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Article

Experimental and Theoretical Investigations of Lithium and Magnesium Derivatives of Bis(*tert*-butylamido)cyclodiphosph(III/V)- and (V/V)azane Mono- and Ditellurides

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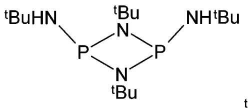
Deprotonation of bis(*tert*-butylamido)cyclophosph(III/III)azane with organolithium or organomagnesium reagents followed by oxidation with elemental tellurium is a viable approach to the preparation of metal cyclodiphosphazane mono- and ditellurides. The reaction of the cyclodiphosph(III)azane [^{t}Bu(H)NP(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**1**) with elemental tellurium in boiling toluene affords the monotelluride [^{t}Bu(H)N(Te)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu] (**9**). A similar reaction involving the magnesium salt Mg[^{t}BuNP(μ-N^{t}Bu)$_2$PN^{t}Bu](THF)$_2$ (**2**) also yields a monotelluride Mg[^{t}BuN(Te)P(μ-N^{t}Bu)$_2$PN^{t}Bu](THF)$_2$ (**10**). By contrast, reaction of the lithium salt Li$_2$[^{t}BuNP(μ-N^{t}Bu)$_2$PN^{t}Bu](THF)$_2$ (**3**) with tellurium results in double oxidation and the formation of the ditellurides Li$_2$[^{t}BuN(Te)P(μ-N^{t}Bu)$_2$P(Te)N^{t}Bu](THF)$_4$ (**11**) and Li$_2$[^{t}BuN(Te)P(μ-N^{t}Bu)$_2$P(Te)N^{t}Bu](tmeda)$_2$ (**12**). Compounds **9**–**12** have been characterized by multinuclear (^{1}H, ^{7}Li, ^{13}C, ^{31}P, and ^{125}Te) NMR, while **9**, **10**, and **12** have also been characterized by X-ray crystallography. The structure of **9** reveals a typical cis/endo,exo arrangement, with no intermolecular contacts to tellurium. The seco-heterocubic structure, observed in **2**, is retained in **10**, with the ligand chelating magnesium in an N,N′,N′′-manner. Unique coordination behavior is exhibited by the ditelluride **12**, in which the dianionic ligand is attached to the two lithium centers in both Te,Te′ and Te,N bonding modes. Multinuclear NMR data are consistent with retention of the solid-state structures of **9**–**12** in solution at low temperatures. The reactivity of cyclodiphosph(III/III)azanes toward chalcogens is rationalized by using theoretical calculations (semiempirical PM3 level of theory), which show an inverse correlation between the charge at the phosphorus center and the ease of oxidation.

Introduction

Dianionic cyclodiphosph(III/III)azanes formed by deprotonation of **1** have been studied extensively as ligands for s- and p-block elements[1,2] as well as transition metals.[3,4b] These complexes typically involve chelation of the element through the exocyclic nitrogen atoms. Additional coordination by an endocyclic nitrogen atom may also occur to give a seco-heterocube arrangement, e.g. the magnesium salt **2**.[2] For monocationic lithium, the exocyclic nitrogen atoms bridge two lithium centers, giving the heterocube **3**.[2]



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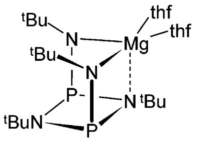

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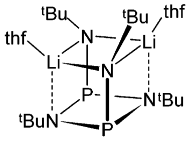

3

The P(III)/P(III) system **1**[5] is readily oxidized by elemental sulfur or selenium to give the corresponding P(V)/P(V) analogues **4**[6] and **5**.[7a] We[7] and others[4] have initiated studies of the coordination chemistry of anions derived from these multidentate ligands.[8] The bonding mode to alkali-metal

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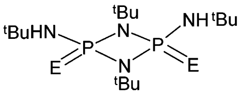
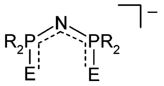
centers varies depending on the cation. For larger cations such as potassium, N,N′ chelation **I**, and E,E′ chelation **II** are observed, whereas N,E chelation **III** is favored for the smaller lithium cation, presumably due to the smaller bite angle of the −N−P−E− motif in **III** compared to those in the alternative chelation modes **I** and **II**.



4, E = S
5, E = Se



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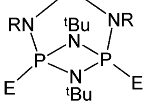
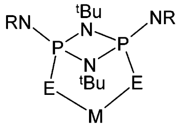
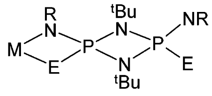


I



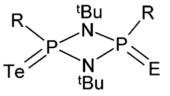
II



III

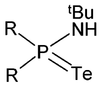
More recent studies have involved mixed oxidation state systems, e.g. $^{t}Bu(H)NP(\mu\text{-}N^{t}Bu)_2P(Se)N(H)^{t}Bu$, which is readily generated by disproportionation of **1** and **5** in a 1:1 molar ratio.[9] The monosulfide analogue cannot be prepared via this method, however, highlighting the increased lability of the P═Se bond compared to the P═S interaction. The even weaker nature of P═Te interactions is demonstrated by the utility of phosphine tellurides as tellurium transfer agents.[10] This is also underlined by the absence of studies involving the elusive ditelluroimidodiphosphonate anion **6** (E = Te), the ligating properties of which have been extensively studied for the oxo, thio and seleno analogues.[11] In addition, only a small number of structurally characterized compounds involving terminal P═Te bonds have been described.[12−15,16a]

The few reported studies of cyclodiphosphazane tellurides have involved exocyclic halide,[17b] alkyl,[12,17] or secondary amino[18] groups on phosphorus, **7**. These substituents do not contain acidic protons, which would permit anion formation. However, tellurophosphinic amides **8** have been prepared and, subsequently, complexed to group 12 metal centers,[16] confirming the chelating potential of the [RN═P−Te−]$^{-}$ arrangement. As a follow-up to a communication on the preparation of the first examples of the monoanion **6** (R = Ph, E = Te) and the dianion $[^{t}BuN(Te)P(\mu\text{-}N^{t}Bu)_2P(Te)N^{t}Bu]^{2-}$,[19] we now report full details of the synthesis and spectroscopic and structural characterization of the monotelluride **9** and its magnesium complex **10**, as well as the dilithium derivatives **11a,b** and **12**. The successful synthesis of **10**−**12** required the formation of the metalated reagents **2** and **3** prior to oxidation with elemental tellurium. This synthetic approach is rationalized via theoretical calculations.

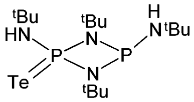


7

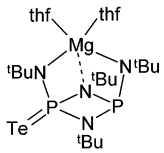
R = ^{t}Bu, Me/Cl, NMe$_2$
E = lone pair, Te



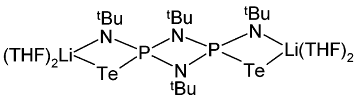
8



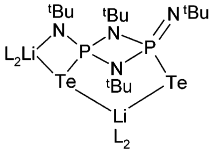
9



10



11a



11b: L = THF
12: L$_2$ = TMEDA

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled over Na/benzophenone prior to use: tetrahydrofuran (thf); toluene; *n*-hexane. Tellurium powder was used as received from Matheson, Coleman & Bell. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (tmeda) was used as received from Aldrich. The bis(*tert*-butylamido)cyclodiphosph(III/III)azanes $[^{t}Bu(H)NP(\mu\text{-}N^{t}Bu)_2PN(H)^{t}Bu]$ (**1**),[5b] $Mg[^{t}BuNP(\mu\text{-}N^{t}Bu)_2PN^{t}Bu](thf)_2$ (**2**),[2] and $Li_2[^{t}BuNP(\mu\text{-}N^{t}Bu)_2PN^{t}Bu](thf)_2$ (**3**)[2] were prepared by literature procedures. All manipulations were performed under an argon atmosphere using standard Schlenk techniques.

Instrumentation. ^{1}H, ^{13}C, ^{31}P, ^{7}Li, and ^{125}Te NMR spectra were recorded on a Bruker DRX 400 NMR spectrometer, with chemical shifts reported relative to Me_4Si in C_6D_6 (^{1}H and ^{13}C), 85% H_3PO_4 in D_2O (^{31}P), 1 M LiCl in D_2O (^{7}Li), and neat Me_2Te (^{125}Te). Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Preparation of $[^{t}Bu(H)N(Te)P(\mu\text{-}N^{t}Bu)_2PN(H)^{t}Bu]$ (9). A mixture of **1** (0.500 g, 1.43 mmol) and Te powder (0.370 g, 2.90 mmol) in toluene (10 mL) was heated at 80 °C for 17 h. After being cooled to 23 °C, the mixture was centrifuged and decanted to remove unreacted tellurium. The resulting pale yellow solution was slowly concentrated to ∼3 mL and kept at −15 °C for 18 h.

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The solution was then centrifuged and decanted to remove crystallized **1** and pumped to dryness. The resulting pale yellow powder was dissolved in *n*-hexane (3 mL) and kept at −15 °C for 18 h to give yellow crystals of **9**. The X-ray-quality crystals were then removed by filtration and pumped dry (0.033 g, 0.069 mmol, 5%). Anal. Calcd for $C_{16}H_{38}N_4P_2Te$: C, 40.43; H, 8.05; N, 11.77. Found: C, 40.61; H, 8.06; N, 11.68. NMR data ([D$_8$]toluene, 225 K): ^{1}H NMR, $\delta = 1.01$ (s, 9H, N^t*Bu*), 1.04 (d, $^4J_{H,P} = 1.3$ Hz, 9H, N^t*Bu*), 1.66 (s, 18H, μ-N^t*Bu*), 2.98 (d, $^2J_{H,P} = 7.6$ Hz, 1H, N*H*), 4.04 (d, $^2J_{H,P} = 19.7$ Hz, 1H, N*H*); ^{13}C{^{1}H} NMR, $\delta = 30.6$ (dd, $^3J_{C,P} = 4.7$ Hz, $^3J_{C,P} = 4.7$ Hz, μ-NC*Me*$_3$), 31.3 (d, $^3J_{C,P} = 4.3$ Hz, NC*Me*$_3$), 32.0 (d, $^3J_{C,P} = 10.3$ Hz, NC*Me*$_3$), 52.1 (d, $^2J_{C,P} = 16.4$ Hz, N*C*Me$_3$), 55.0 (dd, $^2J_{C,P} = 11.8$ Hz, $^2J_{C,P} = 2.7$ Hz, μ-N*C*Me$_3$), 56.3 (d, $^2J_{C,P} = 13.3$ Hz, N*C*Me$_3$); ^{31}P NMR, $\delta = 87.1$ (s), −39.7 (d, $^1J_{P,Te} = 2024$ Hz, $^2J_{P,H} = 20$ Hz); ^{125}Te NMR, $\delta = -188$ (d, $^1J_{Te,P} = 2010$ Hz).

Preparation of {Mg[^{t}BuN(Te)P(μ-N^{t}Bu)$_2$PN^{t}Bu](THF)$_2$}·thf (10·thf). A mixture of **2** (0.282 g, 0.548 mmol) and Te powder (0.140 g, 1.10 mmol) in thf (10 mL) was heated at 80 °C for 4 h. After being cooled to 23 °C, the mixture was centrifuged and decanted to remove unreacted tellurium. The resulting yellow solution was kept at −15 °C for 18 h to give yellow crystals of **10**·thf (0.076 g, 0.11 mmol, 19%). Anal. Calcd for $C_{28}H_{60}MgN_4O_3P_2Te$: C, 47.06; H, 8.46; N, 7.84. Found: C, 46.70; H, 8.27; N, 8.07. NMR data ([D$_8$]tetrahydrofuran, 298 K): ^{1}H NMR, $\delta = 1.22$ (s, 9H, N^t*Bu*), 1.42 (s, 9H, N^t*Bu*), 1.52 (s, 18H, μ-N^t*Bu*), 1.78 (m, CH$_2$*CH*$_2$), 3.62 (m, O*CH*$_2$); ^{13}C{^{1}H} NMR, $\delta = 31.8$ (dd, $^3J_{C,P} = 5.7$ Hz, $^3J_{C,P} = 5.6$ Hz, μ-NC*Me*$_3$), 34.6 (d, $^3J_{C,P} = 9.4$ Hz, NC*Me*$_3$), 36.2 (d, $^3J_{C,P} = 12.4$ Hz, NC*Me*$_3$), 53.6 (s, N*C*Me$_3$), 54.7 (s, N*C*Me$_3$), 55.5 (d, $^2J_{C,P} = 14.9$ Hz, N*C*Me$_3$); ^{31}P{^{1}H} NMR, $\delta = -26.2$ (d, $^1J_{P,Te} = 1856$ Hz, $^2J_{P,P} = 15$ Hz), 107.3 (d, $^1J_{P,P} = 15$ Hz); ^{125}Te NMR, $\delta = -137$ (d, $^1J_{Te,P} = 1851$ Hz).

Preparation of Li$_2$[^{t}BuN(Te)P(μ-N^{t}Bu)$_2$P(Te)N^{t}Bu](thf)$_4$ (11). A mixture of **3** (0.500 g, 0.992 mmol) and Te powder (0.252 g, 1.98 mmol) in thf (10 mL) was heated at 80 °C for 4 h. After being cooled to 23 °C, the mixture was centrifuged and decanted to remove unreacted tellurium. The resulting deep yellow solution was slowly concentrated to 3 mL, layered with 4 mL of *n*-hexane, and kept at −15 °C for 18 h to give yellow crystals of **11**. NMR data ([D$_8$]tetrahydrofuran, 235 K) are as follows. **11a**: ^{31}P{^{1}H} NMR, $\delta = -50.0$ (s, $^1J_{P,Te} = 1790$ Hz); ^{125}Te NMR, $\delta = -124$ (d, $^1J_{Te,P} = 1790$ Hz). **11b**: ^{31}P{^{1}H} NMR, $\delta = -62.9$ (s, $^1J_{P,Te} = 1551$ Hz), −52.0 (d, $^1J_{P,Te} = 1797$ Hz, $^2J_{P,P} = 6$ Hz); ^{125}Te NMR, $\delta = -245$ (d, $^1J_{Te,P} = 1524$ Hz), −135 (d, $^1J_{Te,P} = 1775$ Hz).

Preparation of Li$_2$[^{t}BuN(Te)P(μ-N^{t}Bu)$_2$P(Te)N^{t}Bu](TMEDA)$_2$ (12). Compound **12** was prepared as described previously.[19] Complete multinuclear NMR data are as follows ([D$_8$]toluene, 235 K): ^{1}H NMR, $\delta = 1.62$ (s, 9H, N^t*Bu*), 1.97 (s, 9H, N^t*Bu*), 2.18 (s, 18H, μ-N^t*Bu*), 2.20 (s, 12H, N*Me*$_2$), 2.30 (s/br, 8H, NC*H*$_2$); ^{13}C{^{1}H} NMR, $\delta = 31.8$ (s, μ-NC*Me*$_3$), 34.2 (d, $^3J_{C,P} = 11.2$ Hz, NC*Me*$_3$), 34.8 (d, $^3J_{C,P} = 12.8$ Hz, NC*Me*$_3$), 47.5 (s/ br, N*Me*$_2$), 53.8 (s, μ-N*C*Me$_3$), 55.8 (d, $^2J_{C,P} = 21.2$ Hz, N*C*Me$_3$), 56.3 (d, $^2J_{C,P} = 20.4$ Hz, μ-N*C*Me$_3$), 56.3 (s, N*CH*$_2$); ^{31}P{^{1}H} NMR, $\delta = -113.7$ (d, $^1J_{P,Te} = 1467$ Hz), −75.3 (d, $^1J_{P,Te} = 1309$ Hz); ^{7}Li NMR, $\delta = 0.70$, 3.88; ^{125}Te NMR, $\delta = -289$ (d, $^1J_{Te,P} = 1352$ Hz), −87 (d, $^1J_{Te,P} = 1486$ Hz).

Theoretical Calculations. Calculations were performed by using the HyperChem 6.0 Professional Release (HyperCube, Inc.) software package. Geometry optimizations were performed at the PM3 and AM1 (M = Li) (semiempirical, unrestricted Hartree−Fock) level of theory. Initial parameters for model complexes M[RP(μ-NMe)$_2$PR] (**A**) and M[R(Te)P(μ-NMe)$_2$PR] (**B**) were derived from crystal structure data of known compounds. Methyl groups were substituted for *tert*-butyl groups to minimize computing time.

Table 1. Crystallographic Data for **9** and **10**·thf

	9	**10**·thf
formula	$C_{16}H_{38}N_4P_2Te$	$C_{28}H_{60}MgN_4O_3P_2Te$
fw	476.05	714.65
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.486(2)	14.7600(4)
b, Å	15.535(3)	11.8940(6)
c, Å	15.961(2)	20.375(1)
β, deg	91.40(1)	93.023(1)
V, Å^3	2351.6(7)	3572.0(3)
Z	4	4
F(000)	976	1496
d_{calcd}, g cm^{-3}	1.345	1.329
μ, mm^{-1}	1.41	0.972
T, K	170	153(2)
λ, Å	0.710 69	0.710 73
R$_1$[a]	0.037	0.0501
R$_w$;[b] wR$_2$[c]	0.045[b]	0.1159[c]

[a] $R_1 = [\sum||F_o| - |F_c||]/[\sum F_o|]$ for $I > 2\sigma(I)$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ (all data).

X-ray Structural Analyses. Crystals of **9**, **10**·thf, and **11** were coated with oil (Paratone N, Hampton Research) and mounted on a glass fiber. Measurements were made on Rigaku AFC6S (**9**) and Nonius KappaCCD (**10**·thf and **11**) diffractometers using monochromated Mo Kα radiation. Crystallographic data (for **9** and **10**·thf) are summarized in Table 1.

9. Data were measured using $\omega-2\theta$ scans. A decay of 4.7% was observed, and a linear correction factor was applied. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.22 < 2\theta < 21.21°$. The space group was uniquely determined from the systematic absences. An empirical absorption correction[20] based on azimuthal scans of several reflections was applied, and the data were corrected for Lorentz and polarization effects. The structure was solved by using direct methods[21] and expanded using Fourier techniques.[22] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. Neutral atom scattering factors were taken from Cromer and Waber.[23] Anomalous dispersion coefficients were those of Creagh and McAuley.[24] All calculations were preformed using the teXan[25] crystallographic software package.

10·thf. Data were measured using ϕ and ω scans. Cell parameters were retrieved using the COLLECT[26] software and refined with the HKL DENZO and SCALEPACK software.[27] The space group determination was based on a statistical analysis of intensity distribution and the successful solution and refinement of the

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structure. Data reduction was performed with the HKL DENZO and SCALEPACK software, which corrects for beam inhomogeneity, possible crystal decay, and Lorentz and polarization effects. A multiscan absorption correction was applied (SCALEPACK), and the transmission coefficients were calculated using SHELXL97-2.[28] The structure was solved by using direct methods (SIR-97) and refined by the full-matrix least-squares method on F^2 with SHELXL97-2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon or nitrogen atoms. The methyl carbon atoms of one ^{t}Bu group (labeled as C41, C42, C43, C41′, C42′, and C43′) were disordered over two sites with partial occupancy factors of 0.56(2) and 0.44(2), respectively. Neutral atom scattering factors for non-hydrogen atoms and anomalous dispersion coefficients are contained in the WinGX v1.64.02[30] program library.

Results and Discussion

Synthesis. The preparation of phosphine tellurides R_3PTe typically involves reaction of the phosphine with elemental tellurium powder.[13a,15b,16a,17,18] The reaction of bis(*tert*-butylamido)cyclodiphosph(III/III)azane (**1**) with 2 equiv of tellurium powder in toluene at 80 °C for 17 h produces the monotelluride **9** in $<$ 5% isolated yield. A ^{31}P NMR spectrum showed that the reaction mixture contains primarily unreacted **1**. Variations in the duration or temperature of the reaction did not improve the yield of **9**. This compound is stable indefinitely in the reaction mixture solution and, surprisingly, is air-stable for short periods of time. Decomposition to give elemental tellurium occurs immediately when attempts are made to redissolve **9** at 23 °C. However, the monotelluride is stable in [D$_8$]toluene at low temperature, which has allowed the collection of solution NMR data (vide infra).

Metal salts of cyclodiphosph(V/V)azane dioxides, disulfides, and diselenides are prepared by the reaction of bis(alkyl- or arylamido) derivatives with organoalkali metal or other deprotonating agents.[4,7] In view of the instability of the monotelluride **9** in solution, and the unavailability of the corresponding ditelluride, preparation of metal salts of cyclodiphosphazane tellurides via this method is impractical. As an alternative route, the oxidation of the metal derivatives **2** and **3** with elemental tellurium was chosen.

The reaction of **2** in thf at 80 °C for 4 h gives the cyclodiphosph(III/V)azane monotelluride **10** in ca. 20% yield. Unlike **9**, this magnesium complex undergoes minimal decomposition in thf solution at 23 °C. However, the stability of crystals of **10** is very low in Paratone oil (employed for mounting crystals on glass fibers). The reaction of **3** with elemental tellurium under similar conditions proceeds further, giving the ditelluride **11**, which is extremely air and moisture sensitive. Reaction mixtures and solutions of the impure product in thf are stable at 23 °C; however, the crystalline product was too thermally unstable for the determination of elemental analysis. Solution NMR data were collected at low temperature. A similar reaction in the presence of tmeda also afforded a ditelluride species **12** isolated in ca. 20% yield.[19] These crystals are much more stable than **11** in the solid state and in solution. In contrast to the behavior of **1**, ^{31}P NMR spectra of reaction mixtures revealed that the metalated reagents **2** and **3** are completely consumed in the reactions with elemental tellurium. Consequently, we attribute the low yields of compounds **10**−**12** to the difficulties involved in isolating pure samples of these highly air-sensitive complexes from the reaction mixtures.

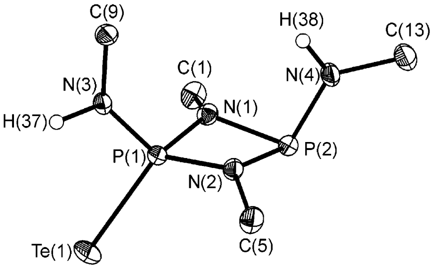

Figure 1. ORTEP diagram of **9** (30% probability ellipsoids). Only the α-carbon atoms of ^{t}Bu groups are shown.

X-ray-quality of crystals of **9**, **10**•thf, and **12** were obtained from reaction mixtures after removal of unreacted tellurium. For compound **9**, unreacted **1** was removed from the reaction mixture by fractional crystallization to prevent cocrystallization with the desired product from *n*-hexane solution. Owing to the high reactivity of **10**•thf and **11** in Paratone oil at room temperature, low-temperature techniques were required for crystal manipulation and data collection.

Structural Analysis. The structure of **9**, shown in Figure 1, is monomeric in the solid state with no significant intermolecular interactions. The exocyclic *tert*-butylamido functionalities adopt an endo,exo arrangement, which is also found for **4**[6] and **5**.[7a] Bond lengths and bond angles for **9** are compared with those of **1** in Table 2. The tellurium−phosphorus bond distance of 2.370(1) Å is at the upper limit of the range of values observed for other phosphine tellurides [2.288(5)−2.368(4) Å],[12−15,16a] while the $\text{P}-\text{N}_{exo}$ bond distances [P(1)−N(3) 1.639(4); P(2)−N(4) 1.655(4) Å] are typical for P(V)−N and P(III)−N single bonds in these systems.[1,8] Also, the $-\text{N}_{endo}-\text{P}-\text{N}_{exo}$ bond angles involving the P(III) center are ca. 9.5° smaller than those involving the P(V) center, reflecting the influence of the lone pair on P(2).

The structure of **10**, depicted in Figure 2, shows retention of the seco-heterocube arrangement observed in the precursor **2**.[2] Bond lengths and bond angles for **10** are compared with those of **2** in Table 2. The Te−P bond distance [2.385(2) Å] is marginally longer than that of **9**. The shortening of P−N bond distances at P(1) reflects the change in oxidation

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Table 2. Selected Bond Lengths (Å) for **1**, **2**, **9**, and **10**·thf

	1[a]	**9**	**2**[b]	**10**·thf
P(1)−Te(1)		2.370(1)		2.385(3)
P(1)−N(1)	1.763(6)	1.678(4)	1.782(4)	1.717(6)
P(1)−N(2)	1.743(5)	1.676(4)	1.748(4)	1.695(6)
P(1)−N(3)	1.619(6)	1.639(4)	1.654(4)	1.620(7)
P(2)−N(1)	1.725(5)	1.758(4)	1.778(4)	1.784(6)
P(2)−N(2)	1.702(6)	1.753(4)	1.760(2)	1.781(6)
P(2)−N(4)	1.710(5)	1.655(4)	1.658(4)	1.649(7)
Mg(1)−N(3)			2.061(4)	2.122(6)
Mg(1)−N(4)			2.059(4)	2.063(6)
Mg(1)···N(1)			2.330(4)	2.423(6)
N(3)−P(1)−Te(1)		104.3(1)		119.5(2)
N(1)−P(1)−Te(1)		119.6(1)		120.4(2)
N(2)−P(1)−Te(1)		119.7(1)		115.5(2)
N(1)−P(1)−N(3)	104.7(3)	114.3(2)	96.5(2)	101.4(3)
N(2)−P(1)−N(3)	105.3(3)	114.6(2)	105.6(2)	110.5(3)
N(1)−P(2)−N(4)	105.0(3)	104.7(2)	95.8(2)	96.9(3)
N(2)−P(2)−N(4)	105.0(3)	105.5(2)	106.1(2)	105.7(3)
N(1)−Mg(1)−N(3)			71.1(2)	68.9(2)
N(1)−Mg(1)−N(4)			70.8(1)	69.4(2)
N(3)−Mg(1)−N(4)			124.6(2)	122.4(3)

[a] Reference 5a. [b] Reference 2.

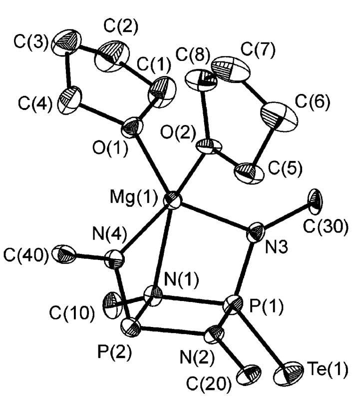
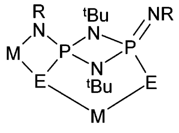


Figure 2. ORTEP diagram of **10** (30% probability ellipsoids). Only the α-carbon atoms of ^{t}Bu groups are shown. The lattice thf molecule is not shown.

state to P(V). This is also accompanied by an opening of the N(1/2)−P(1)−N(3) bond angles compared to those in **2**, creating a further distortion from an ideal seco-heterocubic arrangement. As in **2**, the ligand chelates magnesium in an N,N′,N″ manner; however, the bond distance to the endocyclic nitrogen Mg(1)−N(1) is significantly longer [2.423(6) Å vs 2.330(4) Å in **2**]. This is countered by a shortening of the Mg−O(2) bond distance [2.044(5) Å vs 2.095(4) Å in **2**] of the trans thf oxygen atom. The N(3)−Mg−N(4) bite angle in **10** [122.4(3)°] is slightly smaller than that of **2** [124.6(2)°]. Also, the Mg−N(3) bond distance [2.122(6) Å] in **10** is significantly longer than Mg−N(4) [2.063(6) Å] and the Mg−N(3)/N(4) [2.061(4)/ 2.059(4) Å] distances in **2**, presumably due to the opening of the N(1/2)−P(1)−N(3) bond angles on oxidation (cf. **9**). The geometry around the magnesium center may be considered distorted trigonal bipyramidal, with N(3), N(4), and O(1) occupying the equatorial sites and N(1) and O(2) in the axial positions.

Crystals of **11** were thermally unstable, decomposing to give black elemental tellurium when removed from the reaction mixture. Despite the manipulation and collection of X-ray crystallographic data at low temperature, the crystals were insufficiently stable to give a satisfactory data set. Preliminary studies,[31] however, show two different isomers of $Li_2[{}^tBuN(Te)P(\mu\text{-}N{}^tBu)_2P(Te)N{}^tBu](thf)_4$ in the asymmetric unit. The first molecule **11a** shows the ligand chelating each of the lithium atoms in a N,Te manner (mode **III**), as observed for $Li_2[{}^tBuN(S)P(\mu\text{-}N{}^tBu)_2P(S)N{}^tBu](thf)_4$.[7b] The second molecule **11b**, however, shows two different bonding modes for lithium. Here, the first lithium center is chelated in a N,Te manner (mode **III**), while the second is bound to the ligand in a Te,Te′ manner (mode **II**). This represents an unique combination of bonding modes (**IV**) for dianions of the type $[({}^tBuN)(E)P(\mu\text{-}N{}^tBu)_2P(E)(N{}^tBu)]^{2-}$.



IV

In contrast to **11**, crystals of **12** were sufficiently stable and of suitable quality to allow for a definitive structural characterization. The structure of **12**, which was reported in the preliminary communication,[19] is similar to that of **11b**, with a chelating tmeda ligand replacing two thf molecules coordinated to each lithium atom. The dianionic ligand chelates two lithium centers in Te,N and Te,Te′ manners, thus verifying the preliminary evidence for bonding mode **IV** in **11b**. The P−Te bond distances [2.4243(7) and 2.4515(8) Å] are significantly longer than those in **9** and **10**, suggesting weak phosphorus−tellurium bonding interactions. Further, the P−N bond distances to the "exocyclic" *tert*-butylamido groups are exceptionally short [1.534(2) and 1.574(2) Å] compared to those in **1**, **2**, **9**, and **10** [1.620(7)−1.710(5) Å] (Table 2), suggesting double bond character.

Multinuclear NMR Studies. All NMR data were collected at low temperatures to enhance resolution of small spin−spin couplings. Further, the monotelluride **9** was dissolved in the NMR solvent at 225 K to prevent decomposition. The NMR data are consistent with retention of the solid-state structures of **9**−**12** in solution. However, the equivalence of the cyclodiphosphazane *tert*-butyl groups in the ^{1}H NMR spectrum of **10** at 300 K suggests a labile intramolecular Mg···N interaction, as observed for **2**.[2] The retention of the two P−Te bonds in **11** and **12** in solution is indicated by the observation of single resonances with ^{31}P−^{125}Te coupling in both the ^{31}P and ^{125}Te NMR spectra.

For compound **11**, resonances corresponding to both isomers, **11a,b**, are identifiable in the ^{31}P and ^{125}Te NMR spectra in [D$_8$]thf. The observation of an approximately 1:1 ratio of **11a** to **11b** in the ^{31}P NMR spectrum at 225 K is consistent with the presence of equal amounts of both isomers as found in the solid-state structure.[31] However, this ratio changes to 1:3 at 298 K suggesting that an isomerization process occurs in solution. By contrast, only one set of

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(31) Crystal data for **11**: $C_{64}H_{136}Li_4N_8O_8P_4Te_4$, fw = 1801.92 g mol^{-1}, crystal system triclinic, $P\bar{1}$, $a = 9.849(5)$ Å, $b = 20.999(5)$ Å, $c = 21.903(5)$°, $\alpha = 88.783(5)$°, $\beta = 82.401(5)$°, $\gamma = 88.394(5)$°, $Z = 2$, $d_{calc} = 1.333$ g cm^{-3}.

Table 3. Calculated Charges on Phosphorus(III) Centers for **A** and **B**

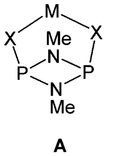
X	M	A	B	Te atoms[a]
NMe	2 H	0.680	0.739	1
NMe	Mg	0.610	0.655	1
NMe	2 Li	0.626[b]		2
NMe	$ZrCl_2$	0.751	0.791	0[c]
^{t}Bu		0.545	0.560	2[d]
Me		0.549	0.612	2[e]
Me, Cl		0.687, 0.860	0.909	1[e,f]

[a] Determined experimentally. [b] AM1 level of theory. [c] Reference 3. [d] Reference 12b. [e] Reference 17b. [f] Attached to PMe.

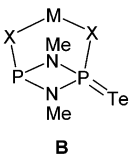
resonances was observed in the NMR spectra of **12** in [D_8]-toluene, consistent with retention of the solid-state structure in solution.

The value of $^1J(^{31}P-^{125}Te)$ decreases in the order **9** > **10** > **11a** ≈ **11b** > **12** (2024, 1856, 1790, 1797/1551, and 1467/1309 Hz, respectively), indicating a decrease in s-orbital character of the P−Te bond, with the weaker couplings for the ditelluride species falling below the observed range for phosphine tellurides (1663−2095 Hz).[32] This trend follows the order of increasing P−Te bond lengths for **9**−**12**, as determined by X-ray crystallography. Further, all ^{125}Te signals (−87 to −289 ppm) are downfield from those observed for tris(alkyl)-, tris(aryl)-, and tris(amido)phosphine tellurides (−492 to −837 ppm).[32]

Theoretical Studies. To provide some insight into our observations regarding the reactions of cyclodiphosph(III)-azanes **1**−**3** with elemental tellurium, theoretical studies (semiempirical PM3 level of theory) were carried out. One issue involves the relative reactivities of cyclodiphosph(III)-azanes toward elemental tellurium. ^{31}P NMR studies of reaction mixtures of **9** show that approximately 70% of **1** remains unreacted after 18 h. In the synthesis of **10** and **11**, on the other hand, **2** and **3** are completely consumed after 4 h. These observations may be rationalized in terms of the relative nucleophilicity of the P(III) centers in **1**−**3**. The formation of a phosphine telluride involves a nucleophilic attack of the phosphorus(III) center on elemental tellurium. Consequently, an increase in electron density at the phosphorus center is accompanied by higher reactivity. Calculated charges at the phosphorus centers of **1**−**3** (Table 3, cyclodiphosph(III/V)azane **A**) show lower values for **2** and **3** (+0.610 and +0.626, respectively) compared to **1** (+0.680), indicating larger electron densities and higher nucleophilicities. This increased electron density is attributable to the partial negative charge on the ligand in these largely ionic Li and Mg complexes. As a result, the yields of **10** and **11** observed via ^{31}P NMR are much higher than that of **9**.



A



B

A related point that requires clarification is the formation of a ditelluride rather than a monotelluride from the dilithium complex **3**. This process involves sequential oxidation of the two phosphorus centers. Therefore, the charges at the P(III) center were calculated for a series of cyclophosph(III/V)-azane monotellurides **B** (X = NMe; M = 2 H, Mg, 2 Li). In each case the oxidation of the first phosphorus atom is accompanied by an increase in the charge (i.e. decrease in electron density) at the second phosphorus center. Although this does explain the stability of the monotelluride **9** [+0.739 charge at P(III)], the corresponding charges for **10** and **11** are lower and similar (+0.655 and +0.626, respectively). Thus, a similar degree of oxidation would be expected for **2** and **3**. This is not the case, however, and other factors such as the conformation of the dilithium monotelluride intermediate or the stability of ditelluride products may be influential.

To further test our hypothesis, similar calculations were performed on precursors of other known cyclodiphosphazane mono- and ditellurides. Cyclodiphosph(III/ III)azanes containing electron-donating alkyl groups (X = ^{t}Bu and Me) were found to have lower positive nuclear charges on phosphorus than those with amido groups (see Table 3). Consequently, it is not surprising that ditelluride species were isolated from these precursors.[12b,17b] Also, in the unsymmetrical cyclodiphosph(III/ III)azane (X = Me and Cl), the strongly electron-withdrawing halide produces a large positive nuclear charge on the adjacent phosphorus center, resulting in the isolation of the monotelluride [MeP(Te)(μ-N^{t}Bu)$_2$PCl].[17b] In the case of the zirconium and halfnium dichloride derivatives of the bis(*tert*-butylamido)cyclodiphosph(III/III)azane dianion, which have seco-heterocubic structures similar to that of the magnesium salt **2**, attempted oxidation with oxygen and sulfur (i.e. stronger oxidizing agents than tellurium) was reported to be unsuccessful.[3] These observations are also consistent with the calculated high positive nuclear charges at the phosphorus centers (+0.751), which result from the electron-withdrawing effect of the transition metal and the larger covalent character of the Zr−N and Hf−N bonding compared to that of the lithium and magnesium salts. The experimental and theoretical data in Table 3 suggest that there is an upper limit of ca. +0.70 for the effective nuclear charge at phosphorus in our model above which phosphine−telluride species are not accessible. This guideline may, therefore, be helpful in predicting the formation of cyclodiphosphazane tellurides with other substituents (X) or different metal centers.

Conclusions

The reaction of lithium or magnesium derivatives of bis(*tert*-butylamido)cyclodiphosph(III)azanes with elemental tellurium is an effective route to the synthesis of bis(*tert*-butylamido)cyclodiphosphazane telluride anions. X-ray crystallographic studies show relatively weak P−Te bonds for the metalated derivatives, retention of the seco-heterocubic structure in **10**, and a novel Te,Te′/Te,N bonding mode (**IV**) for bis(imido)cyclodiphosph(V/V)azane dichalcogenides. Multinuclear NMR studies confirm retention of the cyclodiphosphazane telluride frameworks in solution. Preferential formation of the mono- or ditelluride species may be

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rationalized in terms of the effective nuclear charges at the P(III) centers, which may be employed as a guideline for predicting the accessibility of related cyclodiphosphazane tellurides. Further, this new synthetic approach may be applicable to the preparation of previously inaccessible imidophosphine(V) telluride anions.

Acknowledgment. We thank Mark Krahn for assistance in the preparation of **1**, Dr. Bob MacDonald (University of Alberta) for acquiring X-ray crystallographic data for **10**, Dorothy Fox, Qiao Wu, and Dr. Raghav Yamdagni for assistance in collecting NMR data, and the Natural Sciences and Engineering Research Council of Canada and the University of Calgary for funding.

Supporting Information Available: X-ray crystallographic files in CIF format for **9** and **10**·thf. This material is available free of charge via the Internet at http://pubs.acs.org.

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