metal-organic papers

David Benito-Garagorri,[a] Karl Kirchner[a] and Kurt Mereiter[b]*

[a]Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, A-1060 Vienna, Austria, and [b]Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164SC, A-1060 Vienna, Austria

Correspondence e-mail: kurt.mereiter@tuwien.ac.at

Key indicators

Single-crystal X-ray study
$T = 298$ K
Mean σ(C–C) = 0.011 Å
R factor = 0.046
wR factor = 0.124
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Tetraphenylphosphonium acetonitriletribromoferrate(II)

The title compound, $[P(C_6H_5)_4][FeBr_3(CH_3CN)]$, contains an anionic tetrahedral iron complex arranged in layers between $[P(C_6H_5)_4]^+$ cations. The Fe, one Br, one N and two C atoms have site symmetry m, and the P atom has site symmetry 2.

Comment

cis-[Fe(CO)$_4$Br$_2$], a readily available substance (Hieber & Bader, 1928; Robertson *et al.*, 2000), reacts with various nucleophiles with the release of CO and the consequent formation of iron complexes that are otherwise difficult to obtain. Using this substance, the title compound, (I), was obtained.
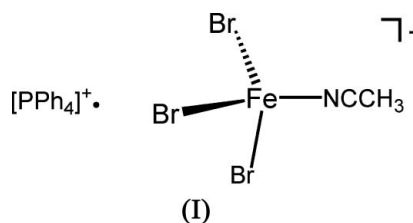
Compound (I) crystallizes in the uncommon space group *Ama*2, and contains an [Fe(CH$_3$CN)Br$_3$]$^-$ anion, with the divalent Fe^{II} atom (site symmetry m) in a tetrahedral coordination (Fig. 1). The mean Fe—Br bond length is 2.404 (3) Å (Table 1). In general, tetrahedral bond angles around Fe vary considerably, but the data for (I) show the expected trend that Br—Fe—Br angles are large and Br—Fe—N angles small. Only a very few [M(CH$_3$CN)X_3]$^-$ complexes (M = divalent transition metal and X = F, Cl, Br or I) have been studied to date by X-ray diffraction analysis. The only other iron compound reported so far contains an [Fe(CH$_3$CN)Cl$_3$]$^-$ anion and an (η^4-2,3-dimethylbutadiene)tricarbonylcobalt(I) cation (Macgregor *et al.*, 1991). It features a geometry similar to the anion in (I), except that, as expected, the Fe—Cl bonds are some 0.15 Å shorter than the Fe—Br bonds in (I). Further anions comparable with (I) are [Zn(CH$_3$CN)X_3]$^-$ (X = Cl or Br; Yoshioka *et al.*, 2001), [Co(CH$_3$CN)Cl$_3$]$^-$ (e.g. Cotton *et al.*, 1998; Hartung *et al.*, 1992) and [Co(CH$_3$CN)Br$_2$Cl]$^-$ (Rabe & Müller, 2001), while Pd and Pt complexes of analogous composition have square-planar coordination (e.g. Muir *et al.*, 1986).

The PPh$_4$ cation in (I) shows the usual geometric features. As pointed out by Müller (1980), PPh$_4$ cations tend to adopt approximate point symmetry $\bar{4}$ in the solid state and to form columns with intracolumnar P···P distances of 7–8 Å and eclipsed juxtaposition of the phenyl rings in order to gain stabilizing C—H—π interactions. PPh$_4$ cations are therefore
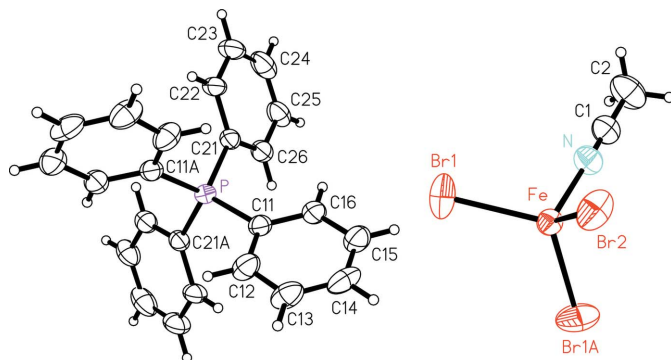
Figure 1
A perspective view of (I). Displacement ellipsoids are drawn at the 30% probability level. Atoms Fe, Br2, N, C1 and C2 are on a mirror plane. Atom Br1A is generated by the symmetry operation $(\frac{1}{2} - x, y, z)$ and the C11A and C21A rings by $(-x, 1 - y, z)$.
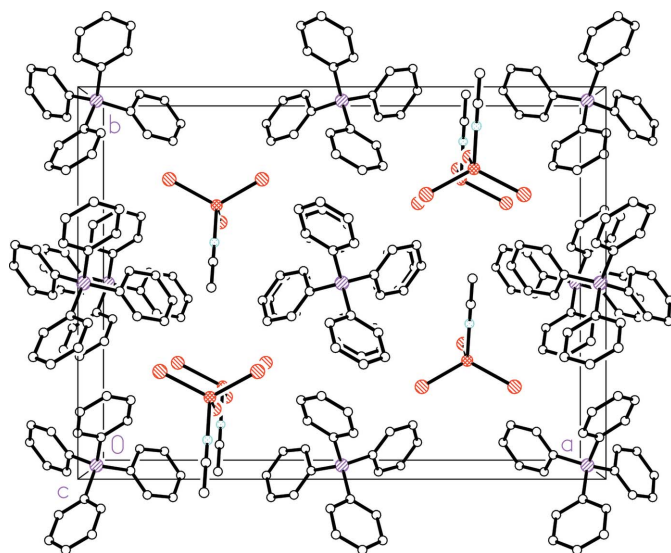

Figure 2
A packing diagram for (I), viewed down c.

structure-directing and inclined to form tetragonal lattices. Such PPh_4 columns are indeed present in (I) along b, but instead of generating a tetragonal lattice, they adopt a layered orthorhombic arrangement which alternates with layers of $[Fe(CH_3CN)Br_3]^-$ anions (Fig. 2). A search of the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002) showed that this architecture combined with space group $Ama2$ was encountered for three other structures with PPh_4 cations and anionic complexes similar in shape to $[Fe(CH_3CN)Br_3]^-$ (Bernard *et al.*, 2004; Finze *et al.*, 2004).

Experimental

cis-$Fe(CO)_4Br_2$ (1 g, 3.05 mmol) (Robertson *et al.*, 2000) was suspended in acetonitrile (50 ml) and stirred under a light Ar stream until CO evolution ended. The volume of the solution was reduced under vacuum to 10 ml, after which a solution of PPh_4Br (1.3 g, 3.05 mmol) in acetonitrile (20 ml) was added, and the mixture was stirred at room temperature for 10 min. Upon addition of Et_2O

(20 ml), a white solid precipitated, which was collected on a glass frit, washed twice with Et_2O and dried under vacuum (yield 649 mg, 64%). Colourless crystals of (I) suitable for X-ray diffraction analysis were obtained by allowing Et_2O to diffuse slowly into a saturated solution of the complex in acetonitrile under Ar.

Crystal data

$(C_{24}H_{20}P)[FeBr_3(C_2H_3N)]$	$Z = 4$
$M_r = 676.00$	$D_x = 1.662$ Mg m^{-3}
Orthorhombic, $Ama2$	Mo $K\alpha$ radiation
$a = 22.3226$ (17) Å	$\mu = 5.07$ mm^{-1}
$b = 16.5842$ (13) Å	$T = 298$ (2) K
$c = 7.2972$ (6) Å	Block, colourless
$V = 2701.4$ (4) Å^3	$0.26 \times 0.23 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	7937 measured reflections
φ and ω scans	2425 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	1946 reflections with $I > 2\sigma(I)$
$T_{min} = 0.25$, $T_{max} = 0.40$	$R_{int} = 0.030$
	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 2.3554P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.124$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.67$ e Å^{-3}
2425 reflections	$\Delta\rho_{min} = -0.45$ e Å^{-3}
154 parameters	Absolute structure: Flack (1983), with 1100 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.001 (17)

Table 1
Selected geometric parameters (Å, °).

Fe—N	2.090 (10)	Fe—Br2	2.4005 (17)
Fe—Br1	2.4058 (10)		
N—Fe—Br1	103.50 (13)	Br1—Fe—Br1^i	116.55 (7)
N—Fe—Br2	110.3 (2)	Br1—Fe—Br2	111.13 (4)

Symmetry code: (i) $-x + \frac{1}{2}, y, z$.

All H atoms were placed in calculated positions (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(carrier).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT*; data reduction: *SAINT*, *SADABS* and *XPREP* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernard, R., Cornu, D., Perrin, M., Scharff, J.-P. & Miele, P. (2004). *J. Organomet. Chem.* **689**, 2581–2585.
Bruker (2003). *SMART* (Version 5.625), *SAINT* (Version 6.36), *SADABS* (Version 2.10), *SHELXTL* (Version 6.10) and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cotton, F. A., Daniels, L. M., Jordan, G. T. IV & Murillo, C. A. (1998). *Polyhedron*, **17**, 589–597.

Finze, M., Bernhardt, E., Willner, H. & Lehmann, C. W. (2004). *Angew. Chem. Int. Ed.* **43**, 4160–4163.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hartung, J., Beyer, L., Gutierrez-Puebla, E., Fernandez, V. & Olk, B. (1992). *Z. Naturforsch. Teil B*, **47**, 183–186.

Hieber, W. & Bader, G. (1928). *Chem. Ber.* **61**, 1717–1722.

Macgregor, S. A., Yellowlees, L. J. & Welch, A. J. (1991). *Acta Cryst.* C**47**, 536–539.

Muir, M. M., Gomez, G. M. & Muir, J. A. (1986). *Acta Cryst.* C**42**, 1699–1701.

Müller, U. (1980). *Acta Cryst.* B**36**, 1075–1081.

Rabe, S. & Müller, U. (2001). *Z. Anorg. Allg. Chem.* **627**, 742–746.

Robertson, E. W., Wilkin, O. M. & Young, N. A. (2000). *Polyhedron*, **19**, 1493–1502.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Yoshioka, K., Kikuchi, H., Mizutani, J. & Matsumoto, K. (2001). *Inorg. Chem.* **40**, 2234–2239.