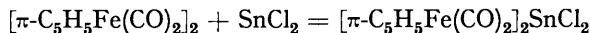


## 29. Interaction of Tin(II) Chloride with Carbonyl- $\pi$ -cyclopentadienyl Complexes of Iron, Molybdenum, and Tungsten.

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Carbonyl- $\pi$ -cyclopentadienyl complexes of iron, molybdenum, and tungsten have been shown to react with tin(II) chloride to give tin-containing complexes of the type  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]\text{SnCl}_2$ .

A NUMBER of  $\pi$ -cyclopentadienyl and carbonyl complexes which contain transition-metal-tin bonds have been prepared,<sup>1,2</sup> for example, by interaction of a sodium salt such as  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$  and tin(IV) halide derivatives such as  $\text{SnClPh}_3$ . In view of the apparent ability of tin(II) chloride as either  $\text{SnCl}_2$  (solvent) or  $\text{SnCl}_3^-$  to behave as a donor, at least towards platinum metals,<sup>3</sup> we have studied the reaction of tin(II) chloride with some typical carbonyl- $\pi$ -cyclopentadienyl complexes in polar solvents such as methanol. Although we do not find additional evidence for tin(II) chloride behaving as a donor, the reactions nevertheless lead to compounds containing metal-tin bonds, *e.g.*;



where the tin is now formally in the IV oxidation state as in the Gorsich<sup>2</sup> complexes. Such reactions could be considered as being due to the "carbenoid" activity of tin(II) chloride,<sup>4</sup> although this stable compound obviously cannot be very reactive in this sense and in any case under the present conditions of reaction must be present as  $:\text{SnCl}_2(\text{H}_2\text{O})$  or  $:\text{SnCl}_2(\text{CH}_3\text{-OH})$ .

The binuclear compound,  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ , reacts according to the above equation, giving an almost quantitative yield of a yellow air-stable compound,  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$ . The infrared spectra show only  $\pi\text{-C}_5\text{H}_5$  and terminal carbon monoxide frequencies, while the nuclear magnetic resonance spectrum shows a single  $\pi\text{-C}_5\text{H}_5$  proton resonance line. The compound is non-conducting in acetone and, as well as being unaffected by boiling 3M-hydrochloric acid, it is decomposed thermally only well above its melting point, yielding ferrocene and carbon monoxide in nearly quantitative yield. Although we were unable to convert it into a hydride by lithium aluminium hydride, the corresponding ethyl derivative  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SnEt}_2$  can be obtained by using ethylmagnesium bromide. The structure of the latter is confirmed by its alternative preparation from the salt,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ , and the chloride,  $\text{Et}_2\text{SnCl}_2$ , in tetrahydrofuran, the product being identical in the two cases.

Reaction of the complex,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ , with tin(II) chloride leads to an orange-yellow compound,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SnCl}_2$ , which appears to be identical with the compound prepared by Gorsich<sup>2</sup> from the complex  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SnPh}_3$  and hydrogen chloride but described as reddish-brown. It is also obtained by treating the compound,  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$ , with tin(IV) chloride under conditions milder than those usually required in such redistribution reactions. A similar tungsten derivative,  $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{SnCl}_2$ , was obtained by interaction of  $\pi\text{-C}_5\text{H}_5\text{WMe}(\text{CO})_3$  and tin(II) chloride, and the corresponding molybdenum derivative was obtained from the binuclear carbonyl with tin(II) chloride.

In conditions similar to those used above, we have been unable to find evidence of

<sup>1</sup> Hieber, Gruber, and Lux, *Z. anorg. Chem.*, 1959, **300**, 275.

<sup>2</sup> Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486, and references cited therein.

<sup>3</sup> Davies, Wilkinson, and Young, *J. Amer. Chem. Soc.*, 1963, **85**, 1692.

<sup>4</sup> Cf. discussion by Volpin, Koreshkov, Dulova, and Kursanov, *Tetrahedron*, 1962, **18**, 107; however, see also Johnson and Gohlke, XIX Internat. Congress, I.U.P.A.C., Abs. AB-4, p. 163, *Tetrahedron Letters*, 1962, 1291.

reaction of stannous chloride with decacarbonyldimanganese or chloropentacarbonylmanganese. With dodecacarbonyltri-iron and stannous chloride, carbon monoxide was evolved and a red substance was isolated which, on addition of tetramethylammonium chloride in 3*M*-hydrochloric, gave a red salt; analyses were, however, irreproducible but iron, tin, chlorine, and carbon monoxide are certainly present in the salt.

We have been unable to obtain evidence for reaction between lead(II) acetate or chloride with the complex  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ .

*Experimental.*—Microanalyses and molecular weights (ebullioscopic in benzene) were by the Microanalytical Laboratory, Imperial College. Infrared spectra (in  $\text{cm}^{-1}$ ) were taken on Perkin-Elmer "Infracord" and model 21 instruments (sodium chloride optics), and nuclear magnetic resonance spectra on a Varian V4300 instrument at 56.4 Mc./sec. by conventional methods ( $\tau$  values are given with internal tetramethylsilane reference). All reactions were carried out initially in nitrogen.

*Dichlorobis(dicarbonyl- $\pi$ -cyclopentadienyliron)tin(IV)*. A solution of the dimeric complex,  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  (5.0 g.), and tin(II) chloride dihydrate (10.0 g.) in methanol (250 ml.) and ethyl acetate (25 ml.) was refluxed for 20 hr. On cooling, yellow crystals (7.0 g.) separated. These were collected, washed with methanol and then ether, and recrystallised from methanol and from toluene–light petroleum (b. p. 100–120°) as the yellow *complex*, m. p. 166–168° {ca. 90% based on  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ } (Found: C, 30.95, 30.9; H, 2.2, 2.4; Cl, 13.2; O, 11.8%; *M*, 586.  $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{Fe}_2\text{O}_4\text{Sn}$  requires C, 30.9; H, 1.85; Cl, 13.1; O, 11.8%; *M*, 543.5).

The compound is insoluble in light petroleum (b. p. 30–40°), water, or 3*M*-hydrochloric acid, sparingly soluble in carbon tetrachloride, carbon disulphide, ether, ethyl acetate, and methanol, but fairly soluble in benzene and acetone. It was recovered unchanged from boiling pyridine after 2 hr. With lithium aluminium hydride in tetrahydrofuran only dark pyrophoric products were obtained. It is stable at ca. 240° under nitrogen but on pyrolysis 0.51 g. of the substance gave ferrocene (0.08 g.) and carbon monoxide (0.0038 mole). It had  $\nu_{\text{max}}$  (Nujol mull) 3115w, 2040sh, 2025vs, 1993vs, 1458m, 1417m, 1368m, 1068w, 1057w, 1015m, 1000m, 878m, 872m, 850s, and 838m  $\text{cm}^{-1}$ .

*Bis(dicarbonyl- $\pi$ -cyclopentadienyliron)diethyltin(IV)*. (1) To ethereal ethylmagnesium bromide (from 0.54 g. of magnesium) was added slowly a suspension of dichlorobis(dicarbonyl- $\pi$ -cyclopentadienyliron)tin(IV) (2.0 g.) in diethyl ether–benzene and the whole was refluxed for 2 hr. After cautious addition of 3*M*-hydrochloric acid (15 ml.) the organic layer was separated, washed with water, and dried ( $\text{CaCl}_2$ ). After removal of the solvent *in vacuo* the residue solidified on cooling. Recrystallisation from methanol gave yellow crystals of the *compound* (0.55 g.), m. p. 76° (decomp.) (Found: C, 40.4; H, 4.2; O, 11.5.  $\text{C}_{18}\text{H}_{20}\text{Fe}_2\text{O}_4\text{Sn}$  requires C, 40.7; H, 3.8; O, 12.1%). The compound is soluble in light petroleum, methylene chloride, chloroform, carbon tetrachloride, and carbon disulphide. Its odour resembles that of dichlorodiethyltin(IV).

(2) To a tetrahydrofuran solution (60 ml.) of the salt,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$  {prepared<sup>5</sup> from the dimer,  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  (3.5 g.)} was added slowly with stirring a solution of dichlorodiethyltin(IV) (3.22 g.) in tetrahydrofuran (15 ml.). After 2 hr. the solution was filtered, the solvent removed under a vacuum, and the residue extracted with light petroleum (b. p. 30–40°). After removal of solvent, the *product* was crystallised from hot methanol (ca. 40 ml.) and light petroleum to give an orange-yellow solid (1.7 g.), m. p. 76°. A mixed m. p. and infrared spectra showed the identity with the product obtained by method (1). It had  $\nu_{\text{max}}$  (in  $\text{CCl}_4$  and  $\text{CS}_2$ ) 3935w, 3140w, 2975s, 2940s, 2910s, 2010vs, 1947vs, 1843w, 1461m, 1431m, 1415m, 1377m, 1363m, 1232w, 1175m, 1117w, 1063w, 1013s, 1003sh, 964m, 930w, and 828s  $\text{cm}^{-1}$ , and (in  $\text{CCl}_4$ )  $\tau$  5.19 (relative area 10;  $\pi\text{-C}_5\text{H}_5$  protons) and 8.69 (relative area 7.8; unresolved  $\text{C}_2\text{H}_5$  group). The methyl and methylene resonances of tetraethyltin are already close together,<sup>6</sup> so that the low concentration of the present complex, even in saturated solution, and its low stability, preclude observation of any of the expected fine structure.

*Trichloro(dicarbonyl- $\pi$ -cyclopentadienyliron)tin(IV)*. (1) A solution of chlorodicarbonyl- $\pi$ -cyclopentadienyliron (1.03 g.) and tin(II) chloride dihydrate (2.25 g.) in methanol (30 ml.) was

<sup>5</sup> Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

<sup>6</sup> Narasimhan and Rogers, *J. Chem. Phys.*, 1961, **34**, 1049.

refluxed for 5 hr. The yellow precipitate which was slowly formed was collected by centrifugation and washed with methanol. The product (0.9 g.) was crystallised from benzene and from benzene-light petroleum (b. p. 30–40°), m. p. 157° (decomp.) (Found: C, 21.4; H, 1.6; Cl, 28.0; O, 8.4%; *M*, 397. Calc. for  $C_8H_5Cl_3FeO_2Sn$ : C, 20.9; H, 1.2; Cl, 26.5; O, 8.0%; *M*, 402). A mixed m. p. and infrared spectra showed the identity with the compound described as reddish-brown.<sup>2</sup>

(2) Dichlorobis(dicarbonyl- $\pi$ -cyclopentadienyliron)tin(IV) (1.03 g.) and tin(IV) chloride (0.33 ml.) in toluene (10 ml.) were heated at 100–110° for 1 hr. The solution was filtered hot. On cooling, a solid separated. The latter was collected and dissolved in dichloromethane, and the yellow product was precipitated by addition of carbon tetrachloride (3 vol.). Mixed m. p. and infrared spectra confirmed the identity of the product, that had  $\nu_{max}$  (Nujol mull) 3120m, 2062vs, 1980vs, 1426s, 1418m, 1358w, 1066w, 1058w, 1016w, 1003w, 901vw, 888vw, 863s, and 834vw  $cm^{-1}$ .

*Trichloro(tricarbonyl- $\pi$ -cyclopentadienyltungsten)tin(IV)*. A solution of tricarbonylmethyl- $\pi$ -cyclopentadienyltungsten<sup>5</sup> (8.27 g.) and tin(IV) chloride (anhydrous; 7.7 g.) in acetone (300 ml.) was refluxed for ca. 3 days. After removal of solvent, the residue was extracted with methylene chloride (3  $\times$  100 ml.). The solvent was again removed, and the residue washed with carbon disulphide (100 ml.; 5  $\times$  30 ml.) to remove unchanged starting material (ca. 5 g.) and crystallised from chloroform, to give yellow crystals (1.3 g.) of the *compound*, m. p. 187° [Found: C, 17.8; H, 1.5; Cl, 19.5; O, 9.7%; *M* (ebullioscopic in benzene), 555.  $C_8H_5Cl_3O_3SnW$  requires C, 17.2; H, 0.9; Cl, 19.1; O, 8.6%; *M*, 558]. It is sparingly soluble in benzene, chloroform, carbon tetrachloride, acetone, or ether but more soluble in methylene chloride. It sublimes in a vacuum at ca. 150° and had  $\nu_{max}$  (Nujol mull) 2990w, 2042s, 1972sh, 1950s, 1924sh, 1421w, 1066w, 1010w, and 863m  $cm^{-1}$ .

*Trichloro(tricarbonyl- $\pi$ -cyclopentadienylmolybdenum)tin(IV)*. A solution of tin chloride dihydrate (7.2 g.) in methanol (200 ml.) was refluxed with tricarbonyl- $\pi$ -cyclopentadienylmolybdenum dimer<sup>5</sup> (1.84 g.) for ca. 2 days. The solvent was partially removed at reduced pressure, giving yellow crystals of the *product* (1.2 g.), which crystallised from methanol, had m. p. 164° (decomp.) [Found: C, 20.5; H, 1.2; Cl, 22.6%; *M*, 470 (Mechrolab osmometer in acetone solution).  $C_8H_5Cl_3O_3MoSn$  requires C, 20.4; H, 1.1; Cl, 22.6%; *M*, 470]. The compound is sparingly soluble in ether, carbon tetrachloride, or methanol, but more so in methylene chloride, chloroform, acetone, or benzene, and insoluble in light petroleum and 3*N*-hydrochloric acid. In Nujol mull it has  $\nu_{max}$  3117w, 2060s, 1996sh, 1972s, 1427w, 1115vw, 1067vw, 1015w, and 863  $cm^{-1}$ .

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