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SYNTHESIS AND REACTIONS OF THE TRANSITION METAL SUBSTITUTED TIN HYDRIDE $HSn[Mo(CO)_3C_5H_5]_3$

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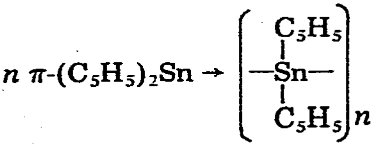
Summary

Reaction of $HMo(CO)_3C_5H_5$ and $Sn(C_5H_5)_2$ produces the tin hydride $HSn[Mo(CO)_3C_5H_5]_3$ (I). Reaction of I with CCl_4, $CHCl_3$, or CH_2Cl_2 gives $ClSn[Mo(CO)_3C_5H_5]_3$ (II). With hydrogen chloride the hydride I reacts to produce the dichloride $Cl_2Sn[Mo(CO)_3C_5H_5]_2$. The first step in this reaction is cleavage of the Sn—H bond to produce the chloride II. The hydride I reacts with acetic acid to produce the diacetate $(CH_3COO)_2Sn[Mo(CO)_3C_5H_5]_2$.

Introduction

The synthesis of metal—metal bonded polymers and oligomers continues to be a goal of several laboratories [1—3]. It is well known that dicyclopentadienyltin(II) (stannocene) undergoes ready conversion to the polystannane shown in eq. 1 [4]. Also many tin(II) compounds are highly associated in the solid state [5].



$$n\ \pi\text{-}(C_5H_5)_2Sn \rightarrow \left[-\overset{\overset{C_5H_5}{|}}{\underset{\underset{C_5H_5}{|}}{Sn}}- \right]_n \qquad (1)$$

Our intention at the outset of this work was to replace the π-cyclopentadienyl group in stannocene with an organotransition metal group and to see if we could then polymerize this diorganotransition metal-tin(II) species in a process analogous to that shown in eq. 1.

Protolysis of dicyclopentadienyltin(II) and its methylcyclopentadienyl analog

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has been shown to yield a variety of divalent derivatives as shown in eq. 2 [6—8].

$$\pi\text{-}(C_5H_5)_2Sn + HX \rightarrow SnX_2 + 2\,C_5H_6 \qquad (2)$$

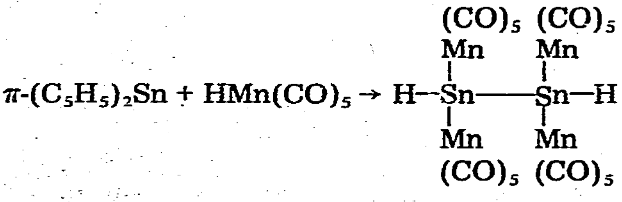
$X = OR, OOCR, SR, CN, Cl, Br$

In some cases this reaction has been shown to occur in two steps, the first of which is shown in eq. 3 [9].

$$\pi\text{-}(C_5H_5)_2Sn + HX \rightarrow \pi\text{-}C_5H_5SnX + C_5H_6 \qquad (3)$$

$X = Cl, OC_6H_5$

Since many organotransition metal hydrides are acidic, reactions analogous to those shown in eq. 3, where X is an organotransition metal group, are of some interest. In this regard, Noltes has reported that the reaction between stannocene and pentacarbonylhydridomanganese(I) yields the product shown in eq. 4 [10].



$$\pi\text{-}(C_5H_5)_2Sn + HMn(CO)_5 \rightarrow \begin{array}{c} \\ \\ H{-}\end{array}\!\!\begin{array}{c}(CO)_5\\ Mn\\ | \\ Sn\\ | \\ Mn\\ (CO)_5\end{array}\!\!\begin{array}{c}\\ \\ \\ {-}{-}{-}\\ \\ \\ \\ \end{array}\!\!\begin{array}{c}(CO)_5\\ Mn\\ | \\ Sn\\ | \\ Mn\\ (CO)_5\end{array}\!\!\begin{array}{c}{-}H\end{array} \qquad (4)$$

Also Harrison has studied the reaction between tricarbonyl(π-cyclopentadienyl)-hydridotungsten(II) and stannocene. Equation 5 summarizes his results as he has most recently formulated them [11].

$$\pi\text{-}(C_5H_5)_2Sn + 2\,HW(CO)_3C_5H_5 \rightarrow Sn[W(CO)_3C_5H_5]_2 + 2\,C_5H_6 \qquad (5)$$

We report here concerning the product of the reaction between stannocene and tricarbonyl(π-cyclopentadienyl)hydridomolybdenum(II) and some of the reactions which it undergoes.

Results and discussion

The reaction between stannocene and tricarbonyl(π-cyclopentadienyl)hydridomolybdenum(II) proceeds rapidly at room temperature in pentane to yield cyclopentadiene quantitatively and tris(tricarbonyl(π-cyclopentadienyl)molybdenum(0))tin(IV) hydride in 88% yield as shown in eq. 6.

$$(\pi\text{-}C_5H_5)_2Sn + 3\,HMo(CO)_3C_5H_5 \rightarrow 2\,C_5H_5 + \underset{(I)}{HSn[Mo(CO)_3C_5H_5]_3} \qquad (6)$$

Compound I was characterized by its molecular weight, its elemental analysis (Table 1), its spectroscopic properties (Table 2), and by its chemical reactions (vide infra). It reacts with halogenated hydrocarbons and it is insoluble in alkanes so the spectroscopic measurements were made in carefully deoxygenated aromatic solvents.

The proton NMR spectrum of compound I shows two signals in the expected 15/1 ratio. The cyclopentadienyl proton signal (τ 5.17 ppm) is very close to the

TABLE 1

ANALYTICAL DATA FOR PREVIOUSLY UNREPORTED COMPOUNDS

Compound	M.p. (°C)	Analysis (Found (calcd.) (%))				
		C	H	Sn	Mo	Cl
$HSn[Mo(CO)_3C_5H_5]_3$ [a] (I)	130 (dec)	33.83 (33.70)	1.99 (1.87)	14.15 (13.89)	32.84 (33.68)	
$ClSn[Mo(CO)_3C_5H_5]_3$ (II)	159—162 (lit. 160) [6]					3.34 (3.99)
$(CH_3CO_2)_2Sn[Mo(CO)_3C_5H_5]_2$ (III)	125	33.08 (33.03)	2.68 (2.20)	16.03 (16.33)	26.67 (26.41)	

[a] Molecular weight: experimental (VPO) 821, theoretical 854.

values (τ 5.2—5.3 ppm) for a series of compounds having the formula $RMo(CO)_3C_5H_5$ [12]. The tin hydrogen proton signal (τ 4.42 ppm) is close to the reported value (τ 4.16 ppm) for the similar compound $[Bu_3PCo(CO)_3]_3SnH$ [13]. Compound I was not soluble enough to allow us to measure J(SnH).

A large number of compounds of the type $XMo(CO)_3C_5H_5$ have been reported. These compounds exhibit two or three carbonyl bands in their IR spectra depending on whether the E mode is resolved into two bands or not [14]. However, compounds of the type $[(C_5H_5CO)_3Mo]_2SnX_2$ often show more than three carbonyl bands, presumably due to conformational effects [15]. As can be seen from Table 2, the position of the CO bands is quite similar in compounds I—IV. The essential difference is the degree to which the additional bands show up.

The characteristic Sn—H absorption is about 1800 cm^{-1} [16]. It is lower for distannanes and higher for stannanes with electronegative substituents on the tin. Noltes and coworkers have reported 1725 cm^{-1} for the Sn—H stretching frequency in $[HSn[Mn(CO)_5]_2]_2$ [10]. Since this latter compound is a distannane the Sn—H stretching frequency in compound I presumably should be at a higher frequency. We observed a weak absorption at 1810 cm^{-1} both in C_6H_6 and in C_6D_6 which disappears in reactions which remove the hydrogen from the tin. We tentatively assign this band to the Sn—H vibration in compound I.

In an attempt to obtain a product containing two molybdenum atoms per tin, we carried out the reaction between $HMo(CO)_3C_5H_5$ and stannocene at low temperature and under conditions where the molybdenum hydride was the limiting reagent. However, compound I was the only organometallic product observed in every case. Also, this reaction was carried out in an NMR tube at 37°C, which allowed continuous monitoring. The only proton signals observed were those due to starting materials and compound I.

In the absence of air, compound I is quite stable in solution at room temperature. The NMR spectrum of a hexadeuteriobenzene solution stored in a sealed NMR tube for 30 days at room temperature changed very little. The chemical properties of I which we have observed indicate that it is a reactive tin(IV) hydride.

Carbon tetrachloride, chloroform and (more slowly) methylene chloride are all reduced at room temperature by I (eq. 7).

TABLE 2

SPECTROSCOPIC DATA

Compound	NMR[a]			IR[b] (cm^{-1})					
	τ (ppm)	Relative integral	Assignment						
HSn[Mo(CO)$_3$C$_5$H$_5$]$_3$ (I)	5.17 4.42	15 1	C$_5$H$_5$ SnH	2026 w	 1810 w	1985 m	1920 s	1907 m	(ν_{CO}) (ν_{SnH})
ClSn[Mo(CO)$_3$C$_5$H$_5$]$_3$ (II)	5.05		C$_5$H$_5$	2026(sh)	2017 m	1986 s	1930 s	1896(sh)	(ν_{CO})
[CH$_3$CO$_2$]$_2$Sn[Mo(CO)$_3$C$_5$H$_5$]$_2$ (III)	4.47[d] 7.90	10 6	C$_5$H$_5$ CCH$_3$	2033 m	2009 s 1623 m (br)		1935 vs (br)[c]		ν_{CO} Ac
Cl$_2$Sn[Mo(CO)$_3$C$_3$H$_5$]$_2$ (IV)[f]	5.15		C$_5$H$_5$	2031 s 2031 s	2010 m 2010 m	1959 m 1960 m	1940 m 1041 m	1917 w[c] 1916 w	ν_{CO} [15]

[a] Approximately 1% solutions in C$_6$D$_6$ with 1% TMS internal standard. Chemical shifts are reported on the τ scale (ppm) with the relative integral values in parentheses. [b] Benzene solution. [c] Benzene solution. [c] Carbon disulfide solution. [d] CDCl$_3$ solution with 1% TMS internal standard. [e] CHCl$_3$ solution. [f] M.p. 199–203°C, lit. 199–201°C [15].

$$\underset{}{HSn[Mo(CO)_3C_5H_5]_3} + CCl_4 \rightarrow \underset{(II)}{ClSn[Mo(CO)_3C_5H_5]_3} + CHCl_3 \qquad (7)$$

Compound II, tris(tricarbonyl-π-cyclopentadienylmolybdenum(0))tin(IV) chloride, has been reported previously but analytical data were not given [17]. It was identified here by its melting point, NMR and IR spectra (Table 2), and chloride analysis (Table 1). When the reaction shown in eq. 7 was done in a sealed NMR tube, the proton signal of the chloroform produced in this reaction was identical in size to that of the tin hydride signal which disappeared.

With an excess of acetic and hydrochloric acids, compound I reacts to produce hydrogen, tricarbonylcyclopentadienylhydridomolybdenum(II) and the other products shown in eq. 8 and 9, respectively. Within experimental error the hydrogen production is quantitative.

$$2\,HAc + HSn[Mo(CO)_3C_5H_5]_3 \rightarrow H_2 + HMo(CO)_3C_5H_5 + \underset{(III)}{[CH_3CO_2]_2Sn[Mo(CO)_3C_5H_5]_2} \qquad (8)$$

$$2\,HCl + HSn[Mo(CO)_3C_5H_5]_3 \rightarrow H_2 + HMo(CO)_3C_5H_5 + \underset{(IV)}{Cl_2Sn[Mo(CO)_3C_5H_5]_2} \qquad (9)$$

Compound III was characterized by its elemental analysis (Table 1) and its NMR spectrum (Table 2) and its mass spectrum (Table 3).

Compound IV has been reported previously [15] and was identified by comparison of its melting point and IR spectrum with literature values and by its NMR and mass spectra.

The reaction between I and a limited amount of hydrogen chloride was shown in a separate experiment to yield hydrogen and compound II (see eq. 10). Interes ingly, compound I does not react with tricarbonyl-π-cyclopentadienylhydridomolybdenum(II), which is a slightly weaker acid than acetic acid [18]. Presumable steric crowding in the product prevents this reaction from occurring.

$$HCl + HSn[Mo(CO)_3C_5H_5]_3 \rightarrow H_2 + ClSn[Mo(CO)_3C_5H_5]_3 \qquad (10)$$

Organotin hydrides are known to react with carbon tetrachloride and with proton sources in a manner analogous to the reactions shown in eq. 7 and 10, respectively [16]. The selective cleavage of one tin—molybdenum bond by excess acid (eq. 9 and 10) is interesting and is receiving further study.

The work reported here and that of Noltes [10] and Harrison [11] indicate that the reaction between organotransition metal hydrides and stannocene is a useful source of interesting new compounds. We are continuing to study this reaction using other metal hydrides.

Experimental

General

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen utilizing Schlenk tube techniques or on a high vacuum apparatus of standard design. Solvents were distilled from calcium hydride before use. All spectra were obtained with solutions prepared in rigorously oxygen and moisture free conditions. Analysis of carbon monoxide and hydrogen was done on the vacuum apparatus by use of a Toepler pump and combustion train of CuO heated in a tube furnace to 410°C. Proton NMR spectra were obtained using a Varian T-60 Spectrometer. In most cases solutions were transferred into the NMR tube under dried, deoxygenated nitrogen. The solution was then degassed and the NMR tube sealed off. Infrared spectra were measured using a Perkin—Elmer 621 grating infrared spectrometer. Mass spectra were obtained by direct insertion of the solid sample into the ionizing chamber of either a Nuclide 12-90-G or a Varian-MAT CH_4 mass spectrometer at an ionizing voltage of 70 eV. Solvents were dried and deoxygenated before use. Starting materials were prepared by published procedures. Analyses and the molecular weight were done by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Preparation of tris(tricarbonyl-π-cyclopentadienylmolybdenum(0))tin(IV) hydride (I)

A solution of 8.0 g (82.1 mmol) $(\pi\text{-}C_5H_5)_2Sn$ in 100 ml of pentane was charged in a three-necked flask equipped with a pressure-equalizing addition funnel and a condenser. The system was maintained under a nitrogen flush while a solution of 30.0 g (121 mmol) of $HMo(CO)_3C_5H_5$ [19] in 100 ml of pentane was added. Within five minutes after addition was complete orange-brown crystals formed. After 3 h standing at room temperature, 24.1 g of solid was recovered by decanting the supernatant liquid. Recrystallization from toluene did not enhance the purity of this material and the analytical and spectroscopic data shown in Tables 1 and 2 were obtained on this sample. The yield was 88%. The mass spectrum obtained from this material was essentially the same as that of bis(tricarbonyl-π-cyclopentadienylmolybdenum), indicating decomposition in the inlet probe.

In a separate experiment carried out in the same manner, the volatile material from the reaction was collected quantitatively. The yield of cyclopentadiene was estimated by comparing the NMR spectrum of an aliquot of the product mixture to that of previously prepared standard solutions.

The above procedure was repeated using the equimolar amounts (excess stannocene) of the two reagents. The solid product recovered from this reaction was shown to be compound I by its NMR spectrum.

In another separate experiment 6 mmol of stannocene and 12 mmol of $HMo(CO)_3C_5H_5$ (excess stannocene) were mixed at —78°C and the mixture was stored overnight at —30°C and then allowed to stand at 0°C for 2 h. Subsequent workup by filtration as above showed the presence of unreacted $(\pi\text{-}C_5H_5)_2Sn$ in the supernatant liquid and the solid product was pure compound I.

Preparation of tris(tricarbonyl-π-cyclopentadienylmolybdenum(0)tin(IV)) chloride (II)

Ten ml of chloroform was added to 1.85 g of compound I in a Schlenk tube. A red solution resulted. Removal of the volatile material and recrystallization of the resulting solid from a slowly evaporating methylene chloride—heptane solution produced 1.4 g (72%) of compound II.

The reaction between I and carbon tetrachloride was carried out in a degassed, sealed NMR tube. Prior to reaction compound I showed signals at τ 4.42 and 5.17 ppm in a ratio of 1/15. After reaction the chloroform to compound II proton (τ 5.05 ppm) ratio was 1/15.

Attempts to recrystallize compound I from methylene chloride gave compound II.

Reaction of compound I with hydrogen chloride

Compound I (0.85 mmol) dissolved in 5 ml of toluene was treated with 4.6 mmol of hydrogen chloride gas for 4 h at room temperature using vacuum line techniques. The non-condensible gaseous product (0.8 mmol) was shown to be hydrogen by combustion analysis. After removing the toluene, the solid residue was washed with pentane. The pentane washings were shown by NMR spectroscopy to contain $HMo(CO)_3C_5H_5$.

The residual solid was recrystallized from methylene chloride/heptane to yield 0.81 mmol (95%) of compound IV.

Analytical and spectroscopic data are shown in Tables 1 and 2. The mass spectrum of this compound is shown in Table 3a.

In a separate experiment, the reagents remained in contact for 24 h but no further molybdenum—tin cleavage was observed. When this reaction was carried out in a degassed, sealed NMR tube using an excess of compound I the product was the monochloride, compound II.

TABLE 3A

MASS SPECTRAL DATA FOR $Cl_2Sn(Mo(CO)_3C_5H_5)_2$

Peak center[a]	Intensity	Assignment[b]
680	1	$SnMp_2Cl_2 = P$
652	16	$P - CO$
624	5	$P - 2\ CO$
596	5	$P - 3\ CO$
568	8	$P - 4\ CO$
540	9	$P - 5\ CO$
512	30	$P - 6\ CO$
477	5	$P - 6\ CO - Cl$
434	17	$SnCl_2Mp$
406	28	$SnCl_2Mp - CO$
378	20	$SnCl_2Mp - 2\ CO$
350	25	$SnCl_2Mp - 3\ CO$
322	50	$[Mo(C_5H_5)]_2$
244	25	$Mo(CO)_3C_5H_5$
216	18	$Mo(CO)_2C_5H_5$
188	25	$Mo(CO)C_5H_5.\ SnCl_2$
160	65	MoC_5H_5
136	26	$Mo(CO)C$
65	11	C_5H_5
64	12	C_5H_4
44	36	CO_2
28	1200	CO

[a] Atomic mass units. [b] $Mp = Mo(CO)_3C_5H_5$.

TABLE 3B

MASS SPECTRAL DATA FOR $Ac_2Sn(Mo(CO)_3C_5H_5)_2$

Peak center [a]	Intensity	Assignment [b]
727	1	$SnMp_2Ac_2 = P$
699	4	$P - CO$
671	20	$P - 2\,CO$
643	20	$P - 3\,CO$
615	4	$P - 4\,CO$
587	7	$P - 5\,CO$
559	30	$P - 6\,CO$
513	9	$SnAcMo_2Cp_2C$
501	13	$P - 6\,CO - Ac$
482	60	$SnAc_2Mo(CO)_3C_5H_5$
454	15	$SnAc_2Mo(CO)_2C_5H_5$
426	22	$SnAc_2Mo(CO)C_5H_5$
398	90	$SnAc_2MoC_5H_5$
370	70	$SnAcMo_2$
322	50	$(MoC_5H_5)_2$
310	30	$SnMo_2$
245	100	$Mo(CO)_3C_5H_5$
237	35	$SnAc_2$
217	100	$Mo(CO)_2C_5H_5$
189	90	$Mo(CO)C_5H_5$
178	100	SnAc
161	400	MoC_5H_5
136	300	Mo(CO)C
119	50	Sn
108	70	MoC
96	55	Mo
81	70	MoC_3H_5 doubly charged ion
59	330	Ac
44	400	CO_2
28	1300	CO

[a] Atomic mass units. [b] $Mp = Mo(CO)_3C_5H_5$, $Ac = CH_3COO$.

Preparation of bis(tricarbonyl-π-cyclopentadienylmolybdenum(0)tin(IV)) diacetate

One ml of glacial acetic acid was added to a solution of 0.39 g (0.46 mmol) of compound I in 10 ml of benzene. The non-condensible gas (unmeasured) was identified as hydrogen by combustion analysis. After the benzene was removed the resulting solid was washed with pentane. The pentane washings were shown by NMR spectroscopy to contain $HMo(CO)_3C_5H_5$. Recrystallization of the residual solid from methylene chloride/heptane yielded 0.26 g (0.36 mmol, 79%) of yellow crystals. The mass spectrum of this compound is shown in Table 3B. Analytical and spectroscopic data are given in Tables 1 and 2.

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