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1-Ferrocenylmethyl-3-(2,4,6-trimethylbenzyl)-1*H*-imidazolidin-3-ium iodide and *trans*-bis(3-benzyl-1-ferrocenylmethyl-1*H*-imidazolidin-2-ylidene)diiodidopalladium(II)

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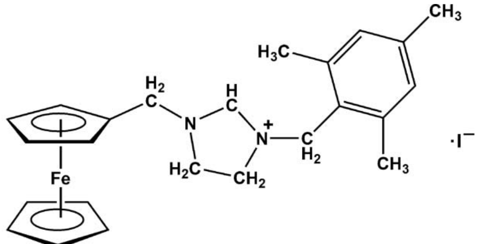
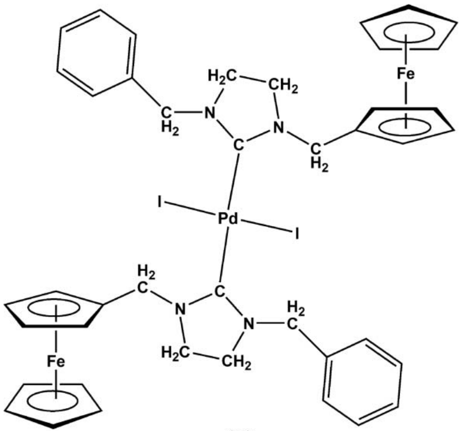
Owing to increasing interest in the use of N-heterocyclic carbenes (NHCs) based on imidazolidinium ions as ligands in the design of highly efficient transition-metal-based homogeneous catalysts, the characterizations of the 1-ferrocenylmethyl-3-(2,4,6-trimethylbenzyl)imidazolidin-3-ium iodide salt, $[Fe(C_5H_5)(C_{19}H_{24}N_2)]I$, (I), and the palladium complex *trans*-bis(3-benzyl-1-ferrocenylmethyl-1*H*-imidazolidin-2-ylidene)diiodidopalladium(II), $[Fe_2Pd(C_5H_5)_2(C_{16}H_{17}N_2)_2I_2]$, (II), are reported. Compound (I) has two iodide anions and two imidazolidinium cations within the asymmetric unit ($Z' = 2$). The two cations have distinctly different conformations, with the ferrocene groups orientated *exo* and *endo* with respect to the N-heterocyclic carbene. Weak C—H donor hydrogen bonds to both the iodide anions and the π system of the mesitylene group combine to form two-dimensional layers perpendicular to the crystallographic *c* direction. Only one of the formally charged imidazolidinium rings forms a near-linear hydrogen bond with an iodide anion. Complex (II) shows square-planar coordination around the Pd^{II} metal, which is located on an inversion centre ($Z' = 0.5$). The ferrocene and benzyl substituents are in a *trans–anti* arrangement. The Pd—C bond distance between the N-heterocyclic carbene ligands and the metal atom is 2.036 (7) Å. A survey of related structures shows that the lengthening of the N—C bonds and the closure of the N—C—N angle seen here on metal complexation is typical of similar NHCs and their complexes.

Comment

In recent years, N-heterocyclic carbenes (NHCs) based on imidazolidinium ions have emerged as useful ligands in the design of highly efficient transition metal-based homogeneous catalysts (Peris & Crabtree, 2004; Cavell & McGuinness, 2004; Glorius, 2007; Sommer & Weck, 2007; Gonzalez *et al.*, 2009; Melaimi *et al.*, 2010). Ferrocenyl-substituted carbenes are interesting compounds because of the influence of the metallocenyl groups with respect to steric protection, electron donation and reversible redox chemistry. Pioneered by Bildstein *et al.* (1998), this expanding field (Bildstein, 2001) contains a broad range of NHCs (Bildstein, Malaun, Kopacka, Ongania & Wurst, 1999; Bildstein, Malaun, Kopacka, Wurst *et al.*, 1999; Jackstell *et al.*, 2002; Demirhan *et al.*, 2003; Bertoog *et al.*, 2005; Siemeling *et al.*, 2009; Varnado *et al.*, 2009), including derivatives with additional donor groups (Yuan *et al.*, 2005; Gischig & Togni, 2005; Labande *et al.*, 2007; Gülcemal *et al.*, 2009) that can be used as multidentate ligands. Such ferrocenyl-substituted carbene ligands have been shown to be effective in transition-metal-catalysed reactions. Some ferrocenyl-substituted NHCs derived from imidazolin-2-ylidene and benzimidazol-2-ylidene have also been structurally characterized by Bildstein and co-workers (Bildstein *et al.*, 1998; Bildstein, Malaun, Kopacka, Ongania & Wurst, 1999; Bildstein, Malaun, Kopacka, Wurst *et al.*, 1999).



(I)



(II)

Recently, we reported the synthesis and electrochemistry (Demirhan *et al.*, 2003) of the title salt 1-ferrocenylmethyl-3-(2,4,6-trimethylbenzyl)-1*H*-imidazolidin-3-ium iodide, (I), and the title complex *trans*-bis(3-benzyl-1-ferrocenylmethyl-1*H*-imidazolidin-2-ylidene)diiodidopalladium(II), (II). The latter is derived from the 1-ferrocenylmethyl-3-benzylimidazolium iodide salt (Demirhan *et al.*, 2003). The ferrocene imidazolidinium salt, (I), can be shown to act as an anion receptor and is used in preparing chiral carbene ligands and their complexes. In complex (II), the ferrocenylmethyl group acts as a pendant group on the N atom of imidazolidin-2-ylidene. This is a new

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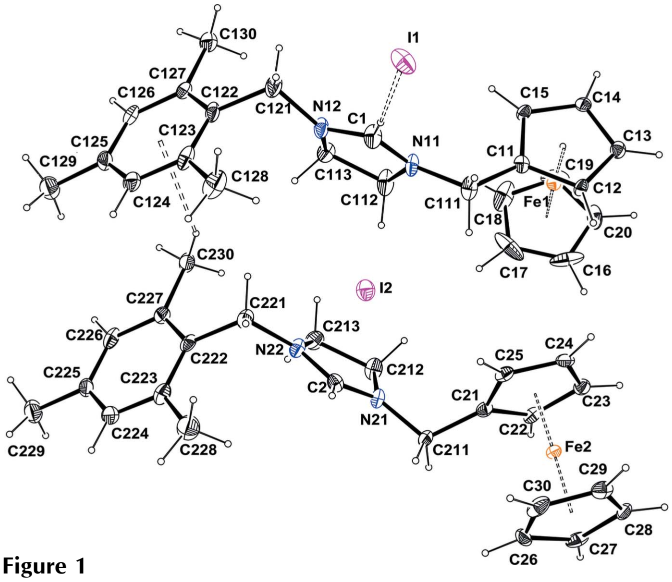

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate C—H$\cdots$I and C—H$\cdots\pi$ interactions.

ferrocenyl-substituted carbene and it is hoped that it may prove useful, given its potential applications in homogenous catalysis and electrocatalysis. Initially, the compounds were isolated as microcrystalline solids that were not suitable for structure determination through X-ray diffraction. After several unsuccessful attempts, X-ray quality crystals were obtained and we report here the crystal structures of (I) and (II).

In compound (I), the asymmetric unit contains two 1-ferrocenylmethyl-3-(2,4,6-trimethylbenzyl)-1*H*-imidazolidin-3-ium cations and two iodide anions ($Z' = 2$, see Fig. 1). The value of the Flack parameter (Flack, 1983) refined to 0.22 (2), and this is normally taken to indicate the occurrence of a twin by inversion. The two cations have different conformations, as is clearly shown in the molecular overlap representation in Fig. 2. In molecule *A*, the N-heterocyclic carbene ring is oriented somewhat *endo* with respect to atom Fe1 and the cyclopentadienyl (Cp) ring to which it is attached, whereas in molecule *B* it is *exo* with respect to atom Fe2 and the related Cp ring. This is clearly shown by the positions of atoms N11 and N21 with respect to the mean planes of the C11–C15 and C21–C25 Cp rings, *viz.* −0.124 (9) Å out of plane for N11 and 1.045 (9) Å for N21. This difference in conformation is also reflected in the C12—C11—C111—N11 and C22—C21—C211—N21 torsion angles, with values of −168.5 (4) and −111.8 (5)°, respectively. The two imidazolidinium rings deviate slightly from planarity, with the largest deviations from the least-squares mean planes being 0.047 (3) and −0.060 (3) Å for methylene atoms C112 and C212, respectively. Thus, the two imidazolidinium groups, N11—C1—N12—C112—C113 and N21—C2—N22—C212—C213, display slightly twisted conformations on, respectively, the C112—C113 bond [puckering parameters Q_2 = 0.079 (5) Å and φ_2 = 313 (4)°; Cremer & Pople, 1975; Evans & Boeyens, 1989] for molecule *A* and the C212—C213 bond [puckering parameters Q_2 = 0.102 (5) Å and φ_2 = 133 (3)°] for molecule *B*. The conformation of molecule *B* of (I) is closely related to that of the salt 1-ferrocenylmethyl-3-benzylimidazolium iodide (Hua *et al.*, 2004). The C—C and C—N distances within the imidazolidinium rings agree with the values observed in this latter salt and with values found in the literature for related Fc-containing compounds (Cambridge Structural Database, *ConQuest*, Version 1.13; Allen, 2002), as can be seen in Table 1. However, it is interesting to note that the N—C—N angles of 114.5 (4) and 113.6 (4)° in (I) are generally larger than the range found for these related species (108.1–113.9°).

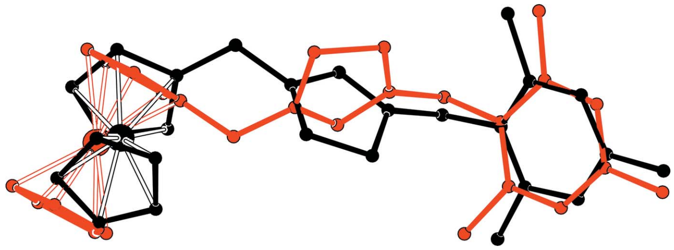

Figure 2
An overlay view, showing the differing molecular geometries of the two independent molecules of (I). The molecule shown in black is molecule *A* and that shown in grey (red in the electronic version of the paper) is molecule *B*.

The least-squares planes of the mesitylene rings and imidazolidinium cations of (I) make dihedral angles of 79.94 (14) and 65.52 (14)° in molecules *A* and *B*, respectively. The bond lengths and angles within the ferrocene moiety are within expected limits. The Cp rings of the Fc groups are slightly twisted away from the ideal eclipsed conformation [by 8.5 (6) and 6.7 (5)°, respectively; mean values calculated from the five possible C—*Cg*—*Cg*—C torsion angles, where *Cg* are the centroids of the Cp rings] and they are also slightly bent, making dihedral angles between the rings of 5.1 (3)° for molecule *A* and 1.9 (3)° for molecule *B*. The displacement parameters for the Cp ring that contains atom C16 indicate some rotational movement, which decreases the accuracy of the geometric parameters associated with this group.

The more pronounced bending for molecule *A* might be related to the rather short and linear C—H$\cdots$I interaction between the carbene and the iodide anion (Table 2). There is no such linear hydrogen-bonding interaction for the *B* cation. Atom C2 does in fact make a closer contact with the iodide anion [3.541 (4) Å in molecule *B* and 3.811 (5) Å in molecule *A*], but only the linear interaction of molecule *A* gives a short H$\cdots$I distance.

The packing within the crystal structure of (I) is governed by weak C—H$\cdots$I and C—H$\cdots\pi$ interactions. The latter involve the centroids of rings C16–C20 (*Cg*1), C122–C127 (*Cg*2) and C26–C30 (*Cg*3) (Table 2), and thus act as a link between cations. All these weak interactions combine to give a layered structure parallel to the (001) plane (Fig. 3).

Compound (II) has a crystallographically imposed centrosymmetric molecular geometry ($Z' = 0.5$), with the Pd1-atom position occupying a centre of symmetry. It shows the expected square-planar coordination with *trans* carbene ligands (Fig. 4). Indeed, the ferrocenylmethyl and benzyl

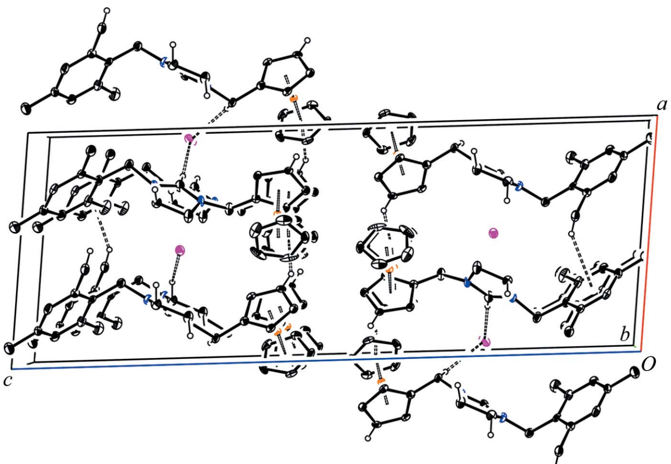

Figure 3
A partial packing view for (I), along the *b* direction, showing the formation of layers parallel to the (001) plane through C—H···I and C—H···π interactions (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

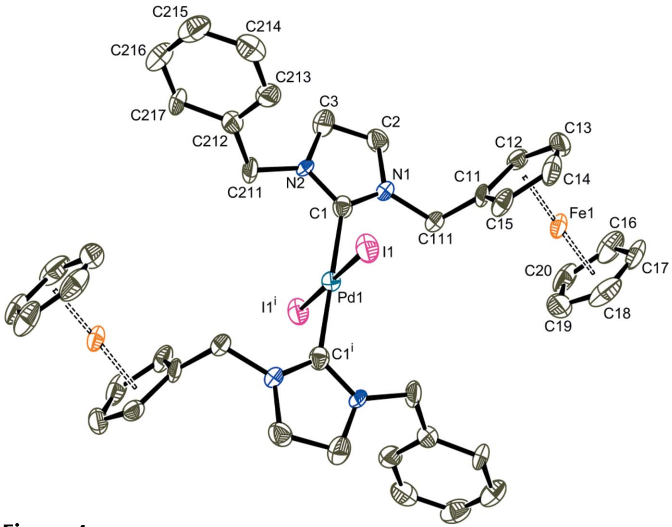

Figure 4
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

substituents in (II) are in a *trans–anti* arrangement. The imidazolidine rings are twisted with respect to the square-planar coordination arrangement by 87.4 (3)°. This is similar to what is observed in other imidazolin-2-ylidene–Pd^{II} complexes. The Cp rings of the Fc group are much more staggered than in (I), with a rotation angle of 33.3 (6)°. They are also slightly bent, as shown by the dihedral angle between the two Cp ring planes of 1.6 (5)°. The bond lengths and angles within the ferrocene moiety are within expected limits. The Pd1—C1 distance of 2.036 (7) Å and the Pd1—I1 distance of 2.6168 (6) Å are also as observed for related square-planar Pd^{II} complexes (Bildstein *et al.*, 1998; Bertoog *et al.*, 2005; Huynh & Wu, 2009).

The carbene-centred N1—C1—N2 ring angle in (II) is 108.4 (6)°. This is within the range of values observed for other NHC–metal complexes, but as with (I) it is at the high end of the range [103.3 (11)–108.4 (12)°; see Table 3]. It is noted that the other large angles are also observed for complexes that contain iodide ligands. The literature survey also shows that coordination of the carbene C atom to metal results, as expected, in a lengthening of the C—N bonds [ranging from 1.329 (8) Å in (II) to 1.41 (2) Å] compared with the free ligands [ranging from 1.292 (5) Å in (I) to 1.339 (9) Å] (Tables 1 and 3). In both (I) and (II), the C—N carbene bond involving the N atom attached to the ferrocene moiety through the methylene bridge is significantly shorter than the C—N bond involving the N atom attached to the mesitylene or phenyl groups. This slight difference is certainly related to an electronic effect caused by the proximity of the electron-rich ferrocene moiety.

Experimental

The syntheses and spectroscopic characterizations of the title compounds have been detailed in the study by Demirhan *et al.* (2003). Crystals of (I) and (II) were grown from methanol–diethyl ether (1:5 *v*/*v*) and dichloromethane–diethyl ether (1:3 *v*/*v*) solvent mixtures, respectively.

Compound (I)

Crystal data

$[Fe(C_5H_5)(C_{19}H_{24}N_2)]I$
$M_r = 528.24$
Monoclinic, $P2_1$
$a = 10.6277\ (12)$ Å
$b = 7.4514\ (8)$ Å
$c = 28.293\ (3)$ Å
$\beta = 95.603\ (9)°$

$V = 2229.8\ (4)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.07$ mm^{-1}
$T = 180$ K
0.44 × 0.29 × 0.03 mm

Data collection

Oxford Xcalibur diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.654$, $T_{max} = 0.964$

19193 measured reflections
10405 independent reflections
7372 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.064$
$S = 0.84$
10405 reflections
512 parameters
1 restraint

H-atom parameters constrained
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}
Absolute structure: Flack (1983), with 4503 Friedel pairs
Flack parameter: 0.220 (15)

Compound (II)

Crystal data

$[Fe_2Pd(C_5H_5)_2(C_{16}H_{17}N_2)_2I_2]$
$M_r = 1076.71$
Monoclinic, $P2_1/n$
$a = 9.5185\ (16)$ Å
$b = 11.7851\ (17)$ Å
$c = 17.569\ (2)$ Å
$\beta = 92.835\ (12)°$

$V = 1968.5\ (5)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.78$ mm^{-1}
$T = 180$ K
0.17 × 0.07 × 0.06 mm

Data collection

Oxford Xcalibur diffractometer
Absorption correction: multi-scan (Blessing, 1997)
$T_{min} = 0.727$, $T_{max} = 0.797$

14178 measured reflections
3890 independent reflections
2082 reflections with $I > 2\sigma(I)$
$R_{int} = 0.084$

Table 1

Comparison of selected C—N distances (Å) and N—C—N angles (°) within the diaminocarbene moiety for Fc-bearing ligands related to (I).

Compound	N—C	C—N	N—C—N	Reference
(I), molecule *A*	1.294 (5)	1.325 (6)	114.5 (4)	This study
(I), molecule *B*	1.292 (5)	1.311 (5)	113.6 (4)	This study
$C_{21}H_{21}FeIN_2$	1.321 (4)	1.317 (4)	109.0 (3)	*a*
$C_{18}H_{17}BF_4FeN_2$	1.332 (5)	1.312 (5)	110.9 (3)	*b*
$C_{19}H_{19}FeIN_2\cdot H_2O\cdot 0.25CH_3OH$	1.339 (9)	1.335 (9)	109.9 (8)	*c*
$C_{25}H_{25}Fe_2IN_2$	1.317 (5)	1.329 (5)	109.0 (3)	*c*
$C_{47}H_{41}BFe_2N_2$	1.334 (5)	1.325 (5)	108.4 (4)	*d*
$C_{23}H_{23}F_6Fe_2N_2P$	1.304 (3)	1.304 (3)	113.9 (3)	*d*
$C_{25}H_{25}Fe_2IN_2$	1.327 (3)	1.332 (3)	108.6 (2)	*e*
$C_{23}H_{21}Fe_2IN_2$	1.329 (8)	1.329 (8)	108.4 (8)	*e*
$C_{59}H_{39}F_{24}Fe_2N_2P_2\cdot I\cdot CH_2Cl_2$	1.336 (8)	1.325 (7)	109.3 (5)	*f*
$C_{26}H_{36}Cl_2FeN_4\cdot CH_2Cl_2$	1.325 (7)	1.326 (7)	108.1 (5)	*g*
$C_{28}H_{28}B_2F_8FeN_4$	1.351 (5)	1.327 (6)	109.6 (4)	*h*
$C_{27}H_{26}BF_4FeN_2PS$	1.324 (5)	1.313 (5)	108.6 (3)	*i*
$C_{27}H_{26}BF_4FeN_2PS$	1.317 (3)	1.309 (4)	109.7 (3)	*i*
$C_{40}H_{38}BF_4FeN_2P$	1.321 (3)	1.331 (3)	110.5 (2)	*j*
$(C_{30}H_{33}FeIN_2)_2$	1.321 (6)	1.321 (6)	110.4 (6)	*j*

References: (*a*) Hua *et al.* (2004); (*b*) Bildstein, Malaun, Kopacka, Ongania & Wurst (1999); (*c*) Bildstein *et al.* (1998); (*d*) Bildstein, Malaun, Kopacka, Wurst *et al.* (1999); (*e*) Bertoog *et al.* (2005); (*f*) Gischig & Togni (2005); (*g*) Coleman *et al.* (2005); (*h*) Varnado *et al.* (2009); (*i*) Labande *et al.* (2007); (*j*) Gülcemal *et al.* (2009).

Table 2

Hydrogen-bond geometry (Å, °) for (I).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C16–C20, C122–C127 and C26–C30 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···I1	0.95	2.87	3.811 (5)	173
C113—H11*E*···I1$^{\rm i}$	0.99	2.98	3.878 (5)	152
C211—H21*B*···I1$^{\rm ii}$	0.99	2.96	3.877 (5)	154
C212—H21*C*···I1$^{\rm iii}$	0.99	2.95	3.797 (5)	145
C213—H21*E*···I2$^{\rm i}$	0.99	2.99	3.860 (6)	148
C24—H24···*Cg*1$^{\rm iv}$	0.95	2.90	3.688 (5)	141
C230—H23*C*···*Cg*2	0.98	2.90	3.781 (5)	150
C14—H14···*Cg*3$^{\rm v}$	0.95	2.70	3.579 (5)	154

Symmetry codes: (i) $x, y+1, z$; (ii) $x-1, y, z$; (iii) $x-1, y+1, z$; (iv) $x, y-1, z$; (v) $x+1, y+1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.091$
$S = 0.85$
3890 reflections
232 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.71$ e Å^{-3}

All H atoms were placed in geometrically idealized positions and treated as riding, with C—H = 0.98 (methyl), 0.99 (methylene) or 0.95 Å (aromatic), and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic and methylene H atoms or 1.5$U_{\rm eq}$(C) for methyl H atoms.

In molecule *A* of (I), the C atoms of the unsubstituted Cp ring display rather elongated displacement ellipsoids, but attempts to model a disordered system did not improve the quality of the refinement. Moreover, the anistropic displacement parameters for all the disordered C atoms were unrealistic and needed to be severely restrained using EADP commands (*SHELXL97*; Sheldrick, 2008). Thus, the nondisordered model was preferred.

Table 3

Comparison of the C—N distances (Å) and N—C—N angles (°) in (II) with those in related complexes found in the literature.

Compound	N—C	C—N	N—C—N	Reference
(II)	1.329 (8)	1.350 (8)	108.4 (6)	This study
$C_{23}H_{16}FeN_2O_5W$	1.384 (7)	1.366 (6)	104.0 (4)	*a*
$C_{40}H_{32}Fe_2N_4O_4W\cdot CH_2Cl_2$	1.41 (2)	1.36 (2)	103.7 (11)	*a*
$C_{34}H_{26}Fe_2N_2O_5W$	1.350 (2)	1.357 (14)	103.3 (11)	*b*
$C_{58}H_{52}Fe_4I_2N_4Pd\cdot 4CH_2Cl_2$	1.355 (9)	1.354 (9)	106.0 (6)	*b*
$C_{38}H_{36}Fe_2Hg_2I_4N_4$	1.348 (10)	1.338 (10)	106.4 (6)	*b*
$C_{70}H_{60}AgBFe_4N_4\cdot 0.5CHCl_3\cdot 1.5MeOH$	1.364 (5)	1.354 (5)	103.8 (3)	*c*
	1.369 (5)	1.350 (5)	104.1 (3)	*c*
$C_{43}H_{39}Fe_2I_2N_2PPd$	1.351 (4)	1.359 (4)	104.9 (3)	*d*
$C_{59}H_{38}F_{24}Fe_2IN_2P_2Pd\cdot PF_6\cdot 3CHCl_3$	1.344 (16)	1.330 (16)	108.4 (12)	*e*
$C_{53}H_{49}Fe_2N_3P_2Pd\cdot 2PF_6\cdot C_2H_6O\cdot C_4H_{10}O$	1.330 (11)	1.330 (11)	106.1 (8)	*e*
$C_{26}H_{34}Cl_2FeN_4Pd\cdot 2CH_2Cl_2$	1.359 (4)	1.363 (4)	104.7 (2)	*f*
$C_{44}H_{50}Cl_2FeIr_2N_4$	1.371 (5)	1.355 (5)	105.8 (3)	*g*
$C_{33}H_{27}Cl_5FeIr_2O_4N_4$	1.353 (5)	1.359 (5)	106.0 (3)	*g*
$C_{35}H_{37}BF_4FeN_2PRh$	1.359 (4)	1.357 (4)	104.5 (2)	*h*
$C_{46}H_{45}BF_4FeN_2PRh$	1.355 (8)	1.362 (8)	105.5 (6)	*i*
$C_{50}H_{51}BF_4FeN_2PRh$	1.367 (5)	1.373 (6)	105.2 (4)	*i*
$C_{36}H_{40}FeIN_2Rh$	1.366 (3)	1.360 (3)	106.02 (18)	*i*

References: (*a*) Bildstein, Malaun, Kopacka, Ongania & Wurst (1999); (*b*) Bildstein *et al.* (1998); (*c*) Bildstein, Malaun, Kopacka, Wurst *et al.* (1999); (*d*) Bertoog *et al.* (2005); (*e*) Gischig & Togni (2005); (*f*) Coleman *et al.* (2005); (*g*) Varnado *et al.* (2009); (*h*) Labande *et al.* (2007); (*i*) Gülcemal *et al.* (2009).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KY3008). Services for accessing these data are described at the back of the journal.

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