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[1,3-Bis(2,3,4,5,6-pentafluorobenzyl)-benzimidazol-2-ylidene]bromido-(η^4-cycloocta-1,5-diene)rhodium(I)

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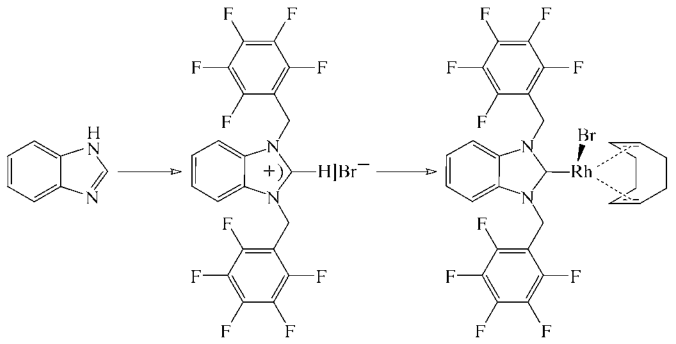
The title complex, [RhBr(C_8H_{12})($C_{21}H_8N_2F_{10}$)], has a slightly distorted pseudo-square-planar geometry. The whole molecule has an approximate mirror symmetry, with the mirror plane passing through the mid-points of the two alkene bonds of the cycloocta-1,5-diene (COD) ligand. The average Rh—C(COD) distance is inversely related to the magnitude of the Rh—C(benzimidazole) distance in this type of compound. The molecules are stacked in columns running along the *a* axis. The crystal structure contains two types of intermolecular C—H···F interactions, as well as two weak π–π stacking interactions.

Comment

Nitrogen-heterocyclic carbenes (NHCs) based on the imidazole ring system are a novel class of ligands in organometallic chemistry (Weskamp *et al.*, 2000) which tend to coordinate very strongly to the metal centre. NHCs and their metal complexes continue to attract interest as components in homogeneous catalysis (Herrmann, 2002*a*). The isolation of the stable imidazolin-2-ylidene and the saturated imidazolidin-2-ylidene derivative sparked renewed interest in the chemistry of N-heterocyclic carbenes and their metal complexes (Hahn, 2006). Recently, transition metal complexes of NHCs have been the focus of considerable attention since they can act as catalysts or catalyst precursors in Rh-catalyzed hydroformylation (Chen *et al.*, 2000), Ru-catalyzed olefin metathesis (Fürstner, 2000), cyclopropanation (Çetinkaya *et al.*, 1997), furan synthesis (Küçükbay *et al.*, 1996; Çetinkaya *et al.*, 2002) and Pd-catalyzed Heck or Suzuki coupling (McGuinnes & Cavell, 2000; Weskamp *et al.*, 1999). However, NHC complexes with fluorinated substituents are rare (Xu *et al.*, 2000). We report here the preparation and characterization of a novel Rh^I complex, (II), bearing the fluorinated NHC ligand (Saunders & McGrandle, 2005).

Complex (II) has a slightly distorted pseudo-square-planar geometry (Fig. 1 and Table 1), if the mid-points of the two double bonds of the cycloocta-1,5-diene (COD) ligand are considered as coordination sites. The metal centre is coordinated to the two alkene bonds of the COD ligand, to a non-substituted C atom of the benzimidazole ring system and to the Br atom. The whole molecule has an approximate mirror symmetry, with the mirror plane passing through the mid-points of the C22═C23 and C26═C27 bonds, and with atoms Rh1, C1 and Br1 lying on the approximate mirror plane. When these mid-points are considered, it can be said that the complex has a *cis* arrangement. The angle between the carbene heterocycle and the coordination plane (Br1/mid-point C22═C23/mid-point C26═C27) is 88.29 (14)°. This value is somewhat lower than that reported by Herrmann (2002*a*), but significantly higher than that reported by Dinçer *et al.* (2006). The COD ring exhibits a boat conformation, with the Rh—C(COD) distances ranging from 2.116 (4) to 2.224 (4) Å. The Rh1—C22 and Rh1—C23 bond distances are shorter than Rh1—C26 and Rh1—C27; this is not unexpected and is due to the *trans* influence of the chelating ligand. These results agree with the values in the literature (Ingleson *et al.*, 2001; Vicente *et al.*, 2001).



(I) (II)

Comparing the average Rh—C(COD) bond length of 2.17 (2) Å and the Rh—C(benzimidazole) bond length of 2.010 (3) Å with literature values, it is observed that Rh—

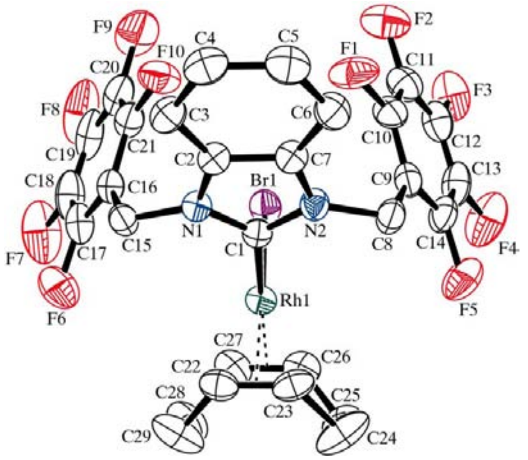


Figure 1
A view of (II), shown with 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

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C(COD) increases with decreasing Rh—C(benzimidazole) distance [2.167 (4) and 2.016 (4) Å (Baker *et al.*, 2004); 2.161 (2) and 2.018 (2) Å (Hahn *et al.*, 2004); 2.143 (3) and 2.059 (3) Å (Duan *et al.*, 2003)]. The C═C bond lengths of the cyclooctadiene ligand differ in that the double bond *trans* to the carbene ligand [C26═C27 = 1.381 (6) Å] is shorter than the C═C bond *trans* to the bromide ligand [C22═C23 = 1.392 (6) Å]. However, these distances fall in the expected range for coordinated olefins (Cambridge Structural Database, Version 5.28; *ConQuest*, Version 1.9; Allen, 2002).

The benzimidazole ring is planar, with a maximum deviation from the plane of −0.012 (2) Å for atom C1, and makes dihedral angles of 88.69 (9) and 88.98 (12)° with the C9–C14 and C16–C21 pentafluorophenyl ring planes, respectively, indicating that two pentafluorophenyl rings are almost perpendicular with respect to the benzimidazole ring. The metal–carbon bond distance between the Rh atom and the NHC ligand is in good agreement with those of other rhodium NHC complexes (Günay *et al.*, 2006; Dinçer *et al.*, 2005, 2006). The N1—C1 and N2—C1 bond distances are both 1.359 (4) Å. These are significantly shorter than the other N—C(carbene) bond distances in (II) (Table 1). The shorter N—C(carbene) bonds are indicative of a greater multiple-bond character due to partial electron donation by the N atom to the carbene C-atom donor (Herrmann, 2002*b*; Fröhlich *et al.*, 1997). Theoretical studies also indicate that the stability of these carbenes is due to electron donation from the N-atom lone pairs into the formally empty $p(\pi)$ orbital on the carbene C atom (Heinemann *et al.*, 1996; Böhme & Frenking, 1996). For this reason, the N1—C1 and N2—C1 bonds are shortened. It is observed that the steric effect of the pentafluorophenyl rings on the Br—Rh—C(carbene) angle and Rh—Br bond results in increased angle [92.82 (9)°] and shortened bond [2.5090 (5) Å] values relative to those in similar compounds (Günay *et al.*, 2006; Dinçer *et al.*, 2005; Herrmann, 2002*b*; Danopoulos *et al.*, 2002).

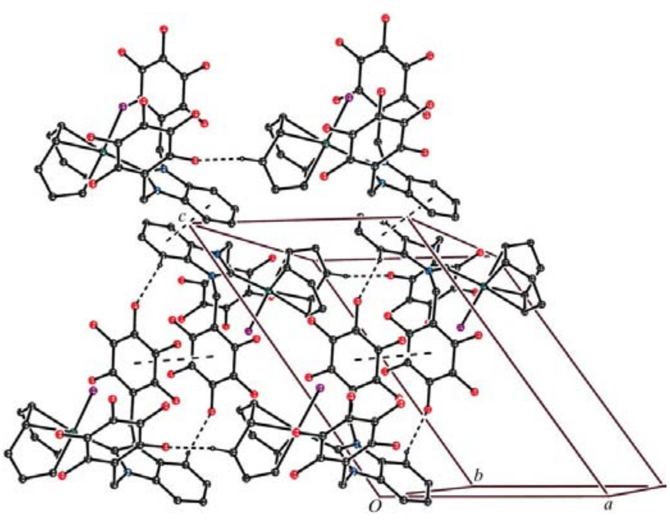

Figure 2
The molecular packing of (II), viewed along the *b* axis. Dashed lines show the C—H···F and π–π interactions.

In the crystal structure of (II) (Fig. 2), molecules are packed in columns running along the *a* axis. The molecules in each column are linked to one another in a zigzag arrangement *via* C25—H25*A*···F1^{i} hydrogen bonds (geometric parameters and symmetry codes for hydrogen bonds are given in Table 2), resulting in the formation of molecular chains along the *a* axis. In addition, there are π–π stacking and C3—H3···F8^{ii} interactions between the molecules in inversion-related columns. In these weak π–π interactions, the C16–C21 pentafluorophenyl ring in the molecule at (x, y, z) stacks above the ring at ($1 - x$, $-y$, $1 - z$), with a distance of 3.956 (8) Å between the ring centroids and a perpendicular distance of 3.402 (8) Å between the rings. Inversion-related columns are connected to similar neighbouring columns by means of another weak π–π interaction. In these π–π interactions, the C2–C7 benzimidazole ring in the molecule at (x, y, z) stacks above the ring at ($2 - x$, $-y$, $2 - z$), with a distance of 3.924 (8) Å between the ring centroids, and a perpendicular distance of 3.537 (8) Å between the rings. There are no other significant intermolecular interactions, such as C—H···π interactions, in the crystal structure of (II).

Experimental

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. The solvents and reagents were obtained from Aldrich, Fluka and Merck. [Rh(μ-OMe)(1,5-COD)]$_2$ (Uson *et al.*, 1985) was synthesized according to literature procedures. A 50 ml Schlenk tube was charged with (I) (Gülcemal, 2005) (111.80 mg, 0.2 mmol), [Rh(OMe)(η^4-COD)]$_2$ (48.40 mg, 0.1 mmol) and 5 ml of dichloromethane. The solution was stirred for 24 h at room temperature and heated under reflux for 2 h. Upon cooling to room temperature, hexane (10 ml) was added to the mixture. The resulting solid was filtered off and recrystallized from CH_2Cl_2/MeOH (1:5 *v*/*v*, 18 ml) (yield 115 mg, 78%; m.p. 509–511 K). Analysis calculated for $C_{29}H_{20}BrF_{10}N_2Rh$: C 46.97, H 2.70, N 3.78%; found: C 46.27, H 2.94, N 3.71%. ^{1}H NMR ($CDCl_3$): δ 1.94 (*q*, *J* = 9.5 Hz, 4H, COD-CH_2), 2.37 (*br*, 4H, COD-CH_2), 3.52 (*s*, 2H, COD-CH), 5.22 (*s*, 2H, COD-CH), 5.92 (*d*, 2H, *J* = 16 Hz, CH_2–C_6F_5), 6.39 (*d*, 2H, *J* = 16 Hz, CH_2–C_6F_5), 7.09 (*q*, *J* = 2.8 Hz, 2H, Ar-H), 7.21 (*q*, *J* = 3.1 Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 27.42 (*d*, *J* = 21.4 Hz, COD-CH_2), 31.88 (*d*, *J* = 22.2 Hz, COD-CH_2), 40.78 (CH_2–C_6F_5), 69.04 (*d*, *J* = 13.8 Hz, COD-CH), 100.28 (*d*, *J* = 6.9 Hz, COD-CH), 108.42, 108.85, 122.13, 133.79, 135.70, 138.16, 139.16, 141.64, 143.37, 145.83 (Ar-C), 199.03 (*d*, *J* = 50.6 Hz, C_{carb}–Rh); ^{19}F NMR ($CDCl_3$): δ −140.98 (2F, F_o), −153.83 (1F, F_p), −161.51 (2F, F_m).

Crystal data

[RhBr(C_8H_{12})($C_{21}H_8N_2F_{10}$)]
M_r = 769.29
Monoclinic, $P2_1/c$
a = 10.3441 (5) Å
b = 21.4937 (10) Å
c = 15.4717 (7) Å
β = 125.629 (3)°
V = 2795.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.13 mm^{-1}
T = 296 K
0.52 × 0.42 × 0.36 mm

Data collection

Stoe IPDSII diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.288, T_{max} = 0.545
36192 measured reflections
6179 independent reflections
4843 reflections with $I > 2\sigma(I)$
R_{int} = 0.056

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.101$
$S = 1.05$
6179 reflections
389 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh1—C1	2.010 (3)	N1—C1	1.359 (4)
Rh1—C22	2.116 (4)	N1—C2	1.392 (4)
Rh1—C23	2.118 (4)	N1—C15	1.456 (4)
Rh1—C26	2.222 (4)	N2—C1	1.359 (4)
Rh1—C27	2.224 (4)	N2—C7	1.400 (4)
Rh1—Br1	2.5090 (5)	N2—C8	1.464 (4)
C1—Rh1—C22	91.62 (14)	C1—N2—C7	111.6 (3)
C1—Rh1—C23	90.43 (14)	C1—N2—C8	124.2 (3)
C22—Rh1—C23	38.38 (17)	C7—N2—C8	124.1 (3)
C1—Rh1—C26	160.15 (16)	N2—C1—N1	104.5 (3)
C1—Rh1—C27	163.35 (16)	N2—C1—Rh1	127.7 (2)
C26—Rh1—C27	36.19 (17)	N1—C1—Rh1	127.8 (2)
C1—N1—C2	111.6 (3)	N2—C8—C9	113.3 (3)
C1—N1—C15	124.2 (3)	N1—C15—C16	113.7 (3)
C2—N1—C15	124.0 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25*A*···F1^{i}	0.97	2.44	3.397 (6)	167
C3—H3···F8^{ii}	0.93	2.50	3.331 (5)	148

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

H atoms were positioned geometrically and treated using a riding model, fixing the C—H bond lengths at 0.97, 0.98 and 0.93 Å for CH_2, CH and aromatic CH groups, respectively. The U_{iso}(H) values were set at $1.2U_{eq}$ of the parent atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3078). Services for accessing these data are described at the back of the journal.

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