Organometallics **1993,** *12,* 4723-4725 4723

Reversible Interconversion of Permethylscandocene Tellurolates and Tellurides. X-ray Structure of $[(C_5Me_5)_2Sc]_2(\mu\text{-}Te)$

Warren E. Piers,[*,†] Leonard R. MacGillivray,[‡] and Michael Zaworotko[‡]

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3

Received July 22, 1993[⊗]

*Summary: Permethylscandocene tellurolates were synthesized by insertion of tellurium into the scandium–carbon bonds of the corresponding alkyl complexes. These tellurolates were found to be thermally unstable toward elimination of TeR_2, forming the dimeric scandium μ-telluride $Cp^*{}_2Sc{-}Te{-}ScCp^*{}_2$ (**2**). Photochemically induced reversion of the thermal reaction was observed when a mixture of **2** and TeR_2 was irradiated under a UV lamp through a Pyrex filter. X-ray analysis of **2** reveals an Sc–Te distance of 2.7528(12) Å and an Sc–Te–Sc angle of 172.07°. These data, coupled with allene-like orientation of the Cp* rings about the Sc–Te–Sc unit, suggest significant π-bonding between scandium and tellurium in this compound. Crystal data for **2**: tetragonal space group $P\bar{4}2_1c$, $a = 15.0324(7)$ Å, $c = 18.8884(14)$ Å, $\alpha, \beta, \gamma = 90°$, $V = 4268.3(4)$ Å^3, $Z = 4$, $R = 0.040$, $R_w = 0.034$ for 2092 reflections with $I > 3\sigma(I)$.*

Early-transition-metal[1] and lanthanide[2] complexes containing tellurium-based ligands are receiving increasing attention, in part due to their potential as low-temperature precursors to various binary materials M_nTe_m.[3] Furthermore, the chemistry of these molecular species can provide glimpses of the molecule-to-bulk solid transformations that occur *en route* to these materials through the observation and isolation of intermediate structures.[2,4] Despite recent advances,[5] synthetic routes to early-metal tellurolates are limited by the lack of general access to suitable tellurium reagents such as stable tellurols[6] or main-group-metal tellurolates.[7] A promising and perhaps more general route involves the direct formation of tellurolate derivatives by reaction of tellurium transfer agents with early-transition-metal alkyl complexes.[8] Herein we describe the facile generation of scandocene tellurolates by this method and their thermal transformation to a dimeric scandocene μ-telluride by loss of a dialkyl telluride. We also report the facile photochemical reversal of this fundamental tellurolate-to-tellurides conversion and the solid-state structure of $[(C_5Me_5)_2Se]_2(\mu\text{-}Te)$.

Treatment of the decamethylscandocene alkyl $Cp^*{}_2ScCH_2SiMe_3$ ($Cp^* = C_5Me_5$) with 1 equiv of elemental tellurium (50–60 °C in hexanes) resulted in the slow uptake of tellurium and formation of the orange, hydrocarbon-stable tellurolate derivative $Cp^*{}_2ScTeCH_2SiMe_3$ (**1a**)[9] (Scheme I). Although attempts to measure the $^{125}Te\{^1H\}$ NMR spectrum of these compounds failed to locate a resonance,[10] tellurium insertion was implicated by the downfield shift of the methylene protons from 0.42 ppm in $Cp^*{}_2Sc(CH_2SiMe_3)$ to 2.42 ppm in **1a**. Alternatively, **1a** was produced rapidly and quantitatively under ambient conditions using $TeP\text{-}n\text{-}Bu_3$[11] as a tellurium transfer agent[4,12] but, because of the high solubility of **1a**, complete removal of PBu_3 proved difficult when this method was used. Use of the phosphine telluride was the method of choice for the synthesis of $Cp^*{}_2ScTeCH_2Ph$ (**1b**), which precipitates from hexane solution upon addition of $TeP\text{-}n\text{-}Bu_3$ to the benzyl derivative. Although **1a** and **1b** are the only well-characterized tellurolates reported here, we have observed tellurium insertions into other Sc–C(sp^3) bonds ($R = CH_3$, $CH_2CH_2\text{-}t\text{-}C_4H_9$) and, thus, the reaction appears to be general.

Heating solutions of **1a** and **1b** at moderate temperatures (90–130 °C, **1a**; 50–70 °C, **1b**) led to slow decomposition by extrusion of TeR_2,[14] yielding a telluride-bridged dimer of composition $Cp^*{}_2Sc{-}Te{-}ScCp^*{}_2$ (**2**). Interestingly, **2** was accessed preparatively via a separate reaction involving $Cp^*{}_2ScD$[13] and 0.5 equiv of $TeP\text{-}n\text{-}Bu_3$.[15] Vigorous evolution of gas, presumably D_2, was observed on mixing,

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† University of Guelph.

‡ Saint Mary's University.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1993.

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[8] (a) Tainturier, G.; Gautheron, B.; Fahim, M.; Trouvé-Bellan, G. *J. Organomet. Chem.* **1989,** *376,* 321. (b) Köpf, H.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1986,** 1192. (c) McGregor, K.; Deacon, G. B.; Dickson, R. S.; Fallon, G. D.; Rowe, R. S.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1990,** 1293.

[9] All new compounds were characterized by microanalysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (see the supplementary material).

[10] The effects of the quadrupolar ^{45}Sc nucleus ($I = {}^7/_2$, 100%) appear to preclude measurement of the ^{125}Te resonance in solution.

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

[12] Treatment of 1 with PMe_3 results in rapid adduct formation, as evidenced by the significant shift in ligand resonances in the ^1H NMR spectrum (see the supplementary material). A similar change in the chemical shift pattern for 1 is not observed in the presence of $P\text{-}n\text{-}Bu_3$; rather, signals for unligated 1 and free $P\text{-}n\text{-}Bu_3$ are observed.

[13] Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987,** *109,* 203.

[14] Gedridge, R. W., Jr.; Higa, K. T.; Nissan, R. A. *Organometallics* **1991,** *10,* 286.

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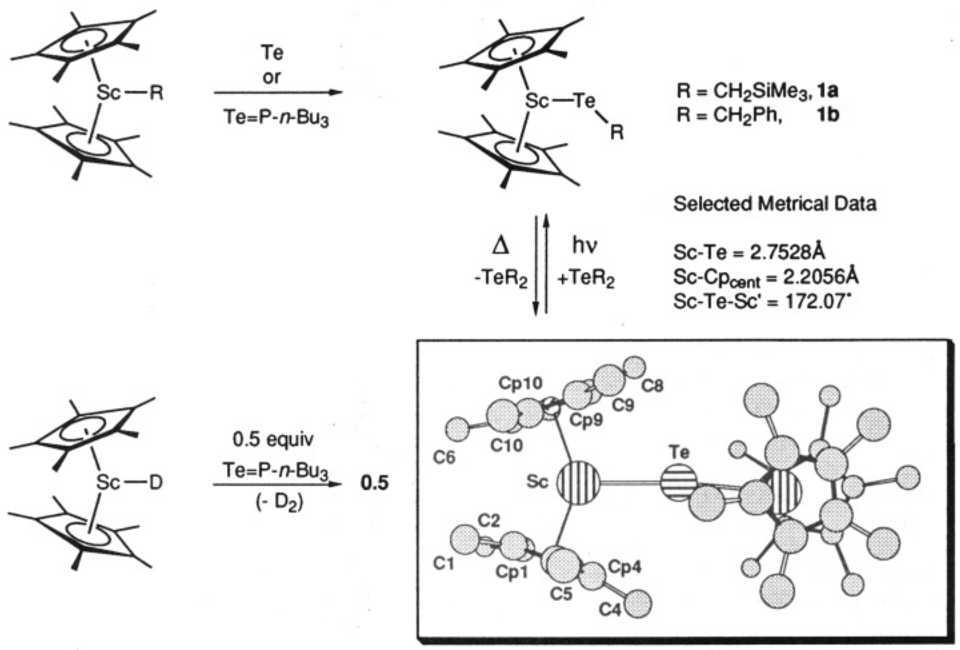
Scheme I



with precipitation upon cooling of an orange solid (85% isolated yield) which was found to be spectroscopically identical with **2** produced via thermolysis of tellurolates **1**. Microanalytical data and X-ray analysis on single crystals of **2** (*vide infra*) confirmed its dimeric structure.

While the extrusion of organic tellurides of form metal tellurides has precedence in early-metal tellurolate chemistry,[1,2] the reverse process has to our knowledge not been observed. We were thus surprised to observe very clean, complete *photochemical* reversal of the process to re-form tellurolate **1**. As Figure 1 shows, an approximately 1:1 mixture of telluride **2** and TeR_2 in benzene-d_6 is converted quantitatively to **1** after 30 min of irradiation through a Pyrex filter using a mercury lamp. Heating the sample at 110 °C results in slow reversion ($t_{1/2} \approx 2$ days) back to the original mixture. While we do not understand this reaction in detail yet, preliminary experiments point to **2** as being the photoactive species in the system, an excited state of which reacts with organotelluride. The absorption spectrum[16] of **2** shows that it absorbs strongly in both the visible and UV portions of the spectrum (297 nm, ϵ = 13 500; 383 nm, ϵ = 15 300; 447 nm, ϵ = 5500); the dialkyl telluride absorbs only in the UV region. Irradiation of a solution of just TeR_2 under identical conditions shows that it is unaffected after 30 min. Likewise, irradiation of a solution of **2** in the absence of a trapping agent leaves the telluride unchanged even after several hours. The remarkable efficiency of the reaction has allowed us to use it preparatively in the synthesis of pure samples of **1a** in high yield, and we are continuing to probe its mechanism, synthetic utility, and generality.

Complex **2** is the first crystallographically characterized compound containing a scandium–tellurium bond. Its molecular structure (Scheme 1) shows that, as expected on the basis of qualitative molecular orbital consider-

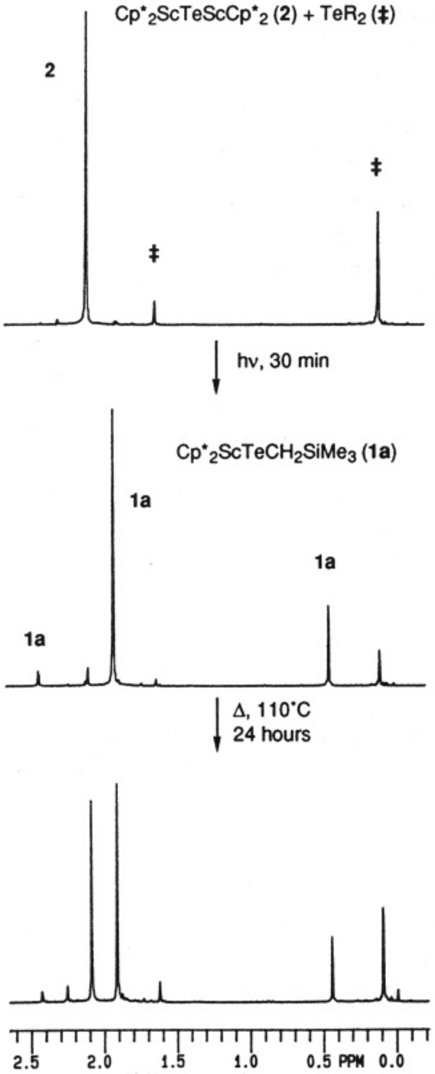


Figure 1. ^1H NMR spectra (200 MHz): (top) a sample of **2** and $Te(CH_2SiMe_3)_2$ in C_6D_6 prior to irradiation; (middle) the same sample after irradiation for 30 min, showing almost complete conversion to **1a**; (bottom) the same sample after heating for 24 h in the dark at 110 °C.

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(15) Group 4 metallocene hydrides produce μ-tellurides when reacted with elemental tellurium: Tainturier, G.; Gautheron, B.; Fahim, M. *J. Organomet. Chem.* **1989**, *373*, 193.

(16) The emission spectrum of **2** shows that irradiation at either 297 or 383 nm gives an emission peak at 525 nm, similar to the photophysical behavior reported recently for related monomeric permethylscandocene complexes: Pfennig, B. W.; Thompson, M. E.; Bocarsly, A. B. *Organometallics* **1993**, *12*, 649.

ations,[17] the two bent Cp^*_2Sc units are arranged in an allene-like array around the μ-telluride.[18] The near-linear geometry (Sc–Te–Sc = 172.07°) of the μ-telluride ligand in **2** is unusual[19] in that all other structurally characterized M–Te–M[20] complexes contain bent μ-telluride ligands, the electronically favored geometry for Te^{2-}.[21] Indeed, the largest M–Te–M angle (165.9°) previously known was found in $[(ddpe)V(CO)_3]_2(\mu\text{-}Te)$[19e] when other members of the series (μ-S, μ-Se) were linear at the chalcogenide. While the angles in **2** and $[(dppe)V(CO)_3]_2(\mu\text{-}Te)$ are essentially linear, an alternate view is that they are as bent as possible, given the constraints of the respective ligand environments. The linear chalcogenide bridges in these and other systems have been attributed to strong π-bonds between the bridging atom and two 15-electron metal centers, forming M≡E≡M units.[22] Such a functionality is impossible in this system (each scandocene unit in **2** is formally a 13-electron fragment, imposing a maximum bond order of 2.0 for the Sc–Te bonds); however, the near-linearity of the Sc–Te–Sc unit, the orientation of the Cp^*_2Sc moieties with respect to each other, and the "shortness" of the Sc–Te bonds (2.7528 Å vs $Sc\text{–}Te_{calc}$ = 2.89[23] or 2.96 Å[24]) indicate significant π-bonding is occurring between scandium and tellurium.

Both the thermal and the photochemical reactions reported here shed fundamental insights on processes important in the production of metal telluride materials from organometallic precursors. The apparent generality of these reactions for organoscandium compounds has made more detailed mechanistic studies possible; we will report these results shortly.

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

Supplementary Material Available: Text giving experimental details and analytical data and tables of spectroscopic data for compounds **1a,b** and **2** and tables of crystal, collection, and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, H atom coordinates, and anisotropic thermal parameters for compound **2** (7 pages). Ordering information is given on any current masthead page.

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[17] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[18] The dihedral angle between the planes defined by each scandium and the Cp centroids associated with it is 91.4°.

[19] The complex $Cp^*_2Yb\text{–}Se\text{–}YbCp^*_2$ is isostructural: Berg, D. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1858.

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[22] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56.

[23] Based on addition of covalent radii: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[24] On the basis of addition of ionic radii Sc^{3+} has a radius of 0.89 Å (Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751) and Te^{2-} a radius of 2.07.[21]