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OCT 80 T S DORY, J J ZUCKERMAN, C D HUFF N00014-77-C-0432
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A Reinvestigation of the Claim that Stannocene and $\text{h}_5^-$Cyclopentadienyltricarbonyltungsten Hydride Form Bis-$\text{h}_5^-$cyclopentadienyltricarbonyltungsten) tin (II).

by

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Prepared for Publication
in
Journal of Organometallic Chemistry

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A Reinvestigation of the claim that stannocene and $h^5$-cyclopentadienyltricarbonyltungsten hydride form bis-($h^5$-cyclopentadienyltricarbonyltungsten) tin(II).

Reinvestigation of the claim that stannocene and $h^5$-cyclopentadienyltricarbonyltungsten hydride form bis-($h^5$-cyclopentadienyltricarbonyltungsten) tin(II), the sole representative of a class of compounds in which tin(II) is attached to electropositive ligands, is revealed to be the facile halogenation product from the recrystallization from halocarbons of the tris-($h^5$-cyclopentadienyltricarbonyltungsten)tin(IV) hydride which actually results from the action of the stannocene on the tungsten hydride. The tris-($h^5$-cyclopentadienyltricarbonyltungsten)tin(IV) hydride, chloride,
and iodide are reported.
A Reinvestigation of the Claim that Stannocene and $h^5$-
Cyclopentadienyltricarbonyltungsten Hydride Form
Bis-($h^5$-cyclopentadienyltricarbonyltungsten)tin(II).

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Of the seven categories of tin(II) compounds which can be potentially distinguished by tin-119m Mössbauer spectroscopy, one category, embracing tin(II) compounds with electropositive ligands, contains a single member, \([h^5\text{-C}_5\text{H}_5(\text{CO})_3\text{W}]_2\text{Sn}\). This vermilion solid was obtained by recrystallization from methylene chloride of the product from the exothermic reaction of bis-\((h^5\text{-methylcyclopentadienyl})\text{tin(II)}\) (methyl stannocene) and \(h^5\text{-cyclopentadienyltricarbonyltungsten hydride}\):

\[
n(h^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Sn}+2n h^5\text{-C}_5\text{H}_5(\text{CO})_3\text{W} \xrightarrow{\text{THF}} \{\text{Sn}[\text{W(}\text{CP})_3\text{C}_5\text{H}_5-h^5]\}_n. \tag{1}
\]

The product gave apparently satisfactory analyses as formulated \([\text{Calcd. for C}_{16}\text{H}_{10}\text{O}6\text{SnW}_2}: \text{C}, 24.5; \text{H}, 1.3\%. \text{ Found: C}, 24.9; \text{H}, 1.7\%\]. The tin-119m Mössbauer spectrum was a doublet with Isomer Shift (I.S.) = 2.08±0.05 and Quadrupole Splitting (Q.S.) = 2.05±0.10 mm s\(^{-1}\). The magnitude of the I.S. value, which lies outside the tin(II) range, was at first attributed to the auto-oligomerization well-known in tin(II) chemistry which gives tin(IV) species with tin-tin bonds. A subsequent report gave the results of an osmometric molecular weight determination in chloroform as 1007 vs. the calculated value of 785 for the monomer \((n = 1)\) product depicted in Eq. 1. The mass spectrum was interpreted in terms of polyisotopic \([\text{P-}n\text{CO}]^+ (n = 4-6)\) and \([\text{P-}C_5\text{H}_5-m\text{CO}]^+ (m = 5,6)\) fragments. The rather large magnitude of the Mössbauer Q.S. value proved more difficult to rationalize, but analogy could be drawn with the dimeric \(\{\text{Sn}[\text{CH}[\text{Si(}\text{CH}_3)_3]_2\}_2\}_2\), I.S. = 2.16; Q.S. = 2.31 mm s\(^{-1}\), which also contains a tin-tin bond. The observed value of 2.05 mm s\(^{-1}\) would require a severely bent W-Sn-W angle, since
there is presumably little difference in electronegativity between these metal atoms. Electron release to tin in the monomeric product would, moreover, tend to give the lone pair predominantly 5p-character and shield the tin nucleus, reducing effective $|\psi(0)|^2$ and diminishing the magnitude of the I.S. value. Opening of the tungsten-tin-tungsten angle by the steric bulk of the cyclopentadienyltricarbonyltungsten moiety would have the same effect,¹ contrary to the high value of the I.S. actually found.²

Experience with the analogous tin-molybdenum derivatives teaches that the action of stannocene on molybdenum carbonyl hydrides is complex, yielding a tris-(molybdenum carbonyl)tin(IV) hydride product. In addition, the tin-hydrogen bonds in this series are readily halogenated by halocarbons under mild conditions.⁶ Thus, because of the unique role of the reported bis-(h⁵-cyclopentadienyltricarbonyltungsten)tin or its oligomers as the sole examples of a novel class of tin compounds,¹ we decided to reinvestigate the reaction depicted in Eq. 1.

We find by analogy to the corresponding reaction in the molybdenum series, that the product from the action of stannocene on h⁵-cyclopentadienyltricarbonyltungsten hydride is tris-(h⁵-cyclopentadienyltricarbonyltungsten)tin(IV) hydride:

$$(h^5-C_5H_5)_2Sn + 3HW(CO)C_5H_5-h^5\overset{THF}{\rightarrow}HSn[W(CP)C_5H_5-h^5]_3 + 2C_5H_6 \quad (2)$$

and not the bis-(h⁵-cyclopentadienyltricarbonyltungsten)tin previously claimed. Further, treatment with methylene chloride, chloroform or carbon tetrachloride produces a deep red solution containing tris-(h⁵-cyclopentadienyltricarbonyltungsten)tin(IV) chloride:⁷
\[
\text{HSn[W(CP)₃C₅H₆-h^5]}_3 + \text{CH}_n\text{Cl}_{14-n} \rightarrow \text{ClSn[W(CP)₃C₅H₆-h^5]}_3
\]
\[+ \text{CH}_n\text{Cl}_{14-n-1} \quad n=0, 1 \text{ and } 2 \]

It is this product that is formed by the procedure used in reference 2. The analytical data reported there fit this formulation [Calcd.: C, 24.98; H, 1.30%] better, the molecular weight of 1153 fits the measured value within experimental error, and the Mössbauer parameters are those expected from a tris-transition metal-substituted tin(IV) chloride. An absorption band is found at 352 cm⁻¹ in the infrared which arises from the ν(Sn-Cl) mode, and the δ(Sn-Cl) is found in the Raman at 151 cm⁻¹. Titration of the starting materials in an nmr tube confirmed the stoichiometry of Eq. 3. No signals arising from intermediates were observed, and the tris-compound is the sole tin-containing product even in an excess of stannocene.

Treatment of the hydride with 1, 3-dibromopropane or methylene bromide, or methyl iodide yields the tris-(h⁵-cyclopentadienyltricarbonyl)tungsten)tin bromide and iodide, respectively.

The properties of the four tris-(h⁵-cyclopentadienyltricarboxyl)tungsten)tin products are listed in Table 1.

Thus the synthesis of a tin(II) compound with electropositive ligands is still awaited.

Acknowledgements

Our work is supported by the Office of Naval Research (to J.J.Z.) and by the National Science Foundation under grant CHE-78-26548 (to J.J.Z.).
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<td>86</td>
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<td>185-189°d.</td>
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<td><strong>1H nmr (ppm)</strong></td>
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<td>Q.S.</td>
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<td>1.86 0.03</td>
<td>1.87±0.01</td>
<td>1.81 0.04</td>
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</table>

**a** W Calcd. = 49.32, Found = 50.09; %Sn Calcd. = 10.61, Found = 10.92.

**b** Lit. 198°.

**c** δ_H-Sn = 5.01 ppm; |J(¹¹⁷,¹¹⁹Sn-H)| = 2066 Hz.

**d** In THF.

**e** In CH₂Cl₂.

**f** Reported as 2012(w,sh), 2004(m), 1982(s), 1968(s), and 1913(s,sh), 1894(vs), 1880(s,sh) and 1866(m) in ref. 2 for the solid, and as 2015(m), 2005(m), 1979(m), 1948(m), 1922(s) and 1905(s,sh) in dichloromethane solution.
References


