

cis-Dicarbonyl-*cis*-dichlorido-*trans*-bis(triphenylphosphine- κP)iridium(III)-tetrafluoridoborate, formed by reaction of (cycloocta-1,5-diene)-bis(triphenylphosphine)iridium tetrafluoridoborate with carbonyl fluoride in dichloromethane solution

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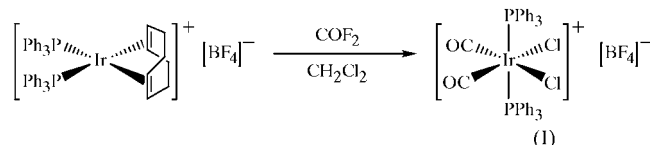
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The reaction between carbonyl fluoride and $[\text{Ir}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$ (COD is cycloocta-1,5-diene) in dichloromethane solution affords the novel title iridium salt, $[\text{IrCl}_2(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{CO})_2]\text{BF}_4$. The cation lies across a twofold rotation axis in the space group $P2_12_12$ and its structure confirms the presence in a *cis* relationship of two metal-bound chlorides, while the phosphine ligands occupy a *trans* pair of sites. The anion also lies across a twofold rotation axis, and the F atoms are disordered over two sets of sites.

Comment

Late transition metal complexes are increasingly being exploited in carbon–fluorine bond cleavages, and the resulting metal–fluoro complexes often exhibit interesting reactivities. Much research has focused on the use of nickel-containing systems (Cornin *et al.*, 1997; Schaub & Radius, 2005), as these have been shown to exhibit remarkable chemoselectivity (Sladek *et al.*, 2002). The viability of homogeneous rhodium-catalysed carbon–fluorine bond activation is well established (Aizenberg & Milstein, 1994, 1995), and carbon–fluorine bond scission using iridium is not unprecedented (Kulawiec *et al.*, 1987). Theoretical studies indicate that carbon–fluorine bond activation at Ir^{I} should be facile (Su & Chu, 1997), and many examples of carbon–fluorine bond activation using other platinum group metals now exist (Braun *et al.*, 2002; Garratt *et al.*, 2005; Torrens, 2005). As part of our ongoing studies into low-valent metal–fluoro complexes, we investigated carbon–fluorine bond activation using $[\text{Ir}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$. Herein, we report the reaction between carbonyl fluoride and $[\text{Ir}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$.

Carbonyl fluoride, on reaction at room temperature with a stirred solution of $[\text{Ir}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$ in dichloromethane, generated a significant amount of precipitate. Removal of all volatiles *in vacuo* yielded an air-sensitive solid, and isolation and purification of this afforded the product, $[\text{IrCl}_2(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4$ (I). Each of the ions lies across a twofold rotation axis. The coordination environment of the iridium is essentially octahedral (Fig. 1), with two *cis*-Cl ligands each *trans* to a CO ligand, so that the two phosphine ligands are *trans* to one another. The tetrafluoridoborate counter-ion exhibits substantial disorder. The absence of a metal-bound fluoride in (I) is surprising and suggests that, if a fluoro complex was initially formed, the fate of the metal-bound fluoride lay in halide exchange with the chlorinated solvent. NMR studies of the crude reaction mixture lends credence to this, with a number of resonances ascribed to varying degrees of solvent fluorination being observed. However, it should be stressed that no spectroscopic evidence for a metal-bound fluoride was observed; the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture indicated quantitative formation of (I).



Although (I) is isoelectronic and isostructural with the well known complexes $[\text{OsCl}_2(\text{CO})_2\text{L}_2]$ (L = phosphine), little work involving either cationic iridium halide or hydride complexes has been reported. Indeed, (I) represents the first iridium carbonyl phosphine chloride complex to be crystallographically characterized, and is one of only a handful of charged iridium halide complexes employing both PPh_3 and CO that have been isolated. Complexes similar to (I) have, however, been observed in iridium hydride chemistry; it has been reported (Malatesta *et al.*, 1974) that reaction of

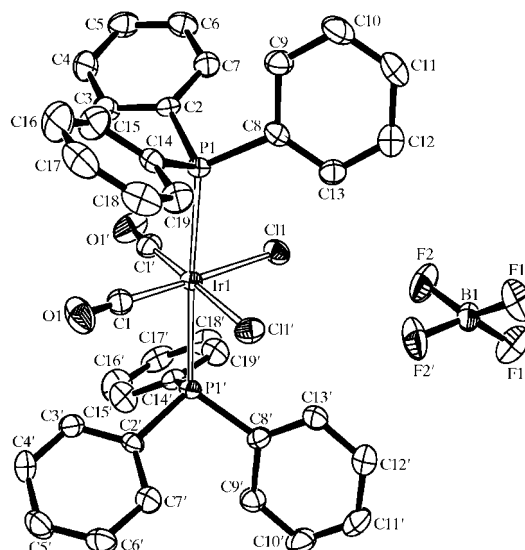


Figure 1
View of the components of (I), shown with 50% probability ellipsoids. H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, z$.]

[Ir(CO)₃(PPh₃)₂] with HClO₄ resulted in the formation of the cation [IrH₂(CO)₂(PPh₃)₂]⁺, while a range of complexes of the type [IrH₂L₂(CO)₂]⁺ (L = phosphine) have also been isolated (Mays *et al.*, 1970). The formation of [IrI₂(CO)₂(PPh₃)₂]⁺ has been inferred (Malatesta *et al.*, 1970), but it could not be purified. Arguably the closest crystallographically characterized comparators to (I) are [IrCl₂(CO)(PEt₃)₂(SOCl)] (Blake *et al.*, 1992), and the isostructural complex [OsCl₂(CO)₂(PEt₃)₂] (Clark *et al.*, 1999). As expected, the metal–phosphine bond lengths in [IrCl₂(CO)(PEt₃)₂(SOCl)] [2.4257 (8) Å] and [OsCl₂(CO)₂(PEt₃)₂] [2.4048 (11) Å] are close to those observed in (I) [2.4258 (8) Å]. The metal–chloride bond lengths of (I) are, however, slightly shorter [2.3629 (8) Å] than those of the isoelectronic [OsCl₂(CO)₂(PEt₃)₂] complex [2.444 (1) Å], indicating a slightly stronger metal–chloride interaction in (I), as expected from the cationic nature of the complex.

Experimental

[Ir(COD)(PPh₃)₂]BF₄ (100 mg, 0.110 mmol) dissolved in dichloromethane (4 ml) was cooled to 195 K and placed under 1100 Torr (1 Torr = 133.322 Pa) of COF₂. The solution was warmed to room temperature and stirred for 3 d whilst the uptake of COF₂ was measured tensimetrically. After removal of the volatiles *in vacuo*, the resulting dark solid was washed twice with cold THF (0.5 ml, 258 K), and the dark solution carefully decanted at 258 K, to afford the product [IrCl₂(CO)₂(PPh₃)₂]BF₄, (I), as an air-sensitive white solid in 32% yield. *m/z* (+ FAB): 815 ([M – BF₄ – CO]⁺), 787 ([M – BF₄ – 2CO]⁺), 751 ([M – BF₄ – 2CO – Cl]⁺), 715 ([M – BF₄ – 2CO – 2Cl]⁺). ¹H (CD₂Cl₂): δ 7.91–7.40 (*m*, 30H, ArH); ¹⁹F{¹H} NMR (CD₂Cl₂): δ –149.7 (*s*), ³¹P{¹H} (CD₂Cl₂): δ –16.2 (*s*). *v*_{max}/cm^{–1} (solid): 2016 (*s*, CO), 1483 (*s*), 1432 (*s*), 1070 (*s*, [BF₄][–]), 683 (*s*). Single crystals of (I) suitable for X-ray diffraction were grown by slow vapour diffusion of hexane into a saturated dichloromethane solution of (I).

Crystal data

[IrCl ₂ (C ₁₈ H ₁₅ P) ₂ (CO) ₂]BF ₄	<i>V</i> = 1753.63 (14) Å ³
<i>M_r</i> = 930.47	<i>Z</i> = 2
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2	Mo <i>K</i> α radiation
<i>a</i> = 11.2488 (5) Å	<i>μ</i> = 4.11 mm ^{–1}
<i>b</i> = 14.6091 (7) Å	<i>T</i> = 150 (2) K
<i>c</i> = 10.6711 (5) Å	0.20 × 0.16 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer	15288 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	4021 independent reflections
<i>T</i> _{min} = 0.504, <i>T</i> _{max} = 0.637	3873 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.044

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.022	Δρ _{max} = 1.47 e Å ^{–3}
<i>wR</i> (<i>F</i> ²) = 0.046	Δρ _{min} = –0.50 e Å ^{–3}
<i>S</i> = 0.99	Absolute structure: Flack (1983),
4021 reflections	1721 Friedel pairs
246 parameters	Flack parameter: –0.015 (5)
H-atom parameters constrained	

All H atoms were treated as riding atoms in geometrically idealized positions, with C–H distances of 0.95 Å and *U*_{iso}(H) values of 1.2*U*_{eq}(C). The F atoms of the tetrafluoroborate ion, which lies across a twofold rotation axis, were found to be disordered over two sets of sites. Free refinement of the two possible positions for F1 and F2 gave final occupancies of 0.50 (3) for each, in the positions shown in Fig. 1.

Table 1

Selected geometric parameters (Å, °).

Ir1–C1	1.911 (4)	C1–O1	1.116 (4)
Ir1–Cl1	2.3629 (8)	B1–F1	1.318 (8)
Ir1–P1	2.4258 (8)	B1–F2	1.361 (7)
C1–Ir1–C1 ⁱ	97.9 (2)	Cl1–Ir1–P1	87.52 (3)
Cl1–Ir1–Cl1 ⁱ	94.77 (5)	O1–C1–Ir1	173.8 (3)
C1–Ir1–P1	90.08 (9)		

Symmetry code: (i) –*x* + 1, –*y* + 1, *z*.

At the end of the refinement, the largest residual electron-density peak in the Fourier difference map was located 0.97 Å from Ir1.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97, PLATON (Spek, 2003), WinGX (Farrugia, 1999) and enCIFer (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3114). Services for accessing these data are described at the back of the journal.

References

- Aizenberg, M. & Milstein, D. (1994). *Science*, **265**, 359–361.
- Aizenberg, M. & Milstein, D. (1995). *J. Am. Chem. Soc.* **117**, 8674–8675.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Blake, A. J., Cockman, R. W. & Ebsworth, E. A. V. (1992). *Acta Cryst.* **C48**, 1658–1660.
- Braun, T., Noveski, D., Neumann, B. & Stammer, H.-G. (2002). *Angew. Chem. Int. Ed.* **41**, 2745–2748.
- Bruker (1998). SMART (Version 5.0) and SAINT (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.
- Clark, H. C. S., Coleman, K. S., Fawcett, J., Holloway, J. H., Hope, E. G., Redding, J. & Russell, D. R. (1999). *Polyhedron*, **18**, 1207–1210.
- Cornin, L., Higgitt, C. L., Karch, R. & Perutz, R. N. (1997). *Organometallics*, **16**, 4920–4928.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Garratt, S. A., Hughes, R. P., Kovacic, I., Ward, A. J., Willemsen, S. & Zhang, D. (2005). *J. Am. Chem. Soc.* **127**, 15585–15594.
- Kulawiec, R. J., Holt, E. M., Carin, M. & Crabtree, R. H. (1987). *Inorg. Chem.* **26**, 2559–2561.
- Malatesta, L., Angoletta, M. & Caglio, G. (1970). *J. Chem. Soc. A*, pp. 1836–1840.
- Malatesta, L., Angoletta, M. & Caglio, G. (1974). *J. Organomet. Chem.* **73**, 265–275.
- Mays, M. J., Church, M. J., Simpson, R. N. F. & Stefanini, F. P. (1970). *J. Chem. Soc. A*, pp. 2909–2914.
- Schaub, T. & Radius, U. (2005). *Chem. Eur. J.* **11**, 5024–5030.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). SADABS. Version 2.10. University of Göttingen, Germany.
- Sladek, M. I., Braun, T., Neumann, B. & Stammer, H.-G. (2002). *J. Chem. Soc. Dalton Trans.* pp. 297–299.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Su, M.-D. & Chu, S.-Y. (1997). *J. Am. Chem. Soc.* **119**, 10178–10185.
- Torrens, H. (2005). *Coord. Chem. Rev.* **249**, 1957–1985.