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

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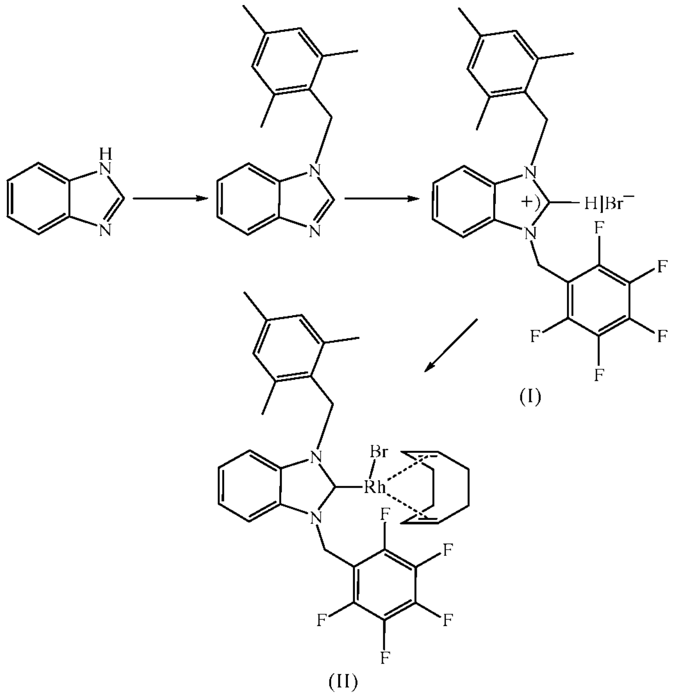
The title complex, $[RhBr(C_8H_{12})(C_{24}H_{19}F_5N_2)]$, has a distorted pseudo-square-planar geometry. The Rh—C bond distance between the N-heterocyclic ligand and the metal atom is 2.022 (3) Å. The angle between the carbene heterocycle and the coordination plane is 75.60 (11)°. It is shown that the average Rh—C(cyclooctadiene) distance is linearly dependent on the Rh—C(imidazole) distance in this type of compound. The crystal structure contains one intramolecular and two intermolecular types of C—H···F interactions, as well as one type of π–π stacking interaction.

Comment

In the past decade, N-heterocyclic carbenes (NHCs) have been the subject of intense research in the field of organometallic chemistry (Scott & Nolan, 2005; Crudden & Allen, 2004; Bourissou *et al.*, 2000; Herrmann & Köcher, 1997; Herrmann *et al.*, 2001). NHCs and their metal complexes continue to attract interest as components in homogeneous catalysis (Herrmann, 2002*a*). Prompted by the novel properties of these carbene ligands, we decided to prepare the supercritical carbon dioxide ($scCO_2$) soluble derivatives in the hope that the resulting carbene complex can be adapted for catalysis in $scCO_2$, which is an attractive alternative to conventional organic liquids for clean synthesis. One of the major limitations of $scCO_2$ as a reaction medium for homogeneous catalysis is its rather low solvent strength towards catalysts derived from common organometallic complexes (Jessop *et al.*, 1999; Smart *et al.*, 1997; Kainz *et al.*, 1997). To solve this problem, the ligands are derivatized with a varying number of fluorine-containing groups. NHC complexes with fluorinated substituents are rare (Xu *et al.*, 2000). In order to accomplish this goal, we required a ligand that has electronic properties similar to those of an NHC ligand but which allows solubility in $scCO_2$. The fluorinated precursor [1-(2,3,4,5,6-pentafluorobenzyl)-3-(2,4,6-trimethylbenzyl)]benzimidazolium bromide, (I), appears to meet the desired criteria. An additional feature of the ligand is that replacing the H substituents on the benzene ring with F atoms slightly increases the steric hindrance in the ligand itself and the coordination compound (II).



Benzimidazole is an interesting heterocyclic ring because it is present in various naturally occurring drugs. For example, omeprazole and lansoprazole are useful drugs in the treatment of peptic ulcers (Nishina *et al.*, 1996), pimobendan is a non-glucosidic cardiotonic drug (Güngör *et al.*, 1992), emedastine difumarate (KG-2413; Sakai *et al.*, 1989) and astemizole (Hismanal; Awouters *et al.*, 1983) were found to be beneficial for the treatment of allergic diseases, and enviroxime is an active drug against rhinoviruses (Victor *et al.*, 1997). Considering the biological importance of substances containing the benzimidazole ring system, we report here the preparation and characterization of the novel Rh^I complex (II), bearing the fluorinated NHC ligand (Saunders & McGrandle, 2005).

Complex (II) has a distorted pseudo-square-planar geometry (Fig. 1 and Table 1), if the cycloocta-1,5-diene (COD) double bonds are considered point ligands. The metal center is coordinated to the two alkene bonds of the COD ligand, to the non-substituted C atom of the benzimidazole ring and to the Br atom. The angle between the carbene heterocycle and the coordination plane (Br1/C25/C32) is 75.60 (11)°. This value is significantly smaller than that in similar complexes (Herrmann, 2002*a*; Dinçer *et al.*, 2005). The Rh—C(COD) distances range from 2.104 (3) to 2.236 (3) Å. The Rh1—C25 and Rh1—C32 bond distances are shorter than Rh1—C28 and Rh1—C29; this is not unexpected and is due to the *trans* influence of the chelating ligand.

Comparing the average Rh—C(COD) bond length of 2.169 (3) Å and the Rh—C(imidazolidine) bond length of

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2.022 (3) Å with literature values, it is observed that Rh—C(COD) increases with increasing Rh—C(imidazolidine) distance [2.159 (5) and 2.015 (5) Å (Günay *et al.*, 2006); 2.204 (2) and 2.039 (2) Å (Dinçer *et al.*, 2005)]. In the COD ligand, the C25═C32 double bond is approximately 0.03 Å longer than the opposite bond C28═C29. However, these distances fall in the expected range for coordinated olefins (Cambridge Structural Database; Version 5.23; Allen, 2002)

The benzimidazole ring is planar, with a maximum deviation from the plane of 0.021 (2) Å for atom C1, and makes dihedral angles of 78.30 (5) and 88.54 (5)° with the trimethylbenzene and pentafluorophenyl ring planes, respectively. The metal–carbon bond distance between the Rh atom and the NHC ligand of 2.022 (3) Å is in good agreement with those of other rhodium NHC complexes (Günay *et al.*, 2006; Dinçer *et al.*, 2005). The N1—C1 and N2—C1 bond distances are 1.357 (3) and 1.356 (4) Å, respectively. These are significantly shorter than the other N—C(carbene) bond distances in (II); for instance, N1—C2 is 1.396 (3) Å. 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). It is observed that the steric effect of the pentafluorophenyl ring on the Br—Rh—C(carbene) angle and Rh—Br bond results in broadening of the angle [to 94.73 (7)°] and shortening of the bond [to 2.4939 (4) Å] relative to those in similar compounds (Günay *et al.*, 2006; Dinçer *et al.*, 2005; Herrmann, 2002*b*; Danopoulos *et al.*, 2002).

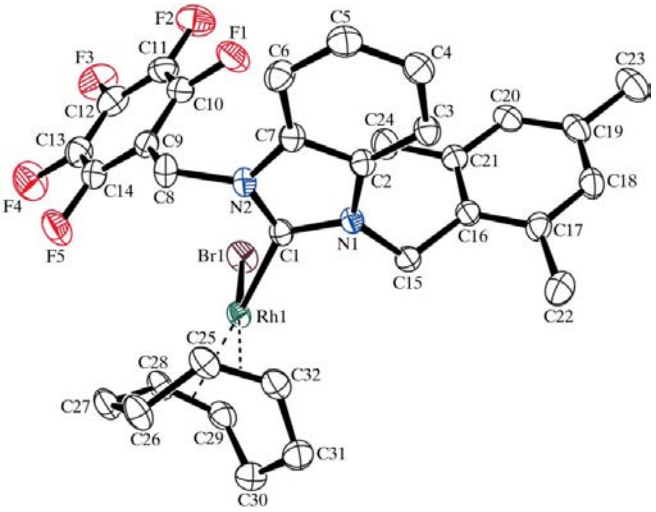

Figure 1
A view of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

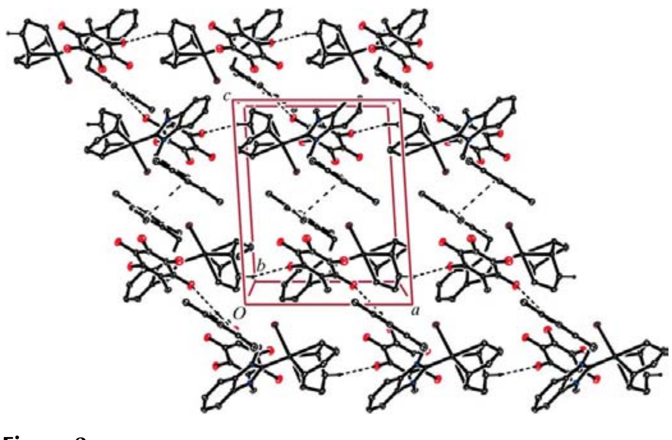

Figure 2
The molecular packing of (II), viewed along the *b* axis. Dashed lines show the C—H···F and π–π interactions. For clarity, only H atoms involved in hydrogen bonding have been included.

In the molecular structure, an intramolecular C8—H8*B*···F5 contact is observed. In the crystal structure (Fig. 2), molecules of the title compound are packed in columns running along the *a* axis. The molecules in each column are linked to one another in a zigzag arrangement *via* C27—H27*A*···F1^{ii} hydrogen bonds, resulting in the formation of molecular chains along the *a* axis. In addition, there are π–π stacking interactions between the molecules in the inversion-related columns. In these π–π interactions, the trimethylbenzene ring in the molecule at (x, y, z) stacks above the ring of the molecule at ($-x$, $-y$, $2 - z$), with a distance of 3.709 (10) Å between the ring centroids and a perpendicular distance of 3.576 (12) Å between the rings. The inversion-related columns are connected to similar neighboring columns by means of linear C24—H24*C*···F5^{i} hydrogen bonds; the detailed geometry of the intra- and intermolecular interactions (including symmetry codes) is given in Table 2. 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. Solvents and reagents were obtained from Aldrich, Fluka and Merck. The solvents were dried by conventional methods and were distilled under argon prior to use. [Rh(μ-OMe)(1,5-COD)]$_2$ (Uson *et al.*, 1985) and 1-(2,4,6-trimethylbenzyl)benzimidazole (Özdemir *et al.*, 2005) were synthesized according to literature methods. A 50 ml Schlenk tube was charged with (I) (Gülcemal, 2005) (102.17 mg, 0.2 mmol), [Rh(OMe)(1,5-COD)]$_2$ (48.40 mg, 0.1 mmol) and dichloromethane (5 ml). The solution was stirred for 24 h at 298 K 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*, 12 ml) (yield 117.5 mg, 82%; m.p. 528–530 K). Analysis calculated for $C_{32}H_{31}BrF_5N_2Rh$: C 53.27, H 4.30, N 3.88%; found: C 53.25, H 4.50, N 3.99%. ^{1}H NMR (CDCl$_3$): δ 1.99 (*br*, 4H, COD-CH$_2$), 2.29 [*s*, 3H, 2,4,6-$CH_2C_6H_2(CH_3)_3$], 2.33 [*s*, 6H, 2,4,6-$CH_2C_6H_2(CH_3)_3$], 2.48 (*br*, 4H, COD-CH$_2$), 3.48 (*br*, 1H, COD-CH), 3.60 (*br*, 1H, COD-CH), 5.24 (*br*, 2H, COD-CH), 5.98 [*d*, 2H, J = 15.2 Hz, 2,4,6-$CH_2C_6H_2(CH_3)_3$], 6.26 (*d*, 1H, J = 16.4 Hz, $CH_2C_6F_5$), 6.38 (*d*, 1H, J = 16.4 Hz, $CH_2C_6F_5$), 6.93 [*s*, 2H, 2,4,6-$CH_2C_6H_2(CH_3)_3$], 6.26–7.38 (*m*, 4H, Ar–H); ^{13}C NMR (CDCl$_3$): δ 21.05 [2,4,6-$CH_2C_6H_2(CH_3)_3$], 21.27 [2,4,6-$CH_2C_6H_2(CH_3)_3$], 28.93 (*d*, J = 25.2 Hz, COD-CH$_2$), 32.96 (*d*, J = 30.7 Hz, COD-CH$_2$), 41.89

(CH_2—Mes), 50.63 (CH_2—C_6F_5), 69.69 (*d*, J = 14.5 Hz, COD-CH), 70.37 (*d*, J = 14.6 Hz, COD-CH), 100.40 (*t*, J = 6.9 Hz, COD-CH), 109.39, 110.00, 111.45, 122.46, 122.91, 128.11, 129.90, 135.32, 138.78 (Ar—C), 198.90 (*d*, J = 50.7 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})($C_{24}H_{19}F_5N_2$)]
M_r = 721.41
Monoclinic, $P2_1/n$
a = 10.3364 (3) Å
b = 21.9437 (9) Å
c = 12.6549 (4) Å
β = 93.517 (3)°
V = 2864.96 (17) Å^3
Z = 4
D_x = 1.673 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.05 mm^{-1}
T = 296 K
Prism, yellow
0.59 × 0.44 × 0.34 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
T_{min} = 0.388, T_{max} = 0.548
41451 measured reflections
6339 independent reflections
5450 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 27.2°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.094
S = 1.05
6339 reflections
374 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 1.3902P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0043 (4)

Table 1
Selected geometric parameters (Å, °).

Rh1—C1	2.022 (3)	N1—C15	1.470 (3)
Rh1—C32	2.104 (3)	N2—C7	1.390 (3)
Rh1—C25	2.125 (3)	N2—C8	1.462 (3)
Rh1—C28	2.210 (3)	C25—C32	1.400 (5)
Rh1—C29	2.236 (3)	C28—C29	1.368 (5)
Rh1—Br1	2.4939 (4)		
C1—Rh1—C32	87.86 (12)	C1—N2—C7	111.4 (2)
C1—Rh1—C25	89.00 (11)	C1—N2—C8	124.3 (2)
C32—Rh1—C25	38.65 (13)	C7—N2—C8	124.2 (2)
C1—Rh1—C28	158.73 (11)	N2—C1—N1	105.5 (2)
C1—Rh1—C29	163.80 (11)	N2—C1—Rh1	126.03 (19)
C28—Rh1—C29	35.83 (12)	N1—C1—Rh1	127.4 (2)
C1—N1—C2	110.9 (2)	N2—C8—C9	113.1 (2)
C1—N1—C15	122.8 (2)	N1—C15—C16	113.4 (2)
C2—N1—C15	126.2 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8B···F5	0.97	2.39	2.831 (4)	107
C24—H24C···F5^{i}	0.96	2.58	3.538 (4)	176
C27—H27A···F1^{ii}	0.97	2.56	3.427 (4)	149

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x - 1, y, z$.

H atoms were positioned geometrically and treated using a riding model, fixing the C—H bond lengths at 0.96, 0.97, 0.98 and 0.93 Å for CH_3, CH_2, CH and aromatic CH groups, respectively. The U_{iso}(H) values were set at 1.2U_{eq} (1.5U_{eq} for methyl) of the pivot 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: *SHELXS97* (Sheldrick, 1997); 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: GZ3014). Services for accessing these data are described at the back of the journal.

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