Reactions of Tin(II) Halides with $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo, and W)

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It is shown that, contrary to previous reports, the insertion of tin(II) halides, SnX_2 (X = F, Cl, Br, or I), into the metal–metal bonds of the dimers $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo, or W) takes place on heating. As well as the $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnX_2$ derivatives, the products may include the $[(\pi\text{-}C_5H_5)M(CO)_3X]$ and $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$ complexes. The results are consistent with the availability of two pathways for these reactions. The first is 'direct insertion', the second is 'indirect', and proceeds *via* the $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$ compounds as detectable intermediates. The route adopted depends on both X and M, the reaction solvent, and the presence, or absence, of light. Many of these reactions also proceed smoothly at room temperatures, or somewhat above, on u.v. irradiation to give a similar range of products. Related reactions of the 'mixed' dimers $[(\pi\text{-}C_5H_5)_2CrW(CO)_6]$ and $[(\pi\text{-}C_5H_5)_2MoW(CO)_6]$ are described. The reactions between $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$ and $[(\pi\text{-}C_5H_5)M'(CO)_3]_2$ (X = Cl, Br, or I; M, M' = Cr, Mo, or W) may be used to prepare $[(\pi\text{-}C_5H_5)M(CO)_3][(\pi\text{-}C_5H_5)M'(CO)_3]SnX_2$, and $[(\pi\text{-}C_5H_5)Fe(CO)_2][(\pi\text{-}C_5H_5)M(CO)_3]SnX_2$ may be similarly obtained.

PREVIOUSLY it has been shown that $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ reacts with tin(II) chloride in refluxing methanol to give a monomolybdenum complex $[(\pi\text{-}C_5H_5)Mo(CO)_3SnCl_3]$, but 'insertion' does not take place.[1] The 'insertion' product, $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnCl_2$, has been obtained from $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$ and $SnCl_2$.[2] Related reactions of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ and $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ do not appear to have been investigated.

We now report that all three $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ complexes (M = Cr, Mo, and W) react with SnX_2 (X = F, Cl, Br, and I) to give $[(\pi\text{-}C_5H_5)M(CO)_3X]$, $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$, or $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnX_2$ depending on M, X, the mole ratio of reactants, the reaction solvent, and the presence or absence of light. We also report, for the first time, the use of u.v. irradiation in bringing about reactions related to the above, but at room temperature. Some reactions of the mixed dimers $[(\pi\text{-}C_5H_5)_2CrW(CO)_6]$ and $[(\pi\text{-}C_5H_5)_2MoW(CO)_6]$ are described, as are other routes to the 'mixed' compounds $[(\pi\text{-}C_5H_5)M(CO)_3][(\pi\text{-}C_5H_5)M'(CO)_3]SnX_2$ and $[(\pi\text{-}C_5H_5)M(CO)_3][(\pi\text{-}C_5H_5)Fe(CO)_2]SnX_2$ (M,M' = Cr, Mo, or W; X = F, Cl, Br, or I).

EXPERIMENTAL

Published methods were used to prepared $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ [3] and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$,[4] whilst $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ was obtained by stirring $[(\pi\text{-}C_5H_5)W(CO)_3Cl]$ [5] and $Na[(\pi\text{-}C_5H_5)W(CO)_3]$ [6] in diglyme at room temperature for three weeks. Similar reactions were used to prepare $[(\pi\text{-}C_5H_5)_2CrW(CO)_6]$ [7] and $[(\pi\text{-}C_5H_5)_2MoW(CO)_6]$ [8] starting from $[(\pi\text{-}C_5H_5)W(CO)_3Cl]$ and either $Na[(\pi\text{-}C_5H_5)Cr(CO)_3]$ [6] or $Na[(\pi\text{-}C_5H_5)Mo(CO)_3]$.[6]

All reactions were carried out in dried and deoxygenated solvents under an atmosphere of nitrogen. They were brought about either by heating a solution of the reactants (*ca.* 1 mmol of dimer) to reflux in a suitable solvent (*ca.* 25 ml), or by u.v. irradiation (Philips HPR 25 W) in acetone at room temperature. When they were complete, their products were isolated by removal of the solvents at reduced pressures. The residues were separated into their constituent compounds by fractional crystallizations or chromatography on alumina. As the halogenotin derivatives could not be eluted from alumina or silica, chromatography could only be used when the compounds containing these moieties had been largely precipitated from solution. The mother-liquors were then chromatographed, and pure samples of the other products obtained. In this way, for example, $[(\pi\text{-}C_5H_5)Mo(CO)_3SnI_3]$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3I]$ could be isolated. The separated compounds were then purified by recrystallization from an alcohol, or from mixtures of heptane with benzene or toluene. The m.p., analyses, and yields of the various products are given in the Table.

I.r. spectra were recorded as described elsewhere.[9] The frequencies and relative peak heights of the absorption bands whose frequencies lie between 1700 and 2100 cm^{-1} are summarised in the Table.

RESULTS

The complexes containing $Sn–M(CO)_3(\pi\text{-}C_5H_5)$ bonds (M = Cr, Mo, or W) are yellow-to-red, air-stable, crystalline solids. The colour darkens as the atomic weight of the halogen increases, but as that of the transition metal decreases.

The reactions between tin(II) halides and $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ may be brought about by heating or by u.v. irradiation. The results of these will be described independently. To avoid repetition, the mole ratio of reactants will be placed in parentheses following the reactants.

Thermal Reactions.—Unless it is stated otherwise, all reactions were carried out in the dark and in refluxing solvents.

When solutions of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $SnCl_2,2H_2O$ (1 : 10) in methanol were heated in the dark, the only compound obtained was $[(\pi\text{-}C_5H_5)Mo(CO)_3SnCl_3]$ (*cf.* ref. 1). In the light, this was a minor product; $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnCl_2$ was given in *ca.* 70% yield, and the reaction time reduced to *ca.* 5 h. Similar results were obtained using ethanol, benzene, and tetrahydrofuran or its mixtures with methanol as solvents. When equimolar quantities of the reactants were used, $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnCl_2$ was the only product, but reaction times were much longer. These were

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[1] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

[2] F. Bonati, S. Cenini, and R. Ugo, *J. Chem. Soc. (A)*, 1967, 932.

[3] S. A. Keppie and M. F. Lappert, *J. Chem. Soc. (A)*, 1971, 3216. (The hydride was decomposed by continued heating of the tetrahydrofuran solution).

[4] R. B. King, *Organometallic Synth.*, 1965, **1**, 109.

[5] E. O. Fischer and K. Fichtel, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[6] R. B. King, *Organometallic Synth.*, 1965, **1**, 156. (Diglyme was used as a solvent, and $Na[(\pi\text{-}C_5H_5)Cr(CO)_3]$ and $Na[(\pi\text{-}C_5H_5)Mo(CO)_3]$ were prepared similarly.)

[7] P. Hackett and A. R. Manning, unpublished work.

[8] E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1960, 1321.

[9] M. Casey and A. R. Manning, *J. Chem. Soc. (A)*, 1970, 2258.

reduced to *ca.* 30 min in n-butanol where the nature of the product was independent of the presence or absence of light. There was no spectroscopic evidence for intermediates in this reaction or that of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ with SnF_2 (1 : 3) in n-butanol where $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnF_2$ was the only product after 4 h.

Only $[(\pi\text{-}C_5H_5)Mo(CO)_3I]$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3SnI_3]$ could be detected in the early stages of the reaction between $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and SnI_2 irrespective of the solvent. These compounds were the only products when a large excess (1 : 10) of tin(II) iodide was used. They may be isolated but the yields were low; after 3 h in tetrahydrofuran they were 6 and 30% for the iodo- and tri-iodotin-molybdenum complexes respectively. When equimolar proportions of the reactants were used the $[(\pi\text{-}C_5H_5)Mo(CO)_3SnI_3]$ first formed reacted further with $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ to give $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnI_2$. This reaction was complete within *ca.* 1 h in n-butanol. The $[(\pi\text{-}C_5H_5)Mo(CO)_3I]$ also formed appears to decompose.

Although the reactions of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ with $SnBr_2$ followed much the same course as those with SnI_2, no $[(\pi\text{-}C_5H_5)Mo(CO)_3Br]$ could be detected at any stage, and they were somewhat slower. For example, equimolar amounts of the reagents in n-butanol gave $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnBr_2$ in 30% yield. The reaction was complete within *ca.* 2·5 h, and proceeded *via* $[(\pi\text{-}C_5H_5)Mo(CO)_3SnBr_3]$.

The reactions of $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ with tin(II) halides were very similar to those of the molybdenum dimer, but were slower. Thus, in n-butanol and in the dark, equimolar quantities of the reagents (1 : 3 for SnF_2) gave $[(\pi\text{-}C_5H_5)W(CO)_3]_2SnX_2$ in reactions which were complete within 24 h for X = F, 5 h for X = Cl and Br, and 4 h when X = I. When X = Br or I, the formation of these products proceeded *via* $[(\pi\text{-}C_5H_5)W(CO)_3SnX_3]$.

The reactions of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ bear some resemblance to those of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, but were much faster and gave more $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2SnX_2$ and less $[(\pi\text{-}C_5H_5)Cr(CO)_3SnX_3]$. Thus equimolar quantities of the chromium dimer and SnX_2 (X = Cl, Br, and I), in butanol, gave the corresponding $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2SnX_2$ derivatives in high yield with no evidence for the formation of reaction intermediates or of other products. All reactions were very fast, and were completed within the time required to run an i.r. spectrum, *i.e.* in less than 5 min.

When the $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2 : SnX_2$ mole ratios were increased to 1 : 10, tin(II) fluoride required a reaction time of 30 min in n-butanol. The only product was $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2SnF_2$. The reactions of the other tin(II) halides in ethanol were complete in less than 5 min. They gave mixtures of the $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2SnX_2$ and $[(\pi\text{-}C_5H_5)Cr(CO)_3SnX_3]$ derivatives. The yields of the dichromium compounds were 70, 54, and 52% for X = Cl, Br, and I respectively, whilst the yields of the trihalogeno-tin complexes increase along the same series, *i.e.* traces, *ca.* 5 and 40% respectively. $[(\pi\text{-}C_5H_5)Cr(CO)_3SnCl_3]$ could not be isolated, but absorption bands due to it were detected in the i.r. spectrum of the reaction mixture. Authentic samples of this compound, and its molybdenum and tungsten analogues, were prepared by another route. They are included in the Table for completeness.

Complexes containing two different transition metals

The melting points, analyses, yields, and i.r. spectra of the products of the reactions of SnX_2 with $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ (X = F, Cl, Br, and I; M = Cr, Mo, and W) and some related compounds

		Found (%)			Required (%)				
Compound	M.p. (°C)[a]	C	H	X[b]	C	H	X[b]	Yield (%)[c]	Absorption bands[d]
$(C_5H_5)Mo(CO)_3I$	140—141	25·6	1·2	34·5	25·8	1·3	34·1	6 (h)	1957(6·7), 1970(10), 2041(8·6)
$(C_5H_5)W(CO)_3I$	147—149	20·4	1·4		20·8	1·1		17 (u)	1950(sh), 1956(10), 2036(7·7)
$(C_5H_5)Cr(CO)_3SnCl_3$	171—174(d)	21·8	1·0	24·9	22·3	1·2	24·8		1957(8·4), 1979(3·3), 2028(10)
$(C_5H_5)Cr(CO)_3SnBr_3$	152—154(d)	16·9	1·0	42·7	17·2	0·9	42·8	18 (u)	1958(8·3), 1977(2·9), 2026(10)
$(C_5H_5)Cr(CO)_3SnI_3$	134—135(d)	13·3	0·7	54·5	13·7	0·7	54·4	47 (u)	1952(7·8), 1970(4·0), 2020(10)
$(C_5H_5)Mo(CO)_3SnCl_3$	164—165	20·3	1·1		20·4	1·1			1964(9·3), 1984(4·0), 2044(10)
$(C_5H_5)Mo(CO)_3SnBr_3$	159—161	15·5	0·7		15·9	0·8		61 (u)	1962(9·7), 1982(4·6), 2041(10)
$(C_5H_5)Mo(CO)_3SnI_3$	162—164	12·3	0·7	51·2	12·8	0·7	51·2	57 (u)	1957(8·3), 1977(3·4), 2036(10)
$(C_5H_5)W(CO)_3SnCl_3$	188—189	16·9	0·9		17·2	0·9			1954(10), 1972(5·0), 2040(10)
$(C_5H_5)W(CO)_3SnBr_3$	178—179	13·5	0·5	34·9	13·9	0·7	34·7	80 (u)	1953(9·3), 1970(4·9), 2037(10)
$(C_5H_5)W(CO)_3SnI_3$	172—173	11·5	0·5	45·1	11·6	0·6	45·8	56 (u)	1947(8·9), 1967(4·0), 2030(10)
$[(C_5H_5)Cr(CO)_3]_2SnF_2$	dec. 188	34·1	1·7	6·6	34·4	1·8	6·8	55 (h)	1909(3·0), 1934(5·3), 1954(4·1), 1992(6·5), 2016(10)
$[(C_5H_5)Cr(CO)_3]_2SnCl_2$	204—205	31·9	1·7	12·2	32·4	1·7	12·0	89 (h)	1911(2·9), 1939(4·5), 1956(6·4), 1994(7·1), 2018(10)
$[(C_5H_5)Cr(CO)_3]_2SnBr_2$	196—198	28·3	1·5	23·2	28·2	1·5	23·4	62 (h)	1911(2·9), 1936(4·5), 1956(7·1), 1933(7·6), 2018(10)
$[(C_5H_5)Cr(CO)_3]_2SnI_2$	dec. 215	24·2	1·1	32·4	24·4	1·3	32·2	47 (h)	1911(2·7), 1933(4·0), 1956(7·3), 1922(7·7), 2014(10)
$[(C_5H_5)Mo(CO)_3]_2SnF_2$	205—206	29·9	1·5	6·25	29·7	1·6	5·9	50 (h)	1913(4·6), 1939(7·0), 1952(4·5), 1961(4·5), 2008(8·0), 2031(10)
$[(C_5H_5)Mo(CO)_3]_2SnCl_2$	199—201	28·5	1·6	10·8	28·6	1·5	10·6	70 (h)	1916(2·5), 1941(4·5), 1960(4·7), 2010(5·9), 2031(10)
$[(C_5H_5)Mo(CO)_3]_2SnBr_2$	210—213	25·3	1·3	20·9	25·0	1·3	20·9	30 (h)	1916(2·4), 1942(4·1), 1960(5·1), 2009(5·9), 2031(10)
$[(C_5H_5)Mo(CO)_3]_2SnI_2$	217—219	21·9	1·1	29·6	22·2	1·2	29·4	37 (h)	1916(2·0), 1942(3·9), 1960(5·4), 2007(5·8), 2029(10)
$[(C_5H_5)W(CO)_3]_2SnF_2$	244—245	22·3	1·1	5·3	23·4	1·2	4·6	73 (h)	1893(sh), 1906(3·5), 1931(10), 1953(3·5), 2004(3·5), 2022(7·3), 2026(sh)
$[(C_5H_5)W(CO)_3]_2SnCl_2$	226—228	22·3	1·1	8·2	22·2	1·1	8·2	66 (h)	1906(2·8), 1935(broad 4·9), 1951(5·3), 2004(5·5), 2025(10)
$[(C_5H_5)W(CO)_3]_2SnBr_2$	220—222	19·9	1·1	17·2	20·3	1·1	17·0	32 (h)	1906(2·4), 1931(sh), 1936(5·1), 1952(7·2), 2004(5·5), 2027(10)
$[(C_5H_5)W(CO)_3]_2SnI_2$	239—240	18·3	1·3	24·6	18·5	1·0	24·6	70 (h)	1906(2·2), 1933(sh), 1937(4·5), 1951(6·2), 2004(5·6), 2024(10)
$[(C_5H_5)Cr(CO)_3][(C_5H_5)Mo(CO)_3]SnBr_2$	189—190	26·4	1·4	21·9	26·5	1·4	22·1	72 (hi)	1909(1·5), 1915(1·9), 1940(4·5), 1955(4·5), 1962(4·5), 1997(4·8), 2000(sh), 2021(sh), 2027(10)
$[(C_5H_5)Cr(CO)_3][(C_5H_5)Mo(CO)_3]SnI_2$	210—211	23·2	1·3	31·4	23·4	1·3	31·0	25 (hi)	1912(1·5), 1939(4·1), 1957(5·6), 1995(4·5), 2019(sh), 2026(10)
$[(C_5H_5)Cr(CO)_3][(C_5H_5)W(CO)_3]SnF_2$	dec. 200°	26·7	1·4		27·8	1·5		5 (u)	1906(4·1), 1932(7·3), 1944(sh), 1954(6·4), 1984(3·2), 1996(5·0), 2003(4·6), 2020(sh), 2025(10)
$[(C_5H_5)Cr(CO)_3][(C_5H_5)W(CO)_3]SnCl_2$	222—223	26·9	1·5	10·0	26·4	1·4	9·8	72 (hi)	1909(3·0), 1935(5·4), 1955(6·5), 1996(5·4), 2000(sh), 2020(sh), 2026(10)
$[(C_5H_5)Mo(CO)_3][(C_5H_5)W(CO)_3]SnF_2$	222—224	26·4	1·4	5·1	26·2	1·4	5·2	6 (u)	1911(4·9), 1938(8·2), 1950(5·8), 1961(4·6), 2007(8·2), 2029(10)
$[(C_5H_5)Mo(CO)_3][(C_5H_5)W(CO)_3]SnCl_2$	210—212	25·9	1·1	10·5	25·4	1·3	9·4	39 (hi)	1910(sh), 1915(2·5), 1940(5·1), 1954(4·8), 1960(sh), 2008(5·7), 2030(10)
$[(C_5H_5)Mo(CO)_3][(C_5H_5)W(CO)_3]SnBr_2$	219—221	22·9	1·4	18·8	22·4	1·2	18·7	35 (hi)	1906(sh), 1914(2·2), 1941(5·0), 1954(5·6), 1960(sh), 2007(5·4), 2029(10)
$[(C_5H_5)Mo(CO)_3][(C_5H_5)W(CO)_3]SnI_2$	226—228	20·1	1·0	27·1	20·2	1·1	26·8	21 (hi)	1909(sh), 1914(2·3), 1942(4·7), 1953(5·4), 1960(sh), 2006(5·2), 2027(10)
$[(C_5H_5)Cr(CO)_3][(C_5H_5)Fe(CO)_2]SnCl_2$	148—151	31·2	1·9	12·2	31·7	1·8	12·5	30 (hi)	1909(4·2), 1915(sh), 1940(2·4), 1954(1·3), 1965(1·0), 1977(3·4), 1994(9·8), 2019(sh), 2026(10)
$[(C_5H_5)Mo(CO)_3][(C_5H_5)Fe(CO)_2]SnCl_2$	154—156	28·9	1·5	11·2	29·4	1·7	11·6	49 (hi)	1917(5·5), 1920(sh), 1949(3·7), 1961(2·1), 1977(4·1), 1980(sh), 2007(5·8), 2028(10)
$[(C_5H_5)W(CO)_3][(C_5H_5)Fe(CO)_2]SnCl_2$	160—163	25·4	1·6	10·0	25·7	1·5	10·0	43 (hi)	1909(3·6), 1914(sh), 1940(2·2), 1978(3·6), 1981(sh), 2004(5·9), 2028(10)

[a] dec. = Decomposes without melting. [b] X = Halogen. [c] (u) = Yield from u.v. irradiation reaction; (h) = Yield from thermal reaction; (hi) = yield from the second step of ' indirect ' thermal reaction (see text). [d] I.r. spectra measured in carbon disulphide solution. Peak positions (cm^{-1}) with relative peak heights in parentheses.

bonded to the same tin atom, $[(\pi\text{-}C_5H_5)M(CO)_3][(\pi\text{-}C_5H_5)M'(CO)_3]SnX_2$ could not be obtained from the direct thermal reaction of $(\pi\text{-}C_5H_5)_2MM'(CO)_6$ with tin(II) halides. For example $[(\pi\text{-}C_5H_5)_2MoW(CO)_6]$ and $SnCl_2$ (1 : 1) in n-butanol gave a mixture of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnCl_2$ and its tungsten counterpart. Some of the desired reactions are best brought about by u.v. irradiation of the reaction mixture as is described in the next section.

The mixed metal compounds may be prepared by the reactions between $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ and $[(\pi\text{-}C_5H_5)M'(CO)_3SnX_3]$ (1 : 1) in n-butanol. In this way we have obtained $[(\pi\text{-}C_5H_5)Cr(CO)_3][(\pi\text{-}C_5H_5)Mo(CO)_3]SnX_2$ (X = Br and I), and $[(\pi\text{-}C_5H_5)Cr(CO)_3][(\pi\text{-}C_5H_5)W(CO)_3]SnCl_2$ starting from $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ and the appropriate trihalogenotin derivative; $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnX_2$ from $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3SnX_3]$ (reaction times = 20 min, 1 h, and 1 h when X = Cl, Br, and I respectively); $[(\pi\text{-}C_5H_5)Mo(CO)_3][(\pi\text{-}C_5H_5)W(CO)_3]SnX_2$ from $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $[(\pi\text{-}C_5H_5)W(CO)_3SnX_3]$ (reaction times 3 h, 1 h, and 1 h when X = Cl, Br, and I respectively); and $[(\pi\text{-}C_5H_5)W(CO)_3]_2SnX_2$ from $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ and $[(\pi\text{-}C_5H_5)W(CO)_3SnX_3]$ (reaction times = 2·5 and 3 h when X = Br and I respectively). When $[\pi\text{-}C_5H_5M(CO)_3SnCl_3]$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (1 : 1) in tetrahydrofuran are heated, $[(\pi\text{-}C_5H_5)Fe(CO)_2][(\pi\text{-}C_5H_5)M(CO)_3]SnCl_2$ are obtained. The reaction times are 120 h, 12 h, and 88 h for M = Cr, Mo, and W respectively. The chromium complex may also be prepared from $[(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3]$ and $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ in tetrahydrofuran. The reaction is completed within 30 min.

U.v. Irradiation Reactions.—All reactions were carried out in acetone using $[(\pi\text{-}C_5H_5)M(CO)_3]_2 : SnX_2$ mole ratios of 1 : 10. Under the influence of the u.v. lamp, the temperatures of the reaction mixtures reached *ca.* 50 °C. In all instances, except where X = F, reaction times were *ca.* 30 min.

No intermediates could be detected in the reactions of tin(II) fluoride. The $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnF_2$ complexes were the only products, obtained in very low yields as extensive decomposition occurred. The reaction times were 30 min, 2 h, and 3 h for M = Cr, Mo, and W respectively. The mixed dimers $[(\pi\text{-}C_5H_5)_2M'W(CO)_6]$ gave only $[(\pi\text{-}C_5H_5)M'(CO)_3][(\pi\text{-}C_5H_5)W(CO)_3]SnF_2$. Reaction times were 30 min and 2·5 h for M′ = Cr and Mo respectively.

All three $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ complexes formed $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnCl_2$ compounds as the major products with tin(II) chloride, but the yields were lower than for the thermal reactions. Small amounts of the $[(\pi\text{-}C_5H_5)M(CO)_3SnCl_3]$ derivatives may also be detected by i.r. spectroscopy (M = Cr, Mo, and W). $[(\pi\text{-}C_5H_5)_2M'W(CO)_6]$ gave $[(\pi\text{-}C_5H_5)M'(CO)_3][(\pi\text{-}C_5H_5)W(CO)_3]SnCl_2$ as the only important products (M′ = Cr and Mo).

Unlike the thermal reactions, the u.v. irradiation reactions between $SnBr_2$ or SnI_2 and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ or $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ do not give any of the $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnX_2$ complexes. The $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$ derivaare the principal products and may be isolated in higher yields than from the thermal reactions. When X = I, some $[(\pi\text{-}C_5H_5)M(CO)_3I]$ may also be isolated (M = Mo and W). $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ gives mixtures of the mono- and dichromium complexes. $[(\pi\text{-}C_5H_5)Cr(CO)_3SnBr_3]$, $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2SnBr_2$, $[(\pi\text{-}C_5H_5)Cr(CO)_3SnI_3]$, and $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2SnI_2$ were isolated in yields of 18, 25, 47, and 11% respectively. The binuclear compound $[(\pi\text{-}C_5H_5)_2MoW(CO)_6]$ and SnI_2 gave a complex mixture of products. These were separated into two fractions which were shown by i.r. spectroscopy, to be mixtures of $[(\pi\text{-}C_5H_5)Mo(CO)_3SnI_3]$ and $[(\pi\text{-}C_5H_5)W(CO)_3SnI_3]$, and of $[(\pi\text{-}C_5H_5)Mo(CO)_3I]$ and its tungsten analogue.

DISCUSSION

The results are consistent with the proposal that the $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ complexes, like $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$,[10] react on heating with tin(II) halides, SnX_2, (M = Cr, Mo, and W; X = F, Cl, Br, and I) by two independent routes. The first of these, the 'direct' reaction, involves insertion of the SnX_2 molecule into the M–M bond with the formation of no detectable intermediates. Potentially, all the dimer may be converted to the 'insertion' product $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnX_2$.

The initial stages of the second, or 'indirect', route yields a mixture of $[(\pi\text{-}C_5H_5)M(CO)_3X]$ and $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$ in comparable amounts. When equimolar quantities of the reactants are used, only about half the dimer is consumed. The remainder reacts further with the trihalogenotin derivative to give $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnX_2$ in an overall maximum possible yield of 50%. The $[(\pi\text{-}C_5H_5)M(CO)_3X]$ also formed appears to decompose under the reaction conditions employed. The first step of the 'indirect' route to the 'insertion' compound is slower than the corresponding reaction involving $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, but it is considerably faster than the second step. Thus if a large excess of SnX_2 is present in the reaction mixture, all the dimer is consumed in the first step, and, under the conditions of the reaction, the $[(\pi\text{-}C_5H_5)M(CO)_3X]$ may be converted to $[(\pi\text{-}C_5H_5)M(CO)_3SnX_3]$ so that this could be obtained in yields of up to 100%.

Previously we have noted that in the 'indirect' reactions of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with SnX_2, the tin(II) halide acts as though it were a tin(IV) halide.[10] This applies equally to the present work. In this context it is worth noting that germanium(II) bromide readily disproportionates to germanium(IV) bromide.[11] Our observations may be explained if a similar disproportionation takes place for tin(II) halides, especially the bromide and iodide, but with the tin(II) and tin(IV) in an equilibrium where the former predominates. This implies that some tin(0) is also produced (*cf.* ref. 10). However, decomposition during the reaction has prevented us from detecting any free metal.

The course of the reaction depends on both the halogen, X, and the transition metal, M. The importance of the 'indirect' route appears to increase along the series M = Cr < Mo ~ W and X = F < Cl < Br < I. Thus tin(II) fluoride apparently always undergoes the 'direct' reaction, and $[(\pi\text{-}C_5H_5)M(CO)_3SnF_3]$ derivatives have never been observed. This does not rule out the possibility that part of the reaction proceeds by an 'indirect' route where the second stage is rapid, but, by comparison with the related reactions of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$,[10] we think it unlikely. However, the

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[10] P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1972, 1487.

[11] M. D. Curtis and P. Wolber, *Inorg. Chem.*, 1972, **11**, 431, and references therein.

formation of traces only of [(π-C_5H_5)M$(CO)_3$$SnCl_3$] even when large amounts of tin(II) chloride are used, and the very high yields of the [(π-C_5H_5M$(CO)_3]_2$$SnCl_2$ derivatives, indicate that for $SnCl_2$ the ' indirect ' route is of minor importance. Although $SnBr_2$ and SnI_2 appear to react primarily by the ' indirect ' route with both [(π-C_5H_5)Mo$(CO)_3]_2$ and [(π-C_5H_5)W$(CO)_3]_2$, it is only at SnX_2: [(π-C_5H_5)Cr$(CO)_3]_2$ mole ratios of 10 : 1 that the yields of [(π-C_5H_5)Cr$(CO)_3$$SnX_3$], arising from the ' indirect ' reactions, become appreciable. They are higher for X = I than for X = Br.

The reactions brought about by u.v. irradiation also take place by two routes, but the ' indirect ' ones appear to be more important than for the thermal reactions as the yields of the [(π-C_5H_5)M$(CO)_3$$SnX_3$] derivatives are generally greater. However, the consequences of changes in temperature may be as important as the presence, or absence, of light. Our investigations of the reaction between tin(II) chloride and [(π-C_5H_5)Mo$(CO_3]_2$ indicates that lower temperatures favour the indirect route in the absence of daylight but the direct route in its presence, whilst at higher temperatures, light has no effect.

We were unable to isolate the mixed complex from the thermal reaction of [(π-$C_5H_5)_2$MW$(CO)_6$] with $SnCl_2$. This was probably due to the disproportionation of the initial product to a mixture of the symmetrical compounds under the conditions of the reactions. However the u.v. irradiation of [(π-$C_5H_5)_2$MW$(CO)_6$] with SnF_2 and $SnCl_2$ (M = Cr and Mo) gave the four mixed metal complexes by the ' direct ' insertion reactions, and they did not disproportionate at the lower temperatures involved. On the other hand, the use of tin(II) iodide with [(π-C_5H_5)MoW$(CO)_6$] gave a complex mixture of products which were identified by i.r. spectroscopy as [(π-C_5H_5)Mo$(CO)_3$I], [(π-C_5H_5)Mo$(CO)_3$$SnI_3$], [($\pi$-$C_5H_5$)W$(CO)_3$I], and [($\pi$-$C_5H_5$)W$(CO)_3$$SnI_3$]. This is exactly what would be expected from the first step of an ' indirect ' reaction.

The second step of the ' indirect ' route has been used to prepare mixed complexes of the type [(π-C_5H_5)M$(CO)_3$][(π-C_5H_5)M'$(CO)_3$]SnX_2 and [(π-C_5H_5)M$(CO)_3$][(π-C_5H_5)Fe$(CO)_2$]$SnCl_2$ (M, M' = Cr, Mo, or W). Such compounds might be prepared by either of the two possible routes, *e.g.* starting from [(π-C_5H_5)M$(CO)_3$$SnX_3$] and [($\pi$-$C_5H_5$)M'$(CO)_3]_2$, or from [($\pi$-$C_5H_5$)M'$(CO)_3$$SnX_3$] and [($\pi$-$C_5H_5$)M$(CO)_3]_2$, but this is not always the case. For example, [(π-C_5H_5)Mo$(CO)_3$$SnCl_3$] and [($\pi$-$C_5H_5$)Fe$(CO)_2]_2$ give the anticipated product, [(π-C_5H_5)Fe$(CO)_2$][(π-C_5H_5)Mo$(CO)_3$]$SnCl_2$, but [(π-C_5H_5)Fe$(CO)_2$$SnCl_3$] and [($\pi$-$C_5H_5$)Mo$(CO)_3]_2$ gave [(π-C_5H_5)Mo$(CO)_3]_2$$SnCl_2$. The reactivity of the [(π-C_5H_5)M$(CO)_3]_2$ dimers decreases along the series M = Cr > Mo > W in this reaction.

The i.r. spectra of the products obtained are consistent with their anticipated structures which have *ca.* tetrahedral co-ordination about the tin atoms and the usual (π-C_5H_5)M$(CO)_3$X co-ordination polyhedron (*cf.* [(π-C_5H_5)Mo$(CO)_3$Cl][12]). The frequencies and relative intensities of absorption bands due to the C–O stretching vibrations are summarised in the Table.

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[12] S. Chaiswasie and R. H. Fenn, *Acta Cryst.*, 1968, **B24**, 525.