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Group 11 Complexes of the *P*,*Te*-Centered Ligand $[TeP^iPr_2NP^iPr_2]^-$: Synthesis, Structures, and Insertion Reactions of the Copper(I) Complex with Chalcogens

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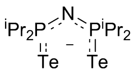
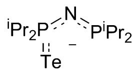
The lithium reagent $[LiTeP^iPr_2NP^iPr_2]$ undergoes metathetical reactions with group 11 chlorides to give the complexes $\{M(TeP^iPr_2NP^iPr_2)\}_3$ (**6:** M = Cu; **7:** M = Ag) and $(Ph_3P)Au(TeP^iPr_2NP^iPr_2)$ (**8**) as yellow crystalline solids. These new complexes were characterized by single crystal X-ray diffraction and multinuclear NMR spectroscopy. The tellurium atoms in the trimeric complexes **6** and **7** occupy bridging positions to give a Cu_3Te_3 ring in a twist-boat conformation with short M···M contacts (M = Cu, Ag). Variable temperature ^{31}P NMR and ESI-MS spectra for **6** and **7** give evidence for the formation of several oligomers in tetrahydrofuran solution. The reactions of **6** with dioxygen (or Me_3NO), elemental sulfur, or red selenium generate the chalcogen-insertion products $\{Cu(TeP^iPr_2NP^iPr_2E)\}_3$ (**9:** E = O; **10:** E = S; **11:** E = Se), which were also structurally characterized by single crystal X-ray diffraction and multinuclear NMR spectroscopy. The lighter chalcogens are two-coordinate while the tellurium centers occupy bridging positions in the trimeric complexes **9**−**11** giving rise to Cu_3Te_3 rings in a chairlike conformation.

Introduction

Tellurium-based ligands have been studied with increasing interest in recent years, especially for the development of metal complexes which are used as single source precursors (SSPs) to solid state metal tellurides. These materials have important applications in electronic devices such as photovoltaic cells or thermoelectric generators. Notably, the bulky tellurolate ligand $[(Me_3Si)_3SiTe]^-$ has been used by Arnold and co-workers to develop group 12 and 14 metal complexes which produce metal telluride thin films or powders upon thermolysis.[1] The group of Bochmann has prepared an *N*,*Te*-chelating class of ligand, $^tBu_2P(Te)NHR$ (R = ^iPr, cyclohexyl), and shown that its group 12 complexes are suitable CVD precursors to group 12 metal telluride thin films.[2] Recent work in our group has focused on using a *Te*,*Te*-chelating ligand, $[(TeP^iPr_2)_2N]^-$ ($\mathbf{L^1}$), to develop metal complexes which are SSPs to these important materials,[3] as well as to investigate their often unique structural chemistry.


$\mathbf{L^1}$


$\mathbf{L^2}$

Homoleptic and heteroleptic metal complexes of this ditellurido-imidodiphosphinato (PNP) ligand have been successfully prepared by metathetical reactions of the sodium salt (tmeda)Na[$\mathbf{L^1}$] with group 12, 13, and 15 metal halides.[4] Some of these complexes have been used to deposit thin films of phase-pure CdTe,[5] Sb_2Te_3,[6] and In_2Te_3,[7] by the method of aerosol-assisted chemical vapor deposition (AACVD). Interestingly, the reaction of (tmeda)Na[$\mathbf{L^1}$] with group 11 halides produces oligomeric complexes of the formula $\{M[\mathbf{L^1}]\}_n$ (**1**: M = Cu, $n = 3$; **2**: M = Ag, $n = 6$),

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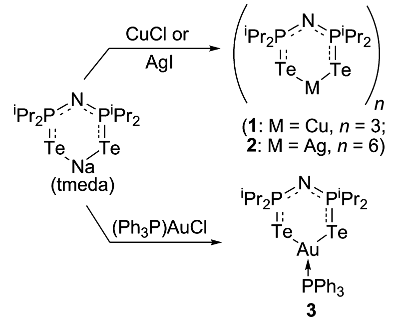
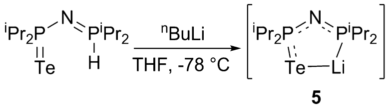
Scheme 1



via the linking of monomeric units through tellurium bridges.[8] In the case of the copper(I) complex **1**, two of the $\mathbf{L}^1$ ligands feature one tellurium center which is two-coordinate and one which is three-coordinate (doubly bridging); the remaining ligand possesses two three-coordinate chalcogens. The complex features two short Cu···Cu distances (2.626(1) and 2.637(2) Å) as a result of this bonding arrangement, which is distorted when compared to the related selenium-based complex $\{\mathrm{Cu}[(\mathrm{SeP}^i\mathrm{Pr}_2)_2\mathrm{N}]\}_3$,[9] where all three ligands feature one singly bridging and one doubly bridging chalcogen center and there are no short Cu···Cu distances. The heteroleptic monomeric complex $(\mathrm{Ph}_3\mathrm{P})\mathrm{Au}[\mathbf{L}^1]$ (**3**) is obtained by using $(\mathrm{Ph}_3\mathrm{P})\mathrm{AuCl}$ (Scheme 1).[8]

Attempts to prepare the homoleptic gallium(III) complex $\mathrm{Ga}[\mathbf{L}^1]_3$ by reaction of GaCl_3 with $(\mathrm{tmeda})\mathrm{Na}[\mathbf{L}^1]$ resulted in an interesting tellurium transfer reaction to give the unprecedented complex $\{\mathrm{Ga}(\mu\text{-Te})[\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2]\}_2$ (**4**), with an accompanying redox process yielding the ditelluride dimer $(\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2\mathrm{Te}\text{-})_2$.[10,11] The presence of the new *P*,*Te* bidentate ligand, $[\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2]^-$ ($\mathbf{L}^2$), in complex **4** prompted attempts to prepare it in a rational manner. The synthesis of the lithium derivative $[\mathrm{LiTeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2]$ (**5**) is readily achieved by deprotonation of the monotelluride $\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP(H)}^i\mathrm{Pr}_2$ with $^n\mathrm{BuLi}$ (eq 1).[12] The complex **5** is stable in tetrahydrofuran (THF) solution, but undergoes decomposition by disproportionation when the solvent is removed. The subsequent reactions of this in situ reagent with group 12 chlorides generate the homoleptic complexes $\mathrm{M}(\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2)_2$ (M = Zn, Cd, Hg) as crystalline solids in good yields.[12]



(1)

5

Since the two ligating atoms of $\mathbf{L}^2$, phosphorus and tellurium, are both soft donors, this ligand is ideally suited for coordination to the electron-rich late transition metals. Several such metal complexes of *P*,*Te*-chelating ligands have been reported, including the mercury(II) complex $\mathrm{Hg}(\mathrm{TePPh}_2\mathrm{CPPh}_2)_2$[13] and the platinum(II) complex $(\mathrm{NCS})_2\mathrm{Pt}(o\text{-PhTe-C}_6\mathrm{H}_4{-}\mathrm{PPh}_2)$.[14] The group 11 metals are also suitable targets, in fact, many of the structurally characterized examples of group 11 complexes containing tellurium are large clusters featuring bridging Te^{2-} or PhTe^- ligands and stabilizing neutral phosphine donors. For instance, in 1993 Fenske and Steck reported a family of compounds with the general formula $[\mathrm{Cu}_x\mathrm{Te}_y(\mathrm{PR}_3)_z]$ ($x + y = 25{-}45$, $z = 8{-}12$), which possess a large core of copper and tellurium centers with copper-bound phosphine ligands on the surface of the cluster.[15] The nonanuclear silver(I) tellurolate complex $[\mathrm{Ag}_9(\mu_3\text{-TePh})_9(\mathrm{PEt}_2\mathrm{Ph})_6]$ was prepared by Fenske et al. in 1997.[16] Since the copper(I) and silver(I) complexes **1** and **2** are trimeric and hexameric in the solid state, respectively, the structural influence of replacing $\mathbf{L}^1$ with $\mathbf{L}^2$ merits investigation.

We now report the reaction of **5** with group 11 halides to generate the homoleptic complexes $\{\mathrm{M}(\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2)\}_n$ (**6**: M = Cu; **7**: M = Ag) and the heteroleptic gold(I) complex $(\mathrm{Ph}_3\mathrm{P})\mathrm{Au}(\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2)$ (**8**), which were structurally characterized in the solid state by single-crystal X-ray diffraction and in solution by multinuclear NMR spectroscopy. A variable-temperature ^{31}P NMR study of **7** was conducted to investigate its aggregation in solution. Spectroscopic evidence for the formation of several oligomers of **7** in THF is presented, a novel finding for the mono- or dichalcogenido PNP class of ligand. The reactions of **6** with elemental chalcogens (E = O, S, Se) provide rare examples of chalcogen-insertion reactions into an M−P bond to generate the new heterodichalcogenido PNP complexes $\{\mathrm{Cu}(\mathrm{TeP}^i\mathrm{Pr}_2\mathrm{NP}^i\mathrm{Pr}_2\mathrm{E})\}_3$ (**9**: E = O; **10**: E = S; **11**: E = Se). The solid-state structures and multinuclear NMR solution spectra of complexes **9**−**11** are discussed.

Experimental Section

Reagents and General Procedures. All solvents were dried and distilled from Na/benzophenone and stored over 4 Å molecular sieves prior to use. Deuterated solvents for NMR studies were degassed using at least three freeze−pump−thaw cycles and stored over 4 Å molecular sieves prior to use. Copper(I) chloride, silver(I) chloride, trimethylamine *N*-oxide (anhydrous), and triphenylphosphinegold(I) chloride were purchased from Aldrich and used as received. Elemental sulfur (Fisher Scientific) was sublimed prior to use. The reagent (tht)AuCl (tht = tetrahydrothiophene) was synthesized from hydrogen tetrachloroaurate by the literature method.[17] Amorphous red selenium was freshly prepared by reduction of selenium dioxide with sodium sulfite according to the method of Bacon and Ingledew.[18] THF solutions of the reagents

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(tmeda)Li(TeP^{i}Pr$_2$NP^{i}Pr$_2$Se)[19] and [LiTeP^{i}Pr$_2$NP^{i}Pr$_2$][12] were prepared according to the literature procedures. All manipulations were performed under an inert atmosphere of argon using standard glovebox and Schlenk techniques. Melting points (uncorrected) were obtained from samples sealed in capillary tubes under argon.

Instrumentation. ^{1}H, ^{31}P, ^{77}Se, and ^{125}Te NMR spectra were recorded on either a Bruker DRX-400 or an AMX-300 NMR spectrometer. Chemical shifts are reported in parts per million (ppm), relative to the external standards Me_4Si (^{1}H), 85% H_3PO_4 (^{31}P), Se_2Ph_2 (^{77}Se), and Te_2Ph_2 (^{125}Te). Spin−spin coupling constants are reported in hertz (Hz). Mass spectra of **6** and **7** were recorded on a Bruker Esquire 3000 mass spectrometer using electrospray ionization and an ion trap analyzer. Elemental analyses were performed by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

{Cu(TeP^{i}Pr$_2$NP^{i}Pr$_2$)}$_3$ (6). A solution of [LiTeP^{i}Pr$_2$NP^{i}Pr$_2$] in THF (30 mL, 1.33 mmol) at −78 °C was added dropwise over 10 min to a suspension of CuCl (131 mg, 1.32 mmol) in THF (20 mL) at room temperature, and the resulting yellow mixture was stirred for 1 h. Removal of the volatiles under vacuum left an oily yellow-orange solid, which was extracted with Et_2O (25 mL) and filtered through Celite over a 0.45 μm filter disk. The resulting orange solution was concentrated to about 5 mL, and overnight storage at −30 °C resulted in the formation of yellow rod-like crystals of **6** (266 mg, 46%, mp 194−198 °C). ^{1}H NMR (CD_2Cl_2) δ: 2.32−2.09 (m, 2H, C*H*(CH_3)$_2$), 2.02−1.78 (m, 2H, C*H*(CH_3)$_2$), 1.46−0.99 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P NMR (CD_2Cl_2) δ: 109.9 (d, $^2J_{P-P}$ = 101, Cu-*P*), 72.9 (d, $^2J_{P-P}$ = 103, $^1J_{Te-P}$ = 1085, Te-*P*). ^{125}Te NMR (CD_2Cl_2) δ: −632.9 (d, $^1J_{Te-P}$ = 1085). Anal. Calcd for $C_{36}H_{84}N_3Cu_3P_6Te_3$: C, 32.80; H, 6.42, N, 3.19. Found: C, 32.90; H, 6.72; N, 3.19. X-ray quality crystals of **6** were grown from a concentrated Et_2O solution at −30 °C.

{Ag(TeP^{i}Pr$_2$NP^{i}Pr$_2$)}$_3$ (7). The silver complex **7** was prepared by using the same procedure as for **6**, with AgCl (190 mg, 1.33 mmol) as the source of silver(I). Recrystallization from Et_2O yielded **7** as a yellow crystalline solid (136 mg, 21%, mp 158−159 °C). ^{1}H NMR (CD_2Cl_2) δ: 2.32−2.10 (m, 2H, C*H*(CH_3)$_2$), 1.94−1.80 (m, 2H, C*H*(CH_3)$_2$), 1.36−0.97 (m, 24H CH(C*H*$_3$)$_2$). ^{31}P NMR (CD_2Cl_2) δ: 112.4 (br dd, $^2J_{P-P}$ = 90, $^1J_{Ag-P}$ = 444, Ag-*P*), 68.2 (d, $^2J_{P-P}$ = 94, $^1J_{Te-P}$ = 1077, Te-*P*). ^{125}Te NMR (CD_2Cl_2) δ: −856.9 ($^1J_{Te-P}$ = 1086). Anal. Calcd for $C_{36}H_{84}N_3Ag_3P_6Te_3$: C, 29.79; H, 5.83, N, 2.90. Found: C, 30.19; H, 5.74; N, 2.86. X-ray quality crystals of **7** were grown from a concentrated Et_2O solution at −30 °C.

(Ph$_3$P)Au(TeP^{i}Pr$_2$NP^{i}Pr$_2$) (8). A solution of [LiTeP^{i}Pr$_2$NP^{i}Pr$_2$] in THF (30 mL, 0.66 mmol) at −78 °C was added dropwise over 10 min to a suspension of (Ph_3P)AuCl (328 mg, 0.66 mmol) in THF (20 mL) at −78 °C, and the resulting pale yellow mixture was stirred for 30 min at −78 °C and 30 min at room temperature. Removal of the volatiles under vacuum left a yellow oil, which was extracted with toluene (25 mL) and filtered through Celite over a 0.45 μm filter disk. Upon removal of the volatiles under vacuum an orange oil remained, which began to crystallize. Dissolution of the material into hot hexanes and cooling to 0 °C afforded yellow crystalline **8** (292 mg, 53%, mp 123−124 °C). ^{1}H NMR (CD_2Cl_2) δ: 7.66−7.57 (m, 6H, P(C_6*H*$_5$)$_3$), 7.48−7.37 (m, 9H, P(C_6*H*$_5$)$_3$), 2.20−1.98 (m, 4H, C*H*(CH_3)$_2$), 1.33−0.99 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P NMR (CD_2Cl_2, 298 K) δ: 137.3 (br m, Au-*P*^{i}Pr$_2$), 74.7 (d, $^2J_{P-P}$ = 62, $^1J_{Te-P}$ = 1189, Te-*P*), 55.7 (br s, Au-*P*Ph$_3$); ^{31}P NMR (CD_2Cl_2, 193 K): 136.2 (d of d, $^2J_{P-P}$ = 230 Hz, $^2J_{P-P}$ = 56, Au-*P*^{i}Pr$_2$), 77.0 (d of d, $^1J_{Te-P}$ = 1181, $^2J_{P-P}$ = 56, $^3J_{P-P}$ = 26, Te-*P*), 54.3 (d of d, $^2J_{P-P}$ = 230 Hz, $^3J_{P-P}$ = 26, Au-*P*Ph$_3$). ^{125}Te NMR (CD_2Cl_2) δ: −532.6 (d, $^1J_{Te-P}$ = 1195). Anal. Calcd for $C_{30}H_{43}NAuP_3Te$: C, 43.14; H, 5.19, N, 1.68. Found: C, 43.09; H, 5.28; N, 1.68. X-ray quality crystals of **8** were grown from a concentrated solution of the complex in hot hexanes which was stored at 5 °C.

Attempted Synthesis of {Au(TeP^{i}Pr$_2$NP^{i}Pr$_2$)}$_n$. The attempted preparation of this gold(I) complex employed a similar procedure as for **8**, with (tht)AuCl (214 mg, 0.67 mmol) as the source of gold(I). The crude red oil product was extracted with toluene (25 mL) and filtered, pumped down to an oil, and extracted with hexanes. The resulting deep red solution was stored at −35 °C and yielded red crystals of the known compound {Au(μ-Te)[TeP^{i}Pr$_2$NP^{i}Pr$_2$]}$_2$,[11] which were identified by their unit cell parameters.

Synthesis of {Cu(TeP^{i}Pr$_2$NP^{i}Pr$_2$O)}$_3$ (9). A solution of **6** (137 mg, 0.10 mmol) in THF (25 mL) containing suspended Me_3NO (23 mg, 0.31 mmol) was stirred at room temperature for 2 d. The volatiles were removed in vacuo, and the residual material was extracted with hexanes, filtered through a 0.45 μm filter disk, concentrated to about 15 mL, and stored at −35 °C for 3 d. Yellow crystals of **9** were isolated from the mother liquor in two crops. Drying the crystals under vacuum resulted in a visual loss of crystallinity, suggesting the product contained a solvent of crystallization that was removed upon exposure of the sample to low pressure. Compound **9** was isolated as a yellow powder (72 mg, 51%, mp 159−160 °C). ^{1}H NMR (CD_2Cl_2) δ: 2.21−2.03 (m, 2H, C*H*(CH_3)$_2$), 1.96−1.78 (m, 2H, C*H*(CH_3)$_2$), 1.39−1.05 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P NMR (CD_2Cl_2) δ: 46.8 (d, $^2J_{P-P}$ = 21, O−P), 11.8 (d, $^2J_{P-P}$ = 21, $^1J_{Te-P}$ = 1119, Te-*P*). ^{125}Te NMR (CD_2Cl_2) δ: −631.8 (d, $^1J_{Te-P}$ = 1119). Anal. Calcd for $C_{36}H_{84}Cu_3N_3O_3P_6Te$: C, 31.65; H, 6.20; N, 3.08. Found: C, 31.61; H, 6.38; N, 3.24. Solvent-free X-ray quality crystals of **9** grew slowly from a solution of **6** in Paratone oil which was exposed to the ambient atmosphere.

Synthesis of {Cu(TeP^{i}Pr$_2$NP^{i}Pr$_2$S)}$_3$ (10). A solution of **6** (0.44 mmol) in THF (50 mL) was prepared as described earlier, and after 1 h of stirring at room temperature it was cooled to −78 °C. This solution was added to a suspension of sulfur (42 mg, 1.31 mmol) in THF (15 mL) at −78 °C. The resulting dark yellow mixture was stirred for 1 h at −78 °C and then warmed up to room temperature, at which point the solution was red-brown in color. Removal of the solvent in vacuo yielded an oily brown product, which was extracted with hot hexanes (20 mL), filtered through a 0.45 mm pore size filter disk, concentrated to 15 mL, and stored at −35 °C. After 5 days, pale yellow hexagonal prismatic crystals were isolated from the mother liquor, which lost solvent upon exposure of the sample to reduced pressure and heating to 100 °C. Complex **10** was isolated as a yellow powder (165 mg, 26%, mp 154−155 °C). ^{1}H NMR (CD_2Cl_2) δ: 2.09−1.95 (m, 4H, C*H*(CH_3)$_2$), 1.34−1.05 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P NMR (CD_2Cl_2) δ: 65.3 (d, $^2J_{P-P}$ = 30, S−P), 21.1 (d, $^2J_{P-P}$ = 30, $^1J_{Te-P}$ = 1173, Te-*P*). ^{125}Te NMR (CD_2Cl_2) δ: −628.7 (d, $^1J_{Te-P}$ = 1170). Anal. Calcd for $C_{36}H_{84}Cu_3N_3P_6S_3Te_3$: C, 30.57; H, 5.99; N, 2.97. Found: C, 30.61; H, 6.05; N, 3.01. X-ray quality crystals of **10**$\cdot$(C_6H_{14})$_n$ grew from a concentrated solution in hexanes at −35 °C.

Synthesis of {Cu(TeP^{i}Pr$_2$NP^{i}Pr$_2$Se)}$_3$ (11). Method A. The complex **11** was prepared using the same procedure as for **10**, by reacting a solution of **6** (0.44 mmol) in THF at −78 °C with a suspension of amorphous red selenium (105 mg, 1.33 mmol) in THF (15 mL) at −78 °C. Yellow crystals of **11** were isolated from the mother liquor in two crops (402 mg, 58%). The ^{31}P NMR spectrum indicated that the sample was about 84% pure, with contamination by {Cu[(SeP^{i}Pr$_2$)$_2$N]}$_3$ and {Cu[(TeP^{i}Pr$_2$)$_2$N]}$_3$ in

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(19) Robertson, S. D.; Chivers, T. *Dalton Trans.* **2008**, 1765.

Table 1. Crystallographic Data for **6**−**11**[a]

	CuL (**6**)	AgL (**7**)	AuL (**8**)	Cu(O,Te) (**9**)	Cu(S,Te) (**10**)	Cu(Se,Te) (**11**)
chemical formula	$C_{36}H_{84}Cu_3N_3P_6Te_3$	$C_{36}H_{84}Ag_3N_3P_6Te_3$	$C_{30}H_{43}AuNP_3Te$	$C_{36}H_{84}Cu_3N_3O_3P_6Te_3$	$C_{36}H_{84}Cu_3N_3P_6S_3Te_3$	$C_{36}H_{84}Cu_3N_3P_6Se_3Te_3$
formula weight	1318.30	1451.29	835.13	1366.30	1414.48	1555.18
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$C2/c$	$C2/c$	$P2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	40.314(8)	39.819(8)	8.2699(5)	14.4878(3)	8.4700(17)	8.4684(17)
b, Å	11.660(2)	11.851(2)	22.988(1)	15.2199(4)	20.327(4)	20.421(4)
c, Å	24.565(5)	24.668(5)	9.3852(6)	15.4833(3)	21.099(4)	21.183(4)
α, deg	90	90	90	108.465(1)	117.28(3)	117.27(3)
β, deg	110.06(3)	109.74(3)	114.38(3)	105.978(2)	96.25(3)	95.65(3)
γ, deg	90	90	90	108.983(2)	90.27(3)	91.29(3)
V, Å^3	10846(4)	10957(4)	1625.1(4)	2776.5(1)	3203.3(14)	3230.8(14)
Z	8	8	2	2	2	2
D_{calcd}, g cm^{-3}	1.615	1.759	1.707	1.634	1.467	1.599
μ (Mo$_{K\alpha}$), mm^{-1}	2.951	2.829	5.573	2.889	2.597	4.168
R_{int}	0.0335	0.0394	0.0641	0.0379	0.0230	0.0356
R_1 [$I > 2\sigma(I)$][b]	0.0407	0.0551	0.0401	0.0526	0.0289	0.0478
wR_2 (all data)[c]	0.1011	0.1769	0.0822	0.1309	0.0905	0.1352
GOF on F^2	1.036	1.066	1.078	1.029	1.097	1.058

[a] λ (Mo$_{K\alpha}$) = 0.71073 Å, $T = -100$ °C. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

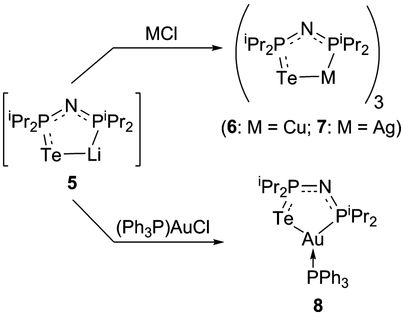
amounts of 10% and 6%, respectively. Further recrystallizations did not improve the purity. ^{1}H NMR (CD$_2$Cl$_2$) δ: 2.20−1.96 (m, 4H, C*H*(CH$_3$)$_2$), 1.30−1.05 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P NMR (CD$_2$Cl$_2$) δ: 58.5 (d, $^2J_{\mathrm{P-P}} = 31$, $^1J_{\mathrm{Se-P}} = 555$, Se−P, **11**), 52.7 (s, $^1J_{\mathrm{Se-P}} = 530$, {Cu[(SeP^{i}Pr$_2$)$_2$N]}$_3$), 28.7 (s, $^1J_{\mathrm{Te-P}} = 1270$, {Cu[(TeP^{i}Pr$_2$)$_2$N]}$_3$), 22.7 (d, $^2J_{\mathrm{P-P}} = 31$, $^1J_{\mathrm{Te-P}} = 1195$, Te-*P*, **11**).

Synthesis of {Cu(TeP^{i}Pr$_2$NP^{i}Pr$_2$Se)}$_3$ (11). Method B. A solution of (tmeda)Li(TeP^{i}Pr$_2$NP^{i}Pr$_2$Se) (2.50 mmol) in THF (40 mL) at −78 °C was added to a suspension of CuCl (248 mg, 2.51 mmol) in THF (20 mL) at −78 °C, and then warmed to room temperature, with stirring, for 30 min. The solvent was removed from the resulting orange/gray solution under vacuum. Extraction with hot hexanes (20 mL) and filtration through Celite over a 0.45 μm filter disk yielded a clear yellow solution. Storage of this solution at −35 °C for several days yielded yellow crystals which contained co-crystallized solvent. Heating to 100 °C under vacuum afforded a solvent-free yellow powder (400 mg, 31%, mp 157−158 °C). ^{1}H NMR (CD$_2$Cl$_2$) δ: 2.20−1.96 (m, 4H, C*H*(CH$_3$)$_2$), 1.30−1.05 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P NMR (CD$_2$Cl$_2$) δ: 58.5 (d, $^2J_{\mathrm{P-P}} = 31$, $^1J_{\mathrm{Se-P}} = 555$, Se−P), 22.7 (d, $^2J_{\mathrm{P-P}} = 31$, $^1J_{\mathrm{Te-P}} = 1195$, Te-*P*). ^{77}Se NMR (CD$_2$Cl$_2$) δ: −292.7 (d, $^1J_{\mathrm{Se-P}} = 557$ Hz). ^{125}Te NMR (CD$_2$Cl$_2$) δ: −650.0 (d, $^1J_{\mathrm{Te-P}} = 1197$). Anal. Calcd for $C_{36}H_{84}Cu_3N_3P_6Se_3Te_3$: C, 27.80; H, 5.44; N, 2.70. Found: C, 28.17; H, 5.22; N, 2.70. X-ray quality crystals of **11**·(C$_6$H$_{14}$)$_n$ grew from a concentrated solution in hexanes at −35 °C.

X-ray Crystallography. A suitable crystal of each complex was selected, coated in Paratone oil, and mounted on a glass fiber. Data were collected at 173 K on a Nonius KappaCCD diffractometer using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) with ω and φ scans. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out by using the Nonius DENZO package. After reduction, the data were corrected for absorption based on equivalent reflections using SCALEPACK (Nonius, 1998). The structures were solved by direct methods with SHELXS-97[20] and refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method by using the SHELXL-97 program.[21] Hydrogen atoms were calculated geometrically and were riding on their respective atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Crystallographic data are summarized in Table 1. No special considerations were needed for the refinement of compound **8**. Some disorder of methyl groups on isopropyl substituents was observed in the data sets for **6**, **7**, and **9**. In these cases the affected carbon atoms were modeled as isotropic mixtures over two positions, with mild geometric restraints. The unit cells for compounds **10** and **11** contained heavily disordered hexane solvent molecules for which no suitable model could be found. The electron density associated with these fragments were removed from the reflection data using the program SQUEEZE (PLATON),[22] leaving voids of about 469 and 445 Å^3 for **10** and **11**, respectively.

Scheme 2



Results and Discussion

Synthesis of {M(TeP^{i}Pr$_2$NP^{i}Pr$_2$)}$_3$ (6: M = Cu; 7: M = Ag) and (Ph$_3$P)Au(TeP^{i}Pr$_2$NP^{i}Pr$_2$) (8). To investigate the coordination chemistry of the lithiated monotellurido ligand [LiTeP^{i}Pr$_2$NP^{i}Pr$_2$] (**5**) toward the group 11 elements, reactions were carried out with CuCl, AgCl, and (Ph$_3$P)AuCl (Scheme 2). Solutions of **5** in THF were prepared according to the established protocol[12] and then reacted with a THF suspension of the corresponding metal chloride in a 1:1 stoichiometry. ^{31}P NMR spectra of reaction aliquots indicated that the metatheses proceeded rapidly (complete in less than 1 h) to give the desired ligand substitution products with minimal unwanted side reactions. Extraction of the products with diethyl ether or hexanes provided an easy method for separation of the LiCl by-product. The copper(I) and silver(I) complexes **6** and **7**, respectively, were crystallized from cold

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Et_2O solutions to give analytically pure X-ray quality yellow crystals in moderate yields (21−46%), and the heteroleptic triphenylphosphinegold(I) complex **8** was likewise isolated from a hexanes solution as yellow crystals (53% yield). So far we have been unable to find a solvent system from which reproducibly high crystalline yields for **6**−**8** are obtained, despite the ^{31}P NMR data indicating they are formed to the exclusion of significant amounts of by-product during their syntheses.

Attempts to prepare a gold(I) complex of $\mathbf{L^2}$ with a more labile supporting ligand were also made; the reaction of (tht)AuCl (tht = tetrahydrothiophene) with **5** at −78 °C initially produced yellow solutions. However, upon workup the color changed to deep red indicating a redox reaction ($Au^I \rightarrow Au^{III}$) had occurred. Recrystallization of the red oil from hexanes gave single crystals of the known complex $\{(Au(\mu\text{-}Te)[TeP^iPr_2NP^iPr_2]\}_2$,[11] the formation of which necessitates the decomposition of the initial product through tellurium abstraction, and hence this sacrificial loss of ligand led to the low yield observed (a few crystals).

The new complexes **6**−**8** all exhibited sharp melting points, but a gradual darkening of the solids while heating and the dark orange to red color of the resulting liquid phases indicated thermal decomposition was likely occurring. Crystalline samples of **6**−**8** are relatively stable to air and moisture; samples left exposed to ambient conditions for days showed no visible signs of decomposition.

Reactions of $\{Cu(TeP^iPr_2NP^iPr_2)\}_3$ (6) with Elemental Chalcogens. During crystallographic studies it was noted that yellow crystals of **6** slowly dissolved in Paratone oil, and over a period of weeks colorless crystalline rods formed from this solution. A single-crystal X-ray analysis determined these new crystals were of the composition $\{Cu(TeP^iPr_2NP^iPr_2O)\}_3$ (**9**). We suggest that this unexpected product is formed by the oxidation of **6** by molecular O_2, resulting in a formal oxygen atom insertion into the Cu−P bond. This interesting observation led to attempts to prepare this new compound by rational synthesis. It was found that the room-temperature reaction of **6** with an oxygen-atom transfer reagent, Me_3NO, in THF resulted in the desired transformation after several days. The heterodichalcogenido complex **9** was obtained as a pure product in 51% yield after recrystallization from hexanes. Interestingly, crystals of the silver(I) monotellurido complex **7** were also observed to form a new crystalline product upon standing in Paratone oil. In this case, however, the product formed was identified as the known ditellurido complex $\{Ag[(TeP^iPr_2)_2N]\}_6$,[8] a result of ligand disproportionation instead of O-atom insertion.

The synthesis of **9** represents the first example of a complex containing a dichalcogenidoimidodiphosphinate ligand $[EPR_2NPR_2E']^-$ with E = Te, E′ = O. All other possible mixed chalcogen ligands of this type have been previously synthesized: for example, the protonated ligands $EPPh_2NHPPh_2E'$ (E = O, E′ = S;[23] E = O, E′ = Se;[24] E = S, E′ = Se[25]) are all known, and the lithium derivatives $(tmeda)Li(TeP^iPr_2NP^iPr_2E)$ (E = S, Se) have been reported recently.[19] With the synthesis of **9** the series of mixed-chalcogen PNP ligands is now complete. Attempts to prepare $(tmeda)Li(TeP^iPr_2NP^iPr_2O)$, a potentially useful source of this ligand, by reaction of Me_3NO and TMEDA with $[LiTeP^iPr_2NP^iPr_2]$ were unsuccessful.

To address the question of whether the reactivity of **6** is general for other elemental chalcogens, we conducted a reaction with elemental sulfur in THF. At room temperature the mixture rapidly darkened in color, and a black precipitate was formed, presumably elemental tellurium. After stirring for 18 h, a reaction aliquot was analyzed by ^{31}P NMR spectroscopy, and resonances corresponding to three major products were identified: one singlet and two sets of mutually coupled doublets, all in comparable quantities. The singlet at δ 59.2 was attributable to the disulfido PNP complex $\{Cu[(SP^iPr_2)_2N]\}_3$, which has been previously reported.[26] One of the other two products was presumed to be the desired complex $\{Cu(TeP^iPr_2NP^iPr_2S)\}_3$ (**10**) [δ 65.3 (d, $^2J_{P-P}$ = 30 Hz), 20.9 (d, $^2J_{P-P}$ = 30 Hz)], and this was later confirmed by its unambiguous synthesis (vide infra). The third compound was tentatively assigned to be $\{Cu(SP^iPr_2NP^iPr_2)\}_3$ [δ 83.1 (d, $^2J_{P-P}$ = 22 Hz), 53.3 (d, $^2J_{P-P}$ = 22 Hz)], as the doublet at δ 53.3 is similar in chemical shift to the other Cu−S−*P* resonances in the mixture, and the downfield resonance at δ 83.1 is consistent with a Cu−*P* moiety.

Based on these data, it was concluded that both the oxidation of the P^{III} center and the nucleophilic displacement of Te by elemental sulfur occur significantly at room temperature, giving the three products observed by ^{31}P NMR. When this reaction was performed under kinetic conditions (slow addition at −78 °C), selective oxidation of the P^{III} center occurred to give **10** almost exclusively, as judged by ^{31}P NMR. The product can be recrystallized from hexanes to give a pure material in 26% yield.

Attempts to insert selenium into the Cu−P bond of **6** using elemental gray selenium were unsuccessful. Although the reaction proceeds at room temperature, complicated mixtures of products are formed; at low temperature no significant reaction is observed. However, freshly prepared amorphous red selenium reacts with **6** under similar conditions as with elemental sulfur to give the selenium-insertion product, $\{Cu(TeP^iPr_2NP^iPr_2Se)\}_3$ (**11**). This product was contaminated by about 16% of the homodichalcogenido complexes $\{(Cu[(EP^iPr_2)_2N]\}_3$ (E = Se, Te), which were not removed by further recrystallizations. A pure sample of **11** was obtained in 31% yield by reaction of the heterodichalcogenido lithium reagent $(tmeda)Li(TeP^iPr_2NP^iPr_2Se)$[19] with CuCl.

The formal insertion of elemental chalcogens into metal−phosphorus bonds has been previously reported but does not appear to be a well-studied transformation compared to, for example, insertions of chalcogens into metal−carbon bonds. The syntheses of **9**−**11** (Scheme 3) therefore represent

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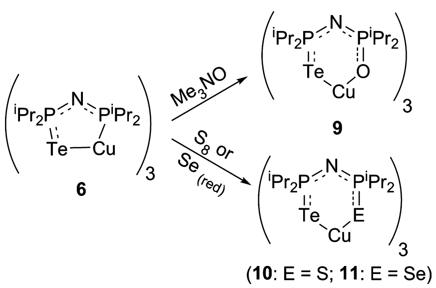
Scheme 3



further cases of this relatively rare reaction. Selected examples include the tin(IV) compound Ph$_2$P-SnEt$_3$, which was reported to react with dioxygen present in air to form Ph$_2$P(O)O-SnEt$_3$,[27] and the reaction of sulfur with the copper(I) complex [(dmp)Cu(PPh$_3$)$_2$][BF$_4$] (dmp = 2,9-dimethyl-1,10-phenanthroline) to yield the phosphine sulfide complex [(dmp)Cu(SPPh$_3$)$_2$][BF$_4$].[28] Stepwise selenium insertion into the Pt−P bonds of [Pt((Ph$_2$P)$_2$CH$_2$)$_2$]Cl$_2$ to give [Pt((Ph$_2$P)$_2$CH$_2$)(SePPh$_2$CH$_2$PPh$_2$)]Cl$_2$ and then [Pt(SePPh$_2$CH$_2$PPh$_2$)$_2$]Cl$_2$ has also been reported.[29] In a closer analogy to the current work, the reaction of elemental sulfur or tellurium with the lithium reagents [LiTeP^{i}Pr$_2$NP^{i}Pr$_2$] (**5**) or [LiSeP^{i}Pr$_2$NP^{i}Pr$_2$], respectively, yielded the heterodichalcogenido PNP complexes (tmeda)Li[TeP^{i}Pr$_2$NP^{i}Pr$_2$E] (E = S, Se).[19]

Crystal Structures of 6−11. The solid-state structures of **6** and **7** are isostructural and reveal a trimeric arrangement with bridging tellurium centers. A representative thermal ellipsoid plot of **6** is shown in Figure 1; selected bond lengths and angles are displayed in Table 2. The trinuclear bonding arrangement is a relatively common motif for group 11 dichalcogenido PNP complexes. For example, the related species {Cu[(EP^{i}Pr$_2$)$_2$N]}$_3$ (E = S,[26] Se,[9] Te[8]) are all trimeric and exhibit a core Cu$_3$E$_3$ ring. In **6** and **7**, the M$_3$Te$_3$ rings are highly distorted from a chairlike arrangement, instead adopting a conformation best described as a twist-boat. Each metal center is coordinated by a *P*,*Te*-chelating ligand, as well as a tellurium atom from an adjacent ligand. The resulting geometries about the metal centers are approximately trigonal planar ($\Sigma_{>(\mathrm{M})}$: M = Cu, 349.3−359.4°; M = Ag, 349.7−358.3°). The endocyclic angles for the central ring are similar in each case: the Te−M−Te angles range from 100.27(3)−131.58(4)° while the M−Te−M values fall within the range 60.97(3)−67.88(3)°.

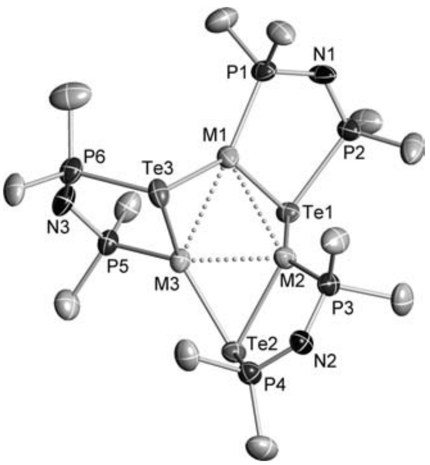


Figure 1. Representative thermal ellipsoid plot (30% probability) of **6** (M = Cu) and **7** (M = Ag). Only α-carbon atoms of isopropyl substituents are shown, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for {M(TeP^{i}Pr$_2$NP^{i}Pr$_2$)}$_3$

	6: M = Cu	**7**: M = Ag
M1−Te1	2.579(1)	2.804(1)
M1−Te3	2.570(1)	2.732(1)
M2−Te1	2.519(1)	2.682(1)
M2−Te2	2.647(1)	2.912(1)
M3−Te2	2.564(1)	2.722(1)
M3−Te3	2.566(1)	2.814(1)
M1−P1	2.277(2)	2.431(3)
M2−P3	2.243(2)	2.403(3)
M3−P5	2.259(2)	2.433(3)
P2−Te1	2.484(2)	2.471(3)
P4−Te2	2.465(2)	2.460(3)
P6−Te3	2.483(2)	2.470(3)
M1−M2	2.847(1)	3.019(2)
M2−M3	2.645(1)	2.924(2)
M3−M1	2.741(1)	3.036(1)
P1−N1	1.635(5)	1.640(12)
P2−N1	1.586(5)	1.577(11)
P3−N2	1.643(5)	1.644(10)
P4−N2	1.586(5)	1.584(11)
P5−N3	1.639(5)	1.646(9)
P6−N3	1.574(6)	1.583(9)
Te3−M1−Te1	128.75(4)	131.58(4)
M1−Te1−M2	67.88(3)	66.74(4)
Te1−M2−Te2	100.27(3)	102.82(4)
M2−Te2−M3	60.97(3)	62.42(3)
Te2−M3−Te3	125.50(3)	125.66(4)
M3−Te3−M1	64.53(3)	66.34(3)
P1−N1−P2	125.3(3)	128.7(6)
P3−N2−P4	124.7(3)	126.3(6)
P5−N3−P6	127.3(3)	129.2(6)

The M−Te distances in **6** and **7** (M = Cu: 2.519(1)−2.647(1) Å; M = Ag: 2.682(1)−2.912(1) Å) are similar to those observed in the complexes {M[(TeP^{i}Pr$_2$)$_2$N]}$_n$ (**1**: M = Cu, *n* = 3; **2**: M = Ag, *n* = 6)[8] and are also comparable to oligomeric copper(I) and silver(I) tellurolate complexes such as [Cu$_2$(μ-TePh)$_2$(PMe$_3$)$_4$] (*d*(Cu−Te) = 2.6316(7)−2.6677(7) Å),[30] or [Ag$_9$(μ_3-TePh)$_9$(PEt$_2$Ph)$_6$] (*d*(Ag−Te) = 2.731(1)−2.932(2) Å).[16] The bond lengths for the M−P connectivities are typical of neutral phosphine donor complexes (*d*(Cu−P) = 2.243(2)−2.277(2) Å; *d*(Ag−P) = 2.403(3)−2.433(3) Å).[31]

Within the ligand framework the P−Te distances are similar for **6** and **7** and range from 2.460(3) to 2.484(2) Å, which are indicative of single-bond character. These values are slightly longer than the analogous bond lengths observed in the homoleptic group 12 complexes M(TeP^{i}Pr$_2$NP^{i}Pr$_2$)$_2$(M

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(31) A search of the Cambridge structural database for R$_3$P-M complexes revealed mean bond distances of *d*(Cu-P) = 2.254(1) Å and *d*(Ag-P) = 2.445(1) Å for 4646 and 2733 instances of each bond, respectively.

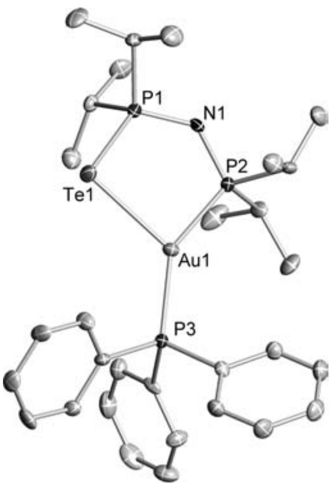

Figure 2. Thermal ellipsoid plot of **8** (30% probability). Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (Ph_3P)Au($TeP^iPr_2NP^iPr_2$) (**8**)

Au1−Te1	2.762(1)	Te1−Au1−P3	120.61(7)
Au1−P2	2.343(3)	Te1−Au1−P2	93.89(7)
Au1−P3	2.298(3)	P2−Au1−P3	145.50(9)
P1−Te1	2.439(3)		
P1−N1	1.599(8)		
P2−N1	1.637(9)		

= Zn, Cd, Hg), which were observed to be 2.430(2)−2.441(2) Å,[12] but are close to the observed distance of 2.453(1) Å in the dimeric Ga^{III} complex {Ga(μ-Te)[$TeP^iPr_2NP^iPr_2$]}$_2$ (**4**).[10] Overall, the metrical parameters suggest a bonding situation best described as a tellurolate/phosphine complex, rather than a phosphine telluride/phosphide donor set. This suggestion is supported by the P−N distances, which are indicative of strong Te−P=N−P character in the ligand backbone, as opposed to Te=P−N=P.

A point of interest in these polynuclear copper(I) and silver(I) complexes is the presence of relatively short M···M intramolecular distances, which are within the sums of the van der Waals radii for Cu−Cu and Ag−Ag (2.8 Å and 3.44 Å, respectively). For **6** the distances range from 2.645(1) to 2.847(1) Å, and for **7** the values are between 2.924(2) and 3.036(1) Å. It is not unusual for short metal−metal distances of this nature to be observed in complexes with bridging ligands,[32] and so it is not clear whether they represent true metallophilic interactions or are imposed by the geometry of ligands. The fact that the metal centers are all very nearly trigonal planar (vide supra) may indicate that only weak interactions, if any, are present.[33]

The crystal structure of **8** is shown in Figure 2, and selected bond parameters are displayed in Table 3.

The complex **8** is monomeric in the solid state, showing no close intermolecular contacts in the unit cell. The gold(I) center is trigonal planar (Σ<(Au1) = 360.0°) with a Au−Te distance of 2.762(1) Å, which is significantly longer than the corresponding distances observed in the ditellurido PNP complex (Ph_3P)Au[(TeP^iPr_2)$_2$N] (2.639(1) and 2.616(7) Å).[8] It is the longest reported Au−Te distance among gold(I) complexes containing a tellurium-based ligand, and in fact only one longer distance was found in the Cambridge Structural Database: the gold telluraborane complex [Et_4N][2-Ph_3P-*closo*-2,1-$AuTeB_{10}H_{10}$] exhibits Au−Te bond lengths of 2.839(3) Å and 2.853(3) Å in two crystallographically unique anions.[34] The two Au−P bond lengths seen in **8** are slightly different, with the triphenylphosphine ligand being closer to the gold center by about 0.05 Å. Complex **8** is the first example of a structurally characterized complex containing a AuP_2Te core. Metrical parameters within the ligand framework are similar to those seen in **6** and **7**; normal P−Te and P−N distances are observed.

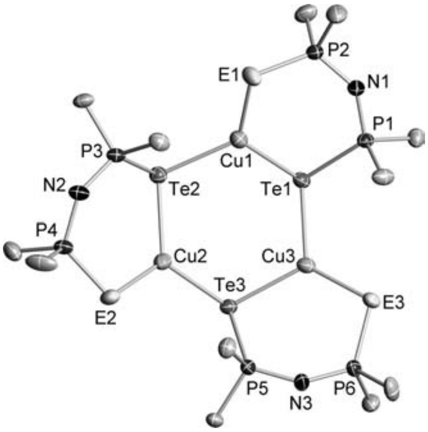

Figure 3. Representative thermal ellipsoid plot (30% probability) of **9** (E = O), **10** (E = S), and **11** (E = Se). Only α-carbon atoms of isopropyl substituents are shown, and hydrogen atoms are omitted for clarity.

The new heterodichalcogenido PNP complexes **9**−**11** were also characterized by single-crystal X-ray crystallography and were found to have similar structures. A representative thermal ellipsoid plot of **10** is shown in Figure 3; selected metrical parameters are presented in Table 4.

As with **6**, the copper(I) complexes **9**−**11** each exhibit a trinuclear bonding arrangement with a central six-membered Cu_3Te_3 ring. The lighter chalcogen occupies the third coordination site at the metal centers, which all possess a trigonal planar geometry (**9**: E = O, Σ<Cu = 359.7−359.9°; **10**: E = S, Σ<Cu = 359.9−360.0°; 11: E = Se, Σ<Cu = 359.7−359.9°). The central Cu_3Te_3 rings in **9**−**11** are chairlike, indicating that the addition of an oxygen, sulfur, or selenium atom to **6** (which has a distorted twist-boat central ring) has a significant influence on the conformation of this ring system. This is reflected by the change in the average endocyclic Cu−Te−Cu angle upon going from **6** (ca. 64°) to **9**−**11** (ca. 89, 109, and 108°, respectively), suggesting there is relief of ring strain in these chalcogenated derivatives. The Cu−Te and P−Te distances are comparable to those present in **6** (vide supra), and the Cu···Cu distances of >3.4 Å suggest no significant intramolecular attractions exist between the metal centers in **9**−**11**. The three outer

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(34) Ferguson, G.; Gallagher, J. F.; Kennedy, J. D.; Kelleher, A.-M.; Spalding, T. R. *Dalton Trans.* **2006**, 2133; The tellurium atoms in this crystal structure are positionally disordered over several boron sites, and the gold(I) center is pentavalent because of multicenter bonding to the telluroborane; hence the quoted Au−Te bond distances may not be representative of a normal two-electron dative bond.

Table 4. Selected Bond lengths (Å) and Angles (deg) for $\{Cu(TeP^iPr_2NP^iPr_2E)\}_3$

	9: E = O	**10**: E = S	**11**: E = Se
Cu1−Te1	2.509(1)	2.519(1)	2.514(1)
Cu1−Te2	2.490(1)	2.526(1)	2.519(1)
Cu2−Te2	2.513(2)	2.516(1)	2.505(1)
Cu2−Te3	2.487(1)	2.534(1)	2.532(1)
Cu3−Te1	2.485(1)	2.531(1)	2.531(1)
Cu3−Te3	2.506(1)	2.516(1)	2.514(1)
Cu1−E1	1.995(6)	2.244(2)	2.352(2)
Cu2−E2	2.012(6)	2.236(1)	2.369(1)
Cu3−E3	2.004(5)	2.241(1)	2.350(1)
P1−Te1	2.470(2)	2.454(1)	2.450(2)
P3−Te2	2.475(3)	2.447(1)	2.431(2)
P5−Te3	2.477(3)	2.456(1)	2.452(2)
P2−E1	1.501(6)	2.021(2)	2.164(2)
P4−E2	1.510(6)	2.020(2)	2.162(2)
P6−E3	1.502(6)	2.026(2)	2.169(2)
Te1−Cu1−Te2	126.49(5)	112.89(4)	113.36(4)
Cu1−Te2−Cu2	87.99(4)	108.06(3)	108.13(4)
Te2−Cu2−Te3	125.92(6)	115.11(3)	116.27(4)
Cu2−Te3−Cu3	91.90(5)	111.08(4)	109.99(4)
Te3−Cu3−Te1	125.38(5)	111.36(3)	112.68(4)
Cu3−Te1−Cu1	88.10(5)	107.87(3)	107.33(4)

Table 5. ^{31}P and ^{125}Te NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for Complexes **6**−**11** in CD_2Cl_2

compound	$\delta(^{31}P)$, *P*-M	$\delta(^{31}P)$, *P*-Te	$\delta(^{31}P)$, *P*-E	$^2J_{P-P}$	$^1J_{Te-P}$	$\delta(^{125}Te)$
6	109.9	72.9		103	1085	−632.9
7	112.4	68.2		94	1077	−856.9
8 (193K)	136.2	77.0		56	1181	−532.6
9		11.8	46.8	21	1119	−631.8
10		21.1	65.3	30	1173	−628.7
11		22.7	58.5	31	1195	−650.0

CuTePNPE rings are all oriented in the same direction, giving the complexes a bowl-like motif. There are indications of weak intermolecular Te···Te contacts in the case of **9** (*d*(Te···Te) = 3.891−4.039 Å, sum of van der Waals radii = 4.12 Å) between adjacent Cu_3Te_3 rings in the unit cell, forming weakly bound dimers.

NMR Characterization of 6−11. The multinuclear (^{31}P, ^{77}Se, ^{125}Te) NMR spectra of **6**−**11** in CD_2Cl_2 provided useful insights into the structures of these compounds in solution (Table 5). The monotellurido complexes **6**−**8** all showed two distinct ^{31}P environments attributable to the $\mathbf{L^2}$ ligand. Since the crystal structures of **6** and **7** both possess six unique phosphorus sites, this indicates the copper(I) and silver(I) complexes of $\mathbf{L^2}$ are conformationally flexible in solution. The metal-bound phosphorus centers exhibit resonances from δ 109.9 to 137.3 and the tellurium-bound centers have values in the narrow range of δ 68.2−74.7. Satellites arising from coupling to ^{125}Te were observed on the latter resonances, with very similar $^1J_{Te-P}$ values of 1085 and 1077 Hz for **6** and **7**, respectively, and 1189 Hz for **8**. The difference of about 100 Hz in values may reflect the bridging (three-coordinate) nature of the tellurium centers in **6** and **7**. A doublet pattern with magnitudes in the range 62−103 Hz was observed in **6**−**8** for the tellurium-bound phosphorus sites, arising from $^2J_{P-P}$ coupling to the metal-bound ^{31}P atoms. A corresponding broad doublet for the metal-bound ^{31}P site was observed for **6**; for the complex **7** the signal was a broad doublet of doublets because of additional spin−spin coupling to the two spin-active silver isotopes (^{107}Ag: *I* = 1/2, 52%; ^{109}Ag: *I* = 1/2, 48%) with an average $^1J_{Ag-P}$ value of 444 Hz. The analogous resonance in complex **8** was very broad with no discernible coupling. The gold(I) complex **8** exhibited an additional broad ^{31}P resonance at δ 55.7 assigned to the PPh_3 ligand. The broad nature of these two resonances in the ^{31}P NMR spectrum of **8** suggested lability of the corresponding two metal-bound phosphorus centers in solution at room temperature. A ^{31}P NMR spectrum of **8** obtained at 193 K exhibited three very sharp resonances, illustrating that ligand exchange processes are slow with respect to the NMR time scale at this temperature. Each resonance displayed a doublet-of-doublets coupling pattern, indicating that the individual ^{31}P centers in **8** are spin−spin coupled to the other two. The intraligand $^2J_{P-P}$ coupling constant was determined to be 56 Hz, while a large $^2J_{P-P}$ value of 230 Hz was observed for the $Ph_3P-Au-P^iPr_2$ unit. A three-bond P−P coupling with a value of $^3J_{P-P} = 26$ Hz across the $Ph_3P-Au-Te-P^iPr_2$ fragment was also apparent.

The ^{125}Te NMR spectra of **6**−**8** exhibited single resonances split into doublets due to $^1J_{Te-P}$ coupling, with values correlating well to those observed in the ^{31}P NMR spectra. The chemical shifts spanned a wide range (δ −632.9, −856.9 and −532.6, respectively), indicating a particular sensitivity to the metal center bound to tellurium. A ^{77}Se NMR spectrum obtained for complex **11** exhibited a doublet at δ −292.7 with a $^1J_{Se-P}$ value of 557 Hz, comparable to the value of 534 Hz for the related complex $\{Cu[(SeP^iPr_2)_2N]\}_3$.[9]

The ^{31}P NMR spectra of the heterodichalcogenido PNP ligand complexes **9**−**11** exhibited a significant upfield shift in both resonances when compared to those of the parent copper(I) complex **6**. The phosphorus centers bonded to the lighter chalcogens resonated at δ 46.8, 65.3, and 58.5, while for the tellurium-bound sites the chemical shifts were δ 11.8, 21.1, and 22.8 for **9**−**11**, respectively. A diminution of the $^2J_{P-P}$ values was also noted (**9**: 21 Hz; **10**: 30 Hz; **11**: 31 Hz), suggesting a notable change in the electronic structure in the P−N−P ligand backbone upon chalcogen insertion into the Cu−P bond. Similar values for chemical shifts and $^2J_{P-P}$ coupling constants were found for the recently prepared lithium derivatives (tmeda)Li[$TeP^iPr_2NP^iPr_2E$] (E = S, Se).[19] The $^1J_{Te-P}$ values for **9**−**11** were found to be 1119, 1177, and 1195 Hz, respectively. The ^{125}Te NMR spectra exhibited doublets with similar chemical shift values (δ −631.2, −628.7, and −650.0 for **9**−**11**, respectively) that closely match that of **6** (−632.9), again suggesting a strong dependence of the ^{125}Te chemical shift on the identity of the metal center.

Variable Temperature NMR and ESI-MS Studies of 6 and 7. Certain features of the room temperature ^{31}P NMR spectrum of the silver(I) complex **7** suggested the occurrence of exchange processes in solution. For example, the resonance corresponding to the silver-bound site was quite broad (fwhm = ca. 600 Hz). Samples at higher dilutions yielded no visible change in the spectra, indicating either an intramolecular process or a rapid intermolecular exchange that is not significantly affected by changes in concentration.

Previously, low-temperature ^{31}P NMR spectra have been obtained in studies of the homodichalcogenido PNP complexes $\{M[(EP^iPr_2)_2N]\}_3$ in solution. The recently

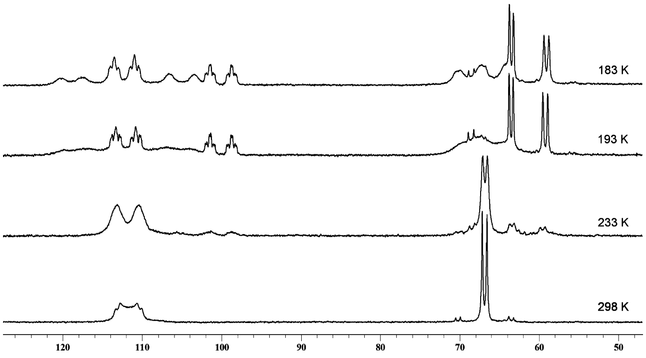

Figure 4. ^{31}P NMR spectra of **7** in d_8-THF at different temperatures.

reported ditellurido PNP complexes $\{M(TeP^iPr_2)_2N\}_n$ (M = Cu, $n = 3$; M = Ag, $n = 6$) exhibited singlet resonances in their ^{31}P NMR spectra, and no change was observed at low temperature.[8] Woollins and co-workers observed a singlet in the ^{31}P NMR spectrum of the disulfido copper(I) complex $\{Cu(SP^iPr_2)_2N\}_3$, and saw no additional signals upon cooling.[26] We recorded low-temperature ^{31}P NMR spectra of **7** to investigate its solution behavior in d_8-THF (Figure 4).

Upon cooling a sample to 233 K both resonances broadened significantly, and new phosphorus environments close to each signal emerged. At 193 K two sets of well-resolved resonances were seen, as well as several very broad signals. When the sample was cooled to 183 K, the latter began to separate into individual resonances but remained broad, indicating that even at this temperature chemical exchange was still rapid on the NMR time scale. At least four unique species could be detected in solution at this temperature, with $^1J_{Ag-P}$ coupling constants ranging from 403 to 513 Hz. No ^{125}Te satellites could be resolved. The apparent doublet-of-triplets patterns observed for the silver-bound ^{31}P resonances are likely due to the overlap of two doublet-of-doublets patterns ($^2J_{P-P}$ and $^1J_{Ag-P}$), where the difference in $^1J_{Ag-P}$ between the two spin-active isotopes of silver (^{107}Ag: $I = 1/2$, 51.82%; ^{109}Ag: $I = 1/2$, 48.18%) is similar to the value of $^2J_{P-P}$. When the sample was warmed to room temperature, the original ^{31}P NMR spectrum was reproduced.

These data indicate that several oligomers of the form $[Ag(TeP^iPr_2NP^iPr_2)]_n$ are rapidly interchanging in d_8-THF solution, possibly via dissociation of the parent trinuclear complex into various $[Ag(TeP^iPr_2NP^iPr_2)]_n$ oligomers in an equilibrium. A repetition of this experiment using a d_8-toluene solution of **7** was performed. Similar results were obtained in that four sets of resonances could be clearly seen; however, no improvement in resolution was achieved. Variable-temperature ^{31}P NMR data for a d_8-THF solution of the copper(I) complex **6** were obtained using similar conditions, and four unique oligomers were also observed in solution at low temperature; however, no coupling constants could be discerned as the signals were quite broad.

In an attempt to acquire more information concerning this equilibrium, electrospray ionization mass spectrometry (ESI-MS) was utilized to analyze THF solutions of **6** and **7**. The spectrum of the copper(I) complex **6** is dominated by three signals at *m/z* 378.25, 442.14, and 753.18 amu, the masses and isotope distributions of which corresponded to $[\mathbf{L^2}]^+$, $[\{Cu(\mathbf{L^2})\} + H]^+$, and $[\{Cu(\mathbf{L^2})\}_2 - Te + H]^+$, respectively. No signal for the trimeric species was observed. These data provide further evidence that an equilibrium between various oligomeric species and the trimer may exist in THF solution. Although no trimer was observed directly, it is possible that larger oligomers are unstable under the conditions of the ESI experiment (the monomer was observed as the protonated parent ion, but the dimer was found to lose Te upon ionization).

An ESI-MS spectrum of **7** in THF consisted of unidentified ions associated with major fragmentation, indicating the silver(I) complex appears to be much more labile under ESI conditions. However, a repetition of this experiment in a 1:1 mixture of THF and acetonitrile yielded an improved spectrum with the most intense signal at *m/z* 486.19 amu, $[\{Ag(\mathbf{L^2})\} + H]^+$. Two less intense but clearly visible signals at *m/*z 840.88 and 968.86 amu were attributable to $[\{Ag(\mathbf{L^2})\}_2 - Te + H]^+$ and $[\{Ag(\mathbf{L^2})\}_2 + H]^+$, respectively. Based on the low temperature ^{31}P NMR and ESI-MS data for complexes **6** and **7**, it is likely that there is a solution equilibrium process in which the trimer is rapidly exchanging with two or more other oligomers.

Conclusions

The first monochalcogenido PNP complexes of copper(I) (**6**), silver(I) (**7**), and gold(I) (**8**) have been synthesized. X-ray structural analysis reveals that **6** and **7** are trinuclear in the solid state, while **8** is a monomer supported by a PPh_3 ligand. Variable-temperature NMR and ESI-MS studies of the complexes **6** and **7** in THF provide evidence for the simultaneous presence of several different oligomers in solution, which may be related to the strain of the M_3Te_3 ring in these complexes. The copper(I) complex **6** reacts readily with elemental oxygen, sulfur, or red selenium via insertion into the Cu−P bond yielding the novel heterodichalcogenido PNP complexes $\{Cu(TeP^iPr_2NP^iPr_2E)\}_3$ (**9**: E = O; **10**: E = S; **11**: E = Se); complex **9** contains the first example of the elusive *O,Te* dichalcogenido PNP ligand. The new complexes **6**−**11** are potential sources of binary or ternary chalcogenides of the coinage metals via AACVD techniques. Such investigations will be the subject of future studies.

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Supporting Information Available: Crystallographic data in CIF file format. This material is available free of charge via the Internet at http://pubs.acs.org.

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