Notes

Synthesis and Structure of Free and Complex-Stabilized Bis(cyclopentadienyl)tellurium: $[\eta^1\text{-}(Me_3Si)_3C_5H_2]_2Te$ and $[\eta^1\text{-}(Me_3Si)_3C_5H_2]_2TeW(CO)_5$

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*Summary: $[\eta^1\text{-}(Me_3Si)_3C_5H_2]_2Te$ (**1**), the first homoleptic cyclopentadienyltellurium compound, is obtained by reacting lithium tris(trimethylsilyl)cyclopentadienide with bis(diethyldithiocarbamato)tellurium. **1** slowly decomposes at room temperature but can be stabilized as $[\eta^1\text{-}(Me_3Si)_3C_5H_2]_2TeW(CO)_5$ (**2**). **1** and **2** are structurally characterized by single-crystal X-ray diffraction.*

Introduction

Cyclopentadienes are the most frequently used ligands in organometallic chemistry.[1] If σ- or π-bonded cyclopentadienyls of main group elements as central atoms are included, most of the elements form such compounds. Of group 16 elements only η^1-$Cp^*{}_2S$[2] and η^1-$Cp^*{}_2Se$[3] are known. Probably as a consequence of the relatively weak Te−C bond and the limited number of Te(II) synthons, no homoleptic cyclopentadienyltellurium compounds have been reported so far. Minkin et al.[4] have isolated several ArTeCp type compounds [Cp = $C_5(CO_2Me)_5$] with stabilizing electron acceptor groups in the ortho position and characterized them by ^1H and ^{13}C NMR spectroscopy.

Results and Discussion

By reaction of bis(diethyldithiocarbamato)tellurium with lithium tris(trimethylsilyl)cyclopentadienide, a so-called supracyclopentadienyl,[1] we now have obtained the first homoleptic cyclopentadienyltellurium compound **1** (Scheme 1).

In solution there are two isomers (**1a**:**1b** = 4:1) with tellurium in a vinylic 2- or 1-position, respectively, which decompose with extrusion of tellurium within a few days. Out of such solutions **1a** crystallizes exclusively. The structure of **1a** was determined X-ray crystallographically at 213 K (Figure 1). Tellurium is σ-bound to the cyclopentadiene rings which are almost perpendicular to each other to minimize the steric strain of the vinylic Me_3Si groups.

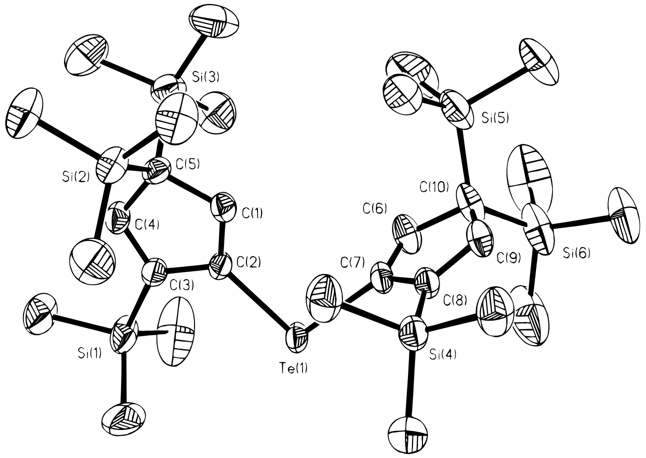
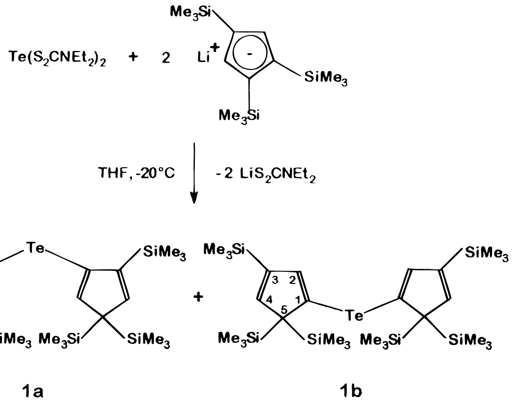


Figure 1. Structure of **1a** with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 1



Analogous reactions with differently substituted lithium cyclopentadienides show a decrease in stability of the respective tellurane in the order $(Me_3Si)_3C_5H_2$ > $(t\text{-}Bu)_2(Me_3Si)C_5H_2$ > $(Me_3Si)_2C_5H_3$ > $(t\text{-}Bu)_2C_5H_3$ > Cp* > Cp, as judged by the approximate half-life in solution, from almost instantaneous extrusion of tellurium (Cp*) to several days. Since alkyl groups invariably occupy vinylic positions and do not exhibit any fluxionial behavior, this means that they effectively compete with tellurium which also favors these positions. Generally organotellurium compounds with tellurium in vinylic positions are more stable than in allylic positions.[5] The latter easily undergo radical decomposition, whereas the stability of the former is usually explained by a favor-

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Table 1. Crystal Data and Structure Refinement for 1a and 2

	1a	**2**
formula	$C_{28}H_{58}Si_6Te$	$C_{33}H_{58}O_5Si_6TeW$
M_r	690.88	1014.78
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (pm)	1023.8(3)	1350.5(2)
b (pm)	1236.3(4)	1828.4(3)
c (pm)	1753.0(3)	1903.1(3)
α (deg)	92.84(2)	90
β (deg)	91.07(2)	100.73(1)
γ (deg)	114.40(2)	90
V (Å^3)	2016.3(9)	4617.1(13)
Z	2	4
D_x (Mg/m^3)	1.138	1.460
temp (K)	213	223
μ (mm^{-1})	0.930	3.309
F(000)	724	2024
cryst size (mm)	0.6 × 0.28 × 0.22	0.58 × 0.39 × 0.12
2θ range (deg)	6.08−48	6.04−46.00
no. of rflns collcd	6621	6704
no. of indep rflns	5428	5943
R(int)	0.0168	0.0262
$T_{\min}$, $T_{\max}$	0.883, 0.946	0.540, 1.000
data, restraints, params	5425, 0, 316	5936, 0, 415
GOF	1.064	1.038
$R1$, w$R2$ [$I > 2\sigma(I)$]	0.0296, 0.0635	0.0370, 0.0919
final max, min Δρ (e Å^{-3})	0.403, −0.429	0.564, −0.544

able interaction of tellurium orbitals with the adjacent π-system. Me_3Si groups on the other hand primarily occupy allylic positions in cyclopentadiene and are fluxionial. They possibly by their −I effect also enhance the interaction of tellurium orbitals with the π-system of the cyclopentadiene ring. In accordance the Te−C bond length (2.116 Å) in **1a** is somewhat shorter than the sum of the covalent radii (2.14 Å), quite in contrast to the S−C bond length in $Cp^*{}_2S$ (1.856 Å compared to 1.81 Å)[2] and the Se-C bond length in $Cp^*{}_2Se$ (2.000 Å compared to 1.94 Å)[3] with sulfur and selenium in allylic positions and almost coplanar Cp* rings. There are of course also steric factors influencing the stability of such compounds.

1a/**1b** interacts with THF·$W(CO)_5$ with formation of **1a**·$W(CO)_5$ (**2**). **2** now is completely stable in solution and in the solid state. The X-ray structure (Figure 2) however shows a structurally almost unchanged **1a**. The change in stability thus is most likely due to kinetic stabilization by steric hindrance of the tellurium which is also seen in packing models. A similar stabilization for an elusive tellurium species has been achieved previously for a tellurourea in a $Cr(CO)_5$ complex.[6] The dense steric packing of **2** also persists in solution. According to the ^{1}H-NMR spectra in **2** the cyclopentadiene rings are no longer freely rotating in contrast to **1a**/**1b**. Tellurium in **2** is coordinated distorted pyramidal (sum of angles: 307.3°). The relative shortening of the W−CO(*trans*) bond (1.969 Å) compared to the mean of the W−CO(*cis*) bonds (2.046 Å) indicates good donor properties of tellurium.[7]

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1a and 2, with Estimated Standard Deviation in Parentheses

Compound **1**			
Te(1)−C(2)	2.111(3)	C(1)−C(5)	1.489(4)
Te(1)−C(7)	2.121(3)	C(6)−C(7)	1.337(4)
C(1)−C(2)	1.354(4)	C(7)−C(8)	1.462(4)
C(2)−C(3)	1.470(4)	C(8)−C(9)	1.363(4)
C(3)−C(4)	1.360(5)	C(9)−C(10)	1.480(5)
C(4)−C(5)	1.481(4)	C(6)−C(10)	1.495(4)
C(2)−Te(1)−C(7)	99.10(12)	interplane angle	83.03(15)
Compound **2**			
Te(1)−C(2)	2.141(7)	C(2)−C(3)	1.463(9)
Te(1)−C(7)	2.137(7)	C(3)−C(4)	1.362(10)
Te(1)−W(1)	2.8385(6)	C(4)−C(5)	1.485(10)
W(1)−C(01)	2.047(9)	C(1)−C(5)	1.494(10)
W(1)−C(02)	2.026(9)	C(6)−C(7)	1.346(9)
W(1)−C(03)	2.054(10)	C(7)−C(8)	1.465(10)
W(1)−C(04)	2.054(10)	C(8)−C(9)	1.354(10)
W(1)−C(05)	1.969(9)	C(9)−C(10)	1.485(10)
C(1)−C(2)	1.339(10)		
C(2)−Te(1)−C(7)	98.5(3)	C(01)−W(1)−C(04)	88.2(3)
C(2)−Te(1)−W(1)	106.9(2)	C(02)−W(1)−C(03)	89.8(3)
C(7)−Te(1)−W(1)	101.9(2)	C(04)−W(1)−C(03)	175.5(3)
C(05)−W(1)−C(01)	90.6(3)	C(02)−W(1)−Te(1)	88.5(2)
C(05)−W(1)−C(02)	89.9(3)	C(04)−W(1)−Te(1)	92.7(2)
C(05)−W(1)−C(04)	88.5(4)	C(02)−W(1)−C(01)	178.0(3)
C(05)−W(1)−C(03)	87.0(4)	C(02)−W(1)−C(04)	89.9(3)
C(05)−W(1)−Te(1)	178.0(3)	C(01)−W(1)−C(03)	92.1(3)
C(01)−W(1)−Te(1)	91.1(2)	C(03)−W(1)−Te(1)	91.8(2)
interplane angle	81.39(31)		

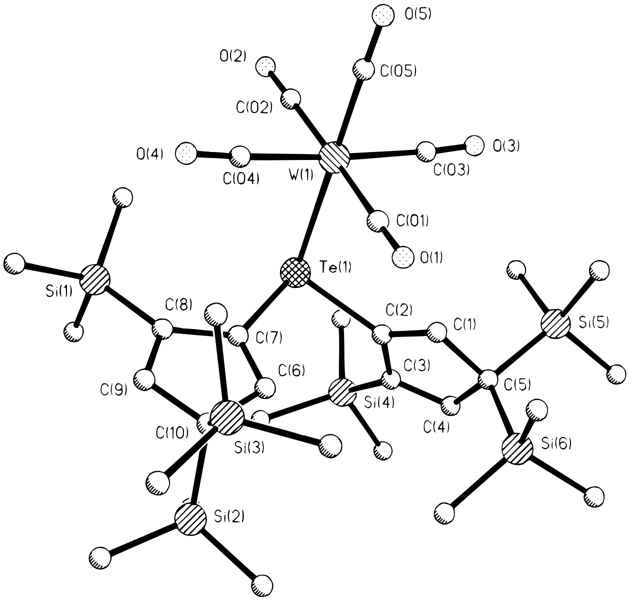

Figure 2. Structure of **2**. For clarity hydrogen atoms are omitted and spheres are plotted instead of ellipsoids.

Experimental Section

General Comments. All reactions were performed under argon by using standard Schlenk techniques. Hexane and THF were purified and dried according to literature methods. $(Me_3Si)_3C_5H_3$[8] and $Te(S_2CNEt_2)_2$[9] were prepared as previously described. $W(CO)_6$ was purchased from Aldrich and used without further purification. Flash chromatography was performed with Merck silica gel (Type 60, 230−400 mesh ASTM) and petroleum ether (fraction 40−60 °C) as the eluent. ^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded on a Bruker AC 200 spectrometer and signals referred to solvent peaks and to external Me_2Te, respectively. Mass spectra (EI) were recorded at 30 eV on a Varian CH-7 spectrometer. Infrared spectra were measured as KBr disks in the range 4000−250 cm^{-1} on a Nicolet 510 FT-IR spectrometer.

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Synthesis of 1. To a solution of $(Me_3Si)_3C_5H_3$ (4.00 g, 14.2 mmol) in 60 mL of THF was added 8.90 mL of methyllithium (14.2 mmol, 1.6 M in hexane) at −30 °C. After the mixture was stirred for 3 h at room temperature, a solution of $Te(S_2CNEt_2)_2$ (3.01 g, 7.10 mmol) in 40 mL of THF was slowly added at −20 °C. The mixture was stirred for 2 h at room temperature. Removal of the solvent *in vacuo*, filtration over silica gel, and chromatography afforded pure **1** as a pale yellow oil which readily turns brown. **1** was crystallized at −20 °C from hexane as pale yellow crystals, which decompose within several days (3.67 g, 74.8%), mp 62−64 °C dec. ^{1}H NMR (200 MHz, C_6D_6): **1a**, δ 0.20 (s, 18H, 5,5-$SiMe_3$), 0.64 (s, 9H, 3-$SiMe_3$), 7.01 (d, J 2.44 Hz, 1H, 4-H), 7.07 (d, J 2.44 Hz, 1H, 1-H); **1b**, δ 0.36 (s, 18H, 5,5-$SiMe_3$), 0.45 (s, 9H, 3-$SiMe_3$), 7.04 (d, J 2.44 Hz, 1H, 4-H), 7.32 (d, J 2.44 Hz, 1H, 2-H). ^{13}C NMR (200 MHz, C_6D_6): **1a**, δ 0.25 (5,5-$SiMe_3$), 0.82 (3-$SiMe_3$), 63.9 (5-C), 144 (2-C), 147 (4-C), 148 (1-C), 151 (3-C); **1b**, δ 0.25 (5,5-$SiMe_3$), 0.82 (3-$SiMe_3$), 64.4 (5-C), 116 (1-C), 148 (2-C), 149 (4-C), 150 (3-C). ^{125}Te NMR (200 MHz, hexane): **1a**, δ 348; **1b**, δ 307. MS [m/z (%)]: 692 (67, M^+), 411 (100, $M^+ - Cp(SiMe_3)_3$).

Synthesis of 2. After UV-irradiating a solution of $W(CO)_6$ (0.400 g, 1.14 mmol) in 30 mL of THF for 3 h,[10] **1** (0.600 g, 0.870 mmol) in 20 mL of THF was slowly added. After stirring of the mixture for 2 h and removal of the solvent, the residue was dissolved in hexane, filtered, and crystallized at −20 °C, affording pure **2** as air stable yellow crystals (0.740 g, 85.0%), mp 148 °C dec. Anal. Calcd for $C_{33}H_{58}O_5Si_6TeW$: C, 39.06; H, 5.76. Found: C, 38.92; H, 5.60. ^{1}H NMR (200 MHz, $CDCl_3$): δ −0.02 (s, 9H, 5-$SiMe_3$), 0.01 (s, 9H, 5-$SiMe_3$), 0.29 (s, 9H, 3-$SiMe_3$), 6.81(d, J 2.44 Hz, 1H, 4-H), 7.02 (d, J 2.44 Hz, 1H, 1-H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 0.29 (5-$SiMe_3$), 0.77 (5-$SiMe_3$), 1.34 (3-$SiMe_3$), 64.9 (5-C), 115 (2-C), 146 (3-C), 149 (1-C), 150 (4-C), 199 [CO(*cis*)], 200 [CO(*trans*)]. ^{125}Te NMR (200 MHz, hexane): δ 237. MS [m/z (%)]: 692 [100, $M^+ - W(CO)_5$]. FT-IR (KBr): ν(CO) = 2068 (s), 1980 (s), 1941 (vs), 1908 (vs), 1872 (w) cm^{-1}.

X-ray Crystallography. Single crystals of **1a** and **2** were grown from hexane at −20 °C. X-ray data were collected on a Siemens P4 diffractometer (graphite monochromator, λ = 0.710 73 Å) by the ω scan method, and absorption corrections were made by the ψ scan method. The structures were solved by direct methods (SHELXS-86)[11] and refined by full-matrix blocked least squares on F^2 (SHELXL-93).[12] The positions of the hydrogen atoms were calculated and included in the refinement with isotropic temperature parameters $U_{eq} = 1.5U_{eq}$ of the parent carbon atoms.

Supporting Information Available: Tables of crystallographic parameters, bond distances and angles, and atom coordinates and thermal parameters for **1a** and **2** (15 pages). Ordering information is given on any current masthead page.

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