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Intramolecularly Coordinated Low-Valent Organotellurium Complexes Derived from 1-(Dimethylamino)naphthalene

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A series of low-valent intramolecularly coordinated organotellurium compounds incorporating the 8-(dimethylamino)-1-naphthyl group has been synthesized by the organolithium route. Insertion of elemental tellurium into the Li−C bond of RLi (**2**) affords the tellurolate RTeLi (**3**) (R = 8-(dimethylamino)-1-naphthyl). Oxidative workup of **3** gives dark red ditelluride **4** in moderate yield. Reaction of **2** with "PhTeBr" afforded telluride **5**. Interestingly, the reaction of **2** with TeI_2 afforded the stable tellurenyl iodide **6** instead of the expected telluride R_2Te. Controlled bromination of ditelluride with bromine in chloroform gave stable tellurenyl bromide **7** whereas bromination with excess bromine leads to the isolation of tellurium(IV) tribromide **8**. Ditelluride **4** was found to be inert to the reactions with diazomethane and reducing agents like $NaBH_4$, NaH, and $LiAlH_4$. The compounds were characterized by elemental analysis, NMR (^1H, ^{13}C, ^{125}Te), and mass spectroscopic techniques. For three of these compounds R_2Te_2 (**4**), RTePh (**5**), and RTeBr (**7**) the molecular structures in the solid state have been determined by X-ray diffraction studies. All the three complexes which have been structurally characterized have a T-shaped geometry around the central tellurium atom. Though there are weak Te···N interactions in the solid state, in solution pyramidal inversion at the N-center is not blocked and as a result, the NMe_2 signals are observed as sharp singlets in the ^1H NMR spectra.

Introduction

Molecules having an intramolecular Te···N interaction have attracted considerable current attention.[1,2] These molecules are remarkably versatile as they afford (a) stable tellurenyl halides,[1b] (b) monomeric volatile tellurolates,[3] and (c) hybrid multidentate ligands containing "hard" nitrogen or oxygen in addition to the "soft" tellurium.[4] Whereas several examples of hybrid ligands incorporating sp^2 nitrogen atoms, e.g. azobenzene,[5] azomethines,[6] and pyridines,[7] are known, very few examples, however, of organotellurium ligands containing sp^3 nitrogen are known.[8]

Recently we reported synthesis of stable tellurenyl halides,[9] hybrid ligands,[10] and volatile selenolates[11] derived from *N*,*N*-dimethylbenzylamine. We report here the preparation, structural characterization, and some observations on reactivity of organotellurium compounds derived from another sp^3 nitrogen-containing substrate, *N*,*N*-dimethylnaphthylamine. This ligand was originally introduced by Van Koten and co-workers in investigations of stereochemistry and fluxionality of organotin and other metal complexes.[12] [8-(Dimethylamino)-1-naphthyl]trimethyltin had an exceptional reactivity in the redistribution reaction with trimethyltin chloride or bromide. Later on this has been extensively used by Corriu and co-workers to synthesize organosilyl compounds,[13] where intramolecular coordination generally results in chelated pentacoordinate

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(1) (a) McWhinnie, W. R. *Phosphorus, Sulphur Silicon* **1992**, *67*, 107. (b) Sudha, N.; Singh, H. B. *Coord. Chem. Rev.* **1994**, *135/136*, 469.

(2) *The Chemistry of Organic Selenium and Tellurium compounds*, Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986, 1987; Vols. 1 and 2.

(3) Bonasia, P. J.; Arnold, J. *J. Organomet. Chem.* **1993**, *449*, 147.

(4) (a) Hope, E. G.; Levason, W. *Coord. Chem. Rev.* **1993**, *122*, 109. (b) Singh, A. K.; Srivastava, V. *J. Coord. Chem.* **1992**, *27*, 237.

(5) Cobbledick, R. E.; Einstein, F. W. B.; McWhinnie, W. R.; Musa, F. H. *J. Chem. Res. (S)* **1979**, *145*; *J. Chem. Res. (M)* **1979**, 1901.

(6) Al-Salim, N.; Hamor, T. A.; McWhinnie, W. R. *J. Chem. Soc., Chem. Commun.* **1986**, 453. (b) Abid, K. Y.; Al Salim, N.; Greaves, M. R.; McWhinnie, W. R.; West, A. A.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1697. (c) Sadekov, I. D.; Maksimenko, A. A.; Maslakov, A. G.; Mehrotra, G. K.; Borodkin, G. S.; Kompan, O. E.; Struchkov, Yu. T.; Fedetov, M. A.; Minkin, V. I. *Metallorg. Khim.* **1989**, *2*, 298. (d) Minkin, V. I.; Sadekov, I. D.; Maksimenko, A. A.; Kompan, O. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1991**, *402*, 331.

(7) Hamor, T. A.; Al-Salim, N.; West, A. A.; McWhinnie, W. R. *J. Organomet. Chem.* **1986**, *310*, C5. (b) Al-Salim, N.; West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2363.

(8) (a) Singh, A. K.; Srivastava, V.; Khandelwal, B. L. *Polyhedron* **1990**, *9*, 495. (b) Kemmitt, T.; Levason, W. *Organometallics* **1989**, *8*, 1303. (c) King, R. B.; Sangokoya, S. A.; Holt, E. M. *Inorg. Chem.* **1987**, *26*, 4307.

(9) Singh, H. B.; Sudha, N.; West, A. A.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1990**, 907.

(10) Kaur, R.; Singh, H. B.; Butcher, R. J. *Organometallics* **1995**, *14*, 4755.

(11) Kaur, R.; Singh, H. B.; Patel, R. P.; Kulshreshta, S. K. *J. Chem. Soc., Dalton Trans.*, in press.

(12) (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) Jastrzebski, J. T. B. H.; van Koten, G.; Goubitz, K.; Arlen, C.; Pfeffer, M. *J. Organomet. Chem.* **1983**, *246*, C75. (c) Jastrzebski, J. T. B. H.; Boersma, J.; Esch, P. M.; van Koten, G. *Organometallics* **1991**, *10*, 930. (d) Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287.

(13) (a) Corriu, R. J. P.; Mazhar, M.; Poirer, M.; Royo, G. *J. Organomet. Chem.* **1986**, *306*, C5. (b) Breliere, C.; Corriu, R. J. P.; Royo, G.; Zwecker, J. *Organometallics* **1989**, *8*, 1834. (c) Carre, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C.; Belin, C. *J. Organomet. Chem.* **1994**, *470*, 43.

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species which are models for the intermediates involved in nucleophilic displacement at silicon. They have also investigated phosphorus derivatives of the ligand. This ligand was expected to facilitate better intramolecular Te···N coordination due to the rigid and planar geometry of the ligand. Here we also compare the reactivity of the new class of compounds with those derived from the more flexible 2-((dimethylamino)methyl)phenyl ligand.[10]

Experimental Section

General Procedures. Air-sensitive reactions were carried out under inert atmosphere. Solvents were purified and dried by standard techniques. All chemicals used, e.g. *N*,*N*-dimethylnaphthylamine (Fluka) and *n*-butyllithium (E Merck), were reagent grade and were used as received. Reagent grade tellurium powder was purified by washing with concentrated hydrochloric acid to remove TeO_2, followed by several washings with water to remove the acid and finally with methanol and diethyl ether, and dried before use. [8-(Dimethylamino)-1-naphthyl]lithium etherate[12b] was prepared by metalation of *N*,*N*-dimethylnaphthylamine with *n*-BuLi in ether at room temperature for 24 h. Diphenyl ditelluride[15] and TeI_2[16] were prepared as reported. The melting points were recorded in capillary tubes on a Veego melting point apparatus and are uncorrected. ^1H (299.94 MHz), ^{13}C (75.42 MHz), and ^{125}Te (94.75 MHz) NMR spectra were recorded on a Varian VXR 300S spectrometer at the indicated frequencies. Chemical shifts cited were referenced to internal TMS (^1H, ^{13}C) and external $Te(Et_2CNS_2)_2$ (^{125}Te). The assignments of carbons in the ^{13}C NMR spectra are in accordance with the figure in ref 17. Elemental analyses were performed on a Carlo Erba elemental analyzer Model 1106. Mass spectra are reported as *m*/*e* (ion percent relative intensity). In the case of an isotopic pattern, the value given is for the most intense peak.

Synthesis of Bis[8-(dimethylamino)-1-naphthyl] Ditelluride (4). To a suspension of [8-(dimethylamino)-1-naphthyl]lithium etherate (**2**) (6 mmol) was rapidly added elemental tellurium (0.8 g, 6 mmol). After 3 h, all tellurium was consumed to give a yellow solution of lithium naphthalenetellurolate **3**. To this, distilled water (10 mL) was added and complete oxidation was affected by passing oxygen for 0.5 h. The resulting organic layer and dichloromethane extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated in *vacuo*. The residue was washed with acetonitrile to separate out the reddish yellow precipitate of ditelluride **4**. Recrystallization of this from chloroform/acetonitrile (1:1) afforded **4** as yellow flakes (0.8 g, 44%, mp 200 °C (dec)). Anal. Calcd for $C_{24}H_{24}N_2Te_2$: C, 48.39; H, 4.06; N, 4.70. Found: C, 48.40; H, 4.11; N, 4.72. ^1H NMR ($CDCl_3$): δ 8.08−7.11 (m, 12H, aromatic H), 2.87 (s, 12H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 150.18 (C_8), 137.45 (C_2), 135.16 (C_{10}), 131.64 (C_9), 127.46 (C_4), 126.89 (C_3), 126.46 (C_5), 125.40 (C_6), 118.53 (C_7), 103.34 (C_1), 47.23 (NMe_2). ^{125}Te NMR ($CDCl_3$): δ −372.6. Mass spectra (EI): *m*/*e* 594 ($M^+ - 2$, 13%), 297 ($C_{10}H_6NMe_2Te$, 80%), 284 ($C_{10}H_6NMeTe$, 13.2%), 169 ($C_{10}H_6NMe_2$, 38%), 154 ($C_{10}H_6NMe$, 100%).

Synthesis of 8-(Dimethylamino)-1-naphthyl Phenyl Telluride (5). A solution of "PhTeBr"[18] was prepared by addition of bromine (0.48 g, 3 mmol) in benzene (6 mL) to a solution of Ph_2Te_2 (1.245 g, 3 mmol) in dry diethyl ether (60 mL) at −78 °C. The solution was stirred for 15 min in an ice bath. The resulting suspension of black "PhTeBr" was transferred to the suspension of [8-(dimethylamino)-1-naphthyl]lithium etherate (**2**) in dry ether. The solution was stirred for 2 h at room temperature, diluted with 150 mL of petroleum ether (60−80 °C), and extracted with aqueous NH_4Cl (500 mL). The organic phase was dried over sodium sulfate and the solvent was removed under vacuum giving a viscous liquid. On being kept overnight, 8-(dimethylamino)-1-naphthyl phenyl telluride (**5**) separated off as off-white needle-shaped crystals. An additional yield was obtained by column chromatography of the mother liquor over silica gel. The unreacted Ph_2Te_2 was removed by elution with petroleum ether (60−80 °C) followed by elution with dichloromethane/petroleum ether (10:90) to afford **5** (0.6 g, 26.3%, mp 119 °C). Anal. Calcd for $C_{18}H_{17}NTe$: C, 57.66; H, 4.57; N, 3.74. Found: C, 58.10; H, 4.62; N, 3.73. ^1H NMR ($CDCl_3$): δ 8.01−7.06 (m, 11H, aromatic H), 2.77 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 150.51 (C_8), 141.19 (C_{12}), 135.40 (C_{10}), 131.47 (C_9), 130.85 (C_2), 129.32 (C_{13}), 128.10 (C_{14}), 126.92 (C_4), 126.55 (C_3), 125.86 (C_5), 125.52 (C_6), 122.61 (C_1), 118.94 (C_7), 115.98 (C_{11}), 47.22 (NMe_2), ^{125}Te NMR ($CDCl_3$): δ −124.6. Mass spectra (EI): *m*/*e* 377 (M^+, 65%), 300 ($C_{10}H_6NMe_2Te$, 25%), 283 ($C_{10}H_6NMeTe$, 14.6%), 270 ($C_{10}H_6NTe$, 5.6%), 205 (C_6H_5Te, 13%), 170 ($C_{10}H_6NMe_2$, 80%), 161 (100%), 155 ($C_{10}H_6NMe$, 56%).

Synthesis of [8-(Dimethylamino)-1-naphthyl]tellurium Iodide (6). To a suspension of [8-(dimethylamino)-1-naphthyl]lithium etherate (**2**) (6 mmol) was added TeI_2 (1.2 g, 3 mmol), and the mixture was stirred for 2 h. Then the reaction mixture was poured into ice water and extracted with diethyl ether. The ether extract was dried over anhydrous sodium sulfate and concentrated in *vacuo*. The residue was chromatographed over SiO_2. The reddish brown solid was eluted out using dichloromethane. Reddish brown needles of **6** were obtained on evaporation of CH_2Cl_2 (0.1 g, 4.2%, mp 150 °C). Anal. Calcd for $C_{12}H_{12}NTeI$: C, 33.93; H, 2.85; N, 3.30. Found: C, 34.33; H, 3.01; N, 3.32. ^1H NMR ($CDCl_3$): δ 8.18−7.45 (m, 6H, aromatic H), 3.17 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 147.58 (C_8), 135.97 (C_2), 134.73 (C_{10}), 131.5 (C_9), 129.06 (C_4), 127.95 (C_3), 126.7 (C_5), 125.75 (C_6), 117.45 (C_7), 108.68 (C_1), 51.76 (NMe_2). ^{125}Te NMR ($CDCl_3$): δ 406. Mass spectra (EI): *m*/*e* 424 ($M^+ - 1$, 22%), 297 ($C_{10}H_6NMe_2Te$, 100%), 284 ($C_{10}H_6NMeTe$, 19.1%), 170 ($C_{10}H_6NMe_2$, 71.6%), 155 ($C_{10}H_6NMe$, 63.4%), 140 ($C_{10}H_6N$, 24%), 127 ($Te/C_{10}H_6$, 72%).

Synthesis of [8-(Dimethylamino)-1-naphthyl]tellurium(II) Bromide (7). A solution of bromine (0.058 g, 0.36 mmol) in chloroform (10 mL) was added to a stirred solution of ditelluride **4** (0.217 g, 0.36 mmol) in chloroform (50 mL) at 0 °C. After addition the solution was stirred for an additional 1 h. The excess of the solvent was evaporated under vacuum to reduce the volume to 20 mL. The product **7** precipitated on cooling as a light brown crystalline solid (0.24 g, 88.8%, mp 143 °C). Anal. Calcd for $C_{12}H_{12}NTeBr$: C, 38.15; H, 3.20; N, 3.71. Found: C, 38.21; H, 3.22; N, 3.59. ^1H NMR ($CDCl_3$): δ 8.17−7.42 (m, 6H, aromatic H), 3.23 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 147.97 (C_8), 134.88 (C_{10}), 131.88 (C_2), 131.40 (C_9), 128.92 (C_4), 128.05 (C_3), 126.16 (C_5), 125.76 (C_6), 117.69 (C_7), 114.73 (C_1), 52.64 (NMe_2). ^{125}Te NMR ($CDCl_3$): δ 678.

Synthesis of [8-(Dimethylamino)-1-naphthyl]tellurium(IV) Tribromide (8). A solution of bromine (0.24 g, 1.5 mmol) in chloroform (10 mL) was added dropwise to a stirred solution of **4** (0.3 g, 0.5 mmol) in chloroform (50 mL) at −5 °C over a period of 1 h. The mixture was stirred for 2 h. The

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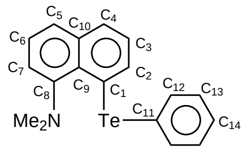
(14) Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reye, C.; Declercq, J. P.; Dubourg, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1430.

(15) Schutz, P.; Klar, G. *Z. Naturforsch. B* **1975**, 30.

(16) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 3rd ed.; Academic Press: New York, 1975−1981.

(17) Figure:



(18) Gysling, H. J.; Luss, H. R. *Organometallics* **1984**, *3*, 596.

Table 1. Crystallographic Data and Measurements for 4, 5, and 7

	compound		
	4	**5**	**7**
	Crystal Data		
empirical formula	$C_{24}H_{24}N_2Te_2$	$C_{18}H_{17}NTe$	$C_{12}H_{12}NTeBr$
color; habit	yellow plate	off-white needle	orange needle
cryst size (mm)	0.39 × 24 × 21	0.5 × 5 × 3	0.3 × 2 × 8
cryst system	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/n$	$Pna2_1$
unit cell dimens $a-c$ (Å)[a]	7.4300(10), 10.1870(10), 29.894(4)	12.495(6), 8.045(2) ($\beta = 92.59(2)°$) 15.252(2)Å	12.228(3), 9.173(1), 10.987(2)
V (Å^3)	2277.9(5)	1531.6(9)	1232.4(7)
Z	4	4	4
fw	595.65	374.93	377.74
D(calc) (Mg/m^3)	1.737	1.626	2.036
abs coeff (mm^{-1})	2.573	1.932	5.60
F(000)	1144	736	712
	Measurement of Intensity Data		
T (K)	173(2)	130(2)	296
θ range for data collcn (deg)	2.11−30	2.06−25	2−25
index range	$0 \le h \le 10, 0 \le k \le 14, 0 \le l \le 42$	$0 \le h \le 14, 0 \le k \le 9, -18 \le l \le 18$	$0 \le h \le 14, 0 \le k \le 10, 0 \le l \le 12$
tot. reflns collcd	3782	2849	1278
indepdt reflns	3782	2704	942
abs corr	semi-empirical from ψ scans	semi-empirical from ψ scans	Lorentz−polarization
max and min transm	0.575 and 0.792	0.537 and 0.570	0.96 and 1.04
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares
data/restraints/params	3781/0/260	2704/0/183	942/0/180
final R indices (%)	$R = 4.41$, w$R2 = 10.82$ [$I > 2\sigma(I)$]	$R = 2.15$, w$R2 = 6.13$ [$I > 2\sigma(I)$]	$R = 2.0$, w$R2 = 2.2$ [$I > 3\sigma(I)$]
largest diff peak and hole (e Å^{-3})	1.98, −1.26	0.302, −0.880	0.28, −0.35

[a] *a* and *b* for **5**.

precipitated tribromide was filtered out and washed with chloroform (0.4 g, 74% mp 200 °C (dec). Anal. Calcd for $C_{12}H_{12}NTeBr_3$: C, 26.81; H, 2.25; N, 2.61. Found: C, 27.04; H, 2.16; N, 2.45. ^{1}H NMR ($CDCl_3$): δ 8.93−7.3 (m, 6H, aromatic H), 3.47 (s, 6H, NMe_2). ^{125}Te NMR (DMSO): δ 585, 563 (major), 542.

X-ray Structural Determinations of 4, 5, and 7. Diffraction-quality single crystals of **4** were obtained by slow evaporation of a solution of **4** in chloroform and acetonitrile (1:1). Yellow plates were formed on standing for 3 days at room temperature. Off-white needles of **5** were obtained on standing the mother liquor overnight which were found to be of X-ray-quality. Red needles of **7** were obtained from chloroform on cooling. Suitable specimens were mounted on glass fibers, and data sets were collected on a Siemens R3m/v diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). For **7** all the measurements were made on a Rigaku AFC65 diffractometer with graphite-monochromated Mo Kα radiation. Details of crystal structure determination and refinement parameters are given in Table 1.

The structure of **4** was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement, based on 3781 observed reflections [$I > 2\sigma(I)$] and 260 variable parameters, converged with unweighted and weighted agreement factors of $R = 4.41$ and w$R2 = 10.82\%$. All calculations were performed using the Siemens SHELXTL PLUS (PC version).[19] For **5**, a total of 2704 independent intensities were measured at 130 K. The data were corrected for absorption by means of ψ scans. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELX-93.[20] The unweighted and weighted agreement factors were $R = 2.15$ and w$R2 = 6.13\%$. For **7**, the data were collected at 293 K using the ω-scan technique. A total of 1278 reflections were collected. An empirical absorption correction using the program DIFABS[21] was applied which resulted in transmission factors ranging from 0.96 to 1.04. Data were corrected for Lorentz and polarization. The structure was solved by direct methods using SHELX[22] and refined by the Texsan package.[23] All non-hydrogens were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[24] The final cycle of full-matrix least-squares refinement based on 942 observed reflection [I > $3.0\sigma(I)$] and 180 variable parameters converged with unweighted and weighted agreement factors of 2% and 2.2%. All hydrogens refined isotropically except H14, which was left at its calculated position.

Results and Discussion

Lithium naphthalenetellurolate **3** (Scheme 1) was generated by the reaction of **2** with tellurium powder. Aqueous oxidative workup of the tellurolate afforded a reddish-yellow ditelluride (**4**). The telluride **5** was synthesized by reacting “PhTeBr” with **2**. Synthon **2** was treated with TeI_2 in order to get R_2Te. The reaction did not occur as expected and gave many products (by TLC). The stable reddish brown product obtained after column chromatography over silica gel was identified as RTeI (**6**). Controlled bromination of **4** (1:1) afforded tellurium(II) bromide (**7**), and with an excess of bromine (1:3) tellurium(IV) tribromide (**8**) was obtained.

RTeLi (**3**) was treated with methyl iodide to get RTeMe. Initially there was indication for the formation of RTeMe (by TLC). However, 0.5 h of stirring followed by workup of the reaction mixture afforded a yellow powder in 70% yield which on analysis was found to be ditelluride **4**. Reduction of ditelluride **4** with $NaBH_4$, NaH, and $LiAlH_4$ was attempted to generate RTeNa (R = *N*,*N*-dimethylnaphthylamine) with the aim to prepare the RTeR^1 type of ligand. However, the reactions were unsuccessful. In all cases workup led to the isolation of the ditelluride. The reaction of ditelluride suspended

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(19) SHELXTL PLUS; X-ray instruments Group, Nicolet Instruments Corp., Madison, WI 53711, 1983.

(20) Sheldrick, G. M. SHELXL 93 Program for the refinement of Crystal Structure, University of Gottingen, Gottingen, Germany, 1993.

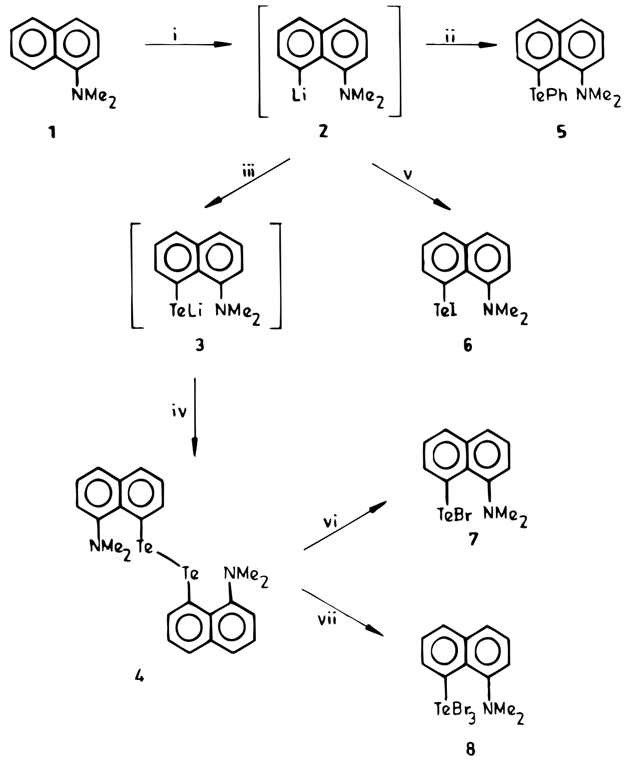
(21) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(22) Sheldrick, G. M. SHLEX 76. Program for crystal Structure Determination, University of Cambridge, England, 1976.

(23) Texray Structure Analysis Package, Molecular Structure Corp., 1985.

(24) Cromer, D. T.; Waber, T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingharm, England, 1974; Vol. IV.

Scheme 1



[a] Key: (i) n-BuLi/Et_2O; (ii) PhTeBr; (iii) Te^0, (iv) [O]; (v) TeI_2; (vi) Br_2 (1/M)/$CHCl_3$; (vii) Br_2 (excess)/$CHCl_3$.

in ether or tetrahydrofuran with diazomethane was also unsuccessful. This may be due to the poor solubility of the ditelluride. The ditelluride is soluble only in dichloromethane or chloroform and insoluble in most polar solvents. No mixed solvents were used to dissolve the ditelluride. The poor reactivity of ditelluride toward diazomethane may also be due to the enhanced stability of the ditelluride due to strong intramolecular coordination (*vide infra*).

Complexation behavior of **4** with $Pd(C_6H_5CN)_2Cl_2$ was studied. Addition of Pd(II) ion to a solution of **4** in dichloromethane resulted in immediate precipitation of a black powder presumably tellurium. Recently Tamao *et al.*[25] have reported related unusual reactivity of the Si···Si bond in trisilanes containing the 8-(dimethylamino)-1-naphthyl group toward palladium-catalyzed reaction. The intramolecular coordination of the dimethylamino group facilitates this transition metal catalyzed cleavage reaction.

These compounds were characterized by elemental analysis, mass spectroscopy, IR and NMR (^1H, ^{13}C, and ^{125}Te) studies. Mass spectra (EI at 70 eV) of **4**−**6** show molecular ion peaks, although in the case of **4** the relative intensity is low. In addition compounds show strong peaks at *m/e* 297, 170, and 155 corresponding to $C_{12}H_{12}NTe$, $C_{12}H_{12}N$, and $C_{11}H_9N$, respectively.

In solution, the Te···N interaction is so weak that the two methyl groups on nitrogen in **4**−**7** are observed as a sharp singlet in ^1H and ^{13}C NMR. This probably indicates a pyramidal inversion at the nitrogen center of the NMe_2 group in solution. The chemical shifts values of the NMe_2 resonances in **4**−**7** are not sensitive to the anticipated Te···N bond. The ^{13}C values of NMe_2 group carbons of **4** and **5** are found at 47.2 ppm, which is close to that of **1** (46.2 ppm). When a bromo (**7**) or iodo (**6**) group is substituted at the tellurium center, a downfield shift of this resonance (51.8, 52.6 ppm, respectively) is observed. The tribromide (**8**) has poor solubility in chloroform, and NMR spectra were recorded both in $CDCl_3$ and DMSO-d_6. The spectrum in $CDCl_3$ was as expected whereas the ^1H NMR spectrum in DMSO-d_6 exhibited additional signals near the NMe_2 region, suggesting the presence of more than one species in the solution which arises due to DMSO coordination.

^{125}Te chemical shifts are cited in the Experimental Section and are found to be sensitive to the nature of the substituent group bonded to the tellurium atom. The R_2Te_2 signal is at a more shielded position (−372.6 ppm) than that for R_2Te (−124.6 ppm). When electronegative groups are bonded to tellurium, the shielding at the tellurium nucleus decreases significantly. Thus chemical shifts for the halides are more positive than those of the ditelluride or telluride. The signals for bromides (**7**, **8**) are observed at deshielded positions (678, 563 ppm, respectively) compared to the iodide (**6**) (406 ppm).

It is interesting to compare the structure and reactivity of these tellurium ligands with the analogous ligands derived from the more flexible 2-((dimethylamino)methyl)phenyl substrate. Whereas $2\text{-}NMe_2CH_2C_6H_4Li$ reacted rapidly with TeI_2 to give $(2\text{-}NMe_2CH_2C_6H_4)_2Te$ in excellent yield,[10] the reaction of **2** with TeI_2 failed to give the desired product. $2\text{-}NMe_2CH_2C_6H_4TeLi$ reacts with methyl iodide to give $RTeCH_3$ in moderate yield, while **3** failed to give the expected product and afforded the ditelluride **4**. A similar behavior of reactivity was observed for the ditelluride **4** toward diazomethane.

The ^{125}Te NMR chemical shifts of tellurium compounds derived from *N*,*N*-dimethylnaphthylamine appear at a downfield position from that of analogous compounds derived from *N*,*N*-dimethylbenzylamine. For example the chemical shift of **5** appears at δ −124.6 whereas that for $2\text{-}Me_2CH_2C_6H_4TePh$ appears at δ −198. The above observations are quite similar to those observed for the related phosphorus derivatives of the 2-((dimethylamino)methyl)phenyl ligand and 8-(dimethylamino)-1-naphthyl ligand.[14] The rigidity of the naphthalene skeleton imposes a close approach of the potential donor nitrogen and acceptor tellurium as evident by the shorter Te···N distance in **5** (2.713(1) Å) compared to the Te···N distance in $(2\text{-}NMe_2CH_2C_6H_4)_2Te$ (3.048, 3.145 Å). Although room-temperature ^1H and ^{13}C NMR data indicate a weaker Te···N interaction in solution, the ^{125}Te NMR data and the observed Te···N distances in the solid state indicate a stronger Te···N interaction in these complexes compared with analogue complexes derived from *N*,*N*-dimethylbenzylamine.

Molecular Geometry and Crystal Structure of Complex 4. The molecular structure of **4** with atom numbering is shown in Figure 1. Selected bond lengths and bond angles are given in Table 2. The crystal structure involves packing of four discrete molecules in the unit cell. The Te(1)−Te(2) bond length of the ditelluride [2.765(1) Å] is slightly higher than the sum of the Pauling single[26] bond covalent radii (2.74 Å). The longer Te−Te distance is presumably due to a strong

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(25) Tamao, K.; Tarao, Y.; Nakagawa, Y.; Nagata, K.; Ito, Y. *Organometallics* **1993**, *12*, 1113.

(26) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

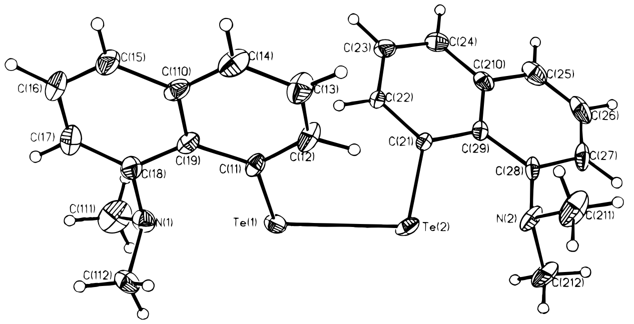

Figure 1. Molecular structure of 8-(dimethylamino)-1-naphthyl ditelluride (**4**).

Table 2. Bond Lengths (Å) and Bond Angles (deg) for 4

Te(1)−Te(2)	2.765(1)	Te(1)−C(11)	2.130(5)
Te(2)−C(21)	2.126(5)	C(19)−C(110)	1.439(8)
C(19)−C(18)	1.436(9)	C(19)−C(11)	1.419(8)
C(110)−C(14)	1.397(9)	C(110)−C(15)	1.417(10)
C(23)−C(22)	1.419(7)	C(23)−C(24)	1.382(8)
C(29)−C(21)	1.418(6)	C(29)−C(210)	1.430(7)
C(29)−C(28)	1.427(7)	C(18)−N(1)	1.435(8)
C(18)−C(17)	1.343(11)	N(1)−C(112)	1.455(7)
N(1)−C(111)	1.436(10)	C(21)−C(22)	1.384(6)
C(210)−C(24)	1.395(9)	C(210)−C(25)	1.409(8)
C(12)−C(11)	1.381(8)	C(12)−C(13)	1.417(9)
N(2)−C(28)	1.406(8)	N(2)−C(212)	1.468(8)
N(2)−C(211)	1.492(8)	C(25)−C(26)	1.360(11)
C(27)−C(28)	1.406(9)	C(27)−C(26)	1.405(10)
C(14)−C(13)	1.361(9)	C(15)−C(16)	1.367(13)
C(16)−C(17)	1.395(13)		

Te(2)−Te(1)−C(11)	100.9(1)	Te(1)−Te(2)−C(21)	99.5(1)
C(110)−C(19)−C(18)	117.9(5)	C(110)−C(19)−C(11)	118.7(5)
C(18)−C(19)−C(11)	123.4(5)	C(19)−C(110)−C(14)	120.3(5)
C(19)−C(110)−C(15)	118.0(6)	C(14)−C(110)−C(15)	121.7(6)
C(22)−C(23)−C(24)	119.0(6)	C(21)−C(29)−C(210)	118.7(4)
C(21)−C(29)−C(28)	122.7(4)	C(210)−C(29)−C(28)	118.6(4)
C(19)−C(18)−N(1)	116.4(5)	C(19)−C(18)−C(17)	119.8(6)
N(1)−C(18)−C(17)	123.7(7)	C(18)−N(1)−C(112)	111.1(5)
C(18)−N(1)−C(111)	115.8(6)	C(112)−N(1)−C(111)	110.3(6)
Te(2)−C(21)−C(29)	121.0(3)	Te(2)−C(21)−C(22)	119.2(3)
C(29)−C(21)−C(22)	119.7(4)	C(29)−C(210)−C(24)	119.7(5)
C(29)−C(210)−C(25)	119.9(5)	C(24)−C(210)−C(25)	120.4(5)
C(11)−C(12)−C(13)	122.4(6)	Te(1)−C(11)−C(19)	121.9(4)
Te(1)−C(11)−C(12)	119.0(4)	C(19)−C(11)−C(12)	118.4(5)
C(23)−C(22)−C(21)	121.2(5)	C(23)−C(24)−C(210)	121.3(5)
C(28)−N(2)−C(212)	113.3(5)	C(28)−N(2)−C(211)	111.6(6)
C(212)−N(2)−C(211)	112.0(5)	C(210)−C(25)−C(26)	120.8(6)
C(28)−C(27)−C(26)	120.8(6)	C(110)−C(14)−C(13)	120.7(6)
C(29)−C(28)−N(2)	118.0(5)	C(29)−C(28)−C(27)	119.2(5)
N(2)−C(28)−C(27)	122.8(5)	C(12)−C(13)−C(14)	119.1(6)
C(110)−C(15)−C(16)	122.4(7)	C(25)−C(26)−C(27)	120.6(6)
C(15)−C(16)−C(17)	118.0(8)	C(18)−C(17)−C(16)	123.4(8)

Te···N interaction. Recently Sandman *et al.*[27] have reported the crystal structures of two conformational polymorphs of bis(2-naphthyl) ditelluride, where Te(1)−Te(2) distances are 2.7089(7) and 2.7179(6) Å. The lower melting polymorph has a transoid conformation (C−Te−Te−C > 90°) while the higher melting polymorph has a cisoid conformation (C−Te−Te−C < 90°), and on the basis of DSC curve, the cisoid structure is found to be more stable. In the case of **4** the C(11)−Te(1)−Te(2)−C(21) torsion angle is −81.2(2)° and thus has a cisoid conformation. Other Te−Te distances from recent X-ray structure determinations of diaryl ditellurides vary from 2.665(2) to 2.746 Å.[6b,28,29] The distances Te(1)−C(11) [2.130(5) Å] and Te(2)−C(21) [2.126(5) Å] are also slightly longer than the sum of the Pauling single-bond covalent radii for a Te−C(sp^2) single bond, 2.11 Å, but are similar to the values found in bis(2-naphthyl) ditellurides [2.135(6), 2.127(5) Å]. The Te(1)−N(1) and Te(2)−N(2) distances (2.743(5) and 2.699(5) Å) are much higher than the sum of the covalent radii but are within the van der Waals distance of 3.61 Å[30] and therefore can be considered as a weak interaction. In fact the Te···N distances in this ditelluride are shorter than those recently reported for bis[2-(hydroxyiminomethyl)phenyl] ditelluride [2.822 and 2.876 Å] where nitrogen is in the sp^2 state.[6b] In bis(dimethylamino)formyl ditelluride, where N is in the sp^3 state, the Te···N distance is 3.019(12) Å.[28] Due to the Te···N interaction the geometry around each central tellurium atom is T-shaped. The Te···Te intermolecular distance is 5.666(1) Å and is greater than the sum of the van der Waals distance (4.4 Å).[30]

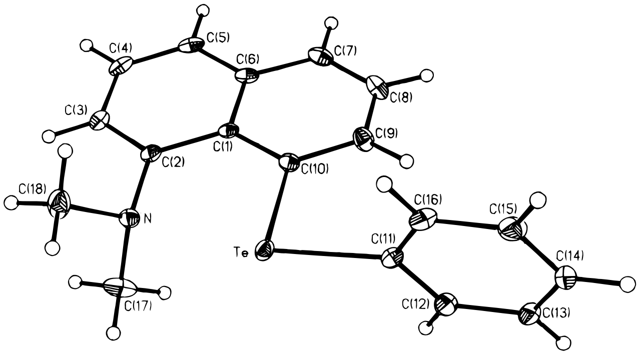

Figure 2. Molecular Structure of 8-(dimethylamino)-1-naphthyl phenyl telluride (**5**).

Molecular and Crystal Structure of Complex 5. The molecular structure of **5** is shown in Figure 2. Selected bond lengths and bond angles are given in Table 3. The crystal structure consists of discrete molecules linked by weak intermolecular Te···Te contacts. The unit cell comprises the packing of four discrete molecules. The tellurium atom is bonded to two carbon atoms with Te−C(10) = 2.138(3) Å and Te−C(11) = 2.151(3) Å. These distances are slightly longer than the sum of the Pauling single-bond covalent radii for a Te−C(sp^2) single bond (2.11 Å) but are in good agreement with related structures [i.e. 2.138(6) and 2.144(6) Å in RTe(C_6H_5OEt-p) (R = 2-(2-pyridyl)phenyl)[7b]]. The bond configuration about tellurium is V-shaped with the angle C(10)−Te−C(11) of 94.19(10)°. The Te−N distance of 2.713(1) Å is much longer than the sum of the covalent radii but is within the van der Waals distance of 3.61 Å[30] and therefore can be considered to represent a weak interaction. An almost identical bond length is shown by bis[(2-isopropyliminomethyl)phenyl] telluride [2.720(2) Å].[6d] If this Te···N interaction is considered as significant, the geometry around tellurium is T-shaped and has a stable 10−Te−3 tellurane structure.

Examination of intermolecular distances shows that the shortest distance between the Te atoms Te(1)···Te(1)^1 [Te(1)^1 is generated by the symmetry operation $1 - x, -y, 2 - z$)] is 3.909(1) Å. This distance is less than the van der Waals distance of 4.12 or 4.4 Å and could be considered as indicating a very weak interaction between the molecules.

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(27) Sandman, D. J.; Li, L.; Tripathy, S.; Stark, J. C.; Acampora, L. A.; Foxman, B. M. *Organometallics* **1994**, *13*, 348.

(28) Zingaro, R. A.; Herrera, C.; Meyers, E. A. *J. Organomet. Chem.* **1986**, *306*, C36.

(29) Kalyankumar, S.; Singh, H. B.; Das, K.; Sinha, U. C. *J. Organomet. Chem.* **1990**, *397*, 161.

(30) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Table 3. Bond Lengths (Å) and Bond Angles (deg) for 5

Te−C(10)	2.138(3)	Te−C(11)	2.151(3)
C(1)−C(2)	1.429(4)	C(1)−C(10)	1.432(4)
C(1)−C(6)	1.438(4)	C(2)−C(3)	1.373(4)
C(2)−N	1.438(3)	C(3)−C(4)	1.404(4)
C(4)−C(5)	1.362(4)	C(5)−C(6)	1.421(4)
C(6)−C(7)	1.418(4)	C(7)−C(8)	1.362(4)
C(8)−C(9)	1.408(4)	C(9)−C(10)	1.381(4)
C(11)−C(12)	1.395(4)	C(11)−C(16)	1.399(4)
C(12)−C(13)	1.390(4)	C(13)−C(14)	1.388(4)
C(14)−C(15)	1.384(4)	C(15)−C(16)	1.390(4)
C(17)−N	1.471(4)	N−C(18)	1.461(4)
C(10)−Te−C(11)	94.19(10)	C(2)−C(1)−C(10)	123.9(2)
C(2)−C(1)−C(6)	117.2(2)	C(10)−C(1)−C(6)	118.9(2)
C(3)−C(2)−C(1)	121.1(3)	C(3)−C(2)−N	121.5(3)
C(1)−C(2)−N	117.4(2)	C(2)−C(3)−C(4)	121.0(3)
C(5)−C(4)−C(3)	120.0(3)	C(4)−C(5)−C(6)	121.0(3)
C(7)−C(6)−C(5)	121.3(3)	C(7)−C(6)−C(1)	119.1(3)
C(5)−C(6)−C(1)	119.6(3)	C(8)−C(7)−C(6)	120.6(3)
C(7)−C(8)−C(9)	120.6(3)	C(10)−C(9)−C(8)	121.4(3)
C(9)−C(10)−C(1)	119.2(2)	C(9)−C(10)−Te	120.2(2)
C(1)−C(10)−Te	120.6(2)	C(12)−C(11)−C(16)	119.1(3)
C(12)−C(11)−Te	120.6(2)	C(16)−C(11)−Te	120.1(2)
C(13)−C(12)−C(11)	120.2(3)	C(14)−C(13)−C(12)	120.3(3)
C(15)−C(14)−C(13)	119.9(3)	C(14)−C(15)−C(16)	120.1(3)
C(15)−C(16)−C(11)	120.4(3)	C(2)−N−C(18)	113.7(2)
C(2)−N−C(17)	112.1(2)	C(18)−N−C(17)	111.9(2)

Table 4. Bond Lengths (Å) and Angles (deg) for 7

Te−Br	2.672(1)	C(3)−C(4)	1.36(1)
Te−N	2.395(6)	C(4)−C(10)	1.40(1)
Te−C(1)	2.109(6)	C(5)−C(6)	1.35(1)
N−C(8)	1.463(9)	C(5)−C(10)	1.41(1)
N−C(11)	1.481(1)	C(6)−C(7)	1.39(1)
N−C(12)	1.49(1)	C(7)−C(8)	1.38(1)
C(1)−C(2)	1.37(1)	C(8)−C(9)	1.40(1)
C(1)−C(9)	1.42(1)	C(9)−C(10)	1.43(1)
C(2)−C(3)	1.41(1)		
Br−Te−N	170.7(1)	C(3)−C(4)−C(10)	120.7(8)
Br−Te−C(1)	93.3(2)	C(6)−C(5)−C(10)	120.7(8)
N−Te(1)−C(1)	77.5(2)	C(5)−C(6)−C(7)	121.3(9)
Te−N−C(8)	106.4(4)	C(6)−C(7)−C(8)	119.2(8)
Te−N−C(11)	109.3(5)	N−C(8)−C(7)	121.4(7)
Te−N−C(12)	108.5(6)	N−C(8)−C(9)	116.8(6)
C(8)−N−C(11)	109.7(6)	C(7)−C(8)−C(9)	121.7(7)
C(8)−N−C(12)	114.2(7)	C(1)−C(9)−C(8)	122.2(7)
C(11)−N−C(12)	108.6(7)	C(1)−C(9)−C(10)	119.8(6)
Te−C(1)−C(2)	125.2(6)	C(8)−C(9)−C(10)	118.0(7)
Te−C(1)−C(9)	114.9(5)	C(4)−C(10)−C(5)	122.7(7)
C(2)−C(1)−C(9)	119.9(7)	C(4)−C(10)−C(9)	118.4(7)
C(1)−C(2)−C(3)	119.5(8)	C(5)−C(10)−C(9)	118.9(7)
C(2)−C(3)−C(4)	121.7(8)		

Molecular and Crystal Structure of Complex 7. Selected bond angles and bond lengths are given in the Table 4. The crystal structure of **7** involves the packing of four discrete molecule in the unit cell. An ORTEP view of this molecule is shown in the Figure 3, which reveals that the configuration at tellurium is T-shaped, a typical geometry for a 10−Te−3 tellurane.[2] The tellurium atom is joined to a carbon atom and a bromine atom, Te−C(1) = 2.109(6) Å and Te−Br = 2.672(1) Å, with a Te···N separation of 2.395(6) Å. These distances may be compared with those of 2-(bromotelluro)-*N*-(p-tolyl)benzylamine, where the Te···N distance is 2.375(13) Å,[31] and (2-((dimethylamino)methyl)phenyl)tellurium(II) iodide where the Te···N distance is 2.366(4) Å.[10] This distance is slightly longer than the typical (sp^2)N···Te distance (2.24 Å);[1a] however, it may be considered significant since it is much shorter than Te···N distances in **4** and **5**. The Te−C(1) bond length compares with the 2.111(6) Å observed for the Te−C distance in (2-(2′-pyridyl)phenyl)tellurium(II) bromide[32] and the 2.125(16) Å observed for 2-(bromotelluro)-*N*-(p-tolyl)benzylamine.[31] The Te−Br distance is characteristic of such distances and is intermediate between the 2.663(3) Å found for 2-(bromotelluro)-*N*-(p-tolyl)benzylamine[30] and the 2.71 Å for (2-(2-pyridyl)phenyl)tellurium(II) bromide.[32]

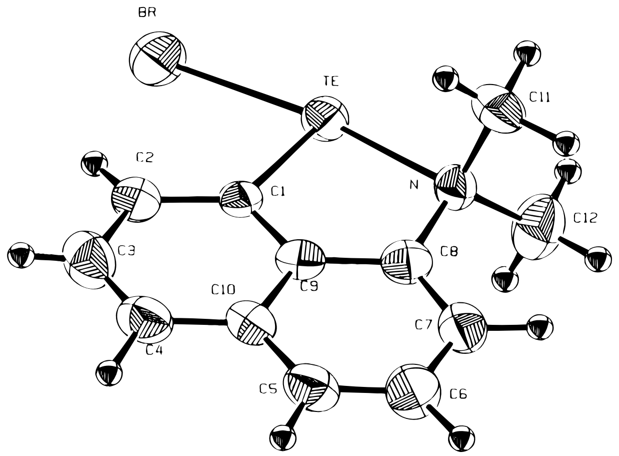

Figure 3. Molecular structure of [8-(dimethylamino)-1-naphthyl]tellurium(II) bromide (**7**).

Conclusions

A new family of intramolecularly coordinated low-valent organotellurium complexes has been prepared and characterized. In these complexes Te···N coordination was found to be stronger than the analgous complexes derived from *N*,*N*-dimethylbenzylamine. The stronger coordination results in enhanced stability of the derivatives. This observation is further corroborated by the lower reactivity of the tellurolate **3** toward methyl iodide and ditelluride **4** toward diazomethane and reducing agents.

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Supporting Information Available: Tables of complete atomic coordinates and *U* values and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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[31] Maslakov, A. G.; McWhinnie, W. R.; Perry, M. C.; Shaikh, N.; McWhinnie, S. L. W.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1993**, 619.

[32] Greaves, M. R.; Hamor, T. A.; Howlin, B. J.; Lobana, T. S.; Mbogo, S. A.; McWhinnie, W. R.; Povey, D. C. *J. Organomet. Chem.* **1991**, *420*, 327.