich coordination chemistry can be predicted for bis(1°-amino)cyclodiphosph(v)azanes. The unique feature of these tetradentate ligands—their bifunctionality—may find applications in catalysis (tethering to surfaces) and materials research (synthesis of metalla-oligomers and -polymers).

Experimental

CAUTION: Organic azides are potentially explosive compounds. We encountered no problems while handling these reagents or their reaction mixtures.

All experiments were performed under an atmosphere of purified nitrogen or argon, using standard Schlenk techniques. Solvents were dried and freed of molecular oxygen by distillation under an atmosphere of nitrogen from sodium or potassium benzophenone ketyl immediately before use. NMR spectra were recorded on Varian VXR-300 and Bruker AVANCE-500 NMR spectrometers. The ^1H, ^{13}C and ^{31}P NMR spectra are referenced relative to C_6D_5H (7.15 ppm), C_6D_6 (128.0 ppm) and $P(OEt)_3$ (137.0 ppm), respectively. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by E and R Microanalytical Services, Parsipanny, NJ, and Desert Analytics, Tucson, AZ. Triethylamine and grey selenium were purchased from Aldrich and used without further purification. Titanium tetrachloride was purchased from Aldrich and used as a 2.0 M stock solution in toluene. Phenyl and *p*-tolyl azide,[23] and *cis*-$[Bu^t(H)N(Bu^tNP)_2N(H)Bu^t]$[6] were synthesized by published procedures.

Syntheses

$\{[(Bu^tNP)_2(NBu^t)_2]TiCl_2\}$ (2). A two-neck 100-mL round bottom flask, equipped with an inlet and stir bar, was charged with a mixture of toluene (20 mL), triethylamine (0.48 mL, 3.5 mmol) and titanium tetrachloride (1.7 mL of a stock solution). To the cooled (−78 °C) flask was added dropwise a toluene solution of **1** (0.601 g, 1.72 mmol). The vigorously stirred orange reaction mixture was allowed to warm and stirred at RT for 12 h. It was then filtered through a medium-porosity frit to remove triethylammonium chloride, and the orange filtrate was concentrated *in vacuo* until crystals formed. These were redissolved and the flask was kept at −12 °C until flaky orange crystals (0.621 g, 77.6%) had formed. The crystals were sublimed under a dynamic vacuum (70 °C, 0.03 Torr) to give orange blocks (0.576 g, 72.0%), mp 200–203 °C (Found: C, 41.11; H, 7.97; N, 11.79. $C_{16}H_{36}Cl_2N_4P_2Ti$ requires C, 41.30; H, 7.80; N, 12.04%); δ_H (C_6D_6) 1.57 (s, 18 H, NBu^t), 1.15 (s, 18 H, NBu^t); δ_C (C_6D_6) 60.2 (d, J_{PC} = 19.3 Hz), 54.6 (t, J_{PC} = 10.2 Hz), 33.7 (d, J_{PC} = 12.2 Hz), 28.3 (t, J_{PC} = 7.2 Hz); δ_P (C_6D_6) 115.5 (s).

{*cis*-[Bu^t(H)N(PhN=PNBu^t)$_2$N(H)Bu^t]·THF} (3). A sample of **1** (5.20 g, 14.9 mmol) was dissolved in THF (50 mL) in a two-necked flask, equipped with an inlet, stir bar, and dropping funnel. Phenyl azide (3.56 g, 29.8 mmol), dissolved in THF (25 mL), was then added dropwise at RT to the clear solution, which slowly evolved gas (N_2). The orange solution was stirred (12 h), then refluxed (2.5 h) and finally transferred to a 250-mL flask, where it was concentrated *in vacuo* until crystals formed. These were redissolved in a minimal amount of THF, and the ensuing solution was refrigerated (−12 °C) to afford off-white crystals (6.62 g, 74.0%), mp 152–154 °C (Found: C, 63.92; H, 9.20; N, 13.99. $C_{32}H_{56}N_6OP_2$ requires C, 63.76; H, 9.36; N, 13.94%); δ_H (C_6D_6) 7.37 (s, 4 H), 7.36 (s, 4 H), 6.97 (m, 2 H), 3.54 (m, 4 H, THF), 1.92 (s, 2 H, NH), 1.68 (m, 4 H, THF), 1.38 (s, 18 H, N(H)Bu^t), 1.34 (s, 18 H, NBu^t); δ_C (C_6D_6) 148.2 (s), 129.1 (s), 124.9 (t, J_{PC} = 9.1 Hz), 119.2 (s), 67.8 (s), 54.0 (s), 53.4 (t, J_{PC} = 2.5 Hz), 31.9 (s), 30.5 (t, J_{PC} = 4.2 Hz), 25.8 (s); δ_P (C_6D_6) −26.7 (s).

***cis*-[Bu^t(H)N(*p*-tolylN=PNBu^t)$_2$N(H)Bu^t] (4).** In a manner identical to that used for the synthesis of **3**, a sample of **1** (1.04 g, 3.00 mmol) was treated with *p*-tolyl azide (0.798 g, 6.00 mmol). After the solution had been refrigerated for several days, colourless rectangular crystals of **4** (1.59 g, 95.0%) were recovered, mp 140–143 °C (Found: C, 63.85; H, 9.31; N, 15.07. $C_{30}H_{52}N_6P_2$ requires C, 64.49; H, 9.38; N, 15.03%); δ_H (C_6D_6) 7.32 (d, 4 H, J_{HH} = 8 Hz), 7.20 (d, 4 H, J_{HH} = 8 Hz), 2.28 (s, 6 H, CH_3), 1.73 (br t, 2 H, NH), 1.39 (s, 18 H, N(H)Bu^t), 1.37 (s, 18 H, NBu^t); δ_C (C_6D_6) 145.6 (s), 129.8 (s), 128.3 (s), 124.7 (t, J_{PC} = 9 Hz), 54.0 (s), 53.3 (s), 31.9 (s), 30.5 (t, J_{PC} = 4.1 Hz), 21.0 (s); δ_P (C_6D_6) −29.2 (s).

{[Bu^t(H)N(PhN=PNBu^t)$_2$NBu^t]TiCl$_3$·0.5C$_6$H$_5$Me} (5). In a cooled (−78 °C) three-neck flask, triethylamine (0.41 mL, 2.9 mmol) and titanium tetrachloride (1.4 mL of a stock solution) were dissolved in toluene (10 mL), producing a dark orange solution. A sample of **3** (0.884 g, 1.47 mmol), dissolved in toluene (10 mL), was then added dropwise to the $TiCl_4/NEt_3$ solution. The dark-red reaction mixture was stirred for 12 h while it warmed to RT. After filtration on a fine frit, the red filtrate was concentrated *in vacuo* until crystals formed. These were redissolved (35 °C), and the warm filtrate was allowed to slowly cool to RT until dark-red crystals of **5** (0.77 g, 76%) had formed, mp 208–210 °C (Found: C, 52.28; H, 7.58; N, 10.85. $C_{31.5}H_{51}Cl_3N_6P_2Ti$ requires C, 51.83; H, 7.05; N, 11.50%); δ_H (C_6D_6) 7.64 (d, 2 H, J_{HH} = 7.6 Hz), 7.31 (s, 1 H), 7.14–7.00 (m, 5 H), 6.88 (m, 2 H), 6.71 (d, 2 H, J_{HH} = 8.5 Hz), 2.10 (s, 1.5 H, C$_6$H$_5$*Me*), 1.92 (s, 1 H, NH), 1.70 (s, 9 H, NBu^t), 1.29 (s, 18 H, NBu^t), 1.17 (s, 9 H, N(H)Bu^t); δ_C (C_6D_6) 148.5 (s), 144.0 (s), 129.4 (s), 129.3 (s), 125.7 (s), 124.9 (d, J_{PC} = 11 Hz), 124.1 (d, J_{PC} = 11 Hz), 120.2 (s), 60.8 (d, J_{PC} = 3.6 Hz), 56.4 (s), 54.2 (d, J_{PC} = 4.1 Hz), 33.1 (d, J_{PC} = 7.8 Hz), 31.4 (d, J_{PC} = 4.9 Hz), 30.8 (t, J_{PC} = 3.9 Hz), 21.4 (s, CH_3); δ_P (C_6D_6) −1.42 (d, J_{PP} = 48 Hz), −50.1 (d, J_{PP} = 48 Hz).

{[Bu^t(H)N(*p*-tolylN=PNBu^t)$_2$NBu^t]TiCl$_3$} (6). In a manner identical to that used for the synthesis of **5**, NEt_3 (0.60 mL, 4.0 mmol), $TiCl_4$ (4.0 mmol) and **4** (1.11 g, 1.97 mmol) were combined in toluene. Upon cooling (−12 °C) the solution for several days, purple needles formed (0.99 g, 74%), mp 200–202 °C (Found: C, 50.58; H, 7.21; N, 11.52; $C_{30}H_{51}Cl_3N_6P_2Ti$ requires C, 50.61; H, 7.22; N, 11.80%); δ_H (C_6D_6) 7.57 (dd, 2 H, J_{HH} = 6.5 Hz), 6.89 (t, 4 H, J_{HH} = 8 Hz), 6.61 (d, 2 H, J_{HH} = 7.8 Hz), 2.18 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 1.96 (s, 1H, NH), 1.71 (s, 9 H, NBu^t), 1.33 (s, 18 H, NBu^t), 1.20 (s, 9 H, N(H)Bu^t); δ_C (C_6D_6) 129.8 (s), 129.3 (s), 125.6 (s), 125.0 (d, J_{PC} = 9.5 Hz), 124.0 (d, J_{PC} = 12.5 Hz), 56.3 (s), 54.0 (s), 32.7 (d, J_{PC} = 8.4 Hz), 31.5 (d, J_{PC} = 5.0 Hz), 30.8 (t, J_{PC} = 4.0 Hz), 20.9 (s), 20.8 (s); δ_P (C_6D_6) −3.04 (d, J_{PP} = 47 Hz), −50.3 (d, J_{PP} = 47 Hz).

***cis*-[Bu^t(H)N(Se=PNBu^t)$_2$N(H)Bu^t] (8).** A mixture of **1** (1.01 g, 2.89 mmol) and grey selenium (0.452 g, 5.72 mmol) was dissolved/suspended in toluene (20 mL) and refluxed until it was clear (*ca.* 6 h). The light yellow solution was concentrated and placed in a freezer (−21 °C). After several days light-yellow, rod-shaped crystals (1.26 g. 86.9%) formed, mp 144–148 °C (Found: C, 37.92; H, 7.28; N, 10.88. $C_{16}H_{38}N_4P_2Se_2$ requires C, 37.95; H, 7.56; N, 11.06%); δ_H (C_6D_6) 3.19 (s, 2 H, NH), 1.78 (s, 18 H, N(H)Bu^t), 1.15 (s, 18 H, NBu^t); δ_C (C_6D_6) 59.2 (s), 55.9 (t, J_{PC} = 2.8 Hz), 32.0 (s), 30.9 (t, J = 4.6 Hz); δ_P (C_6D_6) 40.35 (s, $J(^{77}Se)$ satellites (7.5%) = 886 Hz).

{[Bu^t(H)N(S=PNBu^t)$_2$NBu^t]TiCl$_3$·C$_6$H$_5$Me} (9). In a manner strictly analogous to that used for the syntheses of **5** and **6**, toluene (45 mL), triethylamine (1.4 mL, 10 mmol) and $TiCl_4$ (5 mL of a stock solution) were combined. To this cooled (−78 °C) solution was added dropwise **7** (2.06 g, 5.00 mmol), dissolved in toluene (20 mL). The dark orange solution was allowed to slowly warm to RT and stirred for 12 h. It was then filtered through a medium-porosity frit, and the resulting dark orange solution was concentrated *in vacuo*. The supersaturated solution was stored in a freezer (−12 °C) until orange crystals had formed (1.7 g, 57%), mp 173–175 °C (Found: C, 41.68; H, 7.27; N, 8.90; $C_{23}H_{45}Cl_3N_4P_2S_2Ti$ requires C, 41.99; H, 6.89; N, 8.51%); δ_H (C_6D_6) 7.52–7.05 (m, 5 H, C$_6$*H*$_5$Me), 2.83 (s, 1 H, NH), 2.10 (s, 3 H, C$_6$H$_5$*Me*), 1.59 (s, 9 H, NBu^t), 1.37 (s, 18 H, N^{t}Bu), 1.16 (s, 9 H, N(H)Bu^t); δ_C (C_6D_6) 59.6 (s), 34.1 (s), 32.9 (d, J_{PC} = 7.5 Hz), 31.6 (s), 25.8 (s); δ_P (C_6D_6) 36.2 (d, J_{PP} = 26 Hz); 25.7 (d, J_{PP} = 26 Hz).

{[Bu^t(H)N(Se=PNBu^t)$_2$NBu^t]TiCl$_3$·C$_6$H$_5$Me} (10). In a manner strictly analogous to that used for the synthesis of **9**, $TiCl_4$ (2.1 mL of a stock solution), NEt_3 (0.6 mL, 4.2 mmol) and **8** (1.0 g, 2.0 mmol) were combined in toluene (20 mL). The dark orange solution was allowed to warm to RT and then stirred for 12 h. Yield: 1.2 g, 93%, mp 170 °C (decomp.) (Found: C, 36.46; H, 6.24; N, 7.65; $C_{23}H_{45}Cl_3N_4P_2Se_2Ti$ requires C, 36.70; H, 6.03; N, 7.44%); δ_H (C_6D_6) 7.53–7.05 (m, 5 H, C$_6$*H*$_5$Me), 3.21 (s, 1 H, NH), 2.10 (s, 3 H, C$_6$H$_5$*Me*), 1.61 (s, 9 H, NBu^t), 1.42 (s, 18 H, NBu^t), 1.20 (s, 9H, N(H)Bu^t); δ_C (C_6D_6) 59.3 (s), 32.9 (d, J_{PC} = 7.9 Hz), 31.6 (s), 30.7 (s), 25.8 (s); δ_P (C_6D_6) 22.5 (d, J_{PP} = 14 Hz), 10.1 (d, J_{PP} = 14 Hz).

X-Ray crystallography

Compounds 2, 5 and 10. Suitable, single crystals were coated with oil, affixed to a glass capillary, and centred on the diffractometer in a stream of cold nitrogen. Reflection intensities were collected with a Bruker SMART CCD diffractometer, equipped with an LT-2 low-temperature apparatus, operating at 213 K. Data were measured using ω scans of 0.3° per frame for 30 s until a complete hemisphere had been collected. The first 50 frames were recollected at the end of the data collection to monitor for decay. Cell parameters were retrieved using SMART[24] software and refined with SAINT[25] on all observed reflections. Data were reduced with SAINT, which corrects for Lorentz factor, polarization and decay. An empirical absorption correction was applied with SADABS.[26] The structures were solved by direct methods with the SHELXS-90[27] program and refined by full-matrix least squares methods on F^2 with SHELXL-97,[28] incorporated in SHELXTL Version 5.10.[29]

Compounds 3, 4 and 9. The crystals were sealed inside argon-filled glass capillaries, and the intensity data were collected on a Bruker P4 diffractometer. The structures were solved by direct methods with SHELXL-NT, Version 5.10,[30] and refined analogously to **2**, **5** and **10**.

CCDC reference numbers 158377–158382.

See http://www.rsc.org/suppdata/dt/b0/b007877h/ for crystallographic data in CIF or other electronic format.

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