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Synthesis, Characterization, and Reactivity of New Heteroleptic Heterobimetallic Alkoxide Derivatives of Tin(II): X-ray Crystal Structures of $[ClSn\{M_2(OPr^i)_9\}]_2$ (M = Zr, Hf), $[(C_5H_5)Sn\{Zr_2(OPr^i)_9\}]$, and $[(C_5H_5)Pb(\mu_2\text{-}OBu^t)_2Sn(OBu^t)]$[†]

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The synthesis of new cyclopentadienyl-containing heterobimetallic alkoxides has been accomplished by employing the alkoxide precursors toward cyclopentadienyl reagents (NaCp and $(C_5H_5)SnCl$). The equimolar reactions of anhydrous SnX_2 (X = Cl, I) and $KM_2(OPr^i)_9$ (M = Zr, Hf) offer halide heterobimetallic isopropoxides $[XSn\{M_2(OPr^i)_9\}]_2$ (**1**, M = Hf, X = Cl; **2**, M = Hf, X = I; **3**, M = Zr, X = Cl) in quantitative yields. Both **1** and **3** react with NaCp in benzene−THF to give $(C_5H_5)Sn\{M_2(OPr^i)_9\}$ (**4**, M = Hf; **5**, M = Zr). Alternatively, **4** and **5** are conveniently obtained by the equimolar reaction of $(C_5H_5)SnCl$ with $KM_2(OPr^i)_9$ (M = Zr, Hf). Although the reaction (1:1) of $(C_5H_5)SnCl$ with $[KGe(OBu^t)_3]_n$ affords the expected product $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$ (**6**), the reaction with $[KPb(OBu^t)_3]_n$ shows a transfer of cyclopentadienyl ring from tin to lead to provide $(C_5H_5)Pb(\mu_2\text{-}OBu^t)_2Sn(OBu^t)$ (**7**). The new derivatives have been readily characterized by elemental analysis, multinuclear (^1H, ^{13}C, ^{119}Sn, and ^{207}Pb) NMR studies, molecular weight measurements, and volatility. A single-crystal X-ray diffraction study is reported for the compounds **1**, **3**, and **5**−**7**. The solid state structures of **1**, **3**, and **5** exhibit varying coordination behavior of $M_2(OPr^i)_9^-$ units to SnX^+ (X = C_5H_5, Cl) fragments. In the structural framework of the *tert*-butoxide derivatives, the four membered $MM'(\mu_2\text{-}OBu^t)_2$ (**6**, M = Ge, M′ = Sn; **7**, M = Pb, M′ = Sn) ring is terminated at the metal ends by cyclopentadienyl and *tert*-butoxide ligands and each of the metals, bearing a stereochemically active lone pair, displays a pyramidal geometry.

Introduction

The importance of metallo-organic derivatives as precursors to multimetallic oxide materials has made metal alkoxide chemistry a frontier field of research which includes developments such as designing of single-source precursors and modification of heterometallic systems for reactivity modulation.[1] Although the heterometal alkoxide systems modified by the incorporation of ligands such as carboxylates, β-diketonates, nitrates, halides, etc. are well-known,[2] the cyclopentadienyl heterometallic alkoxides which can bridge the inorganic alkoxides and organometallic systems have not been studied. Metal alkoxides with classical alkoxide ligands (OPr^i, OEt, OMe) often exhibit a pronounced tendency to oligomerize, and thus are not the ideal candidates for the structural and reactivity investigations;[1c] however, in these systems the incorporation of a coligand such as C_5H_5 anion which can occupy several coordination sites is likely to generate more tractable systems. Homometallic mixed-ligand compounds containing both cyclopentadienyl and alkoxide moieties are described in the literature;[3] however, to the best of our knowledge, no structurally characterized example is available for heterometal heteroleptic ($C_5H_5^-/OR^-$) derivatives. In a preliminary communication,[4] we have reported on the rational construction of first heterobimetallic cyclopentadienyl alkoxides where the presence of the cyclopentadienyl anion as a coligand provides a heterobimetallic framework that is not accessible by the use of only alkoxide ligands. We herein describe the synthesis and reactivity of halide/alkali metal heterometallic alkoxides in building new cyclopentadienyl heterobimetallic alkoxides and the single-crystal X-ray crystallography of the derivatives $[ClSnM_2(OPr^i)_9]_2$ (M = Hf, Zr), $[(C_5H_5)Sn\{Zr_2(OPr^i)_9\}]$, and $[(C_5H_5)Pb(\mu\text{-}OBu^t)_2Sn(OBu^t)]$ along with the details of the derivative $[(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)]$.

Results and Discussion

Two synthetic strategies involving the equimolar reactions of cyclopentadienyltin chloride ($(C_5H_5)SnCl$)

[†] Dedicated to Professor Dr. W. Siebert on his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1996.

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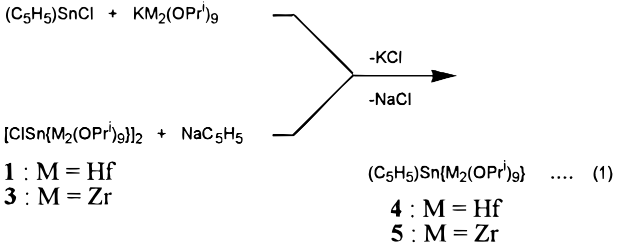
Table 1. Summary of Crystallographic Data for Compounds 1, 3, 6, and 7

	complex			
	1	**3**	**6**	**7**
empirical formula	$C_{27}H_{63}ClHf_2O_9Sn$	$C_{27}H_{63}ClZr_2O_9Sn$	$C_{17}H_{32}GeO_3Sn$	$C_{17}H_{32}O_3PbSn\cdot C_4H_8O$
M_r	1042.89	868.35	475.71	682.41
cryst system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	Pn	$Pnma$
a/Å	23.940(5)	23.916(5)	10.125(9)	9.533(6)
b/Å	16.624(3)	16.532(3)	10.082(9)	10.906(6)
c/Å	20.520(4)	20.414(4)	10.670(9)	25.66(2)
β/deg	94.45(3)	94.26(3)	104.50(7)	90.0
V/Å^3	8142(3)	8049(3)	1055(2)	2667.9(3)
Z	8	8	2	4
F(000)	4064	3552	480	1320
D_c/Mg m^{-3}	1.702	1.433	1.498	1.699
T/°C	293(2)	293(2)	183(2)	293(1)
cryst size/mm	0.6 × 0.4 × 0.3	0.45 × 0.33 × 0.3	0.5 × 0.4 × 0.2	0.4 × 0.3 × 0.2
std reflcns	3	3	3	3
θ range/deg	1.58−22.51	1.59−25.00	2.02−20.03	1.59−25.00
reflcns collcd	10 624	10 858	2018	2705
indepdt reflcns	10 624	10 856	1861	2479
obsd reflcns	7930	6580	1825	1681
GOF on F^2	1.447	1.059	1.170	1.314
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0771$	$R1 = 0.0616$	$R1 = 0.0644$	$R1 = 0.0833$
R indices (all data)	$R1 = 0.1021$	$R1 = 0.1101$	$R1 = 0.0656$	$R1 = 0.1322$

with potassium nonaisopropoxodizirconate (−dihafnate) and/or chloride heterobimetallic alkoxides with sodium cyclopentadienylide (NaCp) represent a simple metathetical approach for the high-yield synthesis of cyclopentadienyl-containing heterobimetallic alkoxides (eq 1).



The chloride and iodide heterometallic alkoxides $[XSn\{Hf_2(OPr^i)_9\}]_2$ (X = Cl (**1**); X = I (**2**)) are conveniently prepared by the 1:1 reaction of $KHf_2(OPr^i)_9$ with anhydrous samples of $SnCl_2$ and SnI_2, respectively. Compounds **1** and **2** are obtained, after the workup of the reaction mixtures, as white and yellow solids, respectively, which can be crystallized from cold (−10 °C) toluene−hexane solution in > 50% yield. Their sublimation in vacuo (**1**, 130 °C/10^{-2} mm; **2**, 140−145 °C/10^{-2} mm) is accompanied with decomposition, leaving appreciable residues. Ambient-temperature ^1H and ^{13}C NMR spectra of **1** in benzene-d_6 or $CDCl_3$ reveal only one type of alkoxide environment in solution and thus do not elaborate the structural pattern existing in the solution. In contrast to **1**, the iodo derivative **2** is stereochemically rigid and exhibits in the ^1H NMR spectrum four methyl doublets in the intensity ratio 4:1:1:3 (δ 1.19−1.34). The methine protons are observed as two multiplets centered at δ 4.60 and 4.40, the latter one results from an overlapping of two septets. The ^{13}C NMR spectrum exhibits four and three signals for the methine and methyl carbons, respectively. For both **1** and **2**, the ^{119}Sn NMR spectra in benzene show two resonances each (**1**, δ −308.83, −333.82; **2**, δ −166.33, −282.15) in 3:1 intensity ratio, the upfield shift belonging to the bigger signal. The tin chemical shifts are in the range commonly observed for four- and/or five-coordinate tin(II) species;[5,6] the relatively downfield shifts in the case of **1** can be attributed to the greater electron affinity of chlorine which results in a more deshielded (in comparison to iodo derivative **2**) tin center. The solution ^{119}Sn NMR chemical shifts of compound **2** in conjunction with the observed molecular complexity (η = 1.3) is suggestive of an equilibrium between two species with differently coordinated tin atoms, possibly a four-coordinate monomer and a five-coordinate dimer. A similar ^{119}Sn NMR spectroscopic pattern (δ −168.50, −275.42) had been observed for the closely related derivative $[ISn\{Zr_2(OPr^i)_9\}]_2$[6] and was shown by variable-temperature ^{119}Sn NMR studies to be consistent with a monomer−dimer equilibrium. A similar intermolecular dynamics is proposed for **2**; on recording the ^{119}Sn NMR spectra at elevated temperatures, the intensity of the peak corresponding to dimeric species decreases while the peak due to lower coordinated (monomer) species shows a relative increase. An opposite effect is observed on lowering the temperature. The ^{119}Sn NMR chemical shifts of $[ClSnZr_2(OPr^i)_9]_2$[5a] (δ −190.16, −322.30) are comparable with those observed for $[ISnM_2(OPr^i)_9]_2$ (M = Zr, Hf)[6] derivatives. However in the case of $[ClSn\{Hf_2(OPr^i)_9\}]_2$ (**1**), the ^{119}Sn chemical shifts are observed rather downfield and the difference between the two values is small (~25 ppm) to account for a change in coordination number. At higher temperatures, the two resonances become broad and move closer; however, a coalescence was not observable till +70 °C. It appears that any dissociative−associative process taking place in solution presumably (in view of the long Sn−Cl and Sn−μ_3-OPr^i contacts; *vide infra*) produces species with similar coordination number.

In an effort to obtain detailed structural information, a single-crystal X-ray structure was determined for **1**. Some of the important bond lengths and angles are

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Hf(1)−O(5)	1.896(11)	Hf(1)−O(6)	1.918(11)
Hf(1)−O(4)	2.096(10)	Hf(1)−O(2)	2.108(11)
Hf(1)−O(1)	2.220(10)	Hf(1)−O(3)	2.328(10)
Hf(3)−O(13)	1.910(11)	Hf(3)−O(14)	1.923(11)
Hf(3)−O(11)	2.099(12)	Hf(3)−O(15)	2.120(10)
Hf(3)−O(10)	2.226(11)	Hf(3)−O(12)	2.305(10)
Hf(2)−O(8)	1.899(14)	Hf(2)−O(7)	1.924(10)
Hf(2)−O(9)	1.953(13)	Hf(2)−O(2)	2.215(10)
Hf(2)−O(1)	2.248(10)	Hf(2)−O(3)	2.343(10)
Hf(4)−O(17)	1.926(14)	Hf(4)−O(16)	1.946(12)
Hf(4)−O(18)	1.948(13)	Hf(4)−O(11)	2.224(11)
Hf(4)−O(10)	2.272(10)	Hf(4)−O(12)	2.362(10)
Sn(2)−O(12)	2.332(10)	Sn(1)−O(3)	2.315(10)
Sn(1)−O(4)	2.191(11)	Sn(2)−O(15)	2.178(11)
Sn(2)−Cl(1)	2.582(5)	Sn(1)−Cl(2)	2.598(5)

O(5)−Hf(1)−O(6)	100.0(5)	O(5)−Hf(1)−O(4)	99.8(5)
O(6)−Hf(1)−O(4)	100.9(5)	O(5)−Hf(1)−O(2)	102.2(5)
O(6)−Hf(1)−O(2)	100.6(5)	O(4)−Hf(1)−O(2)	145.9(4)
O(5)−Hf(1)−O(1)	97.7(5)	O(6)−Hf(1)−O(1)	162.4(4)
O(4)−Hf(1)−O(1)	76.8(4)	O(2)−Hf(1)−O(1)	74.7(4)
O(5)−Hf(1)−O(3)	164.0(5)	O(6)−Hf(1)−O(3)	96.0(4)
O(4)−Hf(1)−O(3)	77.5(4)	O(2)−Hf(1)−O(3)	74.1(4)
O(1)−Hf(1)−O(3)	66.4(3)	O(13)−Hf(3)−O(14)	100.7(5)
O(13)−Hf(3)−O(11)	101.5(5)	O(14)−Hf(3)−O(11)	101.0(5)
O(13)−Hf(3)−O(15)	100.8(5)	O(14)−Hf(3)−O(15)	99.7(5)
O(11)−Hf(3)−O(15)	146.0(4)	O(13)−Hf(3)−O(10)	96.6(5)
O(14)−Hf(3)−O(10)	162.6(4)	O(11)−Hf(3)−O(10)	75.0(4)
O(15)−Hf(3)−O(10)	77.1(4)	O(13)−Hf(3)−O(12)	164.0(5)
O(8)−Hf(2)−O(7)	101.5(6)	O(8)−Hf(2)−O(9)	101.4(6)
O(7)−Hf(2)−O(9)	99.8(5)	O(8)−Hf(2)−O(2)	96.7(5)
O(7)−Hf(2)−O(2)	94.2(5)	O(9)−Hf(2)−O(2)	154.3(5)
O(8)−Hf(2)−O(1)	95.6(5)	O(7)−Hf(2)−O(1)	159.3(5)
O(9)−Hf(2)−O(1)	88.0(5)	O(2)−Hf(2)−O(1)	72.1(4)
O(8)−Hf(2)−O(3)	160.1(5)	O(7)−Hf(2)−O(3)	95.6(5)
O(9)−Hf(2)−O(3)	85.3(4)	O(2)−Hf(2)−O(3)	71.9(4)
O(1)−Hf(2)−O(3)	65.7(3)	O(17)−Hf(4)−O(16)	103.7(6)
O(17)−Hf(4)−O(18)	100.1(6)	O(16)−Hf(4)−O(18)	99.6(5)
O(17)−Hf(4)−O(11)	95.6(5)	O(16)−Hf(4)−O(11)	154.5(5)
O(18)−Hf(4)−O(11)	93.1(5)	O(17)−Hf(4)−O(10)	94.4(5)
O(16)−Hf(4)−O(10)	90.1(5)	O(18)−Hf(4)−O(10)	160.1(5)
O(11)−Hf(4)−O(10)	71.8(4)	O(17)−Hf(4)−O(12)	158.6(5)
O(16)−Hf(4)−O(12)	85.0(4)	O(18)−Hf(4)−O(12)	97.6(4)
O(11)−Hf(4)−O(12)	71.5(4)	O(10)−Hf(4)−O(12)	65.7(3)
O(15)−Sn(2)−O(12)	75.1(4)	O(15)−Sn(2)−Cl(1)	86.7(3)
O(12)−Sn(2)−Cl(1)	96.3(3)	O(4)−Sn(1)−O(3)	76.0(4)
O(4)−Sn(1)−Cl(2)	86.9(3)	O(3)−Sn(1)−Cl(2)	95.7(3)
Hf(1)−O(1)−Hf(2)	95.8(4)	Hf(1)−O(2)−Hf(2)	100.2(4)
Sn(1)−O(3)−Hf(1)	92.6(3)	Hf(1)−O(3)−Hf(2)	90.5(3)
Sn(1)−O(3)−Hf(2)	102.4(4)	Hf(1)−O(4)−Sn(1)	103.0(4)
Hf(3)−O(10)−Hf(4)	95.0(4)	Hf(3)−O(11)−Hf(4)	100.1(4)
Hf(3)−O(12)−Sn(2)	92.8(3)	Sn(2)−O(12)−Hf(4)	101.4(4)
Hf(3)−O(12)−Hf(4)	90.6(3)	Hf(3)−O(15)−Sn(2)	102.8(5)

assembled in Table 2. A ball-and-stick representation giving the atom-numbering scheme used in the table is shown in Figure 1. In the solid state, compound **1** adopts a dimeric form *via* long Sn⋯Cl interactions (average distance = 3.348 Å; sum of van der Waal radii of Sn and Cl = 4.00 Å)[7] between the chlorine of one molecule with the tin of a second molecule. The overall molecular structure in the asymmetric unit comprises a three-coordinate tin(II) center which is coordinated by two isopropoxide oxygens (one terminal, O(15), and one bridging, O(12)) of the $Hf_2(OPr^i)_9$ unit and one chlorine. If the Sn(2)−Cl(2) interaction is taken in account, the coordination sphere of tin may also be described as "3 + 1". The tin atom then shows a distorted trigonal bipyramidal geometry with one of the apical sites being occupied by the nonbonding electron pair of tin. The associated structure (Figure 1) of **1** is remarkably paralleled by the centrosymmetric molecule of $Pb_2Zr_4(OPr^i)_{20}$[8] reported by Caulton et al. which exhibits a similar bidentate ligating mode of the bioctahedral $M_2(OPr^i)_9^-$ unit formed by the interaction of two $Zr_2(OPr^i)_8$ moieties with a $Pb_2(OPr^i)_4$ unit. Owing to the asymmetric coordination mode, the $Hf_2(OPr^i)_9$ unit in **1** is deviated from the bioctahedral form and the distortion around two hafnium centers is evident in the *trans* O−Hf−O angles (Table 2). The Sn−O bond lengths (Sn−(μ_2-OPr^i) = 2.184(11) Å; Sn−(μ_3-OPr^i) = 2.323(10) Å) in **1** are substantially comparable to that observed for analogous $[ISn\{Zr_2(OPr^i)_9\}]_2$[6] (Sn−(μ_2-OPr^i) = 2.196(4) Å; average Sn−(μ_3-OPr^i) = 2.385(4) Å). The Sn(1)−Cl(2) bond distance (2.598(5) Å) is much shorter (sum of their ionic radii = 2.830 Å) and is consistent with the covalent nature and thermal stability of **1**. However the Sn(1)−Cl(1) and Sn(2)−Cl(2) interactions (average 3.348 Å) are significantly longer and correlate nicely to the less associated solution behavior of **1** (molecular complexity, $\eta = 1.2$). The hafnium−oxygen distances (Table 2) in the bioctahedral $Hf_2(OPr^i)_9$ unit show a reasonable variation depending upon the number of metal atoms coordinated to the oxygen which correlates to the lengthening of Hf−O bonds with decreasing nucleophilic character of isopropoxide oxygens on increased bridging: O(3) bonded to three metal atoms is the longest, 2.335(10) Å. O(1) and O(2) bonded to two hafnium atoms show a mean Hf−O distance of 2.197(11) Å. O(4) bonded to tin and hafnium is 2.191(11) Å. The other five terminal oxygens (O(5), O(6), O(7), O(8), and O(9)) bonded to one metal atom have a mean Hf−O distance of 1.918 Å.

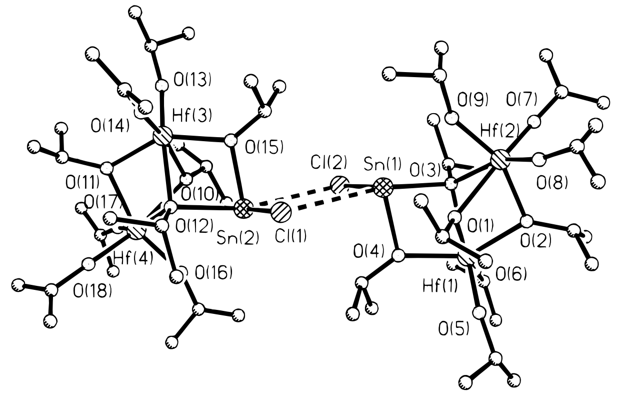

Figure 1. Ball and stick view of the $[ClSn\{Hf_2(OPr^i)_9\}]_2$ (**1**) molecule showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

The synthetic and spectroscopic details of one of the halide derivatives, $[ClSn\{Zr_2(OPr^i)_9\}]_2$[5a] (**3**) employed in the present study, have been previously reported. However, in view of its use as a precursor to cyclopentadienyl heterobimetallic alkoxides **4** and **5** and for the sake of comparison with other related derivatives, the solid-state structure of **3** was established by single-crystal X-ray diffraction analysis and the results obtained are shown in Table 3 and Figure 2. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ and is isomorphous with compound **1** (see Table 1). The bioctahedral $Zr_2(OPr^i)_9$ unit binds the Sn(II) center in a bidentate fashion, and its deviation from the commonly observed tetradentate chelation is presumably due to the presence of a stereochemically active lone pair

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

Zr(1)−O(5)	1.914(8)	Zr(1)−O(6)	1.935(8)
Zr(1)−O(7)	1.943(8)	Zr(1)−O(2)	2.221(7)
Zr(1)−O(3)	2.248(7)	Zr(1)−O(1)	2.371(6)
Zr(3)−O(14)	1.909(8)	Zr(3)−O(15)	1.926(7)
Zr(3)−O(16)	1.946(8)	Zr(3)−O(13)	2.230(7)
Zr(3)−O(12)	2.242(6)	Zr(3)−O(10)	2.369(7)
Zr(2)−O(9)	1.905(8)	Zr(2)−O(8)	1.905(7)
Zr(2)−O(2)	2.093(6)	Zr(2)−O(4)	2.114(7)
Zr(2)−O(1)	2.336(7)	Zr(2)−O(3)	2.250(6)
Zr(4)−O(18)	1.908(8)	Zr(4)−O(17)	1.910(7)
Zr(4)−O(13)	2.085(6)	Zr(4)−O(11)	2.116(6)
Zr(4)−O(10)	2.328(6)	Zr(4)−O(12)	2.250(6)
Sn(2)−O(11)	2.161(7)	Sn(2)−O(10)	2.286(6)
Sn(1)−O(4)	2.154(7)	Sn(1)−O(1)	2.259(6)
Sn(2)−Cl(2)	2.579(4)	Sn(1)−Cl(1)	2.584(4)

O(4)−Sn(1)−O(1)	76.8(2)	O(4)−Sn(1)−Cl(1)	86.6(2)
O(1)−Sn(1)−Cl(1)	95.6(2)	O(11)−Sn(2)−O(10)	76.4(2)
O(11)−Sn(2)−Cl(2)	87.1(2)	O(10)−Sn(2)−Cl(2)	96.4(2)
O(5)−Zr(1)−O(6)	100.2(4)	O(5)−Zr(1)−O(7)	102.0(4)
O(6)−Zr(1)−O(7)	100.4(4)	O(5)−Zr(1)−O(2)	95.3(3)
O(6)−Zr(1)−O(2)	93.9(3)	O(7)−Zr(1)−O(2)	155.1(3)
O(5)−Zr(1)−O(3)	95.6(3)	O(6)−Zr(1)−O(3)	159.7(3)
O(7)−Zr(1)−O(3)	88.7(3)	O(2)−Zr(1)−O(3)	71.8(2)
O(5)−Zr(1)−O(1)	159.0(3)	O(6)−Zr(1)−O(1)	97.2(3)
O(7)−Zr(1)−O(1)	86.2(3)	O(2)−Zr(1)−O(1)	71.8(2)
O(3)−Zr(1)−O(1)	65.1(2)	O(9)−Zr(2)−O(8)	101.0(4)
O(9)−Zr(2)−O(2)	101.8(3)	O(8)−Zr(2)−O(2)	101.2(3)
O(9)−Zr(2)−O(4)	100.7(3)	O(8)−Zr(2)−O(4)	100.7(3)
O(2)−Zr(2)−O(4)	144.7(3)	O(9)−Zr(2)−O(3)	97.8(3)
O(8)−Zr(2)−O(3)	161.2(3)	O(2)−Zr(2)−O(3)	74.1(3)
O(4)−Zr(2)−O(3)	76.2(2)	O(9)−Zr(2)−O(1)	163.4(3)
O(8)−Zr(2)−O(1)	95.5(3)	O(2)−Zr(2)−O(1)	74.7(2)
O(4)−Zr(2)−O(1)	75.9(2)	O(3)−Zr(2)−O(1)	65.6(2)
O(14)−Zr(3)−O(15)	100.0(4)	O(14)−Zr(3)−O(16)	101.5(4)
O(15)−Zr(3)−O(16)	100.6(4)	O(14)−Zr(3)−O(13)	97.2(3)
O(15)−Zr(3)−O(13)	92.4(3)	O(16)−Zr(3)−O(13)	154.9(3)
O(14)−Zr(3)−O(12)	95.2(3)	O(15)−Zr(3)−O(12)	159.2(3)
O(16)−Zr(3)−O(12)	90.1(3)	O(13)−Zr(3)−O(12)	71.5(2)
O(14)−Zr(3)−O(10)	159.3(3)	O(15)−Zr(3)−O(10)	97.8(3)
O(16)−Zr(3)−O(10)	85.6(3)	O(13)−Zr(3)−O(10)	71.4(2)
O(12)−Zr(3)−O(10)	65.0(2)	O(18)−Zr(4)−O(17)	100.1(3)
O(18)−Zr(4)−O(13)	102.2(3)	O(17)−Zr(4)−O(13)	100.9(3)
O(18)−Zr(4)−O(11)	100.3(3)	O(17)−Zr(4)−O(11)	100.9(3)
O(13)−Zr(4)−O(11)	145.2(3)	O(18)−Zr(4)−O(12)	98.6(3)
O(17)−Zr(4)−O(12)	161.3(3)	O(13)−Zr(4)−O(12)	74.1(2)
O(11)−Zr(4)−O(12)	76.6(2)	O(18)−Zr(4)−O(10)	164.2(3)
O(17)−Zr(4)−O(10)	95.7(3)	O(13)−Zr(4)−O(10)	74.7(2)
O(11)−Zr(4)−O(10)	76.4(2)	O(12)−Zr(4)−O(10)	65.6(2)
Sn(1)−O(1)−Zr(2)	93.3(2)	Zr(2)−O(1)−Zr(1)	90.3(2)
Sn(1)−O(1)−Zr(1)	102.9(2)	Zr(1)−O(3)−Zr(2)	95.7(2)
Zr(2)−O(4)−Sn(1)	103.0(3)	Zr(4)−O(10)−Zr(3)	90.6(3)
Sn(2)−O(10)−Zr(4)	92.9(2)	Zr(3)−O(12)−Zr(4)	96.0(2)
Sn(2)−O(10)−Zr(3)	102.3(2)	Zr(4)−O(13)−Zr(3)	101.3(2)
Zr(4)−O(11)−Sn(2)	102.9(3)		

of electrons at tin which inhibits the coordination of a second terminal OPr^i group (O(7) and O(16)). The presence of a stereochemically active lone pair at tin becomes apparent as the sum of angles (∠O(1)−Sn(1)−Cl(1), O(1)−Sn(1)−O(4) and O(4)−Sn(1)−Cl(1)) around tin is 259.0° (Table 3). This shows the preference of tin(II) for a lower coordination number and a pyramidal configuration.[9] The Sn−Cl distances observed in the central Sn_2Cl_2 ring (2.591(7) and 3.350(8) Å) of **3** are consistent with an asymmetric bridging. The trend of Zr−O distances (terminal OR < μ_2-OR < μ_3-OR, Table 3) and short terminal Zr−OR bonds associated with large Zr−O−C angles (average 166.8 °) in **3** agree with the literature reports.[6,10,11] The monoanionic bioctahedral ligands of the general formula $M_2(OR)_9^-$, existing with a number of tetravalent metals (Sn, Ti, Zr, Hf, Ce, Th, U), are a frequently occurring substructure in the heterometal alkoxide chemistry and various examples based on their interactions with "cationic" fragments are known.[6,10] The $Zr_2(OPr^i)_9^-$ unit is a versatile sequestering agent, and besides the frequently encountered tetradentate ligating mode, it is capable of coordinating the metal atom in bi- and tridentate fashion while preserving the structural integrity of the bioctahedral unit. It is relevant to mention that the role of the $Zr_2(OPr^i)_9$ moiety in building novel heterotermetallic alkoxides has been recently reported.[11]

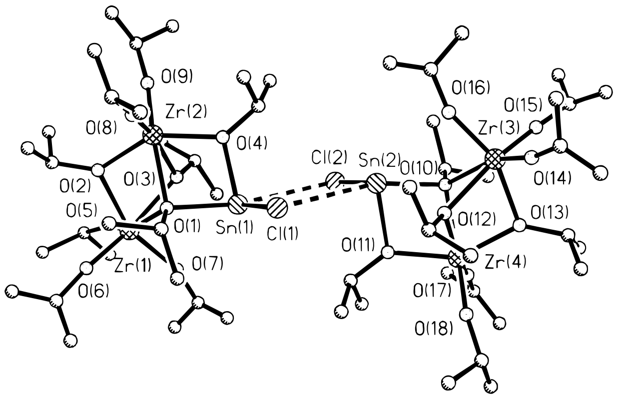

Figure 2. Ball and stick representation of the dimeric $[ClSn\{Zr_2(OPr^i)_9\}]_2$ (**3**) with the atom-numbering scheme used in the tables. Hydrogen atoms are omitted for clarity.

In contrast to the centrosymmetric dimeric form of the iodo derivative $[ISn\{Zr_2(OPr^i)_9\}]_2$,[6] the molecules of **1** and **3** possess no crystallographic symmetry; however, their deviation from C_i symmetry is nevertheless quite small. Although the chloro-bridged dimeric form of **3** is essentially similar to that observed for **1**, the solid-state structures of both **1** and **3** (Figures 1 and 2) differ from the iodo derivative $[ISn\{Zr_2(OPr^i)_9\}]_2$[6] with respect to the coordination behavior of the $M_2(OPr^i)_9^-$ substructure to similar SnX^+ (X = Cl, I) fragments which act as bi- and tridentate sequestering ligands for chloride and iodide derivatives, respectively. It is relevant to note that role of a change in coordination number and nuclearity with respect to the nature of halide ligands has also been observed for Cd−Zr mixed-metal alkoxides. The substitution of chloride in the dimeric $[ClCd\{Zr_2(OPr^i)_9\}]_2$[12] containing a six-coordinate cadmium by larger iodide ligand produces a monomeric species $ICd\{Zr_2(OPr^i)_9\}$ with a five-coordinate cadmium. The interactions of oxygen atoms of the second doubly bridging OPr^i groups in **1** (O(1) and O(10)) and **3** (O(3) and O(12)) with the tin(II) center are substantially long (average 2.59 Å in **1**; 2.61 Å in **3**) to be considered as effective bonding interactions (sum of their ionic radii = 2.33 Å). If these long-range interactions are consid-

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[9] Veith, M.; Käfer, D.; Koch, J.; May, P.; Stahl, L.; Huch, V. *Chem. Ber.* **1992**, *125*, 1033.

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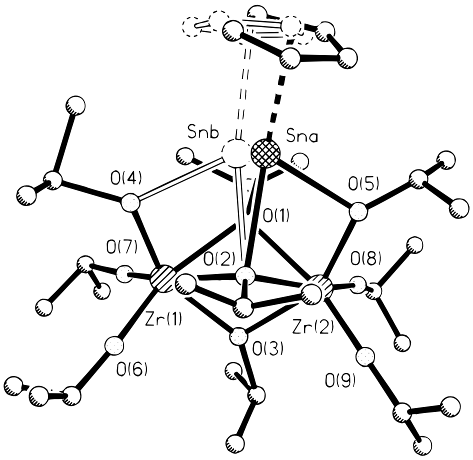

Figure 3. Ball and stick representation of the molecular structure of $(C_5H_5)Sn\{Zr_2(OPr^i)_9\}$ (**5**) with the selected atom labeling. The dotted lines show the positions of the partially occupied tin and cyclopentadienyl sites.

ered in describing the coordination figures, tin(II) atoms in both **1** and **3** can be viewed in a distorted octahedral arrangement with one of the axial sites being occupied by a pair of nonbonding electrons; this provides compound **3** a close structural resemblance with derivatives $[ClCd\{Zr_2(OPr^i)_9\}]_2$[12] and $[(Pr^iO)Ba\{Zr_2(OPr^i)_9\}]_2$.[10f] The molecule can then be described as a union of three face-sharing octahedra built around two zirconium (hafnium) atoms and one tin atom. The central $(Pr^iO)_2Sn_2Cl_2$ unit of both **1** and **3** is different from derivatives $Sn_2(OBu^t)_4$[13a] and $M_2(OBu^t)_2X_2$[13b] (X = Cl, I; M = Sn(II), Ge(II)). The Sn−O distances in **3** are quite short in comparison to that found in Hf derivative **1** (Tables 2 and 3).

Compounds **4** and **5** are obtained as waxy solids, readily soluble in common organic solvents, and could be crystallized from concentrated pentane solutions to obtain colorless plates. In order to establish the structural identity, a single-crystal X-ray diffraction study was performed on compound **5**, and a tentative ball-and-stick drawing of the molecule with the selected atom-numbering scheme is shown in Figure 3. The crystals of compound **5** are low melting (mp ≈ 30 °C). Various attempts of low-temperature diffraction study did not give a better data set. However, the structural data and overall quality of refinement (see Experimental Section) do establish the general connectivities of the atoms. The molecule crystallizes with a disordered structure (presumably due to the low melting nature of **5** or a subtle twinning in the examined crystals which could not be overcome by low-temperature techniques). When seen in the context of related halide precursors, a dimeric structure was anticipated for **5**, but owing to the steric bulk of C_5H_5 anion the compound is observed as a monomer in the solid state.The overall molecular structure of **5** features a tin center (bearing a cyclopentadienyl ligand) coordinated in pseudotridentate fashion (due to the inability of Sn to span the distance between the two terminal alkoxide oxygens (O(4) and O(5)) of the $Zr_2(OPr^i)_9$ unit) by a bioctahedral $Zr_2(OPr^i)_9$ unit. Owing to the above-mentioned disorder, a rigorous discussion involving the data for bond distances and angles has not been made. The crystallographic data are given in the Experimental Section.

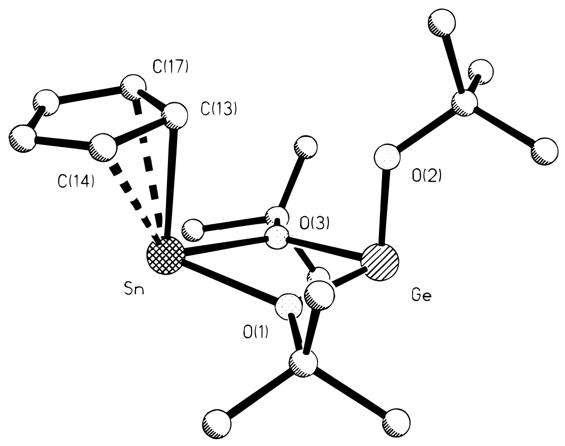

Figure 4. Ball and stick drawing showing the molecular structure of $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$ (**6**).[4]

The freshly synthesized derivatives (**4**−**6**) are colorless products which develop a pale yellow color over a period of few hours. The color deepens on prolonged storage; however, the NMR data remain unaltered. Ambient-temperature ^1H and ^{13}C NMR spectra of both **4** and **5** in benzene-d_6 exhibit only single sets of ligand resonances indicating a fluxional process in the solution and thus are non-informative of the structural pattern existing in the solution. The ^{119}Sn spectra (C_6D_6) of both **4** and **5** show sharp resonances at δ −333.73 and −261.03, respectively, which are consistent with a three-coordinate tin center and suggest the retention of the molecular structure (Figure 3) of **5** in solution. Although no structural determination has been made, the comparable ^{119}Sn NMR chemical shifts and molecular weight data are in agreement of a similar structure for **4**. Despite the long Sn−C(Cp) (av 2.806 Å) and Sn−O (av 2.479 Å) contacts as observed in the solid-state structure of **5**, both **4** and **5** exhibit a remarkable volatile behavior and could be recovered unchanged after a careful distillation (**4**,140 °C/10^{-2} mm; **5**, 150 °C/10^{-2} mm) in a rotary distillation apparatus (see Experimental Section).

Treatment of $(C_5H_5)SnCl$ with an equimolar quantity of $[KGe(OBu^t)_3]_n$ in toluene at 25 °C results *via* salt elimination in the formation of the expected $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$ (**6**).[4] However, a similar reaction between CpSnCl and $[KPb(OBu^t)_3]_n$ did not afford the anticipated "$(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Pb(OBu^t)$", and the multinuclear NMR data indicated a transfer of cyclopentadienyl group from tin to lead which indeed was also observed in the solid-state structure of **7** *(vide infra)*. A preliminary account of the synthesis of both the compounds together with their spectral characterization and a single-crystal X-ray structure of **6** has been quoted in a previous communication.[4] The single-crystal X-ray diffraction of compound **7** has been recently undertaken to provide clue to the correct interpretation of its rather intriguing NMR data. The colorless viscous liquid **6** and the pale yellow solid **7** are fluxional on the ^1H and ^{13}C NMR time scales. The solution ^{119}Sn NMR chemical shift of δ −286.4 for **6** is consistent with a three-coordinate tin(II) center which in view of the observed solid-state structure (Figure 4) shows the retention of the heterobimetallic framework. If the structures of **6** and **7** are considered to be analogous with respect to

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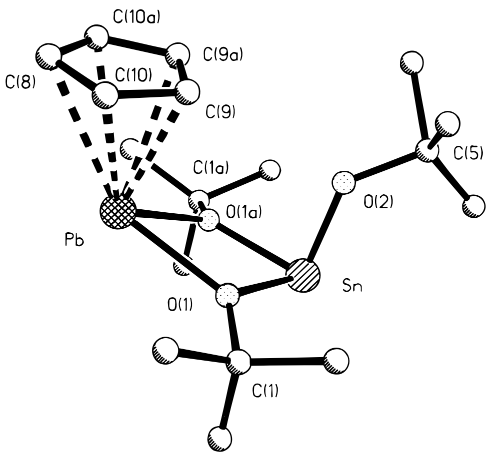


Figure 5. Ball and stick representation of $(C_5H_5)Pb(\mu_2\text{-}OBu^t)_2Sn(OBu^t)$ (**7**) with atom-labeling scheme. The lattice solvent molecule (THF) is not shown and the hydrogen atoms are omitted for clarity.

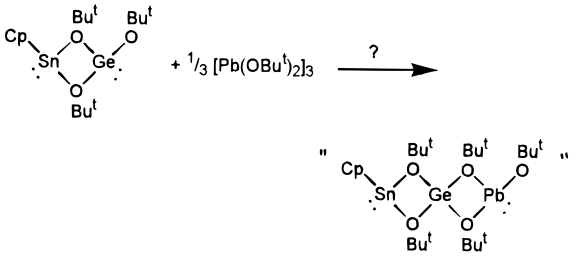
both being formed by the interaction of $CpSn^+$ fragment with the $Ge(OBu^t)_3{}^-$ and $Pb(OBu^t)_3{}^-$ units, respectively, the observation of a larger $^{119/117}Sn-^1H$ coupling constant (14.8 Hz) for **7** in comparison to **6** (4.5 Hz) seems to be in agreement with a more π coordinated complex of **7**. However, this postulation is contrary to the observed ^{119}Sn chemical shift for **7** (δ −106.3) which is relatively low field with respect to **6** (δ −286.4). This value of δ −106.3 on the other hand is close to the ^{119}Sn NMR chemical shift as observed for $[Sn(OBu^t)_2]_2$[15] (δ −93.6) indicating the tin(II) center in **7** to be present in an environment of three *tert*-butoxide oxygens $\{(OBu^t)Sn(\mu_2\text{-}OBu^t)\}^-$. The coupling constant of 14.8 Hz lies in the characteristic range of the third-order lead−hydrogen coupling ($^3J(^{207}Pb-^1H)$).[16] Indeed, the migration of the cyclopentadienyl ring to lead which justifies the above observations was borne out by a single-crystal X-ray analysis. The molecular geometry is shown in Figure 5 with the selected bond lengths and angles collected in Table 4. The structure reveals a nearly planar (358.3°) SnO_2Pb core with both Sn and Pb atoms possessing a pyramidal geometry. The three coordinated Sn and Pb atoms are bridged symmetrically by two OBu^t ligands with typical Pb−O distances of 2.362(11) Å and Sn−O distances of 2.042(11) Å. Within the standard deviation limit (3σ), both tin and germanium in compound **6** are also symmetrically bridged to the two *tert*-butoxy groups.

Table 4. Selected Metrical Parameters for 6 and 7

7		6	
Bond Distances (Å)			
Pb−O(1)	2.362(11)	Sn−O(1)	2.212(9)
Pb−O(1′)	2.362(11)	Sn−O(3)	2.218(9)
Pb−C(9)	2.76(2)	Sn−C(13)	2.41(2)
Pb−C(9′)	2.76(2)	Sn−C(14)	2.73(2)
Pb−C(10)	2.89(2)	Sn−C(17)	2.68(2)
Pb−C(8)	3.09(3)	Ge−O(3)	1.935(9)
Sn−O(1)	2.042(11)	Ge−O(1)	1.960(9)
Sn−O(1′)	2.042(11)	Ge−O(2)	1.839(10)
Sn−O(2)	1.96(2)	C(13)−C(14)	1.44(3)
C(8)−C(10)	1.39(3)	C(14)−C(15)	1.35(4)
C(9)−C(10)	1.25(3)	C(15)−C(16)	1.46(4)
C(9)−C(9′)	1.35(3)	C(16)−C(17)	1.35(4)
		C(13)−C(17)	1.46(3)
Bond Angles (deg)			
O(1′)−Pb−O(1)	66.1(5)	O(1)−Sn−O(3)	66.7(3)
O(1′)−Sn−O(1)	78.2(6)	O(3)−Ge−O(1)	77.4(4)
Sn−O(1)−Pb	107.0(5)	Ge−O(1)−Sn	106.5(4)
C(5)−O(2)−Sn	128(2)	Ge−O(3)−Sn	107.9(12)
C(10′)−C(8)−C(10)	103.0(3)	C(5)−O(2)−Ge	126.2(9)
C(9)−C(10)−C(8)	109(3)	C(13)−C(14)−C(15)	106(2)
C(10)−C(9)−C(9′)	110(2)	C(15)−C(16)−C(17)	108(2)

In view of the similar overall framework, interesting structural comparison can be made between compounds **6** and **7**. The two divalent group 14 elements possessing stereochemically active lone pairs (Sn and Ge in **6** and Sn and Pb in **7**) are bridged by two *tert*-butoxy groups (eclipsed conformation), the oxygen atoms of which have planar coordination. The four-membered ring in both the cases is appended by a exocyclic cyclopentadienyl ring and a *tert*-butoxy group, the pendant groups orienting in *cis* positions (Figures 4 and 5). In contrast to the molecular asymmetry observed in **6** (Figure 4), the solid-state structure of **7** possess a mirror plane passing through Sn, Pb, O(2), and a carbon atom, C(8), of the cyclopentadienyl ring. The O_b-M-O_b [M = Sn (**6**), Pb (**7**)] bond angle (**6**, 66.1°; **7**, 66.6°) is highly acute in both the cases. The most interesting aspect is the difference in the mode of coordination of cyclopentadienyl group to tin in compound **6** and to lead in compound **7**. The tin germanate has been proposed with a peripherally ($\eta^{1/3}$) bonded cyclopentadienyl ring possessing diene character. However, the crystal structure of tin plumbate shows a centrally bonded (η^5) cyclopentadienyl ring with asymmetrical Pb−C(ring) distances. The individual Pb−C distances in **7** differ by as much as 0.33 Å. This variation in Pb−C distances is reflected in the endocyclic C−C interatomic distances of the cyclopentadienyl ring. The two equal bond distances (C(9)−C(10) and C(9′)−C(10′) (1.25(3) Å)) are substantially shorter than the remaining C−C bond distances and also from a normal C−C double bond. The nonequidistant nature of the metal-ring carbon distances and higher degree of shortening of some of C−C distances are also observed in the precursor molecule $CpSnCl$[14] (C−C = 1.22−1.55 Å; Sn−C(Cp) = 2.45−2.74 Å). An interesting observation in the solid-state structures of the newly prepared half-sandwich compounds, **6** and **7**, is the presence of a large scattering of the ring carbon−metal distances (**6**, 2.41−2.73; **7**, 2.76−3.09 Å) indicating a pronounced "ring slippage".

Compounds **6** and **7** owing to the presence of a terminal alkoxy group are attractive precursors for the synthesis of a heterotrimetallic cyclopentadienyl alkoxide by Lewis acid−base reactions. An attempt to produce the heterotermetallic derivative "$(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(\mu_2\text{-}OBu^t)_2Pb(OBu^t)$" was made (eq 2) by reacting $(C_5H_5)Sn(\mu_2\text{-}OBu^t)_2Ge(OBu^t)$ and $Pb_3(OBut)_6$ in 3:1 molar ratio in toluene at room temperature. The



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removal of solvent *in vacuo* followed by crystallization of the isolated product from a THF−hexane mixture at 0 °C incidentally gave compound **7** (30% yield), which was confirmed by the identical spectral data and determination of the unit cell constants of a suitable crystal.

Conclusion

Described in the present study is the synthesis of new cyclopentadienyl heterobimetallic alkoxides of bivalent tin achieved by the reactions between chloro precursors ($(C_5H_5)SnCl$ or $ClSn\{M_2(OPr^i)_9\}$ (M = Hf, Zr)) and an alkali metal salt of the appropriate ligand (NaCp or $KM_2(OPr^i)_9$). As expected at the outset, the degree of association of the modified ($C_5H_5^-$ containing) heterometal systems is drastically different from that of starting materials. The derivatives $[(C_5H_5)SnCl]_n$ and $[KM(OBu^t)_3]_n$ (M = Ge, Pb) are polymeric in nature whereas the products (**6** and **7**) obtained from them are monomeric in both solution and the solid state. Similarly, the substitution of chloride in dimeric $[ClSn\{M_2(OPr^i)_9\}]_2$ by bulkier cyclopentadienyl ligand produces monomeric $(C_5H_5)Sn\{M_2\{OPr^i)_9\}$ (M = Hf, Zr). In contrast to the extraordinary bridging ability of alkoxo groups, a cyclopentadienyl bridging will be thermodynamically disfavored and the terminal position of $C_5H_5^-$ fragment in these heteroleptic derivatives renders the product monomeric. Further, such mixed-ligand systems provide access to a metal stoichiometry not achievable by pure alkoxide compounds; e.g., an equimolar reaction of $[Sn(OBu^t)_2]_2$ and $[Ge(OBu^t)_2]_2$ does not form a Sn−Ge heterobimetallic with 1:1 metal stoichiometry, which is obviously present in $(C_5H_5)Sn(OBu^t)_3Ge$ and in view of the high volatility of **6** can be explored for MOCVD purposes. Furthermore, a controlled alcoholysis of $(C_5H_5)Sn(OBu^t)_3Ge$ is expected, in principle, to offer "$SnGe(OBu^t)_4$". Besides developing the synthetic approaches for combining M−O−C and M−C derivatives, the availability of structural data and the presence of different metals in these novel systems would allow (i) ligand arrrangement (Cp transfer) studies and (ii) a correlation of the hapticity of the cyclopentadienyl ring with respect to the nature of the metal present (ring slippage). In view of the above the present investigations represent the beginning of an elusive class of mixed-ligand (Cp^-/OR^-) heterometallic systems. Further studies to establish the generality of the results and to employ bis(cyclopentadienyl)metal halides are currently underway.

Experimental Section

General Comments. All operations were performed under an atmosphere of prepurified and dry nitrogen. The hydrocarbon solvents were dried and distilled from sodium benzophenone ketyl under an inert atmosphere. Isopropyl alcohol was dried by distillation from Mg turnings and $Al(OPr^i)_3$. Tertiary butyl alcohol was distilled from potassium and stored over molecular sieves. CpSnCl,[14] $[KM(OBu^t)_3]_n$ (M = Ge, Pb),[5a] and $[M(OPr^i)_4{\cdot}Pr^iOH]_2$ (M = Zr, Hf)[17] were prepared according to the literature. The syntheses of $[ClSn\{Zr_2(OPr^i)_9\}]_2$[5b] and $(C_5H_5)Sn(OBu^t)_3Ge$[4] have been reported earlier. $SnCl_2$ was stirred in acetic anhydride, washed with hexanes (3−5 times), and heated *in vacuo* (110 °C/10^{-2} mm) to obtain anhydrous $SnCl_2$ which was analyzed for Sn and Cl contents before use. A commercial sample of SnI_2 was dried by heating *in vacuo*. NMR spectra were obtained on a Bruker AC-200 NMR spectrometer operating at 200.13, 50.3, 74.6, and 41.8 MHz for ^1H, ^{13}C, ^{119}Sn, and ^{207}Pb, respectively. ^{119}Sn and ^{207}Pb NMR chemical shifts in solution are referenced externally to $Sn(Me)_4$ and a 0.1 M solution of $Pb(NO_3)_2$ in D_2O, respectively. Elemental analyses (C and H) were performed on a LECO CHN 900 elemental analyzer. Molecular weights were determined cryoscopically in benzene. Metal and halogen contents were estimated by standard analytical procedures. The distillation of the new derivatives were performed on a micro rotary distillation apparatus (Büchi Co.).

Syntheses and Characterization of Heterometal Heteroleptic Complexes. $[ClSn\{Hf_2(OPr^i)_9\}]_2$ (**1**). A solution of $KHf_2(OPr^i)_9$ [freshly prepared from the interaction of $KOPr^i$ (0.23 g, 2.42 mmol) and $Hf(OPr^i)_4{\cdot}Pr^iOH$ (2.30 g, 4.85 mmol) in benzene (20 mL)] was added slowly to a well-stirred suspension of $SnCl_2$ (0.46 g, 2.42 mmol) in benzene (15 mL). The reaction mixture was stirred for 12 h at room temperature and briefly at 70 °C. Filtration of KCl and removal of volatiles in vacuum yielded a white solid which analyzed as $[ClSn\{Hf_2(OPr^i)_9\}]_2$ (**1**). The product could be purified by crystallization (toluene-hexane, −10 °C) and sublimation (130 °C/10^{-2} Torr) in ~50% yield. Anal. Calcd for $C_{27}H_{63}O_9ClSnHf_2$: C, 10.36; H, 6.04; Cl, 3.39; Sn, 11.37; Hf, 34.22. Found: C, 10.19; H, 6.00; Cl, 3.25; Sn, 11.28; Hf, 33.29. ^1H NMR (C_6D_6, 20 °C): δ 1.35 (d, 54H, J = 6 Hz), 4.62 (septet, 9H, J = 6 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 26.37 (CH_3), 71.02 (CH). $^{119}Sn\{^1H\}$NMR: δ −308.85 and −333.82. Molecular weight: 1043 (calcd), 1260 (found).

$[ISn\{Hf_2(OPr^i)_9\}]_2$ (**2**) was prepared analogously by an equimolar reaction of anhydrous SnI_2 (1.76 g, 4.72 mmol) and $KHf_2(OPr^i)_9$ (4.35 g, 4.69 mmol) in benzene. Yield of crude product: 5.09 g, 94%. Yield of sublimed (140−145 °C/10^{-2} Torr) product: 2.1 g, 40%. Anal. Calcd for $C_{27}H_{63}O_9ISnHf_2$: C, 28.58; H, 5.55; I, 11.18; Sn, 10.46; Hf, 31.46. Found: C, 28.23; H, 5.60; I, 11.01; Sn, 10.93; Hf, 30.96. ^1H NMR (C_6D_6, 20 °C): δ 1.20 (d, J = 6 Hz, 18H), 1.25 (d, J = 6 Hz, 6H), 1.31 (d, J = 6 Hz, 6H), 1.33 (d, J = 6 Hz, 24H), 4.40 (m, J = 6 Hz, 4H), 4.60 (septet, J = 6 Hz, 5H). ^{13}C NMR (C_6D_6, 20 °C): δ 26.20, 26.47, 26.56 (CH_3), 71.80, 73.30, 73.89, 75.82 (CH). $^{119}Sn\{^1H\}$NMR (C_6D_6): δ −166.34 and −282.15. Molecular weight: 1134 (calcd), 1459 (found).

$(C_5H_5)Sn\{Hf_2(OPr^i)_9\}$ (**4**). A benzene (20 mL) solution of $KHf_2(OPr^i)_9$ (2.70 g, 2.91 mmol) was added to a suspension of $(C_5H_5)SnCl$ (0.64 g, 2.92 mmol) in benzene (15 mL), and the resulting mixture was stirred for 24 h at room temperature followed by stirring at 50 °C for 4 h. The precipitated KCl was filtered off, and the filtrate was stripped in vacuo to obtain a viscous product (2.85 g, 91%), which was dissolved in a minimum amount of pentane and placed at −15 °C. Over a period of 2 days, colorless plates were formed (yield, 45%). Anal. Calcd for $C_{32}H_{68}O_9SnHf_2$: C, 35.83; H, 6.34; Sn, 11.07; Hf, 33.28. Found: C, 35.29; H, 6.03; Sn, 11.18; Hf, 32.65. ^1H NMR (C_6D_6, 20 °C): δ 1.34 (d, 54H, J = 6 Hz), 4.50 (sept, 9H, J = 6 Hz), 6.21 (s, 5H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 26.64 (CH_3), 70.09 (CH), 109.67 (C_5H_5). $^{119}Sn\{^1H\}$ NMR: δ −333.73. Molecular weight: 1073 (calcd), 1130 (found).

$(C_5H_5)Sn\{Zr_2(OPr^i)_9\}$ (**5**) could be obtained analogously by the reaction (1:1) of $(C_5H_5)SnCl$ (1.26 g, 5.75 mmol) and $KZr_2(OPr^i)_9$ (4.30 g, 5.71 mmol). Yield: 4.65 g, 90%. Anal. Calcd for $C_{32}H_{68}O_9SnZr_2$: C, 42.79; H, 7.57; Sn, 13.21; Zr, 20.31. Found: C, 42.15; H, 7.13; Sn, 13.13; Zr, 20.86. ^1H NMR (C_6D_6, 20 °C): δ 1.35 (d, 54H, J = 6 Hz), 4.43 (sept, 9H, J = 6 Hz), 6.25 (s, 5H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 26.58 (CH_3), 70.25 (CH), 109.58 (C_5H_5). $^{119}Sn\{^1H\}$ NMR: δ −261.03. Molecular weight: 868 (calcd), 831 (found).

In an alternative method, **4** and **5** could be obtained by the equimolar reactions of chloro derivatives $[ClSn\{Hf_2(OPr^i)_9\}]_2$ (**1**) and $[ClSn\{Zr_2(OPr^i)_9\}]_2$ (**3**) with NaCp in benzene and a small amount of THF at 50 °C after continuously stirring the

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[17] Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*; Longmans: London, 1978.

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reaction mixture for 24 h, the workup of the reactions being similar as described as above.

$(C_5H_5)Pb(OBu^t)_3Sn$ (**7**). To 0.31 g (14.17 mmol) of (C_5H_5)-SnCl in 20 mL of toluene was added $KPb(OBu^t)_3$ (0.66 g, 14.17 mmol). The suspension was stirred for 24 h at room temperature. After removal of the formed KCl by filtration, the solvent was removed in vacuo and a pale yellow solid was obtained. The product was redissolved in a THF−hexane mixture and left to crystallize at 0 °C (yield: 0.73 g, 85%). Anal. Calcd for $C_{17}H_{32}O_3PbSn$: 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. ^1H NMR (C_6D_6, 20 °C): δ 1.27 (s, 27H); 6.33 (s, 5H, $J = 14.8$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 34.47 (CH_3), 71.97 (CH), 109.2 (C_5H_5). $^{119}Sn\{^1H\}$ NMR: δ −106.3 [176.1 Hz]. $^{207}Pb\{^1H\}$ NMR: −2091.9 [163.1 Hz]. Molecular weight: 610 (calcd), 632 (found).

X-ray Crystallography. Crystals of compounds **1**, **3**, and **5**−**7**, suitable for X-ray diffraction studies, were affixed to the end of a glass fiber using silicone grease, transferred into quartz capillaries, and sealed under an inert atmosphere to mount on the goniometer head of a Siemens Stoe AED 2 diffractometer equipped with graphite-monochromated Mo Kα radiation. The data collection ($\omega-\theta$ scan type) was performed using a standard moving crystal−moving detector technique at ambient temperature except for compound **6** for which the data were collected at low temperature (−90 °C). The structures were solved by direct methods using programs SHELXS-86[18] and SHELXL-93[19] and refined by full-matrix least-squares on F^2. A summary of the fundamental crystal data and data collection parameters for **1**, **3**, **6**, and **7** is presented in Table 1.

The X-ray measurements were made on suitable crystals of $[ClSn\{Hf_2(OPr^i)_9\}]_2$ (**1**) and $[ClSn\{Zr_2(OPr^i)_9\}]_2$ (**3**) with approximate dimensions 0.5 × 0.3 × 0.2 mm^3 (**1**) and 0.45 × 0.33 × 0.3 mm^3 (**3**). A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima and symmetry consistent with the monoclinic space group $P2_1/c$. In each case equivalent data were averaged after correction for Lorentz and polarization terms to yield a unique intensities set. Hydrogens were placed in fixed idealized positions for the final cycles of least squares.

Crystals of $(C_5H_5)Sn\{Zr_2(OPr^i)_9\}$(**5**) grown from pentane at −15 °C crystallized in a triclinic crystal system. The space group $P\bar{1}$ was identified and confirmed by successful solution and refinement of the structure. Cell constants and an orientation matrix were obtained from least-squares refinement of 25 carefully centered reflections. That the crystal was not subject to decay during measurements of intensities was monitored by three check measurements at regular intervals. Two peaks with coordination geometry consistent with tin were identified as partially occupied tin sites (SnA and SnB). The Sn atom as well as the carbons of the cyclopentadienyl ring can be tentatively assigned as disordered over two sites such that two sets of $(C_5H_5)Sn^+$ unit were found between the alkoxide "arms" O(4) and O(5) of $Zr_2(OPr^i)_9$ unit and were modeled successfully by assigning two partial occupancies to each of the atoms (Sn(A) = 0.8 occ; Sn(B) = 0.2 occ; C(A) = 0.8 occ; C(B) = 0.2 occ). Crystallographic data for **5**: triclinic space group $P\bar{1}$, with $a = 10.076(10)$ Å, $b = 12.563(12)$ Å, $c = 18.02(2)$ Å, $\alpha = 93.86(8)°$, $\beta = 96.94(8)°$, $\gamma = 103.38(8)°$, $V = 2192(4)$ Å^3, $d_{calc} = 1.361$ Mg m^{-3}, and $Z = 4$. Of the 7730 independent reflections measured, 5955 had $I > 2\sigma(I)$ and were regarded as observed which after the final cycle of refinement converged to $R = 0.0826$ and $wR2 = 0.2459$. The quality of the data set is not satisfactory to be published completely.

Colorless crystals of $[(C_5H_5)Sn(OBu^t)_3Ge]$ (**6**) were obtained from its concentrated toluene solution cooled to −10 °C. The crystal was mounted on a glass capillary with silicone grease, transfered to a Siemens Stoe AED 2 diffractometer, and centered in a steam of cold dinitrogen gas. The data collection was performed at −90 °C. The intensities of 3 standard reflections were measured every 90 min, and no crystal decay was observed over the course of the experiment. After completion of refinement, the structure was found to have monoclinic space group *Pn*. Selected bond lengths and angles are presented in Table 4.

Yellow needles of $[(C_5H_5)Pb(OBu^t)_3Sn]\cdot THF$ (**7**) were obtained by slow cooling of a THF−hexane solution to 0 °C. The structure was solved by direct methods (SHELXS-86) for the orthorhombic space group *Pnma* and refined by full-matrix least-squares on F^2 (SHELXL-93). Compound **7** crystallizes with one molecule of THF which fills the void in the unit cell. The results of the structural study are shown in Table 4 and Figure 5.

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Supporting Information Available: Full listings of X-ray parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and isotropic displacement parameters for compounds **1**, **3**, and **7** (28 pages). Ordering information is given on any current masthead page.

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[18] Sheldrick, G. M. SHELXS-86, University of Göttingen, 1986.

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