Inorg. Chem. **1995,** *34,* 2499−2500 **2499**

Permethyltitanocene Tellurides and Ditellurides. X-ray Structures of $[(C_5Me_5)_2Ti]_2(\mu\text{-}Te)$ and $(C_5Me_5)_2Ti(\eta^2\text{-}Te_2)$

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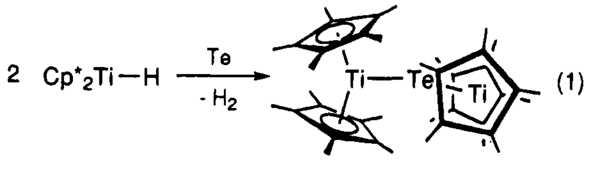
Received January 5, 1995

We have described aspects of the thermal and photochemical interchange between formally d^0 permethylscandocene tellurolates and tellurides.[1] In these compounds, the principle absorptions were tellurium to scandium charge transfer bands which resulted in population of the nonbonding (with respect to tellurium) $1a_1$ orbitals on the metallocene fragment.[2] The observed photochemistry was a consequence of the scandium−tellurium bond weakening which occurred upon irradiation.[1c]

This qualitative picture of the photochemical behavior of Cp^*_2ScTeR and $[Cp^*_2Sc]_2(\mu\text{-}Te)$ led us to postulate that population of the metallocene $1a_1$ orbitals would attenuate the photoreactivity leading to M−Te bond breakage. We have thus initiated development of the analogous permethyltitanocene(III) chemistry. While we have observed similarities between the two manifolds of chemistry, the d^1 titanocene derivatives are indeed less photochemically reactive; on the other hand, new avenues of thermal and redox chemistry not available to the scandium compounds have been uncovered, which we report herein.

Contrary to facile tellurium insertion reactions into scandium−carbon bonds, attempts to generate permethyltitanocene(III) tellurolates[3] via reaction of tellurium with Cp^*_2TiR (R = CH_3, Np) alkyls were not successful; however, treatment of Cp^*_2TiH[4] with 0.5 equiv of elemental tellurium led to the evolution of gas and a dark red solution from which a red-brown, paramagnetic solid, **1**, was isolated (eq 1). A parent ion at *m*/*e* = 766 in the mass spectrum of **1** indicated a dimeric structure which was confirmed via X-ray analysis (Figure 1).[5]



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As in the scandium congener,[1c] an "allene-like" arrangement of opposing Cp^*_2Ti units minimizes steric repulsions between Cp* rings while maximizing π bonding between titanium and tellurium. Significant π-interaction is reflected in the comparatively short Ti−Te distances of 2.705(3) and 2.697(3) Å relative to previously determined Ti−Te lengths of 2.788(1) Å in d^0 $Cp^{Me}{}_2Ti^{IV}(TeR_2)_2$ and 2.912(3) or 2.879(3) Å for crystallographically independent molecules of $Cp_2Ti^{III}(TeR)PMe_3$ (R = $Si(SiMe_3)_3$).[3] The Ti−Te−Ti bond angle of 168.62(8)° deviates from linearity to a slightly greater degree than in the scandium analog where the corresponding angle was 172.07(5)°.

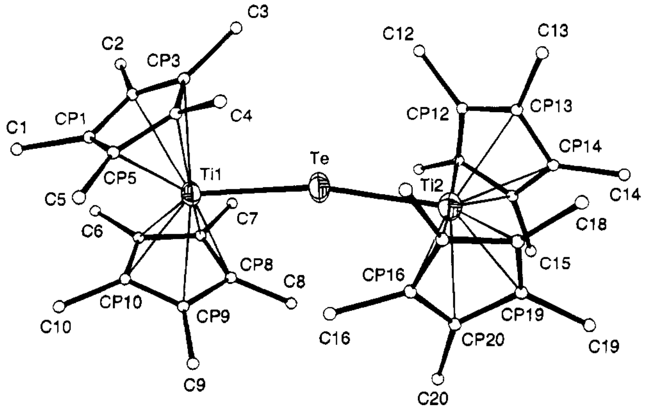

Figure 1. Molecular structure of $[Cp^*_2Ti]_2(\mu\text{-}Te)$, **1**. Selected bond lengths (Å): Ti1−Te, 2.705(3); Ti2−Te, 2.697(3). Selected Bond Angle (deg): Ti1−Te−Ti2, 168.62(8). Dihedral angle between planes containing $Cp^*_{cent}-Ti-Cp^*_{cent}$ (deg): 94.6.

In contrast to other Ti(III)−Ti(III) dimers,[6] no strong evidence was found for magnetic coupling through the tellurium bridge between the Ti(III) centers in **1**. The compound's ESR spectrum (g = 1.977 relative to DPPH, g = 2.0037, in hexanes (10^{-4} M) at 298 K) was broad and featureless. Variable temperature susceptibility measurements showed that, between the range of 80−250 K, normal Curie−Weiss behavior was followed (Θ = −25.6 K, μ_{eff} = 2.1 μ_B per dimer).[7] The lack of significant coupling between the d^1 titanium centers may be due to the fact that the SOMO $1a_1$ bent metallocene orbitals,[2] in which the electrons likely reside, are nonbonding with respect to tellurium, precluding superexchange pathways. Similar magnetic behavior was observed in related bent metallocene μ-chalcogenides of ytterbium and samarium.[8] Thus, the compound behaves as if each titanium center is an individual paramagnet, albeit with a somewhat depressed value of μ_{eff} compared with the expected spin-only value of 2.87 μ_B. The low observed magnetic moment

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

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(5) Crystal data for **1**: $C_{40}H_{60}Ti_2Te$, 0.20 × 0.25 × 0.30 mm, triclinic, $P\bar{1}$ a = 8.9445(17) Å, b = 12.186(2) Å, c = 18.876(4) Å, α = 77.35(4)°, β = 83.60(3)°, γ = 73.638(20), V = 1923.4(6) Å^3, Z = 2, ρ_{calc} = 1.32 mg m^{-3}, $2\theta_{max}$ = 45°, Mo Kα radiation, λ = 0.709 30 Å, ω scan mode, T = 298 K, 5194 measured reflections, 5013 independent, 2671 reflections with $I_{net} > 3.0\sigma(I_{net})$, μ = 1.18 mm^{-1}, min/max transmission = 0.793 and 0.990, $R(F)$ = 0.056, R_w = 0.055, GoF = 2.24.

(6) Jungst, R.; Sekutowski, D.; Davis, J.; Lulu, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.

(7) A maximum at ca. 4 K was observed in the $1/\chi$ vs T plot; however, caution in drawing conclusions based on this plot must be advised due to the low number of data points defining this maximum. Clearly the antiferromagnetic coupling, if present, is very weak in **1**.

(8) Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865.

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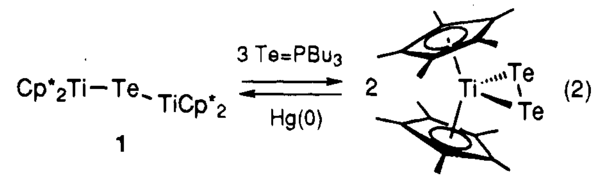
may be a result of intermolecular interactions, a notion which is supported by the non-zero value of Θ.[9,10]

The UV spectrum[11] of **1** is more complex than that of the scandium congener[1c] and, although charge transfer bands are present, **1** does *not* react photochemically with $Te(CH_2SiMe_3)_2$ when irradiated with visible light. Instead, **1** undergoes further thermal reaction with tri-*n*-butylphosphine telluride (3 equiv) to form a deep red, diamagnetic titanium(IV) species of stoichiometry $[Cp^*_2TiTe_2]_n$, **2** (eq 2). A parent ion in the mass spectrum of **2** at 574 *m*/*e* was indicative of a monomeric species.[12] The ^{125}Te and ^{123}Te NMR spectra both had resonances at 1463 ppm (relative to $TeMe_2$ at 0.0 ppm) and in the ^{123}Te spectrum, satellites due to the $^{123}Te-^{125}Te$ isotopomer were observed ($^1J_{Te-Te}$ = 1603 Hz) implying the presence of an η^2-Te_2 ligand.



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(2)

X-ray analysis of **2** (Figure 2)[13] confirmed a monomeric structure in which the η^2-Te_2^{2-} ligand is bonded to the titanium center and lies in the plane bisecting the Cp* rings forming an isosceles triangle with titanium at the apex. The Ti–Te distance of 2.808(3) Å is longer than those found in **1** and more reflective of Ti(IV)–Te single bonds (*vide supra*). The Te–Te distance of 2.7030(18) Å is comparable to those in other η^2-Te_2 complexes[14] and based on Te–Te distances in Te_2 (2.59(2) Å[15]) and elemental tellurium (2.835 Å[16]), the Te–Te bond order in **2** is between 1 and 2.

We have begun to explore the reactivity of **2** and found it to be an efficient "Te" and "Te_2" transfer agent. For example, **2** was converted quantitatively back to the μ-telluride dimer **1** when stirred with excess elemental mercury (eq 2). This reaction was performed to probe the role of "$Cp^*_2Ti{=}Te$",[17] in the production of **2** from **1** and tellurium; however even when **2** was treated with elemental mercury in the presence of Lewis base traps such as pyridine, (*N*,*N*-dimethylamino)pyridine, or PMe_3, the only product isolated from the reactions was **1**.

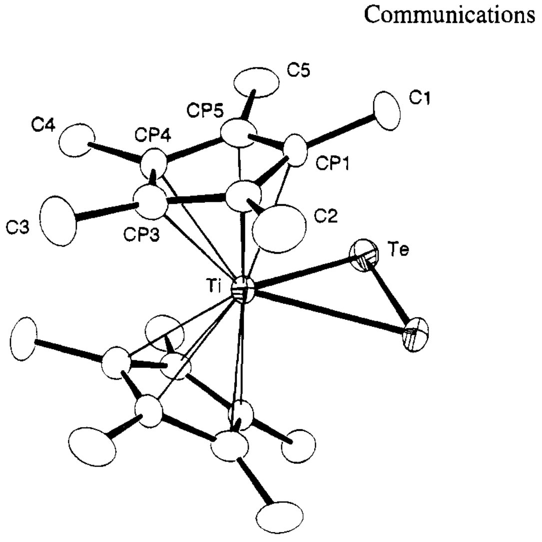
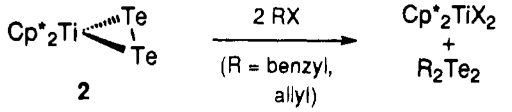


Figure 2. Molecular structure of $Cp^*_2Ti(\eta^2$-$Te_2)$, **2**. Selected bond lengths (Å): Ti–Te, 2.808(3); Te–Te(a), 2.7030(18). Selected Bond Angles (deg): Te(a)–Te–Ti, 61.23(4); Te–Ti–Te(a), 57.53(7).

Ditelluride **2** reacts with alkyl halides in a Te_2 transfer reaction to produce $Cp^*_2TiCl_2$ and ditelluride or telluride derivatives (eq 3). For example, benzyl chloride reacts rapidly with **2** and if the reaction is performed in the dark, dibenzyl ditelluride[18] may be isolated in 60% yield. Allyl bromide initially gives diallyl ditelluride, which rapidly decomposes to diallyl telluride[19] with loss of elemental tellurium. The failure to observe **1** in these reactions suggest that **2** transfers the Te_2 ligand as a unit. We are exploring the scope and mechanism of these reactions further and will report these results in due course.



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(3)

Acknowledgment. Funding from NSERC (Canada) in the form of Research Grants to W.E.P. and M.J.Z. is gratefully acknowledged. W.E.P. thanks Professors Sandro Gambarotta (Ottawa) and Martha Greenblatt (Rutgers) for magnetic moment measurements.

Supplementary Material Available: Text giving experimental details and listings of crystallographic data, atomic parameters, hydrogen parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** and **2** (15 pages). Ordering information is given on any current masthead page.

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[9] Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders: Toronto, 1992; p 475.

[10] Owing to the poor solubility of **1** in hydrocarbon solvents, measurement of the magnetic moment in solution via the Evans method was not possible.

[11] UV/vis of **1** (peak position in nm, ϵ): 715, 900; 581, 4500; 471, 11 900; 424, 9100, 360, 7900; 295, 12 250; 238, 15 850.

[12] Fenske, D.; Grissinger, A. *Z. Naturforsch.* **1990**, *45B*, 1309.

[13] (a) Crystal data for **2**: $C_{20}H_{30}TiTe_2$, 0.30 × 0.30 × 0.35 mm, orthorhombic, *F2dd*, a = 9.266(4) Å, b = 16.902(7) Å, c = 27.356(14) Å, V = 4265(3) Å^3, Z = 8, ϱ_{calc} = 1.79 mg m^{-3}, $2\theta_{max}$ = 50°, Mo Kα radiation, λ = 0.709 30 Å, ω scan mode, T = 298 K, 1054 measured reflections, 1039 independent, 949 reflections with $I_{net} > 3.0\sigma(I_{net})$, μ = 1.18 mm^{-1}, min/max transmission = 0.765 and 0.998, $R(F)$ = 0.037, R_w = 0.044, GoF = 2.92. The enantiomorph was fixed by including Friedel reflections in the least squares refinement and refining Rogers chirality η.[13b] A value of 1.1 was obtained for chirality η. (b) Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734.

[14] Other monomeric η^2-Te_2 complexes: (a) Howard, W. A.; Parkin, G.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 25. (b) Shin, J. H.; Parkin, G. *Organometallics* **1994**, *13*, 2147. (c) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 9822. (d) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916.

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