The Insertion of Tin(II) Halides into Transition Metal–Halogen Bonds

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ALTHOUGH the insertion of tin(II) halides into the metal–chlorine bonds of transition-metal halides is well substantiated,[1] very little is known about the mechanism of this reaction. It has been suggested that the active species in a methanolic solution of tin(II) chloride are free or solvated $SnCl_2$ molecules.[1] An alternative possibility is that the reaction may proceed *via* a displacement of the chloro-group by an $SnCl_3^-$ion in an S_N1 or S_N2 type of reaction.

As an aid in the evaluation of possible mechanisms, the interactions of tin(II) chloride and some π-cyclopentadienylcarbonyl complexes of transition metal iodides have been investigated. π-Cyclopentadienyldicarbonyliodoiron(II) reacts readily with a ten-fold excess of tin(II) chloride in refluxing methanol solution to give an orange–brown product formulated as π-$C_5H_5Fe(CO)_2SnCl_2I,CH_3OH$, m.p. 110°; ν_{CO} = 2040 and 2000 cm.$^{-1}$ in heptane solution.

Under similar conditions, π-cyclopentadienyltricarbonyliodomolybdenum(II) and tin(II) chloride do not react even after two days.

These observations indicate that the π-$C_5H_5Fe(CO)_2I$–$SnCl_2$ reaction does not proceed by the substitution mechanisms as the iodine atom must remain associated with the molecule. A possible course of the reaction would involve the co-ordination of an $SnCl_2$ molecule to the transition metal followed by an intramolecular migration of the iodo-group from the transition metal to the tin atom. As one might expect the formation of a seven co-ordinate intermediate, π-$C_5H_5Fe(CO)_2(SnCl_2)I$, to take place more readily than that of the eight co-ordinate species π-$C_5H_5Mo(CO)_3(SnCl_2)I$, it is not surprising that the insertion reaction proceeds far more slowly for the molybdenum complex than for the iron. It is assumed that both reactions proceed by the same route.

Rate studies are being made on the π-cyclopentadienyldicarbonyliodoiron(II) — tin(II) halide systems in the hope that they may provide further evidence as to the reaction mechanism. Preliminary studies indicate that other π-cyclopentadienyldicarbonyliron(II) derivatives undergo similar insertion reactions with tin(II) halides.

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