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Synthesis, Structure, and Reactivity of Iodo-Functionalized Heterobimetallic Alkoxides of Tin(IV): X-ray Crystal Structures of $[I_2Sn\{Al(OPr^i)_4\}_2]$, $[I_2Sn\{Ti(OPr^i)_5\}_2]$, $[I_3Sn\{Zr(OPr^i)_5(Pr^iOH)\}]$, and $[I_2Sn\{Mo(C_5H_5)(CO)_3\}_2]$

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A series of new iodide heterobimetallic isopropoxides $[I_2Sn\{Al(OPr^i)_4\}_2]$ (**1**), $[I_2Sn\{Ti(OPr^i)_5\}_2]$ (**2**), $[I_2Sn\{Nb(OPr^i)_6\}_2]$ (**3**), and $[I_3Sn\{Zr(OPr^i)_5(Pr^iOH)\}]$ (**4**) obtained on reacting SnI_4 with stoichiometric amounts of alkali-metal reagents $[KAl(OPr^i)_4]_n$, $[KTi(OPr^i)_5]_n$, $[KZr(OPr^i)_5]_n$, and $[KNb(OPr^i)_6]_n$, respectively, is reported. The monomeric formulation and hexacoordination of tin proposed for **1**−**4**, on the basis of microanalytical, cryoscopic, and multinuclear (^1H, ^{13}C, ^{27}Al, and ^{119}Sn) NMR spectral data, was established for **1**, **2**, and **4** by single-crystal X-ray diffraction analysis. The solid-state structures of **1** and **2** feature an approximately octahedral tin(IV) center bearing two terminal iodide ligands and two bidentate $\{Al(OPr^i)_4\}^-$ and $\{Ti(OPr^i)_5\}^-$ moieties, containing aluminum or titanium atoms in a distorted tetrahedral or trigonal-bipyramidal environment of OPr^i ligands, respectively. The crystal structure of **4** represents a bioctahedron formed by the face-sharing interaction of two slightly distorted octahedra built around Sn(IV) and Zr(IV) centers. Compounds **1** and **2**, when allowed to react (1:2) with the transition-metal derivative $Na[Mo(C_5H_5)(CO)_3]$, afford the Sn−Mo-bonded cluster $[I_2Sn\{Mo(C_5H_5)(CO)_3\}_2]$ (**5**) as the only isolable product, in both the cases.

Introduction

The current interest in heterometal alkoxides stems from their significance in both molecule[1] and material[2] chemistry. Recent investigations in alkoxide chemistry have shown that metathesis reactions involving alkali-metal alkoxometalate $[M'M_x(OR)_{x+1}]$ (M' = an alkali metal) and metal halides ($M''X_n$; X = Cl, Br, I) do not always result in the expected anion ($\{M(OR)_x\}^-$) transfer to the nucleophilic metal (M'') center, and no mixed-metal species are formed in several cases.[3] Also, the retention of the salt to form "ate" compounds[4] or complex clustered species with trapped alkali-metal cation(s)[5] or halide anion(s)[6] is frequently observed. Additionally, the nature of the resulting heterometal species may be complicated by the easy formation of oxo complexes,[7] generally resulting from an adventitious hydrolysis from traces of moisture present in the solvents or adsorbed on the reaction vessels; however, incorporation of oxo ligands by other processes such as alkene or ketone elimination[3a,8] or deoxygenation of alcohol to eliminate ether[9] also appear to be plausible mechanisms. Our recent discovery of the switching[10] of metal atoms (between two alkoxometalate fragments) in the formation of heterometallic alkoxide assemblies adds a new facet to such complex changes which can dramatically alter the nature of heterometal species, putative in the solution of alkoxides.

We have recently demonstrated the synthetic potential of well-characterized *monohalo-functionalized* heterobimetallic alkoxides in (i) the construction of molecular alkoxides containing three different metals,[10] (ii) the formation of novel examples of cyclopentadienyl-containing heterobimetallic alkoxide derivatives,[11] and

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(1) (a) Veith, M. *Chem. Rev.* **1990**, *90*, 3. (b) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969. (c) Mehrotra, R. C.; Singh, A.; Sogani, S. *Chem. Rev.* **1994,** *94,* 1643. (d) Mehrotra, R. C.; Singh, A.; Sogani, S. *Chem. Soc. Rev.* **1994**, 215. (e) Herrman, W. A.; Huber, N. W.; Runte, O. *Angew. Chem.* **1995,** *107*, 2371.

(2) (a) Veith, M.; Faber, S.; Hempelmann, R.; Janssen, S.; Prewo, J.; Eckerlde, H. *J. Mater. Sci.* **1996,** *31,* 2009. (b) Veith, M.; Kneip, S. *J. Mater. Sci. Lett.* **1994**, *13*, 335. (c) Sanchez, C.; Ribot, F. *New J. Chem*. **1994,** *18,* 1007. (d) Chandler, C. D.; Roger, C.; Hampden-Smith, M. J. *Chem. Rev.* **1993**, *93*, 1205. (e) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.

(3) (a) Veith, M.; Yu, E. C.; Huch, V. *Chem. Eur. J.* **1995,** *1,* 1. (b) Veith, M.; Mathur, S.; Huch, V. *Inorg. Chem.* **1997,** *36,* 2391.

(4) (a) Clark, D. L.; Hollis, R. V.; Scott, B. L.; Watkin, J. G. *Inorg. Chem*. **1996,** *35,* 667 and references therein.

(5) (a) Evans, W. J.; Sollberger, M. S.; Ziller, J. W. *J. Am. Chem. Soc.* **1993,** *115,* 4120. (b) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994,** *33,* 5903.

(6) (a) Aandersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978,** *17,* 1962. (b) Evans, W. J.; Sollberger, M. S.; Hanusa, T. P. *J. Am. Chem. Soc.* **1988,** *110,* 1841 (c) Evans, W. J.; Sollberger, M. S. *Inorg. Chem*. **1988,** *27,* 4417.

(7) (a) Hubert-Pfalzgraf, L. G. *Polyhedron* **1994,** *13,* 1181. (b) Mehrotra, R. C.; Singh, A. *Chem. Soc. Rev.* **1996,** 1.

(8) Purdy, A.; George, C. F.; Callahan, J. H. *Inorg. Chem.* **1991,** *30,* 2812.

(9) (a) Turova, N. Ya.; Kessler, V. G.; Kucheiko, S. I. *Polyhedron* **1991,** *10,* 2617. (b) Kessler, V. G.; Turova, N. Ya.; Panov, A. *Polyhedron* **1996,** *15,* 335.

(10) (a) Veith, M.; Mathur, S.; Huch, V. *J. Am. Chem. Soc.* **1996,** *118,* 903. (b) Veith, M.; Mathur, S.; Huch, V. *Inorg. Chem.* **1996,** *35,* 7295. (c) Veith, M.; Mathur, S.; Mathur, C.; Huch, V. *J. Chem. Soc., Dalton Trans.* **1997,** 2101.

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more recently (iii) the first synthesis of ionogenic heterometal alkoxides.[12] Furthermore, in contrast to a large number of structurally characterized heterometal alkoxo derivatives of tin(II),[1a,13] the heterometal alkoxides containing tin(IV) are rather scarce and the examples known are limited to $[KSn(OBu^t)_5]_n$,[14] $[Tl_2Sn(OEt)_6]_n$,[15] and $[ICd\{Sn_2(OPr^i)_9\}]$.[16] Finally, tin(IV) alkoxides are precursors to tin(IV)-based oxide materials,[17] which due to their optical transparency and electrical conductivity are important constituents in electrooptical or optical ceramics.[18] In view of the above and the absence of any report on the structurally characterized examples of halide heterometal tin(IV) alkoxides, we describe here the *di*- and *tri-iodo* derivatives.

Results and Discussion

As mentioned at the outset, we are studying[19] the use of alkoxometalate "bricks", e.g., $\{M(OR)_3\}^-$ (M = Mg, Ca, Sr, Ba, Sn, Ge, Pb), $\{M(OR)_4\}^-$ (M = Al, Ga, Sb, Bi), $\{M(OR)_5\}^-$ (M = Ti, Zr), $\{M(OR)_6\}^-$ (M = Nb, Ta), and $\{M_2(OR)_9\}^-$ (M = Sn, Ti, Zr, Hf), for constructing alkoxide-supported *mixed-metal* frameworks with the entity M−O(R)−M′−O(R)−M″. The alkali-metal derivatives of the above-described alkoxometalate anions are generally polymeric and insoluble in nonpolar solvents; however, on treating with the appropriate metal halides, they furnish well-defined building blocks to produce soluble and in many cases volatile molecular compounds with the desired metal ratios. The potential of this strategy in the synthesis of heterometallic alkoxides based on various mixed-metal combinations has been nicely demonstrated by Mehrotra et al.[20]

Tin tetraiodide reacts with potassium isopropoxyaluminate, -titanate, -zirconate, and -niobate in toluene−isopropyl alcohol to give iodide heterobimetallic isopropoxides according to eqs 1 and 2. Owing to the chelating nature of alkoxometalate units, compounds **1**−**3** represent the SnL_2X_2 family (L = a bidentate ligand) of octahedral complexes.[21] The structural investigations (**1** and **2**) reveal a cis-orientation; nevertheless, possibility of other geometrical isomers existing in solution cannot be ruled out. The reaction of SnI_4 with $[KAl(OPr^i)_4]_n$ in toluene, followed by filtration of preciptated KI and removal of solvent in vacuo, gave a yellow solid (90% yield). Dissolving the product in *n*-hexane at −10 °C afforded yellow crystals (35%) of $[I_2Sn\{Al(OPr^i)_4\}_2]$ (**1**). **1** is thermally stable and could be sublimed without decomposition at 120 °C/10^{-2} Torr. The microanalytical data conform to the formulation of **1**, which was found to exist as monomeric species in benzene by cryoscopy. Interestingly, the analogous chloro-derivative $[Cl_2Sn\{Al(OPr^i)_4\}_2]$[22] shows a tendency to associate in solution (molecular complexity = 1.5), and it appears that the larger iodide ligand renders **1** monomeric in solution and the solid state (*vide infra).* A similar effect of the size of the halide ligand on the nuclearity of the compound has been observed in halo-functionalized Cd−Zr mixed-metal alkoxides $[ClCd\{Zr_2(OPr^i)_9\}]_2$[23] and $[ICd\{Zr_2(OPr^i)_9\}]$.[10] In contrast to the deceptively simple spectral features generally observed among heterometal alkoxides, the room-temperature ^1H and ^{13}C NMR data of **1** are structurally informative. The ^1H NMR spectrum consists of seven *gem*-dimethyl resonances in the integrated ratio 1:1:1:1:1:2:1, which suggests the presence of eight OPr^i groups; the methine protons are observed as two distinct septets and a multiplet resulting from two overlapping septets which integrate to 2:2:4. The ^{13}C NMR spectrum contains eight resonances for each of the methyl and methine carbons. Owing to the idealized C_2 symmetry (vide infra), **1** possesses only four distinct methine carbon atoms and the greater number of signals observed can, presumably, result from the presence of isomeric forms in solution. The ^{27}Al NMR chemical shift (δ 60.68) lies in the characteristic range of four-coordinate aluminum and closely matches the value observed for tetrahedral $\{Al(OPr^i)_4\}^-$ moieties in $[Al\{Al(OPr^i)_4\}_3]$ (δ 59.0)[24] and $[Cl_2Sn\{Al(OPr^i)_4\}_2]$ (δ 67.12).[21] The ^{119}Sn NMR spectrum exhibits a single resonance at δ −1540.72, which is considerably upfield in comparison to the ^{119}Sn chemical shift of SnI_4 (δ −1700).[25] The higher frequency shift and a shielded tin

$$\begin{array}{l} SnI_4 + 2/n[K\{M(OPr^i)_x\}]_n \rightarrow \\ \qquad [I_2Sn\{M(OPr^i)_x\}_2] + 2KI \\ \qquad \mathbf{1}\text{: } M = Al,\ x = 4 \\ \qquad \mathbf{2}\text{: } M = Ti,\ x = 5 \\ \qquad \mathbf{3}\text{: } M = Nb,\ x = 6 \end{array} \tag{1}$$

$$\begin{array}{l} SnI_4 + 1/n[KZr(OPr^i)_5]_n \rightarrow \\ \qquad [I_3Sn\{Zr(OPr^i)_5\}(Pr^iOH)] + KI \\ \qquad \qquad \mathbf{4} \end{array} \tag{2}$$

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[11] Veith, M.; Mathur, C.; Mathur, S.; Huch, V. *Organometallics* **1997,** *16*, 1292.

[12] Veith, M.; Mathur, S.; Huch, V. *Chem. Commun.* **1997,** 2197.

[13] (a) Veith, M.; Hans, J.; Stahl, L.; May, P.; Huch, V.; Sebald, A. *Z. Naturforsch., Teil B* **1991,** *46*, 403. (b) Veith, M.; Kaefer, D.; Koch, J.; May, P.; Stahl, L.; Huch, V. *Chem. Ber.* **1992**, *125*, 5, 1033. (c) Veith, M.; Kaefer, D.; Huch, V. *Angew Chem., Int. Ed. Engl.* **1986,** *25,* 375. (d) Veith, M.; Roesler, R. *Z. Naturforsch., Teil B* **1986,** *41b*, 1071.

[14] Veith, M.; Reimers, M. *Chem. Ber.* **1990**, *123*, 1941.

[15] Hampden-Smith, M. J.; Smith, D. E.; Duesler, E. N. *Inorg. Chem.* **1989**, *28*, 3399.

[16] Veith, M.; Mathur, S.; Huch, V. *J. Chem. Soc., Dalton Trans.* **1996,** 2485.

[17] (a) Roger, C.; Hampden-Smith, M. J. *Chemtech* **1993,** *23*, 26. (b) Roger, C.; Schaefer, D. W.; Beaucage, G.; Hampden-Smith, M. J. *J. Sol-Gel Sci. Technol.* **1994,** *2*, 305.

[18] (a) Klein, L. C. *Sol−Gel Technology for Thin Films, Fibres, Preforms, Electronics and Speciality Shapes*; Noyes Publications: Park Ridge, NJ, 1988. (b) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science, The Physics and Chemistry of Sol−Gel Processing*; Academic Press: San Diego, CA, 1990.

[19] Veith, M.; Mathur, S.; Mathur, C. *Polyhedron* **1997** in press.

[20] (a) Mathur, S.; Singh, A.; Mehrotra, R. C. *Ind. J. Chem.* **1995,** *34A*, 454. (b) Mathur, S.; Singh, A.; Mehrotra, R. C. *Polyhedron* **1993,** *12* (9), 1073.(c) Mathur, S.; Singh, A.; Mehrotra, R. C. *Indian J. Chem.* **1993,** *32A*, 585. (d) Gupta, R.; Singh, A.; Mehrotra, R. C. *Indian J. Chem.* **1991,** *30A*, 592. (e) Garg, G.; Dubey, R. K.; Singh, A.; Mehrotra, R. C. *Polyhedron* **1991,** *10*, 1733. (f) Dubey, R. C.; Singh, A.; Mehrotra, R. C. *Inorg. Chim. Acta* **1988,** *143*, 169. (g) Dubey, R. K.; Singh, A.; Mehrotra, R. C. *J. Organomet. Chem.***1988,** *341*, 569. (h) Dubey, R. K.; Singh, A.; Mehrotra, R. C. *Polyhedron* **1987,** *6*, 427. (i) Shah, A.; Singh, A.; Mehrotra, R. C. *Inorg. Chim. Acta* **1988,** *141*, 289.

[21] Denekamp, C. I. F.; Evans, D. F.; Slawin, A. M. Z.; Williams, D. J.; Wong, C. Y.; Woollins, D. J. *J. Chem. Soc., Dalton Trans.* **1992,** 2375 and references therein.

[22] (a) Mathur, S.; Singh, A.; Mehrotra, R. C. *Polyhedron* **1992**, *11*, 341. (b) Mathur, S. Ph.D. Thesis, University of Rajasthan, Jaipur, India, 1992.

[23] Sogani, S.; Singh, A.; Bohra, R.; Mehrotra, R. C.; Noltemeyer, M. *J. Chem. Soc., Chem. Commun.* **1991,** 738.

[24] Folting, K.; Streib, W. E.; Caulton, K. G.; Poncelet, O.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1991,** *10*, 1639.

[25] Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1983**, *16*, 73.

nucleus despite a higher coordination number in **1** could be ascribed to an effective metal−ligand pπ−dπ bonding.

The reaction of $\mathrm{SnI_4}$ with 2 equiv of $\mathrm{KTi(OPr^i)_5}$ in toluene gave $\mathrm{[I_2Sn\{Ti(OPr^i)_5\}_2]}$ (**2**) in high yield. The compound crystallizes as pale yellow platelets from a toluene−isopropyl alcohol solution kept at −20 °C. Molecule **2** is highly fluxional at room temperature, and the NMR (^{1}H and ^{13}C) spectra exhibit time-averaged ligand resonances; however, the alkoxide site exchange slows down on lowering the temperature, and the ^{1}H NMR spectrum at −10 °C shows two doublets in the intensity ratio 6:4, assignable to the six terminal and four bridging $\mathrm{OPr^i}$ groups present in **2**. A further splitting of the signals could not be observed, even at −70 °C. A similar nonrigid behavior has been observed for $\mathrm{[LiTi(OPr^i)_5]_2}$[26] where no structurally diagnostic spectrum could be observed until −120 °C. The spectral observations in **2** are in accord which the observed solid-state structure (*vide infra),* with four bridging and six terminal $\mathrm{OPr^i}$ groups. The structure is also supported by the ^{13}C NMR spectrum which contains two signals for each of methyl and methine carbons. The ^{119}Sn NMR spectrum shows a single resonance at δ −1245.07 ppm, indicating the presence of only one type of tin(IV) species in solution. The molecular complexity of **2**, as determined by cryoscopy, is consistent with the presence of monomeric species in freezing benzene. Attempted volatilization of **2** resulted in its decomposition (135 °C/10^{-2} Torr), liberating $\mathrm{Ti(OPr^i)_4}$ as a volatile fragment and leaving a tin-rich residue (Sn, 34.2%).

$\mathrm{[I_2Sn\{Nb(OPr^i)_6\}_2]}$ (**3**), obtained from an interaction (1:2) of $\mathrm{SnI_4}$ and $\mathrm{KNb(OPr^i)_6}$, shows three doublets in the room-temperature ^{1}H NMR spectrum with relative intensities of 8:2:2 corresponding to the 12 $\mathrm{OPr^i}$ ligands present in **3**. The ^{119}Sn NMR chemical shift (δ −1113.91) is comparable to that observed for derivative **2** and indicates a six-coordinate tin(IV) atom in **3**. Similar to compounds **1** and **2**, the cryoscopic molecular weight determination on **3** indicates a monomeric nature. Protracted attempts for a single-crystal X-ray diffraction analysis of **3** were not successful due to twinning problems. However, in light of the solid-state structures of **1** and **2**, we propose a similar structure for **3** based on the bidentate interaction of two $\mathrm{\{Nb(OPr^i)_6\}^-}$ units with a "$\mathrm{SnI_2}^{2+}$" fragment.

In view of the octahedral configuration observed around tin(IV) due to the bidentate chelation of two monoanionic $\mathrm{\{M(OR)}_x\}^-$ units in **1** and **2**, the stoichiometry was changed to 1:1 in an attempt to obtain a pentacoordinate tin(IV) species. An equimolar reaction of $\mathrm{SnI_4}$ and $\mathrm{KZr(OPr^i)_5}$ in a toluene−isopropyl alcohol mixture (eq 2) afforded, after the workup of the reaction mixture, orange crystals of **4** in 40% yield. The ^{1}H NMR spectrum of **4** at 20 °C reveals four doublets (*gem*-dimethyl resonances), integrating in a ratio of 3:1:1:1; the methine protons are observed as three overlapping septets (δ 4.34−4.65). A sharp resonance in the typical range (δ 3.65) of a hydroxylic hydrogen for a coordinated $\mathrm{Pr^iOH}$ molecule[27,28] along with the characteristic ν(OH) band in the IR spectrum (see Experimental Section) indicates the presence of a neutral $\mathrm{Pr^iOH}$ molecule in **4**. The ^{119}Sn NMR chemical shift (δ −1078.9) is suggestive of a six-coordinate tin(IV) species in a solution of **4**. Indeed, the solid-state structure of **4** (Figure 3) is entirely consistent with the spectral observations (vide infra).

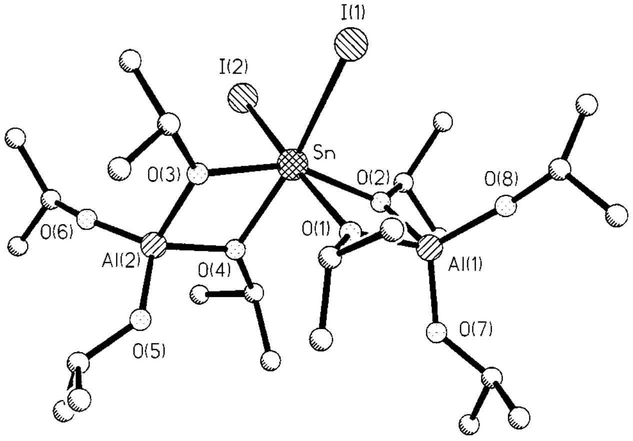

Figure 1. Ball-and-stick drawing of the solid-state structure of $\mathrm{[I_2Sn\{Al(OPr^i)_4\}_2]}$ (**1**) with the atom-numbering scheme used in the table. The hydrogen atoms of the isopropyl moieties are not drawn.

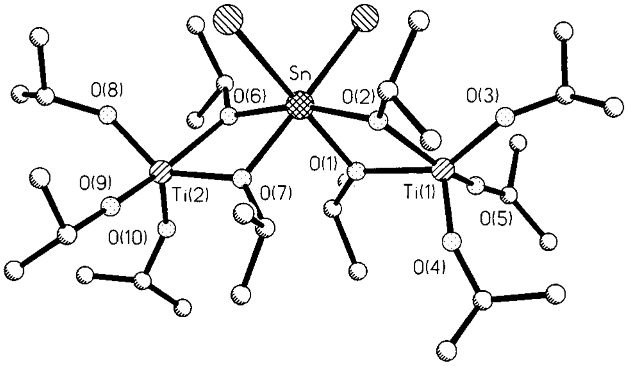

Figure 2. Ball-and-stick diagram of the molecular structure of $\mathrm{[I_2Sn\{Ti(OPr^i)_5\}_2]}$ (**2**).

By virtue of the lability of Sn−I bonds, compounds **1**−**4** are versatile synthons to new heterometallic species via anion-exchange reactions. $\mathrm{Na[(C_5H_5)Mo(CO)_3]}$ is a well-known reagent for obtaining metal−metal-bonded heterometal species by salt elimination reactions. It was anticipated that metathesis of both the Sn−I bonds in **1** and **2** with 2 equiv of $\mathrm{Na[Mo(C_5H_5)(CO)_3]}$ would afford "$\mathrm{[\{(C_5H_5)(CO)_3Mo\}_2Sn\{M(OPr^i)_x\}_2]}$" (M = Al, x = 4; M = Ti, x = 5) derivatives. However, the NMR spectra of the red crystalline material (**5**) isolated in the reaction (1:2) of both **1** and **2** with $\mathrm{Na[Mo(C_5H_5)(CO)_3]}$ shows no resonances in the region characteristic of isopropoxy groups. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **5** at room temperature display one single resonance corresponding to the cyclopentadienyl rings. However, the ^{13}C{^{1}H} NMR spectrum shows three additional resonances (1:1:1) in the diagnostic region of carbonyl carbon atoms, indicating a static conformation about each Mo center. The solution ($\mathrm{CDCl_3}$) IR spectrum exhibits three distinct carbonyl

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(26) Hampden-Smith, M. J.; Williams, D. S.; Rheingold, A. L. *Inorg. Chem.* **1990,** *29,* 4076.

(27) Vaartstra, B. A.; Huffman, J. C.; Gradeff, P. S.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Parrand, S.; Yunulu, K.; Caulton, K. G. *Inorg. Chem.* **1990,** *29,* 3126.

(28) Hampden-Smith, M. J.; Wark, T. A.; Rheingold, A.; Huffman, J. C. *Can. J. Chem.* **1991,** *69,* 121.

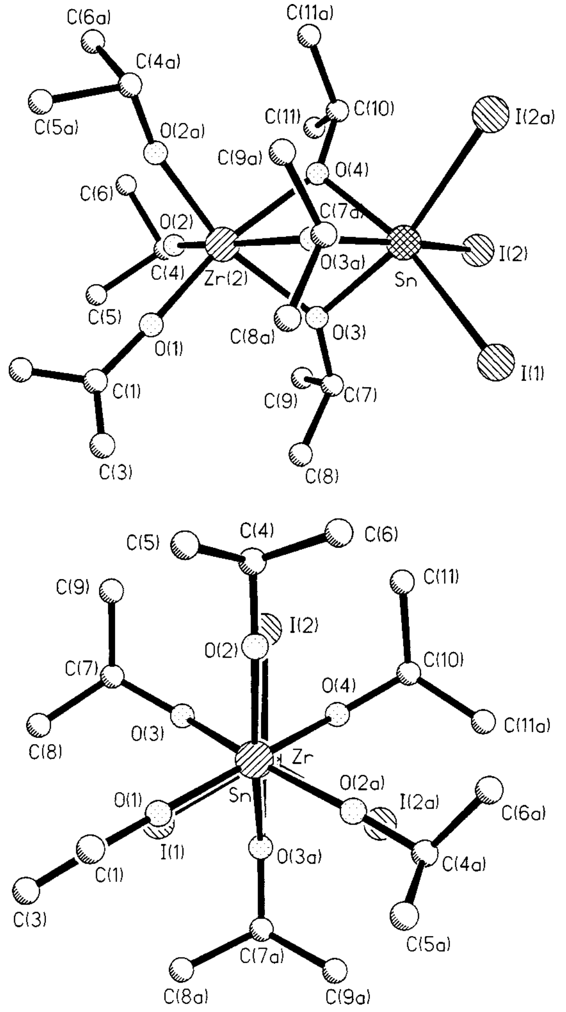

Figure 3. (a) Ball-and-stick drawing of the molecular structure of [$I_3Sn\{Zr(OPr^i)_5(Pr^iOH)\}$] (**4**). (b) A perspective view down the tin−zirconium axis.

stretching frequencies (ν 2031, 2009, 1952 cm^{-1}), as observed in a number of related complexes based on cyclopentadienylmetal tricarbonyl fragments (e.g., [$BiCl\{Mo(CO)_3(C_5H_5)\}_2$]).[29] A single resonance at δ 354.31 in the ^{119}Sn NMR spectrum lies in the range typically observed for organometallic derivatives with a tetracoordinate tin center containing Sn−Mo bonds.[25] A definitive structure elucidation by X-ray crystallography revealed a tetracoordinate tin species devoid of alkoxometalate ligands (vide infra).

Solid-State Structures. Compound **1** crystallizes in the centrosymmetric space group $P\bar{1}$.The molecular structure (Figure 1) of **1** consists of a central tin(IV) atom present in an octahedral configuration of two terminal iodide ligands in a cis position and the four isopropoxide oxygen atoms of two monoanionic bidentate $\{Al(OPr^i)_4\}^-$ moieties, thus belonging to the cis series of octahedral metal complexes.[21] Owing to the chelating properties of the $\{Al(OPr^i)_4\}^-$ moiety, the compound exists in enantiomeric forms (*R* and *S*). The asymmetric unit contains one of the enantiomeric forms; the second kind of molecule within the crystal structure is generated by inversion symmetry. The two four-membered Sn−O(1)−Al(1)−O(2) and Sn−O(3)−Al(2)−O(4) rings are essentially planar (358.94° and 359.40°, respectively) and are oriented in a mutually perpendicular fashion. The octahedral geometry about tin is substantially distorted from ideal parameters, with cis and trans angles ranging from 69.55° to 99.27° and 154.19° to 167.55°, respectively. The two Sn−I bond distances are almost equal (2.727 and 2.745 Å) and in good agreement with the sum of their covalent radii (2.73 Å).[30] The Sn−O distances range from 2.109(3) to 2.117(3) Å and are almost the same with respect to their standard deviations. Remarkably, no trans effect is found for the oxygen atoms O(1) and O(4). The aluminum atoms of the two tetrakis(isopropoxy)aluminate groups have a distorted tetrahedral geometry. Within the four-membered SnO_2Al rings, the Al−O distances are comparable but longer than the terminal bonds (Table 2). The terminal Al−O distances (1.662(4)−1.694(4) Å) in Al−O tetrahedra lie in the range observed for other isopropoxyaluminates.[31−34] A notable feature of the structure of **1** is the Al−O−C bond angles associated with the terminal O(6) and O(8) alkoxide oxygen atoms (162.8° and 160.7°), which are significantly larger in comparison to Al−O−C angles commonly observed in aluminum alkoxides (e.g., Al−O−C in $[Al(OPr^i)_3]_4$ 128°−135°),[24] which is generally considered as crystallographic evidence for a strong π interaction between the oxygen p orbitals and the σ-antibonding orbitals (the contribution of the d orbitals is also accounted for) of aluminum; however, this could also be due to the steric requirements or larger degrees of freedom available to the terminal alkoxy groups. The bidentate chelation of the $\{Al(OPr^i)_4\}^-$ group to a single metal center, which has been observed in the structural characterization of **1**, has been proposed for a large number of heterometallic alkoxyaluminates: $Pr[\{Al(OPr^i)_4\}_2(Pr^iOH)(\mu\text{-}Cl)\}_2]$,[31] $Er\{Al(OPr^i)_4\}_3$,[32] $HfAl_2(OPr^i)_{10}$,[33] and $TiAl_2(OPr^i)_{10}$.[34] However, any prediction of the ligating properties of the $\{Al(OPr^i)_4\}^-$ unit in the absence of single-crystal diffraction studies can prove highly speculative since different coordination modes may be possible. A tetrakis(isopropoxy)aluminate moiety can bridge (i) two different metal centers via single alkoxy bridges (e.g., $Mo_2(O_2CCH_3)_2\{Al(OPr^i)_4\}_2$),[35] (ii) two metal centers via a single alkoxy bridge to one and a double alkoxy bridge to a second (e.g., $Mg_2Al_3(OPr^i)_{13}$),[36] and (iii) two metal centers via two double alkoxy bridges (e.g., $[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_n$).[37]

Compound **2** crystallizes in acentric space group $P2_1$, and the crystal chosen for X-ray diffraction analysis solely contains one of the enantiomeric forms. The absolute conformation was determined (Flack param-

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(29) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C.; Tucker, A. J.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1988,** 2941.

(30) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(31) Tripathi, U. M.; Singh, A.; Mehrotra, R. C.; Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *J. Chem. Soc., Chem. Commun.* **1992,** 152.

(32) Wijk, M.; Norrestam, R.; Nygren, M.; Westin, G. *Inorg. Chem.* **1996,** *35,* 1077.

(33) Turevskaya, E. P.; Berdyev, D. V.; Turova, N. Ya.; Starikova, Z. A.; Yanovsky, A. I.; Struchkov, Y. T.; Belokon, A. I. *Polyhedron* **1997,** *16,* 663.

(34) Tudyka, S.; Pflanz, K.; Aldingeer, F.; Borrmann, H.; Fischer, P.; Brunner, H. *Z. Anorg. Allg. Chem.* **1997,** *623,* 1163.

(35) Lamotte, J.; Oideberg, O.; Dupont, L.; Durfut, P. *Cryst. Struct. Commun.* **1981,** *10,* 59.

(36) Meese-Marktscheffel, J. A.; Fukuchi, R.; Kido, M.; Tachibana, G.; Jensen, C. M.; Gilje, J. W. *Chem. Mater.* **1993,** *5,* 755.

(37) Meese-Marktscheffel, J. A.; Weimann, R.; Schumann, H.; Gilje, J. W. *Inorg. Chem.* **1993,** 32, 5894.

Table 1. Summary of Crystal and Refinement Data for $[I_2Sn\{Al(OPr^i)_4\}_2]$ (1), $[I_2Sn\{Ti(OPr^i)_5\}_2]$ (2), $[I_3Sn\{Zr(OPr^i)_5\}(Pr^iOH)\}]$ (4), and $[I_2Sn\{Mo(C_5H_5)(CO)_3\}_2]$ (5)

empirical formula	$C_{24}H_{56}Al_2I_2O_8Sn$	$C_{30}H_{70}I_2O_{10}SnTi_2$	$C_{18}H_{42}I_3O_6SnZr$	$C_{16}H_{10}I_2Mo_2O_6Sn$
fw	899.14	1059.15	945.13	862.63
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/m$	$P2_1/c$
a (Å)	9.765(2)	11.093(2)	9.963(2)	10.759(2)
b (Å)	12.928(3)	16.366(3)	15.377(3)	13.635(3)
c (Å)	15.780(3)	13.108(3)	11.236(2)	15.483(3)
α (deg)	86.01(3)			
β (deg)	84.77(3)	100.70(3)	111.97(3)	90.05(3)
γ (deg)	78.14(3)			
temp (°C)	20	20	20	20
Z	2	2	2	4
V (Å^3)	1938.8(7)	2338.4(8)	1596.4(5)	2271.3(8)
D_{calcd} (Mg m^{-3})	1.540	1.504	1.966	1.939
μ (Mo Kα) (mm^{-1})	2.331	2.224	4.034	3.024
θ range (deg)	1.61−27.56	1.58−22.49	1.95−24.00	1.89−24.11
no. of colld reflns	8920	6364	2608	2945
no. of indep reflns	8920	6106	2608	2945
no. of obsd reflns	7774	5482	2319	2781
R^a	0.0398	0.0375	0.0438	0.0328
$R_w{}^b$	0.0479	0.0403	0.0497	0.0348
goodness-of-fit	1.109	0.967	1.095	1.072
factors min, max (e Å^3)	1.366, −1.108	0.585, −0.587	1.051, −1.480	0.639, −1.163

[a] $R(F_o^2) = \sum||F_o| - |F_c||/|F_o|$ for observed reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

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

I(1)−Sn	2.7271(8)	I(2)−Sn	2.7456(9)
Sn−O(3)	2.106(3)	Sn−O(4)	2.109(3)
Sn−O(2)	2.112(3)	Sn−O(1)	2.117(3)
Al(1)−O(8)	1.666(4)	Al(1)−O(7)	1.687(4)
Al(1)−O(1)	1.801(3)	Al(1)−O(2)	1.824(3)
Al(2)−O(6)	1.662(4)	Al(2)−O(5)	1.694(4)
Al(2)−O(4)	1.808(3)	Al(2)−O(3)	1.815(3)
O(3)−Sn−O(4)	69.55(10)	O(3)−Sn−O(2)	154.19(11)
O(4)−Sn−O(2)	91.83(11)	O(3)−Sn−O(1)	91.48(11)
O(4)−Sn−O(1)	88.49(11)	O(2)−Sn−O(1)	69.63(10)
O(3)−Sn−I(1)	98.13(8)	O(4)−Sn−I(1)	167.55(7)
O(2)−Sn−I(1)	99.27(8)	O(1)−Sn−I(1)	90.10(8)
O(3)−Sn−I(2)	99.18(8)	O(4)−Sn−I(2)	88.57(8)
O(2)−Sn−I(2)	97.99(8)	O(1)−Sn−I(2)	167.17(7)
I(1)−Sn−I(2)	95.40(4)	O(8)−Al(1)−O(1)	118.3(2)
O(8)−Al(1)−O(7)	116.1(2)	O(8)−Al(1)−O(2)	111.6(2)
O(7)−Al(1)−O(1)	110.5(2)	O(1)−Al(1)−O(2)	83.50(13)
O(7)−Al(1)−O(2)	112.4(2)	O(6)−Al(2)−O(4)	117.8(2)
O(6)−Al(2)−O(5)	115.9(2)	O(6)−Al(2)−O(3)	112.9(2)
O(5)−Al(2)−O(4)	110.6(2)	O(4)−Al(2)−O(3)	83.13(13)
O(5)−Al(2)−O(3)	112.1(2)	Al(1)−O(2)−Sn	102.59(13)
Al(1)−O(1)−Sn	103.22(13)	Al(2)−O(4)−Sn	103.44(12)
Al(2)−O(3)−Sn	103.28(13)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 2

Sn−O(6)	2.063(5)	Sn−O(2)	2.067(5)
Sn−O(1)	2.093(5)	Sn−O(7)	2.106(5)
Sn−I(2)	2.7777(8)	Sn−I(1)	2.7835(8)
Ti(1)−O(5)	1.774(6)	Ti(1)−O(3)	1.796(6)
Ti(1)−O(4)	1.773(6)	Ti(1)−O(1)	2.050(5)
Ti(1)−O(2)	2.137(5)	Ti(2)−O(10)	1.777(6)
Ti(2)−O(9)	1.785(6)	Ti(2)−O(8)	1.814(6)
Ti(2)−O(7)	2.039(5)	Ti(2)−O(6)	2.136(5)
O(6)−Sn−O(2)	164.4(2)	O(6)−Sn−O(1)	96.8(2)
O(2)−Sn−O(1)	71.63(19)	O(6)−Sn−O(7)	71.84(19)
O(2)−Sn−O(7)	96.8(2)	O(1)−Sn−O(7)	87.90(19)
O(6)−Sn−I(2)	91.64(14)	O(2)−Sn−I(2)	98.60(13)
O(1)−Sn−I(2)	168.58(14)	O(7)−Sn−I(2)	87.43(13)
O(6)−Sn−I(1)	98.98(14)	O(2)−Sn−I(1)	91.37(15)
O(1)−Sn−I(1)	89.05(14)	O(7)−Sn−I(1)	169.88(13)
I(2)−Sn−I(1)	97.25(3)	O(5)−Ti(1)−O(4)	103.9(3)
O(5)−Ti(1)−O(3)	96.1(3)	O(5)−Ti(1)−O(1)	92.0(3)
O(3)−Ti(1)−O(4)	106.9(3)	O(4)−Ti(1)−O(1)	106.3(3)
O(3)−Ti(1)−O(1)	142.7(3)	O(3)−Ti(1)−O(2)	87.5(2)
O(5)−Ti(1)−O(2)	154.7(3)	O(1)−Ti(1)−O(2)	70.99(19)
O(4)−Ti(1)−O(2)	98.8(3)	O(10)−Ti(2)−O(8)	109.7(3)
O(10)−Ti(2)−O(9)	103.1(3)	O(10)−Ti(2)−O(7)	105.8(3)
O(9)−Ti(2)−O(8)	96.8(3)	O(8)−Ti(2)−O(7)	139.3(3)
O(9)−Ti(2)−O(7)	93.7(3)	O(9)−Ti(2)−O(6)	158.8(3)
O(10)−Ti(2)−O(6)	95.9(2)	O(7)−Ti(2)−O(6)	71.74(19)
O(8)−Ti(2)−O(6)	85.5(2)	Ti(1)−O(1)−Sn	107.7(2)
Sn−O(2)−Ti(1)	105.6(2)	Ti(2)−O(7)−Sn	107.5(2)
Sn−O(6)−Ti(2)	105.4(2)		

eter 0.01(3)). The solid-state structure of **2** (Figure 2) shows a six-coordinate tin(IV) atom bound to two iodide and two bidentate $\{Ti(OPr^i)_5\}^-$ ligands. In comparison to **1**, the distortions from regular octahedral geometry are decreased, as may be deduced from the *trans* L−Sn−L′ (164.4−169.8°) and *cis* L−Sn−L′ angles (71.8−98.9°) (L = I, L′ = OR). The two Sn−I bonds (Sn−I(1) = 2.7835 Å; Sn−I(2) = 2.7777 Å) are slightly longer than those observed in **1** (Table 2). Among the two $\{Ti(OPr^i)_5\}^-$ fragments, the titanium atoms are present in slightly distorted trigonal-bipyramidal (TBP) environments with O(2), O(5) and O(6), O(9) occupying the axial sites whereas, O(1), O(3), O(4) and O(7), O(8), O(10) are the equatorial ligands for Ti(1) and Ti(2), respectively. The monoanionic $Ti(OPr^i)_5{}^-$ unit in **2** with a TBP arrangement of alkoxo ligands is structurally similar to the five-coordinate titanium observed in the solid-state structures of polymeric $[M\{Ti(OPr^i)_5\}]_n$ (M = Na, K) compounds.[21,38] The Ti−OR distances (Table 3) clearly fall in two ranges, with Ti-μ_2-OR distances (averages 2.082 Å) being longer than terminal Ti−OR distances (average 1.780 Å). The observation of shorter terminal Ti−OR bond lengths with larger Ti−O−C terminal angles (average 155.2°) is a common feature of alkoxides of early transition metals.[10] Interestingly, among the terminal OR ligands on Ti(1) and Ti(2), the angles at the axial O(5) and O(9) alkoxide oxygen atoms are significantly larger (Ti(1)−O(5)−C(13) = 170.4°; Ti(2)−O(9)−C(25) = 178.6°) than that observed for equatorial (O(3), O(4), O(8), and O(10)) OR terminal groups (average Ti−O−C = 145.6°).

The solid-state structure of **4**, as determined by an X-ray diffraction study, is shown in Figure 3a. The molecule is highly symmetrical and possesses a mirror plane passing through Sn, Zr, I(1), O(1), and O(4) (C_m

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(38) Boyle, T. J.; Bradley, D. C.; Hampden-Smith, M. J.; Patel, A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5893.

Table 4. Pertinent Bond Lengths (Å) and Angles (deg) for Compound 4

Sn−O(4)	2.115(6)	Sn−O(3)	2.133(4)
Sn−I(2)	2.7731(9)	Sn−I(1)	2.7750(11)
Zr−O(2)	2.023(5)	Zr−O(1)	1.969(7)
Zr−O(3)	2.179(4)	Zr−O(4)	2.202(6)
O(4)−Sn−O(3)	74.7(2)	O(3a)−Sn−O(3)[a]	74.4(2)
O(4)−Sn−I(2)	93.83(11)	O(3)−Sn−I(2a)[a]	164.76(11)
O(3)−Sn−I(2)	93.09(12)	I(2)−Sn−I(2a)[a]	97.70(4)
O(4)−Sn−I(1)	166.7(2)	O(3)−Sn−I(1)	94.83(11)
I(2)−Sn−I(1)	94.93(3)	O(1)−Zr−O(2)	94.3(2)
O(1)−Zr−O(3)	98.1(2)	O(2)−Zr−O(2a)[a]	92.3(3)
O(2a)−Zr−O(3)[a]	164.3(2)	O(2)−Zr−O(3)	96.2(2)
O(3)−Zr−O(3a)[a]	72.6(2)	O(2)−Zr−O(4)	94.3(2)
O(1)−Zr−O(4)	167.6(3)	O(3)−Zr−O(4)	72.0(2)
Sn−O(3)−Zr	92.8(2)	Sn−O(4)−Zr	92.6(2)

[a] Symmetry transformations used to generate equivalent atoms: a = $x, -y + {}^1/_2, z$.

crystallographic symmetry). From the structural parameters (Table 4), it can be deduced that the higher point symmetry C_{3v} (3m) with the rotation axis passing through the Sn and Zr atoms (Figure 3b) is very close; it can be anticipated that the free molecule might adopt this point symmetry. The overall molecular geometry is best described as a face-sharing fusion of two octahedra built about Sn(IV) and Zr(IV) and is comparable with the solid-state structure of the homoleptic mixed-valence uranium (U(IV)−U(V)) derivative $U_2(OBu^t)_9$.[39] Although **4** does not have a lot of molecular relatives to compare with, the formation of a confacial bioctahedral configuration in the form of chelating $M_2(OPr^i)_9^-$ anions is a feature of the alkoxy chemistry of a large number of tetravalent metals.[9] In contrast to the bidentate ligation of the $\{Al(OPr^i)_4\}^-$ (**1**) and $\{Ti(OPr^i)_5\}^-$ (**2**) anions, as anticipated for a five-coordinate tin(IV) species, the $\{Zr(OPr^i)_5\}^-$ unit in **4** acts as a tridentate sequestering anion to furnish a hexacoordinate tin(IV) atom, which illustrates the ligating versatility of $\{M(OR)_x\}^-$ units with respect to the demand of central metal atom. Zr(IV) achieves hexacoordination by adding an Pr^iOH molecule. The addition of neutral alcohol molecules to attain an octahedral configuration is well-established in dinuclear isopropoxide 2-propanolates $[M_2(OR)_8(ROH)_2]$ of larger tetravalent metals (Sn^{IV}, Zr^{IV}, Hf^{IV}, Ce^{IV}).[10c,27,28] Although the hydroxylic hydrogen atom in **4** could not be located crystallographically, the Zr−O(2) (Zr−O(2a)) and Zr−O(1) bond distances (metal−alkoxide distances being shorter than the metal−alcohol distances) suggest it to be situated between O(2) and O(2a). The shorter O(2)···O(2a) separations (O(2)···O(2a) = 2.917 Å; O(1)···O(2) = 2.931 Å) and the significant bending of Zr−O(2)−C (Zr−O(2a)−C) angles (165.0°) (due to the tendency of the Pr^i moiety to point away from the O···O vector) in comparison to Zr−O(1)−C (176.3°) further supports the presence of an alcohol proton between O(2) and O(2a). The Sn−I distances (average 2.774 Å) are comparable with those observed in **1** and **2**. The Zr−μ-OPr^i distances (Table 4) are in the typical range commonly observed for doubly bridging alkoxide groups in structurally analogous $Zr_2(OPr^i)_9^-$ units.[10,11]

A single-crystal X-ray diffraction analysis of a suitable specimen of **5** revealed four molecules in the crystal unit, related by space group symmetry. The molecule is illustrated in Figure 4 with the atom-labeling scheme used in Table 5. The solid-state structure exhibits a bridging "SnI_2" moiety bonded to two $[(C_5H_5)Mo(CO)_3]$ units via Sn−Mo bonds. The coordination around tin deviates from an ideal tetrahedral geometry. The Mo(1)−Sn−Mo(2) angle (133.96(3)°) is larger than a regular tetrahedral angle while Mo−Sn−I angles (100.91−108.55°) are smaller, indicating a greater s character in the transition-metal−tin bond.[40] If we consider the broadening of the Mo−Sn−Mo angle, it is tempting to ascribe the increase over the tetrahedral angle of 109.5° to steric repulsion between the large transition-metal fragments. This consideration of steric requirements could also explain the significantly different Sn−I contacts (Sn−I(2) 2.6445(9) Å; Sn−I(1) 2.7790 Å) since $Cp(CO)_3Mo(1)$ is more affected by the SnI_2 unit (Figure 4). Nevertheless, the different bonding of the iodide ligands to tin could also be due to electronic factors as no significant intermolecular I···Sn−I(1) interactions are observed in the packing of the molecules. The coordination of the transition metals to tin could result in the withdrawal of electron density from the tin center. Distinctly, one of the iodide ligands (I(2)) is most affected by the coordination of the molybdenum centers to tin. The Sn−I(2) bond is present within a quasi-planar $SnMo_2I$ group (sum of angles = 346.10°). In a tetravalent formalism, the tin coordination can be viewed as $SnMo_2I(2)^+I(1)^-$. The bond angles decrease in the order Mo−Sn−Mo > Mo−Sn−I > I−Sn−I (Table 5). The coordination polyhedron of the Mo atoms approximates an octahedron with three carbonyl groups, a tin atom, and the remaining two sites being occupied by the cyclopentadienyl ring. The metal carbonyl angles Mo-

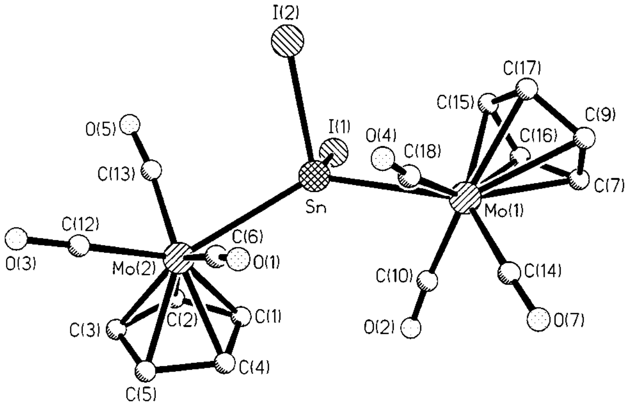

Figure 4. Ball-and-stick representation of $[I_2Sn\{Mo(C_5H_5)(CO)_3\}_2]$ (**5**).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 5

Sn−I(2)	2.6445(9)	Sn−I(1)	2.7790(8)
Sn−Mo(1)	2.9831(10)	Sn−Mo(2)	3.0186(11)
C(1)−Mo(2)	2.272(8)	C(7)−Mo(1)	2.497(9)
C(2)−Mo(2)	2.215(7)	C(9)−Mo(1)	2.452(9)
C(3)−Mo(2)	2.271(9)	C(15)−Mo(1)	2.389(8)
C(4)−Mo(2)	2.237(8)	C(16)−Mo(1)	2.428(9)
C(5)−Mo(2)	2.252(8)	C(17)−Mo(1)	2.344(9)
I(2)−Sn−I(1)	94.23(3)	I(2)−Sn−Mo(1)	104.20(3)
I(1)−Sn−Mo	100.91(3)	I(2)−Sn−Mo(2)	107.94(3)
I(1)−Sn−Mo(2)	108.55(3)	Mo(1)−Sn−Mo(2)	133.96(3)

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(39) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1984,** *23,* 4211.

(40) (a) Zubieta, J. A.; Zuckerman, J. J. *Progress in Inorganic Chemistry;* Volzy, S. J., Ed.; Interscience: New York, 1978; p 251. (b) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989,** *89,* 11.

(1)−C(18)−O(4) (171.6°) and Mo(1)−C(10)−O(2) (175.1°) deviate from linearity in order to bring the carbonyl group close to the tin atom. This partial umbrella effect is evident in the narrowing of Sn−Mo(1)−C(18) (70.7(2)°) and Sn−Mo−C(10) (71.2(3)°). In contrast to other analogous compounds, e.g., $[\{(C_5H_5)Cr(CO)_3\}_2SnCl_2]$[41] and $[\{(C_5H_5)Fe(CO)_2\}_2SnCl_2]$,[42] the cyclopentadienyl rings in **5** exhibit different bonding parameters to the two molybdenum centers. The C−C bond lengths in the cyclopentadienyl ring interacting with the Mo(1) center show the expected occurrence of double bonds at the C(7a)−C(9a) (1.340(2) Å) and C(16)−C(15) (1.339(12) Å) positions, while an appreciably delocalized character is observed for the cyclopentadienyl ring bound to the Mo(2) atom (C−C(Cp) 1.42−1.52 Å). Further, the cyclopentadienyl ring attached to the Mo(2) atom is more strongly bonded, with the Mo−C(Cp) distances lying between 2.21 and 2.27 Å; however, the cyclopentadienyl ring attatched to Mo(1) shows weaker contacts with a larger degree of variation (2.34−2.49 Å). To our knowledge, the two Mo−Sn contacts (2.983(10) and 3.018(11) Å) are the longest ever observed and are significantly longer than Mo−Sn(Ge) distances observed in other related complexes ($[(CO)_5Mo{-}In(OBu^t)_3Sn{-}Mo(CO)_5$, 2.76 Å;[43] $[(C_5H_5)Sn(OBu^t)_3Ge{-}Mo(CO)_5]$, 2.73 Å;[44] $ClSn[C_5H_5Fe(CO)_2]_2[C_5H_5Mo(CO)_3]$, 2.598 Å[45]).

Curiously, the formation of the metal−metal-bonded cluster **5** involves the cleavage of the metal−oxygen bonds in **1** or **2**. The displacement of the $\{Al(OPr^i)_4\}^-$ or $\{Ti(OPr^i)_5\}^-$ anions by $Mo(C_5H_5)(CO)_3^-$ units is intriguing, especially in view of the greater affinity of tin for oxygen, and could possibly be a consequence of the higher covalent nature of Sn−I bonds.

Experimental Section

General Methods and Materials. All manipulations were routinely performed under a dry and deoxygenated dinitrogen atmosphere. Solvents were purified using standard procedures. Commercial (Aldrich) samples of $Ti(OPr^i)_4$ and SnI_4 were purified by distillation and sublimation, respectively, in vacuo and analyzed for metal contents prior to use. $[Zr(OPr^i)_4\cdot Pr^iOH]_2$,[46] $[Nb(OPr^i)_5]_2$,[46] $[Al(OPr^i)_3]_4$,[46] and $Na[(C_5H_5)Mo(CO)_3]$[47] were synthesized according to literature procedures. Elemental analyses were performed on a LECO elemental analyzer CHN 900. ^1H (200.13 MHz), ^{13}C (50.31 MHz), ^{27}Al (52.14 MHz) and ^{119}Sn (74.68 MHz) NMR spectra were recorded on a Bruker MSL 200 spectrometer. ^{27}Al and ^{119}Sn NMR chemical shifts are referenced externally to $Al(NO_3)_3\cdot 6H_2O$ and $SnMe_4$, respectively. IR spectra were recorded on a Bio-Rad FTS-165 spectrometer. Molecular weight determinations were obtained cryoscopically by the freezing-point depression of benzene. Metal and iodine contents were estimated using established procedures.[48]

Synthesis. For brevity sake, the synthesis of only one representative compound (**2**) has been described in detail. Compounds **1**, **3**, and **4** were prepared analogously. The crude yield of all the derivatives (except **5**) are almost quantitative. The extremely high solublity of these derivatives in hydrocarbon solvents drastically reduces the yield of recrystallized material. The figures quoted below refer to the yields of the first recrystallization products, however, in each of the cases another 15−25% product could be recovered from further recrystallization processes.

$[I_2Sn\{Ti(OPr^i)_5\}_2]$ (2). To a toluene (20 mL) solution of freshly sublimed SnI_4 (3.06 g, 4.88 mmol) was added a clear solution of $KTi(OPr^i)_5$ (freshly synthesized by reacting K (0.38 g, 9.71 mmol) and $Ti(OPr^i)_4$ (2.79 g, 9.73 mmol) in a hot (50 °C) mixture of toluene−isopropyl alcohol). A slightly exothermic reaction took place with an immediate formation of KI, and a color change from orange to light yellow was observed. After the reaction mixture was stirred for 12 h at room temperature, it was filtered off, and the volatiles were removed in vacuo to obtain a yellow semisolid (4.5 g, 86%), which could be recrystallized from a toluene−isopropyl alcohol mixture (50/50, v/v) (2.76 g, 54%) at −20 °C. Anal. Calcd for $C_{30}H_{70}I_2O_{10}SnTi_2$: C, 34.01; H, 6.66; Sn, 11.20; I, 23.96. Found: C, 33.56; H, 6.43; Sn, 11.43; I, 23.79. Mol wt found 1118; calcd 1059. Selected IR ($CDCl_3$, cm^{-1}) data: 2971 (s), 2929 (s), 2869 (s), 2627 (s), 1463 (s), 1371 (s), 1365 (s), 1332 (s), 1163 (s), 1123 (s), 993 (m), 907 (s), 853 (m), 812 (m), 732 (s), 650 (w), 543 (s), 431 (m). ^1H NMR (20 °C, C_6D_6): δ 1.27 (d, 60H, CH_3), 4.52 (m, 6H), 4.81 (m, 4H) (CH). ^1H NMR (−10 °C, C_7D_8): δ 1.29 (d, 36H), 1.32 (d, 24H) (CH_3), 4.54 (m, 6H), 4.89 (m, 4H) (CH). ^{13}C NMR (20 °C, C_6D_6): δ 26.59 (CH_3), 76.47, 79.79 (CH). ^{13}C NMR (−10 °C, C_7D_8): δ 26.56, 26.80 (CH_3), 76.33, 79.86 (CH). ^{119}Sn NMR (20 °C, C_6D_6): δ −1245.07.

$[I_2Sn\{Al(OPr^i)_4\}_2]$ (1). Obtained from SnI_4 (2.22 g, 3.54 mmol) and $KAl(OPr^i)_4$ (freshly synthesized by reacting K (0.27 g, 7.09 mmol) and $Al(OPr^i)_3$ (1.44 g, 7.08 mmol) in a mixture of toluene−isopropyl alcohol at 50 °C).Yield: 2.80 g, 90%. Crystallized from *n*-hexane as yellow crystals (1.11 g, 35%). Anal. Calcd for $C_{24}H_{56}Al_2I_2O_8Sn$: C, 32.05; H, 6.22; Al, 3.00; I, 28.22; Sn, 13.20. Found: C, 31.36; H, 6.01; Al, 2.89; I 27.45; Sn, 13.35. Mol wt found 970; calcd 899. Selected IR ($CDCl_3$, cm^{-1}) data: 3090 (s), 3071 (s), 3033 (s), 2962 (s), 2927 (s), 2864 (m), 1480 (s), 1386 (s), 1374 (s), 1331 (m), 1171 (m), 1131 (s), 1111 (s), 1035 (s), 1008 (m), 969 (m), 942 (s), 834 (s), 813 (s), 674 (s), 603 (m), 542 (s), 497 (m), 453 (m). ^1H NMR (20 °C, C_7D_8): δ 1.24 (d, $J = 6$ Hz, 6H), 1.26 (d, $J = 6$ Hz, 6H), 1.32 (d, $J = 6$ Hz, 6H), 1.37 (d, $J = 6$ Hz, 6H), 1.38 (d, $J = 6$ Hz, 6H), 1.58 (d, $J = 6$ Hz, 12H), 1.62 (d, $J = 6$ Hz, 6H) (CH_3), 4.27 (sept, $J = 6$ Hz, 2H), 4.50 (sept, $J = 6$ Hz, 2H), 4.78 (m, 4H) (CH). ^{13}C NMR (20 °C, C_7D_8): δ 24.02, 24.73, 26.09, 26.35, 27.84, 28.02, 28.21, 28.36 (CH_3), 63.86, 63.93, 63.99, 66.11, 66.64, 69.56, 70.34, 70.99 (CH). ^{27}Al NMR (20 °C, C_7D_8): δ 60.68. ^{119}Sn NMR (20 °C, C_7D_8): δ −1540.72.

$[I_2Sn\{Nb(OPr^i)_6\}_2]$ (3). Obtained from SnI_4 (0.71 g, 1.13 mmol) and $KNb(OPr^i)_6$ (freshly synthesized by reacting K (0.09 g, 2.32 mmol) and $Nb(OPr^i)_5$ (0.90 g, 2.30 mmol) in a mixture of toluene−isopropyl alcohol at 50 °C). Yield: 1.23 g, 88%. Crystallized from toluene−*n*-hexane as yellow crystals (0.56 g, 40%). Anal. Calcd for $C_{36}H_{84}I_2O_{12}SnNb_2$: C, 29.97; H, 5.82; I, 17.59; Sn, 8.23. Found: C, 29.36; H, 5.55; I, 17.84; Sn, 8.01 Mol wt found 1325; calcd 1443. Selected IR ($CDCl_3$, cm^{-1}) data: 3091(s), 3071 (s), 3035(m), 2972 (s), 2927 (s), 1479 (s), 1463 (m), 1379 (m), 1365 (m), 1330 (m), 1166 (m), 1112 (s), 1029 (m), 996 (s), 942 (m), 856 (m), 830 (m), 730 (m), 676 (s), 570 (s), 498 (m), 464 (m). ^1H NMR (20 °C, C_6D_6): δ 1.27 (d, $J = 6$ Hz, 48H), 1.32, (d, $J = 6$ Hz, 12H), 1.45 (d, $J = 6$ Hz, 12H) (CH_3); methine protons are observed as three overlapping multiplets centered at δ 4.40, 4.64, and 4.91. ^{13}C NMR (20 °C, C_6D_6): δ 24.82, 25.03, 26.39 (CH_3), 67.97, 74.99, 76.27 (CH). ^{119}Sn (20 °C, C_6D_6): δ −1113.91.

$[I_3Sn\{Zr(OPr^i)_5(Pr^iOH)\}]$ (4). Obtained from SnI_4 (2.10 g, 3.35 mmol) and $KZr(OPr^i)_5$ (freshly synthesized by reacting K (0.132 g, 3.37 mmol) and $Zr(OPr^i)_4\cdot Pr^iOH$ (1.30 g, 3.35 mmol) in a mixture of toluene−isopropyl alcohol at 50 °C). Yield: 2.80 g, 90%. Crystallized from a *n*-hexane−isopropyl alcohol mixture as orange crystals (1.26 g, 40%). Anal. Calcd for

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(41) Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1975,** 230.
(42) O'Connor, J. E.; Corey, E. R. *Inorg. Chem.* **1967,** *6*, 968.
(43) Veith, M.; Weidner, S.; Kunze, K.; Käfer, D.; Hans, J.; Huch, V. *Coord. Chem. Rev.* **1994,** *137*, 297.
(44) Veith, M.; Mathur, C.; Huch, V. *Phosphorous, Sulfur and Silicon* **1997,** in press.
(45) O'Connor, J. E.; Corey, E. R. *J. Am. Chem. Soc.* **1967,** *89*, 3930.
(46) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides;* Academic Press: London, 1978.

$C_{18}H_{42}I_3O_6SnZr$: C, 22.87; H, 4.55; I, 40.28; Sn, 12.55; Zr, 9.65. Found: C, 22.03; H, 4.39; I, 39.40; Sn, 12.38; Zr, 9.50. Mol wt found 1066; calcd 945. Selected IR ($CDCl_3$, cm^{-1}) data: 3190 (br), 3090 (s), 3071 (s), 3033 (s), 2972 (s), 2947 (s), 2897 (m), 1457 (s), 1386 (s), 1350 (s), 1331 (m), 1156 (m), 1132 (s), 1077 (s), 1071 (s), 1014 (m), 982 (m), 946 (s), 832 (s), 812 (s), 668(s), 602 (m), 545 (s), 496 (m), 450 (m). ^1H NMR (20 °C, C_6D_6): δ 1.22 (d, $J = 6$ Hz, 18H), 1.25 (d, $J = 6$ Hz, 6H), 1.29 (d, $J = 6$ Hz, 6H), 1.52 (d, $J = 6$ Hz, 6H) (CH_3), 3.65 (s, 1H, O*H*), 4.34 (sept, $J = 6$ Hz, 3H), 4.46 (sept, $J = 6$ Hz, 1H), 4.65 (br m, 2H) (C*H*). ^{13}C NMR (20 °C, C_6D_6): δ 24.72, 24.91, 25.24, 26.34 (CH_3), 63.55, 66.86, 73.56, 74.25 (*C*H). ^{119}Sn NMR (20 °C, C_6D_6): δ −1078.9.

[$I_2Sn\{Mo(C_5H_5)(CO)_3\}_2$] (5). A THF (25 mL) solution of $Na[Mo(C_5H_5)(CO)_3]$ (0.46 g, 17.16 mmol) was added slowly to a stirred toluene solution of **1** (0.78 g, 8.67 mmol). An immediate color change from yellow to orange was observed. The resulting mixture was then stirred for 6 h at room temperature, during which the color of the solution changed from orange to dark red. The red residue, left after removal of the solvent in vacuo, was extracted with 20 mL of toluene. The toluene solution was reduced in vacuo upon which red crystals were obtained. Yield: 0.22 g, 20% based upon the initial amounts of $Na[Mo(C_5H_5)(CO)_3]$. Anal. Calcd for $C_{16}H_{10}I_2Mo_2O_6Sn$: C, 22.76; H, 1.16; I, 29.42; Sn, 13.76. Found: C, 22.58; H, 1.12; I, 29.30; Sn, 13.58. ^1H NMR (20 °C, C_6D_6): δ 4.82 (s, C_5H_5). ^{13}C NMR (20 °C, C_6D_6): δ 91.84 (C_5H_5), 225.13, 225.33, 230.37 (*C*O). ^{119}Sn NMR (20 °C, C_6D_6): δ 354.31. IR ($CDCl_3$, cm^{-1}): ν(CO) 2031, 2009, 1952.

Crystallographic Studies. Crystal data, collection, and processing parameters for **1**, **2, 4**, and **5** are given in Table 1, whereas significant bond parameters are listed in Tables 2−5.

[$I_2Sn\{Al(OPr^i)_4\}_2$] (1). A yellow rectangular bar (0.70 × 0.50 × 0.35 mm) was affixed to the end of the glass fiber using silicone grease and transferred to a thin-walled Lindemann capillary, under strictly anaerobic conditions. The sealed capillary was then mounted on the goniometer head of a Siemens Stoe AED 2 diffractometer operating with graphite-monochromated Mo Kα X-ray radiation ($\lambda = 0.710\ 73$ Å). Unit cell dimensions were determined from the least-squares refinement of $(\sin \theta/\lambda)^2$ values for 24 accurately centered reflections. The data collection ($\omega-\theta$ scan type) was performed at ambient temperature using a standard moving crystal-moving detector technique. Three reflections chosen as intensity standards were measured every 90 min of X-ray exposure time, no significant decay in the crystal quality was observed. An empirical absorption correction (ψ scans) was applied. A careful examination of the preliminary data set revealed no systematic extinctions or any diffraction symmetry, suggesting the possible space group as $P1$ or $P\bar{1}$. The centrosymmetric space group $P\bar{1}$ was chosen and later proved to be correct by successful refinement of the model. The structure was solved by direct methods (SHELXS-86),[49] which revealed the positions of the heavy atoms. The remaining non-hydrogen atoms were identified from difference Fourier analysis. The overall refinement method used was full-matrix least-squares on F^2 (SHELXS-93).[50] Hydrogen atoms were included in the last refinement cycles as idealized contributions (C−H = 0.96 Å). The final difference Fourier map was essentially featureless.

[$I_2Sn\{Ti(OPr^i)_5\}_2$] (2). A pale yellow plate with approximate dimensions of 0.50 × 0.10 × 0.25 mm was handled in a manner similar to that described for **1.** Data were corrected for Lorentz and polarization effects, and equivalent data were averaged after correction for absorption. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematically absent reflections corresponding to one of the space groups $P2_1$ or $P2_1/m$. Satisfactory solution and refinement of the model revealed the noncentrosymmetric space group to be the correct choice. The positions of the heavy atoms were found by direct methods. All remaining non-hydrogen atoms were located on successive difference electron density maps. Hydrogen atoms were affixed as idealized contributions, and the overall refinement method used was full-matrix least-squares on F^2.

[$I_3Sn\{Zr(OPr^i)_5(Pr^iOH)\}$] (4). An orange cube was cleaved to obtain a suitable specimen (0.30 × 0.45 × 0.50 mm). The crystal mounting, data collection, and reduction procedure was similar to that described for **1**. A systematic search of a limited hemisphere of reciprocal space located a set of data with monoclinic symmetry. The space group $P2_1/m$ was selected and supported at all stages of structure solution and refinement to be the correct choice. The positions of the tin, zirconium, and iodine atoms were easily determined from an initial E-map (direct methods). The remaining atoms were observed in subsequent Fourier syntheses. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms. All hydrogen atoms were refined using the riding model in the HFIX facility in SHELXS-93. The final difference Fourier map showed no significant features.

[$I_2Sn\{Mo(C_5H_5)(CO)_3\}_2$] (5). The crystal mounting, data collection, and reduction procedure of the dark red plate of approximate dimensions 0.20 × 0.25 × 0.30 mm was similar to that described for **1**. The structure of **5** (monoclinic, space group $P2_1/c$) was solved by heavy-atom methods using SHELXS 86 and refined by full-matrix least-squares on F^2 (SHELXS 93). The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were affixed as idealized contributions. Weighting was introduced in the last refinement cycles.

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Supporting Information Available: Tables of atomic coordinates and the corresponding anisotropic thermal parameters for complexes **1**, **2**, **4**, and **5** (23 pages). Ordering information is given on any current masthead page.

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(47) Patil, H. R. H.; Graham, W. A. G. *Inorg. Chem.* **1966,** *5*, 1401.

(48) Vogel, A. I. *A Textbook of Quantitative Analysis;* Longmans, London, 1978.

(49) Sheldrick, G. M. *SHELXS 86*; University of Göttingen: Göttingen, Germany, 1986.

(50) Sheldrick, G. M. *SHELXL 93, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1993.