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Synthesis and Structure of Semi(tetrahydrofuran-*O*)bispotassium Bis(2,3,4,5-tetraethylstibolide)

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*Summary: The reaction of bis(cyclopentadienyl)zircona-2,3,4,5-tetraethylcyclopentadiene (**1**) with antimony trichloride yields 1-chloro-2,3,4,5-tetraethyl-1-stibole (**2**). The reduction with potassium gives semi(tetrahydrofuran-O)bispotassium bis(2,3,4,5-tetraethylstibolide) (**3**). The potassium stibolide columns are linked via K−Sb contacts of 3.618 Å, thus forming a wavelike layer structure. The molecular structure shows three crystallographically different metal cations. One potassium atom is located between two stibolide anions, whereas the other ones show additional K−O and K−Sb contacts of 2.681 and 3.618 Å, respectively.*

Introduction

Cyclopentadienides of the alkali metals are widely used synthons for the preparation of metallocenes of the d-block elements. Their synthesis is straightforward, and an isolation of these reactive species usually is unnecessary to perform ligand transfer reactions.[1,2] The formal substitution of a CH unit by a phosphorus atom gives the well-known phospholides,[3] which show properties similar to those of the hydrocarbon analogues. The aromaticity within the five-membered cycle based on NMR data and theoretical investigations lies in the same order of magnitude,[4] and also the structures of the metallocenes and the phospha-substituted derivatives are often alike.[3] However, in addition to the η^5-coordination phospholides can act as η^1-ligands preferably to 16-electron species of d-block metals. For the alkaline earth metal phospholides, metallocenes[5] (η^5-coordination) and 1-phosphacyclopenta-2,4-dien-1-ides[6] (η^1-coordination) were observed. There are only a few examples of structurally characterized pentelacyclopentadienides of the heavier penteles (pnictogenes). To our knowledge for antimony only the molecular structures of 1,1′-distibaferrocenes have been published.[7−9] Here we report on the synthesis and structure of an alkylated potassium stibolide that exhibits both η^5- as well as η^1-coordination to a potassium cation.

Cyclopentadienides of the heavier alkali metals are of interest not only due to their application as cyclopentadienyl transfer reagents but also due to their structural and physical properties. Very recently, Cloke et al.[10] published the synthesis of (tetrahydrofuran-*O*)-potassium 2,4,5-tri(*tert*-butyl)-1,3-diphosphacyclopentadienide with its columnar structure. Whereas unsubstituted cyclopentadienyllithium, -sodium, and -potassium are polymeric in the solid state,[11] demanding groups and coordination of neutral coligands lead to the formation of monomeric or oligomeric molecules.[1] On the other hand, addition of bases such as THF and the use of substituted cyclopentadienyl groups is necessary to obtain substances soluble in common organic solvents.

Results and Discussion

The reaction of zirconocene dichloride with butyllithium and hex-3-yne at −78 °C in THF yields nearly quantitatively red 1,1-bis(cyclopentadienyl)-2,3,4,5-tetraethyl-1-zirconacyclopenta-2,4-diene (**1**).[12] The transmetalation with antimony trichloride gives the corresponding 1-chloro-2,3,4,5-tetraethyl-1-stibole (**2**) as a yellow oil according to Scheme 1. The reduction of **2** with potassium metal in THF and recrystallization from heptane yields slightly yellow crystals of semi(tetrahydrofuran-*O*)bispotassium bis(2,3,4,5-tetraethyl-1-stibolide) (**3**).

The molecular structure and the numbering scheme of **3** are represented in Figure 1. The unit shown in Figure 1 is part of a column in which potassium cations and stibolide anions alternate. However, there are three crystallographically and chemically different metal centers: K1 lies between two parallel stibolide anions, and at K3 a THF ligand is bonded (K3−O3 2.68(1) Å) and enforces a nonparallel orientation of the neighbor-

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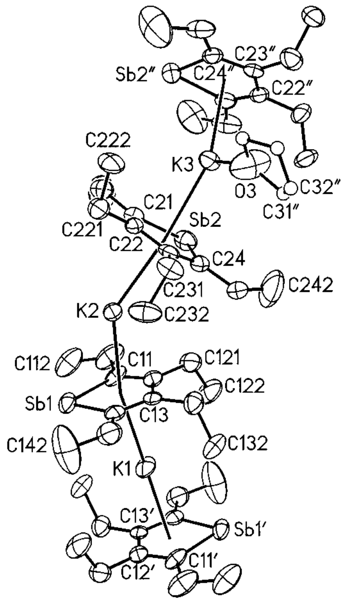
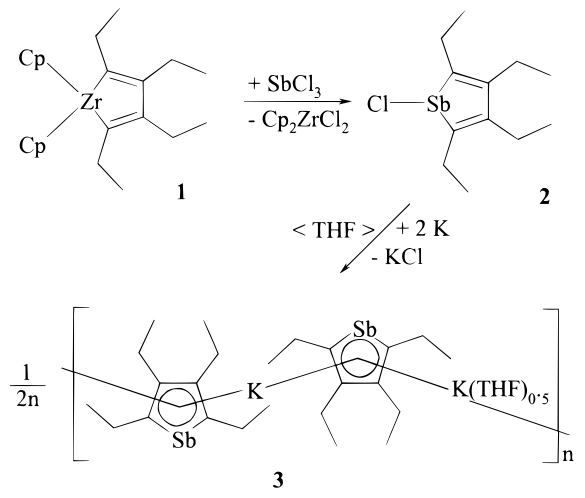


Figure 1. Molecular structure and numbering scheme of **3**. The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity reasons. The carbon atoms of the THF ligand are shown with arbitrary radii. Atoms marked with one prime are generated by an inversion center ($-x$, $-y$, $-z$); those marked with two primes are generated by C_2 symmetry ($-x+1$, y, $-z-0.5$).

Scheme 1. Synthesis of Stibole 2 and Its Reduction with Potassium to Stibolide 3



ing stibolide substituents, whereas K2 displays close contacts to the neighboring column, as shown in Figure 2. As a consequence of the lower coordination number of K1, the distances of K1 to the centers of the neighboring stibolide cycles with values of 2.839 Å are smaller than the corresponding contacts between K2 and K3 to their neighboring anions. The parallel orientation of the anions bonded to K1 is crystallographically enforced by an inversion center. The stibolide anions at K2 and K3 show strong deviations from parallelism, and the angles between the centers of the stibolide cycles show values of 139.5° and 138.2° at K2 and K3, respectively. Along with this bending increasing distances between the stibolide centers and the cations of approximately 290.5 Å are observed. The columns are linked via K2−Sb1‴ contacts of 3.618 Å, thus forming a wavelike layer structure rather than a chain structure.

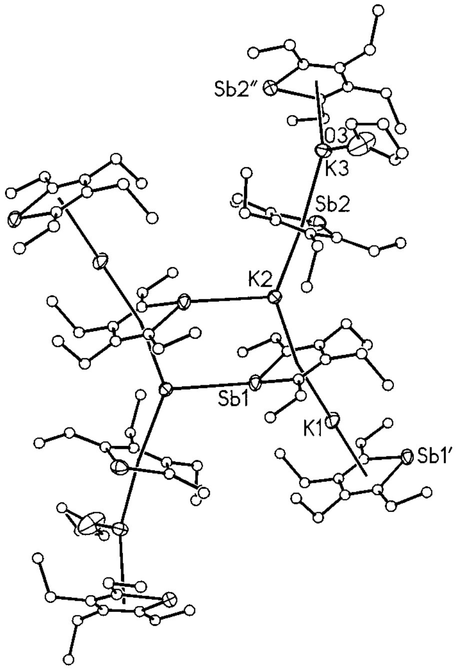


Figure 2. Linkage of two columns in the crystal structure of **3**. All hydrogen atoms are omitted for clarity reasons; all carbon atoms are represented with arbitrary radii. The ellipsoids represent a probability of 40%. Linking of the columns occurs via a K1 and Sb1‴ of the stibolide generated by $-x+1$, $-y$, $-z$. The centers of the stibolide anions are symbolized by Z(n) with n the same number as the corresponding Sb(n). Environment of the potassium centers: distances (Å) K1−Z1 2.839, K2−Z1 2.901, K2−Z2 2.893, K3−Z2 2.922; angles (deg) Z1−K1−Z1′ 180.0, Z1−K2−Z2 139.5, Z1−K2−Sb1‴ 111.8, Z2−K2−Sb1‴ 108.6, Z2−K3−Z2″ 138.2, O3−K3−Z2 110.9, O3−K3−Z2″ 110.9.

As expected, the shortening of the Sb−C bond lengths compared to single bonds is less pronounced. On the other hand these bonds are clearly longer than observed for a Sb═C double bond (2.06 Å),[13] calculated for stibaethene H−Sb═CH$_2$ (2.01 Å)[14] or found for stibabenzene (stibinine, 2.05 Å).[15] Surprisingly, the Sb1−C11 and Sb1−C14 bond lengths of 2.085(8) and 2.087(7) Å are smaller than the values for Sb2−C21 (2.115(8) Å) and Sb2−C24 (2.100(7) Å), although the linkage between the columns leads to a higher coordination number at Sb1. In 2,2′,5,5′-tetramethyl-[7] and octamethyl-1,1′-distibaferrocene[9] mean endocyclic Sb−C bond lengths of 2.11 Å were reported.

Another point of interest concerns the delocalization of the anionic charge within the stibolide anions. Taking the bond length difference between the endocyclic C−C bonds as shown in Table 1 as a criterion, the delocalization should be disturbed since the C(n1)−C(n2) and C(n3)−C(n4) bonds with a mean value of 1.39 Å are shorter than the C(n2)−C(n3) bonds at approximately 1.44 Å. In contrast to this observation the corresponding endocyclic C−C bonds in 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene[8] are alike (mean value 1.43 Å). For octamethyl-1,1′-distibafer-

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Table 1. Selected Bond Lengths (Å) and Angles (deg) of 3

	n = 1	*n* = 2
K1−Sb(*n*)	3.4861(6)	
K2−Sb(*n*)	3.555(2)	3.487(2)
K3−Sb(*n*)		3.501(2)
Sb(*n*)−C(*n*1)	2.085(8)	2.115(8)
Sb(*n*)−C(*n*4)	2.087(7)	2.100(7)
C(*n*1)−C(*n*2)	1.40(1)	1.38(1)
C(*n*2)−C(n3)	1.45(1)	1.44(1)
C(n3)−C(*n*4)	1.38(1)	1.40(1)
C(*n*4)−Sb(*n*)−C(*n*1)	81.1(3)	81.1(3)
Sb(*n*)−C(*n*1)−C(*n*2)	112.5(5)	111.6(5)
C(*n*1)−C(*n*2)−C(*n*3)	116.2(7)	118.0(6)
C(*n*2)−C(*n*3)−C(*n*4)	118.0(6)	117.7(7)
C(*n*3)−C(*n*4)−Sb(*n*)	112.0(5)	111.6(5)

Table 2. NMR Spectroscopic Data of 1, 2, and 3 ([D$_6$]benzene, 25°C)

	1	**2**	**3**
^{1}H:			
δ(CH$_3$)	0.87	0.87	1.01
δ(CH$_2$)	2.19	1.98	2.22
^3J(H,H)	7.6	7.2	broad
δ(CH$_3$)	0.97	1.13	1.01
δ(CH$_2$)	2.31	2.38	2.43/2.83
^3J(H,H)	7.2	7.2	broad
δ	5.91 (Cp)		1.41 (THF) 3.52 (THF)
^{13}C{^{1}H}:			
δ(CH$_3$)	14.31	14.26	15.15/16.05
δ(CH$_3$)	15.96	16.95	18.91/21.22
δ(CH$_2$)	21.19	22.47	23.11/23.74
δ(CH$_2$)	29.41	24.92	26.50/29.05
δ(C2, C5)	133.65	157.59	153.34
δ(C3, C4)	190.67	153.54	150.24
δ	109.60 (Cp)		25.50 (THF) 67.65 (THF)

Table 3. Crystallographic Data of 3 as Well as Details of the Structure Solution and Refinement Procedures

empirical formula	$C_{26}H_{44}K_2O_{0.5}Sb_2$
fw (g mol^{-1})	686.31
temp *T* (K)	193(2)
space group[18]	*C*2/*c* (No. 15)
unit cell dimens	
a (Å)	11.4558(8)
b (Å)	18.331(1)
c (Å)	30.601(2)
β (deg)	100.078(2)
V (Å^3)	6326.8(8)
Z	8
ρ_{calcd} (g cm^3)	1.441
λ (Å)	0.71073
μ (cm^{-1})	1.983
R indices (all data)	5197 (R_{int} = 0.0463)
w*R*2[a]	0.1355
*R*1[a]	0.0985
R indices with $I > 2\sigma(I)$ (data)	3250
R_1[a]	0.0536
goodness-of-fit s[b]on F^2	1.011
residual density (e Å^{-3})	1.277/−0.943

rocene[9] similar results were reported; however, due to less steric strain the bond lengths are in general slightly smaller. All these stibolide anions have a very narrow C−Sb−C angle of approximately 80° in common.

Table 2 summarizes the NMR spectroscopic data. The ethyl groups of **3** are split; we were not able to distinguish whether this splitting arises from two chemically different stibolide anions or from the ethyl substituents of one anion. There is no temperature dependency observed. Therefore, hindered rotation can be ruled out as the reason for this observation.

Conclusion

Interactions between soft cations and heavier p-block elements are of general interest.[16] In the crystal structure of **3** η^5-coordination of the stibolide anions to the potassium cations leads to the formation of columns. These structural motifs are linked by metal centers which are η^1-bonded to the antimony atoms of the neighboring column. The K−Sb distances within a column vary between 3.49 and 3.56 Å, whereas the linkage between the columns shows K−Sb σ-bond lengths of 3.62 Å.

Experimental Section

General Procedures. All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed by using standard Schlenk techniques and dried with thoroughly deoxygenated solvents. NMR spectra were recorded on JEOL spectrometers GSX270 and EX400, and the NMR data are listed in Table 2. A Nicolet 520 FT-IR spectrophotometer was used to record the IR spectra; solid substances were measured in Nujol between KBr plates (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder). The low carbon value of **1** at the elemental analysis results from carbide and carbonate formation during handling and combustion of the compound.

Synthesis of 1,1-Bis(cyclopentadienyl)-2,3,4,5-tetraethyl-1-zirconacyclopenta-2,4-diene (1).[12] A 2.5 M butyllithium solution in hexane (28.43 mL, 71.08 mmol) was dropped slowly into a solution of 10.39 g of zirconocene dichloride (35.54 mmol) and 5.84 g of hex-3-yne (71.08 mmol) in 40 mL of THF at −78 °C. After complete addition and an additional 15 min at this temperature this reddish brown solution was warmed to room temperature. All volatile materials were removed in vacuo, and the residue was dissolved in 40 mL of toluene. All solids were filtered off, and the removal of toluene left 11.51 g of red and analytically pure powder of **1** (29.85 mmol, 84%), mp 57 °C. IR [cm^{-1}]: 1672 s, 1620 s, 1613 s, 1604 s, 1580 s, 1463 s, 1453 s, 1415 m, 1375 s, 1340 m, 1323 m, 1262 m, 1232 m, 1192 m, 1134 s, 1098 s, 1063 s, 1016 vs, 901 m, 893 w, 846 m, 795 vs, 740 s, 676 s, 668 s, 601 m, 540 m, 531 m, 510 m, 493 m, 476 m, 331 w. Anal. Calcd for $C_{22}H_{30}Zr$, 385.68 g mol^{-1}: C, 68.51; H, 7.84. Found: C, 68.26; H, 7.68.

Synthesis of 1-Chloro-2,3,4,5-tetraethyl-1-stibole (2). Antimony trichloride (1.13 g, 4.95 mmol) was added to a solution of 1.91 g of **1** (4.95 mmol) in 25 mL of THF. After 24 h of stirring ar room temperature all volatile materials were removed under vacuum. The yellow residue was extracted with 30 mL of pentane. Removal of the solvent left 1.27 g of an analytically pure yellow oil of **2** (3.95 mmol, 80%). IR [cm^{-1}]: 2967 vs, 2931 vs, 2872 s, 1766 vw, 1735 vw, 1710 vw, 1670 vw, 1721 vw, 1584 vw, 1559 vw, 1550 vw, 1506 vw, 1456 s, 1376 m, 1311 w, 1284 vw, 1259 vw, 1223 vw, 1179 vw, 1156 vw, 1105 vw, 1090 vw, 1063 w, 1050 w, 962 vw, 943 vw, 922 vw, 884 vw, 866 vw, 817 vw, 784 vw, 729 vw, 698 vw, 578 vw, 529 vw, 443 vw, 403 vw, 331 m, 316 m, 281 vw. Anal. Calcd for $C_{12}H_{20}ClSb$, 321.53 g mol^{-1}: C, 44.83; H, 6.27. Found: C, 44.81; H, 6.09.

Synthesis of Semi(tetrahydrofuran-*O*)bispotassium bis(2,3,4,5-tetraethyl-1-stibolide) (3). Potassium (0.33 g, 8.44 mmol) was added to a solution of 1.65 g of **2** (5.13 mmol) in 25 mL of THF. After 2 days of stirring at room temperature all volatiles were removed under reduced pressure. Extraction

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of the residue with 30 mL of heptane and recrystallization from benzene gave 3.69 g of yellow crystals of **3** (5.47 mmol, 72%), dec above 165 °C. IR [cm^{-1}]: 1688 vw, 1641 vw, 1579 w, 1559 w, 1472 vs, 1447 vs, 1402 s, 1372 vs, 1342 w, 1309 s, 1259 vs, 1174 vw, 1144 w, 1078 vs, 1061 vs, 1050 vs, 1024 vs, 996 s, 925 m, 912 m, 900 m, 861 m, 847 m, 810 vs, 756 s, 721 m, 696 m, 664 m, 644 w, 612 w, 531 vw, 521 vw, 482 vw, 438 vw, 388 m, 366 m. Anal. Calcd for $C_{26}H_{44}K_2O_{0.5}Sb_2$, 686.31 g mol^{-1}: C, 45.50; H, 6.46. Found: C, 45.21; H, 6.50.

Crystallographic Analysis of 3. Data were collected on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at −80 °C using oil-coated rapidly cooled single crystals.[17] A total of 11 180 reflections were collected in the range 2.7° < 2θ < 55.5°. A semiempirical absorption correction was applied ($T_{\mathrm{min}}/T_{\mathrm{max}}$ 0.755/0.826). Crystallographic parameters, details of data collection, and refinement procedures are summarized in Table 3.

The structure was solved by direct methods, and 288 parameters were refined with the software packages SHELXL-93 and SHELXL-97.[19] Neutral scattering factors were taken from Cromer and Mann[20] and for the hydrogen atoms from Stewart et al.[21] The non-hydrogen atoms were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms. One of the methyl groups is disordered on two positions with a population ratio C112/C113 of 0.52(2)/0.48(2). This disorder is not represented in Figure 1 due to clarity reasons. We were not able to adopt a split model for the carbon atoms of the THF ligand (C31, C32) with high thermal motion.

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Supporting Information Available: An X-ray crystallographic file for the structure determination of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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