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# *trans*-Bis[1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]dibromopalladium(II)

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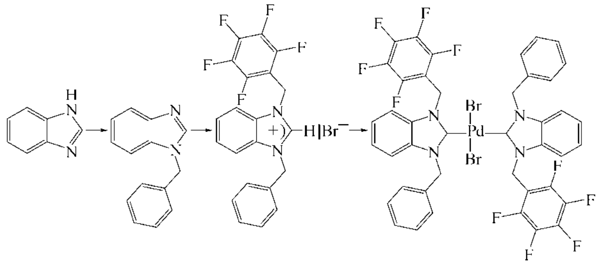
The title compound, $[PdBr_2(C_{21}H_{13}F_5N_2)_2]$, crystallizes with two independent centrosymmetric conformational isomers having a square-planar coordination at the Pd atom. The conformational isomers differ by the ligands having a *cis* or *trans* orientation of their benzyl and pentafluorobenzyl rings with respect to the benzimidazole ring plane. The benzimidazole rings are rotated with respect to the coordination plane of the metal by 79.1 (2) and 75.2 (1)° for molecules *A* and *B*, respectively. The Pd—Br bond lengths are 2.4218 (8) and 2.4407 (10) Å for molecules *A* and *B*, respectively, and the Pd—C bond lengths are 2.030 (8) and 2.018 (9) Å. The crystal structure contains two types of C—H···F and one type of C—H···Br intramolecular contact, as well as C—H···$\pi$ interactions.

## Comment

N-Heterocyclic carbenes (NHCs) have been the subject of intense research in the field of organometallic chemistry (Herrmann *et al.*, 2001; Crudden & Allen, 2004; Scott & Nolan, 2005), and NHCs and their metal complexes continue to attract interest as components in homogeneous catalysis (Herrmann, 2002). NHCs are increasingly used as the major structural units for many organometallic compounds and homogeneous catalysts, but little attention has been paid to the synthesis of NHC derivatives with fluorophilic properties. NHC complexes with fluorinated substituents are rare (Xu *et al.*, 2000; McGrandle & Saunders, 2005; Dinçer *et al.*, 2006; Burling *et al.*, 2006). Prompted by the novel properties of these carbene ligands, we decided to prepare some supercritical carbon dioxide ($scCO_2$) soluble derivatives in the hope that the resulting carbene complexes 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 (Smart *et al.*, 1997; Kainz *et al.*,1997; Jessop *et al.*, 1999). In order to accomplish this goal, we required a ligand that has electronic properties similar to those of an NHC ligand but allows solubility in $scCO_2$. To solve this problem, we synthesized ligands with different numbers of fluorine-containing groups. We report



(I) (II)

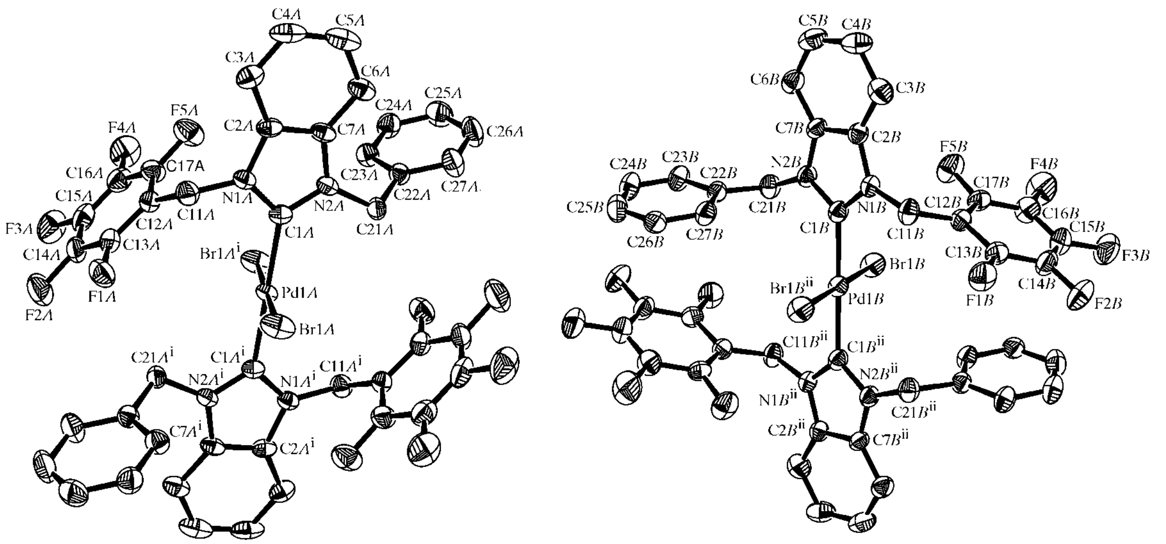


**Figure 1**
The molecular structures of conformational isomers *A* (left) and *B* (right), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y, -z$.]

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here the syntheses of 1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)-benzimidazolium bromide, (I), and the title compound, $[PdBr_2(C_{21}H_{13}F_5N_2)_2]$, (II), and the crystal structure of (II) (Fig. 1).

Compound (II) crystallizes with two independent centrosymmetric conformational isomers, molecules *A* and *B*. While one-half of each molecule is crystallographically independent, the other half is generated by an inversion centre located at the metal centre of the molecule. The conformational isomers differ by the orientations of their benzyl and pentafluorobenzyl rings. The benzyl and pentafluorobenzyl rings within each ligand of molecule *A* are located on the same side of the benzimidazole ring plane, while these rings in molecule *B* are located on opposite sides of the benzimidazole ring plane.

The coordination geometries around the Pd atoms are slightly distorted square planar, formed by the two coordinating C atoms of the benzimidazole rings and two Br atoms in a *trans* arrangement. The *cis* angles deviate by up to 1.1° from the ideal value of 90°. The planes of the benzimidazole rings make dihedral angles of 79.1 (2) and 75.2 (1)° with the coordination planes for molecules *A* and *B*, respectively.

The Pd—Br bond lengths are 2.4218 (8) and 2.4407 (10) Å for molecules *A* and *B*. The Pd—C bond distances between the NHC ligand and the metal atom are 2.030 (8) and 2.018 (9) Å, comparable to those in other palladium(II)–NHC complexes (Magill *et al.*, 2001; Liu *et al.*, 2003; Gökçe *et al.*, 2004). Although both C—N bonds in the NHC rings are single bonds, their distances are different, as found in related complexes (Gökçe *et al.*, 2004, 2006; Karabıyık *et al.*, 2006*a*,*b*). The C—N bond distances involving the carbene C atom bonded to Pd are shorter than the other C—N bond distances (Table 1). This is possibly indicative of a greater partial double-bond character due to partial electron donation by the N atoms to the carbene C-atom donor (Fröhlich *et al.*, 1997; Herrmann *et al.*, 2001). A theoretical study also indicates that the stability of these carbenes is due to electron donation from the N-atom lone pairs into the formally vacant $p(\pi)$ orbital of the carbene C atom (herein C1*A* and C1*B*) (Karabıyık *et al.*, 2005).

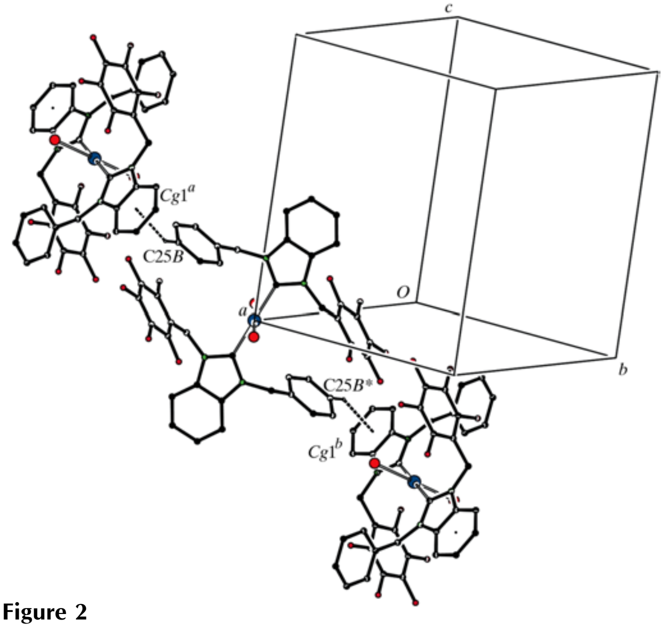

**Figure 2**
Part of the crystal structure of (II), showing the formation of a chain generated by the C—H$\cdots\pi$ interaction involving atom C25*B*. For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (*) $-x+2, -y, -z$; (*a*) $-x+2, -y, -z+1$; (*b*) $-x+1, -y+1, -z$.]

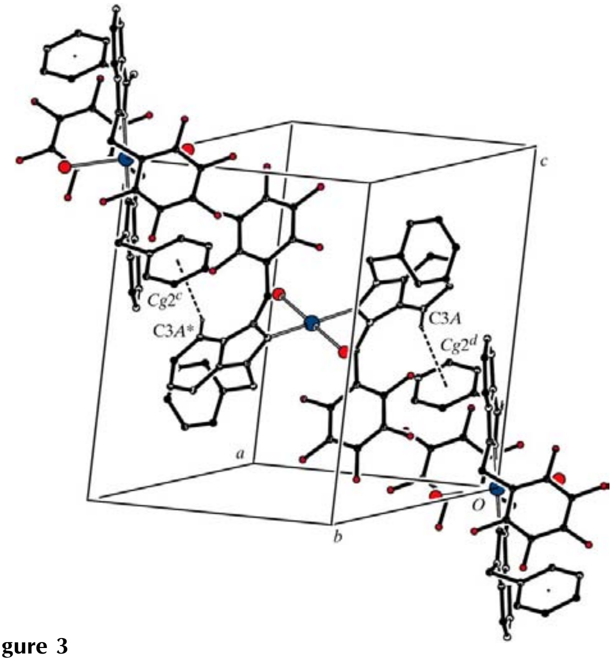

**Figure 3**
Part of the crystal structure of (II), showing the formation of a chain generated by the C—H$\cdots\pi$ interaction involving atom C3*A*. For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (*) $-x+1, -y+1, -z+1$; (*c*) $x, y+1, z+1$; (*d*) $x-1, y, z$.]

There are three short intramolecular contacts in the crystal structure (Table 2), two of C—H$\cdots$F type for molecule *A* and one of C—H$\cdots$Br type for molecule *B*. As shown in Figs. 2 and 3, atoms C25*B* and C3*A* in the molecule at ($x, y, z$) act as C—H$\cdots\pi$ hydrogen-bond donors to the C2*A*–C7*A* ring in the molecule at ($2-x, -y, 1-z$) and the C22*B*–C27*B* ring in the molecule at ($-1+x, y, z$), respectively.

## Experimental

For the synthesis of (I), a mixture of pentafluorobenzyl bromide (2.10 g, 7.96 mmol) and 1-benzylbenzimidazole (1.652 g, 7.94 mmol) was refluxed in toluene (15 ml) for 2 h. The volume of the solution was reduced to *ca* 3–4 ml under vacuum. Diethyl ether (10 ml) was added and the solution was filtered. The remaining white precipitate was dissolved in methanol (4 ml) and diethyl ether was added (15 ml). The resulting white crystals were filtered off and dried under vacuum (yield 3.4 g, 91%; m.p. 418 K). Analysis calculated for $C_{21}H_{14}BrF_5N_2$: C 53.73, H 2.99, N 5.97%; found: C 53.53, H 2.94, N 5.89%. $^1$H NMR ($CDCl_3$): $\delta$ 5.89 (*s*, 2H, $CH_2C_6H_5$), 6.19 (*s*, 2H, $CH_2C_6F_5$), 7.34–7.63 (*m*, 9H, Ar–H), 11.71 (*s*, 1H, CH). $^{13}$C NMR ($CDCl_3$): $\delta$ 39.58 ($CH_2C_6H_5$), 52.01 ($CH_2C_6F_5$), 107.01, 114.58, 127.86, 128.56, 129.48, 131.25, 112.75, 132.63, 136.85, 139.31, 141.30, 143.74, 144.51 (Ar–C), 147.08 (CH). $^{19}$F NMR ($CDCl_3$): $\delta$ −140.75 (2F, $F_o$), −149.76 (1F, $F_p$), −159.22 (2F, $F_m$). For the synthesis of (II), a 50 ml Schlenk tube was charged with (I) (187.60 mg, 0.4 mmol), $Pd(OAc)_2$ (44.88 mg, 0.2 mmol) and tetrahydrofuran (5 ml). The solution was heated under reflux for 24 h, and the colour of the solution changed from orange to yellow. Upon cooling to room temperature, hexane (10 ml) was added to the mixture. The solid was filtered off and then recrystallized from $CH_2Cl_2$/MeOH (1:5 *v*/*v*, 12 ml) (yield 160 mg, 77%; m.p. 541–542 K). Analysis calculated for $C_{42}H_{26}Br_2F_{10}N_4Pd$: C 48.35, H 2.49, N 5.37%; found: C 47.60, H 1.96, N 5.36%. $^1$H NMR ($CDCl_3$): $\delta$ 5.91 (*s*, 4H, $CH_2C_6H_5$), 6.07 (*d*, 4H, *J* = 10 Hz, $CH_2C_6F_5$), 6.99–7.42 (*m*, 18H, Ar–H). $^{13}$C NMR ($CDCl_3$): $\delta$ 53.00 ($CH_2C_6H_5$), 41.30 ($CH_2C_6F_5$), 110.33 (*d*, *J* = 15.3 Hz), 111.96 (*d*, *J* = 10.7 Hz), 123.68, 127.40, 127.65, 128.88, 128.81, 134.56, 134.63, 134.76, 134.89, 135.11, 135.49 (Ar–C), 183.06 (C—Pd). $^{19}$F NMR ($CDCl_3$): $\delta$ −140.82 (2F, $F_o$), −150.57 (1F, $F_p$), −159.44 (2F, $F_m$).

*Crystal data*

$[PdBr_2(C_{21}H_{13}F_5N_2)_2]$
$M_r = 1042.89$
Triclinic, $P\overline{1}$
$a = 11.6122$ (8) Å
$b = 12.1401$ (9) Å
$c = 13.6590$ (11) Å
$\alpha = 92.589$ (6)°
$\beta = 95.610$ (6)°
$\gamma = 92.520$ (6)°
$V = 1912.1$ (2) Å$^3$
$Z = 2$
$D_x = 1.811$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 2.66$ mm$^{-1}$
$T = 293$ (2) K
Prism, colourless
0.18 × 0.16 × 0.09 mm

*Data collection*

Stoe IPDS-II diffractometer
$\omega$ scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\rm min} = 0.646$, $T_{\rm max} = 0.796$
23746 measured reflections
7493 independent reflections
3911 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.121$
$\theta_{\rm max} = 26.0°$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.119$
$S = 0.95$
7493 reflections
535 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.68$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.55$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N1*A*—C1*A* | 1.352 (10) | N1*B*—C1*B* | 1.357 (10) |
| N1*A*—C2*A* | 1.399 (9) | N1*B*—C2*B* | 1.392 (10) |
| N1*A*—C11*A* | 1.448 (10) | N1*B*—C11*B* | 1.453 (10) |
| N2*A*—C1*A* | 1.351 (9) | N2*B*—C1*B* | 1.350 (10) |
| N2*A*—C7*A* | 1.380 (10) | N2*B*—C7*B* | 1.392 (11) |
| N2*A*—C21*A* | 1.461 (10) | N2*B*—C21*B* | 1.460 (10) |
| C2*A*—C7*A* | 1.379 (11) | C2*B*—C7*B* | 1.385 (11) |
| | | | |
| C1*A*—Pd1*A*—Br1*A*$^{\rm i}$ | 89.87 (18) | C1*B*—Pd1*B*—Br1*B*$^{\rm ii}$ | 91.1 (2) |
| C1*A*—Pd1*A*—Br1*A* | 90.13 (18) | C1*B*—Pd1*B*—Br1*B* | 88.9 (2) |
| | | | |
| N2*A*—C21*A*—C22*A*—C27*A* | 131.6 (9) | N2*B*—C21*B*—C22*B*—C27*B* | −34.3 (12) |
| N1*A*—C11*A*—C12*A*—C13*A* | 142.7 (8) | N1*B*—C11*B*—C12*B*—C13*B* | −169.3 (8) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y, -z$.

All H atoms were treated as riding atoms, with C—H distances in the range 0.93–0.97 Å and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

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: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

**Table 2**
The intra- and intermolecular hydrogen-bond interactions in (I) (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C2*A*–C7*A* and C22*B*–C27*B* rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C21*A*—H21*A*··· F1*A*$^{\rm i}$ | 0.97 | 2.45 | 3.19 (1) | 132 |
| C11*A*—H12*A*···F1*A* | 0.97 | 2.39 | 2.80 (1) | 105 |
| C11*B*—H11*B*···Br1*B*$^{\rm ii}$ | 0.97 | 2.89 | 3.70 (1) | 142 |
| C26*B*—H26*B*···F4*B*$^{\rm iii}$ | 0.93 | 2.38 | 3.21 (1) | 148 |
| C25*B*—H25*B*···*Cg*1$^{\rm iv}$ | 0.93 | 2.59 | 3.41 (1) | 148 |
| C3*A*—H3*A*···*Cg*2$^{\rm v}$ | 0.93 | 2.78 | 3.62 (1) | 150 |

Symmetry codes: (iii) $x+1, y, z$; (iv) $-x+2, -y, -z+1$; (v) $x-1, y, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3050). Services for accessing these data are described at the back of the journal.

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