Cleavage of Aryl Carbon–Hydrogen Bonds in Iridium Triphenyl Phosphite Complexes

By E. W. AINSCOUGH and S. D. ROBINSON*
(*Department of Chemistry, King's College, Strand, London* WC2R 2LS)

Summary Reactions of a wide range of iridium triphenyl phosphite complexes in boiling organic solvents yielding products tentatively formulated with metal–*ortho*-carbon bonds are reported.

RECENT interest in the activation and cleavage of aryl C–H bonds in transition-metal complexes[1,2] prompts this report on the most extensive series of such reactions disclosed to date.

We find that $[IrHCl_2(C_8H_{12})]_2$ reacts with $P(OPh)_3$ in boiling benzene to give $IrHCl_2[P(OPh)_3]_3$ (A) (*ca.* 70% yield) and $IrHCl[P(OPh)_2(OC_6H_4)][P(OPh)_3]_2$ (B) (*ca.* 30% yield); the latter complex is tentatively assigned a metal to *ortho* carbon bonded structure on the evidence outlined below. The formation of complex (B) is thought to involve loss of HCl from $[IrHCl_2(C_8H_{12})]_2$ followed by substitution to give $IrCl[P(OPh)_3]_3$ which immediately undergoes an intramolecular oxidative addition reaction involving cleavage of an *ortho* C–H bond to yield the required product. This reaction sequence is supported by our observation of (B) as the sole hydride containing species derived from the reaction of $[IrCl(C_8H_{12})]_2$ with $P(OPh)_3$ under similar conditions. On heating in boiling decalin, $IrHCl_2[P(OPh)_3]_3$

eliminates HCl (1 mole) and H_2 (1 mole) to yield $IrCl[P(OPh)_2(OC_6H_4)]_2[P(OPh)_3]$ (C);† intermediate formation of $IrCl[P(OPh)_3]_3$ is suggested by the transient development of a yellow coloration at an early stage of the reaction. Formation of complex (C) also occurs when $IrHCl[P(OPh)_2(OC_6H_4)][P(OPh)_3]_2$ is heated in boiling decalin.

$IrCl(CO)[P(OPh)_3]_2$ in boiling decalin undergoes a related intramolecular oxidative addition reaction accompanied by elimination of CO (1 mole) and H_2 (1 mole) to give the dimeric species formulated as $\{IrCl[P(OPh)_2(OC_6H_4)]_2\}_2$ (D). Product mixtures isolated after shorter reaction times or using lower reaction temperatures show spectroscopic evidence for the presence of iridium(III) carbonyl and hydride intermediates [i.r. spectrum (Nujol) ν_{CO} 2060,2080 cm^{-1}; n.m.r. spectrum (C_6D_6) τ 17·98 doublet of doublets, $J(P\text{–}H_{trans})$227Hz; $J(P\text{–}H_{cis})$20Hz.]

Carbon monoxide is readily displaced from $IrCl(CO)[P(OPh)_3]_2$ by excess $P(OPh)_3$ in refluxing acetone solution, replacement of the CO in this manner leads to an increase in electron density at the iridium centre and permits an easy oxidative addition to occur. Thus, under these mild conditions, the product isolated is $IrHCl[P(OPh)_2(OC_6H_4)][P(OPh)_3]_2$ (identical with B). Excess iodide ions also rapidly displace CO from $IrCl(CO)[P(OPh)_3]_2$ and initiate a similar series of oxidative addition reactions in boiling acetone.

$IrH[P(OPh)_3]_4$[3] and $IrH(CO)[P(OPh)_3]_3$, prepared by reaction of $IrH_3(PPh_3)_3$ and $IrH(CO)(PPh_3)_3$ respectively with $P(OPh)_3$, react in boiling decalin to give $IrH[P(OPh)_2(OC_6H_4)]_2[P(OPh)_3]$ (E). The postulated iridium(I) intermediate $Ir[P(OPh)_2(OC_6H_4)][P(OPh)_3]_3$ (F) has not been isolated from this reaction, however, the corresponding rhodium(I) complex $Rh[P(OPh)_2(OC_6H_4)][P(OPh)_3]_3$ (G)‡ is formed on heating $RhH[P(OPh)_3]_4$ in boiling n-heptane and may be isolated and characterised. The isolation of (G) may be attributed in part to the smaller tendency of rhodium(I) to undergo oxidative addition. Complexes A, B, C, and D were isolated as white microcrystalline solids and G as a pale yellow solid; all gave good analytical data. All hydride derivatives were characterised by i.r. and by well-defined, high-field n.m.r. patterns. Evolved gases were analysed chemically (HCl) and by mass spectrometry. The presence of the $P(OPh)_2(OC_6H_4)$ group and its formulation as a bidentate ligand co-ordinating through phosphorus and an *ortho*-carbon atom are supported in each case by the observation of sharp bands at 1100 and 800 cm^{-1} in the i.r. spectra. These well-defined bands do not appear to be typical of *ortho* disubstituted aromatic rings,[4] however they have been reported to occur in the spectra of some related ruthenium(II) triphenyl phosphite complexes[1,5] in which the presence of the *ortho* carbon bonded $P(OPh)_2(OC_6H_4)$ group has been established by deuteriation studies.[1] Confirmatory evidence of structure is being sought by *X*-ray crystallography. Related reactions have been observed with the corresponding bromo- and iodo-complexes and with other phosphites. Similar triaryl phosphite complexes of osmium have also been isolated or characterised in solution by n.m.r. spectroscopy.

We thank Dr. J. J. Levison for preliminary studies.

(*Received, May 4th,* 1970; *Com.* 667.)

---

† At this stage of the investigation we cannot entirely discount the possibility that formation of a second metal–*ortho*-carbon bond involves the same phosphite ligand as the first.

‡ The formation of this complex has been noted previously (ref. 1).

[1] W. H. Knoth and R. A. Schunn, *J. Amer. Chem. Soc.*, 1969, **91**, 2400; G. W. Parshall, W. H. Knoth, and R. A. Schunn, *ibid.*, 4990 and references therein.

[2] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139 and references therein.

[3] D. Giusto, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 767.

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958.

[5] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 639.