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A REINVESTIGATION OF THE CLAIM THAT STANNOCENE AND H5 -CYCLO-
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Bis-(h^5-cyclopentadienyl)tin(II), and h^5-cyclopentadienyltricarbonyltungsten hydride form tris-(h^5-cyclopentadienyl)tricarbonyltungsten)tin(IV) hydride which is readily halogenated by the halocarbon solvents used to form the corresponding tin(IV) halides rather than the bis-(h^5-cyclopentadienyltricarbonyltungsten)tin(II) product previously claimed.

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A Reinvestigation of the Claim that Stannocene and h^5-Cyclopentadienyltricarbonyltungsten Hydride Form Bis-(h^5-cyclopentadienyltricarbonyltungsten)tin(II).

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Summary

Bis-(h^5-cyclopentadienyl)tin(II), and $\underline{h}^5$-cyclopentadienyltricarbonyltungsten hydride form tris-($\underline{h}^5$-cyclopentadienyl)tricarbonyltungsten)tin(IV) hydride which is readily halogenated by the halocarbon solvents used to form the corresponding tin(IV) halides rather than the bis-($\underline{h}^5$-cyclopentadienyltricarbonyltungsten)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, embracing tin(II) compounds with electropositive ligands, contains a single member, namely $[\underline{h}^5\text{-}C_5H_5(CO)_3W]_2Sn$.[2] 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) and $\underline{h}^5$-cyclopentadienyltricarbonyltungsten hydride:

$$n(\underline{h}^5\text{-}CH_3C_5H_4)_2Sn + 2n\ \underline{h}^5\text{-}C_5H_5(CO)_3WH \xrightarrow{THF} \{Sn[W(CO)_3C_5H_5\text{-}\underline{h}^5]\}_n \quad (1)$$

The product gave apparently satisfactory analyses as formulated [Calcd. for $C_{16}H_{10}O_6SnW_2$: 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±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 Eq. 1. The mass spectrum was interpreted in terms of polyisotopic $[P-nCO]^+$ (n = 4-6) and $[P-C_5H_5-mCO]^+$ (m = 5,6) fragments.[4]

The action of stannocene on analogous 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.[5] We find that the product from the action of stannocene on $\underline{h}^5$-cyclopentadienyltricarbonyltungsten hydride is tris-($\underline{h}^5$-cyclopentadienyltricarbonytungsten)tin(IV) hydride:

$$(\underline{h}^5\text{-}C_5H_5)_2Sn+3HW(CO)_3C_5H_5\text{-}\underline{h}^5 \xrightarrow{THF} HSn[W(CP)_3C_5H_5\text{-}\underline{h}^5]_3+2C_5H_6 \quad (2)$$

and not the bis-($\underline{h}^5$-cyclopentadienyltricarbonyltungsten)tin previously claimed. Further, treatment with methylene chloride, chloroform or carbon tetrachloride produces a deep red solution containing tris-($\underline{h}^5$-cyclopentadienyltricarbonyltungsten)tin(IV) chloride:[6]

$$HSn[W(CO)_3C_5H_8\text{-}\underline{h}^5]_3+CH_nCl_{4-n} \rightarrow ClSn[W(CO)_3C_5H_5\text{-}\underline{h}^5]_3 + CH_{n+1}Cl_{4-n-1} \quad (3)$$

n=0, 1 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,[4] and the Mössbauer parameters are those expected from a tris-transition metal-substituted tin(IV) chloride.[3,7-9] 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($\underline{h}^5$-cyclopentadienyltricarbonyltungsten)tin bromide and iodide, respectively.

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

Thus the synthesis of a tin(II) compound with electropositive ligands[1] is still awaited.

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Table 1. Properties of $ESn[W(CO)_3C_5H_5\text{-}\underline{h}^5]_3$

	E = H[a]	Cl[b]	Br[b]	I[b]
Yield	72	86	68	83
m.p.	196-203°d.	212°d.[c]	210-214°d.	185-189°d.
^1H nmr (ppm)	4.93[d]	5.02	5.03	5.03
Infrared $\nu(CO)(cm^{-1})$	2016(m)[e]	2025(s)[f,g]	2026(sh)[f]	2028(sh)[f]
	2000(m)	2005(s)	2011(m)	2018(m)
	1970(s)	1985(m)	1985(s)	1982(s)
	1920(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] Lit. 198°.[6]

[d] $\delta H\text{-}Sn$ = 5.01 ppm; $|^1J(^{117,119}Sn\text{-}^1H)|$ = 2066 Hz.

[e] In THF.

[f] In CH_2Cl_2.

[g] 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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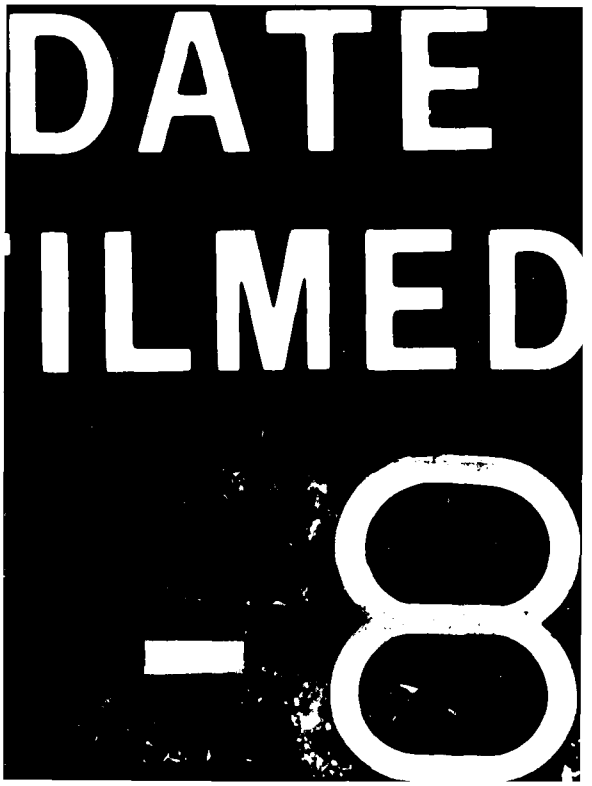
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