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Interaction of Tin(1) Halides with Compounds having Mercury–Metal Bonds

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Tin(II) halides react with mercury compounds such as RR'Hg $[R = \pi - C_5 H_5 Fe(CO)_2, \pi - C_5 H_5 Mo(CO)_3,$ π -C₅H₅W(CO)₃, Co(CO)₄, Co(CO)₃(Buⁿ₃P); R = R or CI] to yield compounds with tin-metal bond(s) such as RR'SnX₂ or RSnX₃. The nature of the reaction is discussed.

CARBONYL compounds with transition metal-tin bonds have generally been synthesised by the classical route¹ involving the use of an ionic derivative of a metal carbonyl and of an appropriate non-transition metal compound; another route was described by us²⁻⁴ and others.5

When a mercury(II) derivative such as $R_{a}Hg$ (R = aryl) is treated with tin(II) halide reaction (1) takes place.⁶ We find that formally the same reaction takes

$$R_{2}Hg + SnX_{2} = Hg + R_{2}SnX_{2} (X = CI, Br)$$
(1)

place in dipolar aprotic solvents, such as acetone or ethyl acetate, when R is an organometallic moiety instead of an aryl group. In all cases listed in the Table compounds with transition metal-tin bond(s) were formed. [Fe(CO)₂NO(Ph₃P)]₂Hg and [Fe(CO)₃NO]₂Hg, however, did not afford any isolable compound. In a few cases some RSnX₃ was isolated together with the expected R₂SnX₂. Only the former was isolated when R was $[Co(CO)_{3}(Bu_{3}^{n}P)]$ and X was Br, in spite of the fact that [(CO)₃(Buⁿ₃P)Co]₂SnBr₂ is stable and was isolated by us³ by a different synthetic procedure. A similar fact had been observed, leading to the isolation of $[(\pi - C_5H_5)MO(CO)_3]SnCl_3^2$ $[(\pi - C_5H_5)W(CO)_3]SnCl_3^2$ and [(CO)₃{(Ph₂PCH₂)₂}Mn]SnCl₃.⁷ Similarly, even the reaction of sodium pentacarbonylmanganese(I) with pure trimethyl-lead chloride was reported ¹ to yield a mixture of $[(CO)_5Mn]Pb(CH_3)_3$ and $[(CO)_5Mn]_2Pb(CH_3)_2$, although the former was stable and did not yield the latter on heating, either neat or as tetrahydrofuran solution. We allowed tin(II) halides to react also with compounds of the type RHgX $[X = Cl, CH_3CO_2, and$ $R = \pi - C_5 H_5 Fe(CO)_2$, $Co(CO)_4$, $Co(CO)_3 (Bu_3^nP)$] obtained by the equilibrium (2). All these compounds reacted

$$R_2Hg + HgX_2 = 2 RHgX$$
 (2)

simply and with good vields as in reaction (3). Only

$$RHgX + SnX_2 \longrightarrow RSnX_3 + Hg$$
(3)

 $[\pi-C_5H_5Fe(CO)_2]Hg(CH_3CO_2)$ showed a different reactivity in that the compound $[\pi-C_5H_5Fe(CO)_2]_2SnCl_2$

- ¹ F. Hein, H. Pobloth, and E. Heuser, Z. anorg. Chem., 1941, 248, 84; R. D. Gorsich, J. Amer. Chem. Soc., 1962, 84, 2486. ² F. Bonati and G. Wilkinson, J. Chem. Soc., 1964, 179. ³ F. Bonati, S. Cenini, D. Morelli, and R. Ugo, J. Chem. Soc.
- (A), 1966, 1052. ⁴ F. Bonati, S. Cenini, D. Morelli, and R. Ugo, Autumn

was formed but no acetate-containing derivative. When an equimolecular mixture of $[\pi-C_5H_5Mo(CO)_3]_2Hg$ and $[(CO)_3(Bu^n_3P)Co]_2Hg$ was allowed to react with SnCl₂, no mixed compound such as

 $[(CO)_{3}(Bu_{3}^{n}P)CO]SnCl_{2}[\pi-C_{5}H_{5}MO(CO)_{3}]$ was obtained but [(CO)₃(Buⁿ₃P)Co]₂SnCl₂ was isolated in very good yield with some $[\pi-C_5H_5Mo(CO)_3]_2SnCl_2$ and unchanged $[\pi-C_5H_5Mo(CO)_3]_2$ Hg. However, if an equimolecular mixture of $[\pi-C_5H_5Fe(CO)_2]_2Hg$ and $[\pi-C_5H_5Mo(CO)_3]_2Hg$ was allowed to react a compound which possibly is $[\pi - C_5 H_5 Fe(CO)_2]$ SnCl₂ $[\pi - C_5 H_5 Mo(CO)_3]$ was obtained although in poor yield.

Some conclusions can be drawn about the exchange equilibrium between the organometallic moieties bonded to the mercury. When the two organometallic moieties are very different, e.g., $R = Co(CO)_3(Bun_3P)$ and R' = π -C₅H₅Mo(CO)₃, the equilibrium (4) seems to move

$$R_{2}Hg + R'_{2}Hg - 2 RR'Hg$$
(4)

to the left. When the two organometallic moieties are analogous, such as π -C₅H₅Mo(ČO)₃ and π -C₅H₅Fe(CO)₂, a considerable amount of

 $[\pi-C_5H_5Mo(CO)_3]Hg[\pi-C_5H_5Fe(CO)_2]$ may be present at the equilibrium with perhaps a roughly statistical distribution.⁸ Moreover, the reactivities towards SnX₂ of the symmetrical and the asymmetrical derivative should be comparable because

 $[\pi-C_5H_5M_0(CO)_3]$ SnCl₂ $[\pi-C_5H_5F_6(CO)_2]$ seems to be present in the mixture from the reaction. This method of synthesis of compounds with two different metals directly bonded to a tin atom is therefore suitable only in few cases when the Hg-M bonds (M = Co, Mo, Fe, W) are of comparable reactivity. We tried to understand the nature and the possible mechanism of this new interaction of tin(II) halides. The reaction does not go through compounds with a homogeneous metal-metal bond which might be obtained as in reaction (5). Indeed,

$$R_{2}Hg \longrightarrow R-R + Hg [R = \pi - C_{5}H_{5}Fe(CO)_{2}, (CO)_{3}(Bu^{n}_{3}P)Co] (5)$$

no mercury was liberated when $[(CO)_3(Bun_3P)Co]_2Hg$ was allowed to stand in the reaction conditions in the absence of tin(II) halide; the compound was recovered

- ⁵ D. J. Patmore and W. A. G. Graham, Inorg. Chem., 1966.
- 5, 1405. ⁶ K. A. Kocheshkow and A. N. Nesmeyanow, Chem. Ber., 1931, **64**, 628.
- 7 F. Bonati and R. Ugo, Istituto Lombardo (Rend. Sci.), 1964, A, 98, 607.
- ⁸ W. E. French, N. Inamoto, and G. F. Wright, Canad. J. Chem., 1964, 42, 2228.

Meeting of the Chemical Society, Nottingham, Sept. 1965, Abs. B9; F. Bonati, S. Cenini, D. Morelli, and R. Ugo, Inorg. Nuclear Chem. Letters, 1965, 1, 107.

unaltered after two days. Moreover, metallic mercury separated quickly only on addition of tin(II) halides. We think that the possible initial step of the reaction is the "carbene" insertion (6) of SnX₂.^{2,3} The inter-

$$R-Hg-R + SnX_2 \longrightarrow [R-Hg-Sn-R]$$
(6)

mediate, which should be very unstable because of a mercury-tin bond, breaks down as in (7). Although

$$[R-Hg-Sn-R] \longrightarrow Hg + R_2SnX_2$$
(7)

on the basis of our results we cannot certainly demonstrate this path, it seems to be supported by the following evidence. (a) The reactivity of the mercurial compounds with SnCl₂ depends on the stability and the nature of the mercury-metal bond. (b) The CO exchange on $Hg[Co(CO)_4]_2$ seems to go through a Hg-Co CO insertion mechanism,9 although other mechanisms can (c) By reaction of dichlorocarbene with operate. dialkylmercurials, compounds of type RHg-Cl₂R¹⁰ $(R = Pr^{i}, Bu^{s}, Bu^{n})$ were obtained. (d) The bonds Hg-Si and Hg-Ge are subject to ready fission, giving mercury and Si-Si or Ge-Ge species 11 and this type of reaction might well extend to tin. However, the mercury-tin fission seems to be not homolytic as for Hg-Si and Hg-Ge bonds.¹¹ In fact, the reaction is not hindered by addition of quinol or chloranil. For the reaction (3) a different mechanism can operate, as indi-

$$HgX + SnX_2 \longrightarrow RSnX_3 + Hg$$
 (3)

cated by the much higher yields, although the first mechanism cannot be ruled out. A nucleophilic attack of SnX_3^- on the RHg⁺ or on the [RHg(solvent)]⁺ cation could take place instead of the electrophilic SnX₂ (8) 12 insertion. Reaction $[R = \pi - C_5 H_5 Fe(CO)_2,$

$$RHgX + Y^{-} \longrightarrow RHgY + X^{-}$$
(8)

 $Co(CO)_3(Bu^n_3P)$ and $X^- = Cl^-$; $Y^- = Br^-$, I^- , $CH_3 \cdot CO_2^{-}$ is very rapid and easy with good nucleophiles as I⁻ and supports the existence of the above-mentioned cation.

In conclusion, this method of synthesis of compounds with metal-tin bonds seems suitable in many cases. because many mercurial compounds have been recently made available through the reaction of HgX₂ with complex hydrides 13,14 or compounds in low oxidation states.15,16 Preliminary results confirm that $MCl_2(HgCl)CO(PPh_3)_2~(M=Ir, Rh)$ react with $SnCl_2$ in this way.

EXPERIMENTAL

Infrared spectra were taken on Perkin-Elmer model 137 and 237 instruments (Nujol mull, unless otherwise

⁹ S. Breitschaft and F. Basolo, J. Amer. Chem. Soc., 1966, 88, 2702.

stated). ¹H n.m.r. spectra were recorded on a Perkin-Elmer R-10 instrument operating at 60 Mc./sec. with tetramethylsilane as internal standard and CDCl₃ as solvent. Melting points were determined on a Leitz Heitztischmikroskop and were not corrected. Reactions were carried out initially in nitrogen, with evaporation under vacuum (water pump).

Anhydrous tin(II) halides and anhydrous solvents were The tin compounds obtained are listed in the used. Table.

			Yields	Compounds
R	R'	X	(%)	obtained*
Co(CO) ₃ Bu ⁿ ₃ P	R	Cl	85	R_2SnCl_2
Co(CO) ₃ Bu ⁿ ₃ P	Cl	Cl	80	RSnCl ₃
Co(CO) ₃ Bu ⁿ ₃ P	R	Br	50	RSnBr ₃
Co(CO)	R	Cl	20-40 †	R_2SnCl_2
π -C ₅ H ₅ Fe(CO) ₂	\mathbf{R}	Cl	25	R ₂ SnCl ₂
π -C ₅ H ₅ Fe(CO) ₂	Cl	Cl	50	RSnCl ₃
π -C ₅ H ₅ Fe(CO) ₂	R	\mathbf{Br}		$R_2SnBr_2 +$
				RSnBr ₃
π -C ₅ H ₅ Fe(CO) ₂	CH ₃ CO ₂	Cl	30	R ₂ SnCl ₂
π -C ₅ H ₅ Mo(CO) ₃	R	Cl		$R_2SnCl_2 +$
				RSnCl ₃
π -C ₅ H ₅ Mo(CO) ₃	Cl	Cl	35	RSnCl ₃
π -C ₅ H ₅ W(CO) ₃	Cl	C1	50	RSnCl ₃
π -C ₅ H ₅ Mo(CO) ₃	π -C ₅ H ₅ Fe(CO) ₂	Cl	30	RR'SnCl ₂

* Compounds obtained by reaction of RR'Hg with SnX2. † Isolated as Ph₂P or Ph₃As derivative.

Chloro(tetracarbonylcobalt)mercury.--Mercury(II) chloride (0.32 g) in ethyl acetate (25 ml) was added to a solution of bis(tetracarbonylcobalt)mercury (0.50 g.) in ethyl acetate (20 ml.). After a few minutes the solvent was removed under vacuum, and the residue was extracted with methanol. On evaporation of the filtered solution, pale orange needles (0.68 g.) separated, m. p. 105-107° $\{86\% \text{ based on } [Co(CO)_4]_2Hg\}$ (Found: C, 11.0; Co, 13.6. Calc. for C₄ClCoHgO₄: C, 11.8; Co, 14.4%).

The compound is insoluble in light petroleum, hexane, and ligroin, sparingly soluble in methanol and ethanol, and fairly soluble in acetone and ethyl acetate; v_{max} 2088m, 2044w, 2032m, 2008s, 1996sh cm.⁻¹.

Bis(tricarbonyltri-n-butylphosphinecobalt)mercury.— A solution of bis(tetracarbonylcobalt)mercury (2.8 g.) in benzene (90 ml.) was treated at room temperature with tri-n-butylphosphine (2.13 g.) in the same solvent (40 ml.). After 3 hr. the solvent was removed in vacuo and the residue was extracted with acetone. After addition of methanol, the filtered solution was evaporated giving a yellow compound, m. p. 108-109° {80% based on [Co(CO)₄]₂Hg} (Found: C, 40.0; H, 6.1; Co, 13.0. C₃₀H₅₄Co₂HgO₆P₂ requires C, 40.4; H, 6.1; Co, 13.2%), fairly soluble in organic solvents but sparingly soluble in methanol and ethanol; v_{max}, 1970m, 1940s, 1920s, 1890sh, 1410vw, 1220vw, 1200vw, 1080w, 1060w, 905m, 780w, 750vw, 730m cm.⁻¹.

Chloro(tricarbonyltri-n-butylphosphinecobalt)mercury.---Mercury(II) chloride (0.18 g.) in ethyl acetate (25 ml.) was added to a solution of bis(tricarbonyltri-n-butylphosphinecobalt)mercury (0.45 g.) in ethyl acetate (25 ml.). After a

¹¹ N. S. Vyazankin, G. A. Razuvaev, and E. N. Gladyshev, Doklady Akad. Nauk S.S.S.R., 1964, **155**, 830.

- ¹² F. Bonati and R. Ugo, unpublished results.
 ¹³ R. S. Nyholm and K. Vrieze, J. Chem. Soc., 1965, 5331.
 ¹⁴ R. S. Nyholm and K. Vrieze, J. Chem. Soc., 1965, 5337.
 ¹⁵ M. C. Ganorkar and M. H. B. Stiddard, Chem. Comm., 1965,
- 22. ¹⁶ D. M. Adam, D. J. Cook, and R. D. W. Kemmitt, Chem. Comm., 1966, 103.

¹⁰ J. A. Landgrebe and R. Mathis, J. Amer. Chem. Soc., 1964, 86, 5Ž4.

few minutes the solvent was removed under vacuum and the residue was extracted with methanol. On evaporation of the filtered solution, a yellow *compound* separated, m. p. 115—117° {*ca.* 75% based on $[Co(CO)_3(Bu^3_3P)]_2Hg$ } (Found: C, 30.9; H, 4.9; Co, 9.5. $C_{15}H_{27}ClCoHgO_3P$ requires C, 30.9; H, 4.7; Co, 10.1%). It exists as a yellow and a green isomer; it is possible to change the green into yellow isomer by dissolution and crystallisation. Infrared spectrum shows v_{max} 2020m, 1955vs broad, 1910sh, 1400vw, 1210vw, 1090w, 910vw, 900w, 890vw, 780sh, 770w, 725m cm.⁻¹.

Chloro(dicarbonyl- π -cyclopentadienyliron)mercury.— Mercury(II) chloride (0.72 g.) in ethyl acetate (15 ml.) was added to a solution of bis(dicarbonyl- π -cyclopentadienyliron)mercury (1 g.) in ethyl acetate (35 ml.). After 1 hr. at room temperature, the solution was filtered and on evaporation a yellow-orange compound separated, m. p. 110° (decomp.) (Found: C, 20.56; H, 1.28; Cl, 8.0. C₇H₅ClFeHgO₂ requires C, 20.4; H, 1.21; Cl, 8.6%), sparingly soluble in organic solvents. The ¹H n.m.r. spectrum shows only one signal at 5.02 τ ; ν_{max} 3030vw, 2000vs, 1950vs broad, 1420vw, 1410w, 1060w, 1015w, 995w, 940vw, 870sh, 865w, 855s, 835w cm.⁻¹.

Acetato(dicarbonyl- π -cyclopentadienyliron)mercury.— Bis-(dicarbonyl- π -cyclopentadienyliron)mercury (0.41 g.) in ethyl acetate (50 ml.) was treated at room temperature, with stirring, with mercury(II) acetate (0.32 g.). After 25 hr. the resulting limpid solution was evaporated to dryness and the residue was crystallised from carbon tetrachloride giving a mustard-yellow compound, m. p. 77— 79° (Found: C, 24.9; H, 1.8. C₉H₈FeHgO₄ requires C, 24.8; H, 1.8%), sparingly soluble in organic solvents. The ¹H n.m.r. spectrum has two broad signals at *ca*. 5.05 and 8.0 τ , of relative area 5:3; 3030vw, 2000s, 1990s, 1955s, 1945s, 1905sh, 1600shm, 1585m, 1425w, 1415w, 1315m, 1020vw, 925vw, 870sh, 860w, 840sh, 725vw, 680w cm.⁻¹.

Dichlorobis(tricarbonyltri-n-butylphosphinecobalt)tin.— Tin(11) chloride (0.34 g.) in acetone (25 ml.) was added to a solution of bis(tricarbonyltri-n-butylphosphinecobalt)mercury (0.99 g.) in acetone (25 ml.). After being kept for two days at room temperature the solution was evaporated to dryness and the residue was extracted with methanol. On evaporation of the filtered solution orange-yellow prisms separated, m. p. 92—95° (Found: C, 40.9; H, 6.2. Calc. for C₃₀H₅₄Cl₂Co₂P₂O₆Sn: C, 40.9; H, 6.1%). The infrared spectrum in solution and m. p. are in accord with those reported; ³ v_{max.} 2036vw, 2020m, 1970vs, 1960sh s, 1925sh, 1410vw, 1210vw, 1190vvw, 1095vw, 1070vvw, 1050vw, 970vw, 915w, 905sh, 875vvw, 740w, 725w cm.⁻¹.

 $\label{eq:tricarbonyltri-n-butylphosphinecobalt)tin.-Tin(II) chloride (0.09 g.) in acetone (30 ml.) was added to a solution of chloro(tricarbonyltri-n-butylphosphinecobalt)mercury (0.19 g.) in acetone (25 ml.). After 36 hr. at room temperature the solution was evaporated to dryness. The residue was extracted with methylene dichloride and the compound was crystallised from methanol as yellow needles, m. p. 128-130° (Found: C, 31.6; H, 4.7; Co, 10.2. C_{15}H_{27}Cl_3COO_3PSn requires C, 31.5; H, 4.7; Co, 10.3%); v_{max.} 2060w, 2000s broad, 1960sh, 1410vw, 1215w, 1200vw, 1180vw, 1080w, 1050w, 1005vvw, 960w, 910m, 775m broad, 725m cm.^-1.$

Tribromo(tricarbonyltri-n-butylphosphinecobalt)tin.— Tin(II) bromide (0.1 g.) in acetone (15 ml.) was added to a solution of bis(tricarbonyltri-n-butylphosphinecobalt)mer-

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cury (0·3 g.) in acetone (25 ml.). After one day at room temperature, the solution was evaporated to dryness, the residue was extracted with methylene dichloride, and the orange-yellow *compound* was crystallised from methanol. It had m. p. 115° (Found: C, 25·1; H, 4·2; Co, 7·9. $C_{15}H_{27}Br_3CoO_3PSn$ requires C, 25·6; H, 3·8; Co 8·3%), is soluble in chloroform and methylene dichloride, and sparingly soluble in methanol; ν_{max} 2030w, 1980s, 1950sh, 1400vw, 1310vw, 1270vvw, 1255w, 1220w, 1200w, 1100w, 1080w, 1060w, 910m, 780w, 750vw, 725m cm.⁻¹.

Dichlorobis(tricarbonyltriphenylphosphinecobalt)tin.— Tin(II) chloride (0·42 g.) in ethyl acetate was added to a solution of bis(tetracarbonylcobalt)mercury (1·1 g.) in ethyl acetate. After three days at room temperature the solution was evaporated to dryness. The residue was extracted with benzene and a stoicheiometric amount of triphenylphosphine in benzene was added to the filtered solution. After one day, on evaporation of the solution, yellow crystals separated. On recrystallisation from methanol, a yellow compound separated, identified ³ by m. p. and infrared spectrum in solution; v_{max} . 2078w, 2021w, 2000s, 1940vs, 1910m, 1580vw, 1480m, 1435s, 1310vw, 1260w, 1185vw, 1100s, 1070sh, 1030m, 1000w, 805m, 755s, 715m, 700s cm.⁻¹.

Dichlorobis(tricarbonyltriphenylarsinecobalt)tin.— The compound was prepared as the preceding one, and identified ³ through its m. p. and its spectrum in CH₂Cl₂; ν_{max} . 2076m, 2026w, 1998s, 1955vs, 1911m, 1580vw, 1480w, 1440m, 1310vw, 1185vw, 1085m, 1030vw, 1005w, 750s, 700s cm.⁻¹.

Dichlorobis(dicarbonyl- π -cyclopentadienyliron)tin.— (1) Tin(II) chloride (0.82 g.) in acetone was added to a solution of bis(dicarbonyl- π -cyclopentadienyliron)mercury (2 g.) in acetone. The solution was refluxed for 5 hr. and evaporated to dryness. The residue was extracted with methylene dichloride and the solvent was removed under vacuum. The solid residue was washed with methanol to give a yellow compound, identified ² by m. p. and infrared spectrum. The ¹H n.m.r. spectrum shows one signal at 4.98 τ .

(2) Mercury(II) acetate (0.32 g.) was added at room temperature, with stirring, to a solution of bis(dicarbonyl- π -cyclopentadienyliron)mercury (0.4 g.) in ethyl acetate (50 ml.). After 25 hr. the solution was treated with tin(II) chloride (0.4 g.) and after 36 hr. the solution was evaporated to dryness. The residue was extracted with carbon tetra-chloride and the solvent was removed under vacuum. The compound was identified through the m. p. and infrared spectrum.²

Trichloro(dicarbonyl- π -cyclopentadienyliron)tin.— Tin(II) chloride (0·12 g.) in acetone was added to a solution of chloro(dicarbonyl- π -cyclopentadienyliron)mercury (0·2 g.) in acetone. The solution was refluxed for 16 hr. and evaporated to dryness. The residue was extracted with CH₂Cl₂ and the compound was crystallised from methanol; on evaporation a yellow compound was obtained, identified by its m. p. and infrared spectrum.² The ¹H n.m.r. spectrum shows only one signal at 4·82 τ .

Dibromo(dicarbonyl- π -cyclopentadienyliron)tin.—(1) According to a general method,² we prepared this compound by interaction of tin(II) bromide with the dimeric complex $[\pi$ -C₅H₅Fe(CO)₂]₂, obtaining orange-yellow needles, m. p. 177—179° (decomp.) {ca. 70% based on [CpFe(CO)₂]₂ (Cp = cyclopentadiene)} [Found: C, 26.7; H, 1.5; M (in benzene), 685. C₁₄H₁₀Br₂Fe₂O₄Sn requires C, 26.5; H, 1.5%; M, 632]. The ¹H n.m.r. spectrum shows a signal

at 4.98 $\tau; \nu_{max}$ 3100vw, 2010s, 1970w, 1955s, 1935m, 1910w, 1430vw, 1414vw, 880vw, 860m, 780w cm.⁻¹.

(2) Tin(II) bromide (0.5 g.) in acetone was added to a solution of bis(dicarbonyl- π -cyclopentadienyliron)mercury (0.7 g.) in acetone. The solution was refluxed for 6 hr. and evaporated to dryness. The residue was extracted with methylene dichloride and the solvent was removed under vacuum. The residue was washed with ethanol to give a yellow-orange mixture, m. p. ca. 140—145°. By recrystallisation from benzene-n-hexane red-orange needles were obtained with the same m. p. The ¹H n.m.r. spectrum showed two signals of comparable intensity at 4.97 τ {[CpFe(CO)₂]₂SnBr₂} and 4.83 τ . The signal at 4.83 τ is very likely due to [CpFe(CO)₂]SnBr₃, as can be seen on comparison with signals of similar chlorinated compounds. The infrared spectrum contains all the bands present in [CpFe(CO)₂]₂SnBr₂.

 $Dichlorobis(tricarbonyl-\pi-cyclopentadienylmolybdenum)tin.$ -Tin(II) chloride (0.1 g.) in acetone was added to a solution of bis(tricarbonyl-π-cyclopentadienylmolybdenum)mercury (1.32 g.) in acetone. The solution was refluxed for five days and evaporated to dryness. The residue was extracted with methylene dichloride; the solvent was removed under vacuum and the residue was crystallised from acetoneligroin. On evaporation of the solution a red oil separated; the solution was decanted and on further concentration gave an yellow-orange mixture (0.93 g.), m. p. ca. 150°. The ¹H n.m.r. spectrum showed three signals at 4.34 τ { $[CpMo(CO)_3]SnCl_3$ }, 4.41 τ { $[CpMo(CO)_3]_2SnCl_2$ } and $4.59 \tau \{ [CpMo(CO)_3]_2 Hg \}$ in a molar ratio, respectively, of 37: 29.6: 33.4%. The signals were compared with those of the analytically pure compounds. Thin-layer chromatography confirmed this result. After recrystallisation from benzene-ligroin, with cooling to -20° , golden-yellow needles were obtained, m. p. 199-200° (Found: C, 28.6, H, 1.6; Cl, 10.4. Calc. for C₁₆H₁₀Cl₂Mo₂O₆Sn: C, 28.2; H, 1.4; Cl. 10.4). The ¹H n.m.r. spectrum shows a signal at 4.4 τ ; v_{max.} 3030vw, 2010s, 1960m, 1920s, 1410w, 1070vw, 1020vw, 1010vw, 1000vw, 870vw, 855vw, 845w, 840w, 830w cm.⁻¹. The compound has analysis and m. p. in accord with those described.17

 $Trichloro(tricarbonyl-\pi-cyclopentadienylmolybdenum)tin.$ Mercury(II) chloride (0.62 g.) in acetone was added to a solution of bis(tricarbonyl- π -cyclopentadienylmolybdenum)-mercury (1.57 g.) in acetone. After being kept at room temperature for 30 min., a solution of tin(II) chloride (0.85 g.) in acetone was added. The resulting solution was refluxed for three days and evaporated to dryness. The residue was extracted with methylene dichloride and the solvent was removed under vacuum. The residue was washed with ethanol to give a yellow compound whose ¹H n.m.r. spectrum shows signals at 4.34 τ . Infrared spectrum and m. p. were in accord with those described.²

Trichloro(tricarbonyl-π-cyclopentadienyltungsten)tin.—Mercury(II) chloride (0.27 g.) in acetone (40 ml.) was added to a solution of bis(tricarbonyl-π-cyclopentadienyltungsten)mercury (0.83 g.) in acetone (80 ml.). After 1 hr. at room temperature a solution of tin(II) chloride (0.75 g.) in acetone (45 ml.) was added. After three days at room temperature, the resulting solution was evaporated to dryness. The residue was extracted with methylene dichloride and solvent was removed under vacuum. The residue was washed with chloroform, giving a yellow compound (0.5 g.) (Found: C, 16.9; H, 0.8. Calc. for C₈H₅Cl₃O₃SnW: C, 17.2; H, 0.8%). The ¹H n.m.r. spectrum shows a signal at 4.4 τ. Analysis, infrared spectrum, and m. p. were in accord with those described.²

Dichloro(dicarbonyl- π -cyclopentadienyliron)(tricarbonyl- π cyclopentadienylmolybdenum)tin.—To a solution of bis-(dicarbonyl- π -cyclopentadienyliron)mercury (0.55 g.) and bis(tricarbonyl- π -cyclopentadienylmolybdenum)mercury (0.69 g.) in acetone (110 ml.) was added a solution of tin(II) chloride (0.6 g.) in acetone (40 ml.). After 4 days at room temperature the solution was refluxed for one day and evaporated to dryness. The residue was extracted with methylene dichloride and the filtered solution was evaporated to ca. 20 ml. By addition of n-hexane a red oil separated. The solution was decanted and by further addition of n-hexane a yellow compound was obtained, m. p. 133—135°. This seems to transform on crystallisation from solvents (Found: C, 28.0; H, 1.3; Fe, 9.5; Sn, 17.9.

 $C_{15}H_{10}Cl_2FeMoO_5Sn$ requires C, 29.4; H, 1.6; Fe, 9.0; Sn, 19.5%). The ¹H n.m.r. spectrum shows two signals at 4.33 and 4.59 τ with a 1:1 ratio; $\nu_{max.}$ 3070vw, 2050w, 1990s, 1955s, 1885sh, 1870vs, 1420vw, 1415vw, 1055vw, 1010w, 855vw, 845w, 835vw, 825w, 820m cm.⁻¹.

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¹⁷ A. N. Nesmeyanov, K. N. Anisimov, N. E. Kalobova, M. Ya Zakharova, *Doklady Akad. Nauk S.S.S.R.*, 1964, **156**, 612.