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A REINVESTIGATION OF THE CLAIM THAT STANNOCENE AND H5-  
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A Reinvestigation of the Claim that Stannocene and  $h_1^5$ -Cyclopentadienyltricarbonyltungsten Hydride Form Bis-( $h^5$ -cyclopentadienyltricarbonyltungsten) tin (II).

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Reinvestigation of the claim that stannocene and $h^5$ -cyclopentadienyltri- carbonyltungsten 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 halo- genation 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, →		

20 → bromide and iodide are reported. ←

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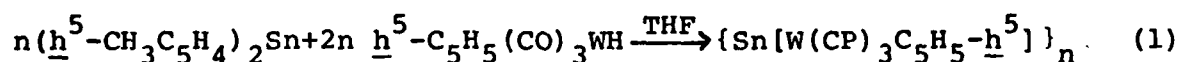
A Reinvestigation of the Claim that Stannocene and  $\underline{h}^5$ -  
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Of the seven categories of tin(II) compounds which can be potentially distinguished by tin-119m Mössbauer spectroscopy,<sup>1</sup> one category, embracing tin(II) compounds with electropositive ligands, contains a single member,  $[\underline{h}^5\text{-C}_5\text{H}_5(\text{CO})_3\text{W}]_2\text{Sn}$ .<sup>2</sup> This vermilion solid was obtained by recrystallization from methylene chloride of the product from the exothermic reaction of bis-( $\underline{h}^5$ -methylcyclopentadienyl)tin(II) (methyl stannocene) and  $\underline{h}^5$ -cyclopentadienyl-tricarbonyltungsten hydride:



The product gave apparently satisfactory analyses as formulated [Calcd. for  $\text{C}_{16}\text{H}_{10}\text{O}_6\text{SnW}_2$ : C, 24.5; H, 1.3%. Found: C, 24.9; H, 1.7%]. The tin-119m Mössbauer spectrum was a doublet with Isomer Shift (I.S.) =  $2.08 \pm 0.05$  and Quadrupole Splitting (Q.S.) =  $2.05 \pm 0.10 \text{ mm s}^{-1}$ . The magnitude of the I.S. value, which lies outside the tin(II) range,<sup>3</sup> 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  $[\text{P-nCO}]^+$  ( $n = 4-6$ ) and  $[\text{P-C}_5\text{H}_5\text{-mCO}]^+$  ( $m = 5,6$ ) fragments.<sup>4</sup> The rather large magnitude of the Mössbauer Q.S. value proved more difficult to rationalize, but analogy could be drawn with the dimeric  $[\text{Sn}\{\text{CH}[\text{Si}(\text{CH}_3)_3]\}_2]_2$ , I.S. = 2.16; Q.S. =  $2.31 \text{ mm s}^{-1}$ , which also contains a tin-tin bond.<sup>5</sup> The observed value of  $2.05 \text{ mm s}^{-1}$  would require a severely bent W-Sn-W angle, since

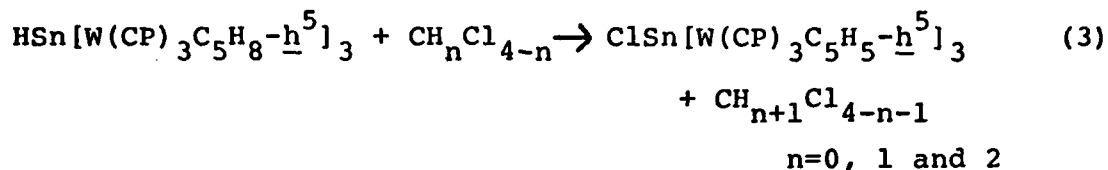
there is presumably little difference in electronegativity between these metal atoms. Electron release to tin in the monomeric product would, moreover, tend to give the lone pair predominantly 5p-character and shield the tin nucleus, reducing effective  $|\psi(0)|^2$  and diminishing the magnitude of the I.S. value. Opening of the tungsten-tin-tungsten angle by the steric bulk of the cyclopentadienyltricarbonyltungsten moiety would have the same effect,<sup>1</sup> contrary to the high value of the I.S. actually found.<sup>2</sup>

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.<sup>6</sup> Thus, because of the unique role of the reported bis-( $\eta^5$ -cyclopentadienyltricarbonyltungsten)tin or its oligomers as the sole examples of a novel class of tin compounds,<sup>1</sup> 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  $\eta^5$ -cyclopentadienyltricarbonyltungsten hydride is tris-( $\eta^5$ -cyclopentadienyltricarbonyltungsten)tin(IV) hydride:



and not the bis-( $\eta^5$ -cyclopentadienyltricarbonyltungsten)tin previously claimed. Further, treatment with methylene chloride, chloroform or carbon tetrachloride produces a deep red solution containing tris-( $\eta^5$ -cyclopentadienyltricarbonyltungsten)tin(IV) chloride:<sup>7</sup>



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,<sup>4</sup> and the Mössbauer parameters are those expected from a tris-transition metal-substituted tin(IV) chloride.<sup>3,8-10</sup> An absorption band is found at  $352 \text{ cm}^{-1}$  in the infrared which arises from the  $\nu(\text{Sn-Cl})$  mode, and the  $\delta(\text{Sn-Cl})$  is found in the Raman at  $151 \text{ cm}^{-1}$ . 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-( $\text{h}^5$ -cyclopentadienyltricarbonyltungsten)tin bromide and iodide, respectively.

The properties of the four tris-( $\text{h}^5$ -cyclopentadienyltricarbonyltungsten)tin products are listed in Table 1.

Thus the synthesis of a tin(II) compound with electropositive ligands<sup>1</sup> is still awaited.

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Table 1. Properties of  $\text{ESn}[\text{W}(\text{CO})_3\text{C}_5\text{H}_5\text{-h}^5]_3$

	<u>E = H</u> <sup>a</sup>	<u>Cl</u>	<u>Br</u>	<u>I</u>
<u>Anal.</u>				
%C Calcd.	25.75	24.98	24.06	23.15
Found	25.88	24.78	25.33	23.48
%H Calcd.	1.43	1.30	1.25	1.21
Found	1.59	1.25	1.87	1.44
%E Calcd.	-	3.08	6.67	10.21
Found	-	3.36	7.07	9.97
Yield	72	86	68	83
m.p.	196-200°d.	212°d. <sup>b</sup>	210-214°d.	185-189°d.
<sup>1</sup> H nmr (ppm)	4.93 <sup>c</sup>	5.02	5.03	5.03
Infrared $\nu(\text{CO})$ (cm <sup>-1</sup> )	2016(m) <sup>d</sup> 2000(m)	2025(s) <sup>e, f</sup> 2005(s)	2026(sh) <sup>e</sup> 2011(m)	2028(sh) <sup>e</sup> 2018(m)
	1976(s) 1920(s) 1900(s)	1985(m) 1948(m) 1930(s)	1985(s) 1920(s) 1888(sh)	1982(s) 1912(s) 1890(sh)
Mössbauer (mm s <sup>-1</sup> )				
I.S.	1.79±0.02	1.98±0.02	1.99±0.01	1.95±0.01
Q.S.	---	1.86 0.03	1.87±0.01	1.81 0.04

<sup>a</sup>%W Calcd. = 49.32, Found = 50.09%; %Sn Calcd. = 10.61, Found = 10.92%.

<sup>b</sup>Lit. 198°<sup>7</sup>.

<sup>c</sup> $\delta_{\text{H-Sn}} = 5.01$  ppm;  $|^1J(^{117,119}\text{Sn-}^1\text{H})| = 2066$  Hz.

<sup>d</sup>In THF.

<sup>e</sup>In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>f</sup>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.

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