Bimolecular Extrusion of TeR_2 from *β*-Diketiminato Supported Scandium Bis-tellurolates

Lisa K. Knight,[a] Warren E. Piers,*[a] and Robert McDonald[b]

Abstract: Reaction of the well-defined, base-free dialkyl scandium compounds $L^nSc(CH_2SiMe_3)_2$ supported by the *β*-diketiminato ligands ArNC(R)CHC(R)NAr (Ar = 2,6-diisopropyl; R = Me, L^1; R = *t*Bu, L^2) with two equivalents of $nBu_3P{=}Te$ gives the bis-tellurolate complexes $L^nSc(TeCH_2SiMe_3)_2$, **1b** (L^1) and **2b** (L^2). Tellurolate **2b** was isolated and fully characterized, including an X-ray structure analysis, and exhibits two chemically distinct tellurolate ligands in solution on the NMR time scale. Tellurolate **1b** is only moderately stable and decomposes with elimination of two equivalents of $Te(CH_2SiMe_3)_2$ to form the dimeric bis-telluride **1d**. This compound was characterized by X-ray crystallography and elemental analysis. In contast, tellurolate **2b** decomposes with loss of only one equivalent of $Te(CH_2SiMe_3)_2$, leading to the formation of a dinuclear complex with one bridging telluride unit joining two $L^2Sc(TeCH_2SiMe_3)$ fragments. This compound was also structurally characterized. The solution behavior of this material is complex, as it exists as three conformational isomers that undergo slow exchange on the NMR time scale. The production of dimer **2c**, along with the results of crossover experiments, suggest strongly that TeR_2 elimination from these bis-tellurolates is bimolecular.

Keywords: ligand effects · scandium · tellurides · tellurium

The organometallic chemistry of well-defined, monomeric, bis-alkyl derivatives of Sc, Y, and the lanthanides has been hampered by the synthetic difficulties associated with their preparation and their prediliction to undergo metalation, dimerization, or complexation by salts.[1] We recently reported the preparation of a new family of discrete bis-alkyl scandium compounds supported by sterically demanding *β*-diketiminato ligands[2] and have now begun to explore their chemistry.

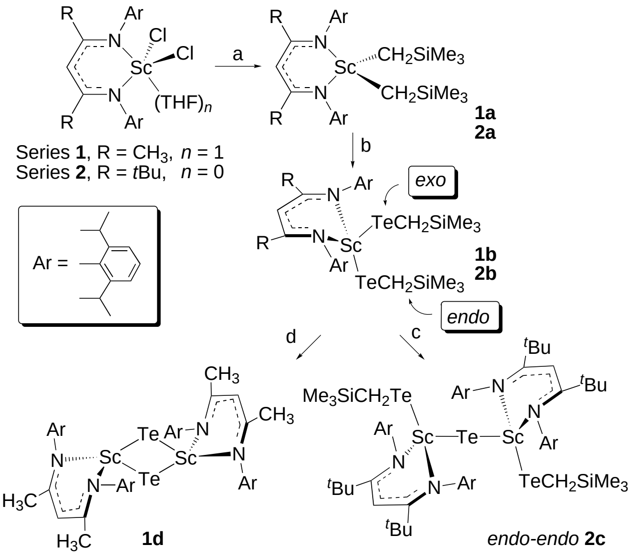
We have previously shown that elemental tellurium inserts smoothly into the Sc–C bonds of a variety of $[Cp^*_2ScR]$ derivatives to form scandium tellurolates, which undergo a thermal or photochemical extrusion of TeR_2 to yield the *μ*-telluride $[\{Cp^*_2Sc\}_2(Te)]$.[3] This telluride-forming reaction has been observed in other tellurolates,[4] those of Group 4,[5] 5[6] and lanthanide[7],[8] in particular, and is thought to be an important process for the deposition of binary metal tellurides from tellurolate precursors.[9] Clearly, in mono-tellurolate derivatives, the mechanism must be bimolecular, but in bis-tellurolates, the loss of TeR_2 may also occur in a unimolecular sense, producing an intermediate terminal tellurido complex which usually oligomerizes. For example, Arnold and Gindelberger have used kinetic data to show this is the pathway for loss of $Te(SiPh_3)_2$ from $[Cp^{tBu}_2Zr\{Te(SiPh_3)_2\}]$, producing the dimeric $[\{Cp^{tBu}_2Zr\}_2(\mu\text{-}Te)_2]$.[5a] Significantly, this reaction proceeds only in the presence of a Lewis base. In contrast, the experiments described here convincingly show that extrusion of TeR_2 from $LSc(TeR)_2$ (L = *β*-diketiminato) *in the absence of a Lewis base* is bimolecular.

The *β*-diketiminato ligands employed here[10] incorporate the bulky Ar group 2,6-iPr-C_6H_3 and differ in the iminoacyl substituent of the diketiminato framework: CH_3 for series **1** (L^1) and *t*Bu for compounds **2** (L^2; Scheme 1). Ligand L^2 offers a slightly greater degree of steric protection than the CH_3-substituted ligand L^1, since the *t*Bu group pushes the aryl group forward into the scandium's coordination sphere more effectively than the methyl group of series **1**.[11] Bis-trimethylsilylmethyl derivatives of each LSc unit were prepared by alkylation of the dichloride precursors with organolithium reagents, giving **1a** and **2a** in isolated yields of around 40–45%. Reaction of either of these compounds with two equivalents of $nBu_3P{=}Te$,[12] a source of soluble "Te", proceeds upon mixing as evidenced by a rapid color change from light yellow to a darker orange-red. The products are both thermally and photochemically sensitive and only one (**2b**) has been isolated, characterized, and identified as the expected bis-tellurolate. Analytically pure **2b** is an orange-yellow solid which is moderately stable in solution at ambient

---

[a] Prof. W. E. Piers, L. K. Knight
Department of Chemistry
University of Calgary
2500 University Dr. NW, T2N 1N4 (Canada)
Fax: (+1)403-289-9488
E-mail: wpiers@ucalgary.ca

[b] Dr. R. McDonald
Department of Chemistry, University of Alberta
Edmonton, AB (Canada)



Scheme 1. a) 2.1 LiCH$_2$SiMe$_3$; b) 2 Te=PnBu$_3$, toluene; c) R = tBu, hν, – Te(CH$_2$SiMe$_3$)$_2$; d) R = CH$_3$, hν, – Te(CH$_2$SiMe$_3$)$_2$.

temperatures if protected from light. The solid-state structure of **2b** was determined by X-ray crystallography (Figure 1).[13] The Sc–Te1 and Sc–Te2 distances of 2.8177(5) and 2.8097(5) Å, respectively, in the two chemically distinct tellurolate ligands (*endo* and *exo* as labeled in Scheme 1) are comparable to that of 2.8337(14) Å found in the benzyl tellurolate [Cp$^*_2$ScTeCH$_2$Ph].[3a] The orientation of the two tellurolate ligands with respect to each other is striking in that the structure appears geometrically predisposed to elimination of TeR$_2$ in an intramolecular fashion: the C2-Te2-Sc-Te1 torsion angle is only 16.04(10)°.

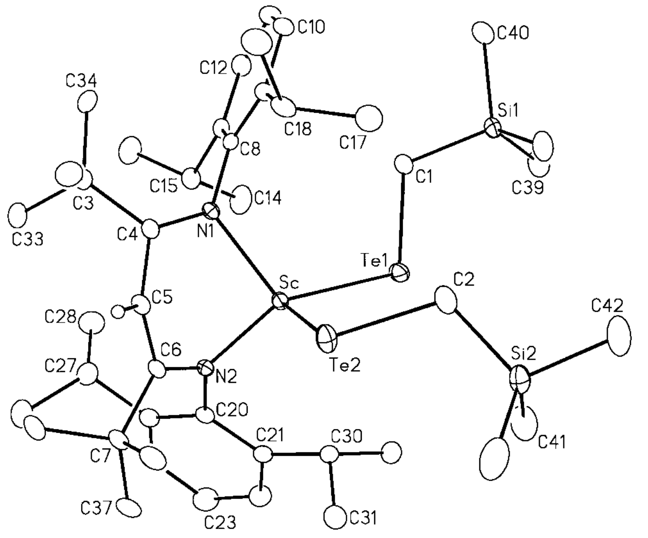


Figure 1. Molecular structure of **2b**. Selected distances [Å] and angles [°]: Sc–Te1 2.8177(5), Sc–Te2 2.8097(5), Sc–N1, 2.136(2), Sc–N2 2.080(2), N1–C4 1.318(3), N2–C6 1.368(3), C4–C5 1.451(3), C5–C6 1.389(4), Sc–C4 2.788(3), Sc–C5 2.695(2), Sc–C6 2.619(2); Te1-Sc-Te2 107.999(17), N1-Sc-N2 93.41(8), Sc-N1-C4 105.15(16), Sc-N2-C6 96.67(15), C4-C5-C6 133.9(2).

NMR spectroscopy on **2b** suggests the structure shown is static on the NMR time scale, since two TeCH$_2$SiMe$_3$ groups are apparent in the ^{1}H and ^{125}Te{^{1}H} NMR spectra. For example, two signals appear in the ^{1}H NMR spectrum at $\delta = 2.40$ and 1.17 for the TeCH$_2$ protons and in the ^{125}Te NMR spectrum, separate signals are observed at $\delta = 266.7$ and 62.9. Attempts to assign these resonance signals specifically to the *exo* and *endo* positions by ^{1}H ROESY experiments did not lead to a clear conclusion on this issue. The static solution structure for **2b** contrasts with the behavior of the dialkyl starting materials, in which the two alkyl groups are equivalent by NMR spectroscopy under similar conditions. This is likely due to a dynamic process involving flipping of the β-diketiminato ligand.[14] The barrier to this process in alkyl derivatives **a** and related compounds appears to be related to the steric bulk of the alkyl group, with larger groups having more difficulty passing through the channel defined by the bulky aryl groups. Since the tellurolate ligands in compounds **b** are more bulky still, the process exchanging them is slow on the NMR time scale for these ligands.

In contrast to **2b**, bis-tellurolate **1b** is only fleetingly observed spectroscopically, and pure samples were not isolable. In solution, loss of Te(CH$_2$SiMe$_3$)$_2$ from **1b** is facile and clear yellow crystals can be harvested from these reactions. Spectroscopic data for this highly insoluble product were not obtainable in solvents it did not react with; however, it was identified as the μ-telluride species **1d** by X-ray crystallography (Figure 2). The β-diketimato ligand in **1d** ligates the scandium atom in a primarily σ-bonding mode as indicated by a rather long Sc–C3 non-bonded distance of 3.328(3) Å and a relatively small deviation of Sc from the N-C-C-C-N plane of 0.676(3) Å. Although a center of inversion coincides with the centroid of the Sc$_2$Te$_2$ core of the molecule, the Sc–Te and Sc′–Te bond lengths are slightly different at 2.7604(5) and 2.7634(6) Å, respectively. These parameters compare favorably to the Sc–Te bond length of

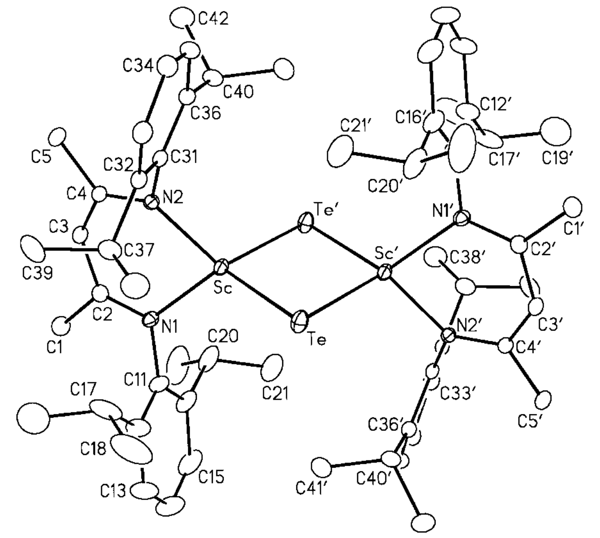
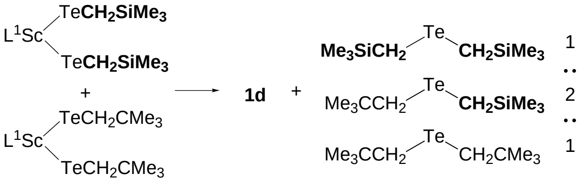


Figure 2. Molecular structure of **1d**. Selected distances [Å] and angles [°]: Sc–Te 2.7604(5), Sc′–Te 2.7634(6), Sc–N1 2.131(2), Sc–N2 2.119(2), N1–C2 1.337(3), N2–C4 1.345(3), C2–C3 1.409(3), C3–C4 1.383(4), Sc–C2 3.058(3), Sc–C3 3.328(3), Sc–C4 3.048(2); Sc-Te-Sc′ 79.398(16), Te-Sc-Te′ 100.602(16), N1-Sc-N2 88.80(8), Sc-N1-C2 122.07(17), Sc-N2-C4 121.65(17), C2-C3-C4 130.3(2).

2.7528(12) Å found for [{Cp_2^*Sc}$_2$(μ-Te)],[3a] where π-bonding between Sc and Te probably occurs.

While it is conceivable that the conversion of **1b** to **1d** involves intramolecular loss of TeR_2 followed by rapid dimerization of "$L^1Sc{=}Te$", the following observations convincingly show that this process is bimolecular. First, attempts to trap "$L^1Sc{=}Te$" by allowing **1b** to decompose in the presence of PMe_3 or PhC≡CPh (species which might be expected to trap a terminal tellurido intermediate), only compound **1d** is observed. Furthermore, attempts to dissociate the dimeric structure of **1d** with various Lewis bases leads to decomposition of the compound. Second, a crossover experiment which utilizes the in situ generated neopentyl substituted bis-tellurolate in concert with **1b** gives a statistical mixture of $Te(CH_2CMe_3)_2$, $Te(CH_2SiMe_3)_2$, and $(Me_3SiCH_2)Te(CH_2CMe_3)$[15] (1:1:2) upon production of **1d** [Eq. (1)]; only the first two products would be expected in an intramolecular extrusion.[16] Finally, when the isolated bis-tellurolate compound **2b** (vide supra) is allowed to decompose by exposing a hexane solution to light, half an equivalent of $Te(CH_2SiMe_3)_2$ is produced and deep yellow crystals of the μ-tellurido bis-tellurolate complex **2c** deposit from the solution (Scheme 1). This species, which was analyzed by X-ray crystallography (Figure 3), is produced from bimolecular extrusion of $Te(CH_2SiMe_3)_2$ from **2b**. Likely, this tellurolate–telluride is an intermediate on the way to a (μ-Te)$_2$ species analogous to **1d**, although we have not observed clean conversion of **2c** to such a species as of yet. Presumably, the greater steric presence of the *t*Bu substituted diketiminato ligand stabilizes this compound towards further loss of $Te(CH_2SiMe_3)_2$.



(1)

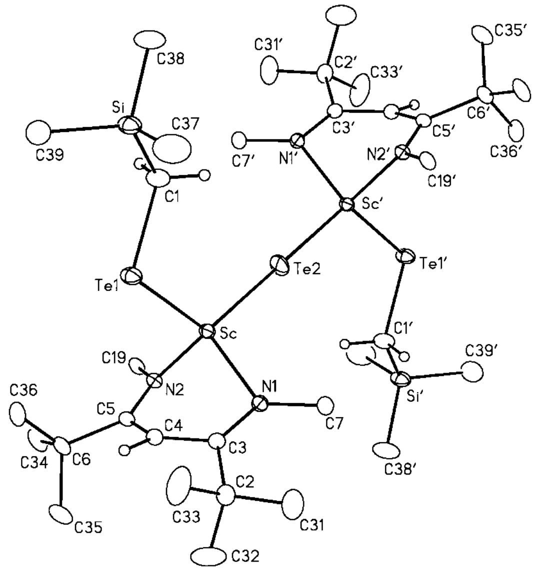
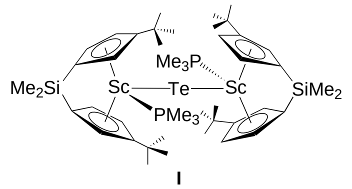


Figure 3. Molecular structure of **2c**; for clarity, only the *ipso*-carbons of the β-diketiminato aryl groups are shown. Selected distances [Å] and angles [°]: Sc–Te1 2.8326(4), Sc–Te2 2.7088(4), Sc–N1 2.1002(16), Sc–N2 2.0905(17), N1–C3 1.332(2), N2–C5 1.341(2), C3–C4 1.425(3), C4–C5 1.420(3), Sc–C3 2.7054(19), Sc–C4 2.693(2), Sc–C5 2.6859(19); Sc-Te2-Sc′ 180.0, Te1-Sc-Te2 121.180(14), N1-Sc-N2 97.34, Sc-N1-C3 101.69(12), Sc-N2-C5 100.74(12), C3-C4-C5 136.60(18), Sc-Te1-C1 101.18(6), Te1-C1-Si 111.47(11).

Structurally, the β-diketiminato ligand in **2c** exhibits a greater degree of π-donation to the scandium center as supported by the significantly shorter Sc to C3, C4, and C5 distances in **2c** as compared to those in **1d**, and the greater deviation of Sc from the plane defined by the five ligand atoms (1.2506(17) Å). The linear geometry at Te2 is unusual for tellurium; a previous example from our group, **I**,[17] was rationalized on the basis of the steric requirements of the ancillary ligand set. While Te2 is also rather sterically protected in **2c**, the very short Sc–Te2 distance of 2.7088(4) Å (cf. the distance of 2.8798(5) Å for the Sc–Te interatomic distance in **I**) is indicative of significant π bonding between Sc and Te; thus, there may be a contributing electronic impetus for the linearity at Te2 in this compound.



I

As can be seen in Figure 3, in the solid state, the $TeCH_2SiMe_3$ ligands of **2c** occupy the *endo* sites at scandium, underneath the plane of the β-diketiminato ligand. However, ^1H NMR spectroscopy on crystals of **2c** revealed a complex spectrum consistent with the presence of three conformational isomers which we label the *endo–endo*, *exo–exo*, and *endo–exo* isomers of **2c**, based on the orientation of the tellurolate ligands at each scandium center (Figure 4). Although the spectrum is complicated, the regions of the spectrum for the backbone CH ($\delta = 5.5-5.8$) and the $SiCH_3$ ($\delta = -0.1-0.5$) protons clearly indicate the presence of two symmetrical and one unsymmetrical species in a 1.0:0.5:0.8 ratio. At room temperature, these isomers do not exchange on the NMR time scale. However, ^1H EXSY NMR spectroscopy (Figure 4, inset) indicates that the isomers do interconvert, presumably by the flipping of the β-diketiminato ligands. As can be seen, the backbone C*H* signals for the unsymmetrical *endo–exo* **2c** ($\delta = 5.50$ and 5.61) exhibit crosspeaks with both symmetrical isomers ($\delta = 5.55$ and 5.76), but crosspeaks between the signals for the *exo–exo* and *endo–endo* isomers and between the two resonance signals for the *endo–exo* isomer are absent. This is presumably because two flipping events (k_{flip}) are required in order to carry out these latter exchanges, while only one is necessary for the former. Again, it is difficult to specifically assign the peaks in this spectrum to the isomers; we have assumed for the purposes of Figure 4 that the major symmetrical isomer in solution is that found in the solid state (i.e. *endo–endo* **2c**), but it is conceivable that this is erroneous.

In summary, we have shown that extrusion of TeR_2 from the scandium bis-tellurolates **1b** and **2b** occurs via a bimolecular

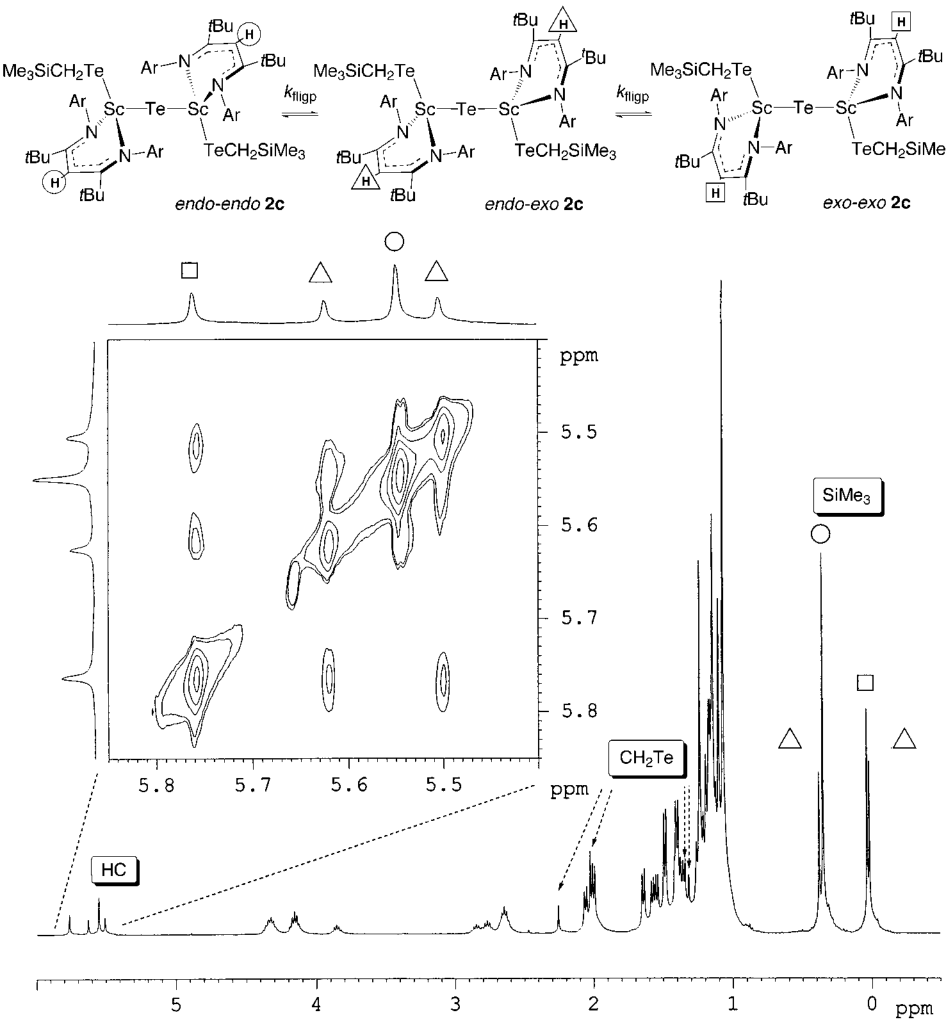


Figure 4. 400 MHz ^{1}H NMR spectrum of the equilibrating mixture of conformational isomers of **2c**. For clarity, the aromatic region of the spectrum is not shown. Inset: ^{1}H-^{1}H EXSY map of the ligand backbone CH region of the spectrum.

pathway, in contrast to previously characterized unimolecular eliminations from Group 4 bis-tellurolates. In the latter cases, the TeR_2 extrusions were initiated in the presence of an excess of a Lewis base. Under such conditions, the molecular orbitals necessary for bimolecular transition states are unavailable; furthermore, coordination of the Lewis base to the metal center likely forces the tellurolate ligands closer together in the metal's coordination sphere, facilitating unimolecular elimination of TeR_2. In the bimolecular reactions described here, we suggest that the scandium tellurolates serve as their own Lewis base inducer of elimination through dimerization. To test these ideas, we are examining the elimination of TeR_2 from compounds **b** in the presence of external Lewis bases.

Experimental Section

^{1}H, ^{13}C{^{1}H}, ^{125}Te{^{1}H}, and HMQC NMR experiments were performed on Bruker AC-200 or WH-400 MHz spectrometers and were recorded in C_6D_6, unless otherwise noted. Data are reported in ppm relative to solvent signals for ^{1}H and ^{13}C spectra; for ^{125}Te spectra, the data are referenced relative to external $TeMe_2$ (0.0 ppm). The ligand HL (L = ArNC(R)CHC(R)NAr, where Ar = 2,6-*i*Pr-C_6H_3 and R = *t*Bu) was prepared by a literature procedure.[11a] Compounds **1a** and **2a** were prepared by alkylation of the $LScCl_2$ precursors;[2] full details will be reported separately.[14]

Preparation of [$L^2Sc(TeCH_2SiMe_3)_2$] (2b): Toluene (10 mL) was vacuum transferred (−78 °C) into a flask containing **2a** (0.391 g, 0.54 mmol) and two equivalents of solid TeP*n*Bu$_3$ (0.357 g, 1.08 mmol). The reaction mixture was warmed to room temperature and allowed to stir for 5 min. The toluene was removed in vacuo and replaced with hexanes (5 mL); an orange precipitate was isolated by means of a cold filtration. The solid was washed twice with cold hexanes to remove *n*Bu$_3$P and the solid was recrystallized from hexanes, giving **2b** (0.288 g, 55 %). ^{1}H NMR: $\delta = 7.07$ (m, 4H; C_6H_3), 6.97 (m, 2H; C_6H_3), 5.66 (s, 1H; CH), 4.30, 2.68 (m, 2 × 2H; C*H*(CH$_3$)$_2$), 2.34 (brs, 2H; ScTeCH$_2$),1.88, 1.50 (brs, 2 × 6H; CH(C*H$_3$*)$_2$), 1.16 (brs, 12H; CH(C*H$_3$*)$_2$), 1.10 (brs, 20H; NCC(CH$_3$)$_3$ and ScTeCH$_2$), 0.30, 0.01 (s, 2 × 9H; TeCH$_2$Si(C*H$_3$*)$_3$); ^{13}C{^{1}H} NMR: $\delta = 172.5$ (N*C*C(CH$_3$)$_3$), 144.3 (C_{ipso}), 128.7, 128.2, 127.0, 127.1, 124,2 (C_6H_3), 87.7 (CH), 45.7 (NC*C*(CH$_3$)$_3$), 32.4 (NCC(*C*H$_3$)$_3$), 32.0, 28.9 (*C*H(CH$_3$)$_2$), 29.3, 25.4 (CH(*C*H$_3$)$_2$), 0.4, −0.1 (Si(CH$_3$)$_3$), −22.1, −22.2 (ScTeCH$_2$); ^{125}Te{^{1}H} NMR: $\delta = 266.7$, 62.9 (ScTeCH$_2$Si(CH$_3$)$_3$); elemental analysis calcd for $C_{43}H_{75}N_2Si_2Te_2Sc$ (%): C 52.90, H 7.74, N, 2.87; found: C 52.57, H 7.59, N 2.88.

Preparation of [{L^1Sc}$_2$(μ-Te)$_2$] (1d): Two equivalents of TeP*n*Bu$_3$ and one equivalent of **1a** were dissolved separately in toluene (10 mL for **1a** and 5 mL for TeP*n*Bu$_3$). The two reagents were combined and allowed to stir at room temperature for half an hour. The solution changed to a deep orange color; the reaction mixture was left at room temperature for two days during which time, yellow crystals formed and deposited from the solution. The yellow solid was isolated by filtration and dried in vacuo, giving **1d**

(0.175 g, 57 %); elemental analysis calcd for $C_{58}H_{82}N_4Te_2Sc_2$ (%): C 59.02, H 7.00, N 4.75; found: C 58.99, H 6.67, N 4.52.

Preparation of $[\{L^2Sc(TeCH_2SiMe_3)\}_2(\mu\text{-}Te)]$ (2c): Compound **2b** (0.061 g, 0.063 mmol) was dissolved in hexanes (3 mL) and the homogeneous yellow solution was stirred while exposed to light at room temperature for 24 h. Cubic, yellow crystals deposited from this solution. The solvent was decanted and the crystals were washed three times with cold hexanes (0.2 mL) to yield **2c** (0.026 g, 50.0 %). There are three conformational isomers in solution (see text); by symmetry, the ^1H NMR spectrum of these isomers contains eight methine peaks ($\delta = 4.16$, 3.86, 2.85, 2.77, two at $\delta =$ 2.64 and 4.32) and sixteen methyl resonances ($\delta = 2.06$, 2.00, 1.64, 1.57, 1.54, 1.49, 1.39, 1.36 with eight more resonance signals between $\delta = 1.26$ and 1.06). The aryl resonance signals for the three isomers range from $\delta = 7.17$ to 6.98; the remaining peaks are assigned as follows for the ^1H NMR: *endo–endo* **2c**: $\delta = 5.55$ (s, 2H; CH), 2.03 (s, 4H; $ScTeCH_2$), 1.07 (s, 36H; $NCC(CH_3)_3$), 0.36 (s, 18H; $\mathrm{TeCH_2Si(C}\mathit{H}_3)_3$); *exo–exo* **2c**: $\delta = 5.76$ (s, 2H; CH), 1.34 (s, 4H; $ScTeCH_2$), 1.26 (s, 36H; $NCC(CH_3)_3$), 0.04 (s, 18H; $TeCH_2Si(CH_3)_3$); *endo–exo* **2c**: 5.63 (s, 1H; CH), 5.51 (s, 1H; CH), 2.26 (s, 2H; $ScTeCH_2$), 1.32 (s, 2H; $ScTeCH_2$), 1.14 (s, 18H; $NCC(CH_3)_3$), 1.10 (s, 18H; $NCC(CH_3)_3$), 0.38 (s, 9H; $\mathrm{TeCH_2Si(C}\mathit{H}_3)_3$), 0.02 (s, 9H; $\mathrm{TeCH_2\text{-}Si(C}\mathit{H}_3)_3$). Complete assignment of the $^{13}C\{^1H\}$ NMR spectrum was not possible, and the data is reported by carbon type: $\delta = 172.8$, 172.4, 171.6, 171.3 ($\mathrm{N}\mathit{C}\mathrm{C(CH_3)_3}$); 145.0, 144.7, 144.4, 143.2, 143.0, 141.4, 141.3, 141.0, 140.6, 127.4, 127.1, 126.9, 125.4, 125.2, 125.1, 124.2 ($\mathit{C}_6\mathrm{H}_3$); 89.5, 89.0, 87.8, 87.7 ($\mathit{C}\mathrm{H}$); 45.5, 45.3, 45.1, 44.9 ($\mathrm{NC}\mathit{C}\mathrm{(CH_3)_3}$); 33.0, 32.9, 32.73, 32.67 ($\mathrm{NCC(}\mathit{C}\mathrm{H_3)_3}$); 32.5, 31.6, 31.2, 31.0, 30.8, 29.8, 29.7, 29.1, 29.0, 28.95, 28.89, 28.8, 27.0, 26.9, 26.7, 26.6, 26.0, 25.8, 25.5, 24.7, 24.6, 24.5, 24.3 (23 of 24 peaks are observed for ($\mathit{C}\mathrm{H(CH_3)_2}$) and ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$)); 0.51, 0.48, 0.04, -0.04 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$); -24.0, -24.1, -24.4, -24.8 ($\mathrm{ScTe}\mathit{C}\mathrm{H_2}$); elemental analysis calcd for $C_{78}H_{128}N_4Si_2Te_3Sc_2$ (%): C 56.75, H 7.82, N 3.39; found: C 56.67, H 8.16, N 3.42.

Crossover experiment: To separate solutions of **1a** (0.011 g, 0.016 mmol) and $L^1Sc(CH_2CMe_3)_2$[14] (0.011 g, 0.016 mmol) in C_6D_6 were added two equivalents of $\mathrm{TeP}\mathit{n}\mathrm{Bu_3}$. The resulting solutions of **1b** and $L^1Sc(TeCH_2CMe_3)_2$ were combined in an NMR tube; two days later, the supernatant containing dialkyl tellurides, was decanted from the deposited yellow crystals of **1d** and assayed by ^1H and ^{125}Te NMR spectroscopy. ^1H NMR: $\delta = 2.58$ (s, 2H; $\mathrm{Te(C}\mathit{H}_2\mathrm{C(CH_3)_3)(CH_2Si(CH_3)_3)}$), 2.55 (s, 4H; $\mathrm{Te(C}\mathit{H}_2\mathrm{C(CH_3)_3)_2}$), 1.63 (s, 4H; $\mathrm{Te(C}\mathit{H}_2\mathrm{Si(CH_3)_3)_2}$), 1.57 (s, 2H; $\mathrm{Te(CH_2C(CH_3)_3)(C}\mathit{H}_2\mathrm{Si(CH_3)_3)}$), 0.97 (brs, 27H; $\mathrm{Te(CH_2C(C}\mathit{H}_3)_3)_2)$ and $\mathrm{Te(CH_2C(C}\mathit{H}_3)_3)\mathrm{(CH_2Si(CH_3)_3)}$), 0.09 (brs, 27H; $\mathrm{Te(CH_2Si(C}\mathit{H}_3)_3)_2)$ and $\mathrm{Te(CH_2C(CH_3)_3)(CH_2Si(C}\mathit{H}_3)_3)$); $^{125}Te\{^1H\}$ NMR: $\delta = 36.7$ ($Te(CH_2C\text{-}(CH_3)_3)_2)$), 34.5 ($Te(CH_2C(CH_3)_3)(CH_2Si(CH_3)_3)$), 33.9 ($Te(CH_2Si\text{-}(CH_3)_3)_2$).

Acknowledgement

Financial support for this work was provided by the Petroleum Research Fund (no. 33436-AC3) as administered by the American Chemical Society. L.K.K. and W.E.P. thank Ms. Q. Wu for help with NMR spectroscopy. W.E.P. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1996–2000).

---

[1] a) H. Schumann, J. A. Meese-Marktscheffel, L Esser, *Chem. Rev.* **1995**, *95*, 865; b) F. T. Edelmann in *Comprehensive Organometallic Chemistry II, Vol. 4* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**.

[2] L. W. M. Lee, W. E. Piers, M. R. J. Elsegood, W. Clegg, M. Parvez, *Organometallics* **1999**, *18*, 2947.

[3] a) W. E. Piers, L. R. MacGillivray, M. J. Zaworotko, *Organometallics* **1993**, *12*, 4723; b)W. E. Piers, D. J. Parks, L. R. MacGillivray, M. J. Zaworotko, *Organometallics* **1994**, *13*, 4547; c) W. E. Piers, *J. Chem. Soc. Chem. Commun.* **1994**, 309.

[4] a) J. Arnold, *Prog. Inorg. Chem.* **1995**, *43*, 353, and references therein; b) U. Siemeling, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 67.

[5] a) D. E. Gindelberger, J. Arnold, *Organometallics* **1994**, *13*, 4462; b) V. Christou, J. Arnold *J. Am. Chem. Soc.* **1992**, *114*, 6240; c) C. P. Gerlach, V. Christou, J. Arnold, *Inorg. Chem.* **1996**, *35*, 2758.

[6] a) V. Christou, J. Arnold, *Angew. Chem.* **1993**, *105*, 1551; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1450; b) C. P. Gerlach, J. Arnold, *Inorg. Chem.* **1996**, *35*, 5770.

[7] a) D. R. Cary, J. Arnold, *J. Am. Chem. Soc.* **1993**, *115*, 2520; b) D. R. Cary, J. Arnold, *Inorg. Chem.* **1994**, **33**, 1791; c) D. R. Cary, G. E. Ball, J. Arnold, *J. Am. Chem. Soc.* **1995**, *117*, 3492.

[8] Related aluminum chalcogen chemistry: a) C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2000**, *112*, 1885; *Angew. Chem. Int. Ed.* **2000**, *39*, 1815; b) C. Cui, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, *Organometallics* **1999**, *18*, 5120.

[9] Binary scandium tellurides: a) J. G. White, J. P. Dismukes, *Inorg. Chem.* **1965**, *4*, 1760; b) P. A. Maggard, J. D. Corbett, *Angew. Chem.* **1997**, *109*, 2062; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1974.

[10] B. Qian, W. J. Scanlon, M. R. Smith III, *Organometallics* **1999**, *18*, 1693, and references therein.

[11] a) P. H. M. Budzelaar, A. B. van Oort, A. G. Orpen, *Eur. J. Inorg. Chem.* **1998**, 1485; b) a similar phenomenon has been noted in related aminidinato complexes: S. Dagorne, R. F. Jordan, V. G. Young, Jr., *Organometallics* **1999**, *18*, 4619.

[12] R. A. Zingaro, B. H. Steeves, K. J. Irgolic, *J. Organomet. Chem.* **1965**, *4*, 320.

[13] a) Crystals were grown from toluene or benzene solution, with hexanes added to varying degrees. The structures were solved by using direct methods with or without a fragment search using either DIRDIF-96[13b] or SHELXS-86[3c] software. Refinement was performed with a full-matrix least squares analysis on F^2 using SHELXL-93.[13d] Crystal data for **2b**: $C_{46}H_{82}N_2ScSi_2Te_2$, $M_r = 1019.48$, $0.36 \times 0.29 \times 0.18$, monoclinic, $P2_1/c$, $a = 14.9661(9)$, $b = 17.8415(12)$, $c = 20.4884(14)$ Å, $\beta = 102.4175(14)°$, $V = 5342.8(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.267$ g cm^{-3}, $Mo_{K\alpha}$ ($\lambda = 0.71073$), $T = -80$ °C, no. of reflections = 26048, independent reflections = 10941, $2\theta_{max} = 52.82$, $\mu = 1.282$ mm^{-1}, min/max transmission = 0.6711–0.8433, $R_1 = 0.0307$, $wR_2 = 0.0713$, GOF = 0.928, no. of parameters = 461, largest difference peak/hole = 0.556/ – 0.533 e Å^3. Crystal data for **1d**: $C_{58}H_{82}N_4Sc_2Te_2$, $M_r = 1180.40$, $0.26 \times 0.18 \times 0.16$, monoclinic, $P2_1/n$ (a nonstandard setting of $P2_1/c$), $a = 13.5911(8)$, $b = 14.6989(8)$, $c = 15.4220(8)$ Å, $\beta = 108.1600(10)°$, $V = 2927.5(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.339$ g cm^{-3}, MoKα ($\lambda = 0.71073$), $T = -80$ °C, no. of reflections = 16458, independent reflections = 5574, $2\theta_{max} = 51.40$, $\mu = 1.246$ mm^{-1}, min/max transmission = 0.6702–0.8310, $R_1 = 0.0306$, $wR_2 = 0.0768$, GOF = 0.969, no. of parameters = 300, largest difference peak/hole = 0.404/ – 0.372 e Å^3. Crystal data for **2c**: $C_{78}H_{128}N_4Sc_2Si_2Te_3$, $M_r = 1650.74$, $0.61 \times 0.48 \times 0.44$, monoclinic, $P2_1/n$ (a nonstandard setting of $P2_1/c$), $a = 14.5576(8)$, $b = 20.4943(11)$, $c = 14.8955(8)$ Å, $\beta = 104.5719(9)°$, $V = 4301.1(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.275$ g cm^{-3}, $Mo_{K\alpha}$ ($\lambda = 0.71073$), $T = 0$ °C, no. of reflections = 21036, independent reflections = 8801, $2\theta_{max} = 52.80$, $\mu = 1.222$ mm^{-1}, min/max transmission = 0.4915–0.6697, $R_1 = 0.0275$, $wR_2 = 0.0745$, GOF = 1.040, no. of parameters = 403, largest difference peak/hole = 0.688/ – 0.347 e Å^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145090 (**2b**), CCDC-145089 (**1d**), and CCDC-145091 (**2c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk); b) P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israil, J. M. M. Smits, The DIRDIF Program System, Crystallographic Laboratory, University of Nijmegen, The Netherlands, **1996**; c) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467; d) G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Determination, Universität Göttingen, Germany, **1993**.

[14] P. G. Hayes, L. K. Knight, L. W. M. Lee, W. E. Piers, M. Parvez, unpublished results.

[15] These compounds were identified by separate synthesis: R. W. Gedridge, Jr., K. T. Higa, R. A. Nissan, *Organometallics* **1991**, *10*, 286.

[16] A control experiment showed that scrambling of $Te(CH_2CMe_3)_2$ and $Te(CH_2SiMe_3)_2$ did not occur in the presence of **1d**.

[17] W. E. Piers, G. Ferguson, J. F. Gallagher, *Inorg. Chem.* **1994**, *33*, 3784.

Received: August 30, 2000 [F2701]