Inorg. Chem. **1994**, *33*, 3784–3787

Sterically Enforced Linearity in a Bridging Telluride Ligand. X-ray Structure of $\{(CH_3)_2Si[(t\text{-}C_4H_9)C_5H_3]_2Sc(PMe_3)\}_2(\mu\text{-}Te)\cdot C_6H_6$

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Received March 23, 1994®

Insertion of elemental tellurium into the scandium–carbon bond of $\{meso\text{-}(CH_3)_2Si[(t\text{-}C_4H_9)C_5H_3]_2\}Sc(CH_2SiMe_3)$ (DpScR) occurs readily at 50 °C in hexane solution to produce the scandocene tellurolate DpScTeR (**1**) in 78% isolated yield. Alternatively, when $TePBu_3$ is employed as a tellurium transfer agent, **1** is produced rapidly in high yield (100% by NMR) at room temperature. Heating tellurolate **1** leads to expulsion of TeR_2 and production of the dimeric μ-telluride DpSc–Te–ScDp (**2**), which was separately synthesized by the reaction of $[DpScH]_2$ with 0.5 equiv of $TePBu_3$ (74% yield). Telluride **2** was further characterized as the benzene solvate of its bis(trimethylphosphine) adduct $DpSc(PMe_3)\text{–}Te\text{–}Sc(PMe_3)Dp$ (**3**), the subject of an X-ray diffraction analysis (triclinic space group $P\bar{1}$, $a = 10.6755(6)$ Å, $b = 11.8654(6)$ Å, $c = 23.8264(14)$ Å, $\alpha = 92.415(4)°$, $\beta = 102.808(5)°$, $\gamma = 106.513(4)°$, $V = 2803.7(3)$ Å^3, $Z = 2$, $R = 0.029$, $R_w = 0.036$ for 7994 reflections with $I > 3\sigma(I)$). The asymmetric unit is comprised of two "half"-molecules with the Te atom in each case lying on an inversion center; the Sc–Te–Sc coordination is as a consequence precisely linear, and the mean Sc–Te bond distance is 2.875(5) Å.

Introduction

Many examples of complexes in which a bare main group element bridges two or more transition metal centers exist,[1] although the number of examples for elements within a given group tend to decrease for the heavier members of the group. For example, in group 16, many μ-oxo and sulfido derivatives are known for metals from across the transition series[2] but only a handful of low-nuclearity μ-telluride complexes have been prepared. Since complexes of this type provide basic information on the nature of metal/non-metal bonds,[3] the comparatively fewer number of μ-telluride (and to a lesser degree μ-selenide) complexes implies a weaker understanding of metal–tellurium interactions. However, recent reports in the literature have begun to address this gap. Several of these accounts deal with monomeric compounds and have provided insight into the character of terminal M–Te bonds.[4] The nature of tellurium interactions with two or more metals is potentially more complicated and is not as well understood.

In dimeric μ-telluride derivatives, $L_nM\text{–}Te\text{–}ML_n$, the degree of multiple bonding between the metal and tellurium is, not surprisingly, dependent mainly on the formal electron count of the metal fragment in question. Thus, for 17-,[5] 16-,[6] and 15-electron[7] L_nM fragments maximum M–Te bond orders of 1, 2, and 3, respectively, are anticipated. Along with a shortening of M–Te bond length, increasing bond order (*i.e.*, the amount of π character in the M–Te bond) should result in expansion of the $L_nM\text{–}Te\text{–}L_nM$ bond angle, which approaches 180° as the bond order increases. Although a strictly linear M–Te–M moiety has not yet been observed, such a functionality has been seen in M–E–M complexes of the lower chalcogens[7,8] and has always been attributed to strong π bonding between M and E (bond order = 3). In this article, we report the synthesis and characterization of a dimeric scandium telluride with a linear Sc–Te–Sc linkage which cannot be rationalized with an electronic argument; rather the steric features of the supporting ligand appear to dictate the geometry at tellurium.

Experimental Section

General Procedures. General experimental operations have been described in detail elsewhere.[9] Sc_2O_3 was purchased from Boulder Scientific Co., P.O. Box 548, Mead, CO 80542, and converted to $ScCl_3\cdot 6H_2O$ by dissolving in 6 M HCl. $ScCl_3\cdot 3THF$ was prepared by a literature procedure.[10] Elemental tellurium (100 mesh) and tri-*n*-butylphosphine (P-*n*-Bu$_3$) were purchased from Aldrich Chemical Co. and used to prepare Te=P-*n*-Bu$_3$ by a literature procedure.[11] $^{31}P\{^1H\}$ NMR spectra were recorded at 161.9 MHz on a Varian Unity 400 instrument and referenced to external H_3PO_4 at 0.0 ppm.

Preparation of $DpScTeCH_2SiMe_3$ (1). $DpScCH_2SiMe_3$[12] (1.69 g, 3.9 mmol) and elemental tellurium (0.473 g, 3.7 mmol) were suspended in hexanes (50 mL), and the suspension was stirred vigorously at 50–60 °C for 6 h, during which time slow uptake of the tellurium and a deepening of the solution's orange coloration were observed. The resulting solution was filtered, and the filtrate was concentrated to about 25 mL and cooled to –78 °C. The orange precipitate was collected by cold filtration. Yield: 1.68 g, 78% yield. ^1H NMR (C_6D_6, ppm): $(t\text{-}C_4H_9)C_5H_3$, 7.37, 6.06, 5.22 (m); $TeCH_2SiMe_3$, 2.48 (s); $(t\text{-}C_4H_9)C_5H_3$, 1.12 (s); $Si(CH_3)_2$, 0.73, 0.26 (s); $TeCH_2Si(CH_3)_3$, 0.32 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): $(t\text{-}C_4H_9)C_5H_3$, 149.7, 119.5, 118.3, 112.2, one peak obscured by C_6D_6;

® Abstract published in *Advance ACS Abstracts*, July 1, 1994.

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Table 1. Summary of Data Collection and Structure Refinement Details for Dp(PMe$_3$)Sc–Te–Sc(PMe$_3$)Dp (**3**)

empirical formula	$C_{46}H_{78}P_2Si_2Sc_2Te\cdot C_6H_6$	V, Å^3	2803.7(3)
fw	1044.9	space group	$P\bar{1}$
cryst syst	triclinic	Z	2
a, Å	10.6755(6)	F(000)	1096
b, Å	11.8654(6)	d_{calc}, g cm^{-3}	1.24
c, Å	23.8264(14)	μ, cm^{-1}	8.8
α, deg	92.415(4)	temp, °C	21
β, deg	102.808(5)	R, R_w^{a}	0.029, 0.036
γ, deg	106.513(4)	GoF^a	1.44

[a] $R = \sum(|F_o - F_c|)/\sum|F_o|$; $R_w = \{\sum[w(F_o - F_c)^2]/\sum(wF_o^2)\}^{1/2}$; GoF = $\{\sum[w(F_o - F_c)^2]/(\text{no. of reflns} - \text{no. of params})\}^{1/2}$.

Te*C*H$_2$SiMe$_3$, –17.65; (t-*C*$_4$H$_9$)C$_5$H$_3$, 32.6, 31.3; TeCH$_2$Si(*C*H$_3$)$_3$, 4.1; Si(*C*H$_3$)$_2$, –3.7, –6.0. Anal. Calcd for $C_{24}H_{41}Si_2ScTe$: C, 51.63; H, 7.40. Found: C, 52.79; H, 7.36.

Reaction of 1 with PMe$_3$. Complex **1** (0.033 g, 0.06 mmol) was dissolved in about 0.6 mL of benzene-d_6, and the solution was loaded into a sealable 5-mm NMR tube. The solution was degassed via two freeze–pump–thaw routines on a vacuum line, ≈1 equiv of PMe$_3$ was vacuum-transferred into the tube from a calibrated volume, and the tube was flame-sealed. ^{1}H NMR (C$_6$D$_6$, ppm, room temperature): (t-C$_4$H$_9$)C$_5$*H*$_3$, 6.44, 6.07, 5.29 (m); TeC*H*$_2$SiMe$_3$, 2.07 (s); (t-C$_4$*H*$_9$)C$_5$H$_3$, 1.41 (s); P(C*H*$_3$)$_3$, 0.82 (d); Si(C*H*$_3$)$_2$, 0.65, 0.17 (s); TeCH$_2$Si(C*H*$_3$)$_3$, 0.27 (s). ^{31}P{^{1}H} NMR (C$_7$D$_8$, ppm): at room temperature, –36.0 (br s); at –90 °C, –15.2 (s), –56.6 (s).

Preparation of DpSc–Te–ScDp (2). In a glovebox [DpScH]$_2$[12] (0.384 g, 0.56 mmol) and TeP-n-Bu$_3$ (0.0.092 g, 0.27 mmol) were loaded into a 25-mL round-bottomed flask that was attached to a swivel frit apparatus. The assembly was attached to a vacuum line and evacuated, and 15 mL of toluene was transferred into the vessel at –78 °C. The reaction mixture was allowed to warm to room temperature. During warming, gas evolution was accompanied by darkening of the solution to a deep purple color. After a further 15 min of stirring, the toluene was removed *in vacuo* and the residue recrystallized from hexanes. The solid was isolated by filtration, washed twice with cold hexanes, and dried *in vacuo*. Yield: 0.334 g, 74%. ^{1}H NMR (C$_6$D$_6$, ppm): (t-C$_4$H$_9$)C$_5$*H*$_3$, 7.64, 6.01, 5.59 (m); (t-C$_4$*H*$_9$)C$_5$H$_3$, 1.38 (s); Si(C*H*$_3$)$_2$, 0.83, 0.53 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm): (t-C$_4$H$_9$)*C*$_5$H$_3$, 150.2, 122.0, 117.9, 117.5, 112.2; (t-*C*$_4$H$_9$)-C$_5$H$_3$, 32.9, 31.7; Si(*C*H$_3$)$_2$, –3.1, –6.0. Anal. Calcd for $C_{40}H_{60}Si_2Sc_2Te$: C, 58.98; H, 7.42. Found: C, 60.90; H, 8.45. (The sample was contaminated by 12% P-n-Bu$_3$ by ^{1}H NMR. Anal. Calcd for mixture: C, 60.45; H, 8.14).

Preparation of DpSc(PMe$_3$)–Te–Sc(PMe$_3$)Dp (3). Telluride dimer **2** (0.028 g, 0.03 mmol) was dissolved in benzene-d_6, and the solution was loaded into a sealable 5-mm NMR tube. The solution was degassed on a vacuum line and 2 equiv of PMe$_3$ vacuum-transferred into the tube from a calibrated volume. Reaction was signaled by an immediate precipitation of a red-purple solid. Upon heating (70 °C), the solid dissolved and NMR spectra were obtained. Attempts to isolate **3** via drying under vacuum led to partial removal of PMe$_3$ and mixtures of **2** and **3**. ^{1}H NMR (C$_6$D$_6$, ppm): (t-C$_4$H$_9$)C$_5$*H*$_3$, 6.94, 6.21, 5.51 (m); (t-C$_4$*H*$_9$)C$_5$H$_3$, 1.41 (s); Si(C*H*$_3$)$_2$, 0.74, 0.35 (s); P(C*H*$_3$)$_3$, 0.91 (br s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm): (t-C$_4$H$_9$)*C*$_5$H$_3$, 150.6, 128.7, 117.1, 116.3, 110.8; (t-*C*$_4$H$_9$)C$_5$H$_3$, 33.1, 32.2; Si(*C*H$_3$)$_2$, –2.9, –5.8; P(*C*H$_3$)$_3$, 16.5 (d, J_P = 6.8 Hz).

Structural Analysis for DpSc(PMe$_3$)–Te–Sc(PMe$_3$)Dp (3). Crystal data for molecule **3** are summarized in Table 1; full acquisition and refinement details are available in the supplementary material. Molecule **3** crystallized in the triclinic system, and the space group was determined by cell reduction and successful refinement as $P\bar{1}$. The structure was solved by the heavy atom method, which revealed the positions of the tellurium and scandium atoms. The remaining non-hydrogen atoms were located in difference Fourier syntheses. The asymmetric unit consists of two independent half-molecules (the tellurium atom resides on an inversion center), which differ only slightly in conformation. Positional and thermal parameters are given in Table 2, and selected metrical data are found in Table 3. Refinement was by full-matrix least-squares calculations on F, initially with isotropic and later with anisotropic thermal parameters for all non-hydrogen atoms using the NRCVAX[13] programs to an R value of 0.029, R_w = 0.036, and GoF = 1.44. The hydrogen atoms were positioned geometrically and included as riding atoms in the structure factor calculations (C–H = 0.95 Å). The figures were prepared using ORTEPII.[14]

Table 2. Positional and Thermal Parameters and Theor Esd's for Dp(PMe$_3$)Sc–Te–Sc(PMe$_3$)Dp (**3**)

atom	x	y	z	B_{iso}, Å^2
Te(1)	0.00	0.00	0.00	2.980(13)
Sc(1)	0.08965(5)	–0.17041(5)	–0.05700(2)	2.599(24)
P(1)	0.20668(9)	–0.20434(8)	0.05373(4)	3.57(4)
Si(1)	0.18952(10)	–0.36412(8)	–0.12263(5)	4.29(5)
C(1A)	0.32740(38)	–0.07139(32)	0.09577(15)	4.99(19)
C(2A)	0.30337(37)	–0.30980(32)	0.06912(16)	4.97(19)
C(3A)	0.08684(39)	–0.25423(37)	0.09729(15)	5.32(21)
C(4A)	0.28763(40)	–0.44781(32)	–0.07678(21)	6.16(24)
C(5A)	0.16586(47)	–0.41275(38)	–0.20018(20)	7.14(25)
C(11A)	0.20035(30)	–0.12427(27)	–0.13936(13)	3.33(14)
C(12A)	0.26065(30)	–0.20122(25)	–0.10643(14)	3.34(15)
C(13A)	0.33465(30)	–0.13250(27)	–0.05333(14)	3.41(15)
C(14A)	0.32111(29)	–0.01735(26)	–0.05426(13)	3.22(14)
C(15A)	0.24019(29)	–0.01069(25)	–0.10870(12)	3.00(13)
C(16A)	0.21880(32)	0.09829(26)	–0.13428(13)	3.42(14)
C(17A)	0.25421(35)	0.20154(28)	–0.08785(15)	4.28(18)
C(18A)	0.31047(45)	0.13145(35)	–0.17624(17)	5.82(22)
C(19A)	0.07159(41)	0.07373(33)	–0.16823(16)	5.13(19)
C(21A)	–0.07039(32)	–0.32568(27)	–0.13666(13)	3.58(14)
C(22A)	0.02658(32)	–0.37538(25)	–0.10430(15)	3.84(16)
C(23A)	–0.00317(32)	–0.38563(25)	–0.04966(15)	3.82(16)
C(24A)	–0.11624(32)	–0.34580(27)	–0.04887(14)	3.64(14)
C(25A)	–0.16000(30)	–0.31097(25)	–0.10328(13)	3.29(13)
C(26A)	–0.29128(32)	–0.28337(29)	–0.12697(14)	3.93(15)
C(27A)	–0.35181(33)	–0.25162(32)	–0.07845(15)	4.56(18)
C(28A)	–0.26860(38)	–0.18226(36)	–0.16498(15)	5.10(20)
C(29A)	–0.39099(38)	–0.39606(38)	–0.16431(19)	6.52(22)
Te(2)	0.50	0.50	0.50	2.935(13)
Sc(2)	0.58212(5)	0.34359(5)	0.43087(2)	2.668(25)
P(2)	0.68739(9)	0.27333(8)	0.53465(4)	3.70(4)
Si(2)	0.66812(10)	0.16591(8)	0.34875(5)	4.37(5)
C(1B)	0.81298(40)	0.39167(34)	0.58419(16)	5.41(20)
C(2B)	0.77312(38)	0.15903(33)	0.53937(17)	5.24(20)
C(3B)	0.56318(40)	0.21404(35)	0.57565(17)	5.41(21)
C(4B)	0.75297(43)	0.05936(33)	0.38195(21)	6.39(25)
C(5B)	0.64190(45)	0.14916(37)	0.26889(18)	6.43(23)
C(11B)	0.70148(31)	0.41288(28)	0.35287(13)	3.50(14)
C(12B)	0.75249(31)	0.32361(27)	0.37859(14)	3.56(16)
C(13B)	0.82654(30)	0.37489(28)	0.43527(14)	3.57(16)
C(14B)	0.82227(30)	0.49193(26)	0.44357(13)	3.26(14)
C(15B)	0.74691(30)	0.51718(26)	0.39182(12)	3.12(14)
C(16B)	0.73560(33)	0.63682(27)	0.37553(13)	3.61(15)
C(17B)	0.77266(38)	0.72576(29)	0.42904(16)	4.63(20)
C(18B)	0.83622(42)	0.68183(34)	0.33769(18)	5.74(22)
C(19B)	0.59406(39)	0.62559(33)	0.34052(16)	5.10(19)
C(21B)	0.41836(32)	0.21628(28)	0.34309(13)	3.71(15)
C(22B)	0.50738(33)	0.15349(27)	0.36916(14)	3.83(15)
C(23B)	0.47246(33)	0.12470(26)	0.42197(15)	3.82(17)
C(24B)	0.36408(32)	0.16722(26)	0.42692(14)	3.62(15)
C(25B)	0.32769(30)	0.22200(26)	0.37738(13)	3.42(14)
C(26B)	0.20179(31)	0.25822(30)	0.35798(13)	3.81(15)
C(27B)	0.14148(32)	0.27871(31)	0.40880(15)	4.28(17)
C(28B)	0.09786(38)	0.15520(39)	0.31510(17)	6.26(21)
C(29B)	0.22973(39)	0.36927(37)	0.32673(15)	5.26(21)
C(1)	0.18059(68)	0.82833(59)	0.27685(18)	7.76(36)
C(2)	0.31025(76)	0.88441(44)	0.27307(24)	8.44(34)
C(3)	0.38130(52)	0.81829(64)	0.25516(23)	7.93(32)
C(4)	0.32993(62)	0.70258(59)	0.24094(20)	7.30(32)
C(5)	0.20427(68)	0.64802(41)	0.24389(21)	7.43(33)
C(6)	0.12846(52)	0.70940(61)	0.26200(21)	7.61(32)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Results and Discussion

The chemistry reported herein is summarized in Scheme 1. By analogy to chemistry we recently reported,[15] elemental tellurium

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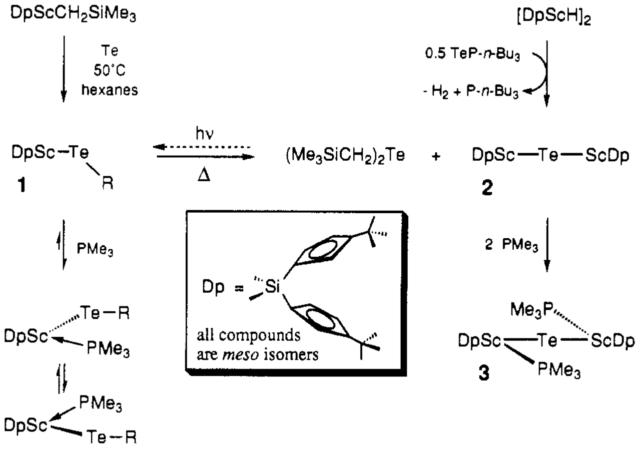
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Dp(PMe$_3$)Sc–Te–Sc(PMe$_3$)Dp (3)

Bond Lengths: Molecule A					
Te(1)–Sc(1)	2.8798(5)	Sc(1)–P(1)	2.7563(10)	Sc(1)–C(11A)	2.510(3)
Sc(1)–C(12A)	2.480(3)	Sc(1)–C(13A)	2.505(3)	Sc(1)–C(14A)	2.603(3)
Sc(1)–C(15A)	2.652(3)	P(1)–C(1A)	1.814(4)	Si(1)–C(4A)	1.858(4)
Si(1)–C(12A)	1.853(3)	C(11A)–C(12A)	1.426(4)	C(11A)–C(15A)	1.409(4)
C(12A)–C(13A)	1.412(4)	C(13A)–C(14A)	1.415(4)	C(14A)–C(15A)	1.409(4)
C(15A)–C(16A)	1.506(4)	C(16A)–C(17A)	1.518(5)	Cp$_{Cent}$–Sc(1)	2.2415(16)
Bond Lengths: Molecule B					
Te(2)–Sc(2)	2.8693(5)	Sc(2)–P(2)	2.7470(10)	Sc(2)–C(11B)	2.517(3)
Sc(2)–C(12B)	2.478(3)	Sc(2)–C(13B)	2.506(3)	Sc(2)–C(14B)	2.609(3)
Sc(2)–C(15B)	2.652(3)	P(2)–C(1B)	1.803(4)	Si(2)–C(4B)	1.861(4)
Si(2)–C(12B)	1.861(3)	C(11B)–C(12B)	1.424(4)	C(11B)–C(15B)	1.411(4)
C(12B)–C(13B)	1.415(5)	C(13B)–C(14B)	1.409(4)	C(14B)–C(15B)	1.409(4)
C(15B)–C(16B)	1.518(4)	C(16B)–C(17B)	1.524(5)	Cp$_{Cent}$–Sc(2)	2.2441(16)
Bond Angles: Molecule A					
Sc(1)–Te(1)–Sc(1)^a	180.0	Te(1)–Sc(1)–P(1)	84.743(24)		
Te(1)–Sc(1)–C(11A)	122.24(7)	Te(1)–Sc(1)–C(12A)	145.88(7)		
Te(1)–Sc(1)–C(13A)	120.46(7)	Te(1)–Sc(1)–C(14A)	92.83(7)		
Te(1)–Sc(1)–C(15A)	94.02(6)	Sc(1)–P(1)–C(1A)	113.77(12)		
Sc(1)–P(1)–C(2A)	123.09(13)	Sc(1)–P(1)–C(3A)	113.47(12)		
C(4A)–Si(1)–C(5A)	109.87(21)	C(12A)–Si(1)–C(22A)	96.41(13)		
C(11A)–C(12A)–C(13A)	104.85(25)	C(12A)–C(13A)–C(14A)	109.6(3)		
C(13A)–C(14A)–C(15A)	108.4(3)	C(11A)–C(15A)–C(14A)	106.2(3)		
C(12A)–C(11A)–C(15A)	110.8(3)				
Bond Angles: Molecule B					
Sc(2)–Te(2)–Sc(2)^b	180.0	Te(2)–Sc(2)–P(2)	85.093(24)		
Te(2)–Sc(2)–C(11B)	122.28(8)	Te(2)–Sc(2)–C(12B)	146.03(7)		
Te(2)–Sc(2)–C(13B)	120.74(8)	Te(2)–Sc(2)–C(14B)	93.21(7)		
Te(2)–Sc(2)–C(15B)	94.22(7)	Sc(2)–P(2)–C(1B)	113.69(12)		
Sc(2)–P(2)–C(2B)	122.46(13)	Sc(2)–P(2)–C(3B)	113.76(12)		
C(4B)–Si(2)–C(5B)	110.72(20)	C(12B)–Si(2)–C(22B)	96.42(13)		
C(11B)–C(12B)–C(13B)	105.3(3)	C(12B)–C(13B)–C(14B)	109.5(3)		
C(13B)–C(14B)–C(15B)	108.3(3)	C(11B)–C(15B)–C(14B)	106.7(3)		
C(12B)–C(11B)–C(15B)	110.1(3)				

^{a} Refers to the following equivalent position: $-x, -y, -z$. ^{b} Refers to the following equivalent position: $1 - x, 1 - y, 1 - z$.

Scheme 1



inserts readily into the scandium–carbon bonds of the *ansa*-scandocene alkyl {*meso*-(CH$_3$)$_2$Si[(*t*-C$_4$H$_9$)C$_5$H$_3$]$_2$}Sc(CH$_2$SiMe$_3$) (DpScR). The reaction proceeds in 4–5 hours when fine-mesh tellurium is used or upon mixing when the tellurium transfer agent Te=P-*n*-Bu$_3$ is employed. However, complete separation of the byproduct P-*n*-Bu$_3$ from the highly soluble tellurolate is difficult, and so to obtain pure samples of *meso*-DpScTeR (**1**), use of elemental tellurium is the pathway of choice.

Tellurolate **1** reacts with PMe$_3$ to form a mixture of rapidly exchanging diastereomeric adducts differentiated by the direction of approach taken by the incoming PMe$_3$ base. A broad resonance at −36.0 ppm was observed in the room-temperature $^{31}P\{^1H\}$ NMR spectrum which collapsed and sharpened into two resonances at −15.2 and −56.6 ppm as the temperature was lowered.[16] The ratio of diastereomers was 2.4:1 at −90 °C. The data do not allow for definitive assignment of the predominant diastereomer's structure; attempts to isolate solid samples of these adducts failed largely due to the lability of the PMe$_3$ ligand, which is slowly pumped away under high vacuum.

Upon standing for lengthy periods of time (2 weeks), solutions of **1** and PMe$_3$ deposit ruby red cube-shaped crystals suitable for X-ray analysis. This study revealed the compound to be a PMe$_3$-ligated μ-telluride dimer of composition DpSc(PMe$_3$)–Te–Sc(PMe$_3$)Dp (**3**; *vide infra*). The unligated dimer DpSc–Te–ScDp (**2**) can be synthesized via thermolysis of **1** at 90 °C or by reaction of [DpScH]$_2$ with Te=P-*n*-Bu$_3$. The former reaction occurs with concomitant extrusion of TeR$_2$,[17] while the latter is accompanied by vigorous H$_2$ evolution. Dimer **2** rapidly takes up 2 equiv of PMe$_3$ to form **3**, which immediately precipitates almost completely from benzene solution as a powdery bright purple solid.[18] In light of these observations, it is likely that the slow thermal decomposition of **1** at room temperature produces the unligated dimer **2**, which is trapped as the highly insoluble PMe$_3$ adduct **3**, which gradually crystallizes as a monobenzene solvate over the course of several days.

The asymmetric unit of **3**·C$_6$H$_6$ consists of two independent half-molecules (the tellurium atom resides on an inversion center), which differ only slightly in conformation. Figure 1 shows views of **3** (a) along and (b) above the plane that bisects the cyclopentadienyl rings on each metal center and contains the atoms P, Sc, Te, Sc′, and P′. The phosphines fill vacancies in each scandium's coordination sphere and give the molecule an American football shape in three dimensions, perhaps accounting for its low-solubility hydrocarbon solvents. The mean Sc–P

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(16) Free PMe$_3$ (neat) resonates at 62 ppm relative to H$_3$PO$_4$: Grim, S. O.; McFarlane, W.; Davidoff, E. F. *J. Org. Chem.* **1967**, *32*, 781.

(17) The thermolysis reaction is reversed quantitatively upon irradiation of mixtures of **3** and Te(CH$_2$SiMe$_3$)$_2$.[15]

(18) Attempts to isolate **3** in this fashion were unsuccessful due to facile loss of PMe$_3$ when samples were exposed to vacuum. Samples suitable for microanalysis were thus not obtainable.

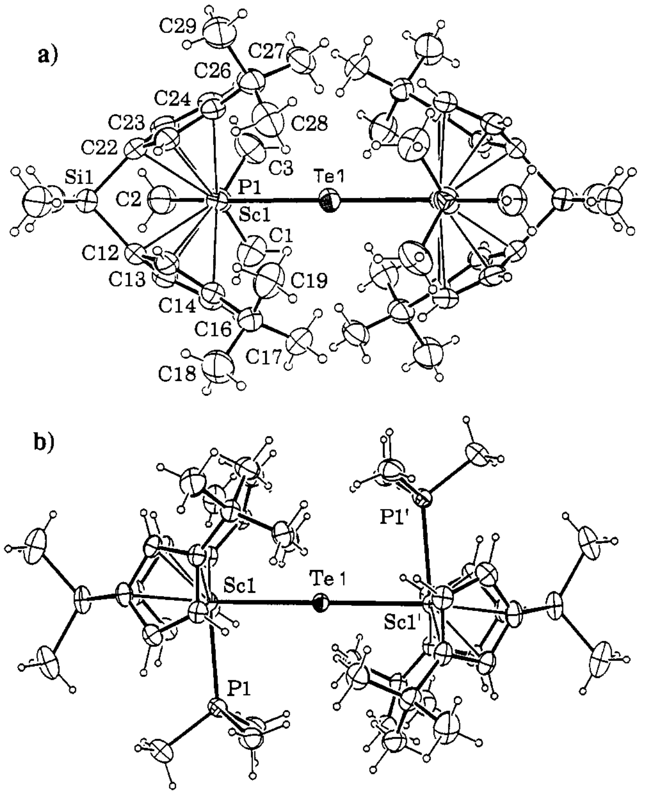
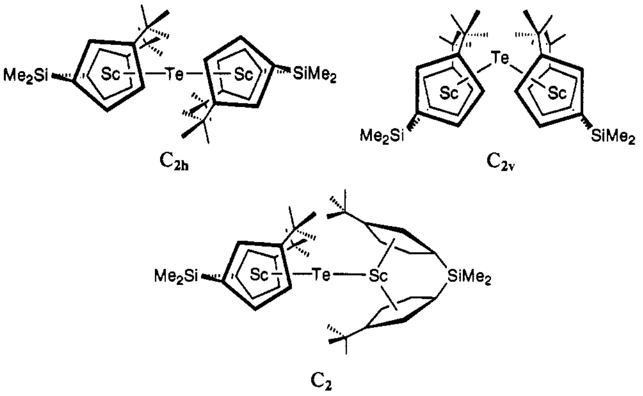


Figure 1. ORTEP diagrams showing two views of DpSc(PMe_3)–Te–Sc(PMe_3)Dp (**3**) (molecule A): (a) along the P–Sc–Te–Sc′–P′ plane; (b) above the P–Sc–Te–Sc′–P′ plane.

distance of 2.752(5) Å is in line with other reported Sc–P bonds.[19] In light of the commonly accepted molecular orbital scheme for bent Cp_2M fragments,[20] the arrangement of the DpSc units with respect to each other is surprising, since only one unhybridized 5p orbital on Te can participate in π bonding to Sc orbitals of proper symmetry. There is thus a maximum bond order of 1.5 possible for the Sc–Te bonds of **3**. This contrasts with the structures observed for $Cp^*_2ScTeScCp^*_2$[15] and other complexes of this type[21] in which the Cp^*_2M units are disposed in an allene-like array across the M–E–M vector and π interaction is optimized (maximum bond order of 2). The attenuated π bonding for **3** is reflected in the mean Sc–Te bond distance of 2.875(5) Å compared to 2.7528(12) Å found for $Cp^*_2ScTeScCp^*_2$.

Given the diminished role of π bonding between Sc and Te in **3**, the perfect linear geometry (Sc–Te–Sc = 180.0°) of the μ-telluride ligand is unexpected. For diorganotellurides and H_2Te the X–Te–X angles are generally found to be close to 90° [22] due in part to the larger, more sterically accommodating Te atom and partially to the fact that weaker Te–X bonds do not compensate for the energy required for hybridization. Although unsupported by theory, experimental results to date suggest that a similar tendency toward bent geometry occurs in M–Te–M complexes, since most structurally characterized L_nM–E–ML_n[5-7] complexes contain bent μ-telluride ligands. Even for L_nM–E–ML_n complexes where L_nM is a 15-electron fragment and linear M–E–M bridges are most favored, synthetic attempts to prepare the telluride members of the series have either met with failure or resulted in structures not strictly linear at tellurium.[7] Thus the observed structure of **3** is somewhat unusual both because of the linear geometry at tellurium and because this linearity apparently is a result of the steric properties of the ligand set employed and *not* electronic factors. Use of models suggests that any bending of the Sc–Te–Sc vector in the plane bisecting the cyclopentadienyl rings almost immediately results in significant steric problems involving a set of *tert*-butyl groups and the PMe_3 ligand on the opposing Sc center. Thus, the role of the PMe_3 ligands in terms of enforcing linearity in **3** may be crucial and the geometry at tellurium in the unligated dimer **2** may be significantly different. Our NMR data, which show only one set of ligand resonances, rule out the C_2 structure shown in Chart 1. Such a conformation would require rotation of one of the DpSc units by 90°, and although this structure would lead to optimal π bonding, the ligand architecture precludes such a rotation from occurring. Unfortunately, X-ray-quality crystals of **2** could not be obtained and though the structure of the ligated species **3** is suggestive of a linear conformation for **2**, the spectroscopic data for **2** cannot distinguish between the C_{2h} linear and C_{2v} bent structures shown in Chart 1.

Chart 1



Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supplementary Material Available: Tables of crystal, collection, and refinement data, bond lengths and angles, H atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, torsion angles, and mean plane data for compound **3** (17 pages). Ordering information is given on any current masthead page.

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