Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

The synthesis and structure of bis-μ-(diphenylphosphido)dicarbonylbis(triphenylphosphine)diiridium

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(Received October 16th, 1972)

SUMMARY

The reaction of $IrH(CO)(PPh_3)_3$ in boiling decalin gives a purple crystalline product which X-ray diffraction establishes as $[Ir(PPh_2)(CO)(PPh_3)]_2$, a complex containing a metal–metal bond of length 2.554Å and order two.

Many tertiary phosphine and phosphite complexes of the platinum metals undergo intramolecular aromatic substitution in boiling organic solvents to give products containing metal–*ortho*-carbon bonds[1]. We have previously described[2] particular reactions of this type involving iridium triphenylphosphite complexes and it was of obvious interest to study related triphenylphosphine systems under similar conditions.

A suspension of $IrH(CO)(PPh_3)_3$ in decalin dissolves readily on warming to give a clear orange solution which, on boiling, rapidly (ca. 5 min) turns an opaque red-brown colour and then deposits well-formed purple crystals in ca. 50% yield. The insolubility of these crystals has prevented solution molecular weight studies or NMR investigations; their infrared spectrum (nujol mull) shows only a single, strong band (1920 cm^{-1}) in the region 2500–1600 cm^{-1}.

The crystals are monoclinic with a = 11.499, b = 13.762, c = 16.529Å, β = 96.75°; space group $P2_1/n$; Z = 2. Four-circle diffractometry (Mo-K_α) provided 2986 independent reflexions $[I_{obs}/\sigma(I_{obs}) \geqslant 2.0]$; least squares analysis of atomic coordinates using anisotropic thermal parameters for the iridium and phosphorus atoms and isotropic thermal factors for the remaining carbon and oxygen atoms has converged R to 0.038 [e.s.d.'s average 0.001 (Ir–Ir), 0.002(Ir–P), 0.009(Ir–C), 0.010(P–C) and 0.012Å(C–C and C–O)].

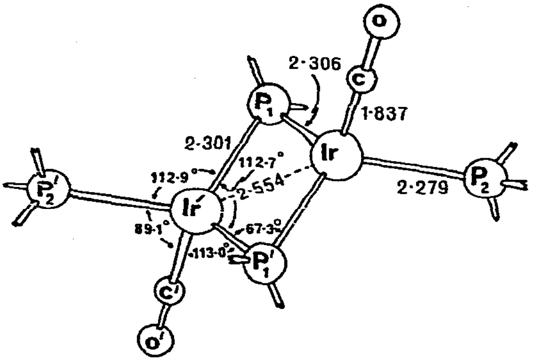

Fig.1. Stereochemical structure of the $[Ir(PPh_2)(CO)(PPh_3)]_2$ complex.

The stereochemistry of the complex, which has C_i symmetry in the crystal, is illustrated in Fig.1. The rare gas rule would imply that four electrons should be allocated to metal–metal bonding and the Ir–Ir bond length of 2.554Å is consistent with this in that the length for unit bond order must be ca. 2.70Å; the acute angles at the bridging phosphorus atoms (67.3°) are also taken as indicative of strong metal–metal interactions.

The isoelectronic ruthenium nitrosyl derivative $[Ru(PPh_2)(NO)(PPh_2Me)]_2$, reported[3] while this communication was in preparation, also has a slightly distorted tetrahedral coordination geometry, with a Ru–Ru bond length of 2.629Å and a Ru–P–Ru bond angle of 69.7(1)°; these data are interpreted in terms of a strong metal–metal interaction corresponding to a formal bond order two.

Attempts to isolate other products from the pyrolysis of $IrH(CO)(PPh_3)_3$ in decalin, and to elucidate the mechanism of the reaction are in progress.

We are grateful to the S.R.C. for special support of our studies in organometallic chemistry.

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