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First Synthesis and Spectroscopic Characterization of Novel Cyclopentadienyl Heterobimetallic Alkoxides: Crystal Structure of $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$[†]

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Summary: Novel half-sandwich complexes of the type $CpSn(OBu^t)_3M$ ($M = Ge^{II}$, Sn^{II}, Pb^{II}; $Cp = C_5H_5$) have been prepared conveniently by salt elimination reactions of CpSnCl with potassium alkoxometalates, $[KM(OBu^t)_3]_n$. The single-crystal X-ray crystallographic analysis performed on $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$ reveals an average effect of η^3 and η^1 bonding modes of the cyclopentadienyl ring to the tin atom.

Simple metallocene alkoxides[1,2] constitute a weakly established family of compounds, and only a few reports on their structural aspects are available in the literature. Although a great number of cyclopentadienyl compounds of group 14 elements[3−8] are known, however, to date no attempt has been made to prepare cyclopentadienyl alkoxides of the group 14 elements in their +4 or +2 oxidation states and also the use of alkali-metal alkoxometalates to prepare cyclopentadienyl heterobimetallic alkoxides remains to be explored. The notion of bridging group 14 elements in their subvalent state among themselves via alkoxy bridges was also taken into account, although there is a precedent for this type of bridging in lead stannates and germanates, which have been well characterized by Veith et al.,[9] but efforts made to prepare tin germanates proved to be unsuccessful. Keeping in view that these model compounds would be novel examples of mixed-ligand systems containing both cyclopentadienyl and alkoxometalate units, we report in this communication our investigations on the chemical reactivity of *tert*-butoxometalates of the type $\{M(OBu^t)_3\}^-$ ($M = Ge^{II}$, Sn^{II}, Pb^{II}) toward $(\eta^5\text{-}C_5H_5)SnCl$.

The syntheses[10] of this elusive class of compounds is illustrated in eq 1, and these new derivatives were isolated in high yields (>80%) by the reaction of CpSnCl[11] with $[KM(OBu^t)_3]_n$[9] in a 1:1 molar ratio in toluene at 25 °C.

Table 1. Spectral (^{1}H, ^{13}C, ^{119}Sn, and ^{207}Pb NMR) Data[a,b] for Compounds 1−3

compd	^{1}H	^{13}C{^{1}H}	^{119}Sn{^{1}H}/ ^{207}Pb{^{1}H}
1[c]	1.36 (s), 1.46(s) ($OC(CH_3)_3$); 6.60 (s) (Cp) [4.5 Hz]	32.77 (CH_3) [7 Hz]; 73.55 (CH); 111.03 (Cp) [8 Hz]	−286.4
2	1.35 (s), 1.43 (s) ($OC(CH_3)_3$); 6.60 (s) (Cp) [4.5 Hz]	33.74 (CH_3) [7 Hz, 14 Hz]; 73.23 (CH); 111.10 (Cp) [8 Hz]	−79.56; −362.9 [45.6 Hz]
3	1.27 (s), ($OC(CH_3)_3$); 6.33 (s) (Cp) [14.8 Hz]	34.47 (CH_3); 71.97 (CH); 109.2 (Cp) [31.8 Hz]	−106.3 [176.1 Hz]; −2091.9 [163.1 Hz][d]

[a] Conditions: C_6D_6, ppm, 296 K. [b] The coupling constants $J_{^{119/117}Sn}$ are given in brackets. Abbreviations: s = strong, m = medium, b = broad. [c] IR (KBr disk; cm^{-1}) of compound **1**: 2974.3 (b), 1364.9 (s), 1238.1 (s), 1177.2 (s), 803.8 (m), 752.1 (s), 610.5 (s), 575.8 (s). [d] ^{207}Pb{^{1}H}.

$$CpSnCl + KM(OBu^t)_3 \rightarrow \underset{\mathbf{1-3}}{CpSn(OBu^t)_3M} + KCl\downarrow \quad (1)$$

$$M = Ge^{II}\ (\mathbf{1}),\ Sn^{II}\ (\mathbf{2}),\ Pb^{II}\ (\mathbf{3});\ Cp = C_5H_5$$

The spectral data (Table 1), satisfactory elemental analyses, and averaged molecular complexity ($\eta = 1.1-1.2$) corresponding to the presence of monomers in solution are compatible with the formulation of the above-mentioned compounds. Compounds **1** and **2** are volatile colorless viscous liquids which distill at 95 °C/10^{-2} mmHg (**1**) and 100 °C/10^{-2} mmHg (**2**), respectively. Compound **3** is isolated as a pale yellow solid after recrystallization from THF/hexane. It decomposes on attempted sublimation (70 °C/10^{-2} mmHg) to give Cp_2Pb as one of the volatile fragments (^{1}H NMR evidence).

To gain a better understanding of the structural aspects of these molecules, an X-ray diffraction study was carried out on a single crystal of compound **1**, which was grown from a toluene solution.[12] In view of the low melting point (20 °C) of the compound, the data collec-

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[†] Dedicated to Prof. Dr. M. Baudler on the occasion of her 75th birthday.

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(10) Experimental procedure: CpSnCl (0.65 g, 2.96 mmol) and $KGe(OBu^t)_3$ (0.98 g, 2.96 mmol) were stirred in toluene for 24 h. KCl was removed by filtration, and the solvent from the filtrate was removed in vacuo. The colorless viscous liquid obtained was crystallized (−10 °C) from toluene. Yield of **1**: 1.15 g, 81%. Anal. Calcd for $C_{17}H_{32}GeO_3Sn$ (**1**): C, 42.91; H, 6.78; Sn, 24.95. Found: C, 42.84; H, 6.88; Sn, 24.42. Compounds **2** and **3** were prepared analogously using $KSn(OBu^t)_3$ and $KPb(OBu^t)_3$, respectively. Anal. Calcd for $C_{17}H_{32}O_3Sn_2$ (**2**): C, 39.12; H, 6.18; Sn, 45.49. Found: C, 39.05; H, 6.15; Sn, 45.24. Yield of **2**: 82%. Anal. Calcd for $C_{17}H_{32}O_3PbSn$ (**3**): C, 33.45; H, 5.28; Sn, 19.45; Pb, 33.94. Found: C, 33.28; H, 5.31; Sn, 19.32; Pb, 33.82. Yield of **3**: 85%. The $[KM(OBu^t)_3]_n$[9] (M = Ge, Sn, Pb) compounds were prepared according to the literature procedures.

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(12) Crystal data for $C_{17}H_{32}GeO_3Sn$: monoclinic system with cell dimensions at 183(2) K of $a = 10.125(9)$ Å, $b = 10.082(9)$ Å, $c = 10.670(9)$ Å, $\beta = 104.5(7)°$, and $V = 1055(2)$ Å^3. The space group is *Pn* with $Z = 2$ and $D_{calcd} = 1.498$ Mg/m^3. The structure was solved by direct methods and refined by full-matrix least-squares techniques using 1825 reflections having $I > 2\sigma(I)$, resulting in $R = 0.0610$ and $R_w = 0.0621$.

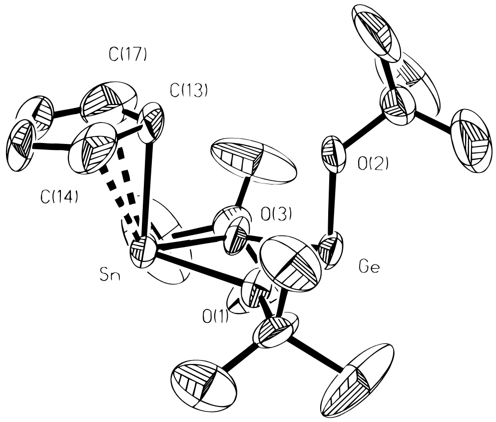

Figure 1. ORTEP drawing of $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$ (**1**). Selected bond distances (Å) and angles (deg): Sn−O(1), 2.212(9); Sn−O(3), 2.218(9); Sn−C(13), 2.41(2); Ge−O(1), 1.960(9); Ge−O(3), 1.935(9); Ge−O(2), 1.839(10); O(1)−Sn−O(3), 66.7; O(3)−Sn−O(13), 97.0(5); O(1)−Ge−O(3), 77.4(4); Sn−O(3)−Ge, 107.2(4); Ge−O(1)−Sn, 106.5(4).

tion was made at low (183(2) K) temperature, and an ORTEP view of $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$ is depicted in Figure 1. The significant geometric details worthy of comment can be summarized as follows.

(a) A nearly planar four-membered SnO_2Ge ring is terminated at Sn^{II} by the cyclopentadienyl ring and at Ge^{II} by the OBu^t group, the terminators occupying *cis* positions with respect to the plane of the ring.

(b) Pyramidally configured Sn^{II} and Ge^{II} centers are bridged by two *tert*-butoxy (μ) groups which have a nearly planar environment (Σ of angles of O_b 359.8, 359.9°) and are in an eclipsed conformation.

(c) There is a stereochemically active lone pair at Ge^{II} and Sn^{II}, as the sum of angles surrounding germanium and tin (including C(13)) totals 264.2 and 256.5°, respectively.

(d) Symmetrical bridging Sn−O bond lengths (2.21 Å) are larger than comparable[13] Sn^{II}−O bond lengths, which average ~2.07 Å, and they are also greater than the sum of their covalent radii.

(e) The Ge−O distance involving a terminal alkoxide ligand (1.839(10) Å) is shorter than the two Ge−O distances involving bridging alkoxides (1.960(9) and 1.935(9) Å, consistent with other related examples such as $[Ni(CO)_3Ge(OBu^t)_2]_2$.[14]

(f) The smallest endocyclic O(1)−Sn−O(3) bond angle yet observed, 66.7°, is highly acute and is much smaller than that observed in $[Sn(OBu^t)_2]_2$[15,16] ($\angle O_b-Sn-O_b = 73.2(2)°$), supporting a congested geometry at tin.

(g) A noteworthy feature of the structure is the notation of the hapticity of the cyclopentadienyl ligand. The Sn−C(13) bond distance (2.41 Å) is substantially larger than that normally found for σ-coordinated Sn^{II} (~2.1−2.3 Å) organometallic compounds[17] and does not favor η^1 bonding of the cyclopentadienyl ring. However, examination of the C−C distances in the cyclopentadienyl ring shows the presence of two pairs of essentially equivalent bond lengths, i.e. C(14)−C(15)) = C(16)−C(17) (1.35(4) Å) and C(13)−C(17) = C(15)−C(16) (1.46(3) Å), supporting the presence of a σ-bonded diene ring.[18] A further interesting observation is the angle between Sn−C(13) and the vector from C(13) to the center of the cyclopentadienyl ring being only 80.4°, which indicates the absence of a tetrahedral geometry, as would be expected for η^1 coordination. Hence, a η^3 mode of coordination can be anticipated for the compound with the involvement of the longer but comparable Sn−C(14) (2.73(2) Å) and Sn−C(17) (2.68(2) Å) distances alongwith Sn−C(13) in bonding. The ^1H NMR spectrum of a toluene solution of compound **1** cooled to −65 °C also shows only a single resonance for the Cp ring, implying the typical fluxional behavior observed for the η^1- and $\eta^{2/3}$-bonded metallacyclopentadienes.[3] The evidence found in support of both η^1 and η^3 modes of coordination in the solid state makes us conclude that the η^3 and η^1 coordination modes of the cyclopentadienyl ligand to the Sn^{II} atom are competing with each other and an average effect is observed. A comparison of the crystal structures of compound **1** and CpSnCl[11] shows a ring slippage which changes the bonding mode of the cyclopentadienyl ring from η^5 in CpSnCl to an averaged $\eta^1-\eta^3$ bonding in compound **1**.

(h) The C(13)···O(2) distance of 3.29 Å supports a weak intramolecular hydrogen bond interaction[19] between O(2) and the hydrogen atom present on C(13) of the Cp ring, which together with other factors might influence the crystallization of **1** in only the *cis* molecular conformation, as observed in the solid state.

The presence of only one type of *tert*-butoxy group, as observed in the NMR spectrum, indicates compound **3** to be fluxional in solution. The larger $^{119/117}Sn-^1H$ coupling constant observed for compound **3** (14.8 Hz) in comparison to compound **1** and **2** (4.5 Hz) in the ^1H NMR spectra seems to be in accord with the more highly coordinated π complex **3** (probably η^5 coordination of the Cp ring to the tin atom).

Isolation of these cyclopentadienyl heterobimetallic alkoxides has provided a platform to integrate the inorganic alkoxides and organometallic systems together. The very weak Cp−Sn bond supports its increased reactivity, and hence, the nucleophilic substitution of these complexes is being explored. The high volatility of these compounds at low temperatures could prove advantageous for use as precursors in MOCVD processes. The demonstration of the above-mentioned ideas is likely to be a subject of future reports.

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Supporting Information Available: Tables of crystal data and refinement details, positional and thermal parameters, and bond distances and angles for compound **1** (6 pages). Ordering information is given on any current masthead page.

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