On the Differing Lewis Basicity of InI Compared with SnII in Molecular Indium-Tin and Thallium-Tin Alkoxides

By Michael Veith* and Klaus Kunze

In the thallium-tin alkoxide I,[1] which we synthesized for the first time some years ago, each of the two metal atoms has a lone pair. Therefore, it could act as a double Lewis base toward electrophilic metal centers, whereby both Sn and TI can engage in bonding. When I is allowed to react thermally or photochemically with chromium or molybdenum hexacarbonyl in excess, however, only the monoaat 2 or 3, respectively, is obtained, as shown in Equation (a).

\[
\text{[Sn(OrBu)2Ti] + [M(CO)6] \rightarrow [CO]_2M-Sn(OrBu)2Ti} \quad (a)
\]

An X-ray structure analysis (Fig. 1 and Table 1) confirms that the tin atom in 3 is bonded to the molybdenum atom.

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**Fig. 1.** Molecular structure of 3 [2] determined by X-ray analysis [2, 9]. The unshaded spheres are carbon atoms; hydrogen atoms are omitted. The Mo-Sn···TI angle is 178.9(1)°.

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Table 1. Results of the X-ray structure analyses of 3, 4, 8, and 10 [2].

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>hexagonal</th>
<th>monoclinic</th>
<th>orthorhombic</th>
<th>monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P61,cm</td>
<td>P21/n</td>
<td>Pmma</td>
<td>P21/n</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.867(9)</td>
<td>9.952(8)</td>
<td>15.11(1)</td>
<td>10.51(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.867(9)</td>
<td>17.95(1)</td>
<td>14.71(1)</td>
<td>30.30(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.21(1)</td>
<td>15.15(1)</td>
<td>15.76(1)</td>
<td>10.74(7)</td>
</tr>
<tr>
<td>Angle [°]</td>
<td>γ = 120</td>
<td>β = 100(20)</td>
<td>β = 107.36(7)</td>
<td></td>
</tr>
<tr>
<td>In-O [Å] (Ti-O)</td>
<td>2.4314(4)</td>
<td>2.557(15)</td>
<td>2.144(6)</td>
<td>2.21(1)</td>
</tr>
<tr>
<td>Sn-O [Å]</td>
<td>2.032(4)</td>
<td>2.017(9)</td>
<td>2.122(9)</td>
<td>2.07(1)</td>
</tr>
<tr>
<td>Sn-Mo [Å]</td>
<td>-</td>
<td>2.707(2)</td>
<td>2.761(1)</td>
<td></td>
</tr>
<tr>
<td>Sn-Cr [Å]</td>
<td>-</td>
<td>-</td>
<td>2.653(6)</td>
<td></td>
</tr>
<tr>
<td>In-Mo [Å]</td>
<td>-</td>
<td>-</td>
<td>2.742(4)</td>
<td>2.734(2)</td>
</tr>
<tr>
<td>O-In-O [Å]</td>
<td>66.7(1)</td>
<td>63.98(8)</td>
<td>73.2(3)</td>
<td>70.8(5)</td>
</tr>
<tr>
<td>O-Sn-O [Å]</td>
<td>81.5(1)</td>
<td>84.29(9)</td>
<td>74.9(3)</td>
<td>76.6(5)</td>
</tr>
<tr>
<td>In-Sn-Sn [Å] (Tl)</td>
<td>3.290(3)</td>
<td>3.298(1)</td>
<td>3.079(1)</td>
<td>3.08(2)</td>
</tr>
<tr>
<td>R value</td>
<td>0.037</td>
<td>0.062</td>
<td>0.058</td>
<td>0.068</td>
</tr>
</tbody>
</table>

Compared with the starting compound 1 (Sn-O = 2.023(9), Ti-O = 2.595(7), and Tl-Sn = 3.306(2) Å [13]), all metal–oxygen distances are slightly shortened; the distance between thallium and tin is decreased. Characteristic of the monoadducts 2 and 3 are the high CO wave numbers (v(A19Sn) bands) and a strong downfield shift of the 119Sn NMR signals relative to those of compound 1 (Δδ = 97.04; Table 2). Even under drastic conditions (large excess of metal carbonyl, higher temperature, longer reaction time), no complex fragment becomes bonded to the thallium atom of 2 or 3.

We therefore attempted to replace thallium by its homologue indium. The desired compound 4 may be obtained starting either from 1 or from the sodium salt [(Na(OtBu)2Sn)2]13 in a heterogeneous reaction with InBr [Eq. (b)].

\[
\text{[Tl(OtBu)2Sn]} \quad 1 \quad \xrightarrow{\text{InBr}} \quad [\text{In(OtBu)2Sn}] \quad 4
\]

\[
1/2[\text{Na(OtBu)2Sn}]_2
\]

Toluene, used as solvent, apparently causes partial dissolution of InBr via formation of an arenec complex. The monomeric product 4, like 1, is soluble in nonpolar solvents, exhibits a similar 119Sn NMR absorption (Table 2), and forms isostructural crystals (Table 1). According to an X-ray structure analysis, 4 has a distorted bipyramidal In4O4Sn structure with In and Sn in apical positions and the three oxygens in equatorial positions. Compared with 1, the indium atom is closer to the O2 plane than the thallium atom, as expected; the distances to the oxygen atoms lie in the normal range (see also indium 2,4,6-tris( trifluoromethyl)phenoxides [13]).

Reaction of 4 with [Cr(CO)5] or [Mo(CO)5] in THF either thermally or photochemically in analogy to Equation (a) likewise results in formation of monoadducts 5 and 6, respectively. Use of an excess of the metal carbonyl or longer reaction times results in further reaction to give the diadducts 7 and 8, respectively [Eq. (c)].

\[
\frac{[\text{In(OtBu)2Sn}]}{[\text{Snd(OtBu)2In-M(CO)5}]} + \frac{[\text{In(OtBu)2Sn}]}{[\text{Snd(OtBu)2In-M(CO)5}]} + \frac{[\text{M(CO)5}]}{[\text{In(OtBu)2Sn}]} \xrightarrow{\Delta T or hr} \frac{[\text{In(OtBu)2Sn}]}{[\text{Snd(OtBu)2In-M(CO)5}]} + \frac{[\text{M(CO)5}]}{[\text{In(OtBu)2Sn}]} + \text{THF}
\]

\[
5, \text{ M} = \text{Cr} \quad 6, \text{ M} = \text{Mo}
\]

\[
\frac{[\text{In(OtBu)2Sn}]}{[\text{Snd(OtBu)2In-M(CO)5}]} + \frac{[\text{In(OtBu)2Sn}]}{[\text{Snd(OtBu)2In-M(CO)5}]} + \frac{[\text{M(CO)5}]}{[\text{In(OtBu)2Sn}]} \xrightarrow{\Delta T or hr} \frac{[\text{In(OtBu)2Sn}]}{[\text{Snd(OtBu)2In-M(CO)5}]} + \frac{[\text{M(CO)5}]}{[\text{In(OtBu)2Sn}]} + \text{THF}
\]

\[
7, \text{ M} = \text{Cr} \quad 8, \text{ M} = \text{Mo}
\]

In contrast to 2 and 3, the transition-metal atoms in 5 and 6 are not coordinated to the tin atom but rather to the indium atom. This is revealed by the upfield shift of the 119Sn NMR signal (Δδ = -95.96) compared with that of 4 and by the wave numbers of the v(A19Sn) stretching band, which indicate a different electron density trans to the CO group (see Table 2).

This is shown especially clearly on going from the monoadducts 5 and 6 to the diadducts 7 and 8. The second v(A19Sn) bands due to the M(CO)5 units on tin lie in the absorption region observed for compounds 2 and 3 (Table 2).

The result of an X-ray structure analysis of 8 is shown in Figure 2. The four metal atoms, Mo, Sn, In, and Mo are arranged nearly linearly (Mo-Sn-In = 174.2°, Mo-In-Sn = 178.8°), with metal single bonds between Mo and In and between Mo and Sn (distances in Table 1); as found in the starting compound 4, In and Sn are bridged by three tert-butoxy groups. The coordination of Mo(CO)5 units on indium and tin results in withdrawal of electron density from indium, so that the In-Sn distance is significantly less than that in 4. The electron density on Sn is increased to a comparable extent; that is, the Sn-O distances are longer than those in 3. If the whole molecule is considered, however, 4 acts as an electron donor toward the Mo(CO)5 units, since the In-Sn distance in 8 is less than that in 4 by 0.122 Å (Table 1).

The preferential coordination of the fragments [Cr(CO)5] and [Mo(CO)5] to indium in the monoadducts can be explained by the electron density trans to the CO group.

Table 2. 1H and 119Sn NMR data (δ values in benzene) and CO wave numbers (cm⁻¹) for compounds 1–10.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>δ(H)</th>
<th>δ(119Sn)</th>
<th>v(A19Sn)</th>
<th>v (other CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Tl(OtBu)2Sn]</td>
<td>1.32</td>
<td>-78.72[a]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>[In(OtBu)2Sn]</td>
<td>1.37</td>
<td>-77.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>[Tl(OtBu)2Sn-Cr(CO)5]</td>
<td>1.31</td>
<td>-</td>
<td>2060 (m)</td>
<td>1970 (sh)</td>
</tr>
<tr>
<td>4</td>
<td>[In(OtBu)2Sn-Mo(CO)5]</td>
<td>1.31</td>
<td>+18.32</td>
<td>2033 (m)</td>
<td>1900 (sh)</td>
</tr>
<tr>
<td>5</td>
<td>[Sn(OtBu)2In-Cr(CO)5]</td>
<td>1.23</td>
<td>-</td>
<td>2070 (m)</td>
<td>1912 (vs)</td>
</tr>
<tr>
<td>6</td>
<td>[Sn(OtBu)2In-Mo(CO)5]</td>
<td>1.23</td>
<td>-173.23</td>
<td>2051 (m)</td>
<td>1925 (vs)</td>
</tr>
<tr>
<td>7</td>
<td>[Cr2(CO)5Sn(OtBu)2In-Cr(CO)5]</td>
<td>1.27</td>
<td>-</td>
<td>2058 (m)</td>
<td>1975 (sh)</td>
</tr>
<tr>
<td>8</td>
<td>[Mo(CO)(SnOEt)(SnOEt)Mo(CO)5]</td>
<td>1.28</td>
<td>-</td>
<td>2041 (m)</td>
<td>1925 (vs, br)</td>
</tr>
<tr>
<td>9</td>
<td>[Cr2(CO)5In(OtBu)2Sn-Mo(CO)5]</td>
<td>1.28</td>
<td>-</td>
<td>2051 (m)</td>
<td>1925 (vs, br)</td>
</tr>
<tr>
<td>10</td>
<td>[Cr2(Mo(CO)(SnOEt)(SnOEt)Mo(CO)5]</td>
<td>1.28</td>
<td>-</td>
<td>2051 (m)</td>
<td>1925 (vs, br)</td>
</tr>
</tbody>
</table>

[a] δ(195, 205) Ti-Sn = 1293 Hz.
ploited chemically. As shown in Equations (d) and (e) reaction of 5 and 6 with the THF adduct of the corresponding metal pentacarbonyl affords the positional isomers 9 and 10, respectively, which contain four different metal atoms.

\[
\begin{align*}
5 & \quad \text{[(CO)\textsubscript{3}Cr - In(OtBu)\textsubscript{2}Sn] + [Mo(CO)\textsubscript{3}(thf)] \rightarrow \text{THF}} \\
6 & \quad \text{[(CO)\textsubscript{3}Mo - In(OtBu)\textsubscript{2}Sn - Cr(CO)\textsubscript{3}]} \\
\end{align*}
\]

Compounds 9 and 10 are clearly distinguished by their CO wave numbers (Table 2) and crystal data (Table 1). The X-ray structure analysis of 10 (Fig. 3, Table 1) again reveals an almost linear arrangement of the metal atoms (Mo-In⋯Sn = 178.1(1)°, Cr-Sn⋯In = 179.7(1)°). Interchange of the Sn and In positions in the structure analysis leads here and for 8 to poorer U values. As found for 8, addition of $[\text{M(CO)}\textsubscript{3}]$ fragments to 4 results in a decrease in the separation of the main-group metals ($\Delta d = 0.113$ Å) and a charge shift from indium to tin. However, owing to the shorter Cr-Sn bond compared with the Mo-Sn bond in 8, the charge shift is less pronounced.

**Experimental Procedure**

4. [TI(OtBu)\textsubscript{2}Sn] (1.0 mmol) [1] or $[[\text{Na(OtBu)\textsubscript{2}Sn}],] (0.5 \text{ mmol}) [3]$ was stirred with indium(1) bromide (1.4 mmol) in 15 mL of toluene at 110°C for 5 or 40 h, respectively. The insoluble material, which may contain some indium, was removed by filtration and the filtrate was concentrated. Sublimation of the residue at 30°C/10\textsuperscript{-7} Torr afforded 0.42 g (92%) or 0.41 g (90%), respectively, of 4: m.p. 41°C.

2, 3, and 5–10: A stirred solution of 1 or 4 and $[\text{Cr(CO)}\textsubscript{3}]$ or $[\text{Mo(CO)}\textsubscript{3}]$ in toluene was heated to reflux. Alternatively, the metal carbonyl was first photolyzed in THF and then allowed to react with 1 or 4 in toluene. Preparation of 9 and 10 starts with 5 and 6, respectively, whose synthesis must be carried out with exact molar ratios of starting materials. All of the compounds were purified by sublimation or recrystallization and gave correct elemental analyses (C, H, metal).

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CAS Registry numbers:  
1. 83437-08-5; 2. 131010-15-6; 3. 131010-16-7; 4. 131010-17-8; 5. 131010-18-9; 6. 131010-19-0; 7. 131010-20-3; 8. 131010-21-4; 9. 131010-22-5; 10. 131010-23-6; [Cr(CO)\textsubscript{3}], 13007-92-6; [Mo(CO)\textsubscript{3}]., 13939-06-5; [Na(OtBu)\textsubscript{2}Sn], 105803-03-0; [Cr(CO)\textsubscript{3}(thf)], 15038-41-2; [Mo(CO)\textsubscript{3}(thf)], 53248-43-4; In, 7440-74-6; Mo, 7439-98-7; Cr, 7440-47-5; Sn, 7440-31-5.

Efficient Stereoselective Total Synthesis of Denticulatins A and B**

By Marc W. Andersen, Bernhard Hildebrandt, and Reinhard W. Hoffmann*

The stereoselective synthesis of natural products of polyketide origin, particularly those which contain the stereotriad D, remains a challenge to the preparative chemist. Among such substances are the denticulatins 3,[1] two polypropionates isolated from *Siphonaria*, whose biological significance remains unclear. Denticulatin is a polyhydroxypolyketo compound and exists in the form of a semiacetal. For the synthesis of the denticulatins it is of interest whether open-chain precursors such as 2 cyclize to the correct denticulatin isomer 3, as well as whether other semiacetals such as 1 isomerize to the desired product (Scheme 1).

**Scheme 1**. Possible synthetic routes to denticulatin. PG = protecting group.

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