

0277-5387(95)00209-X

COMMUNICATION

TRIS(PENTAFLUOROPHENYL)PHOSPHINE COMPLEXES OF IRIDIUM: MOLECULAR STRUCTURE OF *TRANS*-IrBr(CO) $\{P(C_6F_5)_3\}_2$

JOHN H. HOLLOWAY, ERIC G. HOPE, DAVID R. RUSSELL and GRAHAM C. SAUNDERS*

Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

and

MALCOLM J. ATHERTON

BNFL Fluorochemicals Ltd, Springfields, Salwick, Preston PR4 0XJ, U.K.

(Received 3 March 1995; accepted 1 May 1995)

Abstract—The first tris(pentafluorophenyl)phosphine complexes of iridium, IrX (CO){ $P(C_6F_5)_3$ }₂ (X = Cl, Br), formed by the reaction between IrX₃ and $P(C_6F_5)_3$ in 2-methoxyethanol, are described and the crystal structure of *trans*-IrBr(CO){ $P(C_6F_5)_3$ }₂ is reported.

In contrast to the ubiquity of triphenylphosphine as a ligand in transition metal chemistry, tris (pentafluorophenyl)phosphine has received little attention and only complexes of rhodium,^{1,2} palladium¹ and platinum,^{1,3} and one complex of osmium,⁴ have been reported. The greater bulk and weaker σ -donor ability of P(C₆F₅)₃ compared with those of PPh₃ are expected to lead to transition metal complexes possessing significantly different chemical and physical properties to those of their PPh₃ analogues. We now report the first tris(pentafluorophenyl)phosphine complexes of iridium.

Treatment of $IrCl_3 \cdot 3H_2O$ with an excess of $P(C_6F_5)_3$ in refluxing MeOCH₂CH₂OH yields the tris(pentafluorophenyl)phosphine analogue of

Vaska's complex $IrCl(CO){P(C_6F_5)_3}_2$ (1) in quantitative yield. Complex 1 was characterized by elemental analysis† and ¹⁹F NMR, ³¹P NMR and IR spectroscopies. The ³¹P NMR spectrum shows a single broad resonance at -31.30 ppm, and the ¹⁹F NMR spectrum has three broad resonances at -158.56, -144.67 and -126.20 ppm, assigned to the meta-, para- and ortho-fluorine atoms, respectively. The broad nature of these resonances indicates restricted rotation about the P-C bonds, as has been observed in other transition metal complexes of $P(C_6F_5)_3$.³ The IR spectrum exhibits $v(C \equiv O)$ at 1995 cm⁻¹ and bands characteristic of the $P(C_6F_5)_3$ ligand at 1642, 1522, 1296, 1096 and 986 cm⁻¹. The value of $v(C \equiv O)$ is 40 cm⁻¹ higher than that for $IrCl(CO)(PPh_3)_2$,⁵ indicative of the poorer σ -donor ability of P(C₆F₅)₃ compared with that of PPh₃.6

Treatment of $IrBr_3 \cdot 3H_2O$ with $P(C_6F_5)_3$ in refluxing MeOCH₂CH₂OH yields the bromo analogue of complex 1, $IrBr(CO) \{P(C_6F_5)_3\}_2$ (2), in low yield (<5%). Complex 2 was characterized by ¹⁹F NMR, ³¹P NMR and IR spectroscopies. The ³¹P NMR spectrum displays a broad resonance at

^{*}Author to whom correspondence should be addressed.

[†] Analytical data for 1. Found: C, 34.7; Cl, 2.8; P, 5.2. Calc. for $C_{37}ClF_{30}IrOP_2$: C, 33.7; Cl, 2.7; P, 4.7%. Samples of 1 invariably contained small amounts of $P(C_6F_5)_3$ from which it could not be separated. Thus, satisfactory analysis could not be obtained.

- 34.64 ppm and the ¹⁹F NMR spectrum exhibits three broad resonances at -158.62, -144.76 and -125.50 ppm, assigned to the *meta-*, *para-* and *ortho-*fluorine atoms, respectively. The IR spectrum is similar to that of complex 1, exhibiting $v(C \equiv O)$ at 1996 cm⁻¹.

Complex 2 has been structurally characterized by X-ray crystallography.* The molecular structure is shown in Fig. 1. Unlike the structures of most IrX- $(CO)(PR_3)_2$ complexes, that of 2 shows no disorder of the X and CO ligands. The geometry about the iridium atom is distorted square planar. The P—Ir—P angle is $169.8(1)^{\circ}$ and the Br—Ir—C angle is $175.5(2)^{\circ}$, such that the ligands are displaced in the same direction from square planar geometry. This configuration is forced on the molecule by the bulk of the phosphine ligands. Two of the C_6F_5 rings of each ligand are almost parallel to a plane orthogonal to the respective Ir-P bond, whilst the third lies almost perpendicular to this plane. This leads to two of the fluorine atoms, F(16)and F(46), being close to the iridium atom, at 3.129 and 3.161 Å, respectively. These distances are slightly shorter than the sum of the van der Waals' radii (3.25 Å⁸). The distance between these two fluorine atoms is 2.847 Å. The Ir—C bond length of 1.866(7) is longer by ca 0.08 Å than that found in $IrCl(CO)(PPh_3)_2$,⁹ and the C=O bond length of 1.061(9) Å is shorter by ca 0.10 Å, consistent with the IR spectral data. The Ir-P bond lengths differ

* Crystal data for $C_{37}F_{30}$ IrBrOP₂, **2**: M = 1364.4, triclinic, space group $P\bar{1}$, a = 11.268(3), b = 12.224(3), Å, $\alpha = 75.113(16)$, $\beta = 89.97(2),$ c = 16.019(3) $\gamma = 68.76(2)^\circ$, U = 1977.1(9) Å³, Z = 2, $D_c = 2.292$ Mg m^{-3} , Mo- K_{α} radiation, $\lambda = 0.71073$ Å, μ (Mo- K_{α}) = 4.645 mm^{-1} , F(000) = 1284, T = 293 K. The crystals were yellow prisms. The crystal used for data collection had the dimensions $0.2 \times 0.4 \times 1.0$ mm. The intensities of 10,885 reflections were collected on a Siemens P4/m diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) using an ω -scan technique (range $4 \le 2\theta \le 56^\circ$; $-1 \le h \le 12$, $-15 \le k \le 16$, $-22 \leq l \leq 22$). Three standard check reflections monitored every 100 reflections indicated no crystal decay. The data merged to give 9414 unique reflections $(R_{int} = 0.0123)$ and were corrected for Lorentz and polarization effects to yield 8023 data $[F > 4.0\sigma(F)]$ regarded as observed. A semi-empirical absorption correction was applied to the data with the maximum and minimum transmission factors of 1.0000 and 0.4586, respectively. The structure was solved by direct methods using the TREF option of SHELXTL-pc⁷ and refined by full matrix least squares. All atoms were refined with anisotropic thermal parameters. Final R = 0.0408, $R_{\rm w} = 0.0592 \ [{\rm w}^{-1} = \sigma^2(F) + 0.0013F^2]$ for 649 variables, $(\Delta/\sigma)_{\rm max} = 0.144.$



Fig. 1. Molecular structure of $IrBr(CO) \{P(C_6F_5)\}_2$ (2). Selected bond lengths (Å) and angles (°): Ir-Br 2.460(1), Ir—C(1) 1.866(7), Ir—P(1) 2.289(1), Ir—P(2) 2.279(1), C(1)-O(1) 1.061(9), P(1)-C(11) 1.814(5), P(1) - C(21)1.842(6),P(1) - C(31)1.815(7),P(2)-C(41) P(2) - C(51)1.829(6), 1.831(6), P(2) - C(61)1.838(7);P(1)—Ir—P(2)169.8(1),Br - Ir - C(1)175.5(2), Ir-C(1)-O(1)178.4(5). Ir - P(1) - C(11) = 119.3(2), Ir - P(1) - C(21) = 118.1(2),Ir—P(1)—C(31) 106.7(2), Ir—P(2)—C(41) 119.7(2), Ir—P(2)—C(51) 117.5(2), Ir—P(2)—C(61) 106.3(2).

by 0.01 Å, with a mean value of 2.284 Å, consistent with the values of the Pt-P bond lengths of 2.280(1) and 2.292(6) Å for $PtCl_4{P(C_6F_5)_3}_2^{10}$ and $PtI_{2}{P(C_{6}F_{5})_{3}}_{2}$,¹¹ respectively, but shorter by *ca* 0.05 Å than the Ir—P distances of $IrCl(CO)(PPh_3)_2$. The mean P-C distances for each phosphine ligand are 1.824 and 1.833 Å, such that the shorter mean P-C distance corresponds to the longer Ir-P distance. The C-C bond lengths lie in the range 1.331(13)-1.409(11) Å and the C-F bond lengths lie in the range 1.309(8)-1.372(7) Å, consistent with the C-C and C-F bond lengths of $PtI_{2}{P(C_{6}F_{5})_{3}}_{2}^{11}$ and $P(C_{6}F_{3})_{3}^{12}$ The C—P—C, P—C—C, C—C—C and C—C—F angles are similar to those in $PtI_2{P(C_6F_5)_3}_2$.¹¹

Acknowledgements—We thank Dr R. D. W. Kemmitt for helpful discussion, BNFL Fluorochemicals Ltd for support (to G. C. S.) and Johnson Matthey plc for the generous loan of iridium trichloride.

REFERENCES

- R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, J. Chem. Soc., Chem. Commun. 1967, 2149; R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, J. Chem. Soc. A, 1968, 2149.
- R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, J. Chem. Soc. A 1968, 1898.
- J. B. Docherty, D. S. Rycroft, D. W. A. Sharp and G. A. Webb, J. Chem. Soc., Chem. Commun. 1979, 336.

- H. G. Ang, W. L. Kwik, W. K. Leong and J. A. Potenza, Acta Cryst. 1989, C45, 1713.
- 5. L. Vaska, Science 1963, 140, 809.
- J. Chatt, D. P. Melville and R. L. Richards, J. Chem. Soc. A 1969, 2481.
- 7. SHELXTL-pc, Release 4.2, program package for structure solution and refinement. Siemens Analytical Instruments Inc., Madison, WI (1990).
- 8. R. J. Kulawiec, E. M. Holt, M. Lavin and R. H. Crabtree, *Inorg. Chem.* 1987, **26**, 2559.
- M. R. Churchill, J. C. Fettinger, L. A. Buttrey, M. D. Barkan and J. S. Thompson, J. Organomet. Chem. 1988, 340, 257.
- W. P. Schaefer, D. K. Lyon, J. A. Labinger and J. E. Bercaw, Acta Cryst. 1992, C48, 1582.
- 11. W. N. Hunter, K. W. Muir and D. W. A. Sharp, *Acta Cryst.* 1986, C42, 1743.
- 12. A. Karipidies and C. M. Cosio, *Acta Cryst.* 1989, C45, 1743.