Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

[1,3-Bis(2-ethoxyphenyl)imidazolidin-2-ylidene]bromo(cycloocta-1,5-diene)rhodium(I)

Muharrem Dinçer,[a] Namık Özdemir,[a]* M. Emin Günay,[b] Bekir Çetinkaya[c] and Orhan Büyükgüngör[a]

[a]Department of Physics, Arts and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey, [b]Department of Chemistry, Arts and Sciences Faculty, Adnan Menderes University, 09010 Aydın, Turkey, and [c]Department of Chemistry, Sciences Faculty, Ege University, 35100 Izmir, Turkey
Correspondence e-mail: namiko@omu.edu.tr

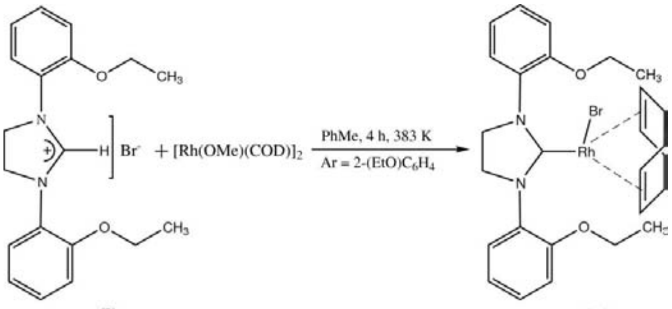
Received 28 February 2005
Accepted 27 April 2005
Online 9 July 2005

The title complex, $[\mathrm{RhBr(C_8H_{12})(C_{19}H_{22}N_2O_2)}]$, has a distorted square-planar geometry. There are two molecules, *A* and *B*, in the asymmetric unit. The Rh—C bond distance between the N-heterocyclic ligand and the metal atom is 2.039 (2) Å in molecule *A* and 2.042 (2) Å in molecule *B*. The angle between the carbene heterocycle and the coordination plane is 87.56 (12)° in molecule *A* and 87.03 (11)° in molecule *B*. It is shown that the average Rh—C(COD) (COD is cyclooctadiene) distance is linearly dependent on the Rh—C(imidazolidine) distance in this type of compound. This can be ascribed to the steric hindrance produced by the packing. The crystal structure contains intramolecular C—H···O and intermolecular C—H···Br interactions.

Comment

N-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. Side chains containing hemilabile functionalities should trigger the chemistry at the metal centre and, at the same time, enhance the stability of the catalyst (Bourissou *et al.*, 2000; Hermann, 2002*a*). For example, NHC complexes with methoxyethyl substituents have been used as catalysts in cyclopropanation reactions (Çetinkaya *et al.*, 1997). The objective of the present work was to seek a metal–carbene complex, $L_nM\text{–}\mathrm{C}\overline{\mathrm{N(Ar)CH_2CH_2N}}\mathrm{(Ar)}$, in which the aryl (Ar) group has an *o*-ethoxy functionality, so that the carbene ligand has potential as a bidentate chelating or bridging ligand. We describe here the crystal structure of the title compound, (II).

The structures of the two independent molecules, *A* and *B*, of (II) have very similar molecular dimensions (Fig. 1 and Table 1). In the following discussion, parameters for molecule *B* are quoted in square brackets. The two molecules are separated by van der Waals interactions and one weak hydrogen bond. Atom C43 of the ethoxyphenyl group forms a hydrogen bond with the Br1 ligand. Similarly, atom C16 of the ethoxyphenyl group forms a C—H···Br contact with the Br2 ligand (Table 2). This arrangement results in the formation of infinite chains running along the *a* axis in the crystal (Fig. 2).



(I) (II)

Complex (II) has a distorted square-planar geometry (Fig. 1 and Table 1), the metal centre being coordinated to the centres of the two alkene bonds of the cycloocta-1,5-diene (COD) ligand, to the non-substituted C atom of the imidazolidine ring and to one Br atom. The angle between the carbene hetero-

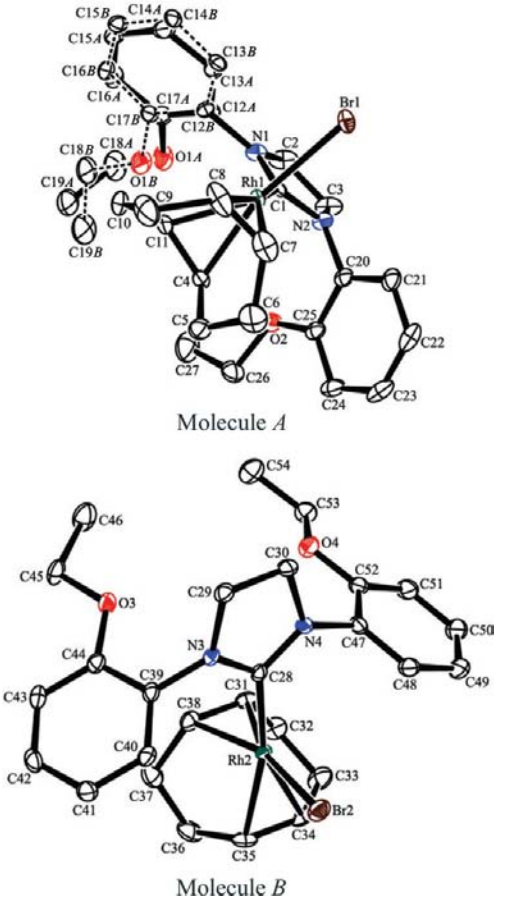


Figure 1
The two molecules of (II), shown with 50% probability displacement ellipsoids and illustrating the atom-numbering scheme. H atoms have been omitted for clarity.

cycle and the coordination plane (Br1/C4/C11) is 87.56 (12)° [87.03 (11)° for Br2/C31/C38]. This value is somewhat smaller than in similar complexes (Hermann, 2002*a*). The Rh—C(COD) distances range from 2.123 (2) to 2.274 (3) Å [2.132 (2)–2.274 (2) Å]. The bond distances Rh1—C4 and Rh1—C11 are shorter than Rh1—C7 and Rh1—C8. This is not unexpected and is due to the *trans* influence of the chelating ligand.

Comparing the average Rh—C(COD) bond length, 2.204 (2) Å [2.198 (2) Å], and the Rh—C(imidazolidine) bond length, 2.039 (2) Å [2.042 (2) 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.*, 2005]. This suggests that the bond lengths involving the Rh atom are more affected by steric hindrance of the packing than by electronic effects. In the COD moiety, the C4═C11 [C31═C38] double bonds are longer than those opposite, C7═C8 [C34═C35]. In molecule *A*, the ethoxyphenyl group (O1/C12–C19) attached to the imidazolidine ring shows positional disorder.

Although the imidazolidine ring is planar [maximum deviation −0.012 (3) Å for atom C1], the imidazolidine ring in molecule *B* is close to a very shallow envelope conformation, with atom C30 displaced by −0.052 (3) Å from the plane. The imidazole ring makes dihedral angles of 52.8 (3) (major component, C12*A*–C17*A*), 62.8 (7) (minor component, C12*B*–C17*B*) and 78.08 (14)° (C20–C25) with the ethoxyphenyl ring planes [68.24 (13) and 72.22 (13)°], respectively.

The metal–carbon bond distance between Rh and the NHC ligand of 2.039 (2) Å [2.042 (2) Å] is longer than in other rhodium NHC complexes [2.015 (5) Å; Günay *et al.*, 2005], mainly due to the presence of a Br ligand instead of a Cl ligand. The N1—C1 and N2—C1 bond distances are 1.354 (3) and 1.358 (3) Å, respectively [N3—C28 and N4—C28 are 1.348 (3) and 1.361 (3) Å, respectively]. These are significantly shorter than the other N—C(carbene) bond distances in these complexes. For instance, N1—C2 is 1.514 (3) Å [N3—C29 is 1.503 (3) Å], possibly indicative of a greater partial double-bond character due to partial electron donation by N to the carbene C-atom donor (Hermann, 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 vacant $p(\pi)$ orbital of the carbene C atom (McGuinness *et al.*, 1998). The Br—Rh—C(carbene) angle of 87.89 (6)° [86.98 (6)°] is somewhat smaller than for similar compounds (Herrmann, 2002*b*; Danopoulos *et al.*, 2002).

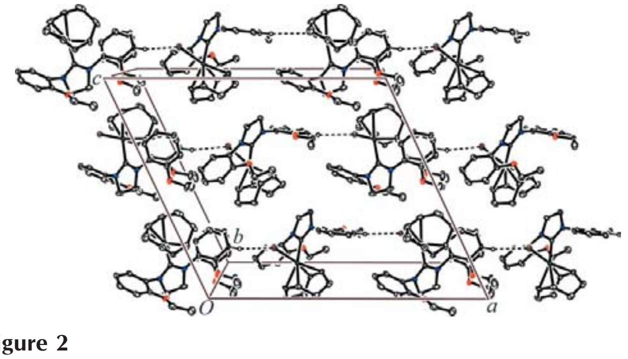


Figure 2
A projection of (II) approximately along *b*, showing the one-dimensional polymer built *via* intermolecular C—H···Br interactions.

The O atoms of the *o*-ethoxy substituents of the benzene ring do not interact with the Rh atoms. Instead, there are four intramolecular C—H···O interactions (Table 2). The interactions involving the imidazolidine ring form a six-membered closed ring, which is fused with both the imidazolidine ring and the benzene rings. These intramolecular interactions strongly influence the orientation of the ethoxyphenyl rings, resulting in a tilting of these rings towards the imidazolidine rings.

Experimental

All reactions were conducted under argon using standard Schlenk cannula techniques. The solvents were purified using the system described by Pangborn *et al.* (1996). The imidazolinium salt (Günay, 2004) and $[Rh(OMe)(COD)]_2$ (Uson *et al.*, 1985) were synthesized according to the published procedures. A 50 ml Schlenk tube was charged with compound (I) (0.196 g, 0.5 mmol), $[Rh(OMe)(\eta^4\text{-}COD)]_2$ (0.121 g, 0.25 mmol) and toluene (5 ml). The solution was heated under reflux for 4 h. Upon cooling to room temperature, hexane (10 ml) was added to the mixture. The resulting solid was filtered off and then recrystallized from CH_2Cl_2–Et_2O (1:3 *v*/*v*, 8 ml) (yield: 0.242 g, 80%; m.p. 493–495 K). Analysis calculated for $C_{27}H_{34}BrN_2O_2Rh$: C 53.92, H 5.70, N 4.66%; found: C 53.87, H 5.62, N 4.45%. ^1H NMR ($CDCl_3$): δ 1.42 [*s*, 6H, 2-$(OCH_2CH_3)C_6H_4$], 1.43 (*m*, COD-CH), 1.63 (*m*, COD-CH_2), 3.79 (*m*, COD-CH), 3.76–3.81 (*m*, 2H, NCH_2CH_2N), 4.00–4.07 [*m*, 2H, 2-$(OCH_2CH_3)C_6H_4$], 4.10–4.16 [*m*, 2H, 2-$(OCH_2CH_3)C_6H_4$], 4.41–4.54 (*m*, 2H, NCH_2CH_2N), 4.66 (*d*, *J* = 2.80 Hz, COD-CH), 6.93 [*dd*, 2H, *J* = 7.20 and 1.20 Hz, 2-$(OCH_2CH_3)C_6H_4$], 7.08–7.12 [*tt*, 2H, *J* = 6.8, 1.6 and 1.2 Hz, 2-$(OCH_2CH_3)C_6H_4$], 7.30–7.34 [*tt*, 2H, *J* = 6.0, 2.0 and 1.6 Hz, 2-$(OCH_2CH_3)C_6H_4$], 8.50 [*dd*, 2H, *J* = 6.0 and 1.60 Hz, 2-$(OCH_2CH_3)C_6H_4$]; ^{13}C NMR ($CDCl_3$): δ 15.1 [2-$(OCH_2CH_3)C_6H_4$], 28.7 (COD-CH), 32.2 (COD-CH_2), 51.2 (NCH_2CH_2N), 63.8 [2-$(OCH_2CH_3)C_6H_4$], 68.3 [2-$(OCH_2CH_3)C_6H_4$], 97.1 (COD-CH), 111.6 [2-$(OCH_2CH_3)C_6H_4$], 120.8 [2-$(OCH_2CH_3)C_6H_4$], 128.7 [2-$(OCH_2CH_3)C_6H_4$], 130.3 [2-$(OCH_2CH_3)C_6H_4$], 132.6 [2-$(OCH_2CH_3)C_6H_4$], 154.4 [2-$(OCH_2CH_3)C_6H_4$], 213.95 (*d*, *J* = 45.8 Hz, C_{carb} Rh).

Crystal data

$[RhBr(C_8H_{12})(C_{19}H_{22}N_2O_2)]$
M_r = 601.38
Monoclinic, $P2_1/c$
a = 19.7510 (6) Å
b = 17.6450 (6) Å
c = 17.1978 (7) Å
β = 114.982 (3)°
V = 5432.8 (3) Å^3
Z = 8
D_x = 1.471 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 75141 reflections
θ = 1.3–27.3°
μ = 2.12 mm^{-1}
T = 100 K
Prism, yellow
0.45 × 0.32 × 0.20 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.488, T_{max} = 0.683
76907 measured reflections
10685 independent reflections
9007 reflections with $I > 2\sigma(I)$
R_{int} = 0.088
θ_{max} = 26.0°
$h = -24 \rightarrow 24$
$k = -21 \rightarrow 21$
$l = -21 \rightarrow 21$

m374 Dinçer *et al.* • $[RhBr(C_8H_{12})(C_{19}H_{22}N_2O_2)]$ *Acta Cryst.* (2005). C**61**, m373–m375

Table 1
Selected geometric parameters (Å, °).

Rh1—Br1	2.5722 (3)	Rh2—Br2	2.5627 (3)
Rh1—C4	2.168 (2)	Rh2—C31	2.169 (2)
Rh1—C7	2.249 (3)	Rh2—C34	2.218 (2)
Rh1—C8	2.274 (3)	Rh2—C35	2.274 (2)
Rh1—C11	2.123 (2)	Rh2—C38	2.132 (2)
N2—C3	1.508 (3)	N4—C30	1.497 (3)
C2—C3	1.533 (4)	C29—C30	1.549 (3)
C4—C11	1.418 (3)	C31—C38	1.421 (4)
C7—C8	1.353 (5)	C34—C35	1.393 (4)
C1—Rh1—C4	91.67 (9)	C28—Rh2—C31	92.99 (9)
C1—Rh1—C7	153.69 (11)	C28—Rh2—C34	157.62 (10)
C1—Rh1—C8	171.40 (11)	C28—Rh2—C35	166.22 (10)
C1—Rh1—C11	92.41 (10)	C28—Rh2—C38	92.81 (9)
C1—N1—C12*A*	124.7 (4)	C28—N3—C39	122.66 (19)
C1—N2—C20	120.79 (19)	C28—N4—C47	122.61 (19)
C2—N1—C12*A*	120.8 (4)	C39—N3—C29	123.72 (18)
C11—Rh1—C4	38.56 (9)	C47—N4—C30	122.11 (19)
C20—N2—C3	121.60 (19)	N3—C28—N4	107.3 (2)
N1—C1—N2	106.9 (2)	N3—C28—Rh2	127.04 (17)
N1—C1—Rh1	130.22 (17)	N4—C28—Rh2	125.67 (16)
N2—C1—Rh1	122.79 (17)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.062$
$S = 1.02$
10685 reflections
680 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 2.0889P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96, 0.97, 0.98 and 0.93 Å for CH_3, CH_2, CH and aromatic H atoms, respectively. The displacement parameters of the H atoms were constrained as $U_{iso}(H) = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl) of the parent atom. In molecule *A*, the ethoxyphenyl group (O1/C12–C19) shows positional disorder and the refined site-occupancy factors of the disordered parts, *viz.* O1*A*/C12*A*–C19*A* and O1*B*/C12*B*–C19*B*, are 73 (6) and 27 (6)%, respectively. The disordered atoms were refined using the following restraints: SIMU, DELU, FLAT and SAME (*SHELXL97*; Sheldrick, 1997).

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*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···O1*A*	0.97	2.20	2.795 (6)	118
C3—H3*A*···O2	0.97	2.51	3.030 (4)	114
C16*B*—H16*B*···Br2^{i}	0.93	2.88	3.798 (2)	167
C29—H29*B*···O3	0.97	2.49	3.007 (4)	113
C30—H30*A*···O4	0.97	2.60	3.121 (3)	114
C43—H43···Br1	0.93	2.83	3.745 (3)	167

Symmetry code: (i) $x + 1, y, z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1125). Services for accessing these data are described at the back of the journal.

References

Bourissou, D., Guerret, O., Gabbai, F. P. & Bertrand, G. (2000). *Chem. Rev.* **100**, 39–92.
Çetinkaya, B., Özdemir, İ. & Dixneuf, P. (1997). *J. Organomet. Chem.* **534**, 153–158.
Danopoulos, A. A., Winston, S. & Hursthouse, M. B. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3090–3091.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fröhlich, N., Pidun, U., Stahl, M. & Frenking, G. (1997). *Organometallics*, **16**, 442–448.
Günay, M. E. (2004). PhD thesis, Ege University, İzmir, Turkey.
Günay, M. E., Aygün, M., Kartal, A., Çetinkaya, B. & Kendi, E. (2005). *Cryst. Res. Technol.* In the press.
Hermann, W. A. (2002*a*). *Angew. Chem. Int. Ed.* **41**, 1290–1309.
Hermann, W. A. (2002*b*). *Adv. Organomet. Chem.* **48**, 1–69.
McGuinness, D. S., Green, M. J., Cavell, K. J., Skelton, B. W. & White, A. H. (1998). *J. Organomet. Chem.* **565**, 165–178.
Pangborn, A. B., Giardollo, M. A., Grubbs, R. H., Rosen, R. K. & Timmers, F. J. (1996). *Organometallics*, **15**, 1518–1520.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
Uson, R., Oro, L. A. & Cabeza, J. A. (1985). *Inorg. Synth.* **23**, 126–130.
Weskamp, T., Böhm, V. P. W. & Hermann, W. A. (2000). *J. Organomet. Chem.* **600**, 12–22.

Acta Cryst. (2005). C**61**, m373–m375 Dinçer *et al.* • $[RhBr(C_8H_{12})(C_{19}H_{22}N_2O_2)]$ **m375**