

***trans*-Bis[1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]-dibromopalladium(II)**Aytaç Gürhan Gökçe,^{a*} Süleyman Gülcemal,^b Muhittin Aygün,^a Bekir Çetinkaya^b and Orhan Büyükgüngör^c^aDepartment of Physics, Dokuz Eylül University, 35160 Buca-Izmir, Turkey,^bDepartment of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey, and^cDepartment of Physics, Ondokuz Mayıs University, 55139 Kurupelit-Samsun, Turkey

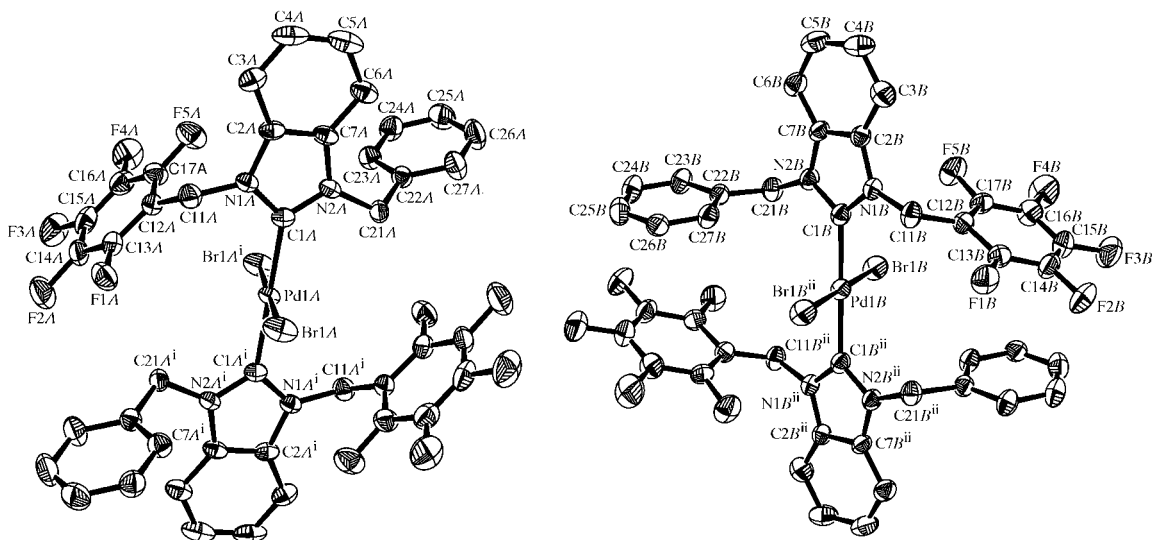
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Received 12 September 2006

Accepted 26 September 2006

Online 31 October 2006

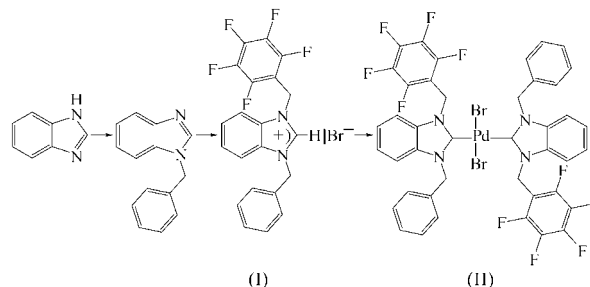
The title compound, [PdBr₂(C₂₁H₁₃F₅N₂)₂], crystallizes with two independent centrosymmetric conformational isomers having a square-planar coordination at the Pd atom. The conformational isomers differ by the ligands having a *cis* or *trans* orientation of their benzyl and pentafluorobenzyl rings with 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... π interactions.

**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) $-x + 2, -y, -z$.]

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 (scCO₂) soluble derivatives in the hope that the resulting carbene complexes can be adapted for catalysis in scCO₂, which is an attractive alternative to conventional organic liquids for clean synthesis. One of the major limitations of scCO₂ 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 scCO₂. To solve this problem, we synthesized ligands with different numbers of fluorine-containing groups. We report

here the syntheses of 1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)-benzimidazolium bromide, (I), and the title compound, $[\text{PdBr}_2(\text{C}_{21}\text{H}_{13}\text{F}_5\text{N}_2)_2]$, (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 $75.2(1)^\circ$ 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

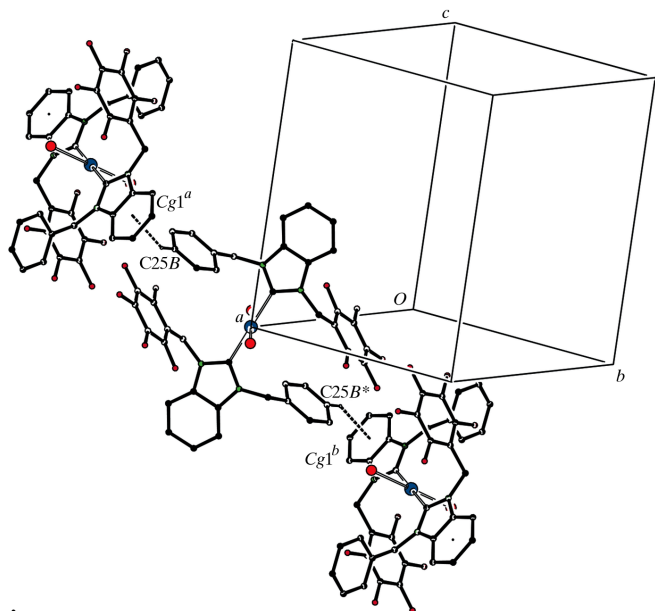


Figure 2
Part of the crystal structure of (II), showing the formation of a chain generated by the C—H... π interaction involving atom C25B. For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (*) $-x + 2, -y, -z$; (a) $-x + 2, -y, -z + 1$; (b) $-x + 1, -y + 1, -z$.]

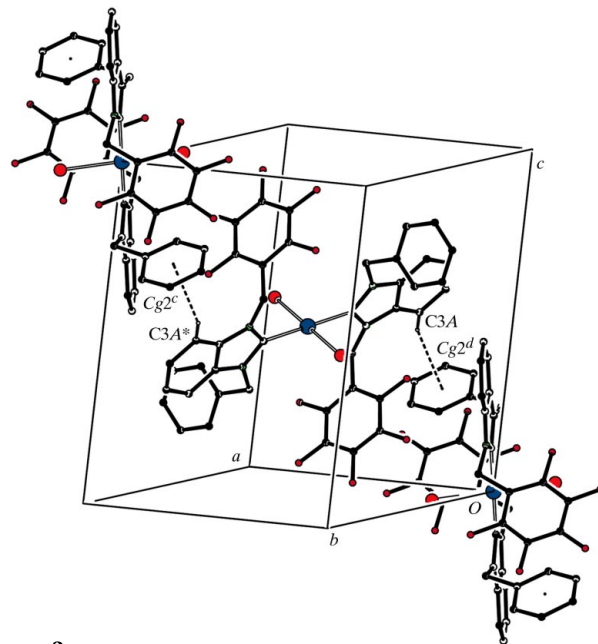


Figure 3
Part of the crystal structure of (II), showing the formation of a chain generated by the C—H... π interaction involving atom C3A. For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (*) $-x + 1, -y + 1, -z + 1$; (c) $x, y + 1, z + 1$; (d) $x - 1, y, z$.]

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 C1A and C1B) (Karabıyık *et al.*, 2005).

There are three short intramolecular contacts in the crystal structure (Table 2), two of C—H...F type for molecule *A* and one of C—H...Br type for molecule *B*. As shown in Figs. 2 and 3, atoms C25B and C3A in the molecule at (x, y, z) act as C—H... π hydrogen-bond donors to the C2A—C7A ring in the molecule at $(2 - x, -y, 1 - z)$ and the C22B—C27B 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 $\text{C}_{21}\text{H}_{14}\text{BrF}_5\text{N}_2$: C 53.73, H 2.99, N 5.97%; found: C 53.53, H 2.94, N 5.89%. ^1H NMR (CDCl_3): δ 5.89 (s, 2H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.19 (s, 2H, $\text{CH}_2\text{C}_6\text{F}_5$), 7.34–7.63 (m, 9H, Ar—H), 11.71 (s, 1H, CH). ^{13}C NMR (CDCl_3): δ 39.58 ($\text{CH}_2\text{C}_6\text{H}_5$), 52.01 ($\text{CH}_2\text{C}_6\text{F}_5$), 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): δ -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), $\text{Pd}(\text{OAc})_2$ (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 CH₂Cl₂/MeOH (1:5 v/v, 12 ml) (yield 160 mg, 77%; m.p. 541–542 K). Analysis calculated for C₄₂H₂₆Br₂F₁₀N₄Pd: C 48.35, H 2.49, N 5.37%; found: C 47.60, H 1.96, N 5.36%. ¹H NMR (CDCl₃): δ 5.91 (s, 4H, CH₂C₆H₅), 6.07 (d, 4H, *J* = 10 Hz, CH₂C₆F₅), 6.99–7.42 (*m*, 18H, Ar–H). ¹³C NMR (CDCl₃): δ 53.00 (CH₂C₆H₅), 41.30 (CH₂C₆F₅), 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). ¹⁹F NMR (CDCl₃): δ –140.82 (2F, F_o), –150.57 (1F, F_p), –159.44 (2F, F_m).

Crystal data

[PdBr ₂ (C ₂₁ H ₁₃ F ₅ N ₂) ₂]	<i>V</i> = 1912.1 (2) Å ³
<i>M_r</i> = 1042.89	<i>Z</i> = 2
Triclinic, <i>P</i> 1	<i>D_x</i> = 1.811 Mg m ^{−3}
<i>a</i> = 11.6122 (8) Å	Mo <i>K</i> α radiation
<i>b</i> = 12.1401 (9) Å	<i>μ</i> = 2.66 mm ^{−1}
<i>c</i> = 13.6590 (11) Å	<i>T</i> = 293 (2) K
<i>α</i> = 92.589 (6)°	Prism, colourless
<i>β</i> = 95.610 (6)°	0.18 × 0.16 × 0.09 mm
<i>γ</i> = 92.520 (6)°	

Data collection

Stoe IPDS-II diffractometer	23746 measured reflections
<i>ω</i> scans	7493 independent reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	3911 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.646, <i>T_{max}</i> = 0.796	<i>R_{int}</i> = 0.121
	<i>θ_{max}</i> = 26.0°

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.059	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.035 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.119	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 0.95	(Δ/ <i>σ</i>) _{max} = 0.002
7493 reflections	Δρ _{max} = 0.68 e Å ^{−3}
535 parameters	Δρ _{min} = −0.55 e Å ^{−3}

Table 1

Selected geometric parameters (Å, °).

N1A–C1A	1.352 (10)	N1B–C1B	1.357 (10)
N1A–C2A	1.399 (9)	N1B–C2B	1.392 (10)
N1A–C11A	1.448 (10)	N1B–C11B	1.453 (10)
N2A–C1A	1.351 (9)	N2B–C1B	1.350 (10)
N2A–C7A	1.380 (10)	N2B–C7B	1.392 (11)
N2A–C21A	1.461 (10)	N2B–C21B	1.460 (10)
C2A–C7A	1.379 (11)	C2B–C7B	1.385 (11)
C1A–Pd1A–Br1A ⁱ	89.87 (18)	C1B–Pd1B–Br1B ⁱⁱ	91.1 (2)
C1A–Pd1A–Br1A	90.13 (18)	C1B–Pd1B–Br1B	88.9 (2)
N2A–C21A–C22A–C27A	131.6 (9)	N2B–C21B–C22B–C27B	−34.3 (12)
N1A–C11A–C12A–C13A	142.7 (8)	N1B–C11B–C12B–C13B	−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*_{iso}(H) values of 1.2*U*_{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, °).

Cg1 and Cg2 are the centroids of the C2A–C7A and C22B–C27B rings, respectively.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C21A–H21A...F1A ⁱ	0.97	2.45	3.19 (1)	132
C11A–H12A...F1A	0.97	2.39	2.80 (1)	105
C11B–H11B...Br1B ⁱⁱ	0.97	2.89	3.70 (1)	142
C26B–H26B...F4B ⁱⁱⁱ	0.93	2.38	3.21 (1)	148
C25B–H25B...Cg1 ^{iv}	0.93	2.59	3.41 (1)	148
C3A–H3A...Cg2 ^v	0.93	2.78	3.62 (1)	150

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

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased under grant No. F.279 of the University Research Fund) and Dokuz Eylül University Research Funds (project No. 04.KB.FEN.100).

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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