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An Iridium Complex of Tris(2,4,6-trimethoxyphenyl)phosphine

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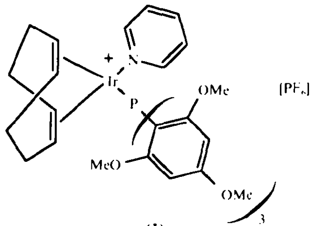
(*Received* 1 *June* 1993; *accepted* 7 *September* 1993)

Abstract

The structure determination of (η^4-1,5-cyclooctadiene)(pyridine)[tris(2,4,6-trimethoxyphenyl)phosphine]iridium(I) hexafluorophosphate, $[Ir(C_{27}H_{33}O_9P)(C_8H_{12})(C_5H_5N)][PF_6]$ revealed approximate square-pyramidal geometry at the Ir atom with one of the methoxy groups of the phosphine ligand being weakly bound in the apical position [Ir$\cdots$O = 2.857 (4) Å].

Comment

We have been interested for some time in the structures and conformation in solution of cationic iridium phosphine complexes, particularly those involving hindered phosphines (Abbassioun, Hitchcock & Chaloner, 1989; Abbassioun, Chaloner & Hitchcock, 1990; Abbassioun, Chaloner, Hitchcock & Koziorowski, 1991; Chaloner, Hitchcock & Reisinger, 1992; Bedford, Chaloner & Hitchcock, 1993). Many such complexes have been used as catalysts for the homogeneous hydrogenation of hindered alkenes (Crabtree, 1979). There has been considerable interest in the use of the basic hindered phosphine tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) (Wada & Higashizaki, 1984) as a ligand in organometallic chemistry and a number of structures of complexes involving this ligand have been determined (Dunbar, Haefner & Pence, 1989; Chen & Dunbar, 1990, 1991; Dunbar, Haefner & Burzynski, 1990; Dunbar, Haefner & Quillevéré, 1990; Haefner, Dunbar & Bender, 1991). The related ligand tris(2,6-dimethoxyphenyl)phosphine may be expected to be equally sterically demanding, but a little less basic.



(I)

The complex (I) was prepared by reaction of $[Ir(cod)(py)_2][PF_6]$, where cod is 1,5-cyclooctadiene and py is pyridine, with tris(2,4,6-trimethoxyphenyl)phosphine (Crabtree & Moorehouse, 1986) and its structure is shown in Fig. 1. The Ir atom adopts a distorted square-pyramidal geometry due to the bulk of the phosphine ligand. There is one short contact between an ether O atom and the metal centre, Ir$\cdots$O = 2.857 (4) Å, and the ether may be described as occupying an approximately apical site in the square-based pyramid. It is relevant to compare this distance with the related parameter in the structure of $[Ir(cod)(py)\{P(C_6H_4\text{-}2,6\text{-}\{OMe\}_2)_3\}][PF_6]$, Ir$\cdots$O = 2.724 (6) Å. We may postulate that

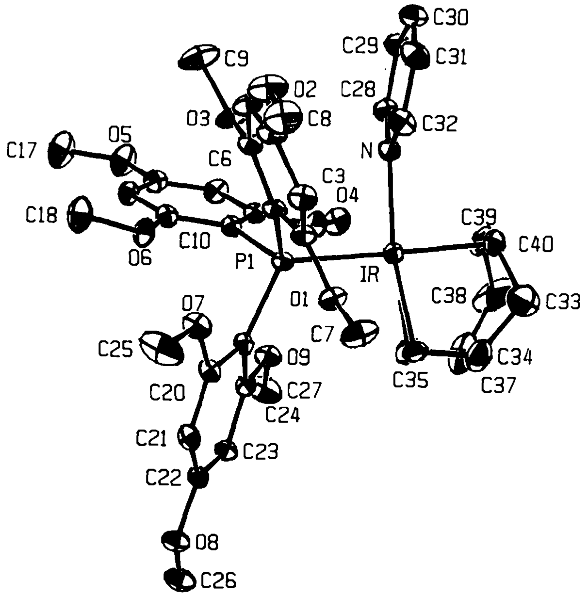


Fig. 1. Molecular structure and atom-numbering scheme of the title compound.

the longer distance in this case might be due to some intermolecular crowding. The metal–oxygen distance is quite long when compared with other related interactions and the relatively long bond between the ether and the metal suggests that this will be labile in solution. The molecule does indeed show interesting fluxional behaviour in its NMR spectra, and this will be reported in detail elsewhere (Avent, Bedford & Chaloner, 1992).

Experimental

Crystal data

$[Ir(C_{27}H_{33}O_9P)(C_8H_{12})(C_5H_5N)][PF_6]$
$M_r = 1057.0$
Monoclinic
$P2_1/n$
$a = 11.282\ (4)$ Å
$b = 18.801\ (4)$ Å
$c = 20.592\ (6)$ Å
$\beta = 94.19\ (3)°$
$V = 4356.1$ Å^3
$Z = 4$

$D_x = 1.61$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7$-$9°$
$\mu = 3.20$ mm^{-1}
$T = 293$ K
Blocks
0.2 × 0.2 × 0.15 mm
Orange-yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.66$, $T_{max} = 1.46$
8260 measured reflections
7855 independent reflections

5296 observed reflections $[|F^2| > 2\sigma(F^2)]$
$R_{int} = 0.026$
$\theta_{max} = 25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 22$
$l = -24 \rightarrow 24$
2 standard reflections
frequency: 60 min
intensity variation: −1.2%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.039$
$S = 1.46$
5296 reflections
532 parameters
H-atom parameters not refined, fixed at calculated positions, $U_{iso}(H) = 1.3 \times U_{eq}(C)$

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Atomic scattering factors from Enraf-Nonius *MolEN* (Fair, 1990) programs

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ir	0.15021 (2)	0.02559 (1)	0.19188 (1)	0.045 (1)
P1	−0.04587 (12)	0.01348 (6)	0.22671 (7)	0.035 (1)
P2	−0.6227 (2)	0.1671 (1)	0.4795 (1)	0.072 (1)
F1	−0.5649 (5)	0.1650 (4)	0.4152 (2)	0.161 (5)
F2	−0.7291 (4)	0.1214 (3)	0.4477 (3)	0.122 (3)
F3	−0.5592 (6)	0.0983 (3)	0.5030 (3)	0.186 (5)
F4	−0.6886 (5)	0.2363 (3)	0.4571 (3)	0.156 (4)
F5	−0.5172 (4)	0.2137 (2)	0.5113 (2)	0.102 (3)
F6	−0.6850 (6)	0.1718 (3)	0.5440 (3)	0.184 (5)
O1	−0.0534 (4)	−0.1023 (2)	0.1378 (2)	0.051 (2)
O2	−0.0578 (5)	−0.2968 (2)	0.2914 (2)	0.080 (3)
O3	−0.0254 (4)	−0.0593 (2)	0.3623 (2)	0.059 (2)
O4	0.1021 (3)	0.1328 (2)	0.2847 (2)	0.051 (2)
O5	−0.1354 (4)	0.1965 (2)	0.4553 (2)	0.083 (3)
O6	−0.2475 (3)	0.0049 (2)	0.3077 (2)	0.056 (2)
O7	−0.2782 (3)	−0.0727 (2)	0.1755 (2)	0.057 (2)
O8	−0.4409 (3)	0.1049 (2)	0.0332 (2)	0.058 (2)
O9	−0.0996 (3)	0.1525 (2)	0.1813 (2)	0.050 (2)
N	0.2184 (4)	−0.0284 (2)	0.2774 (2)	0.048 (2)
C1	−0.0532 (4)	−0.0809 (3)	0.2494 (3)	0.040 (3)
C2	−0.0545 (5)	−0.1302 (3)	0.1989 (3)	0.041 (3)
C3	−0.0575 (5)	−0.2035 (3)	0.2103 (3)	0.053 (3)
C4	−0.0552 (6)	−0.2265 (3)	0.2739 (3)	0.056 (3)
C5	−0.0456 (6)	−0.1803 (3)	0.3251 (3)	0.057 (3)
C6	−0.0425 (5)	−0.1064 (3)	0.3127 (3)	0.045 (3)
C7	−0.0667 (8)	−0.1481 (4)	0.0831 (3)	0.083 (5)
C8	−0.0862 (7)	−0.3470 (3)	0.2418 (4)	0.083 (5)
C9	−0.0300 (9)	−0.0819 (4)	0.4268 (4)	0.102 (6)
C10	−0.0723 (4)	0.0671 (3)	0.2982 (3)	0.038 (3)
C11	0.0043 (5)	0.1230 (3)	0.3193 (3)	0.041 (3)
C12	−0.0193 (5)	0.1648 (3)	0.3718 (3)	0.054 (3)
C13	−0.1207 (6)	0.1515 (3)	0.4036 (3)	0.057 (3)
C14	−0.1985 (5)	0.0992 (3)	0.3844 (3)	0.049 (3)
C15	−0.1743 (5)	0.0569 (3)	0.3315 (3)	0.043 (3)
C16	0.1726 (6)	0.1945 (3)	0.2979 (3)	0.067 (4)
C17	−0.2365 (8)	0.1872 (4)	0.4897 (4)	0.106 (5)
C18	−0.3431 (6)	−0.0177 (4)	0.3429 (4)	0.085 (5)
C19	−0.1761 (4)	0.0370 (3)	0.1714 (3)	0.038 (3)
C20	−0.2718 (5)	−0.0061 (3)	0.1486 (3)	0.042 (3)
C21	−0.3566 (5)	0.0171 (3)	0.1021 (3)	0.048 (3)
C22	−0.3527 (5)	0.0868 (3)	0.0793 (3)	0.044 (3)
C23	−0.2668 (5)	0.1331 (3)	0.1040 (3)	0.044 (3)
C24	−0.1832 (5)	0.1085 (3)	0.1505 (3)	0.040 (3)
C25	−0.3707 (7)	−0.1187 (4)	0.1555 (5)	0.111 (5)
C26	−0.4472 (6)	0.1767 (4)	0.0122 (3)	0.072 (4)
C27	−0.1071 (6)	0.2264 (3)	0.1699 (4)	0.079 (4)
C28	0.2716 (6)	0.0044 (3)	0.3290 (3)	0.053 (3)
C29	0.3384 (6)	−0.0308 (4)	0.3772 (3)	0.067 (4)
C30	0.3491 (6)	−0.1037 (4)	0.3731 (3)	0.069 (4)
C31	0.2921 (6)	−0.1378 (4)	0.3222 (4)	0.075 (4)
C32	0.2272 (6)	−0.1003 (3)	0.2754 (3)	0.063 (4)
C33	0.2872 (9)	−0.0283 (7)	0.0786 (4)	0.206 (8)
C34	0.1680 (7)	−0.0155 (5)	0.0500 (4)	0.090 (5)
C35	0.0910 (5)	0.0288 (4)	0.0910 (3)	0.059 (3)
C36	0.1157 (6)	0.0975 (3)	0.1121 (3)	0.072 (4)
C37	0.2256 (8)	0.1390 (4)	0.0963 (4)	0.115 (6)
C38	0.3309 (9)	0.1229 (7)	0.1350 (5)	0.208 (8)
C39	0.3267 (6)	0.0546 (7)	0.1745 (4)	0.140 (7)
C40	0.3079 (7)	−0.0107 (6)	0.1493 (4)	0.128 (6)

Table 2. *Selected geometric parameters* (Å, °)

*M*1 and *M*2 are the midpoints of the C35—C36 and C39—C40 bonds, respectively.

Ir—P1	2.386 (1)	Ir—N	2.127 (5)
Ir—*M*1	2.022 (8)	Ir—*M*2	2.027 (8)
Ir—C35	2.136 (6)	Ir—C36	2.141 (7)
Ir—C39	2.120 (8)	Ir—C40	2.151 (8)
*M*1—Ir—*M*2	85.3 (2)	*M*1—Ir—N	169.1 (2)
*M*1—Ir—P	97.1 (2)	*M*2—Ir—N	87.0 (2)
*M*2—Ir—P	172.6 (2)	P1—Ir—N	89.6 (1)

We thank the University of Sussex for a bursary (to RBB) and Johnson Matthey PLC for a generous loan of iridium salts.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71618 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1063]

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Acta Cryst. (1994). C**50**, 358–362

Structure du Bis(tétraéthylammonium) Tétrachlorocuprate(II) Hémihydrate, $[(C_2H_5)_4N]_2[CuCl_4].0,5H_2O$

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(*Reçu le* 8 *octobre* 1992, *accepté le* 9 *juillet* 1993)

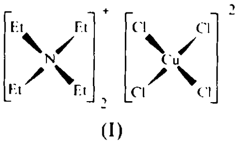
Abstract

The cell of the title compound, $[C_2H_5N]_2[CuCl_4].0.5H_2O$, contains disordered tetraethylammonium ions in a 'swastika' configuration and two non-equivalent $CuCl_4^{2-}$ ions. One $CuCl_4^{2-}$ ion is linked to a water molecule and forms a rigid group having approximate square-based-pyramidal geometry. This group is disordered around a fourfold axis.

Commentaire

De nombreux travaux sur les transitions de phases dans les solides font référence à des composés de la famille A_2BX_4 où A est un cation, B un métal et X un halogène. En particulier, les composés contenant un tétraméthylammonium $[(CH_3)_4N]^+$ ou un tétraméthylphosphonium $[(CH_3)_4P]^+$ (notés respectivement TMA et TMP par la suite), comportent des séquences de phase qui présentent des propriétés physiques intéressantes {ferroélectricité, ferroélasticité, transitions commensurable-incommensurable: $[(CD_3)_4N]_2[CuCl_4]$ (Asahi, Hasebe & Gesi, 1988; Hasebe, Asahi, Tanisaki & Gesi, 1988); $(TMA)_2[FeCl_4]$ (Ruiz-Larrea, Lopez-Echarri & Tello, 1988); $(TMA)_2[ZnCl_4]$ (Le Bihan, Averty, Hilczer & Szczepanska, 1989); $(TMA)_2[BCl_4]$, B = Mn, Fe et Cu (Gesi, 1989); $[(CH_3)_4Z]_2[BX_4]$, Z = P, As et Sb, B = Co, Cu et Zn, X = Cl, Br et I (Pressprich, Bond & Willet, 1991); $[(CH_3)_4P]_2[CuBr_4]$ (Saint Grégoire, Almairac, Astito, Lapasset & Moret, 1991)}. Par contre, la série de composés semblables où A est un tétraéthylammonium $[(C_2H_5)_4N]^+$ (noté TEA dans la suite) a suscité moins d'études structurales, bien que ces composés présentent des séquences de transitions de phase aussi riches que dans les $(TMA)_2[BX_4]$. Par exemple, les composés $(TEA)_2[BCl_4]$ et $(TEA)_2[BBr_4]$, où B = Co, Mn, Cu, Zn et Cd, présentent de nombreuses transitions dans le domaine de température 77–300 K (Uehara, Iimura, Shimizu, Morita, Yoshifuji, Tsuchiya, Imai, Uemori, Nakagawa & Kyuno, 1984; De, Ghosh & Ray Chaudhuri, 1986; Ghosh, De & Chaudhuri, 1986; Wolthuis, Huiskamp, De Jongh & Carlin, 1986; Kahrizi & Steinitz, 1989, 1990).

Les quelques études structurales effectuées sur ces composés montrent que la majorité des $(TEA)_2[BX_4]$ ont, à la température ambiante, un groupe d'espace commun $P4_2/nmc$, des paramètres de valeurs semblables (Tableau 1), et possèdent des organisations isomorphes. Ces structures sont constituées d'anions BX_4^{2-}, de géométrie pseudo-tétraèdrique, et de cations TEA désordonnés. Le $(TEA)_2[CuCl_4]$, par son groupe d'espace différent ($P4/n$) ainsi que par la valeur de ses paramètres, constitue une exception dans cette série de composés (Tableau 1). La raison de cette anomalie a pu être trouvée dès la cristallogénèse. Nous avons montré que le produit étudié, identique à celui cité dans la littérature, comportait en réalité une demi molécule d'eau par groupement formulaire. Cette étude concerne donc le composé $[(C_2H_5)_4N]_2[CuCl_4].0,5H_2O$ (I).



(I)

Acta Crystallographica Section C
ISSN 0108-2701 © 1994