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# Unusual Sandwiching of the Cyclopentadienyl Anion in $[K_4(C_5H_5)_2M_2(OBu^t)_6(CH_3OCH_2CH_2OCH_3)_2]_n$ (M = Ge, Sn)

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Our recent studies on monomeric mixed-ligand ($Cp^-/OR^-$) heterometal systems of the type $[(C_5H_5)MM'(OBu^t)_3]$ (M = Sn, Pb; M′ = Ge, Sn) and $[(C_5H_5)Sn\{M_2(OPr^i)_9\}]$ (M = Zr, Hf) prepared via salt elimination reactions have shown that both cyclopentadienyl and alkoxide ligands can bond simultaneously to different metal centers to afford molecular compounds.[1,2] Lewis acid−base interactions of $KOBu^t$ with *tert*-butoxides of subvalent group 14 elements, $[M(OBu^t)_2]_n$, afford the well-characterized series of heterometal alkoxides $[KM(OBu^t)_3]_n$ (M = Ge, Sn, Pb),[3] which have been used as anion transfer reagents ($\{M(OBu^t)_3{}^-\}$) to construct a variety of heterometal alkoxides.[3a,4] To substitute a monodirectional $-OBu^t$ ligand, in $[KM(OBu^t)_3]_n$, by a "two-dimensional" $C_5H_5{}^-$ ligand, we have carried out the reactions of $KC_5H_5$ with $[M(OBu^t)_2]_n$ derivatives. These reactions follow a similar path with respect to the Lewis acid−base interactions of the molecular entities when compared with the homoleptic alkoxide derivatives, but the mixed-ligand products differ in composition due to the incorporation of an additional molecule of $KC_5H_5$. The heterometal coordination polymers, self-assembled by the formal cyclopentadienyl and $M(OBu^t)_3{}^-$ anions and the potassium cations, involve an unusual interaction of a cyclopentadienyl ring with four K atoms as evident in the crystal structure of $[K_4(C_5H_5)_2Sn_2(OBu^t)_6)(CH_3OCH_2CH_2OCH_3)_2]_n$, which strikingly differs from the heretofore known coordination modes or interactions of a cyclopentadienyl moiety with metal centers.[5]

## Experimental Section

**Methods and Materials.** All the complexes are highly air and moisture sensitive and were handled under rigorous exclusion of air and moisture in an inert atmosphere of dried nitrogen using modified Schlenk techniques. Solvents were dried with appropriate drying agents and freshly distilled before use. Potassium cyclopentadienylide[6] and $[M(OBu^t)_2]_2$ (M = Ge, Sn)[7] were prepared according to the literature procedures. NMR spectra were recorded in $C_6D_6$ or $C_7D_8$ on a Bruker AC-200 spectrometer. The $^1H$ NMR chemical shifts (ppm) are reported relative to protio impurities of deuterated solvents, whereas the solution $^{13}C$ NMR spectra are referenced to the solvent resonances. The solution and solid-state $^{119}Sn$ NMR chemical shifts are externally referenced to $Sn(Me)_4$. For the measurement of solid-state NMR spectra, a polycrystalline sample (ca. 200 mg) was filled in an airtight insert, sealed by a threaded Teflon plunger. Spectra ($^{13}C$ and $^{119}Sn$) were obtained on a Bruker MSL 200S spectrometer using the cross polarization magic angle spinning (CP MAS) technique with proton decoupling. Microanalyses (C and H) were performed on a LECO Elemental Analyzer CHN 900. Melting points were recorded in sealed capillaries and are uncorrected.

**Synthesis of $[K_4(C_5H_5)_2Sn_2(OBu^t)_6(CH_3OCH_2CH_2OCH_3)_2]_n$ (2).** A solution of CpK (0.405 g, 3.88 mmol) in 5 mL of THF was slowly added to a colorless solution of $[Sn(OBu^t)_2]_2$ (1.03 g, 3.88 mmol) in 10 mL of toluene at room temperature, followed by stirring for ∼12 h. The volatiles were removed under vacuo, and the pink viscous mass obtained was dissolved in a DME−*n*-hexane mixture (5/1 v/v). The solution, when allowed to stand overnight at 0 °C, afforded the product **2** as colorless prisms. Yield: 0.75 g, 67% (based on initial amounts of CpK). Anal. Calcd for $C_{42}H_{84}K_4O_{10}Sn_2$: C, 44.13; H, 7.40; Sn, 20.77. Found C, 44.09; H, 7.44; Sn, 20.55. Mp: 118−120 °C. $^1H$ NMR ($C_6D_6$, 296 K): $\delta$ 1.34 (s, 54H, $OC(CH_3)_3$), 3.10 (s, 12H, $OCH_3$), 3.27 (s, 8H, $OCH_2$), 6.30 (s, 10H, $C_5H_5$). $^1H$ NMR ($C_7D_8$, 203K): $\delta$ 1.55, 1.53, 1.51 ($OC(CH_3)_3$), 3.07($OCH_3$), 3.11($OCH_2$), 6.27, 6.57 ($C_5H_5$). $^{13}C$ NMR ($C_6D_6$, 296 K): $\delta$ 34.88 ($OC(CH_3)_3$), 58.14 ($OCH_3$), 69.26 ($OC(CH_3)_3$), 71.51 ($OCH_2$), 105.66 ($C_5H_5$). $^{13}C$ NMR ($C_7D_8$, 203 K): $\delta$ 34.45, 35.60, 36.00 ($OC(CH_3)_3$), 58.88 ($OCH_3$), 70.04 ($OC(CH_3)_3$), 76.68 ($OCH_2$), 105.57, 106.19 ($C_5H_5$). $^{119}Sn$ NMR ($C_6D_6$, 296K): $\delta$ 190.24. $^{13}C$ CP MAS NMR: $\delta$ 35.60, 35.83, 36.13 ($OC(CH_3)_3$), 59.35 ($OCH_3$), 69.42, 69.95 ($OC(CH_3)_3$), 73.55 ($OCH_2$), 103.82, 104.70 ($C_5H_5$). $^{119}Sn$ CP MAS NMR: $\delta$ 202.6.

Compound **1** was prepared and crystallized analogously using 0.467 g (4.48 mmol) of CpK and 0.980 g (4.47 mmol) of $[Ge(OBu^t)_2]_2$. Yield: 0.69 g, 59% (based on initial amounts of CpK). Anal. Calcd for $C_{42}H_{84}K_4O_{10}Ge_2$: C, 48.00; H, 8.05; Ge, 13.82. Found C, 47.91; H, 7.98; Ge, 13.94. Mp: 112−114 °C. $^1H$ NMR ($C_6D_6$, 296K) 1.35 (s, 54H, $OC(CH_3)_3$), 3.10 (s, 12H, $-OCH_3$), 3.29 (s, 8H, $-OCH_2$), 6.20 (s, 10H, $C_5H_5$).$^{13}C$ NMR ($C_6D_6$, 296 K): $\delta$ 33.70 ($OC(CH_3)_3$), 58.15 ($OCH_3$), 69.54 ($OC(CH_3)_3$), 71.62 ($OCH_2$), 104.88 ($C_5H_5$).

**X-ray Crystallography of 2.** A suitable specimen of **2** grown from DME−hexane mixture was sealed in a glass capillary using inert gas techniques. Data collection was performed on a STOE imaging plate diffraction system. Out of 9381 reflections measured, 4376 were independent, of which 3678 strong ($I > 2\sigma(I)$) reflections were averaged to give $R_{int} = 0.0429$. The structure was solved (SHELXS-86)[8] using direct methods which revealed most of the heavy atoms from the electron difference maps. The remaining non-hydrogen atoms were located in the several following difference Fourier cycles. All non-hydrogen atoms (except the splitted carbon atoms of the cyclopentadienyl rings and one of the *tert*-butyl groups) were refined (SHELXL-97)[9] with anisotropic displacement parameters. In the observed crystal system, $P1$ and $P\bar{1}$ are the only two choices for the space group. The initial statistics indicated a mean $|E^2 - 1| = 0.865$, which is almost the mean value between the centrosymmetric (0.968) and noncentrosymmetric (0.736) models. The structure refined well in both the space groups. The clearly observed centrosymmetric positions of the heavy atoms, which correlates to the observed Flack parameter $x =$

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(1) (a) Veith, M.; Mathur, C.; Huch, V. *Organometallics* **1996**, *15*, 2858. (b) Veith, M.; Mathur, C.; Huch, V. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1997**, *124*, 489.

(2) (a) Veith, M.; Mathur, C.; Mathur, S.; Huch, V. *Organometallics* **1997**, *16*, 1292. (b) Veith, M.; Mathur, S.; Mathur, C. *Polyhedron* **1998**, *5*,1005.

(3) (a) Veith, M.; Hans, J.; Stahl, L.; May, P.; Huch, V.; Sebald, A. *Z. Naturforsch Teil B* **1991**, *46*, 403. (b) Veith, M.; Roesler, R. *Z. Naturforsch. Teil B* **1986**, *41*, 1071.(c) Veith, M. *Chem. Rev.* **1990**, *90*, 3.

(4) Veith, M.; Kaefer, D.; Koch, J.; May, P.; Stahl, L.; Huch, V. *Chem. Ber.* **1992**, *125*, 1033.

(5) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(6) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855.

(7) (a) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 939. (b) Veith, M.; Hobein, P.; Roesler, R. *Z. Naturforsch, Teil B* **1989**, *44*, 1067.

(8) Jordan, V.; Behrens, U.; Olbrich, F.; Weiss, E. *J. Organomet. Chem.* **1996**, *517*, 81.

(9) Sheldrick, G. M. *SHELXS-86 Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

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**Table 1.** Crystallographic Data for **2**

| | | | |
|---|---|---|---|
| empirical formula | $C_{42}H_{84}K_4O_{10}Sn_2$ | $\gamma$, deg | 82.69(3) |
| fw | 1142.87 | $V$, Å$^3$ | 1477.3(5) |
| space group | $P\bar{1}$ | $Z$ | 4 |
| $a$, Å | 9.907(2) | $D$(calcd), g/cm$^3$ | 5.085 |
| $b$, Å | 10.722(2) | $T$ | 293(2) K |
| $c$, Å | 14.162(3) | $\lambda$ (Å) | 0.71073 |
| $\alpha$, deg | 81.95(3) | $R^a$ | 0.0460 |
| $\beta$, deg | 89.62(3) | $R_w{}^a$ | 0.0543 |

[a] $R = \sum||F_o| - |F_c||/\sum F_o$. $R_w = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **2**

| | | | |
|---|---|---|---|
| Sn−O(1) | 2.072(3) | Sn−O(2) | 2.059(4) |
| Sn−O(3) | 2.076(3) | K(1)−O(1) | 2.811(4) |
| K(1)−O(2) | 2.634(4) | K(1)−O(3) | 2.767(4) |
| K(1)−O(4) | 2.884(6) | K(1)−O(5) | 2.718(5) |
| K(2)−O(1) | 2.751(3) | K(2)−O(3) | 2.768(4) |
| K(2)−C(17) | 3.145(9) | K(2)−C(18) | 3.078(9) |
| K(2)−C(19) | 3.143(10) | K(2)−C(17′) | 3.042(8) |
| K(2)−C(18′) | 3.118(9) | K(2)−C(20) | 3.061(10) |
| K(2)−C(21′) | 3.136(13) | K(2)−C(22A) | 3.310(15) |
| K(1)−C(20) | 3.307(10) | K(1)−C(21) | 3.383(11) |
| O(2)−Sn−O(1) | 89.39(15) | O(2)−Sn−O(3) | 90.72(14) |
| O(1)−Sn−O(3) | 79.64(13) | O(2)−K(1)−O(3) | 65.97(11) |
| O(3)−K(1)−O(1) | 56.87(10) | | |

0.43(5) (together with the strong correlations for heavy atoms, in $P1$), suggested the centrosymmetric space group. To decide whether $P1$ or $P\bar{1}$ was correct, the carbon atoms of the cyclopentadienyl rings were analyzed in more detail. While in the accentric structure the carbon atoms were found in distinct places but with unusually high $U_{ij}$ values, the refinement in $P\bar{1}$ gave split positions due to inversion centers. The $U_{ij}$ values were nevertheless better and therefore the refinement in $P\bar{1}$ was preferred. The cyclopentadienyl carbon atoms in $P\bar{1}$ have been refined by splitting the atoms C17, C18, C19, C20, C21 (partial occupancy factor = 0.835), C22A and C22B (partial occupancy = 0.41). Crystallographic data and bond lengths and angles are summarized in Tables 1 and 2.

## Results and Discussion

The room temperature reaction of freshly synthesized $KC_5H_5$ with an equivalent of $[M(OBu^t)_2]_2$ (M = Ge, Sn)[7] in a THF−toluene solution (eq 1) followed by crystallization from DME−

$$4\,(C_5H_5)K + 4\,[M(OBu^t)_2] \xrightarrow{DME} 1/n\,[K_4(C_5H_5)_2\,M_2(OBu^t)_6(CH_3OCH_2CH_2OCH_3)_2]_n + 2\,\text{“}(C_5H_5)MOBu^t\text{”} \quad (1)$$

**1** : M = Ge
**2** : M = Sn

hexane mixture (5/1, v/v) affords $[K_4(C_5H_5)_2M_2(OBu^t)_6(CH_3OCH_2CH_2OCH_3)_2]_n$ as the only isolable products in moderate yields. These compounds could also be prepared in higher yields by 2:1 molar reaction of $KC_5H_5$ and $[M(OBu^t)_2]_2$ (M = Ge, Sn), respectively.

The cyclopentadienyl-modified potassium *tert*-butoxy germanates (stannates) are highly moisture and air sensitive and sparingly soluble in common hydrocarbon solvents, but they dissolve readily in the presence of small amounts of donor solvents (THF, $Et_2O$, $C_4H_8O_2$). Attempted sublimation of both **1** and **2** resulted in their decomposition at 180 °C/$10^{-2}$ Torr, which markedly contrasts the sublimable nature of the corresponding homoleptic $[KM(OBu^t)_3]_n$ (M = Ge, Sn) compounds.

The molecular structure of **2** (Figure 1) reveals a bent sandwich polymer strand devoid of terminal ligands. The backbone of the polydecker chain of **2** consists of a two-dimensional zigzag $[K(C_5H_5)]_n$ string interlocked at potassium atoms by “molecular” $KSn(\mu\text{-}OBu^t)_3\cdot(CH_3OCH_2CH_2OCH_3)$ units. The repeating Cp−K−Cp−K− units, in **2**, are severely bent ($Cp_{centroid}$−K2−$Cp'_{centroid}$ = 129.0°) when compared with that found in $[(Et_2O)K(C_5H_5)]_n$ ($Cp_{centroid}$−K−$Cp'_{centroid}$ = 148.3°).[10] A fragment of **2**, as illustrated in Figure 1, emphasizes the alternating presence of two types of bridging cyclopentadienyl rings. Both the bridging ($\mu$) cyclopentadienyl groups lying on crystallographic inversion centers are disordered. One type of the cyclopentadienyl ring is almost symmetrically sandwiched, in a $\eta^5$-coordination mode (av K−C = 3.095 Å) between K2 and K2′ (arising from the next repeating unit (Figure 1)). The K(2)−$Cp_{centroid}$ ($\eta^5$) distance of 2.880 Å is slightly longer than that found in similar $K-C_5H_5$ derivatives: $[KC_5H_4SiMe_3]_n$ (K−$Cp_{centroid}$ = 2.787 Å),[11] $[(Et_2O)KC_5H_5]_n$ (K−$Cp_{centroid}$ = 2.768 Å).[8] The second type of the cyclopentadienyl ring is unusually enveloped by 4 K atoms. It displays a heterodentate behavior with the cyclopentadienyl carbon atoms showing significantly different contacts to K2 (K2′) (av K−C = 3.058 Å) and K1 (K1′) (av K−C = 3.254 Å). Although the intra/intermolecular interactions of a metal center with three or four cyclopentadienyl rings with different coordination modes have been observed in a number of cases, e.g., $[KC_5H_4SiMe_3]_n$,[11] $[(Et_2O)K(C_5H_5)]_n$,[10] $[(C_5H_5)_2Ca]_n$,[12] $[(C_5H_5)Tl]_n$,[13] $[(C_5H_5)_3In]_n$,[14] the reverse situation of a cyclopentadienyl ring being sandwiched among four metal atoms is unprecedented, to our knowledge. Besides the interactions of the carbon atoms of the two bridging cyclopentadienyl rings, the remainder of the coordination sphere of each of the K2 atoms is completed by two triply bridging oxygen atoms of the *tert*-butoxy groups. The coordination environment around each of the tin atoms formed by three asymmetrically bridged *tert*-butoxy groups represents a trigonal pyramid, whereas the K1 centers, bonded additionally by a bidentate dimethoxyethane molecule and showing a K−C contact, display a distorted octahedral geometry. The “$Sn(\mu\text{-}OBu^t)_3K$” substructure in **2** is essentially similar to the trigonal pyramidal core observed in molecular compounds $[Sn(\mu\text{-}OBu^t)_3$-

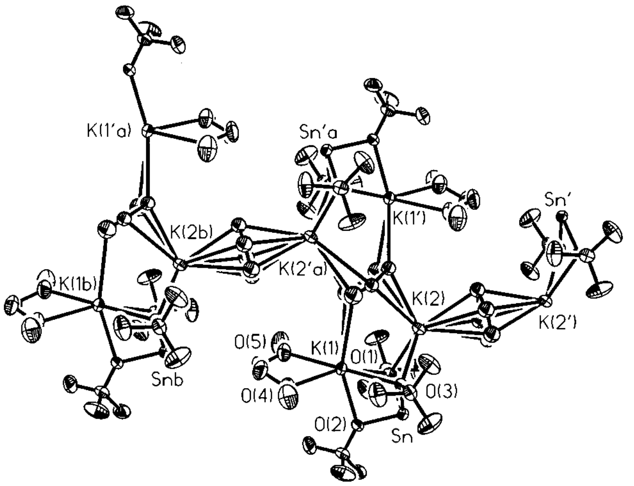

**Figure 1.** An ORTEP view of a section of the coordination polymer **2** using 35% probability ellipsoids. Only one of the positions of the disordered cyclopentadienyl rings is drawn.

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(10) Sheldrick, G. M. *SHELXL-97 Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(11) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 583.

(12) Zerger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, *80*, 7.

(13) Beachley, O. T. Jr.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051.

(14) Einstein, F. W. B.; Gilbert, M. M.; Tuck, D. G. *Inorg. Chem.* **1972**, *11*, 2832.

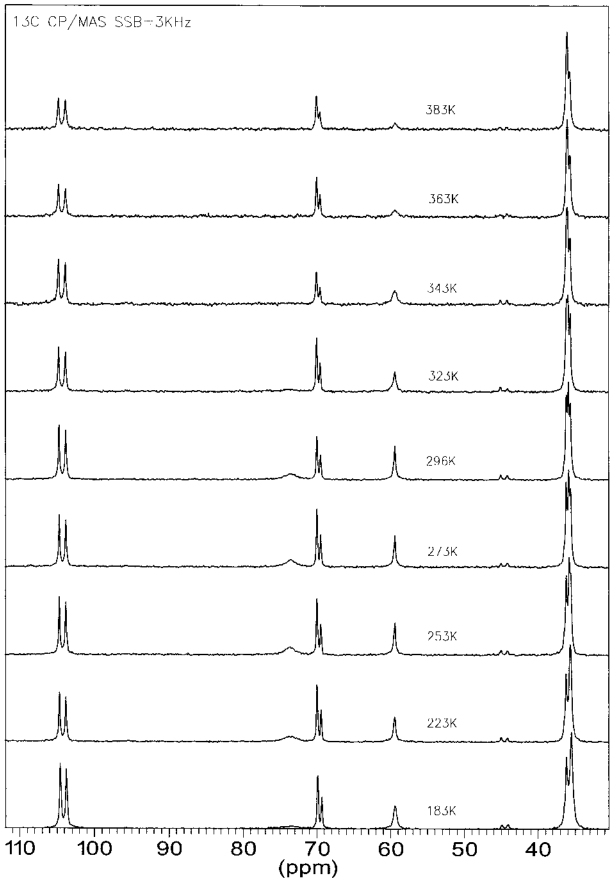

**Figure 2.** A stack plot of the VT ( −90 to +110 °C) $^{13}$C CP MAS spectrum of **2**. The changes in the signals at *δ* 35.60, 35.83, and 36.13 are due to the restricted rotation of the *tert*-butoxy groups. The peaks at *δ* 59.35 and 73.55 belongs to dimethoxyethane.

Tl][15] and [Sn($\mu$-OBu$^t$)$_3$In][3c] as well as in the polymeric [KSn($\mu$-OBu$^t$)$_3$]$_n$.[3b] The Sn−O distances (av 2.069 Å) in **2** are comparable with those observed in [KSn(OBu$^t$)$_3$]$_n$ (av 2.067 Å); however, the K−O distances (2.634(4)−2.811(4) Å) are significantly shorter in **2** (cf. [KSn(OBu$^t$)$_3$]$_n$, av K−O = 2.94 Å).[3b] The ether oxygen atoms of the chelating DME ligand bind the potassium atom in an asymmetric fashion (K(1)−O(4), 2.884(6); K(1)−O(5), 2.718(5)) accompanied by an acute O−K−O bite angle (O(5)−K(1)−O(4), 60.14(18)°).

The more symmetrical nature of the NMR spectra ($^1$H and $^{13}$C) of both **1** and **2** at ambient temperature with single resonances each for the *tert*-butoxy and cyclopentadienyl ligands does not match with the chemical inequivalence of the ligands observed in the solid-state structure of **2**. Apparently, the solution spectral features result from dynamics or dissociative equilibria active in the solution. The low-temperature (−70 °C, $C_7D_8$) NMR spectra on the contrary show two and three distinct signals of equal intensity for the cyclopentadienyl and *tert*-butoxy groups, respectively, which correlates to the solid-state $^{13}$C CP MAS NMR spectrum of **2** (Figure 2). The two closely associated signals in the intensity ratio 1:1 for the two types of the cyclopentadienyl groups in the $^{13}$C CP MAS NMR spectrum showed no temperature dependence and also do not coalesce till 110 °C, indicating the absence of any ligand (Cp−) movement. The $^{119}$Sn NMR chemical shift values of **2** in solution (*δ* −190.24) and the solid state (*δ* −202.6) match closely and are symptomatic of a tin center coordinated by three oxygen atoms.[16]

## Conclusion

The spontaneous generation of cyclopentadienyl-modified potassium *tert*-butoxo germanate (stannate) reported here, represents new metallo-organic examples with a supramolecular motif formed by [$KC_5H_5$]$_n$ and DME adduct of [KM(OBu$^t$)$_3$]$_n$. It is known that heterometal alkoxides, containing only alkoxide ligands, show a pronounced tendency of dissociation into homometallic species, which makes the rational construction of mixed-metal alkoxide framework a rather difficult task. In this context, the assembling and multidentate role of cyclopentadienyl anions to build up a new family of hydrocarbon-soluble coordination polymers provide optmism for synthesizing multimetallic heteroleptic (Cp$^-$/OR$^-$) systems; however, the development of this process as a useful synthetic strategy necessitates further understanding of the subject. Also, the cyclopentadienyl moiety can be used as a potential leaving group for the functionalization of the title compounds. Our investigations in this direction are underway.

**Acknowledgment.** We thank Dr. Michael Zimmer for recording the $^{13}$C and $^{119}$Sn CP MAS NMR spectra for compound **2**.

**Supporting Information Available:** X-ray crystallographic files, in CIF format, for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Veith, M.; Roesler, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 858.

(16) Wrackmeyer, B. *Annu. Rep. NMR Spec.* **1985**, *16*, 84.