Oxidative Addition of Alkyl Halides to Iridium(I) Complexes; the Inversion of Configuration at Carbon

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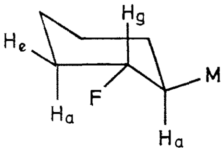
Summary The oxidative addition of an alkyl halide to a d^8 square planar Ir^I complex is shown to proceed with inversion of configuration at carbon.

THE term oxidative addition has been used extensively to classify, with no particular implication of the mechanism involved, a broad range of reactions in which a covalent molecule XY adds to a co-ordinatively unsaturated metal complex.[1] One of the best known examples of this process involves the reactions of certain planar iridium(I) complexes, *e.g.*

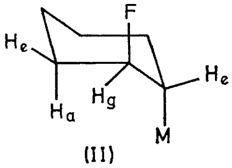
$$XY + trans\text{-}[Ir(PPh_3)_2COCl] \rightarrow [Ir(PPh_3)_2COCl(X)(Y)]$$

where XY can be any one of a variety of molecules such as molecular hydrogen, alkyl and acyl halides, *etc.* In these reactions, cleavage of the XY bond occurs and both the X and Y fragments are found to be co-ordinated separately to the metal in the resultant complex. The mode of cleavage of this bond, however, has not been elucidated. Kinetic studies indicate that these reactions are bimolecular and it was suggested that an S_N2 process might operate.[2] Other studies have been concerned with the resultant stereochemistry about the metal in the product.[3] We report results concerning the change in configuration at carbon when an alkyl halide undergoes an oxidative addition to a metal complex.

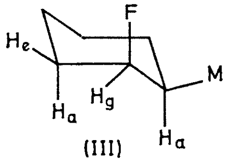
We chose as a substrate *trans*-1-bromo-2-fluorocyclohexane[4] [(Ia) and (IIa)], whose *trans*-configuration was confirmed by study of its ^{19}F spectrum. At 25° (1 : 2 v/v in diethyl ether) the ^{19}F spectrum shows a broad doublet (splitting *ca.* 50 Hz) at +88·3 p.p.m.† On cooling the solution, the spectrum initially broadens and then by −80° two separate resonances have appeared: a doublet at +87·5 p.p.m. [J(F–H$_g$) 48 Hz, intensity *ca.* 5·5] and a broad unresolved resonance centred at +91·5 p.p.m. (intensity *ca.* 1). It is clear that (a) the major conformer in this rapid equilibration process has only one large ^{1}H–^{19}F coupling constant‡ (*ca.* 50 Hz) and (b) this conformer will have bromine in the preferred equatorial position, enabling (Ia) to be assigned as the major conformer which at room temperature rapidly equilibrates with (IIa).



(I)



(II)



(III)

(a) M = Br
(b) M = Ir(PMe$_3$)$_2$(CO)ClBr

The reaction of this substrate with the d^8 complex *trans*-[Ir(PMe$_3$)$_2$COCl] at 25° in dichloromethane solution can be conveniently followed by i.r. and n.m.r. methods. Over several hours the strong, sharp band at 1945 cm^{-1} (ν_{CO}) of the Ir^{I} complex gradually disappears with the concomitant growth of a band at 2030 cm^{-1} characteristic of the Ir^{III} adduct. At the same time the ^{19}F spectrum shows corresponding changes. The resonance at +88·3 p.p.m. due to *trans*-1-bromo-2-fluorocyclohexane decreases while a new signal centred at +64·2 p.p.m. increases in intensity (Figure). This resonance appears as a quartet with peak separation *ca.* 50 Hz.§ Thus three large and comparable ^{1}H–^{19}F couplings occur in the adduct. This pattern is consistent only with structure (IIIb) which has a *cis*-configuration. Moreover, no change in the spectrum of the adduct is observed on cooling the solution. The adduct is thus conformationally stable at room temperature which would be expected for structure (IIIb), which has the bulky metal complex in an equatorial position.

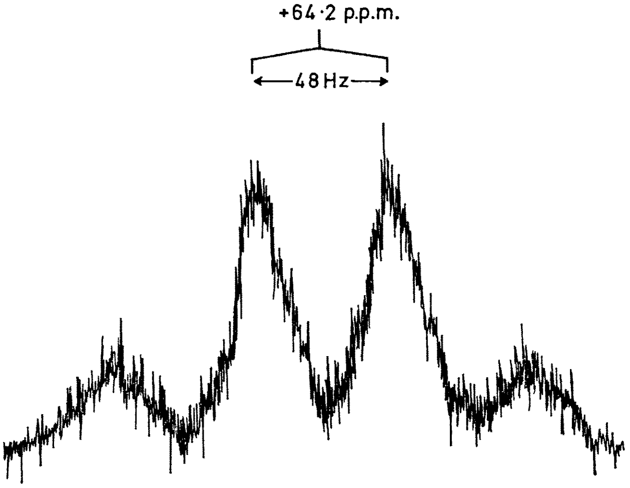


FIGURE. ^{19}F *spectrum of* [Ir(PMe$_3$)$_2$(CO)ClBr(C$_6$H$_{10}$F)] *using an* HA-100 *spectrometer at* 94·1 *MHz with a Varian* C-1024 *time-averaging computer.*

Overall, the oxidative addition of the secondary alkyl halide to the Ir^{I} complex proceeds with inversion of configuration at the carbon centre. This strongly indicates that these reactions follow an S_N2 mechanism, and that the process of oxidative addition is very similar to the nucleophilic displacement reactions of anionic Fe^0 [6] and Co^{I} [7] complexes.

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† Relative to CF$_3$CO$_2$H as external reference.

‡ The values of ^{19}F–^{1}H coupling constants in fluorocyclohexanes are well documented (ref. 5). It is found that J(F–H$_g$) (geminal proton) is *ca.* 50 Hz; J(F$_a$–H$_a$) (with both fluorine and vicinal proton axial) is also *ca.* 50 Hz; all other ^{19}F–^{1}H coupling constants are approximately an order of magnitude smaller (*ca.* 5 Hz).

§ The ^{19}F spectrum measured at 56·4 MHz shows an identical pattern but with small differences in peak spacing, indicating some second order contribution to the spectrum.

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