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Reactions of Tin(II) Halides with Dienyl Metal Carbonyl Complexes of Fe, Cr, Mo and W containing Transition Metal to Halogen Bonds

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The reactions between equimolar amount of tin(II) halides, SnX_2, and the transition metal halides $[(\eta\text{-}C_5H_5)Fe(CO)_2Y]$, $[(\eta\text{-}C_5H_5)Fe(CO)\{P(OPh)_3\}Y]$, $[(\eta\text{-}C_7H_9)Fe(CO)_2I]$, $[(\eta\text{-}C_5H_5)Mo(CO)_3Y]$, and $[(\eta\text{-}C_5H_5)W(CO)_3Y]$ give, in most instances, the tin(IV) derivatives $[(\eta\text{-}C_5H_5)Fe(CO)_2SnX_2Y]$, $[(\eta\text{-}C_5H_5)Fe(CO)\{P(OPh)_3\}SnX_2Y]$, $[(\eta\text{-}C_7H_9)Fe(CO)_2SnX_2I]$, $[(\eta\text{-}C_5H_5)Mo(CO)_3SnX_2Y]$, and $[(\eta\text{-}C_5H_5)W(CO)_3SnX_2Y]$ [X and Y = Cl, Br, or I; and C_7H_9 = cycloheptadienyl]. However, $[(\eta\text{-}C_5H_5)Fe(CO)(L)SnI_2Y]$ [Y = Cl, Br, or I; L = CO or $P(OPh)_3$] and $[(\eta\text{-}C_5H_5)Mo(CO)_3SnX_2Y]$ [X or Y = I] could not be isolated from the appropriate reactions although SnX_3 or SnY_3 derivatives were obtained occasionally.

Introduction

It was previously reported from these laboratories that the product of the reaction of $[(\eta\text{-}C_5H_5)Fe(CO)_2I]$ with $SnCl_2 \cdot 2H_2O$ in refluxing methanol was $[(\eta\text{-}C_5H_5)Fe(CO)_2SnCl_2I \cdot MeOH]$ [1]. Others were unable to repeat this work, and have suggested that as the observation was a figment of the author's imagination, it had best be disregarded [2]. After much thought on the part of one of us, the problem was reapproached. The original reaction, which was not reproducible, was modified and extended to include other $[(\eta\text{-}C_5H_5)Fe(CO)_2Y]$, $[(\eta\text{-}C_5H_5)Fe(CO)\{P(OPh)_3\}Y]$, $[(\eta\text{-}C_7H_9)Fe(CO)_2I]$, $[(\eta\text{-}C_5H_5)Mo(CO)_3Y]$, $[(\eta\text{-}C_5H_5)W(CO)_3Y]$, and SnX_2 [X and Y = Cl, Br, and I; C_7H_9 = cycloheptadienyl]. In most instances the hoped-for $-SnX_2Y$ derivatives were obtained.

Experimental

Previously published methods were used to prepare $[(\eta\text{-}C_5H_5)Fe(CO)_2Y]$ (Y = Cl [3], Br [3], and I [4]), $[(\eta\text{-}C_5H_5)Fe(CO)\{P(OPh)_3\}Y]$ (Y = Br [5], and I [5]), $[(\eta\text{-}C_7H_9)Fe(CO)_2I]$ [6], $[(\eta\text{-}C_5H_5)Mo(CO)_3Y]$ (Y = Cl [7], Br [7], and I [10]). Other chemicals were obtained from the usual commercial sources.

The reactions were carried out under an atmosphere of nitrogen. Solvent purification had little effect on their course.

The transition metal halide (1 g) and an equimolar amount of the anhydrous or hydrated tin(II) halide were heated to reflux in *ca.* 30–50 ml of the selected solvent. When the colour change indicated that the reaction was complete, the solution was filtered, some of the solvent removed at reduced pressure, and the remainder cooled to –25 °C. The precipitated product was filtered off, washed with water or pentane, and dried. Further concentration and cooling of the filtrate usually gave a second crop of crystals.

The solvents used for the compounds of iron were tetrahydrofuran (THF) or 3:1 CH_2Cl_2/EtOH except for $[(\eta\text{-}C_5H_5)Fe(CO)_2Cl]/SnBr_2$ where ether was found to be satisfactory. Tetrahydrofuran was generally used for the reactions of $[(\eta\text{-}C_5H_5)Mo(CO)_3Y]$ except for Y = I where n-butanol was also used. All of the reactions involving $[(\eta\text{-}C_5H_5)W(CO)_3Y]$ were carried out in n-butanol except when Y = Cl where tetrahydrofuran was found to be suitable.

The reaction times varied from 20 min to *ca.* 5 hr, but were usually less than 1 hr.

The yields of the SnX_2Y derivatives varied between *ca.* 10% and 70%, but were generally *ca.* 35%. These values are undoubtedly much lower than the true yields as product purity was considered to be of primary importance.

The melting points, analyses, and infrared spectra of the products are summarised in Table I. The i.r. spectra were obtained as described previously [11].

Results and Discussion

The reactions of the various dienyl metal carbonyl halides $[(\eta\text{-dienyl})M(CO)_n(L)_mY]$ with SnX_2 (M = Fe, Mo, or W; Y = Cl, Br, or I; and X = Cl, Br, or Y)

TABLE I. Melting Points, Analyses, and Infrared Spectra of Compounds Described in the Text.

Compound[a]	M.p. (°C)[b]	Analyses[c]				Infrared Spectra[d]		
		%C	%H	%X	%Y			
$(C_5H_5)Fe(CO)_2SnCl_3$	155–6	20.8(20.9)	1.1(1.2)	27.0(26.5)		2005	2045	
$(C_5H_5)Fe(CO)_2SnCl_2Br$	156–8	18.6(18.8)	0.9(1.1)	15.9(15.9)	18.1(17.9)	2002	2042	
$(C_5H_5)Fe(CO)_2SnCl_2I$	130–2	17.4(17.1)	0.8(1.0)	14.4(14.3)	25.7(25.7)	2003	2042	
$(C_5H_5)Fe(CO)_2SnBr_2Cl$	158–60	17.3(17.1)	0.9(1.2)	32.8(32.4)	6.9(7.2)	2001	2041	
$(C_5H_5)Fe(CO)_2SnBr_3$	168–9	15.3(15.7)	0.8(0.9)	44.9(44.7)		2002	2040	
$(C_5H_5)Fe(CO)_2SnBr_2I$	150–1	14.5(14.5)	0.8(0.9)	27.0(27.1)	21.2(21.1)	2001	2039	
$(C_7H_9)Fe(CO)_2SnCl_2I$	104–6	20.2(20.7)	1.6(1.7)	13.0(13.6)	24.6(24.3)	1994	2032	
$(C_7H_9)Fe(CO)_2SnBr_2I$	117–9	17.3(17.7)	1.7(1.5)			1996	2032	
$(C_7H_9)Fe(CO)_2SnI_3$	119–21	15.0(15.3)	1.5(1.3)	54.4(54.2)		1993	2028	
$(C_5H_5)Fe(CO)\{P(OPh)_3\}SnBr_3$	204–6	35.3(35.2)	2.4(2.4)	29.1(29.3)			1988	
$(C_5H_5)Fe(CO)\{P(OPh)_3\}SnBr_2I$	dec. 160	33.0(33.3)	2.3(2.3)	18.1(18.5)	14.3(14.7)		1987	
$(C_5H_5)Mo(CO)_3SnCl_3$	165–7	19.9(20.4)	1.2(1.1)	23.0(22.7)		1964	1982	2042
$(C_5H_5)Mo(CO)_3SnCl_2Br$	156–8	18.5(18.6)	1.0(1.0)	13.5(13.8)	15.5(15.7)	1963	1982	2041
$(C_5H_5)Mo(CO)_3SnBr_2Cl$	155–6	17.0(17.1)	1.1(0.9)	29.5(28.6)	6.1(6.3)	1961	1981	2040
$(C_5H_5)Mo(CO)_3SnBr_3$	159–60	15.5(15.9)	0.8(0.8)	39.7(39.7)		1962	1981	2041
$(C_5H_5)W(CO)_3SnCl_3$	180–2	16.9(17.2)	0.5(0.9)	19.5(19.0)		1952	1970	2037
$(C_5H_5)W(CO)_3SnCl_2Br$	176–7	15.5(15.9)	0.8(0.8)	11.6(11.7)	13.5(13.2)	1952	1969	2035
$(C_5H_5)W(CO)_3SnCl_2I$	147–9	15.2(14.7)	0.7(0.7)	10.9(10.9)	19.5(19.4)	1951	1967	2032
$(C_5H_5)W(CO)_3SnBr_2Cl$	172–4	14.8(14.8)	0.5(0.8)	24.8(24.7)	5.1(5.5)	1951	1968	2035
$(C_5H_5)W(CO)_3SnBr_3$	174–6	13.6(13.9)	1.0(0.7)	34.7(34.7)		1951	1967	2035
$(C_5H_5)W(CO)_3SnBr_2I$	152–3	12.9(12.9)	0.6(0.7)	21.2(21.6)	17.3(17.2)	1948	1965	2031
$(C_5H_5)W(CO)_3SnI_3$	154–6	11.4(11.5)	0.4(0.6)	45.5(45.7)		1942	1962	2027

[a] The formulae are quoted as $(dienyl)M(L)_nSnX_2Y$ arising from the reactions of $(dienyl)M(L)_nY$ with SnX_2. [b] Measured in sealed tubes. dec. = decomposes without melting. [c] Found values with the required figures in parentheses. [d] Peak positions (cm^{-1}) of absorption bands due to ν(CO) vibrations. Measured in carbon disulphide solution.

give the hoped for $[(\eta\text{-dienyl})M(CO)_n(L)_mSnX_2Y]$ derivatives in most instances. These compounds are stable crystalline solids. Their colours vary from yellow to brown for the iron complexes, whilst those of molybdenum and tungsten are more red. They darken as the atomic numbers of X or Y increase.

Some reactions did not follow this pattern, especially those of SnI_2. With $[(\eta\text{-}C_5H_5)Fe(CO)_2Y]$ (Y = Cl), $[(\eta\text{-}C_5H_5)Fe(CO)_2SnI_3]$ and $[(\eta\text{-}C_5H_5)Fe(CO)_2I]$ were obtained in low yields together with SnI_4 in some instances; with Y = Br no products could be isolated; and with Y = I no reaction appeared to take place although iodine was present in the reaction mixture (*cf.* ref. 2).

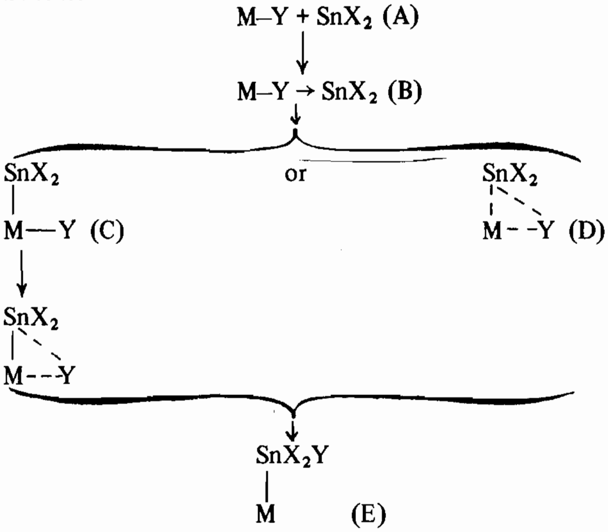
Similarly $[(\eta\text{-}C_5H_5)Mo(CO)_3Y]$ failed to react with SnI_2 in refluxing tetrahydrofuran (Y = Cl or Br) or n-butanol (Y = I). Also $[(\eta\text{-}C_5H_5)Mo(CO)_3I]$ did not give the anticipated products with SnX_2; only $[(\eta\text{-}C_5H_5)Mo(CO)_3SnCl_3]$ or $[(\eta\text{-}C_5H_5)Mo(CO)_3SnBr_3]$ could be isolated in low yield from the reaction mixtures when X = Cl or Br respectively.

In contrast with the above, $[(\eta\text{-}C_7H_9)Fe(CO)_2SnI_3]$ may be obtained in high yields, and all $[(\eta\text{-}C_5H_5)W(CO)_3Y]$ react with all SnX_2 (X and Y = Cl, Br, or I) although we did not attempt that where X = I and Y = Br.

In all instances care had to be taken to prevent redistribution reactions. For example, at higher temperatures (refluxing tetrahydrofuran or ethanol/CH_2Cl_2 mixture) the $[(\eta\text{-}C_5H_5)Fe(CO)_2Cl]/SnBr_2$ reaction gives $[(\eta\text{-}C_5H_5)Fe(CO)_2SnBr_3]$ rather than the $[(\eta\text{-}C_5H_5)Fe(CO)_2SnBr_2Cl]$ obtained in refluxing ether. Also, the isolated product of the reaction between $[(\eta\text{-}C_5H_5)Fe(CO)\{P(OPh)_3\}I]$ and $SnBr_2$ in refluxing tetrahydrofuran is $[(\eta\text{-}C_5H_5)Fe(CO)\{P(OPh)_3\}SnBr_3]$ after 90 min, but $[(\eta\text{-}C_5H_5)Fe(CO)\{P(OPh)_3\}SnBr_2I]$ after only 30 min.

The $[M(CO)_5Cl]^-$ anions undergo related reactions with SnX_2 to give $[M(CO)_5SnX_2Cl]^-$ (M = Cr, Mo, or W; X = F or I) [12]. Similar ions may also be obtained from $[M(CO)_5(THF)]$ and $[SnX_2Y]^-$ [13]. However, it should be mentioned that with other systems *e.g.* $[(\eta\text{-}C_7H_7)Mo(CO)_2Y]$ [14] and $[(\eta\text{-}C_5H_5)Co(CNC_6H_4OMe\text{-}p)I_2]$ [15], attempts to prepare the corresponding SnX_2Y derivatives have not been successful.

Scheme



The reactions described here may be related to those of other [(η-C_5H_5)Fe$(CO)_2$Y] complexes which, with SnX_2, afford [(η-C_5H_5)Fe$(CO)_2$$SnX_2Y$] *e.g.* Y = Me [16], alkyl [17], or (η-C_5H_5)Fe$(CO)_2$ [18] when X = Cl. However, when X = Br or I other reactions take place to give [(η-C_5H_5)Fe$(CO)_2$$SnX_3$].

The results presented here are consistent with our earlier observation [1], and with that of Mays and Pearson [2]. The unsymmetrical trihalotin- derivatives, *e.g.* [(η-C_5H_5)Fe$(CO)_2$$SnX_2Y$], are the first products formed in the insertion reaction, as we observed [1], but under more vigorous conditions are converted to the symmetrical trihalotin-complexes *e.g.* [(η-C_5H_5)Fe$(CO)_2$$SnX_3$]. This may be brought about by longer rection times (*cf.* [(η-C_5H_5)Fe(CO){P$(OPh)_3$}I]/$SnBr_2$), higher temperatures (*cf.* [(η-C_5H_5)Fe$(CO)_2$Cl]/$SnBr_2$), or an excess of SnX_2 (*cf.* ref. 2).

We feel that the suggested mechanism is valid *i.e.* that an intermediate such as [(η-C_5H_5)Fe$(CO)_2$-SnX_2)Y] is formed and that the halogen Y migrates from iron to tin. However it is possible that there may be an initial interaction of the type [(η-C_5H_5)Fe-$(CO)_2$Y → SnX_2] similar to that observed between transition metal halides or pseudo halides and strong Lewis acids *e.g.* [(η-C_5H_5)Fe$(CO)_2$CN → BF_3] [19]. A plausible reaction scheme is illustrated. The metal–SnX_2 interaction may take the form shown in C with the formation of an intermediate compound having a definite metal–tin coordinate bond*. On the other hand, it may involve only a three-centre transition state, D, in a single-step conversion of B or A into the product E. We are not able to distinguish between these alternatives on the basis of our data.

The ease of the insertion reaction appears to decline for Y = Cl > I and X = Cl > I. This may be a consequence of the differing electronegativities of the halogen atoms, but these are also of different sizes so that steric factors cannot be ruled out.

The infrared spectra of the products are similar to those of related derivatives [23–24]. Thus it is probable that they have the structures usually associated with [(η-C_5H_5)Fe(CO)(L)Y] (*e.g.* L = CO, Y = $SnCl_3$ [25]) and [(η-C_5H_5)Mo$(CO)_3$Y] complexes (*e.g.* Y = Cl [26]). Although the presence of two different groups in the SnX_2Y moiety allows the presence of isomers arising from restricted rotation about the Sn–Fe or Sn–M bonds, we can find no unequivocal evidence for it.

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*If C is formed, SnX_2 may act as a Lewis base as it does in [X_2Sn → W$(CO)_5$] [20] or [X_2Sn → Fe$(CO)_4$] [21] or as a Lewis acid comparable to mercury(II) chloride in [Cl_2Hg ← Co$(CO)_2$(η-C_5H_5)] [22].