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Mechanistic Aspects of the Thermal and Photochemical Interconversion of Permethylscandocene Tellurolates and Tellurides. X-ray Structures of $(C_5Me_5)_2ScTeCH_2C_6H_5$, $[(C_5Me_5)_2Sc]_2(\mu\text{-}Te)$, and $[(C_5Me_5)_2Sc]_2(\mu\text{-}Se)$

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Treatment of $Cp^*{}_2ScR$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = CH_2SiMe_3, $CH_2C_6H_5$, *erythro*-CH(D)CH(D)-*t*-C_4H_9, $CH_2CH(D)CH_2CH_2CH{=}CMe_2$, C_6H_5, $CH_2(c\text{-}C_5H_9)$) with 1 equiv of elemental tellurium or Te=P-*n*-Bu_3 yields the tellurolates $Cp^*{}_2ScTeR$ (**1a-e,g**) in moderate to good yields (31−71%). The tellurolates are monomeric, as inferred from the X-ray structure of **1b** (Sc-Te = 2.8337(14) Å; Sc−Te−C = 121.61(21)°). Insertion of elemental selenium into the Sc−C bond of $Cp^*{}_2ScCH_2SiMe_3$ produces selenolate **3** (55%). Reaction of 0.5 equiv of tellurium or selenium with the deuteride $Cp^*{}_2ScD$ results in elimination of D_2 and production of chalcogenide dimers $[Cp^*{}_2Sc]_2(\mu\text{-}E)$ (E = Te (**2**), Se (**4**)). Evidence that the production of **2** proceeds via $Cp^*{}_2ScTeD$ is presented. The X-ray structures of **2** (Sc−Te = 2.7528(12) Å; Sc−Te−Sca = 172.07(5)°) and **4** (Se−Sc = 2.5425(16) Å; Sc−Se−Sca = 173.74(10)°) were performed and are reported for comparison. Telluride dimer **2** was also produced via the thermal (70−110 °C) or photochemical (λ > 290 nm) extrusion of TeR_2 from tellurolates **1a**−**d**. Further thermal reactions between **2** and TeR_2 were observed at higher temperatures, leading to a new scandium telluride of empirical formula Cp*ScTe. Experiments utilizing tellurolates **1c,d** indicate that both the thermal and photochemical eliminations of TeR_2 proceed without involving Te−C bond cleavage, leading to $R^\bullet$ intermediates. Photochemical reactions between **2** and TeR_2 substrates showed that the elimination process is photochemically reversible, leading to varying mixtures of compounds **1**, **2**, and TeR_2, depending on the nature of R. Use of $Te[(CH_2)_4CH{=}CH_2]_2$, which contains an alkyl group sensitive to the presence of $R^\bullet$, shows cyclization in the 5-hexenyl group leading to **1g**, indicating the involvement of radicals in the back-photoreaction. The presence of a photostationary equilibrium in these systems is further evidenced in the slow conversion of $Cp^*{}_2ScTe(CH_2)_4CH{=}CH_2$ (**1f**) to **1g** over prolonged irradiation periods. Comparison of the UV−visible spectra and the photochemistry associated with these tellurium compounds with their selenium congeners indicates that the primary photoevents in these reactions involve Te → Sc ligand to metal charge-transfer absorptions. Crystallographic data for **1b**, **2**, and **4** are as follows: **1b**, monoclinic, space group $P2_1/c$, a = 14.932(5) Å, b = 10.8122(8) Å, c = 17.496(8) Å, β = 113.64°, V = 2587.5(15) Å^3, Z = 4, R = 0.041, R_w = 0.038; **2**, tetragonal, space group $P42_1c$, a = 15.0324(7) Å, c = 18.8884(14) Å, V = 4268.3(4) Å^3, Z = 4, R = 0.040, R_w = 0.034; **4**, tetragonal, space group $P\bar{4}2_1c$, a = 14.7663(12) Å, c = 19.101(4) Å, Z = = 4, V = 4164.9(9) Å^3, R = 0.050, R_w = 0.043.

Introduction

The "inorganometallic" chemistry of molecular compounds containing transition metals and the heavier group 16 elements has undergone swift development over the past several years. The primary motivation for these advances has been the potential for homoleptic $M(ER)_n$ species to serve as convenient, low-temperature precursors of a wide variety of binary materials containing transition metals and selenium or tellurium in more controlled synthetic procedures.[1] While the materials of most interest are based on group 12/group 16 combinations,[2] early-transition-metal or lanthanide/group 16 element compounds have been important as model systems for studying the mechanisms by which metal chalcogenolates (MER) decomposed to $(ME_x)_n$ materials via metal chalcogenide (M=E) intermediates (eq 1).[3] The

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$$[M(ER)_2]_n \xrightarrow{\Delta} [ME]_n + nER_2 \qquad (1)$$

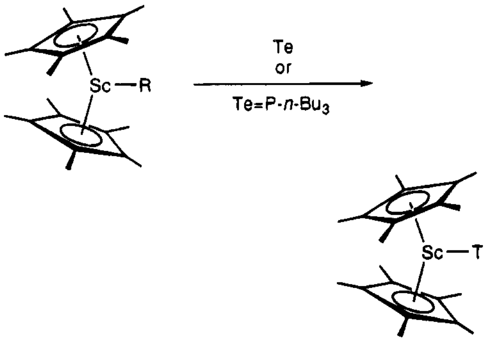
most relevant studies in this regard include those from the groups of Arnold, Bianconi, and Brennan, wherein homoleptic $M(ER)_n$ ($R = Si(SiMe_3)_3$, $E = Te$, $M = Zr$,[4] $M = La$,[5a] Eu;[5b] $R = 2,4,6\text{-}Me_3\text{-}C_6H_2$, $E = Te$, $M = Yb$;[6] $R = C_6H_5$, $E = Se$, $M = Eu$;[7] $R = C_6H_5$, $E = Se$, $M = Yb$[8]) derivatives were observed to thermally decompose with concomitant loss of TeR_2. In some instances, discreet molecular telluride complexes were trapped during the decomposition process. The subsequent conversion of these telluride precursors to metal telluride materials clearly implicated this tellurolate to telluride transformation as being important on the path from molecules to bulk materials.

Although numerous examples of this mode of decomposition now have been reported,[2d,4–8,9] relatively little is known concerning its intimate mechanistic details. Given the apparent generality of the dialkyl telluride extrusion process, it would be desirable to develop a more accurate picture of the mechanism (or mechanisms) by which this transformation takes place. Such information could, for example, be employed in the more logical design of molecular precursors to solids of defined stoichiometry and possibly structure. Since many of the systems in which this reaction has been observed are complicated by multiple extrusions, a mechanistic investigation would require a simplified, well-characterized model system in which the extrusion process may be isolated from further TeR_2 eliminations or other side reactions.

It occurred to us that molecules of general formula $Cp_2M(TeR)_n$ (M = group 4 metal, $n = 2$; M = group 3 metal, $n = 1$) would serve as useful models for intra- and intermolecular extrusion reactions, respectively. Arnold *et al.* have reported some chemistry concerned with the group 4 systems,[10] while we have focused on some permethylscandocene tellurolate derivatives, Cp^*_2ScTeR ($Cp^* = C_5Me_5^-$), which were observed to decompose thermally via the elimination of TeR_2 to form the dinuclear μ-telluride derivative $[Cp^*_2Sc]_2(\mu\text{-}Te)$.[11] The generality of the synthetic chemistry involved has allowed us to perform some mechanistic studies[12] which provided some information on the nature of this bimolecular extrusion process. An important finding which has emerged from our studies concerns the photoactivity of the tellurolate and telluride derivatives with respect to the process given in eq 1; we report here full details on the synthetic chemistry as well as our results concerning both the thermal and photochemical interconversion between permethylscandocene tellurolates and the telluride derivative $[Cp^*_2Sc]_2(\mu\text{-}Te)$.

Synthesis and Characterization of Permethylscandocene Chalcogenolates and Chalcogenides

The chemistry described herein began with the discovery of the facile insertion of tellurium into the scandium–carbon bond of $Cp^*_2ScCH_2SiMe_3$.[13] Use of either elemental tellurium or the tellurium transfer agent $Te{=}P\text{-}n\text{-}Bu_3$ allowed for incorporation of one tellurium atom to form the permethylscandocene tellurolate **1a** in good yield. This reaction was extended to include several different scandocene alkyl and aryl groups and appears to be quite general for $Sc{-}C_{sp^3}$ and $Sc{-}C_{sp^2}$ scandium–carbon bonds (eq 2).[14] Insertion reactions involving stronger $Sc{-}C_{sp}$ linkages[15] have not yet been attempted. The heterogeneous reaction proceeded slowly over the course of several hours, while the insertion occurred essentially upon mixing using $Te{=}P\text{-}n\text{-}Bu_3$ as the tellurium source; however, complete removal of the byproduct tri-*n*-butylphosphine in the latter method was in some cases difficult. While the phosphine does not coordinate the scandium center, some of the tellurolate products are highly soluble materials even in hexanes, making it difficult to wash the products thoroughly enough to be fully rid of trace amounts of the phosphine.



(2)

$R =$ $-CH_2SiMe_3$, **1a**
$-CH_2C_6H_5$, **1b**
erythro-$CH(D)CH(D)\text{-}t\text{-}C_4H_9$, **1c**
$-CH_2CH(D)(CH_2)_2CH{=}CMe_2$, **1d**
$-C_6H_5$ **1e**
$-CH_2(c\text{-}C_5H_9)$ **1g**

Taken together, microanalytical data, ^1H and $^{13}C\{^1H\}$ NMR spectra (Table 1), and an X-ray structural analysis on the benzyl tellurolate derivative **1b** (*vide infra*) convincingly demonstrated that tellurium insertion had

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[14] For the tellurolate **1a**, reaction with a further 0.5 equiv of tellurium was observed when excess tellurium was present. A red-brown compound that was analyzed for the formula $[Cp^*_2ScTeCH_2SiMe_3]_2(Te)$ was isolated (Anal. Calcd for $C_{48}H_{78}Sc_2Si_2Te_3$: C, 48.69; H, 6.64. Found: C, 48.82; H, 6.44). The structure of this compound is unknown, but the ^1H NMR spectrum indicates it possesses a high degree of symmetry (C_6D_6, ppm: 2.32, $TeCH_2$; 1.95, $C_5(CH_3)_5$; 0.31, $Si(CH_3)_3$). Interestingly, the benzyl tellurolate **1b** does *not* undergo further reaction with tellurium; therefore, it is not clear how general this reaction will be; nevertheless, these observations do illustrate the need for carefully controlling the stoichiometry of these insertion reactions.

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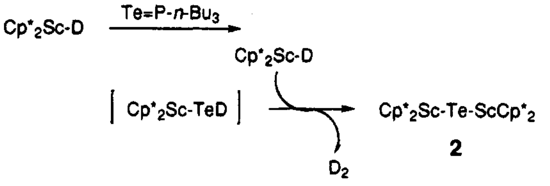
Table 1. ^{1}H and ^{13}C{^{1}H} NMR Data for Isolated New Compounds[a]

	^{1}H NMR[b]			^{13}C{^{1}H} NMR[b]		
compd	δ (ppm)	assign	*J* (Hz)	δ (ppm)	assign	*J* (Hz)
$\mathrm{Cp^*_2ScTeCH_2Si(CH_3)_3}$ (**1a**)	1.86	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		120.9	$\mathit{C}_5\mathrm{(CH_3)_5}$	
	2.42	$\mathrm{TeC}\mathit{H}_2$		11.7	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
	0.43	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$		5.7	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$	
				−23.8	$\mathrm{Te}\mathit{C}\mathrm{H_2}$	$J_{\mathrm{CTe}} = 190.3$
						$J_{\mathrm{CSi}} = 53.3$
						$J_{\mathrm{CH}} = 128.1$
$\mathrm{Cp^*_2ScTeCH_2C_6H_5}$ (**1b**)	1.88	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		123.1	$\mathit{C}_5\mathrm{(CH_3)_5}$	
	7.57	*o*-C*H*		12.1	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
	7.19	*m*-C*H*		148.3	*ipso*	
	7.02	*p*-C*H*		128.9	Ph	
	4.82	$\mathrm{TeC}\mathit{H}_2$		127.6	Ph	
				122.5	Ph	
				−1.8	$\mathrm{Te}\mathit{C}\mathrm{H_2}$	$J_{\mathrm{CTe}} = 164.8$
						$J_{\mathrm{CH}} = 142.3$
erythro-$\mathrm{Cp^*_2ScTeCH(D)CH(D)}$-*t*-$\mathrm{C_4H_9}$ (**1c**)	1.94	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		123.0	$\mathit{C}_5\mathrm{(CH_3)_5}$	
	3.45	$\mathrm{TeC}\mathit{H}\mathrm{(D)}$	13.6	12.1	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
	0.99	$\mathrm{C(C}\mathit{H}_3\mathrm{)_3}$		52.1	$\mathrm{TeCH(D)}\mathit{C}\mathrm{H(D)}$	$J_{\mathrm{CD}} = 19.5$
	c	$\mathrm{C}\mathit{H}\mathrm{(D)}$		33.4	$\mathit{C}\mathrm{(CH_3)_3}$	
				29.1	$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	
				−10.4	$\mathrm{Te}\mathit{C}\mathrm{H(D)CH(D)}$	$J_{\mathrm{CD}} = 20.9$
$\mathrm{Cp^*_2ScTeCH_2CH(D)CH_2CH_2CH{=}CMe_2}$ (**1d**)	1.95	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		122.4	$\mathit{C}_5\mathrm{(CH_3)_5}$	
	5.24(q)	$\mathrm{C}\mathit{H}\mathrm{{=}CMe_2}$	6.7	12.8	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
	3.27(m)	$\mathrm{C}\mathit{H}_2\mathrm{CH(D)}$	7.5	127.8	$\mathrm{{=}}\mathit{C}\mathrm{Me_2}$	
	2.08(m)	$\mathrm{C}\mathit{H}_2\mathrm{CH{=}}$		119.7	$\mathrm{{=}}\mathit{C}\mathrm{HCH_2}$	
	1.94	$\mathrm{C}\mathit{H}\mathrm{(D)}$		34.9	$\mathit{C}\mathrm{H(D)}$	$J_{\mathrm{CD}} = 19.7$
	1.66	$\mathrm{{=}CC}\mathit{H}_3\mathrm{Me}$		32.9	$\mathit{C}\mathrm{H_2CH{=}}$	
	1.60(m)	$\mathrm{CH(D)C}\mathit{H}_2$	7.7	27.9	$\mathit{C}\mathrm{H_2CH_2CH{=}}$	
	1.56	$\mathrm{{=}CC}\mathit{H}_3\mathrm{Me}$		25.9	$\mathrm{{=}C(}\mathit{C}\mathrm{H_3)}$	
				17.8	$\mathrm{{=}C(}\mathit{C}\mathrm{H_3)}$	
				−1.1	$\mathrm{Te}\mathit{C}\mathrm{H_2}$	
$\mathrm{Cp^*_2ScTeC_6H_5}$ (**1e**)	1.86	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		123.5	$\mathit{C}_5\mathrm{(CH_3)_5}$	
	8.14	*o*-C*H*		12.1	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
	7.10	*p*-C*H*		143.2	*ipso*	
	7.03	*m*-C*H*		128.4	Ph	
				125.4	Ph	
$\mathrm{[Cp^*_2Sc]_2(\mu\text{-}Te)}$ (**2**)	2.08	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		122.4	$\mathit{C}_5\mathrm{(CH_3)_5}$	
				13.7	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
$\mathrm{Cp^*_2ScSeCH_2Si(CH_3)_3}$ (**3**)	1.92	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		122.4	$\mathit{C}_5\mathrm{(CH_3)_5}$	
	2.43	$\mathrm{SeC}\mathit{H}_2$		11.8	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
	0.39	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$		5.1	$\mathrm{Se}\mathit{C}\mathrm{H_2}$	
				−0.7	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$	$J_{\mathrm{CSe}} = 77.8$
						$J_{\mathrm{CSi}} = 54.0$
$\mathrm{[Cp^*_2Sc[_2(\mu\text{-}Se)}$ (**4**)	2.06	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		121.2	$\mathit{C}_5\mathrm{(CH_3)_5}$	
				12.5	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
$\mathrm{Cp^*_2ScCH_2SiMe_3}$	1.86	$\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$		120.9	$\mathit{C}_5\mathrm{(CH_3)_5}$	
	0.42	$\mathrm{C}\mathit{H}_2\mathrm{Si}$		11.7	$\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$	
	0.37	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$			$\mathit{C}\mathrm{H_2SiMe_3}$	
				5.7	$\mathrm{CH_2Si(}\mathit{C}\mathrm{H_3)_3}$	

[a] NMR spectroscopic data for unisolated compounds are given in the Experimental Section. [b] C_6D_6, ppm, referenced to solvent (7.15 ppm for residual protons, 128.0 for carbon). [c] Resonance obscured.

taken place. Attempts to confirm this with ^{127}Te NMR spectroscopy on **1a** and **2** failed; presumably the broadening effects due to strong coupling to the neighboring quadrupolar ^{45}Sc center ($I = {}^7/_2$, 100%) precluded location of a resonance. Nevertheless, tellurium insertion was evidenced in the downfield shift in the $\mathrm{TeC}\mathit{H}_2$ protons by 2−3 ppm in comparison to the shift for the starting alkyl derivatives and by the detection of tellurium satellites around the ^{13}C resonance for the $\mathrm{TeCH_2}$ carbons of **1a** ($J_{\mathrm{C-Te}} = 190$ Hz) and **1b** ($J_{\mathrm{C-Te}} = 165$ Hz).

As discussed below, the tellurolates **1a**−**e** are both thermally and photochemically unstable toward extrusion of $\mathrm{TeR_2}$, yielding the *μ*-telluride permethylscandocene dimer $\mathrm{[Cp^*_2Sc]_2(\mu\text{-}Te)}$ (**2**). A cleaner route to **2** involved reaction of $\mathrm{Cp^*_2ScD}$[16] and 0.5 equiv of Te=P-*n*-$\mathrm{Bu_3}$ (eq 3). Along with production of the dimer, vigorous evolution of gas (presumably D_2) was observed upon mixing of the two reagents. Several lines of experimental evidence suggest that this reaction proceeds via insertion of Te into the Sc−D bond to form $\mathrm{Cp^*_2ScTeD}$, which reacts rapidly with the remaining 0.5 equiv of $\mathrm{Cp^*_2ScD}$ to liberate D_2 and produce **2**. For example, when *in situ* generated $\mathrm{Cp^*_2ScH}$ was treated with 1.1 equiv of Te=P-*n*-$\mathrm{Bu_3}$ at −78 °C under 1−2 atm of H_2, a resonance at −6.88 ppm attributable to $\mathrm{Cp^*_2ScTe}\mathit{H}$ was observed. This chemical shift compares favorably to that recently observed for the related



(3)

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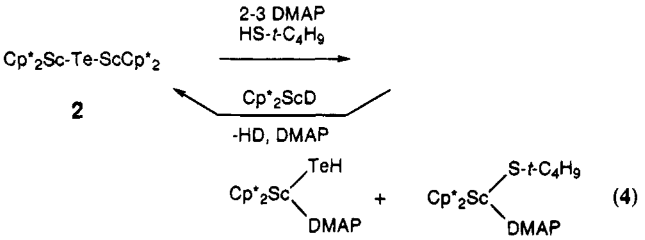
[16] Bercaw *et al.* have found that permethylscandocene hydride is unstable in the absence of dihydrogen.[21c] Evidently the isotope effect on this decomposition process is sufficient to allow for isolation of the deuteride $\mathrm{Cp^*_2ScD}$, which we find to be a convenient starting material for many experiments.

tellurol $(C_5Me_4Et)_2Zr(Te\mathit{H})[\eta^1\text{-}OC(C_6H_5){=}CH_2]$ of −7.0 ppm.[17] While production of this species was reproducible, it was not the major species in solution and was observed to decompose to unknown products at warmer temperatures.[18] However, this permethylscandocene tellurol was trapped as a DMAP (DMAP = 4-(dimethylamino)pyridine) adduct via the reaction shown in eq 4. In the presence of excess DMAP,[19] the μ-telluride permethylscandocene dimer was treated with 1 equiv of 2-methyl-2-propanethiol (pK_a = 11.1;[20] use of stronger acids, such as pyridinium salts, resulted in loss of Cp*H). Strong signals at 2.01 and −7.67 ppm (J_{Te-H} = 76 Hz) in a 30:1 ratio were observed, as well as signals for $Cp^*_2Sc(S\text{-}t\text{-}C_4H_9)(DMAP)$. Resonances attributable to the DMAP in the system were broadened, possibly due to rapid exchange processes, which were not further probed. Isolation of $Cp^*_2ScTeH(DMAP)$ form this system was difficult because of the thiolato byproduct, but it was stable in solution for several hours, decomposing slowly via liberation of Cp*H. Treatment of solutions generated in this manner with Cp^*_2ScD resulted in visible evolution of gas and regeneration of **2**·*n*DMAP, providing strong evidence for the reaction path noted in eq 2.



(4)

For our mechanistic studies it was necessary to synthesize the selenium analogs of tellurolate **1a** and telluride **2**. A similar methodology was thus employed to prepare $Cp^*_2ScSeCH_2SiMe_3$ (**3**) and $[Cp^*_2Sc]_2(\mu\text{-}Se)$ (**4**), shown in eqs 5 and 6, respectively. The reactions proceeded cleanly and efficiently using elemental selenium, and thus complications stemming from phosphine byproducts were avoidable. Similar evidence for the introduction of selenium was observed for **3** as for tellurium insertion in compounds **1** (δ(SeCH_2) 2.42 ppm; J_{C-Se} = 77 Hz) in addition to an observable resonance in the $^{77}Se\{^1H\}$ NMR spectrum at −595 ppm relative to Me_2Se (fwhm = 89 Hz). This selenolate did *not* decompose thermally via SeR_2 extrusion to the selenide dimer **4** at temperatures up to 110 °C. However, **4** was conveniently produced, as shown in eq 6.

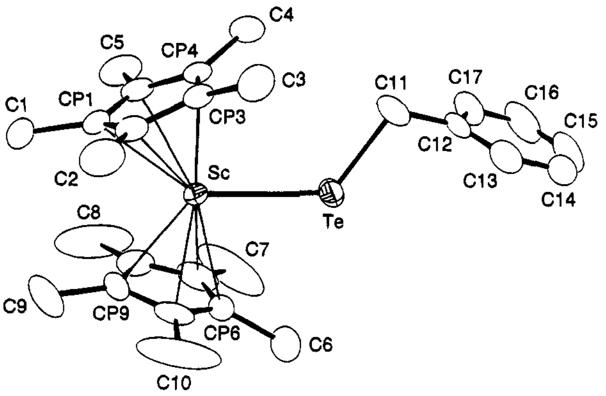


Figure 1. Molecular structure of $Cp^*_2ScTeCH_2C_6H_5$ (**1b**).

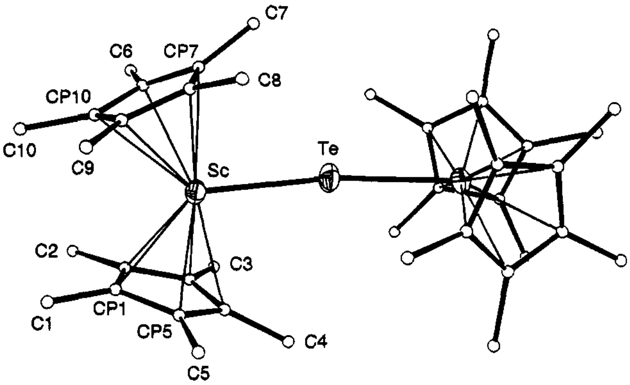


Figure 2. Molecular structure of $[Cp^*_2Sc]_2(\mu\text{-}Te)$ (**2**).

$$\underset{}{Cp^*_2Sc{-}CH_2SiMe_3} \xrightarrow[\text{hexanes}]{\text{Se (1 equiv)}} \underset{\mathbf{3}}{Cp^*_2Sc{-}SeCH_2SiMe_3} \qquad (5)$$

$$Cp^*_2Sc{-}D \xrightarrow[\text{hexanes}]{\text{Se (0.5 equiv)}} \underset{\mathbf{4}}{Cp^*_2Sc{-}Se{-}ScCp^*_2} \qquad (6)$$
$$-D_2$$

Molecular Structures of 1b, 2, and 4

The molecular structures of **1b**, **2**, and **4** are shown in Figures 1−3; complex **2** is isostructural with **4**. Selected metrical data for the three compounds are given in Table 2. Parameters associated with the Cp^*_2-Sc portion of these molecules are not significantly different from those for the handful of other permethylscandocene structures reported;[21] full listings of structural parameters for these compounds are given in the supplementary material.

The benzyl tellurolate **1b** is monomeric in the solid state, with the tellurolate ligand occupying the central position of the metallocene wedge. The ligand features an sp^2-hybridized tellurium atom (Sc−Te−C1 = 121.61(21)°) which on symmetry grounds[22] may σ donate to the metallocene's $2a_1$ orbital and π donate to its b_2 orbital in a dative π bond. The extent to which π

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[17] Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.

[18] The disappearance of the signal for Te*H* at −6.88 ppm was accompanied by the appearance of resonances for Cp*H. While data on the pK_a's of M−TeH tellurols are to our knowledge nonexistent, it is possible that Cp^*_2ScTeH is acidic enough to react with the protiolytically sensitive Cp*Sc moiety. The pK_a of H_2Te is 2.6: Jensen, K., A.; Kjaer, A. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1986; Vol. 1, p 1.

[19] Although the colors of solutions of **2** and DMAP are not visually different from those of **2**, ^1H NMR shows that some sort of adduct formation takes place. This is further substantiated by the fact that reactions of **2** with $HS\text{-}t\text{-}C_4H_9$ occur much faster in the presence of DMAP than in its absence. Reaction of **2** with excess $HS\text{-}t\text{-}C_4H_9$ takes place over several hours, producing transient amounts of the unligated tellurol Cp^*_2ScTeH, elemental tellurium, and $Cp^*_2ScS\text{-}t\text{-}C_4H_9$. ($^1H$ NMR (C_6D_6, ppm): 1.94, $C_5(CH_3)_5$; 1.78, $C(CH_3)_3$. $^{13}C\{^1H\}$ (C_6D_6, ppm): 123.3, $C_5(CH_3)_5$; 12.3, $C_5(CH_3)_5$; 38.3, $C(CH_3)_3$; 34.9, $C(CH_3)_3$.) Reaction of **2** with 1 equiv of $HS\text{-}t\text{-}C_4H_9$ in the presence of DMAP occurs rapidly within minutes of mixing. It is likely, therefore, that adduct formation causes the linear Sc−Te−Sc linkage to bend and render the molecular core more accessible to the protonating reagent.

[20] In aqueous solution: Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 3224.

[21] (a) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525. (b) Shapiro, P. J.; Henling, L. M.; Marsh, R. E.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 4560. (c) 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.

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

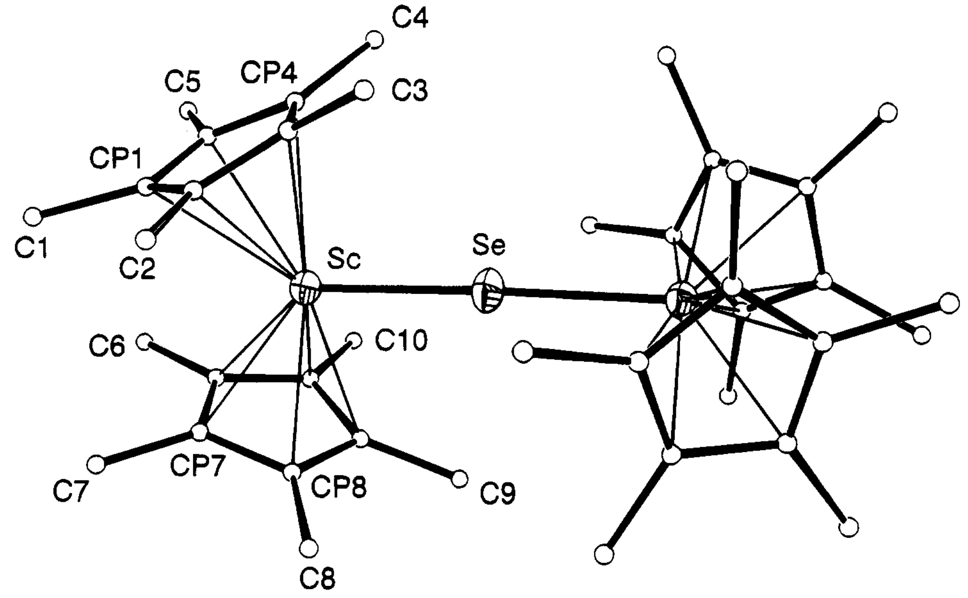

Figure 3. Molecular structure of $[Cp^*_2Sc]_2(\mu\text{-}Se)$ (**4**).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Cp^*_2ScTeCH_2C_6H_5$ (1b), $(Cp^*_2Sc)_2Te^*$ (2), and $(Cp^*_2Sc)_2Se$ (4)

distances		angles	
		Complex 1b	
Te—Sc	2.8337(14)	Sc—Te—C11	121.61(21)
Te—C11	2.199(7)	Te—C11—C12	108.2(5)
C11—C12	1.501(11)	C11—C12—C13	120.0(10)
C12—C13	1.374(16)	C11—C12—C17	121.4(10)
C12—C17	1.376(17)	C13—C12—C17	118.6(8)
C13—C14	1.358(16)	C12—C13—C14	120.8(9)
C14—C15	1.335(21)	C13—C14—C15	120.2(10)
C15—C16	1.367(22)	C14—C15—C16	121.1(10)
C16—C17	1.372(18)	C15—C16—C17	119.2(10)
Sc—Cent1	2.1632(14)	C12—C17—C16	120.2(9)
Sc—Cent2	2.1809(12)	Te—Sc—Cent1	114.84(5)
		Cent1—Sc—Cent2	142.65(6)
		Te—Sc—Cent2	102.50(5)
		Complex 2	
Sc—Te	2.7528(12)	Sc—Te—Sca	172.07(5)
Sc—Cent1	2.2056(14)	Te—Sc—Cent1	109.83(5)
Sc—Cent2	2.2058(14)	Te—Sc—Cent2	109.64(5)
		Cent1—Sc—Cent2	140.52(6)
		Complex 4	
Se—Sc	2.5425(16)	Sc—Se—Sca	173.74(10)
Sc—Cent1	2.1970(19)	Se—Sc—Cent1	110.30(8)
Sc—Cent2	2.2012(19)	Se—Sc—Cent2	110.38(7)
		Cent1—Sc—Cent2	139.29(8)

interaction contributes to the Sc—Te bond is difficult to judge on the basis of the observed Sc—Te bond distance of 2.8337(14) Å. Slightly shorter than a calculated Sc—Te single bond of 2.89[23] or 2.96 Å,[24] the distance is also significantly longer than the same parameter in **2**, which features an Sc—Te bond of 2.7528(12) Å. We have previously noted[11] that the orientation of the Cp^*_2Sc fragments with respect to each other in **2** allows for maximum π overlap between the μ-telluride ligand and each scandium center. On the basis of observed bond lengths, π bonding is stronger in **2** than in **1b**. In a related complex, $\{(CH_3)_2Si[(t\text{-}C_4H_9)C_5H_3]_2Sc(PMe_3)\}_2(\mu\text{-}Te)$,[25] Sc—Te π bonding is attenuated because the ligand structure prevents the Cp_2Sc fragments from assuming an "allene" like arrangement similar to that observed in **2**; the Sc—Te distance in this species is slightly longer than that in **1b** at 2.875(5) Å. Thus, the Sc—Te interaction in **1b** is best described as being intermediate between a single and a double bond.

The μ-chalcogenide dimers **2** and **4** are slightly distorted from idealized D_{2d} symmetry. The Sc—E bond distances of 2.5425(16) Å for E = Se and 2.7528(12) Å for E = Te (Δ = 0.210 Å) are comparable to the distances found for the terminal selenido and tellurido derivatives $(C_5Me_4Et)_2Zr{=}E(NC_5H_5)$.[17] Given the similarity between the ionic radii for Zr^{4+} (0.86 Å) and Sc^{3+} (0.89 Å),[24] it is clear that there is significant double-bond character to the Sc—E bonds of **2** and **4**, resulting in nearly linear Sc—E—Sc bridges. The minor deviations from linearity at the chalcogen in each structure (Sc—E—Sc is 173.74(10)° for Se and 172.07(5)° for Te) may result from a tendency for the heavier chalcogens to assume bent geometries.[26] The steric properties of the Cp^*_2Sc fragments place severe limits on the extent of bending from linearity, which is larger in **2** because of the longer Sc—Te bonds compared with the Sc—Se distances in **4**.

Thermolysis of Permethylscandocene Tellurolates

The tellurolates **1a–e** were synthesized to model the decomposition of metal tellurolates to metal tellurides via extrusion of dialkyl tellurides. At moderate temperatures (60–110 °C) in the absence of visible light the tellurolates **1a–d** extrude TeR_2, yielding **2** as the major scandium-containing product (eq 7). Attempts to push these reactions to several half-lives resulted in further thermal reactions between **2** and TeR_2 (*vide infra*), precluding reproducible kinetic measurements on the

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

[24] Based on addition of ionic radii. Sc^{3+} = 0.89 Å: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. Te^{2-} = 2.07 Å.[23]

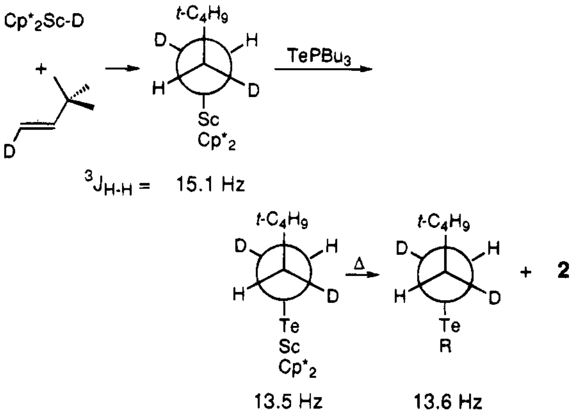
[25] Piers, W. E.; Ferguson, G.; Gallagher, J. F. *Inorg. Chem.*, in press.

[26] (a) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 91–109. (b) Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1986; Vol. 1, Chapter 2.

$$\underset{\mathbf{1a-d}}{\mathrm{Cp^*_2Sc{-}TeR}} \xrightarrow{60-110\ ^\circ\mathrm{C,\ dark}} \underset{\mathbf{2}}{\mathrm{Cp^*_2Sc{-}Te{-}ScCp^*_2}} + \mathrm{TeR_2} \tag{7}$$

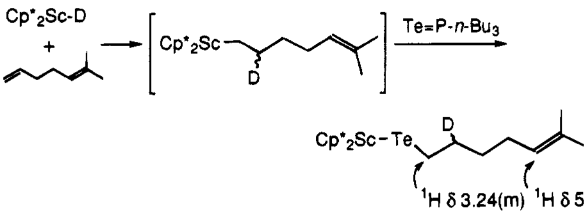
process of interest. Qualitatively the relative rates of extrusion appeared to correlate with the steric bulk associated with R. For example, the tellurolate **1a** required temperatures of 110 °C ($t_{1/2} \approx$ 2 days) to eliminate $Te(CH_2SiMe_3)_2$, while **1c**,**d** extruded TeR_2 at 70 °C ($t_{1/2} \approx$ 2 days) and **1b** decomposed at lower temperatures still (60 °C, $t_{1/2} \approx$ 24 h).

While one might equally conclude that these qualitative rates coincide with the stability of R•,[27] we have obtained good evidence that this extrusion reaction proceeds by a concerted pathway which does not involve Te—C bond homolysis. As we have reported,[12] **1c** can be synthesized via insertion of Te into the Sc—C bond of *erythro*-$Cp^*_2ScCH(D)CH(D)$-*t*-C_4H_9[28] (J_{H-H} = 15.1 Hz) prepared readily by insertion of (*E*)-1-deuterio-3,3-dimethyl-1-butene into the Sc—D bond of Cp^*_2ScD (eq 8). Consistent with a variety of other insertions into early-metal—carbon bonds,[29] tellurium insertion into the *erythro*-neohexyl derivative proceeded with retention of configuration in the probe to yield **1c** (J_{H-H} = 13.6 Hz). Extrusion of TeR_2 from this compound produced *erythro*,*erythro*-Te[CH(D)CH(D)-*t*-$C_4H_9]_2$ with greater than 90% retention of stereochemistry in the probe (J_{H-H} = 13.4 Hz) strongly suggesting a transition state involving concerted bond breaking and making in this extrusion process.

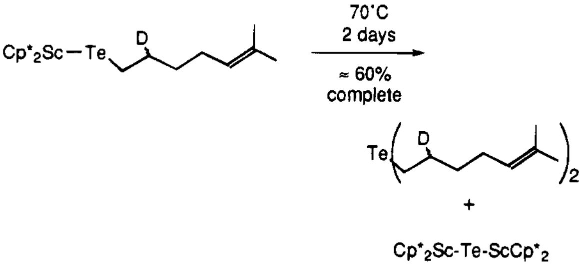


(8)

Further evidence along these lines was obtained from experiments entailing loss of TeR_2 from tellurolate **1d**. This compound contains an R group which is sensitive to cyclization should radicals be involved at any stage of the reaction. Selective insertion of the monosubstituted double bond of 6-methyl-1,5-heptadiene into Sc—D as shown in eq 9 leads to the scandocene alkyl precursor to **1d**,[30] which was not isolated but reacted immediately with Te=P-*n*-Bu_3. Tellurolate **1d** is characterized by a distinguishing multiplet resonance in its ^1H NMR spectrum at 3.24 ppm due to $TeCH_2$ and a triplet at 5.25 ppm for the olefinic proton. As shown in eq 10, we observed no cyclization in the TeR_2 product thermally extruded from **1d**; only one new set of characteristic resonances arose (2.47 and 5.16 ppm) for $Te[CH_2CH(D)CH_2CH_2CH{=}CMe_2]_2$ and no resonances attributable to cyclopentyl deuterium atoms appeared in the $^2H\{^1H\}$ NMR spectrum.

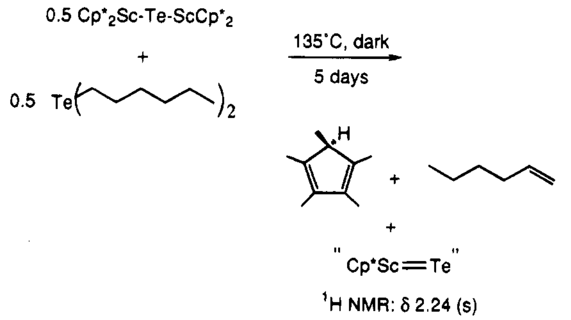


(9)



(10)

At higher temperatures (>135 °C), the dimeric telluride **2** reacts with the extruded TeR_2 in a process which involves abstraction of tellurium from TeR_2 and liberation of Cp*H to produce a new scandium-containing product characterized by a single Cp* resonance at 2.24 ppm. Although the precise structure of this species is not known, the product mixture observed for the reaction of **2** with $Te[(CH_2)_5CH_3]_2$ suggests that it has the empirical formula "Cp*ScTe" (eq 11).[31] Details of how this reaction proceeds are scarce at the present.



(11)

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[27] Stabilities of alkyl radicals are inversely related to the corresponding R—H bond strengths.[27a] While the benzyl C—H bonds of toluene are quite weak at 88 kcal mol^{-1}, the bond strengths of $(CH_3)_4Si$ and $H{-}CH_2CH_2CH_2R$ are comparable at ~99 kcal mol^{-1}.[27b] Also arguing against thermal homolysis of Te—C in this process is our failure to observe *any* R—R or ScTeTeSc coupling products. (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 162–166. (b) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boston, 1990; pp 9–95.

[28] Reversible *β*-elimination occurs in complexes of general structure $Cp^*_2ScCH_2CH_2R$: Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566. Over long periods of time, $Cp^*_2ScCH(D)CH(D)$-*t*-C_4H_9 undergoes epimerization presumably by this mechanism. However, the half-life of this process is estimated to be ~3 days because of the large *tert*-butyl substituent on the *β*-carbonyl and is thus not kinetically significant in these experiments.

[29] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 355.

[30] Initially, we attempted to use 1,5-hexadiene for this experiment. In analogy to chemistry observed in more open *ansa*-type scandocene derivatives (Bercaw, J. E.; Piers, W. E.; Shapiro, P. J.; Bunel, E. E. *Synlett.* **1990**, *1*, 74), rapid cyclization of this substrate to the methylcyclopentyl derivative $Cp^*_2ScCH_2(c\text{-}C_5H_9)$ was observed, nullifying its utility as a probe for radicals. In addition, some product arising from insertion of both ends of the diene was observed. Methylation of one end of the diene solved both of these problems.

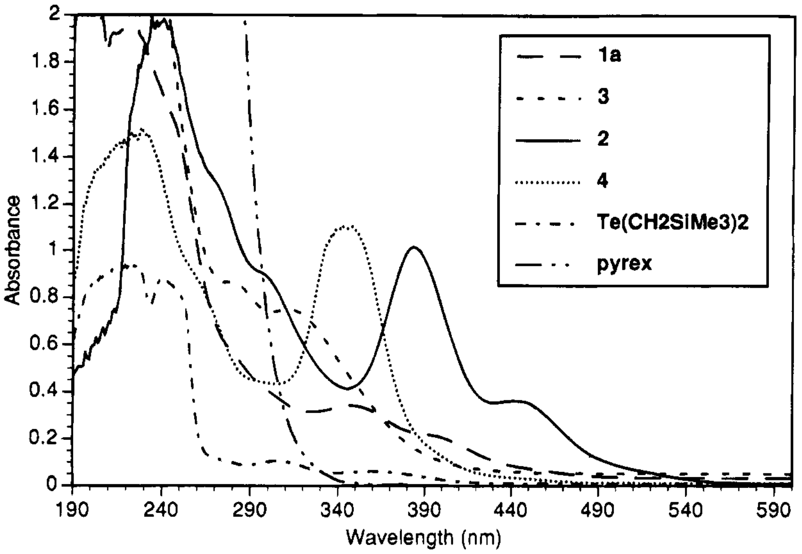
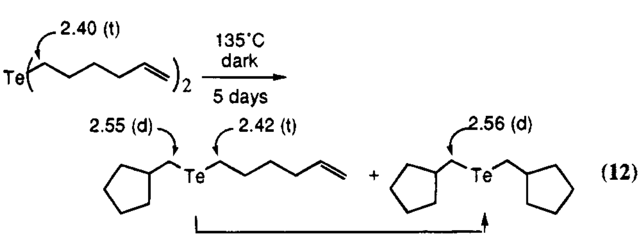


Figure 4. UV–visible spectra of Cp*$_2$ScTeCH$_2$SiMe$_3$ (**1a**; – –), Cp*$_2$ScSeCH$_2$SiMe$_3$ (**3**; - -), [Cp*$_2$Sc]$_2$Te (**2**; —), [Cp*$_2$Sc]$_2$Se (**4**; •••), Te(CH$_2$SiMe$_3$)$_2$ (– - – -), and the Pyrex filter employed in all irradiations (– - - –). The spectra have been normalized using Beer's law to a concentration of 6.64 × 10^{-4} M for direct comparison.

However, the following experiments provide some clues and have some bearing on the photochemical reaction between **2** and TeR$_2$ (*vide infra*). When a sample of Te[(CH$_2$)$_5$CH$_3$]$_2$ was heated under the same conditions (135 °C, 5 days in the dark) no visible or spectroscopic evidence for decomposition of the dialkyl telluride was found. However, if the dialkyl telluride Te[(CH$_2$)$_4$-CH=CH$_2$]$_2$ was subjected to the same thermal stress, progressive cyclization in the hexenyl group was observed over the course of 5 days (equation 12). This



(12)

process was easily followed by ^{1}H NMR by monitoring the 2.3–2.6 ppm region of the spectrum where the protons α to tellurium typically resonante and was very clean in that no products due to homocoupling of R$^•$ or RTe$^•$ radicals were formed. These observations suggest that thermal Te—C bond homolysis is occurring at these higher temperatures but that in this temperature regime the radicals do not break from their solvent cage.[32] Only when **2** is present do they react via a process which eventually produces "Cp*ScTe". The major organic byproducts in the reaction of **2** and Te[(CH$_2$)$_5$CH$_3$]$_2$ are Cp*H and 1-hexene, indicating that the sources of the proton in the former product were the hexyl groups of the starting telluride.

Photochemistry

Irradiation of solutions of **2** and Te(CH$_2$SiMe$_3$)$_2$ (0.05–0.06 M) with a medium-pressure mercury lamp through Pyrex filters resulted in facile reversal of the extrusion reaction described above to regenerate tellurolate **1a**. We have not measured quantum yields for this photoreaction, but solutions of this concentration required only 20–30 min of irradiation to completely revert to **1a**. For other dialkyl tellurides, similar photoreactions were observed; however, complete conversion to the tellurolate was only observed for R = CH$_2$SiMe$_3$. Indeed, irradiation of solutions of pure tellurolates **1b–d** resulted in the *photochemical* extrusion of TeR$_2$ and produced photostationary mixtures of tellurolate, dialkyl telluride, and **2** (eq 13). For **1a**, the position of this

$$2\mathrm{Cp}^*{}_2\mathrm{ScTeR} \xrightleftharpoons{h\nu,\ >290\ \mathrm{nm}} \mathrm{Cp}^*{}_2\mathrm{Sc{-}Te{-}ScCp}^*{}_2 + \mathrm{TeR}_2 \quad (13)$$

photostationary state lies in favor of the tellurolate; irradiation of solutions of **1a** for several hours had no effect on the composition of the system.[33] However, for **1b,d**, unchanging ratios of tellurolate to telluride of ~2:1 were observed after 1 h of irradiation. (Further irradiation of **1d** resulted in decomposition processes; *vide infra*.)

UV–vis spectra for **1a**, **2–4**, Te(CH$_2$SiMe$_3$)$_2$, and the Pyrex filter used are shown in Figure 4. The principal absorptions for each compound and their extinction

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(31) With this empirical formula, by analogy to some recently reported aluminum chemistry (Schulz, S.; Roesky, H. W.; Kock, H. J.; Sheldrick, G. W.; Stalke, D.; Kuhn, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729), this compound is likely tetrameric. Efforts to synthesize larger quantities of this potentially interested compound are underway.

(32) Thermal decomposition of dialkyl tellurides at higher temperatures (>160 °C) has been shown to involve Te—C bond homolysis: Stevenson, J.; Bell, W.; Ferry, J.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1993**, *449*, 141.

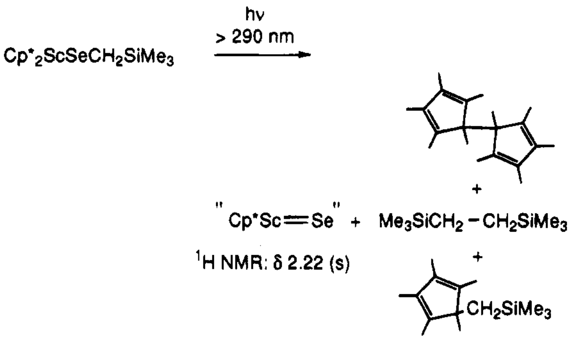
(33) Although essentially a kinetic phenomenon, the position of a photostationary state may be influenced by the ground-state stabilities of the system components if the wavelength of impinging light remains constant. It is not clear why tellurolate **1a** should be more stable than the others in the series, but it is possible that an organometallic γ-silicon effect (Alelyunas, Y. W.; Baenziger, N. C.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1994**, *13*, 148) may be providing extra stabilization for the electrophilic scandocene center. In the absence of definitive structural data, we note the significant upfield shifts of the Te*C*H$_2$ carbon and proton NMR signals for **1a** in comparison to the other scandocene tellurolates and Te(CH$_2$SiMe$_3$)$_2$. In addition, the J_{CTe} coupling constant of 190.3 Hz is 15–25 Hz larger than normal values (for example, J_{CTe} = 164.8 Hz for **1b** and 175.0 Hz for Te(CH$_2$SiMe$_3$)$_2$). On the other hand, using predicted bond distances for Sc—Te (2.83 Å) and Te—C (2.14 Å and an Sc—Te—C bond angle of 85° results in a relatively long (3.3 Å) Sc—C$_\beta$ contact.

Table 3. UV–Visible Absorption Bands for 1a and 2–4

$Cp^*_2ScTeCH_2Si(CH_3)_3$ (**1a**)	349	5 000
	392	3 275
$Cp^*_2ScSeCH_2Si(CH_3)_3$ (**3**)	279	13 500
	311	11 275
$[Cp^*_2Sc]_2(\mu\text{-}Te)$ (**2**)	297 (sh)	13 500
	383	15 300
	447	5 500
$[Cp^*_2Sc]_2(\mu\text{-}Se)$ (**4**)	262 (sh)	17 000
	342	19 500

coefficients are given in Table 3. Since the scandocene complexes are d^0 derivatives, the character of the transitions observed must be ligand to metal charge transfer (LMCT).[34] This is supported by the large extinction coefficients observed for the absorptions, which are comparable to those for LMCT transitions observed in related bent-scandocene compounds.[35] The observed LMCT bands may be due to charge transfer from the π electrons of the Cp* rings or involve electron transfer from the lone-pair electrons of the chalcogen. To help distinguish between these two possibilities, the selenium analogs of **1a** and **2** were prepared to compare both the spectra and photoreactivity of the congeneric pairs.

The lowest energy transition for **4** is shifted to shorter wavelength in comparison to those observed for **2**, and the spectra of the two compounds are markedly different in appearance. The photoactivities of these compounds are also in sharp contrast. Under conditions identical with the photoreactions of **2** with dialkyl tellurides, selenide **4** does not react photochemically with TeR_2. Indeed, **4** was quite stable under prolonged irradiation and eventually decomposed to unknown scandium products via a process which involved loss of pentamethylcyclopentadienyl radicals. Comparison of the chalcogenolate congeners **1a** and **3** shows that they give rise to similar appearing spectra which contain two main absorptions in the visible portion of the spectrum. The positions of the selenolate's absorptions are shifted by 70–80 nm to higher energy and are more intense than the tellurolate absorption bands. Significantly, **3** decomposes rapidly when irradiated by loss of $Cp^{*\bullet}$ radicals (eq 14). Dimerized $Cp^{*\bullet}$ was identified by comparison to reported proton chemical shift data,[36] and signals attributable to $C_5Me_5CH_2SiMe_3$ and $Me_3SiCH_2CH_2SiMe_3$ were also present. In addition, a new Cp* resonance at 2.22 ppm indicates a single scandium-containing product analogous to the telluride compound of unknown structure observed in the thermal reactions of **2** with TeR_2, *i.e.* "Cp*ScSe". This mode of reactivity is in marked contrast to the observed photostability of **1a** and the photoextrusion of TeR_2 seen upon irradiation of the other tellurolates.



(14)

The differences in reactivity observed for the selenium congeners of **1a** and **2** clearly show that, in the tellurium compounds, the low-energy LMCT transitions are Te → Sc in nature, while for the selenium analogs ring → Sc charge transfer is favored. This is a commonly observed phenomenon in the electronic structures of early-metal bent metallocenes as one progresses to heavy-element congeners of a family of compounds. For example, the titanocene dihalides Cp_2TiX_2 have been studied extensively, and while there has been some disagreement as to the precise ordering of molecular orbitals, it is accepted that for X = F, Cl, Br the low-energy transition is ring → Ti in character.[37] However, as progression down the group occurs, the energy of the lone pairs on X rises while the energy of the Cp π electrons steadily decreases until, when X = I, the relative energies switch and I → Ti becomes the low-energy transition. Similar effects have been noted by Thompson *et al.* for monomeric permethylscandocene halides, Cp^*_2ScX.[35] Thus, while precise assignments for the bands observed in the UV–vis spectra of **1a** and **2** have not been made, literature precedent and our observations strongly suggest that the principal transitions are Te → Sc in character.

It is thus likely that in the photoreactions observed for **2** and tellurolates **1b–d** the Te → Sc LMCT bands serve as the primary chromophore. As can be seen in Figure 4, light of wavelength shorter than ~290 nm was removed by the Pyrex filter. While it is possible that the TeR_2 substrates were the absorbing species in these reactions, several observations suggest that this was not the case. The TeR_2 compounds employed are pale yellow liquids with only weak absorbances in the visible region compared to **2** (Figure 4). While these compounds are known to decompose upon irradiation,[38] the n → σ^* transitions generally require photons from the ultraviolet region which have been filtered out in our experiments. Indeed, control experiments involving irradiation of solutions of the dialkyl tellurides employed showed that they are stable for several hours. Finally, the chemistry depicted in eqs 11 and 12 and discussed above show that *thermally* generated $RTe^\bullet$ and $R^\bullet$ radicals give rise to products in the presence of **2** different from those observed in the *photochemical* reaction of **2** and TeR_2, arguing against photochemical Te–C bond homolysis as the primary photoevent in this process.

Nonetheless, at some point in the reaction Te–C bond cleavage is a necessary step in going from **2** and TeR_2 to the tellurolates. While they are not likely generated photochemically, we have strong evidence that $R^\bullet$ radicals are formed in a subsequent step of the reaction. For example, when solutions of **2** and *erythro,erythro*-$Te[CH(D)CH(D)\text{-}t\text{-}C_4H_9]_2$ (formed by thermal extrusion

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[34] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; Chapter 1.

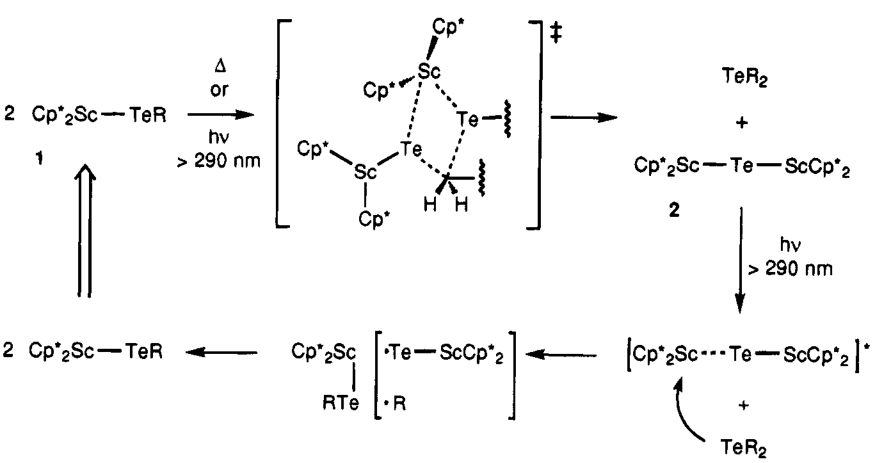
[35] Pfennig, B. W.; Thompson, M. E.; Bocarsly, A. B. *Organometallics* **1993**, *12*, 649.

[36] (a) Culshaw, P. N.; Walton, J. C.; Hughes, L.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1993**, 879. (b) Davies, A. G.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 692. (c) Davies, A. G.; Lusztyk, J. *J. Chem. Soc., Chem. Commun.* **1980**, 554.

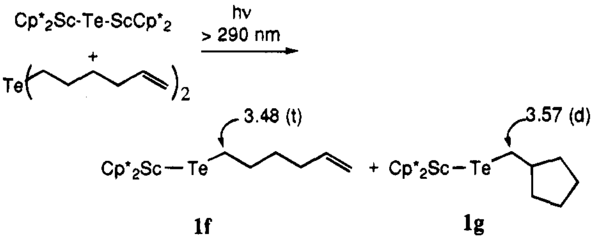
[37] Kenney, J. W., III; Boone, D. R.; Striplin, D. R.; Chem, Y.-H.; Hamar, K. B. *Organometallics* **1993**, *12*, 3671 and references therein.

[38] Golschmidt, Z. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1987; Vol. 2, p 275.

Scheme 1



from *erythro*-**1c**; eq 8) were irradiated, **1c** was regenerated as a mixture of the *threo* and *erythro* isomers. This observation was suggestive of the formation of R• on the path back to **1c**. This notion was supported by the observation of cyclization in the 5-hexenyl substituent when **2** was irradiated with Te[(CH$_2$)$_4$CH=CH$_2$]$_2$ (eq 15).



(15)

1f **1g**

Irradiation Time (min)	Ratio 1f:1g
10	2.73
20	2.22
40	2.05
60	1.65
90	1.45
120	1.16
150	0.97
185	0.80
305	0.51

During short irradiation times, the tellurolates Cp*$_2$ScTe(CH$_2$)$_4$CH=CH$_2$ (**1f**) and Cp*$_2$ScTeCH$_2$(*c*-C$_5$H$_9$) (**1g**) were formed in ~2.7:1 ratio. Since only one Te—C bond is cleaved in a given reaction between **2** and TeR$_2$, a preponderance of **1g** over **1f** should not be observed at early reaction times. However, as shown in the table accompanying eq 15, over longer irradiation periods, the product mixture was converted slowly to the cyclized tellurolate **1g** until eventually it was the only tellurolate product in the system (also present was ~10% **2** and a small amount of [Cp*ScTe]$_n$). At first glance, the photoconversion of **1f** to **1g** implies that the permethylscandocene tellurolates are sensitive toward photolytic cleavage of Te—C. However, the photoextrusion of TeR$_2$ from Cp*$_2$ScTeR does not necessarily begin with Te—C bond homolysis. Indeed, since the transitions which are most likely with the wavelength of light present are Te → Sc in character (*vide supra*), a more probable interpretation of the observed photoconversion of **1f** to **1g** is that it is a consequence of the reversible, photostationary equilibria present in these Cp*$_2$ScTeR/Cp*$_2$ScTeScCp*$_2$ + TeR$_2$ systems in which R• radicals are only involved in the photoreaction leading from **2** and TeR$_2$ to the tellurolates. The detection of small quantities of the dialkyl telluride [H$_2$C=CH(CH$_2$)$_4$]TeCH$_2$(*c*-C$_5$H$_9$) during the irradiation shown in eq 15 is entirely consistent with this scenario. Lastly, when **1d** was irradiated for short periods of time (20–30 min), extrusion of Te[CH$_2$CH(D)CH$_2$CH$_2$CH=CMe$_2$]$_2$ exclusively was observed with no cyclization of the alkyl group present, as determined by both ^{1}H and ^{2}H{^{1}H} NMR spectroscopy.[39]

Summary and Concluding Remarks

A variety of permethylscandocene tellurolates have been prepared via insertion of tellurium into the scandium–carbon bonds of Cp*$_2$ScR derivatives. Their thermal and photochemical interconversion with the dimeric permethylscandocene telluride **2** and TeR$_2$ has been studied with a variety of mechanistic experiments. While in the absence of more sophisticated flash photolysis experiments details concerning the structures of the excited states of tellurolates **1** and telluride **2** are sketchy, our experiments have mapped out the general features of this system, which are summarized in Scheme 1. Our experiments with tellurolates **1c,d** showed that the thermal extrusion of TeR$_2$ proceeded from a transition state characteristic of a concerted elimination with retention of configuration in the stereochemical probe employed. Whether the photochemical extrusion process proceeds via a similar transition state which is rendered more accessible by charge transfer from Te → Sc (and lengthening of the Te—Sc bond) or by a fundamentally different pathway is unknown, although our results are consistent with the former scenario.

Our observations concerning the photoaddition of TeR$_2$ to **2** are consistent with the sequence of events shown in Scheme 1. Absorption of a photon by **2** leads to an excited state in which one of the Sc—Te bonds has been weakened by charge transfer from Te to Sc. This may allow the Sc—Te—Sc vector to bend and open the dimer to attack by TeR$_2$. It appears that the presence of the lone pairs in the trapping agent is essential for

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[39] Prolonged irradiation of **1d** resulted in a variety of products, including [Cp*ScTe]$_n$, Cp*H, and olefinic products resulting from decomposition of R•. We postulate that this is a result of the inefficient coupling (for steric reasons) of Cp*$_2$ScTe• and the tertiary radical formed via cyclization of the alkyl group. However, at early stages of the irradiation the process is very clean and unequivocally shows no cyclization in the radical sensitive alkyl group.

productive photoreaction of **2**. For example, when it is irradiated in the presence of potential trapping agents which do not contain lone pairs (HSn-*n*-Bu_3, $Me_3SnSnMe_3$), **2** remains unchanged indefinitely. Whatever the structure of **2***, reaction with TeR_2 results in cleavage of one Te—C bond to form 1 equiv of **1** and a $Cp^*_2ScTe^{\bullet}/R^{\bullet}$ radical pair, as evidenced by the observed cyclization in 5-hexenyl alkyl substituents. This pair must be short lived ($<10^{-5}$ s[40]), as evidenced by incomplete cyclization of the 5-hexenyl radical at short irradiation times and the lack of observation of products done to homocoupled $Cp^*_2ScTe^{\bullet}$ or $R^{\bullet}$ at any time during these reactions. Coupling of this pair leads to the second equivalent of **1**.

The production of metal tellurides from metal tellurolates has generally been observed to be thermally driven and to be irreversible. Herein, we have uncovered a molecular example of the reverse reaction which occurs under impingement of visible light. While this photobehavior may be solely a consequence of the bent-scandocene framework used as a template for studying the tellurolate/telluride interchange, it is not inconceivable that, for other d^0 systems at least, Te → M charge transfer absorptions may provide a much milder means of depositing metal telluride materials. Indeed, the recently reported compounds $Ln[ESi(SiMe_3)_3]_2(TMEDA)_2$ were reported to decompose to unknown products under ambient lighting conditions.[5b] Lastly, the photoreversibility of the process also has implications for the efficiency of metal telluride production by this route if the extruded TeR_2 is not removed from the system.

Experimental Section

General Considerations. All operations were performed under a purified argon atmosphere in a Braun MB-150 inert-atmosphere glovebox or on high-vacuum lines using standard techniques.[41] Solvents were purified as follows: toluene was distilled from sodium benzophenone ketyl and stored over "titanocene";[42] tetrahydrofuran (THF) was predried with activated (10^{-4} Torr, 200 °C, 3 h) 3 Å molecular sieves and distilled from and stored over sodium benzophenone ketyl; hexanes were distilled from lithium aluminum hydride (Aldrich) and stored over "titanocene"; dichloromethane was distilled from CaH_2; benzene-d_6 was dried sequentially over activated 3 Å sieves and "titanocene" and stored in the glovebox; other NMR solvents were dried analogously to the perprotio solvents.

Sc_2O_3 was purchased from Boulder Scientific Co. and used to prepare $ScCl_3(THF)_3$ via a literature procedure.[43] Cp^*_2ScCl ($Cp^* = C_5Me_5$) alkyl derivatives Cp^*_2ScR and Cp^*_2ScD were prepared as described by Bercaw *et al.*[21c] Literature procedures were employed to prepare $Te{=}P$-*n*-Bu_3[44] and $Te(CH_2SiMe_3)_2$,[45] while other dialkyl tellurides were synthesized via reaction of RBr with *in situ* generated Li_2Te according to the method of Clive *et al.*[46] (*E*)-1-deuterio-3,3-dimethyl-1-butene[47] was synthesized by hydrozirconation of 3,3-dimethyl-1-butyne followed by quenching with D_2O and rigorous drying over CaH_2. Deuterium gas was obtained from Matheson Gas Products and purified by passing through glass towers containing MnO on vermiculite and molecular sieves. 6-Methyl-1,5-heptadiene was purchased from Wiley Organics and dried and distilled over CaH_2; all other materials were obtained from Aldrich Chemical Co. and either used as received or dried and distilled prior to use.

^1H and $^{13}C\{^1H\}$ NMR spectra were accumulated on a Varian Gemini 200 or Unity 400 instrument using Wilmad 528-PP NMR tubes. UV–vis spectra were measured on a Perkin-Elmer Lambda 6 spectrometer using a sealable 1 mm path length quartz cell. Extinction coefficients were calculated using Beer's law by averaging absorbances measured at two different concentrations. Thermolyses were performed in sealed NMR tubes (0.05–0.10 M solutions) in the dark in a thermostated oil bath. GC analyses were carried out on a Varian Model 3400 gas chromatograph. Microanalyses were performed by Onieda Research Services, Inc., One Halsey Rd., Whitesboro, NY 13492.

$Cp^*_2ScTeCH_2SiMe_3$ (1a). Method A. In a glovebox $Cp^*_2ScCH_2SiMe_3$ (0.102 g, 0.26 mmol) was loaded into a 1 dram vial and dissolved in ~1 mL of hexanes. Solid TeP-*n*-Bu_3 (0.084 g, 0.26 mmol) was added with agitation. The mixture was cooled to −30 °C for 12 h, and the orange precipitate was isolated by pipetting away the mother liquor, washing once with cold hexanes, and allowing it to dry in the glovebox atmosphere. Yield: 0.042 g, 31%.

Method B. $Cp^*_2Sc{-}Te{-}ScCp^*_2$ (0.442 g, 0.58 mmol) and $Te(CH_2SiMe_3)_2$ (0.177 g, 0.58 mmol) were loaded into a sealable 9 mm i.d. Pyrex tube and dissolved in benzene (~3 mL). The sample was degassed, sealed under 740 Torr of argon, and irradiated with a mercury UV lamp at 0 °C for 4–5 h. The tube was opened and the solution transferred in a glovebox to a frit assembly. The benzene was removed *in vacuo* and replaced with 1–2 mL of hexanes. The solution was cooled to −78 °C and the resulting orange microcrystalline precipitate collected via a cold filtration. Yield: 0.496 g, 71%. Anal. Calcd for $C_{24}H_{41}ScSiTe$: C, 54.37; H, 7.79. Found: C, 54.24; H, 7.71.

$Cp^*_2ScTeCH_2C_6H_5$ (1b). In a glovebox, $Cp^*_2ScCH_2C_6H_5$ (0.500 g, 1.2 mmol) was dissolved in hexanes (10 mL). Solid TeP-*n*-Bu_3 (0.402 g, 1.2 mmol) was added slowly with agitation; a yellow precipitate formed. The flask was attached to a swivel frit apparatus, and the yellow solid was filtered off and washed once with cold hexanes. Yield: 0.468 g, 71%. Anal. Calcd for $C_{26}H_{37}ScTe$: C, 60.71; H, 6.98. Found: C, 60.44; H, 7.04.

***erythro*-d_2-$Cp^*_2ScTeCH(D)CH(D)$-*t*-C_4H_9 (1c).** In a glovebox, Cp^*_2ScD (0.720 g, 2.3 mmol) was dissolved in hexanes (10 mL). A solution of (*E*)-1-deuterio-3,3-dimethyl-1-butene (0.195 g, 2.3 mmol) in 1 mL of hexanes was added dropwise and the flask attached to a swivel frit apparatus. The yellow solution was concentrated and cooled and the yellow precipitate isolated by cold filtration. Yield: 0.410 g, 45%. $^1H\{^2H\}$ NMR data for *erythro*-d_2-$Cp^*_2ScCH(D)CH(D)$-*t*-C_4H_9 (400 MHz, C_6D_6, ppm): 1.86, $C_5(CH_3)_5$; 1.19, $C(CH_3)_3$; 1.08, $ScCH(D)$ (d, $^3J_{HH} = 15.1$ Hz); 0.52. $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): 120.0, $C_5(CH_3)_5$; 11.3, $C_5(CH_3)_5$; 43.1, $CH(D)CH(D)$ ($J_{CD} = 18.3$ Hz); 33.8, $CH(D)CH(D)$ (br m); 33.4, $C(CH_3)_3$; 29.8, $C(CH_3)_3$. This solid (0.330 g, 0.8 mmol) was dissolved in hexanes (5 mL), and a solution of $Te{=}P$-*n*-Bu_3 (0.269 g, 0.8 mmol) in 1 mL of toluene was added dropwise with agitation. The solvent was removed under reduced pressure and replaced with pure hexanes (≈5 mL). The resulting solution was cooled to −78 °C, and the orange precipitate collected via a cold filtration. The product was washed once with cold hexanes and dried *in vacuo*. Yield: 0.168 g, 39%. Anal. Calcd for $C_{26}H_{41}D_2ScTe$: C, 59.90; H, 8.54. Found: C, 57.81; H, 8.13.

$Cp^*_2ScTeCH_2CH(D)CH_2CH_2CH{=}CMe_2$ (1d). In a glovebox, Cp^*_2ScD (0.426 g, 1.3 mmol) was dissolved in hexanes (5 mL). A solution of 6-methyl-1,5-heptadiene (0.148 g, 1.3 mmol) in 1 mL of hexanes was added dropwise with agitation, resulting in a yellow solution. To this was added *immediately*[48]

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a solution of Te=P-*n*-Bu$_3$ (0.420 g, 1.27 mmol) in 1 mL of toluene with swirling. The solvent was removed *in vacuo* and replaced with pure hexanes ($\approx$3 mL) and the resulting solution cooled to −78 °C. The precipitate was cold filtered and washed once with cold hexane. Yield: 0.387 g, 52%. Anal. Calcd for $C_{28}H_{44}DScTe$: C, 60.57; H, 8.34. Found: C, 58.35; H, 7.70. This compound may have decomposed slightly while being transported for microanalysis.

Cp*$_2$ScTeC$_6$H$_5$ (1e). In a glovebox, Cp*$_2$ScC$_6$H$_5$ (0.412 g, 1.05 mmol) was dissolved in hexanes (10 mL). Solid Te=P-*n*-Bu$_3$ (0.346 g, 1.05 mmol) was added slowly with agitation; a yellow precipitate formed. The flask was attached to a swivel frit apparatus, and the yellow solid was filtered off and washed once with cold hexanes. Yield: 0.371 g, 68%. UV−vis (λ_{max}, nm; ϵ, M^{-1} cm^{-1}): 262, 23 500; 288, 12 500; 334, 6250; 392, 2900. Anal. Calcd for $C_{26}H_{35}ScTe$: C, 60.04; H, 6.78. Found: C, 59.83; H, 6.90.

Cp*$_2$Sc−Te−ScCp*$_2$ (2). In a glovebox Cp*$_2$ScD (0.327 g, 1.0 mmol) and Te=P-*n*-Bu$_3$ (0.167 g, 0.5 mmol) were loaded into a 25 mL round-bottomed flask and 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 warmed to room temperature. During warming, gas evolution was accompanied by darking of the solution to a deep orange. After the solution was stirred a further 15 min, 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: 0.330 g, 85%. Anal. Calcd for $C_{40}H_{60}Sc_2Te$: C, 63.35; H, 7.97. Found: C, 63.59; H, 8.00.

Cp*$_2$ScSeCH$_2$SiMe$_3$ (3). Cp*$_2$ScCH$_2$SiMe$_3$ (**5**; 0.420 g, 1 mmol) and elemental selenium (100 mesh, 0.080 g, 1 mmol) were combined in a small round-bottom flask, and ~5 mL of hexanes was added. The flask was attached to a swivel frit apparatus, and the heterogeneous suspension was stirred for 2 h at room temperature, during which time uptake of selenium was observed with concurrent yellowing of the solution. The solution was filtered and cooled to −78 °C. The resulting yellow microcrystalline product was isolated by cold filtration. Yield: 0.275 g, 55%. ^{77}Se{^{1}H} NMR (C$_6$D$_6$, ppm, relative to (C$_6$H$_5$)$_2$Se$_2$ at −460 ppm, upfield of Me$_2$Se[49]): −598.2 (fwhm = 89 Hz). Anal. Calcd for $C_{24}H_{41}ScSe$: C, 59.86; H, 8.58. Found: C, 58.95; H, 8.34.

Cp*$_2$Sc−Se−ScCp*$_2$ (4). In a glovebox Cp*$_2$ScD (0.152 g, 0.48 mmol), elemental selenium (100 mesh, 0.026 g, 0.33 mmol), and hexanes (5 mL) were loaded into a small round-bottomed flask and attached to a swivel frit apparatus. Gas evolution along with the precipitation of a yellow solid was observed; the reaction mixture was stirred until gas evolution ceased (~30 min). Hexane was removed *in vacuo* and replaced with toluene. The excess selenium was removed by filtration, and the yellow solution was concentrated. Hexanes (~1−2 mL) was added to precipitate the product, which was isolated by filtration. Yield: 0.147 g, 77%. Anal. Calcd for $C_{40}H_{60}Sc_2Se$: C, 67.69; H, 8.52. Found: C, 65.44; H, 7.95.

Cp*$_2$ScCH$_2$SiMe$_3$. Cp*$_2$ScCl (2.0 g, 5.7 mmol) was loaded into a round-bottom flask and attached to a swivel frit apparatus. The apparatus was evacuated, and hexanes (~30 mL) was transferred into the vessel. The solution was cooled to 0 °C, and under a strong flow of argon, a solution of LiCH$_2$SiMe$_3$ (6.0 mL of a 1.0 M solution in pentane) was added dropwise over the course of 15 min. The resulting suspension was stirred for a further 1 h and filtered. The filtrate was concentrated and cooled to −78 °C. After the filtrate stood for several hours at this temperature, the white crystalline product was collected by cold filtration and washed once with cold hexanes. Yield: 1.568 g, 68%. Anal. Calcd for $C_{24}H_{41}ScSi$: C, 71.60; H, 10.26. Found: C, 71.14; H, 10.36.

Generation of Cp*$_2$ScTeH(DMAP). Complex **2** (0.032 g, 0.04 mmol) and DMAP (0.011 g, 0.09 mmol) were dissolved in C$_6$D$_6$ and loaded into a sealable NMR tube, which was affixed to a constant-volume bulb. The sample was degassed via two freeze−pump−thaw routines, and 1 equiv of H-S-*t*-C$_4$H$_9$ (22 Torr in 34.2 mL) was vacuum-transferred into the sample. The tube was sealed under 0.95 atm of argon and warmed rapidly with shaking to room temperature. After the orange to yellow color change was complete (~10 min), the NMR spectrum was accumulated. ^{1}H NMR analysis revealed a 1:1 mixture of Cp*$_2$ScS-*t*-C$_4$H$_9$(DMAP) (2.08, C$_5$(C*H*$_3$)$_5$; 1.92, t-C$_4$*H*$_9$) and Cp*$_2$ScTeH(DMAP) (2.01, C$_5$(C*H*$_3$)$_5$, 30H; −7.67, Te*H*, 1H, J_{TeH} = 76 Hz). DMAP resonances were broad: aromatic C*H*, 9.35, 8.42, 6.04; C*H*$_3$, 2.15.

Attempted Synthesis of Cp*$_2$ScTeCH$_2$CH(D)(CH$_2$)$_2$CH=CH$_2$ (*d*-1f). Cp*$_2$ScD (0.032 g, 0.10 mmol) was dissolved in 0.4 mL of C$_6$D$_6$. A solution of 1,5-hexadiene (0.008 g, 0.10 mmol) in 0.2 mL of C$_6$D$_6$ was added in one portion and was followed *immediately* with a solution of Te=P-*n*-Bu$_3$ (0.033 g, 0.10 mmol) in 0.2 mL of C$_6$D$_6$. ^{1}H NMR analysis revealed a 1:6 mixture of *d*-**1f**:*d*-**1g**. ^{1}H NMR for *d*-**1g**, Cp*$_2$ScTeCH$_2$(*c*-C$_5$H$_9$) (C$_6$D$_6$, ppm): 1.93, C$_5$(C*H*$_3$)$_5$; 3.57, TeC*H*$_2$ (d, $^3J_{HH}$ = 6.8 Hz); 2.48, CH$_2$C*H* (m); 1.4−1.7, cyclopentyl ring protons. ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm): 3.5, TeCH$_2$; 46.4, TeCH$_2$CH; 24.8, 24.7, α-ring CH$_2$; 25.8, β-ring CH$_2$; 25.5, β-ring CH(D) (t, J_{CD} = 19.7 Hz).

Thermolysis of Te[(CH$_2$)$_4$CH=CH$_2$]$_2$. Te[(CH$_2$)$_4$CH=CH$_2$]$_2$ (0.027 g, 0.09 mmol) was dissolved in C$_6$D$_6$ ($\approx$0.13 M) and loaded into a sealable NMR tube. The sample was sealed under 0.95 atm of argon and heated in a thermostated oil bath in the dark at 135 °C for 5 days with periodic monitoring by ^{1}H NMR spectroscopy. NMR data for Te[(CH$_2$)$_4$CH=CH$_2$]$_2$: ^{1}H NMR (C$_6$D$_6$, ppm): 5.70 (ddt, 1H, *J* = 6.7, 10.4, 17.1 Hz); 4.99 (dtt, 1H, *J* = 1.2, 2.0 Hz); 4.96 (ddt, 1H, *J* = 1.6 Hz); 2.40, (t, 2H, *J* = 8.0 Hz); 1.91, (dt, 2H, *J* = 6.8, 7.2 Hz); 1.60 (m, 2H, *J* = 7.6 Hz); 1.31 (m, 2H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm): 138.7, 114.8, 33.4, 32.1, 31.5, 2.1. ^{1}H NMR data for Te[CH$_2$(*c*-C$_5$H$_9$)]$_2$ (C$_6$D$_6$, ppm): 2.56 (d, 2H, *J* = 7.1 Hz); 1.98 (m, 1H); 1.77, 1.50, 1.11 (m, 8H). Partial ^{1}H NMR data for mixed telluride Te[(CH$_2$)$_4$CH=CH$_2$][CH$_2$(*c*-C$_5$H$_9$)]: 2.55 (d, 2H, *J* = 7.1 Hz); 2.42 (t, 2H, *J* = 7.3 Hz).

Thermolysis of Te[(CH$_2$)$_5$CH$_3$]$_2$ and 2. Complex **2** (0.018 g, 0.02 mmol) and Te[(CH$_2$)$_5$CH$_3$]$_2$ (0.008 g, 0.03 mmol) were dissolved in C$_6$D$_6$ (~0.03 M), loaded into a sealable NMR tube, and sealed under 0.95 atm of argon. The sample was heated at 135 °C in the dark in a thermostated oil bath with periodic monitoring by ^{1}H NMR spectroscopy.

General Irradiation Procedures. Irradiations were carried out using a water-cooled Hanovia medium-pressure mercury arc lamp in a ventilated stainless steel photolysis box. Solutions were loaded into NMR tubes in the glovebox, placed in a 2 mm Pyrex filter tube, and irradiated through a glass cooling jacket made from Pyrex and containing tap water. The progress of these reactions was followed by ^{1}H NMR spectroscopy. Cooling of the samples was not necessary, since minimal heating of the sample occurred even for uninterrupted irradiations of over 1 h. Alternatively, ambient sunlight through window glass was used as a milder source of light.

X-ray Crystallography. Single crystals suitable for X-ray crystallography were mounted in thin-walled glass capillaries and optically centered in the X-ray beam of an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions were determined via least-squares refinement of the setting angles of 24 high-angle reflections, and intensity data were collected using the ω-2θ scan mode. Data were corrected for Lorentz, polarization, and absorption effects but not for extinction. Pertinent data collection and structure refinement parameters are presented in Table 4. All structures were solved using direct methods. In **2** and **4** the Te and Se atoms were found to lie on

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(48) Subsequent to selective insertion of the monosubstituted end of the diene, conversion to another product via a process possibly involving σ-bond metathesis with one of the six pendant allylic C−H bonds occurs over the course of 2−3 h.

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Table 4. Summary of Data Collection and Structure Refinement Details for 1b, 2 and 4

	1b	**2**	**4**
formula	$C_{27}H_{37}ScTe$	$C_{43}H_{67}Sc_2Te$	$C_{43}H_{67}Sc_2Se$
fw	534.14	801.52	752.87
cryst syst	monoclinic	tetragonal	tetragonal
a, Å	14.932(5)	15.0324(7)	14.7663(12)
b, Å	10.8122(8)		
c, Å	17.496(8)	18.8884(14)	19.101(4)
β, deg	113.64		
V, Å^3	2587.5(15)	4268.3(4)	4164.9(9)
space group	$P2_1/c$	$P\bar{4}2_1c$	$P\bar{4}2_1c$
Z	4	4	4
F(000)	1088	1676	1604
d_{calc}, mg m^{-3}	1.37	1.25	1.20
μ, mm^{-1}	1.40	1.01	1.21
R	0.041	0.040	0.050
R_w	0.038	0.034	0.043
GOF	3.11	3.41	2.27

crystallographic 2-fold axes, respectively, meaning that only one Cp*$_2$Sc moiety is present in the asymmetric unit. All nonhydrogen atoms were refined with anisotropic thermal parameters except in **2** and **4**, for which solvent hexane carbon atoms were observed to be disordered and refined with fixed thermal parameters and site occupancy as a variable. Methyl and methylene hydrogen atoms were located via inspection of difference Fourier maps and fixed, temperature factors being based upon the carbon atom to which they are bonded. In **2** and **4** the enantiomorph was fixed by refining η.[50] A weighting scheme based upon counting statistics was used with the weight modifier k in kF_o^2 being determined via evaluation of variation in the standard reflections that were collected during the course of data collection. Neutral atom scattering factors were taken from ref 51. Values of R and R_w are given by $R = (F_o - F_c)/\Sigma F_o$ and $R_w = [\Sigma(w(F_o - F_c))^2/\Sigma(wF_o^2)]^{1/2}$. All crystallographic calculations were conducted with the PC version of the NRCVAX program package[52] locally implemented on an IBM compatible 80486 computer.

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, atomic coordinates and isotropic thermal parameters, H atom coordinates, anisotropic thermal parameters, and all bond lengths and angles for compounds **1a**, **2**, and **4** (15 pages). Ordering information is given on any current masthead pages.

OM940532M

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