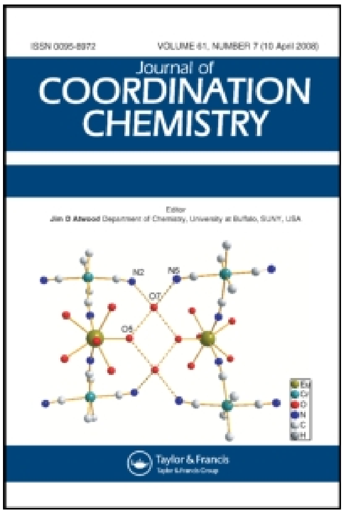

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and structural characterization of (1,3-bis(methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene)chloro(1,5-cyclooctadiene)rhodium(I)

Hasan Karabiyik[a]; Rafet KilinÇarslan[b]; Muhttn Aygün[a]; Bekİr Çetnkaya[b]; Orhan Büyükgüngör[c]
[a] Department of Physics, Dokuz Eylul University, 35160 - Buca, İzmir, Turkey [b] Department of Chemistry, Ege University, 35100 - Bornova, İzmir, Turkey [c] Department of Physics, Ondokuz Mayıs University, 55139 - Samsun, Turkey

To cite this Article Karabiyik, Hasan , KilinÇarslan, Rafet , Aygün, Muhttn , Çetnkaya, Bekİr and Büyükgüngör, Orhan(2006) 'Synthesis and structural characterization of (1,3-bis(methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene)chloro(1,5-cyclooctadiene)rhodium(I)', Journal of Coordination Chemistry, 59: 3, 343 — 350

To link to this Article: DOI: 10.1080/00958970500344946

URL: http://dx.doi.org/10.1080/00958970500344946

Journal of Coordination Chemistry
Vol. 59, No. 3, 15 February 2006, 343–350

Taylor & Francis
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Synthesis and structural characterization of (1,3-bis(methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene)chloro(1,5-cyclooctadiene)rhodium(I)

HASAN KARABIYIK*†, RAFET KILINÇARSLAN‡, MUHİTTİN AYGÜN†,
BEKİR ÇETİNKAYA‡ and ORHAN BÜYÜKGÜNGÖR§

†Department of Physics, Dokuz Eylul University, 35160 – Buca, İzmir, Turkey
‡Department of Chemistry, Ege University, 35100 – Bornova, İzmir, Turkey
§Department of Physics, Ondokuz Mayıs University, 55139 – Samsun, Turkey

(*Received in final form 17 June 2005*)

A new *N*-heterocyclic carbene (NHC) ligand with bulky substituents and functionalized methoxy-donor side arms complexed with Rh(I) was synthesized and characterized by elemental analysis, ^{1}H and ^{13}C NMR, and IR spectroscopy. The crystal and molecular structure was determined by single-crystal X-ray diffraction techniques. Two carbon atoms in the cyclooctadiene ring and three *ortho* methyl groups have positional and orientational disorder, respectively. Rhodium has square-planar coordination geometry.

Keywords: Crystal structure; Rhodium(I); *N*-Heterocyclic carbine; Cyclooctadiene

1. Introduction

Recently, transition metal complexes of *N*-Heterocyclic carbenes (NHC) have been the focus of considerable attention since they can act as catalysts or catalyst precursors in Rh-catalyzed hydrogenation [1], hydroformylation [2], hydrosilylation [3], Ru catalyzed olefin metathesis [4–6], cyclopropanation [7], furan synthesis [8, 9], Pd-catalyzed Heck or Suzuki coupling [10–12] and CO–C_2H_4 copolymerization [13]. These useful catalytic reactions prompt the search for new catalysts with high activity. This has led us to consider the preparation of carbene–metal complexes containing a potentially hemi-labile carbene ligand, one that is strongly linked to the metal but with pendant functional groups that are able to coordinate reversibly.

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*Corresponding author. Email: hasan.karabiyik@deu.edu.tr

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500344946

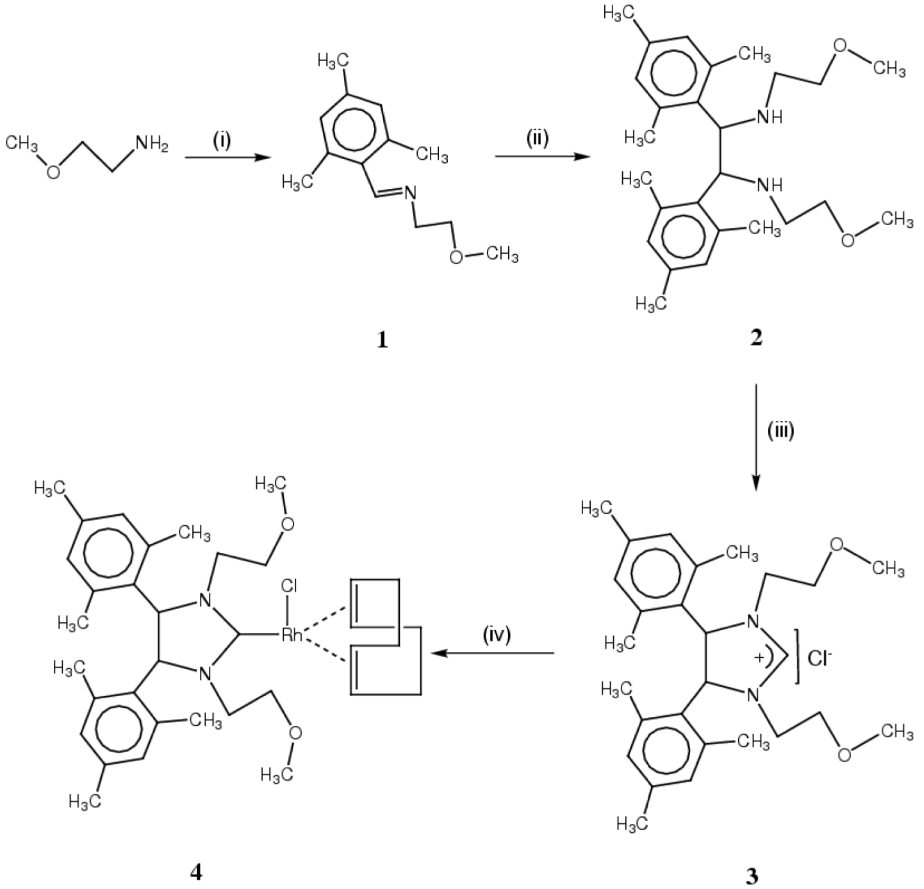

Figure 1. Synthetic scheme for **4**; (i): 2,4,6-(CH3)$_3$–C_6H_2–CHO, room temperature (RT); (ii): Al(Hg), H_2O, Et_2O, RT; (iii): $CH(OEt)_3$, NH_4Cl, 130°C; (iv): $[Rh(\mu\text{-}OMe)(1,5\text{-}COD)]_2$, CH_2Cl_2, RT.

NHC, particularly five-membered heterocycles, have emerged as an important ligand class in organometallic chemistry [14]. The close analogy of NHCs to trialkylphosphines and their excellent s-donating properties make them ligands of choice for the preparation of certain organometallic catalysts for organic synthesis [15]. NHC-containing catalysts are found to be much more effective than conventional catalysts, for instance, in C–C bond formation [16] and olefin metathesis [17]. Much work has focused on the study of structure–reactivity relationships. Thus, useful information has been collected about the influence of several structural factors, including the steric bulk of the carbene carbon [18], the presence of electron withdrawing groups in the imidazole backbone [19] and the presence or absence of unsaturation at the C_4–C_5 bond in the imidazole–dihydroimidazole series [20]. To our surprise, there is no information available concerning the effect of steric bulk at the C_4–C_5 positions. Here, we describe Rh–NHC complexes that probe this effect. Proligand **3** was prepared from **2** according to figure 1. Subsequent treatment with $[Rh(\mu\text{-}OMe)(1,5\text{-}COD)]_2$ afforded the NHC complex.

2. Experimental

2.1. *Materials and methods*

Syntheses of 1,3-bis(methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl) imidazolinium salt **3** and the rhodium complex **4** were performed under dry argon with standard Schlenk techniques. Solvents were of analytical grade and distilled after drying. NMR spectra were recorded at 297 K on a Varian spectrometer at 400 MHz (^{1}H) and 100.56 MHz (^{13}C). IR spectra (KBr pellets) were recorded in the range 400–4000 cm^{-1} on an ATI UNICAM 2000 spectrophotometer. Elemental analyses were carried out by the analytical service of TUBITAK using a Carlo Erba 1106 apparatus.

2.2. *Synthesis*

A mixture of 1,3-bis(methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl) imidazolinium chloride (0.25 g, 0.54 mmol) and $[Rh(\mu\text{-OMe})(1,5\text{-COD})]_2$ (0.13 g, 0.27 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 2 h. The solution was concentrated and pentane (15 cm^3) added. The resulting solid was filtered off and recrystallized from CH_2Cl_2/pentane (1 : 3; v/v), the brown crystals filtered off, washed with pentane (3 × 5 cm^3) and dried under vacuum. Yield: 0.310 g, 86%, m.p. = 198–200°C. Anal. Calcd for $C_{35}H_{50}N_2O_2ClRh$ (%): C, 62.82; H, 7.53; N, 4.19. Found: C, 62.86; H, 7.59; N, 4.23. ^{1}H-NMR (δ, $CDCl_3$): 1.88–1.99 [m, 4H, COD–CH_2]; 2.04 [s, 6H, 2,4,6-$(CH_3)_3C_6H_2$]; 2.08 [s, 6H, 2,4,6-$(CH)_3C_6H_2$]; 2.11 [s, 6H, 2,4,6-$(CH)_3C_6H_2$]; 2.28–2.47 [m, 4H, COD-CH_2]; 3.27 [s, 6H, $NCH_2CH_2OCH_3$]; 3.31–3.38 [m, $NCH_2CH_2OCH_3$]; 3.66 [d, 2H, $J = 2.8$ Hz, COD–CH]; 3.80–3.85 [m, 2H, $NCH_2CH_2OCH_3$]; 4.04–4.09 [m, 2H, $NCH_2CH_2OCH_3$]; 4.92–4.97 [m, 2H, $NCH_2CH_2OCH_3$]; 5.01 [d, 2H, $J = 3.6$ Hz, COD–CH]; 5.69 [s, 2H, NCHCHN]; 6.52 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2$]; 6.59 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2$]. ^{13}C-NMR (δ, $CDCl_3$): 20.9, 21.0, 21.6 [2,4,6-$(CH_3)_3C_6H_2$]; 28.8, 33.2 [COD-CH_2]; 48.2 [$NCH_2CH_2OCH_3$]; 58.9 [$NCH_2CH_2OCH_3$]; 66.0 [NCHCHN]; 67.8 [d, $J = 14.58$ Hz, COD–CH]; 72.3 [$NCH_2CH_2OCH_3$]; 98.9 [d, $J = 6.94$ Hz, COD–CH]; 127.5, 129.9, 131.3, 137.4, 138.6 [2,4,6-$(CH_3)_3C_6H_2$]; 216.4 [d, $J = 46.76$ Hz, $C_{carbene}$].

2.3. *Crystal structure*

A suitable crystal of the title compound of dimensions 0.52 × 0.45 × 0.35 mm^3 was mounted on a STOE IPDS 2 diffractometer employing graphite-monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) and crystallographic data recorded at room temperature. A summary of crystallographic data and details of the structure refinement are given in table 1. Cell parameters were determined using X-AREA software [21] on setting angles of 40,746 reflections [$1.77° < \theta < 25.56°$]. Absorption corrections were achieved by the integration method via X-RED software [21]. For determining the crystal structure, a total of 29364 reflections was recorded, with indices $h_{min} = -47$, $h_{max} = 48$, $k_{min} = -48$, $k_{max} = 48$, $l_{min} = -12$, $l_{max} = 12$. The structure was solved by SHELXS-97 [22] and refined by full-matrix least-squares techniques on F^2 using the SHELXL-97 [23]. All non-hydrogen atoms were refined anisotropically. Throughout the refinement process, two carbon atoms (C30 and C35, see figure 2) in the

Table 1. Crystal data and details of the structure refinement for the complex.

Formula	$C_{35}H_{50}N_2O_2RhCl$
Colour/Shape	Brown/Prismatic
Formula weight	669.14
Crystal system	Trigonal
$F(000)$	6336
Space group	$R\overline{3}$
Cell constants (Å)	$a = 39.9042(14)$ $c = 10.6423(3)$
Cell volume (Å^{-3})	14675.8(9)
Formula units/unit cell	18
D_x (g cm^{-3})	1.363
μ (Mo-$K\alpha$) (mm^{-1})	0.639
Calculated $T_{\min}/T_{\max}$	0.724/0.800
Temperature (K)	293(2)
Extinction coefficient	0.00016(2)
Unique reflections measured	6103
Independent/observed reflections	6103/5201
Data/restraints/parameters	6103/2/406
Final R indices [$I > 2\sigma(I)$]	$R = 0.0301$, $R_w = 0.0803$
R indices (all data)	$R = 0.0373$, $R_w = 0.0830$
Goodness-of-fit on F^2	1.05
Highest peak (e Å^{-3})	0.39
Deepest hole (e Å^{-3})	−0.42
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 15.05P]$, where $P = [F_o^2 + 2F_c^2]/3$

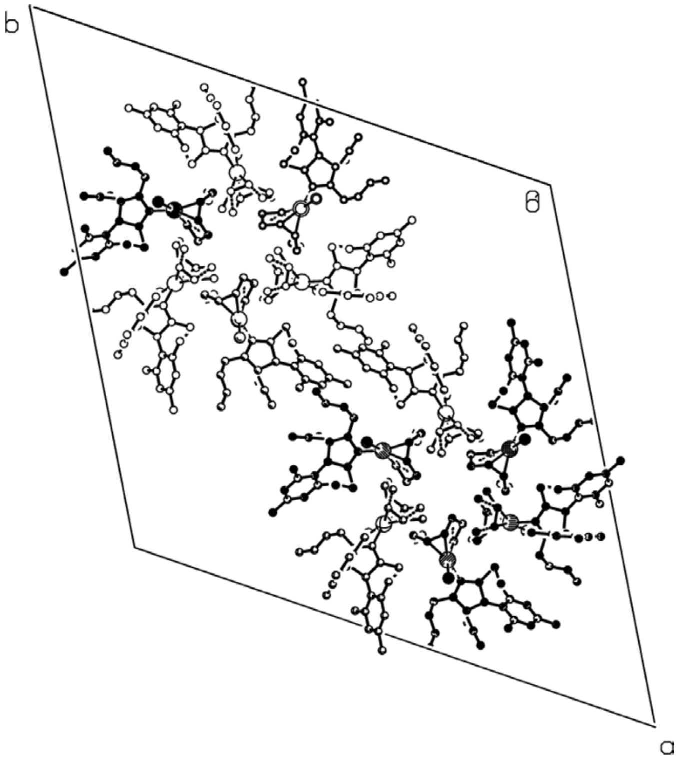

Figure 2. Orientations of the non-hydrogen atoms in the unit cell.

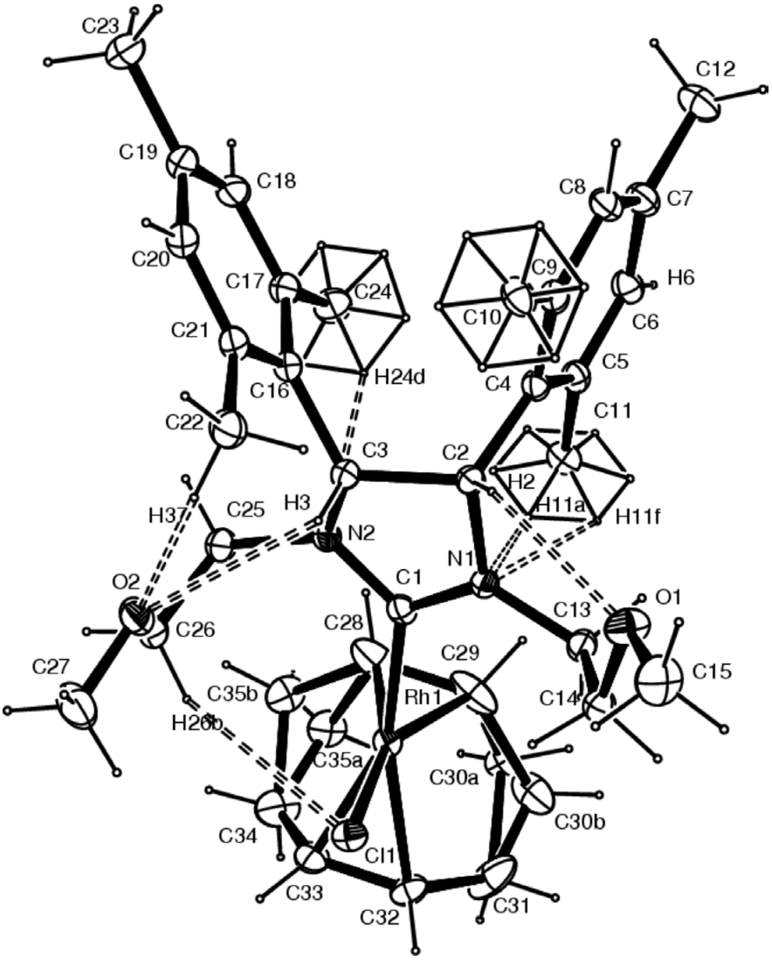

Figure 3. ORTEP drawing of the complex showing the atom numbering scheme with displacement ellipsoids plotted at the 30% probability level. Dashed lines denote weak intramolecular hydrogen bonds.

cyclooctadiene (COD) ring were treated as being disordered over two positions. In addition, three *ortho* methyl groups linked to the 2,4,6-trimethylphenyl rings were refined as idealized disordered methyl groups (two positions).

3. Results and discussion

Elemental analyses and NMR spectra are in agreement with the proposed structure. The clearest spectroscopic evidence identifying **4** as a carbene complex is the appearance of a highly deshielded ^{13}C NMR doublet for $C_{carbene}$ at 216.43 ppm ($J_{RhC} = 46.7$ Hz). The IR spectrum shows a strong band at 1485 cm^{-1} attributable to $\nu(CN_2)$. Bands in the 1400–1650 cm^{-1} region arise from skeletal vibrations of aromatic rings.

An ORTEP [24] drawing of the complex is shown in figure 3. The NHC ring (weighted average ring bond distance 1.446 Å) adopts the envelope conformation.

Table 2. Selected geometrical parameters (lengths in ångstroms, angles in degrees) for the complex.

Rh1–Cl1	2.3774(6)	N1–C1	1.341(3)
Rh1–C1	2.032(3)	N1–C2	1.478(3)
N2–C1	1.345(4)	C2–C3	1.555(4)
N1–C13	1.447(4)	Rh1–C28	2.096(3)
Rh1–C29	2.103(3)	Rh1–C32	2.216(3)
Rh1–C33	2.200(3)	C28–C29	1.397(6)
C32–C33	1.371(4)	C2–C4	1.532(3)
C28–C35B	1.528(6)	C28–C35A	1.620(10)
C29–C30B	1.668(12)	C29–C30A	1.386(13)
C30A–C31	1.661(11)	C30B–C31	1.272(11)
C34–C35B	1.548(9)	C34–C35A	1.345(8)
C31–C32	1.509(6)	C33–C34	1.510(4)
Cl1–Rh1–C1	87.08(6)	C1–N1–C2	113.6(2)
N1–C2–C3	98.32(18)	N2–C3–C2	100.9(2)
C1–N1–C13	124.8(2)	C1–N2–C25	124.6(2)
N1–C2–C4	116.5(2)	N2–C3–C16	117.9(2)
C28–Rh1–C29	38.87(17)	C32–Rh1–C33	36.16(11)
C32–C33–C34	124.1(3)	Cl1–Rh1–C32	89.45(8)
C28–Rh1–C33	81.38(12)	C29–Rh1–C32	81.11(13)
Cl1–Rh1–C1–N1	75.17(19)	Cl1–Rh1–C1–N2	−96.7(2)
Cl1–Rh1–C32–C31	−142.6(2)	Cl1–Rh1–C33–C34	153.7(2)
C1–N1–C2–C4	−107.9(2)	C1–N2–C3–C16	163.3(2)
C1–N1–C2–C3	20.7(2)	C13–N1–C1–N2	178.1(2)
C25–N2–C3–C16	−43.1(3)	C13–N1–C2–C4	71.4(3)

Deviation of the C3 atom from average NHC plane is −0.187(2) Å. As in similar carbene complexes [15, 25–28], C–N bonds in the NHC ring are different, although all are single bonds. C1–N1 and C1–N2 bonds are shorter than N1–C2 and N2–C3 bonds (see table 2). Theoretical studies indicate that the stability of these carbenes is due to electron donation from the nitrogen lone pairs into the formally vacant $p(\pi)$ orbital of the carbene carbon (C1) [10, 25]. For this reason, C1–N1 and C1–N2 bonds are shortened. The Cl–Rh–C1 angle of 87.08(6)° is in agreement with related compounds in the literature [15, 26–29]. C30 and C35 atoms in the cyclooctadiene ring are disordered over two sites with occupancies of 0.426/0.574. In addition, three *ortho* methyl groups are disordered by steric effects arising from the fact that they are close to each other. When midpoints of C28–C29 and C32–C33 are considered, it can be considered that the complex has a *cis* arrangement. These midpoints, the chlorine atom and C1 exhibit slight distortion from planarity (see table 2). As expected for a 16e Rh(I) complex, the coordination geometry about the rhodium centre is nearly square-planar. One of the 2,4,6-trimethylphenyl rings (R1, C4, ⋯, C9) is attached to NHC pseudo-equatorially and the other ring (R2, C16, ⋯, C21) is attached to NHC bisectionally (neither pseudo-axial nor pseudo-equatorial). C2 and C3 atoms have *S* and *R* configurations, respectively.

Although there are no classical hydrogen bonds in the structure, weak interactions, of which details are given in table 3, are observed. There are two π–π stacking interactions, in which R1 and R2 rings participate. The perpendicular distances of these π–π stacking interactions (R1–R2 and R2–R2) are 3.326 and 3.634 Å. Since both are smaller than 3.8 Å, it is considered that both stacking interactions contribute significantly to the stabilization of the lattice. Additionally, an edge-to-face (X–H ⋯ Cg (π-ring)) interaction, in which R2 ring is included, is observed in the crystal structure. The perpendicular distance H ⋯ (π-ring) and X–H ⋯ (π-ring) angle for the interaction

Table 3. Intramolecular and intermolecular hydrogen bonding data (lengths in Å, angles in °) for the complex.*

D–H···A	D–H	H···A	D···A	∠D–H···A
C6–H6···Cl1[a]	0.93	2.81	3.706(3)	161
C2–H2···O1	0.98	2.42	3.099(5)	126
C3–H3···O2	0.98	2.59	3.118(4)	114
C11–H11A···N1	0.96	2.15	2.929(3)	137
C11–H11F···N1	0.96	2.57	2.929(3)	103
C24–H24D···N2	0.96	2.38	3.110(4)	132
C26–H26B···Cl1	0.97	2.82	3.635(4)	142
C22–H37···O2	0.96(4)	2.58(4)	3.432(5)	149(3)

*D, donor; A, acceptor.

[a] Symmetry transformation used to generate equivalent atoms is x, y, $1+z$.

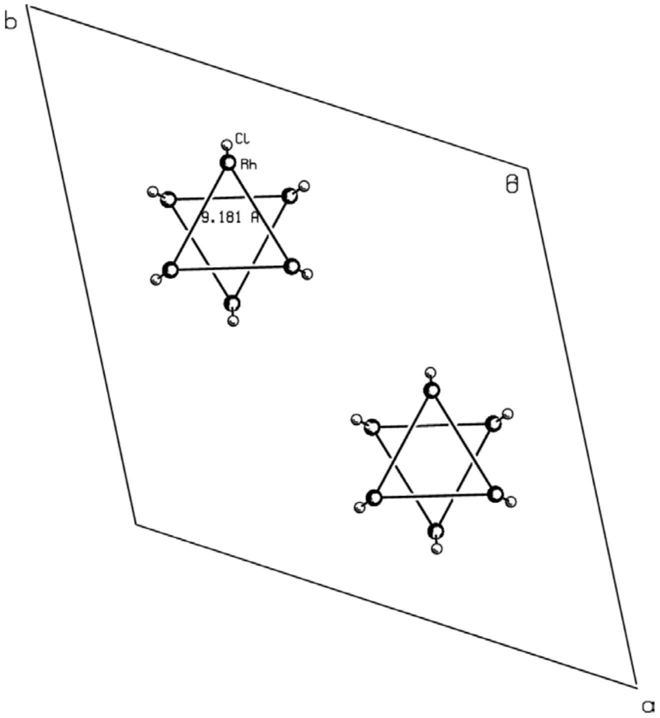

Figure 4. Equilateral triangles formed by Rh atoms in the unit cell.

are 2.862 Å and 153.42°. Rh atoms in the crystal structure form exactly equilateral triangles whose edge length is 9.181 Å (figure 4). Since these triangles are aligned in layers, they make tunnels in the crystal structure at the nano-scale along the c axis of the unit cell.

Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication

CCDC 272728. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

Dokuz Eylül and Ege University Research Funds are gratefully acknowledged for their financial support (Project numbers 04.KB.FEN.100 and 03.FEN.020). Additionally, Hasan Karabıyık would like to thank TÜBİTAK (The Scientific and Technical Research Council of Turkey) for financial support.

References

[1] M.F. Lappert. In *Transition Metal Chemistry*, Müller, E. Diemann (Eds), p. 287, Verlag, Weinheim (1981).
[2] A.C. Chen, L. Ren, A. Decken, C.M. Crudden. *Organometallics*, **19**, 3459 (2000).
[3] W.A. Herrmann, L.J. Goossen, C. Köcher, G.R.J. Artus. *Angew. Chem., Int. Ed. Engl.*, **35**, 2805 (1996).
[4] A. Fürstner. *Angew. Chem. Int. Ed.,* **39**, 3012 (2000).
[5] A. Fürstner, M. Liebl, C.W. Lehmann, M. Picauet, R. Kunz, C. Bruneau, D. Touchhard, P.H. Dixneuf. *Chem. Eur. J.*, **6**, 1847 (2000).
[6] L. Ackermann, D.E. Torn, A. Firstner. *Tetrahedron*, **56**, 2195 (2000).
[7] B. Cetinkaya, I. Ozdemir, P.H. Dixneuf. *J. Organomet. Chem.*, **534**, 153 (1997).
[8] H. Küçükbay, B. Çetinkaya, S. Guesmi, P.H. Dixneuf. *Organometallics*, **15**, 2434 (1996).
[9] B. Cetinkaya, N. Gürbüz, T. Seçkin, I. Özdemir. *J. Mol. Catal.*, **1**, 3514 (2002).
[10] D.S. McGuinnes, K.J. Cavell. *Organometallics*, **19**, 741 (2000).
[11] T. Weskamp, V.P.W. Böhm, W.A. Herrmann. *J. Organamet. Chem.*, **585**, 348 (1999).
[12] C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan. *J. Org. Chem.*, **64**, 3804 (1994).
[13] M.G. Gardiner, W.A. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler. *J. Organomet. Chem.*, **572**, 239 (1999).
[14] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand. *Chem. Rev.*, **100**, 39 (2000).
[15] W.A. Herrmann. *Angew. Chem., Int. Ed. Engl.*, **41**, 1290 (2002).
[16] O. Navarro, R.A. Kelly, S.P. Nolan. *J. Am. Chem. Soc.*, **125**, 16194 (2003).
[17] C. Morrill, T.W. Funk, R.H. Grubbs. *Tetrahedron Lett.*, **45**, 7733 (2004).
[18] M.K. Denk, A. Thadani, K. Hatano, A.J. Lough. *Angew. Chem., Int. Ed. Engl.*, **36**, 2607 (1997).
[19] A.J. Arduengo, F. Davidson, H.V.R. Dias, J.R. Goerlich, D. Khasnis, W.J. Marshall, T.K. Prakasha. *J. Am. Chem. Soc.*, **119**, 12742 (1997).
[20] A.J. Arduengo, J.R. Goerlich, W.J. Marshall. *J. Am. Chem. Soc.*, **117**, 11027 (1995).
[21] Stoe & Cie. *X-ARAEA (Version 1.18) and X-RED32 (Version 1.04)*, Darmstadt (2002).
[22] G.M. Sheldrick. *SHELXS-97, Program for the Solution of Crystal Structures*, University of Gottingen, (1997).
[23] G.M. Sheldrick. *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Gottingen, (1997).
[24] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).
[25] H. Karabıyık, R. Kılınçarslan, M. Aygün, B. Çetinkaya, O. Büyükgüngör. *Z. Naturforshung* (In press).
[26] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R. Artus. *Angew. Chem., Int. Ed. Engl.*, **34**, 2371 (1995).
[27] W.A. Herrmann, L.J. Goossen, M.J. Spiegler. *J. Organomet. Chem.*, **547**, 357 (1997).
[28] T. Weskamp, V.P.W. Böhm, W.A. Herrmann. *J. Organomet. Chem.*, **12**, 600 (2000).
[29] W.A. Herrmann, C. Köcher. *Angew. Chem., Int. Ed. Engl.*, **36**, 2163 (1997).