Inorg. Chem. **2002**, *41*, 1958–1965

Inorganic Chemistry
Article

Redox Chemistry of Tellurium Bis(*tert*-butylamido)cyclodiphosph(V)azane Disulfide and Diselenide Systems: A Spectroscopic and Structural Study

Glen G. Briand, Tristram Chivers,* and Gabriele Schatte

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received November 12, 2001

The redox chemistry of tellurium–chalcogenide systems is examined via reactions of tellurium(IV) tetrachloride with Li[^{t}BuN(E)P(μ-N^{t}Bu)$_2$P(E)N(H)^{t}Bu] (**3a**, E = S; **3b**, E = Se). Reaction of $TeCl_4$ with 2 equiv of **3a** in THF generates the tellurium(IV) species $TeCl_3[HcddS_2][H_2cddS_2]$ **4a** [$cddS_2$ = ^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N^{t}Bu] at short reaction times, while reduction to the tellurium(II) complex $TeCl_2[H_2cddS_2]_2$ **5a** is observed at longer reaction times. The analogous reaction of $TeCl_4$ and **3b** yields only the tellurium(II) complex $TeCl_2[H_2cddSe_2]_2$ **5b**. The use of 4 equiv of **3a** or **3b** produces $Te[HcddE_2]_2$ (**6a** (E = S) or **6b** (E = Se)). NMR and EPR studies of the 5:1 reaction of **3a** and $TeCl_4$ in THF or C_6D_6 indicate that the formation of the Te(II) complex **6a** via decomposition of a Te(IV) precursor occurs via a radical process to generate H_2cddS_2. Abstraction of hydrogen from THF solvent is proposed to account for the formation of **2a**. These results are discussed in the context of known tellurium–sulfur and tellurium–nitrogen redox systems. The X-ray crystal structures of **4a**·$[C_7H_8]_{0.5}$, **5a**, **5b**, **6a**·$[C_6H_{14}]_{0.5}$, and **6b**·$[C_6H_{14}]_{0.5}$ have been determined. The cyclodiphosph(V)azane dichalcogenide ligand chelates the tellurium center in an E,N (E = S, Se) manner in **4a**·$[C_7H_8]_{0.5}$, **6a**·$[C_6H_{14}]_{0.5}$, and **6b**·$[C_6H_{14}]_{0.5}$ with long Te–N bond distances in each case. Further, a neutral H_2cddS_2 ligand weakly coordinates the tellurium center in **4a**·$[C_7H_8]_{0.5}$ via a single chalcogen atom. A similar monodentate interaction of two neutral ligands with a $TeCl_2$ unit is observed in the case of **5a** and **5b**, giving a trans square planar arrangement at tellurium.

Introduction

Interest in the chemistry of tellurium has grown due to the observed activity of ammonium trichloro(diethylene-*O*,*O′*)tellurate (AS101) and other related organotellurium(IV) compounds as immunomodulators.[1] The thiol-dependent expression of this biological activity[2] has focused attention on the thiolate chemistry of tellurium,[3,4] with recent chemical studies of the interactions of bioactive tellurium compounds with cysteine-containing biomolecules.[5] The rich redox chemistry of tellurium−sulfur systems is likely involved, as tellurium(IV) thiolate complexes are not stable and are readily reduced to tellurium(II) thiolates.[3,4,6]

The inherent redox behavior of such systems is controlled by the nature of the sulfur-containing ligand; it results in the reduction of tellurium and oxidation of the ligand to a disulfide RS−SR. In the case of thiolate ligands, redox processes are prevalent,[3,4,6] with only a few spectroscopically characterized examples of homoleptic tellurium(IV) thiolates.[7] Several structurally characterized examples of homoleptic tellurium(II) thiolates have been reported.[3,4,6,8−10] Dithiocarbamate ligands, on the other hand, appear to have a stabilizing effect, and their use has enabled the isolation

---

* To whom correspondence should be addressed. Phone: (403) 220-5741. Fax: (403) 289-9488. E-mail: chivers@ucalgary.ca.

(1) (a) Sredni, B.; Caspi, R. R.; Klein, A.; Kalechman, Y.; Danziger, Y.; Ben Ya'akov, M.; Tamari, T.; Shalit, F.; Albeck, M. *Nature* **1987**, *330*, 173−176. (b) Shani, A.; Tichler, T.; Catane, R.; Gurwith, M.; Rozenszajn, L. A.; Gezin, A.; Levi, E.; Schlesinger, M.; Kalechman, Y.; Michlin, H.; Shalit, F.; Engelsman, E.; Farbstein, H.; Farbstein, M.; Albeck, M.; Sredni, B. *Nat. Immun. Cell Growth Regul.* **1990**, *9*, 182−190.

(2) Deuticke, B.; Lutkemeier, P.; Poser, B. *Biochim. Biophys. Acta.* **1992**, *1109*, 97−107.

(3) Fleischer, H.; Stauf, S.; Schollmeyer, D. *Inorg. Chem.* **1999**, *38*, 3725−3729.

(4) Fleischer, H.; Schollmeyer, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 3705−3706.

(5) Albeck, A.; Weitman, H.; Sredni, B.; Albeck, M. *Inorg. Chem.* **1998**, *37*, 1704−1712.

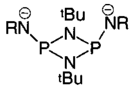
(6) (a) Mazurek, W.; Moritz, A. G.; O'Connor, M. J. *Inorg. Chim. Acta* **1986**, 143−146. (b) von Deuten, K.; Schnabel, W.; Klar, G. *Cryst. Struct. Comm.* **1980**, *9*, 161−165.

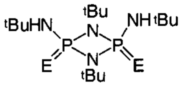
10.1021/ic011151l CCC: $22.00

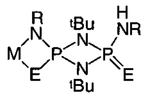
and structural characterization of several homoleptic tellurium(IV) species.[11] The degree of this stabilizing ability, however, depends on the nature of the R group in $[S(S)CNR_2]^-$.[12] Other known tellurium(II)−sulfur ligand systems involving potential secondary donor functionalities include xanthates,[13,14] thiocarboxylates,[15] thiosulfates,[14,16] organothiosulfonates,[17] diorganodithiophosphates,[18,19] diorganodithiophosphinates,[19,20] and imidodithiodiphosphinates.[21] None of these monoanionic ligands have been demonstrated to slow redox processes appreciably. Further, no examples of structurally characterized homoleptic tellurium(IV) complexes have been reported, with the exception of a dianionic monothiopyrocatecholate complex.[6b]

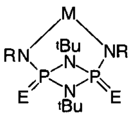
For tellurium complexes involving selenium-bound ligands, the redox behavior is expected to be more pronounced. These systems have been much less studied with only a few structurally characterized tellurium(II) complexes involving 1,1-thiolateselenolates,[9] 1,1-diselenolates,[9] thioselenophosphinates,[22] imidodiselenodiphosphinates,[21a] and selenocyanates.[23] The latter also incorporate coordinated thiourea or selenourea ligands for stability.

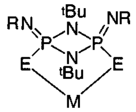
Bis(*tert*-butylamido)cyclodiphosph(III)azane dianions **1** have proven to be interesting and useful ligands for main group elements,[24] as well as transition metals.[25] More recently, the cyclodiphosph(V)azane dichalcogenides (e.g., **2a,b**) have also been found to be convenient sources of versatile mono- and dianionic ligands for s- and d-block metal centers, via reagents of the type Li[^{t}BuN(E)P(μ-N^{t}Bu)$_2$P(E)N(H)^{t}Bu] (**3a**, E = S; **3b**, E = Se).[26] These ligands provide the advantages of a multidentate system, possessing several chelation modes **I**−**III** for the stabilization and isolation of novel structural types. These ligands also contain several NMR active nuclei, notably ^{31}P, allowing for comprehensive assessment of solution chemistry. In this investigation, we have used the tellurium center to probe the redox behavior of the monoanionic ligands derived from **2a** and **2b** via NMR and EPR methods. As a prerequisite to this investigation, the X-ray crystal structures of **4a**·[C$_7$H$_8$]$_{0.5}$, **5a**, **5b**, **6a**·[C$_6$H$_{14}$]$_{0.5}$ and **6b**·[C$_6$H$_{14}$]$_{0.5}$ were determined.

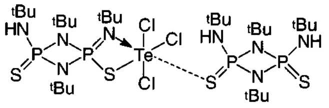

1

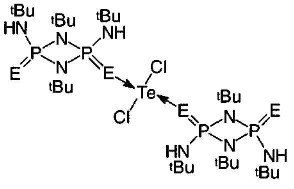

2a, E = S
2b, E = Se

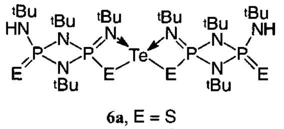

I


II


III


4a


5a, E = S
5b, E = Se


6a, E = S
6b, E = Se

Experimental Section

Reagents and General Procedures. The following solvents were dried and distilled over Na/benzophenone prior to use: tetrahydrofuran (THF), toluene, and *n*-hexane. Tellurium tetrachloride was used as received from Alfa Aesar. Lithium cyclodiphosph(V)azane dichalcogenides Li[^{t}BuN(E)P(μ-N^{t}Bu)$_2$P(E)N(H)^{t}Bu]·(THF)$_2$ [**3a**·

---

(7) (a) Nakhdjavan, B.; Klar, G. *Liebigs Ann. Chem.* **1977**, 1683−1691. (b) Ogawa, S.; Yamashita, M.; Sato, R. *Tetrahedron Lett.* **1995**, *36*, 587−590.

(8) Golic, L.; Dietzsch, W.; Kohler, K.; Stach, J.; Kirmse, R. *J. Chem. Soc., Dalton Trans.* **1988**, 97−100.

(9) Hummel, H.-U.; Fischer, T.; Wolski, A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1483−1488.

(10) Allan, R. E.; Gornitzka, H.; Karcher, J.; Paver, M. A.; Rennie, M.-A.; Russell, C. A.; Raithby, P. R.; Stalke, D.; Steiner, A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1996**, 1727−1730.

(11) (a) Kumar, V.; Aravamudan, G. *Acta Crystallogr.* **1990**, *C46*, 2100−2102. (b) Rout, G. C.; Seshasayee, Aravamudan, G.; Radha, K. *Acta Crystallogr.* **1984**, *C40*, 1142−1145. (c) Husebye, S. *Acta Chem. Scand.* **1979**, *A33*, 485−490. (d) Sejekan, B. G.; Janakiram, C.; Aravamudan, G. *J. Inorg. Nucl. Chem.* **1978**, *40*, 211−213. (e) Esperas, S.; Husebye, S. *Acta Chem. Scand.* **1975**, *A29*, 185−194. (f) Husebye, S.; Svaeren, S. E. *Acta Chem. Scand.* **1973**, *27*, 763−778. (g) Esperas, S.; Husebye, S. *Acta Chem. Scand.* **1973**, *27*, 706−707.

(12) (a) Kumar, V.; Aravamudan, G.; Seshasayee, M.; Selvam, P.; Yvon, K. *Acta Crystallogr.* **1990**, *C46*, 2081−2083. (b) Ganesh, V.; Seshasayee, M.; Chidambaram, S.; Aravamudan, G.; Goubitz, K.; Schenk, H. *Acta Crystallogr.* **1989**, *C45*, 1506−1509.

(13) (a) Foss, O. *Inorg. Synth.* **1953**, *4*, 91−93. (b) Brondmo, N. J.; Esperas, S.; Graver, H.; Husebye, S. *Acta Chem. Scand.* **1973**, *27*, 713−715.

(14) Foss, O. *Acta Chem. Scand.* **1949**, *3*, 1385−1399.

(15) Subrahmanyan, T.; Aravamudan, G.; Rout, G. C.; Seshasayee, M. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 239−248.

(16) Foss, O. *Acta Chem. Scand.* **1952**, *6*, 521−530.

(17) (a) Foss, O.; Lyssandtrae, N.; Maartmann-Moe, K.; Tysseland, M. *Acta Chem. Scand.* **1973**, *27*, 218−228. (b) Ase, K. *Acta Chem. Scand.* **1969**, *23*, 3206−3216. (c) Foss, O. *Acta Chem. Scand.* **1951**, *5*, 115−120.

(18) Refaat, L. S.; Maartmann-Moe, K.; Husebye, S. *Acta Chem. Scand.* **1984**, *A38*, 147−155.

(19) Husebye, S. *Acta Chem. Scand.* **1965**, *19*, 1045−1050.

(20) Te(I) species: Newton, M. G.; King, R. B.; Haiduc, I.; Silvestru, A. *Inorg. Chem.* **1993**, *32*, 3795−3796.

(21) (a) Birdsall, D. J.; Novosad, J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2000**, 435−439. (b) Novosad, J.; Tornroos, K. W.; Necas, M.; Slawin, A. M. Z.; Woollins, J. D.; Husebye, S. *Polyhedron* **1999**, *18*, 2861−2867. (c) Bjornevag, S.; Husebye, S.; Maartmann-Moe, K. *Acta Chem. Scand.* **1982**, *A36*, 195−202. (d) Bjornevag, S.; Husebye, S.; Maartmann-Moe, K. *Acta Crystallogr.* **1981**, *A37*, C240.

(22) Husebye, S. *Acta Chem. Scand.* **1969**, *23*, 1389−1397.

(23) (a) Ase, K.; Foss, O.; Roti, I. *Acta Chem. Scand.* **1971**, *25*, 3808−3820. (b) Foss, O.; Maartmann-Moe, K.; Maroy, K. *Acta Chem. Scand.* **1987**, *A41*, 77−86. (c) Foss, O.; Maartmann-Moe, K.; Maroy, K. *Acta Chem. Scand.* **1986**, *A40*, 685−694.

(24) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203−250 and references cited therein.

(25) Grocholl, L.; Stahl, L.; Staples, R. J. *Chem. Commun.* **1997**, 1465−1466.

Table 1. Crystallographic Data

	4a·$[C_7H_8]_{0.5}$	**5a**	**5b**	**6a**·$[C_6H_{14}]_{0.5}$	**6b**·$[C_6H_{14}]_{0.5}$
formula	$C_{35.5}H_{79}Cl_3N_4P_4S_4Te$	$C_{32}H_{76}Cl_2N_8P_4S_4Te$	$C_{32}H_{76}Cl_2N_8P_4Se_4Te$	$C_{35}H_{81}N_8P_4S_4Te$	$C_{35}H_{81}N_8P_4Se_4Te$
fw	1104.14	1023.63	1211.23	993.80	1181.40
crystal size (mm)	0.35 × 0.25 × 0.04	0.49 × 0.23 × 0.20	0.25 × 0.14 × 0.13	0.31 × 0.22 × 0.20	0.56 × 0.06 × 0.05
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	*Pnma* (no. 62)	*Pnma* (no. 62)
a (Å)	8.9730(6)	10.4577(9)	10.5642(8)	15.457(2)	15.554(2)
b (Å)	40.818(3)	18.5301(17)	18.4039(14)	26.520(4)	26.697(4)
c (Å)	15.3064(11)	13.7709(13)	14.0532(11)	14.061(2)	14.2637(19)
β (deg)	100.1394(16)	111.9974(17)	111.3418(13)	90	90
V (Å^3)	5518.6(7)	2474.3(4)	2544.9(3)	5763.5(14)	5923.0(14)
Z	4	2	2	4	4
F(000)	2300	1068	1212	2092	2380
ρ_{calcd} (g/cm^3)	1.329	1.374	1.581	1.145	1.325
μ (cm^{-1})	9.84	10.39	37.07	8.01	30.96
T (°C)	−80	−80	−80	−80	−80
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
$R_1{}^a$	0.0493	0.0351	0.0424	0.0492	0.0555
w$R_2{}^b$	0.1005	0.0922	0.1102	0.1594	0.1804

[a] $R_1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ for $[F_o{}^2 > 2\sigma(F_o{}^2)]$, $[I > 2\sigma(I)]$. [b] w$R_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$, (all data).

$(THF)_2$, E = S; **3b**·$(THF)_2$, E = Se][26b] were prepared by literature procedures. All manipulations were performed under an argon atmosphere using standard Schlenk techniques.

Instrumentation. Reaction mixtures were monitored by ^{31}P NMR on a Varian XL 200 spectrometer. EPR spectra were recorded on a Bruker EMX-10/12 EPR spectrometer. Infrared spectra were recorded as Nujol mulls on a Nicolet Nexus 470 FT-IR spectrometer in the range 4000−400 cm^{-1}. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Preparation of $TeCl_3[{}^tBuN(S)P(\mu\text{-}N{}^tBu)_2P(S)N(H){}^tBu][{}^tBu(H)N(S)P(\mu\text{-}N{}^tBu)_2P(S)N(H){}^tBu][C_7H_8]_{0.5}$, 4a·$[C_7H_8]_{0.5}$. A solution of **3a**·$(THF)_2$ (0.500 g, 0.891 mmol) in THF (5 mL) was added dropwise to a slurry of $TeCl_4$ (0.240 g, 0.445 mmol) in THF (3 mL) at −90 °C to give an immediate yellow solution and a yellow precipitate. The mixture was allowed to warm to 23 °C, and after 3 h, the slightly cloudy yellow-orange solution was evacuated to dryness. Toluene (7 mL) was added, and the mixture was centrifuged; the supernatant was decanted to remove insoluble material. The solution was layered with *n*-hexane (2 mL) and stored at −15 °C for 2 days to yield yellow needlelike crystals (0.094 g, 0.085 mmol, 19%). Anal. Calcd for $C_{35.5}H_{79}Cl_3N_8P_4S_4Te$: C, 38.62; H, 7.21; N, 10.15. Found: C, 39.20; H, 7.50; N, 10.24.

Preparation of $TeCl_2[{}^tBu(H)N(S)P(\mu\text{-}N{}^tBu)_2P(S)N(H){}^tBu]_2$, 5a. A solution of **3a**·$(THF)_2$ (0.500 g, 0.891 mmol) in THF (10 mL) was added dropwise to a slurry of $TeCl_4$ (0.240 g, 0.445 mmol) in THF (5 mL) at −90 °C to give a yellow solution and a yellow precipitate. The solution was allowed to warm to 23 °C, and after 21 h, the solvent was removed from the cloudy deep orange solution under vacuum. Toluene (4 mL) was added, and the mixture was centrifuged. The supernatant was decanted and reduced in volume to 3 mL. After 3 days at 23 °C, orange prismlike crystals (0.053 g, 0.052 mmol, 12%) were obtained. Anal. Calcd for $C_{32}H_{76}Cl_2N_8P_4S_4Te$: C, 37.54; H, 7.48; N, 10.95. Found: C, 37.58; H, 7.36; N, 10.70.

Preparation of $TeCl_2[{}^tBu(H)N(Se)P(\mu\text{-}N{}^tBu)_2P(Se)N(H){}^tBu]_2$, 5b. A solution of **3b**·$(THF)_2$ (0.250 g, 0.381 mmol) in THF (3 mL) was added dropwise to a slurry of $TeCl_4$ (0.052 g, 0.191 mmol) in THF (2 mL) at −90 °C to give a yellow-brown solution and white precipitate. The solution was allowed to warm to 23 °C, and after 3.5 h, the solvent was removed under vacuum. Toluene (4 mL) was added, and the mixture was centrifuged. The supernatant solution was decanted and reduced in volume to 2 mL. After 7 days at 23 °C, orange prismlike crystals (0.074 g, 0.061 mmol, 32%) were obtained. Anal. Calcd for $C_{32}H_{76}Cl_2N_8P_4Se_4Te$: C, 31.73; H, 6.32; N, 9.25. Found: C, 32.73; H, 6.55; N, 8.55.

Preparation of $Te[{}^tBu(H)N(S)P(\mu\text{-}N{}^tBu)_2P(S)N{}^tBu]_2[C_6H_{14}]_{0.5}$, 6a·$[C_6H_{14}]_{0.5}$. A solution of **3a**·$(THF)_2$ (0.250 g, 0.445 mmol) in THF (3 mL) was added dropwise to a slurry of $TeCl_4$ (0.030 g, 0.111 mmol) in THF (2 mL) at 23 °C to give a yellow solution that turns deep pink over time. After 1 h, the solution was evacuated to dryness. *n*-Hexane (3 mL) was added, and the mixture was centrifuged. The deep pink supernatant was stored at 23 °C for 1 day to yield red-blue crystals of **6a**·$[C_6H_{14}]_{0.5}$ (0.030 g, 0.030 mmol, 27%) and colorless crystals of **2a**. Anal. Calcd for $C_{35}H_{81}N_8P_4S_4Te$: C, 42.30; H, 8.21; N, 11.28. Found: C, 42.86; H, 8.18; N, 10.81.

Preparation of $Te[{}^tBu(H)N(Se)P(\mu\text{-}N{}^tBu)_2P(Se)N{}^tBu]_2[C_6H_{14}]_{0.5}$, 6b·$[C_6H_{14}]_{0.5}$. A solution of **3b**·$(THF)_2$ (0.250 g, 0.381 mmol) in THF (3 mL) was added dropwise to a slurry of $TeCl_4$ (0.026 g, 0.098 mmol) in THF (2 mL) at 23 °C to give a yellow solution that quickly turns brown. The solution was stirred for 40 min, and the solvent was removed under vacuum. *n*-Hexane (2.5 mL) was added, and the mixture was centrifuged. The dark brown supernatant solution was concentrated to 2 mL and stored at 23 °C for 3 days to yield red-brown crystals of **6b**·$[C_6H_{14}]_{0.5}$ (0.035 g, 0.030 mmol, 30%). Anal. Calcd for $C_{35}H_{81}N_8P_4Se_4Te$: C, 35.58; H, 6.90; N, 9.49. Found: C, 34.91; H, 6.63; N, 9.80.

Solution ^{31}P NMR Studies. The progress of redox reactions was monitored in the following manner: 4−5 equiv of **3a**·$(THF)_2$ or **3b**·$(THF)_2$ was added to a suspension of $TeCl_4$ (0.098 mmol) in THF or benzene-d_6 (5 mL) at −90 °C. Spectra were recorded at 23 °C within 5−10 min and at regular intervals for 90 min, and again at 5 and 24 h. The relative distribution of products given in Table 4 was calculated by dividing the sum of the integrated resonances for the specified product by the sum of the integrated resonances for all products.

Theoretical/EPR Studies. Molecular orbital calculations were performed using the HyperChem 6.0 Professional Release (HyperCube, Inc.) software package. Geometry optimizations and vibrational analyses were performed at the PM3 (semiempirical, unrestricted Hartree−Fock) level of theory. Initial parameters for

---

(26) (a) Briand, G. G.; Chivers, T.; Krahn, M. *Coord. Chem. Rev.* **2001**, accepted for publication. (b) Chivers, T.; Krahn, M.; Parvez, M. *Chem. Commun.* **2000**, 463−464. (c) Chivers, T.; Krahn, M.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 2547−2553. (d) Chivers, T.; Fedorchuk, C.; Krahn, M.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 1936−1942. (e) Lief, G. R.; Carrow, C. J.; Stahl, L.; Staples, R. J. *Organometallics* **2001**, *20*, 1629−1635. (f) Moser, D. F.; Carrow, C. J.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1246−1252.

Table 2. Selected Bond Distances (Å)

	$\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$	**5a**	**5b**	$\mathbf{6a}\cdot[\mathrm{C_6H_{14}}]_{0.5}$	$\mathbf{6b}\cdot[\mathrm{C_6H_{14}}]_{0.5}$
Te−Cl(1)	2.496(2)	2.5765(9)	2.590(1)		
Te−Cl(2)	2.531(2)				
Te−Cl(3)	2.472(2)				
Te−E(1)	2.426(2)	2.7280(7)	2.8310(5)	2.534(1)	2.628(1)
Te−N(3)	2.300(4)			2.535(4)	2.616(8)
Te−S(3)	3.149(2)				
P(1)−E(1)	2.070(2)	2.003(1)	2.161(1)	2.034(2)	2.190(2)
P(2)−E(2)	1.923(3)	1.924(1)	2.085(1)	1.932(2)	2.088(2)
P(3)−S(3)	1.956(3)				
P(4)−S(4)	1.927(3)				
P(1)−N(3)	1.571(5)	1.610(2)	1.617(4)	1.556(4)	1.546(6)
P(2)−N(4)	1.627(5)	1.623(2)	1.632(4)	1.630(4)	1.625(7)
P(3)−N(7)	1.628(5)				
P(4)−N(8)	1.635(5)				

Table 3. Selected Bond Angles (deg)

	$\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$	**5a**	**5b**	$\mathbf{6a}\cdot[\mathrm{C_6H_{14}}]_{0.5}$	$\mathbf{6b}\cdot[\mathrm{C_6H_{14}}]_{0.5}$
Cl(1)−Te−Cl(2)	174.48(7)				
E(1)−Te−N(3)	71.6(1)			67.81(9)	68.4(2)
S(1)−Te−Cl(3)	86.22(6)				
E(1)−Te−Cl(1)	91.33(7)	90.67(3)	91.31(3)		
Te−E(1)−P(1)	86.21(8)	110.64(4)	107.07(3)	88.52(5)	86.34(6)
E(1)−Te−E*(1)				82.25(6)	83.07(4)
N(3)−Te−N*(3)				142.1(2)	140.2(3)

Table 4. ^{31}P NMR Data for $\mathrm{TeCl_4} + 5\mathrm{Li(HcddS_2)}$ Reaction in THF (benzene-d_6)$^{a-c}$

t (min)	$\mathrm{Li(HcddS_2)}^{d}$	$\mathrm{Te^{IV}(HcddS_2)_4}^{e}$	$\mathrm{H_2cddS_2}^{f}$	$\mathrm{Te^{II}(HcddS_2)_2}^{g}$	$\mathrm{(HcddS_2)_2}^{h}$
0	100				
10	40	23	19	18	
15	26	4	32	38	
20	22	0	36	42	
30	20	0	37	43	
50	20	0	37	43	
60	22 (13)	0 (6)	39 (22)	39 (38)	(22)
5 h	20	0	42	38	
24 h	19	0	46	35	

^{a} $\mathrm{cddS_2}$ = [^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)N^{t}Bu]. ^{b} Numbers refer to relative amounts (%) of ligand as the reactant and products as determined by integration of ^{31}P NMR resonances. ^{c} Numbers in parentheses refer to benzene-d_6 as the solvent. ^{d} δ ^{31}P (THF): −37.0/16.4 ppm, $^2J(^{31}\mathrm{P}-^{31}\mathrm{P})$ = 19 Hz. ^{e} δ ^{31}P (THF): −34.3/−12.4 ppm, $^2J(^{31}\mathrm{P}-^{31}\mathrm{P})$ = 35 Hz. ^{f} δ ^{31}P (THF): −39 ppm. ^{g} δ ^{31}P (THF): −35.1/−9*, $^2J(^{31}\mathrm{P}-^{31}\mathrm{P})$ = 29 Hz, where an asterisk denotes unresolved coupling. ^{h} δ ^{31}P ($\mathrm{C_6D_6}$): − 35.2/−45*, $^2J(^{31}\mathrm{P}-^{31}\mathrm{P})$ = 25 Hz, where an asterisk denotes unresolved coupling.

the model complex were derived from crystal structure data of [^{t}Bu(H)N(S)P(μ-N^{t}Bu)$_2$P(S)N(H)^{t}Bu].[27] Methyl groups were substituted for *tert*-butyl groups to minimize computing time. Radical intermediates were monitored in the following manner: THF was added to a mixture of **3a** and $\mathrm{TeCl_4}$ (4:1) at −90 °C to give a yellow solution. A spectrum was recorded at 23 °C after 15 min of reaction time.

X-ray Structural Analyses. Crystals of $\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$, **5a**, **5b**, $\mathbf{6a}\cdot[\mathrm{C_6H_{14}}]_{0.5}$, and $\mathbf{6b}\cdot[\mathrm{C_6H_{14}}]_{0.5}$ were coated with oil (Paratone N, Hampton Research) and mounted on a glass fiber. Measurements were made on Bruker AXS P4/RA/SMART 1000 ($\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$) and Bruker AXS Platform/SMART 1000 CCD diffractometers using monochromated Mo Kα radiation (λ = 0.71073 Å) at −80 °C. Crystallographic data are summarized in Table 1.

Data were measured using ω (and ϕ for $\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$) scans. A decay of less than 0.1% was observed in all cases; thus, no decay corrections were employed. Cell parameters were retrieved using SMART[28] software and refined with SAINT[29] software. Space group determinations were based on a statistical analysis of intensity distribution and the successful solution and refinement of the structure.

Data reduction was performed with the Bruker-AXS SHELXTL XPREP software,[30] which corrects for Lorentz and polarization effects. Empirical absorption corrections based on the appropriate transmission factor range were applied (SADABS[31]).

The structures were solved using direct methods (the heavy atom method for $\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$) and refined by the full-matrix least-squares method on F^2 with SHELXL97-2.[32] The non-hydrogen atoms (except the carbon atoms of the toluene molecule in $\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$) were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C−H and N−H bond distances of 0.95 Å) 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 atom. Neutral atom scattering factors for non-hydrogen atoms and anomalous dispersion coefficients are contained in the SHELXTL-NT 5.1[30] program library.

$\mathbf{4}\cdot[\mathrm{C_7H_8}]_{0.5}$. The toluene solvent molecule was disordered around the inversion center. Only one of the two possible orientations was refined. Due to the high degree of disorder, the carbon atoms could only be refined isotropically. The C−C bond distances in the aromatic ring were constrained to 1.36(1) Å and the C−$\mathrm{CH_3}$ bond distance was set to 1.45(1) Å. In addition, the carbon atoms of the toluene molecule were restrained to be coplanar.

5a and 5b. The methyl carbon atoms in one of the ^{t}Bu groups showed a high degree of disorder (C21, C22, C23). Therefore, the

---

(27) Hill, T. G.; Haltiwanger, R. C.; Thompson, M. L.; Katz, S. A.; Norman, A. D. *Inorg. Chem.* **1994**, *33*, 1770−1777.

(28) *SMART V 5.0, Software for the CCD Detector System*; Bruker AXS, Inc.: Madison, WI, 1998.

(29) *SAINT V 5.0, Software for the CCD Detector System*; Bruker AXS, Inc.: Madison, WI, 1998.

(30) *SHELXTL-NT 5.1, XPREP, Program Library for Structure Solution and Molecular Graphics*; Bruker AXS, Inc.: Madison, WI, 1998.

(31) *SADABS, V 2.01 (WindowsNT, Service Pack 6), Software for Area-Detector Absorption and other Corrections*; Bruker AXS, Inc.: Madison, WI, 2000. This version was obtained from Prof. G. M. Sheldrick (Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammanstr. 4, 37077 Göttingen, Germany; March 20, 2000).

(32) Sheldrick, G. M. *SHELXL97-2, Program for the Solution of Crystal Structures;* University of Göttingen: Göttingen, Germany, 1997.

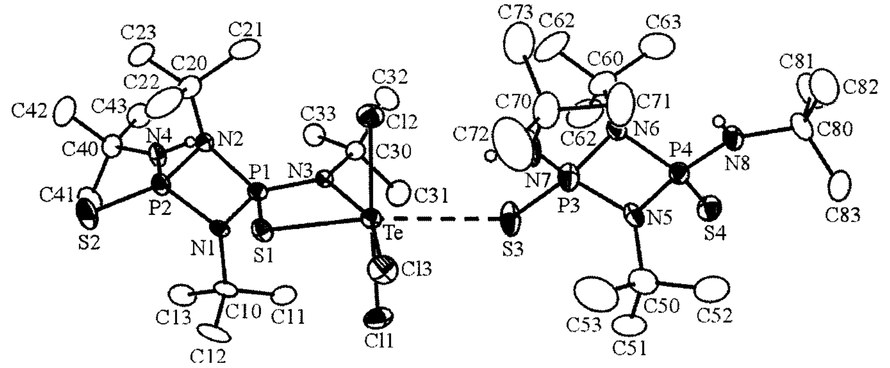


Figure 1. ORTEP diagram of **4a** (30% probability ellipsoids).

C−C bond distances in this ^{t}Bu group were constrained during the refinement in the following manner: 1.540(9) Å for C20−C21, C20−C22, C20−C23, C20′−C21′, C20′−C22′, and C20′−C23′ and 2.480(9) Å for C21−C22, C21−C23, C22−C23, C21′−C22′, C21′−C23′, and C22′−C23′. Partial occupancy factors were allowed for these atoms in the refinement of the structure.

6a·[C_6H_{14}]$_{0.5}$ and 6b·[C_6H_{14}]$_{0.5}$. The solvent molecule, sitting on a mirror plane, showed a high degree of disorder, and as a result the carbon atoms could only be refined isotropically. The C−C bond distances were constrained during the refinement in the following manner: 1.54(1) Å for C1S−C2S, C2S−C3S, C3S−C4S, C4S−C5S, and C5S−C6S and 2.52(1) Å for C1S...C3S, C2S...C4S, C3S...C5S, and C4S...C6S. The partial occupancy factors were set to 0.25 during the refinement of the structure.

Results and Discussion

Syntheses. The reaction of $TeCl_4$ with 2 equiv of lithium bis(*tert*-butylamido)cyclodiphosph(V)azane disulfide **3a** at short reaction times (∼3 h) gives the tellurium(IV) trichloride species **4a** in moderate yield (19%). This complex incorporates both a monoanionic and a neutral cyclodiphosph(V)-azane disulfide ligand **2a** (vide infra). A 1:1 reaction stoichiometry gave an insoluble product that was not further characterized. Presumably, the coordinated neutral ligand in **4a** enhances the solubility of $TeCl_3[^tBuN(S)P(\mu\text{-}N^tBu)_2P(S)N(H)^tBu]$. Attempts to prepare a selenium analogue of **4a** using 1:1 or 1:2 reaction stoichiometries were unsuccessful, and only tellurium(II) species were isolated.

An extension of the reaction time to 18 h resulted in reduction of the tellurium(IV) intermediate to tellurium(II) dichloride diadducts **5a** and **5b** and a small amount of elemental tellurium. Attempts to redissolve the isolated products in organic solvents resulted in further reduction to tellurium metal and formation of protonated ligand **2a** or **2b** (by ^{31}P NMR), which occurs more slowly at low temperatures. The instability of these complexes is not surprising as the $TeCl_2$ molecule is itself unstable and disproportionates to Te^0 and $TeCl_4$.[33] However, tellurium(II) chloride has been successfully stabilized in complexes of the type $Cl_2Te^{II}L_n$ ($n = 1, 2$), where L is a thiourea or selenourea donor ligand.[34]

Reaction of $TeCl_4$ with 4 equiv of **3a** or **3b** also produces a tellurium(II) species (**6a** or **6b**, respectively) and neutral ligand **2a** or **2b**, respectively. Although relatively short reaction times (∼1 h) were used, tellurium(IV) complexes were not isolated, suggesting that these species are much less stable than tetrakis(dithiocarbamato)tellurium(IV) analogues.[11] Longer reaction times or redissolving the isolated products results in further reduction to elemental tellurium.

Despite several attempts, the thermal instability of isolated materials has precluded extensive characterization (e.g., multinuclear NMR), particularly in solution. Nevertheless, the identities of these redox products were confirmed by X-ray crystallography (vide infra). In addition, reactions were monitored via ^{31}P NMR and EPR in order to elucidate the nature of redox processes.

X-ray Structures. Crystals of suitable quality and stability for X-ray analysis were obtained for compounds **4a**, **5a**, **5b**, **6a**, and **6b**. X-ray structures of **4a**, **5a**, and **6a** are shown in Figures 1−3. Selected bond distances and angles are given in Tables 2 and 3.

Compound **4a** (Figure 1) shows a tellurium(IV) center equatorially chelated by a single bis(*tert*-butylamido)cyclodiphosph(V)azane disulfide ligand in an S,N manner (mode **I**), with a bite angle of 71.61(12)°. Chelation by the ligand is accompanied by a change in the formal bond orders, i.e., the tellurium-bound sulfur atom is now linked to phosphorus via a single bond [S(1)−P(1) 2.070(2) Å vs S(2)−P(2) 1.923(3) Å], while the corresponding P−N bond length is closer to the length of a double bond [N(1)−P(1) 1.571(5) Å vs N(4)−P(2) 1.627(5) Å]. The Te−S(1)$_{\text{equatorial}}$ bond distance of 2.426(2) Å is shorter than the Te−S$_{\text{axial}}$ bond distances typically observed in Te(IV)−S systems (ca. 2.48−2.66 Å)[35] (vide infra), while the Te−N(3) distance of 2.300(4) Å suggests a weak interaction (cf. Te(IV)−N single bond ∼2.0 Å).[36] The Te−S(1)−P(1) bond angle of 86.21(8)° also reflects the interaction of N(3) with the tellurium center. The remaining equatorial positions are occupied by a chlorine

---

[33] Rabeneau, R.; Rau, H. *Z. Anorg. Allg. Chem.* **1973**, *395*, 273−279.

[34] (a) Eide, J.; Foss, O.; Maartmann-Moe, K.; Maberg, O.; Scheie, A. *Acta Chem. Scand.* **1987**, *A41*, 67−76. (b) Foss, O.; Maartmann-Moe, K. *Acta Chem. Scand.* **1987**, *A41*, 121−129. (c) Foss, O.; Johnson, K.; Maartmann-Moe, K.; Maroy, K. *Acta Chem. Scand.* **1966**, *20*, 113−122. (d) Foss, O.; Johannessen, W. *Acta Chem. Scand.* **1961**, *15*, 1940−1941.

[35] See for example: (a) Drake, J. E.; Khasrou, L. N.; Mislankar, A. G.; Ratnani, R. *Inorg. Chem.* **1999**, *38*, 3994−4004. (b) Drake, J. E.; Drake, R. J.; Silvestru, A.; Yang, J. *Can. J. Chem.* **1999**, *77*, 356−366.

[36] See for example: (a) Chivers, T.; Gao, X.; Parvez. *J. Am. Chem. Soc.* **1995**, *117*, 2359−2360. (b) Roesky, H. W.; Münzenberg, R. B.; Noltemeyer, M. *J. Organomet. Chem.* **1991**, *418*, 339−348.

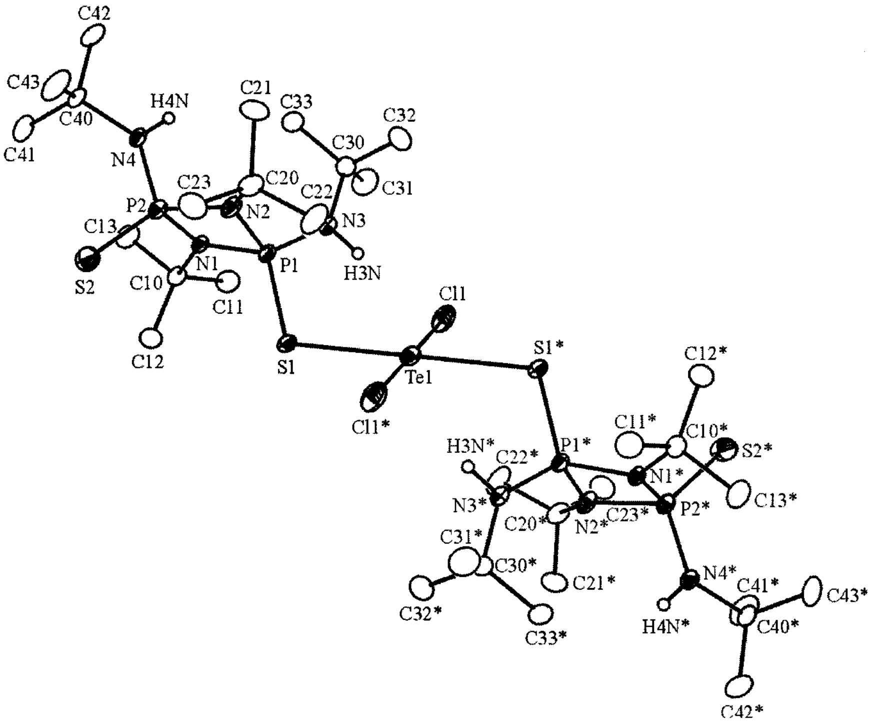


Figure 2. ORTEP diagram of **5a** (30% probability ellipsoids).

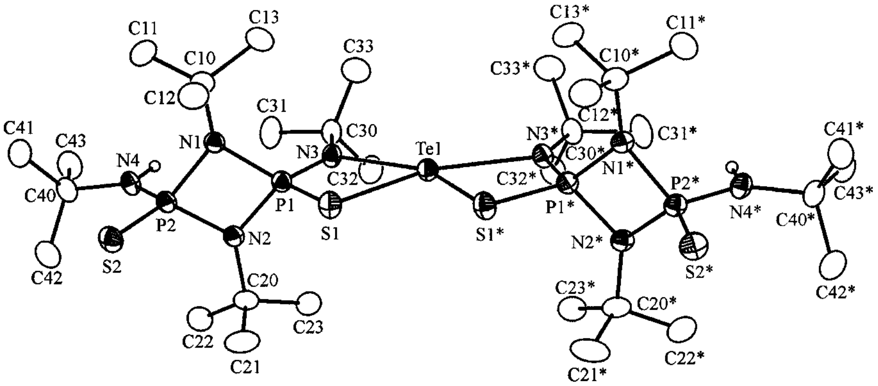


Figure 3. ORTEP diagram of **6a** (30% probability ellipsoids).

atom and the lone electron pair, while the axial sites are occupied by two chlorine atoms [∠ Cl(1)−Te−Cl(2) 174.48(7)°]. As expected, axial Te−Cl bond distances are slightly longer than those of equatorial Te−Cl bonds, and are all within expected values.[21b,37] The $TeCl_3$ complex is weakly linked to a molecule of **2a** via a sulfur atom to the open face of the coordination sphere, a common phenomenon in coordinatively unsaturated tellurium(IV) compounds.[21b,38] Despite the apparent weakness of this interaction [S(3)···Te 3.149(2) vs 2.762 Å av for $Cl_4Te(dppmS_2)$)],[38] it causes a slight lengthening of the adjacent P−S bond compared to that of uncoordinated **2a** [P(3)−S(3) 1.956(3) Å vs P−S 1.933(1) Å, respectively]. This suggests some electron density donation from the sulfur atom, which does not affect the $P-N_{exo}$ bond length [P(3)−N(5) 1.627(5) Å vs P−N 1.631 Å av for **2a**].

Compounds **5a** and **5b** are isostructural (Figure 2). They are composed of a linear $Cl-Te^{II}-Cl$ unit, imposed by a center of symmetry, and two chalcogen-bound neutral ligands, **2a** and **2b**, respectively. The result is a slightly distorted trans square planar geometry around tellurium, which may be considered pseudo-octahedral when the two axial lone pairs are considered. Square planar geometry is commonly observed for $X_2Te^{II}L_2$ adducts, with several examples of the cis arrangement[34b−c,39,40] and only three examples of the trans arrangement[40,41] reported for X = Cl systems. Adoption of the trans configuration is likely preferred in **5a** and **5b** in order to minimize steric repulsion.[40] Further, the longer Te−S bond distance in **5a** compared to that in *trans*-$TeCl_2(tmtu)_2$ [2.7280(7) vs 2.684 Å av, respectively] suggests that the ligand **2a** is a poorer donor than

---

[37] See for example: Sundberg, M. R.; Laitalainen, T.; Bergman, J.; Uggla, R.; Matikainen, J.; Kaltia, S. *Inorg. Chem.* **1998**, *37*, 2786−2791.

[38] Carmalt, C. J.; Norman, N. C.; Farrugia, L. J. *Polyhedron* **1995**, *14*, 1405−1413.

[39] Fredin, K. S.; Maroy, K.; Slogvik, S. *Acta Chem. Scand.* **1975**, *A29*, 212−216.

[40] Husebye, S.; Törnroos, K. W.; Zhu, H. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1921−1927.

[41] Foss, O.; Maartmann-Moe, K. *Acta Chem. Scand.* **1986**, *A40*, 675−684.

tmtu toward $TeCl_2$; this may account for the relative instability of **5a**. The absence of any structural information on *trans*-$TeCl_2$(selenourea)$_2$ adducts precludes a direct comparison for **5b**. However, the slightly longer Te−Cl bond distance in **5b** [2.590(1) Å] compared to that in **5a** [2.577(1) Å] suggests that **2b** is a stronger electron donor than **2a**. In view of the appreciably shorter Te−S bond distance [Te−S(1) 2.7280(7) vs 3.149(2) Å] and the larger covalent radius of Te(II) [1.39 vs 1.37 Å for Te(IV)],[42] it is clear that **2a** is much more strongly coordinated to Te in **5a** than in **4a**. Consequently, the lengthening of the adjacent P−S bond is more pronounced in **5a** [P(1)−S(1) 2.003(1) vs 1.933(1) Å], while the shortening of the adjacent P−N bond distance is now also significant [P(1)−N(1) 1.610(2) Å vs P−N 1.630(3) Å for **2a**].

Compounds **6a** and **6b** are also isostructural (Figure 3). They are comprised of a tellurium(II) center E,N-chelated by two symmetry-related cyclodiphosph(V)azane dichalcogenide ligands. The Te−E(1) bond distances [**6a** 2.534(1) and **6b** 2.628(1) Å] are within the observed distances for corresponding Te^{II}−S/Se systems,[22,23,43] while the long Te−N(3) distances [**6a** 2.535(4) and **6b** 2.616(8) Å] suggest very weak interactions.[10,44] The ligand bite angles are 67.81(9) and 68.4(2)° for **6a** and **6b**, respectively, and the chalcogen atoms occupy cis positions in the coordination sphere. The E_2N_2 unit is planar within the experimental error; the tellurium center lies only 0.011(3) and 0.001(5) Å out of the plane for **6a** and **6b**, respectively. The geometry at tellurium may therefore be considered trapezoid planar. Like **4a**, the asymmetry of the ligand generates a change in the formal bond orders in **6a**, as indicated by variations in bond lengths [P(1)−S(1) 2.034(2) Å vs P(2)−S(2) 1.932(2) Å; P(1)−N(3) 1.556(4) Å vs P(2)−N(4) 1.630(4) Å]. Further, **4a**, **6a**, and **6b** represent the first examples of an S,Se/N-chelation mode for tellurium.

Solution ^{31}P NMR Studies. To gain insight into the nature of the redox processes leading to the formation of tellurium(II) species, the reaction of 5 equiv of **3a** or **3b** with $TeCl_4$ in THF was monitored by ^{31}P NMR. After the solution was mixed for 10 min, the reaction of **3a** shows a large resonance at $\delta \sim 39$ ppm corresponding to the formation of neutral ligand H_2cddS_2 **2a** [$cddS_2 = {}^tBuN(S)P(\mu\text{-}N^tBu)_2P(S)N^tBu$] (Table 4). A pair of doublets at δ 37.0 and 16.4 ppm [$^2J(^{31}P-^{31}P) = 19$ Hz] corresponding to $LiHcddS_2$ **3a** and another pair of doublets at δ 34.3 and −12.4 ppm [$^2J(^{31}P-^{31}P) = 35$ Hz] assigned to $Te^{IV}(HcddS_2)_4$ are also evident. A fifth doublet at δ 35.1 ppm [$^2J(^{31}P-^{31}P) = 29$ Hz] appears to be paired to a broad resonance at approximately δ −9 ppm with unresolved coupling; these resonances are assigned to $Te^{II}(HcddS_2)_2$. The concentration of $LiHcddS_2$ decreases over the first approximately 20 min, as it reacts to form $Te^{IV}(HcddS_2)_4$. Concomitantly, the concentration of $Te^{IV}(HcddS_2)_4$ decreases to zero, and those of $Te^{II}(HcddS_2)_2$ and H_2cddS_2 (**2a**) increase quickly, presumably as a result of the decomposition of the Te(IV) complex. Subsequently, $Te^{II}(HcddS_2)_2$ begins to decompose slowly to give Te(0) and H_2cddS_2. The gradual increase in the concentration of H_2cddS_2 after ca. 50 min corresponds to this decomposition.

The formation of the neutral ligand H_2cddS_2 rather than the S−S coupled dimer $(HcddS_2)_2$ from the decomposition of the Te(IV) and Te(II) complexes suggests a hydrogen abstraction by the radical $[HcddS_2]^\bullet$, formed by the homolysis of Te−S bonds. A radical mechanism has been proposed for the formation of $Te(NR_2)_2$ and HNR_2 from $TeCl_4$ and $LiNR_2$, and the solvent was invoked as the source of the hydrogen atom.[10,44]

To confirm involvement of the THF solvent in the formation of H_2cddS_2, the ~5:1 reaction of disulfide **3a** with $TeCl_4$ was repeated in benzene-d_6. The $H-C_6H_5$ bond dissociation energy ($D°_{298} = 473.1$ kJ/mol) is much higher than that of *H*-tetrahydrofuran-2-yl ($D°_{298} = 385$ kJ/mol).[45] Consequently, dimerization may be preferred over hydrogen abstraction in benzene solvent. Two notable differences were observed in comparison to the THF reaction (Table 4). First, an observable concentration of $Te^{IV}(HcddS_2)_4$ is evident even after 60 min. Second, the presence of a new doublet at δ 35.2 ppm [$^2J(^{31}P-^{31}P) = 25$ Hz] together with a broad peak at approximately δ −45 ppm is observed. These resonances are tentatively assigned to the dimer $(HcddS_2)_2$, which was not observed in the THF reaction. These results are consistent with the involvement of the solvent in the redox and hydrogen abstraction processes.

The reaction of 4 equiv of the diselenide ligand **3b** with $TeCl_4$ in THF shows a large resonance at δ 24.1 ppm after 10 min, which corresponds to the formation of **2b**. In addition, a larger number of peaks were observed than in the corresponding reaction of **3a**, and unambiguous assignments were not possible. Reaction mixtures of **3a** are yellow initially and slowly fade to a reddish color, indicative of the transformation from a tellurium(IV) complex to the tellurium(II) species **6a**. In the case of **3b**, the transition to a red color occurs almost instantaneously, suggesting immediate conversion to the tellurium(II) species **6b**.

Theoretical/EPR Studies. To investigate the involvement of radical processes in the decomposition of these tellurium(IV) species and the formation of H_2cddS_2, theoretical and EPR studies were performed. Semiempirical MO calculations of the model system $[Me(H)N(S)P(\mu\text{-}NMe)_2P(S)NMe]^\bullet$ indicate a nitrogen-based SOMO (spin population at nitrogen = 0.957). The prediction of a nitrogen-based vs a sulfur-based radical appears to be valid, as it would elucidate the preference for hydrogen abstraction vs S−S coupling [e.g., formation of $(HcddS_2)_2$]. The detection of a weak signal in the EPR spectrum of a 4:1 mixture of **3a** with $TeCl_4$ in THF after 15 min confirms radical formation, while the predominance of a 1:1:1 three-line pattern ($g = 2.011$, $a_N = 11.7$)

---

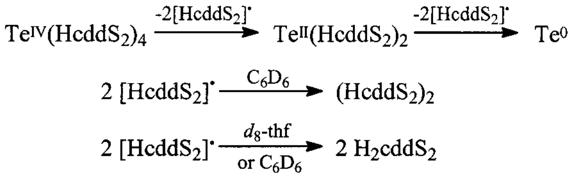
(42) Pauling, L. *The Nature of the Chemical Bond, 3rd Ed.*; Cornell University Press: Ithaka, NY, 1960.

(43) (a) Hoskins, B. F.; Oliver, P. J.; Winter, G. *Inorg. Chim. Acta* **1984**, *86*, L21−L23. (b) Al-Salim, N.; West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2363−2371. (c) Rajashree, S.; Krishna Kumar, R.; Udupa, M. R.; Seshasayee, M. *Acta Crystallogr., Sect. C* **1996**, *52*, 707−709.

(44) Björgvinsson, M.; Roesky, H. W.; Pauer, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, *29*, 5140−5143.

(45) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 82nd ed.; CRC Press LLC: Cleveland, 2001.

Scheme 1



$$\mathrm{Te^{IV}(HcddS_2)_4} \xrightarrow{-2[\mathrm{HcddS_2}]^\bullet} \mathrm{Te^{II}(HcddS_2)_2} \xrightarrow{-2[\mathrm{HcddS_2}]^\bullet} \mathrm{Te^0}$$

$$2\,[\mathrm{HcddS_2}]^\bullet \xrightarrow{C_6D_6} (\mathrm{HcddS_2})_2$$

$$2\,[\mathrm{HcddS_2}]^\bullet \xrightarrow[\text{or } C_6D_6]{d_8\text{-thf}} 2\,\mathrm{H_2cddS_2}$$

suggests a nitrogen-based radical. These observations support a hydrogen abstraction mechanism, as was proposed in the synthesis of $\mathrm{Te(NR_2)_2}$ (vide supra).[10,44]

Attempts to detect a $[\mathrm{HcddS_2}]^\bullet$ radical by monitoring the oxidation of **3a** with I_2 in THF by EPR were unsuccessful, although the protonated ligand $\mathrm{H_2cddS_2}$ **2a** was determined to be the reaction product by ^{31}P NMR. Presumably, hydrogen abstraction by the radical ligand occurs too rapidly to allow detectable concentrations to form under these conditions.

Taken together, the ^{31}P NMR and EPR data for the 5:1 reaction of **3a** with $\mathrm{TeCl_4}$ suggests that the decomposition of the Te(IV) and, subsequently, Te(II) complexes involves the radical processes represented in Scheme 1.

Conclusions

An investigation of tellurium complexes of the monoanion derived from **2a,b** has provided valuable insights into the coordination and redox behavior of this ambidentate ligand. Short reaction times and low ligand:$\mathrm{TeCl_4}$ stoichiometries enable the isolation of a tellurium(IV) species, while long reaction times result in redox processes and the isolation of tellurium(II) complexes. A novel E-monodentate bonding mode has been demonstrated for **2a,b**, and the first examples of S/Se,N-chelation of a tellurium center have been characterized, demonstrating the potential of bis(*tert*-butylamido)cyclodiphosph(V)azanes for accessing novel bonding situations. ^{31}P NMR and EPR studies indicate that the redox processes involve sequential elimination of ligand radicals followed by hydrogen abstraction from the solvent. These observations provide important background information for forthcoming studies of the interaction of **3a** and **3b** with transition metals centers that are susceptible to reduction.

Acknowledgment. We thank the following for helpful contributions: Mark Krahn for assistance in the preparation of **2a** and **2b**; Bob MacDonald (University of Alberta) for acquiring X-ray crystallographic data; Dorothy Fox, Qiao Wu, and Dr. Raghav Yamdagni for assistance in collecting NMR data; Dr. René Boeré (University of Lethbridge) for discussions of the EPR data; and the Natural Sciences and Engineering Research Council of Canada and the University of Calgary for funding.

Supporting Information Available: FT-IR data, an EPR spectrum, and X-ray crystallographic files in CIF format for **4a·**$[\mathrm{C_7H_8}]_{0.5}$, **5a**, **5b**, **6a·**$[\mathrm{C_6H_{14}}]_{0.5}$, and **6b·**$[\mathrm{C_6H_{14}}]_{0.5}$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011151L