Preliminary communication

The reactions of tin(II) halides with $[(\pi\text{-Ring})Fe(CO)_2]_2$ complexes (Ring = C_5H_5, MeC_5H_4, or C_9H_7)

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Bonati and Wilkinson showed that tin(II) chloride undergoes an oxidative addition with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ to give $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$[1]. Since then many related reactions have been described which give complexes of this type as the sole product[2].

We now report that $[(\pi\text{-Ring})Fe(CO)_2]_2$ derivatives (Ring = C_5H_5, MeC_5H_4, or C_9H_7) react with SnX_2 (X = F, Cl, Br, or I) to give $(\pi\text{-Ring})Fe(CO)_2X$, $(\pi\text{-Ring})Fe(CO)_2$-$SnX_3$, $[(\pi\text{-Ring})Fe(CO)_2]_2SnX_2$, or $[(\pi\text{-Ring})Fe(CO)_2]_3SnX$ depending on X, the π-bonded ring, the mole ratio of reactants, and the reaction conditions.

For example, when $SnBr_2 \cdot 2H_2O$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (I) (mole ratio = 10/1) are heated in methanol, tetrahydrofuran, or benzene, (I) is consumed rapidly to give $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ (II) and $(\pi\text{-}C_5H_5)Fe(CO)_2SnBr_3$ (III) in comparable amounts. These are the only products, and both have been isolated. During longer reaction times (II) is converted to (III) so that this is the final product (yield > 70%).

When $SnBr_2 \cdot 2H_2O$ and (I) are used in equimolar quantities, the principal final product is $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnBr_2$ (IV). It appears to arise from the reaction (I) + (III) → (II) + (IV) rather than by a direct insertion of $SnBr_2$ into the Fe—Fe bond of (I). This type of reaction has been used to prepare mixed complexes *e.g.* $[(\pi\text{-}C_5H_5)Fe(CO)_2]$-$[(\pi\text{-}MeC_5H_4)Fe(CO)_2]SnBr_2$ (V), and $[(\pi\text{-}C_5H_5)Fe(CO)_2][(\pi\text{-}C_5H_5)Mo(CO)_3]SnCl_2$ (VI)[3], and although rather slow in the three solvents quoted, it is much more rapid in refluxing xylene or light petroleum (100—120°). These solvents have the added advantage that at ca. 120° the second product, *e.g.* (II), decomposes.

Similar results have been obtained for the methylcyclopentadienyl and indenyl complexes, and for reactions with tin(II) iodide although reaction rates differ. However with $SnCl_2$ or SnF_2, (I) yields little or no mono-iron compounds comparable to (II) or (III). Even with large excesses of these tin(II) salts, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ (VII) or $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnF_2$ (VIII) are the only important products (yields 90 and 80% respectively).

If an excess of the dimer, *e.g.* (I), is used, a further reaction occurs to give $[(\pi\text{-}C_5H_5)Fe(CO)_2]_3SnCl$ (IX) or its fluoro analogue (X). It is slow, but takes place more rapidly in xylene. This type of reaction may be used to prepare mixed complexes such as $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2[(\pi\text{-}MeC_5H_4)Fe(CO)_2]SnCl$ (XI), and $[(\pi\text{-}C_5H_5)Fe(CO)_2]$-$[(\pi\text{-}MeC_5H_4)Fe(CO)_2][Bu_3PCo(CO)_3]SnCl$ (XII).

TABLE 1

MELTING POINTS AND INFRARED SPECTRA (1700–2100 cm^{-1}) OF SOME COMPOUNDS DESCRIBED IN THE TEXT

Compound	M.p.[a] (°C)	Absorption bands[b]							
IV	181–182 (d)	1955(2.6)			1975(5.3)	1999(5.5)		2025(10)	
V	122–125	1953(2.5)			1972(5.9)	2000(5.6)		2022(10)	
VII	168–169	1954(2.9)			1974(5.4)	2000(5.4)		2024(10)	
VIII	175–177	1955(4.1)			1974(7.5)	1999(7.5)		2025(10)	
VI	154–156	1916(4.6)	1921(sh)	1946(3.1)	1960(2.5)	1976(4.5)	1982(sh)	2024(7.4)	2028(10)
IX	Dec. 220	1933(sh)	1937(3.5)	1949(4.6)	1973(4.2)	1985(10)	2003(1.8)	2011(2.9)	
X	228–229 (d)	1930(sh)	1934(4.1)	1945(5.3)	1976(3.9)	1983(10)	2001(1.7)	2010(2.3)	
XI	156–159	1933(sh)	1938(3.3)	1948(4.7)	1974(4.3)	1986(10)	2003(2.4)	2010(2.3)	
XII	106–108	1928(3.8)	1946(10)	1951(sh)	1980(6.0)	1991(9.4)	2016(3.8)	2010(3.1)	

^{a}(d) = melts with decomposition; Dec. = decomposes without melting. ^{b}CS$_2$ solution; peak positions (cm^{-1}) with relative peak heights in parentheses.

These reactions often give high yields of the products, and provide a useful synthetic pathway to polymetallic transition metal derivatives of tin, and, perhaps, of other non-transition elements. Many compounds are new *e.g.* (VIII)–(XII), and are probably difficult to prepare in any other way. Melting points and infrared spectra of some of the complexes are given in Table 1.

REFERENCES

1 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 179.
2 J.F. Young, *Advan. Inorg. Radiochem.*, 11 (1968) 91.
3 F. Bonati, S. Cenini and R. Ugo, *J. Chem. Soc. (A)*, (1967) 932.