

Reinvestigation of the Claim that Bis-(η^5 -cyclopentadienyl)tin(II) and (η^5 -Cyclopentadienyl)tricarbonyltungsten Hydride form Bis-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin(II)

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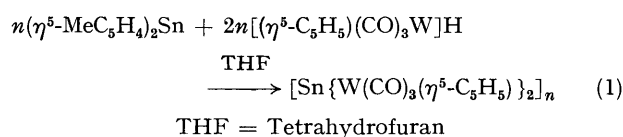
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Summary Bis-(η^5 -cyclopentadienyl)tin(II) and (η^5 -cyclopentadienyl)tricarbonyltungsten hydride form tris-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin(IV) hydride which is readily halogenated by halogenated hydrocarbon solvents to form the corresponding tin(IV) halides rather than the bis-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin(II) product previously claimed.

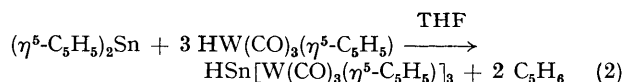
Of the seven categories of tin(II) compounds which can be potentially distinguished by tin-119m Mössbauer spectroscopy,¹ one category, namely embracing tin(II) compounds with electropositive ligands, contains a single member, [(η^5 -C₅H₅)(CO)₃W]₂Sn,² obtained as a vermilion solid by recrystallization from methylene dichloride of the product from the exothermic reaction of bis-(η^5 -methylcyclopentadienyl)tin(II) and (η^5 -cyclopentadienyl)tricarbonyltungsten hydride (equation 1). The product gave apparently



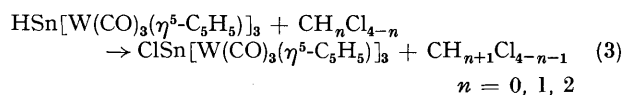
satisfactory analyses as formulated. (Calc. for C₁₆H₁₀O₆SnW₂: C 24.5; H, 1.3%. Found: C, 24.9; H, 1.7%). The tin-119m Mössbauer spectrum of the product was a doublet with isomer shift (I.S.) = 2.08 ± 0.05 and quadrupole splitting (Q.S.) = 2.05 ± 0.10 mm s⁻¹. The magnitude of the I.S. value, which lies outside the tin(II) range,³ 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 equation (1). The mass spectrum was interpreted in terms of polyisotopic [$M - n\text{CO}$]⁺ ($n = 4-6$) and [$M - \text{C}_5\text{H}_5 - m\text{CO}$]⁺ ($m = 5, 6$) fragments.⁴

The action of bis-(η^5 -cyclopentadienyl)tin(II) on analogous molybdenum carbonyl hydrides is complex, yielding a tris-(molybdenum carbonyl)tin(IV) hydride product. In addition, the tin-hydrogen bonds in these compounds are readily halogenated by halogenated hydrocarbons under mild conditions.⁵ We find that the product from the reaction of bis-(η^5 -cyclopentadienyl)tin(II) with (η^5 -cyclopentadienyl)tricarbonyltungsten hydride is tris-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin(IV) hydride (equation 2) and not the bis-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin previously claimed. Further, treatment with methylene dichloride, chloroform, or carbon tetrachloride



produces a deep red solution containing tris-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin(IV) chloride⁶ (equation 3). It is this product that is formed by the procedure used



in reference 2. The analytical data reported there fit this formulation (Calc.: C, 25.0; H, 1.3%) better, the molecular weight of 1153 fits the measured value within experimental error,⁴ and the Mössbauer parameters are those expected from a tris(transition metal-substituted)tin(IV) chloride.^{3,7}

TABLE. Properties of complexes ESn[W(CO)₃(η^5 -C₅H₅)₃].

	E = H ^a	Cl ^b	Br ^b	I ^b
% Yield	72	86	68	83
M.p. °C	196—203	212 ^d	210—214	185—189
¹ H n.m.r., δ	4.93 ^e	5.02	5.03	5.03
$\nu(\text{CO})/\text{cm}^{-1}$	2016(m) ^f	2025(s) ^{g,h}	2026(sh) ^g	2028(sh) ^g
	2000(m)	2005(s)	2011(m)	2018(m)
	1970(s)	1985(m)	1985(s)	1982(s)
	1029(s)	1948(m)	1920(s)	1912(s)
	1900(s)	1930(s)	1888(sh)	1890(sh)
Mössbauer (mm s ⁻¹)				
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

^a Satisfactory analyses were obtained for C, H, Sn, and W. ^b Satisfactory analyses were obtained for C, H, and the halogen. ^c All the complexes decomposed at the melting point. ^d Lit.⁶ 198 °C. ^e $\delta(\text{H-Sn})$ 5.01; $|J(^{117,119}\text{Sn}-^1\text{H})|$ 2066 Hz. ^f In THF. ^g In CH₂Cl₂. ^h Reported as 2012(w,sh), 2004(m), 1982(s), 1968(s), 1913(s,sh), 1894(vs), 1880(s, sh), and 1866(m) cm⁻¹ for the solid, and as 2015(m), 2005(m), 1979(m), 1948(m), 1922(s), and 1905(s,sh) cm⁻¹ in dichloromethane solution (ref. 2).

An absorption band at 352 cm^{-1} in the i.r. spectrum arises from the $\nu(\text{Sn-Cl})$ mode, and the $\delta(\text{Sn-Cl})$ band is found in the Raman spectrum at 151 cm^{-1} . Titration of the starting materials in an n.m.r. tube confirmed the stoichiometry of equation (3). No signals arising from intermediates were observed, and the tris-compound is the sole tin-containing product, even with an excess of bis-(η^5 -cyclopentadienyl)-tin.

Treatment of the hydride with 1,3-dibromopropane or methylene dibromide, or methyl iodide yields the tris-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin bromide and iodide, respectively.

The properties of the four tris-[(η^5 -cyclopentadienyl)tricarbonyltungsten]tin products are listed in the Table.

Thus, the synthesis of a tin(II) compound with electro-positive ligands¹ is still awaited.

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