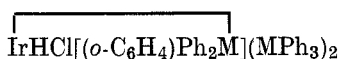


HYDROGEN ABSTRACTION FROM THE COORDINATED LIGAND IN AN IRIIDIUM-TRIPHENYLPHOSPHITE COMPLEX

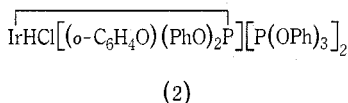
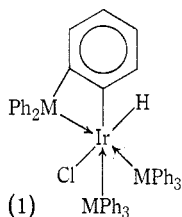
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We have shown¹ that planar iridium(I) complexes of the type $\text{IrCl}(\text{MPh}_3)_3$ ($\text{M} = \text{P, As, or Sb}$) readily isomerize on heating to give iridium(III) hydrides of general formula



the hydrogen atom on the metal being derived from an *ortho*-position of one of the phenyl groups. A metal-carbon σ -bond is formed at the *ortho*-position so as to complete octahedral coordination about the metal. The stereochemistry of the hydrides is as shown in (1). This note records our attempts to study the same phenomenon in the corresponding iridium(I) complex of triphenylphosphite, $\text{P}(\text{OPh})_3$.



Experimental

Infrared spectra in the range $4000\text{--}400\text{ cm}^{-1}$ were measured as liquid films, as benzene or chloroform solutions, or as Nujol mulls on a Perkin-Elmer 225 spectrophotometer. Spectra in the range $450\text{--}200\text{ cm}^{-1}$ were measured as Nujol mulls on the same instrument using either high-density polythene windows or caesium iodide plates. Proton resonance spectra (0–10 p.p.m.) downfield of TMS as internal reference were measured on a Varian Associates HA-100 at 100 MHz. The high field lines were recorded at 60 MHz on a JEOL C60 HL instrument using TMS as internal reference. Microanalyses were carried out at the John Curtin School of Medical Research, A.N.U., (Dr Joyce Fildes and associates) and at the Research School of Chemistry, A.N.U., (Miss Brenda Stevenson and associates). Molecular weights were measured on a Mechrolab vapour pressure osmometer at 25° .

Reaction of Triphenylphosphite with Chlorobis(cyclooctene)iridium(I)

To $\text{IrCl}(\text{C}_8\text{H}_{14})_2$ (0.2 g, 1 mol. propn.) suspended in sodium-dried benzene (5 ml) was added dropwise triphenylphosphite (0.46 g, 3.3 mol. propn.). The yellow suspension dissolved almost immediately to give a colorless solution. Solvent was removed at 15 mm and the residual

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¹ Bennett, M. A., and Milner, D. L., *J. Am. chem. Soc.*, 1969, **91**, 6983.

² Shaw, B. L., and Singleton, E., *J. chem. Soc. (A)*, 1967, 1683.

oil dissolved in sodium-dried ether (5 ml). The solution deposited white crystals after several hours at 0°. Two recrystallizations from ether gave 0.4 g (77%) of white crystals of the triphenylphosphite complex (2), m.p. 146–147° (Found: C, 56.0; H, 3.8; Cl, 2.8; P, 7.9; mol. wt. (CHCl₃), 1149. Calc. for C₅₄H₄₅ClIrO₃P₃: C, 56.0; H, 3.9; Cl, 3.1; P, 8.0%; mol. wt., 1158).

Reaction of Triphenylphosphite with Chlorobis(cyclooctene)rhodium(I)

This was carried out as above, using RhCl(C₈H₁₄)₂³ (1 mol. propn.) and triphenylphosphite (6 mol. propn.). The oil, after recrystallization from methanol or ether, gave yellow crystals of RhCl[P(OPh)₃]₃ identical with those obtained by treating either [RhCl(CO)₂]₂ or [RhCl(1,5-C₈H₁₂)]₂ with P(OPh)₃.^{4,5}

Infrared Spectra between 1400 and 400 cm⁻¹

P(OPh)₃ (liquid film): 1390w, 1330w, 1280w, 1225s, 1200–1180vs, 1160vs, 1100w, 1070s, 1020vs, 1000m, 950sh, 920–850vs, 820s, 775–760vs, 719vs, 685vs, 610m, 593w, 555w, 493vs, 460sh, 440sh.

RhCl[P(OPh)₃]₃ (Nujol mull): 1377vs, 1286m, 1230–1150vs, 1070s, 1025vs, 1005s, 930–880vs, 825s, 780–750vs, 725s, 685vs, 622m, 615–610s, 592vs, 562m, 540w, 495sh, 487vs, 451s, 410w.

Complex (2) (Nujol mull): 1375vs, 1285m, 1240–1150vs, 1120s, 1105s, 1070s, 1038ms, 1025vs, 1005vs, 960–880vs, 820s, 799vs, 780–740vs, 715s, 705s, 685vs, 620sh, 615s, 598–590vs, 570sh, 540w, 490vs(br), 438w (italicized frequencies refer to bands which are clearly absent from the spectra of P(OPh)₃ and RhCl[P(OPh)₃]₃).

Results and Discussion

A general method for preparing planar iridium(I) complexes of the type IrCl(ligand)₃ is to displace cyclooctene from the complex IrCl(C₈H₁₄)₂ with an excess of the ligand.¹ Attempts to prepare the triphenylphosphite complex IrCl[P(OPh)₃]₃ by this method give a colourless, crystalline solid in almost quantitative yield, which is formulated as (2) on the basis of analytical and spectroscopic data. The same complex is obtained by treating IrCl(PPh₃)₃ with three equivalents of triphenylphosphite, and has also been reported briefly and independently of our work as a product of the reaction of triphenylphosphite with the cycloocta-1,5-diene complexes [IrHCl₂(C₈H₁₂)]₂ and [IrCl(C₈H₁₂)]₂, or with IrCl(CO)[P(OPh)₃]₂.⁶ The complex is monomeric in chloroform, and its infrared spectrum shows a band at 2080 cm⁻¹ assignable to ν(Ir–H). In addition to complex aromatic absorption in the region δ 6.6–7.4, the proton n.m.r. spectrum shows a widely spaced pair of 1:2:1 triplets centred at δ –9.75. The infrared frequency, the chemical shift, and the large splitting (*J*_{P,H} 277.5 Hz) are all characteristic of hydrogen *trans* to a phosphorus donor in an octahedral hydroiridium(III) complex,⁷ although *J*_{P,H} is larger than the values generally observed when tertiary phosphines such as PEt₃ are present (130–163 Hz). The 1:2:1 triplet pattern presumably arises from further coupling with two equivalent, strongly coupled, mutually *trans* phosphorus atoms (*J*_{P,H} 18 Hz), which are both *cis* to the hydrogen. This behaviour has been observed previously in hydrides of the type *mer*-IrHX₂L₃ (X = Cl or Br; L = PEt₃ or PEt₂Ph)⁷ (3), and we suggest that the phosphite complex has a similar stereochemistry (2a) with a metal–carbon σ-bond

³ Porri, L., Lionetti, A., Allegra, G., and Immirzi, A., *Chem. Commun.*, 1965, 336.

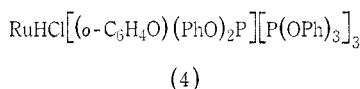
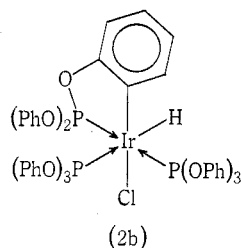
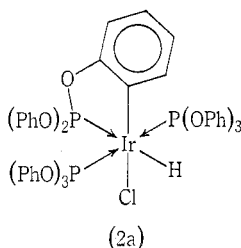
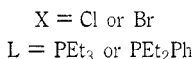
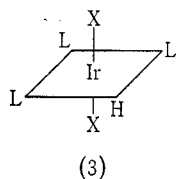
⁴ Vallarino, L., *J. chem. Soc.*, 1957, 2473.

⁵ Haines, L. M., *Inorg. Chem.*, 1970, 9, 1517.

⁶ Ainscough, E. W., and Robinson, S. D., *Chem. Commun.*, 1970, 863.

⁷ Chatt, J., Coffey, R. S., and Shaw, B. L., *J. chem. Soc.*, 1965, 7391.

to the *ortho*-position of one of the phenyl rings. An alternative stereochemistry (2b) cannot be entirely excluded on the basis of the available evidence, because the mutually *trans* phosphorus atoms, although not equivalent, could be equally coupled to the hydrogen atom.



The infrared spectrum of the iridium complex shows strong bands at 1105, 1038, and 800 cm⁻¹ which are absent from the spectra of triphenylphosphite and the rhodium(i) and complex RhCl[P(OPh)₃]₃. Absorptions at 1100 and 800 cm⁻¹ have been observed in the infrared spectrum of the chelate *σ*-phenyl complex (4)^{8,9} which is formed by the reversible loss of hydrogen from RuHCl[P(OPh)₃]₄. In this case, involvement of the *ortho*-position was proved by deuteration studies,⁸ and we assume that the same is true for the iridium complex by analogy with the ruthenium system and with our previous work on IrCl(PPh₃)₃.¹ The far-infrared spectrum of the iridium triphenylphosphite complex shows bands at 312, 291, and 219 cm⁻¹, but we cannot at present make any clear assignment of ν(Ir-Cl) without further study of other complexes of triphenylphosphite.

The initial product of the reaction between IrCl(C₈H₁₄)₂ is probably IrCl[P(OPh)₃]₃ which then undergoes rapid isomerization to the *σ*-phenyl hydride. As pointed out previously,⁹ hydrogen migration and metal-*ortho*-carbon bond formation are likely to occur more readily in triphenylphosphite complexes than in triphenylphosphine complexes, owing to the stability of the chelate five-membered ring compared with that of the strained four-membered ring.

Acknowledgments

We thank Mr. C. Arandjelovic for running the n.m.r. spectra and Johnson Matthey Co. Ltd (England) for a generous loan of iridium salts.

⁸ Parshall, G. W., Knoth, W. H., and Schunn, R. A., *J. Am. chem. Soc.*, 1969, **91**, 4990.

⁹ Levison, J. J., and Robinson, S. D., *J. chem. Soc. (A)*, 1970, 639.