

# The Synthesis, Structural Characterization and Conformational Analysis of (1,3-Bis(2-methyl-4-diethylaminophenyl)imidazolidin-2-ylidene)chloro(1,5-cyclooctadiene)rhodium(I)

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A four-coordinated Rh(I) complex with a new heterocyclic carbene ligand, functionalized by amino donor pendants, **4**, was synthesized and characterized by elemental analyses, NMR and IR spectroscopy, and the molecular structure of the title compound has been determined by X-ray crystallography. Crystallographic data: monoclinic,  $P2_1/m$ ,  $a = 7.9307(5)$ ,  $b = 25.0061(12)$ ,  $c = 8.0780(6)$  Å,  $\beta = 101.366(6)^\circ$ ,  $V = 1570.58(17)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.3515(1)$  g cm<sup>-3</sup>,  $Z = 2$ . The experimentally obtained structural parameters for compound **4** compare reasonably well with those calculated at the semi-empirical ZINDO/1 level of theory carried out to elucidate conformational flexibility and steric hindrances.

**Key words:** *N*-Heterocyclic Carbenes, Rhodium Complexes, Carbene Ligand, Crystal Structure, ZINDO/1

## Introduction

The renaissance of metal complexes of *N*-heterocyclic carbenes began after their use as alternatives for phosphine complexes used in homogeneous catalysis [1–5]. The use of CC-saturated imidazolidin-2-ylidene ligands results in even higher catalytic activity. Examples of such reactions include the Heck olefination of haloarenes [6], hydroformylation [6], the asymmetric hydrosilylation of acetophenone [7, 8], hydrogenation [9] and cyclopropanation of alkenes [10].

The nature of the *N*-substituents of the carbene ligand has a pronounced effect upon the catalytic activity of the complexes [10, 11]. On the other hand, biphasic catalysis consisting of a water-phase containing catalytic species and a non-miscible organic phase continues to attract interest in view of industrial applications [12]. For this purpose a number of attempts have been made to introduce hydrophilic functional groups on convenient ligands, mainly phosphines [12–15]. Despite their similar catalytic behaviour, examples of hydrophilic carbene complexes are rare [16, 17]. The employment of highly reactive nucleophiles as well as electrophiles at different stages of the imidazolidin-2-

ylidene metal complex synthesis precludes the presence of many types of functional groups [17, 18]. As a possible system for this research, we have chosen 4-diethylamino-2-methylphenyl as the *N*-substituent. The presence of peripheral –NEt<sub>2</sub> group is expected to improve water solubility through quaternization of this group.

## Experimental Section

### Materials and methods

All manipulations were performed by using Schlenk-type flasks under dry argon and standard high vacuum-line techniques. The solvents were analytical grade and distilled after drying. NMR spectra were recorded at 297 K on a Varian instrument at 400 MHz (<sup>1</sup>H), 100,56 MHz (<sup>13</sup>C). Elemental analyses were carried out by the analytical service of TUBITAK with a Carlo Erba Strumentazione Model 1106 apparatus. Crystallographic data from single crystal X-ray diffraction have been collected with the STOE IPDS2 diffractometer.

### Preparation of the title compound

A mixture of 1,3-bis(2-methyl-4-diethylaminophenyl)imidazolinium chloride (0.37 g, 0.86 mmol) and [Rh( $\mu$ -

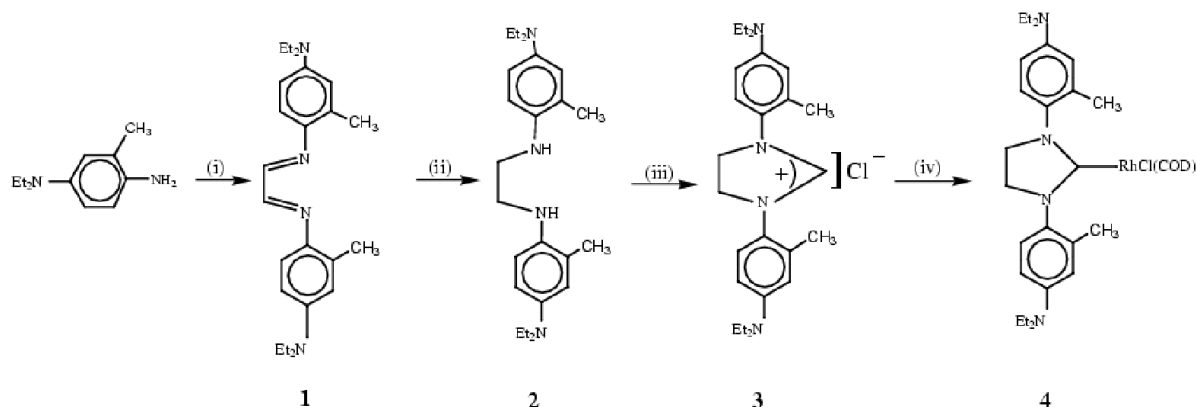


Fig. 1. Synthesis of **4**. (i) Glyoxal, EtOH, RT; (ii) NaBH<sub>4</sub>, EtOH, 78 °C; (iii) CH(OEt)<sub>3</sub>, NH<sub>4</sub>Cl, 130 °C; (iv) [Rh(μ-OMe)(1,5-COD)]<sub>2</sub>, 110 °C, PhMe.

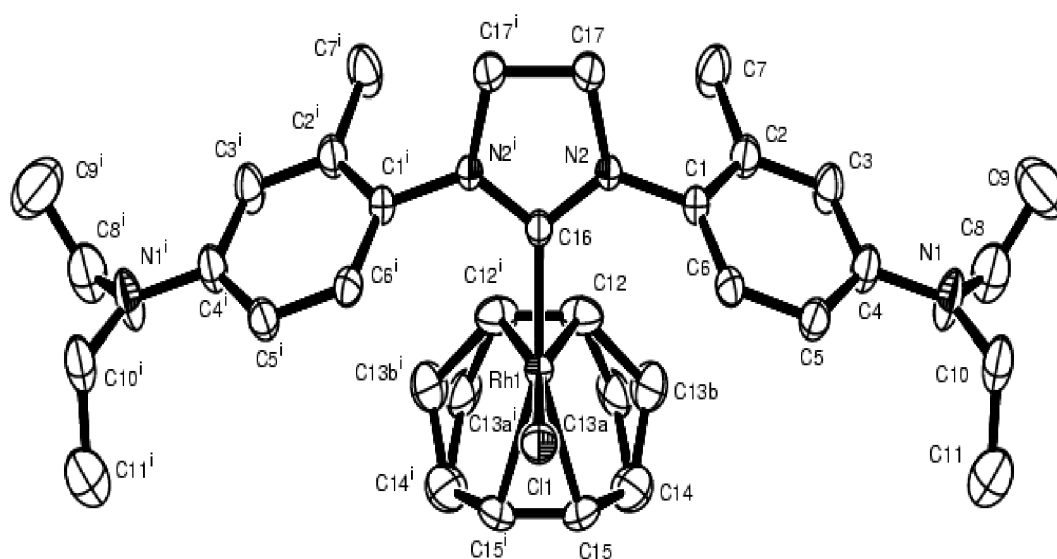


Fig. 2. ORTEP3 drawing of the title compound showing the atomic numbering scheme for non-hydrogen atoms. Displacement ellipsoids of non-H atoms are shown at the 30% probability level. [(i):  $x, y + 3/2, z$ ]

OMe)(1,5-COD)]<sub>2</sub> (0.208 g, 0.43 mmol) in toluene (5 cm<sup>3</sup>) was heated under reflux for 2 h. The solution was cooled to room temperature and hexane (15 ml) was added. The solid was filtered off and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (1 cm<sup>3</sup>/3 cm<sup>3</sup>), filtered and dried. Yield: 0.360 g. (68%, m.p.: 248–250 °C. Analysis for RhClC<sub>33</sub>H<sub>48</sub>N<sub>4</sub>: calcd. C 62.19, H 7.59, N 8.79) (found: C 62.23, H 7.76, N 8.83). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.95 (d,  $J$  = 8.58 Hz, 2H, C<sub>6</sub>H<sub>3</sub>); 6.68 (dd,  $J$  = 8.77 Hz, 2H, C<sub>6</sub>H<sub>3</sub>); 6.53 (d,  $J$  = 2.73, 2H, C<sub>6</sub>H<sub>3</sub>); 4.57 (s, 2H, COD<sub>vinyl</sub>); 3.96 (t,  $J$  = 18.33 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>); 3.84 (t,  $J$  = 18.33, 2H, NCH<sub>2</sub>CH<sub>2</sub>); 3.42–3.37 (m, 8H, NCH<sub>2</sub>CH<sub>3</sub>); 3.06 (s, 2H, COD<sub>vinyl</sub>); 2.32 (s, 6H, 2-(CH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>); 1.75–1.52 (m, 8H, COD<sub>allyl</sub>); 1.2 (t,  $J$  = 14.04, 12H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR

(d, CDCl<sub>3</sub>): δ 214.80 (d,  $J$  = 47.26 Hz, C<sub>carb</sub>=Rh); 147.53, 135.26, 131.87, 128.92, 113.25, 110.16 (C<sub>aren</sub>); 97.16 (d,  $J$  = 6.83 Hz, COD(CH=CH)); 66.99 (d,  $J$  = 15.28 Hz, COD(CH=CH)); 52.8 (NCH<sub>2</sub>CH<sub>2</sub>N); 44.76 (NCH<sub>2</sub>CH<sub>3</sub>); 32.49 (COD(CH<sub>2</sub>)); 28.40 (COD(CH<sub>2</sub>)); 19.18 (2-CH<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>); 12.8 (NCH<sub>2</sub>CH<sub>3</sub>).

#### X-ray crystallography

Suitable crystals were obtained directly from the synthesis as yellow needles. The structure was solved by the Patterson method (SHELXS-97) [19] and refined by full-matrix least squares techniques (SHELXL-97) [20]. Details

Table 1. Crystal data and structure refinement details for the title compound.

Crystal data	Data collection	Refinement
Chemical formula	RhClC <sub>33</sub> H <sub>48</sub> N <sub>4</sub>	Unique reflections
Formula weight	639.11	3162
Cryst. system	monoclinic	Refined parameters
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i> (No:11)	197
Wavelength [Å]	0.71073 (Mo-K $\alpha$ )	<i>R</i> <sub>1</sub> (for all data)
<i>a</i> [Å]	7.9307(5)	0.0481
<i>b</i> [Å]	25.0061(12)	<i>wR</i> <sub>2</sub> (for all data)
<i>c</i> [Å]	8.0780(6)	0.0826
$\beta$ [°]	101.366(6)	<i>R</i> <sub>1</sub> ( $F_o > 4\sigma(F_o)$ )
<i>V</i> [Å <sup>3</sup> ]	1570.58(17)	0.0367
<i>Z</i> / <i>F</i> (000)	2/672	<i>wR</i> <sub>2</sub> ( $F_o > 4\sigma(F_o)$ )
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.352	0.082
$\mu$ (Mo-K $\alpha$ ) [cm <sup>-1</sup> ]	6.57	GoF
Crystal size (mm)	0.60 × 0.53 × 0.22	0.859
		Reflns. with ( $F_o > 4\sigma(F_o)$ )
		2261
		Deepest hole (e Å <sup>-3</sup> )
		−0.62
		Highest peak (e Å <sup>-3</sup> )
		0.81
		Mean shift / esd
		0.0020
		Max. shift / esd
		0.0140
		Max. shift
		0.0010

Table 2. Atomic fractional coordinates and equivalent isotropic displacement parameters of the atoms in the asymmetric unit (in Å<sup>2</sup> with ESDs in parentheses). *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> [Å <sup>2</sup> ]
Rh1	0.34683(5)	1/4	0.35422(4)	0.0365(1)
Cl1	0.52785(14)	1/4	0.14913(14)	0.0502(4)
N1	0.2493(4)	−0.00732(10)	0.2432(4)	0.0766(13)
N2	0.0635(3)	0.20680(8)	0.0884(3)	0.0404(8)
C1	0.1098(3)	0.15220(10)	0.1321(4)	0.0391(10)
C2	−0.0008(4)	0.11912(12)	0.1985(4)	0.0496(11)
C3	0.0483(5)	0.06641(12)	0.2336(5)	0.0588(13)
C4	0.2030(4)	0.04564(11)	0.2072(4)	0.0530(11)
C5	0.3120(4)	0.08011(11)	0.1428(4)	0.0488(11)
C6	0.2642(4)	0.13261(11)	0.1057(4)	0.0430(10)
C7	−0.1718(5)	0.13802(14)	0.2298(6)	0.0762(14)
C8	0.1675(6)	−0.03953(17)	0.3596(6)	0.0905
C9	0.0369(7)	−0.0705(2)	0.2673(8)	0.140(3)
C10	0.3833(6)	−0.03279(15)	0.1747(6)	0.0674(15)
C11	0.5562(6)	−0.02982(18)	0.2867(6)	0.095(2)
C12	0.2021(4)	0.22236(14)	0.5260(4)	0.0630(12)
C13B	0.306(2)	0.1772(9)	0.636(3)	0.071(5)
C13A	0.307(2)	0.1997(10)	0.685(3)	0.072(5)
C14	0.4875(6)	0.18904(17)	0.6766(5)	0.0880(17)
C15	0.5604(4)	0.22284(12)	0.5537(4)	0.0553(11)
C16	0.1422(5)	1/4	0.1658(5)	0.0342(11)
C17	−0.0707(5)	0.21965(13)	−0.0596(5)	0.0556(11)

of the crystal data\*, parameters for data collection, the solution and refinement procedures are given in Table 1. All non-hydrogen atoms were anisotropically refined and an extinction correction (extinct. coeff. = 0.00746) was applied in the refinement process. Scattering factors were taken from International Tables for X-ray Crystallography [21].

\*CCDC 243199 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

There is half an independent molecule in the asymmetric unit.

#### Computational details

The initial molecular structure obtained from the X-ray crystallographic study was optimized by ZINDO/1 [22] semi-empirical quantum mechanical calculations at the spin-Restricted Hartree-Fock (RHF) level [23, 24] without any symmetry constraints. ZINDO/1 has been parameterized to generate geometries of molecules including transition metals. The optimized geometry was obtained by the application of the sequential conjugate gradient method, called the Polak-Ribiere [25] and Eigenvector Following [26] optimization algorithm with a convergence limit of 0.01 kcal/mol and an RMS gradient of 0.05 kcal/Å mol. The semi-empirical calculations were carried out using the HyperChem 6.0 program package [27]. After geometry optimization, to obtain the molecular energy profile versus the selected torsion angle [T(C17-N2-C1-C6)], this torsion angle was varied from −180° to +180° in steps of 10°, and the energy profile of the molecule was obtained by single point calculations on the computed potential energy surface. Probability-weighted coordinates of C13, which is disordered in the crystal, were used in the computations.

#### Results and Discussion

The key intermediates **1–3** were obtained readily by the condensation of 2-methyl-4-diethylaminoaniline with glyoxal. The resulting Schiff base **1** underwent a smooth reduction providing the ethylenediamine **2** which was converted to the corresponding imidazolinium chloride by treatment with CH(OEt)<sub>3</sub> in the presence of NH<sub>4</sub>Cl. Next, the salt **3** was deprotonated in situ with [Rh(μ-OMe)(1,5-COD)]<sub>2</sub> to afford the desired complex **4**.

Elemental analyses and NMR spectra were in agreement with the proposed structure. The clearest spectroscopic evidence identifying **4** as a carbene complex is the appearance of a highly deshielded  $^{13}\text{C}$  NMR doublet for  $\text{C}_{\text{carb}}$  at 214.80 ppm ( $J_{\text{RhC}} = 47.3$  Hz). The IR spectrum of **4** shows a strong band at  $1520\text{ cm}^{-1}$  attributable to  $\nu(\text{CN}_2)$ . The absorption bands in the  $1400\text{--}1600\text{ cm}^{-1}$  regions arise from the skeletal vibrations of the aromatic rings of the ligand.

A thermal ellipsoid drawing of compound **4** is shown in Fig. 2 [28]. Fractional atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are listed in Table 2. Single crystal X-ray diffraction analysis confirmed the monomeric structure of **4**. Several features of this structure, including the planar geometry around the Rh atom and the short  $\text{N-C}_{\text{carb}}$  distances ( $\sim 1.34\text{ \AA}$ ), are consistent with a carbene complex structure. Rh1, C11 and C16 atoms have special positions ( $y = 1/4$ ). No chiral centers are found in the molecule, which has two-fold symmetry on the mid points of the  $\text{C12-C12}^i$  and  $\text{C15-C15}^i$  bonds. Rh1, C11 and C16 are located on the mirror plane and the whole molecule has mirror plane through the Rh1-C16 bond. Weighted average ring bond distances in the cyclooctadiene and carbene rings are 1.4395 and 1.3908  $\text{\AA}$ , respectively. The COD ring exhibits a boat conformation with the  $\text{Rh-C}_{\text{COD}}$  distances ranging from 1.994(4) to 2.203(4)  $\text{\AA}$ . The bond distances  $\text{Rh1-C12}$  and  $\text{Rh1-C12}^i$  are shorter than  $\text{Rh1-C15}$  and  $\text{Rh1-C15}^i$ . These results agree with the literature values [29,30]. Bond distances between C and N atoms in the *N*-heterocyclic carbene ring have considerable differences. Although both  $\text{C16-N2}$  and  $\text{C17-N2}$  are single bonds,  $\text{C16-N2}$  [1.339(3)  $\text{\AA}$ ] is shorter than the others. Similar arguments can be proposed for the  $\text{C17}^i\text{-N2}^i$  and  $\text{C16-N2}^i$  bonds. The 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 atom linked to rhodium is relatively higher than on other carbon atoms in the molecule, whereas excess charges located on the nitrogen atoms in the carbene ring are lower than on other nitrogen atoms in the molecule (see Fig. 5). The  $\text{Cl-Rh-C}_{\text{carbene}}$  angle of  $88.89(12)^\circ$  is in consistency with this type of compounds in the literatures [1, 2, 6, 16, 32–34]. The dihedral angle between planes defined by  $\text{Rh-C12-C12}^i$  and  $\text{Rh-C15-C15}^i$  is  $87.3(3)^\circ$ . The deviation of the chlo-

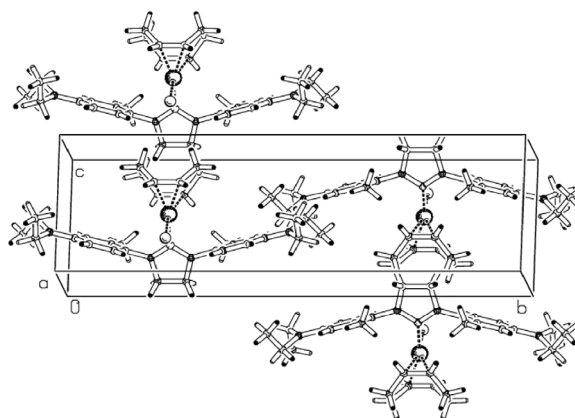


Fig. 3. Molecular packing diagram of the unit cell.

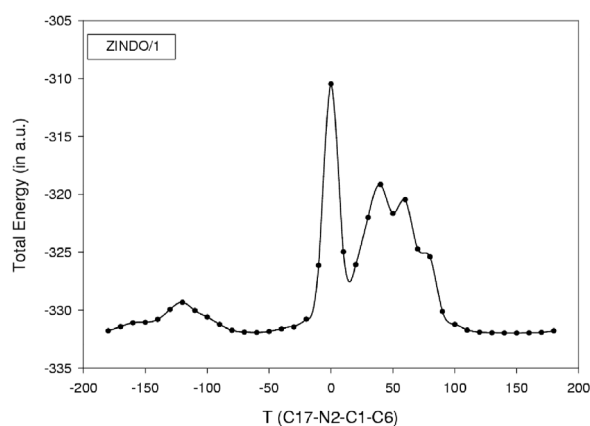
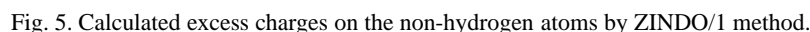


Fig. 4. Calculated energy profile from ZINDO/1 of the title molecule *versus* the torsion angle  $T(\text{C17-N2-C1-C6})$ .

rine atom from the plane  $\text{Rh-C12-C12}^i$  is  $0.045(1)\text{ \AA}$ , and the deviation of  $\text{C}_{\text{carbene}}$  from the plane  $\text{Rh-C15-C15}^i$  is  $0.005(3)\text{ \AA}$ . When midpoints of  $\text{C12-C12}^i$  and  $\text{C15-C15}^i$  are considered, it can be stated that the title compound is a *cis* isomer. These midpoints, the chlorine atom and  $\text{C}_{\text{carbene}}$  exhibit a slight distortion from exact planarity at the rhodium atom. The coordination geometry about the rhodium center is approximately square-planar, as expected for a  $16\text{ e}^-$  Rh(I) complex. Throughout the refinement process, C13 was treated as disordered. C13 is located in C13A and C13B positions with probabilities of 48.2% and 51.8%. There is weak  $\pi$ - $\pi$  stacking [symm. code:  $-x, -y, -z$ ] among 2-methyl-4-diethylaminophenyl rings (centroid, Cg16) in the crystal. The distance between the ring centroids is  $5.9731(18)\text{ \AA}$ , and two  $\text{C-H}\cdots\pi$  interactions are also found in the structure. For the  $\text{C9}\cdots\text{H23b}\cdots\text{Cg16}$  interaction [sym. code:  $-x, -y, -z$ ], the  $\text{H23b}\cdots\text{Cg16}$ ,

— Bond distances —			— Bond angles —			— Torsion angles —		
	X-ray	ZINDO/1		X-ray	ZINDO/1		X-ray	ZINDO/1
C17-C17 <sup>i</sup>	1.518(5)	1.473	C11-Rh1-C16	88.89(12)	98.15	C15-Rh1-C12-C13B	−27.2(9)	−24.05
N2-C17	1.471(5)	1.414	C11-Rh1-C15	91.53(9)	85.65	C15-Rh1-C12-C12 <sup>j</sup>	106.2(2)	109.09
N2-C16	1.339(3)	1.337	C11-Rh1-C12	160.61(10)	162.77	C16-Rh1-C12-C13B	135.8(9)	137.93
Rh1-C16	1.994(4)	1.887	C12-Rh1-C15	81.70(12)	88.20	C16-Rh1-C12-C12 <sup>j</sup>	−90.73(18)	−88.93
Rh1-C12	2.085(3)	2.047	C12-Rh1-C16	92.06(14)	83.15	C12 <sup>j</sup> -Rh1-C12-C13B	−133.4(9)	−133.14
Rh1-C15	2.202(3)	2.068	C15-Rh1-C16	162.03(8)	162.24	C15 <sup>j</sup> -Rh1-C12-C13	−61.3(9)	−59.86
Rh1-C11	2.3965(12)	2.284	N2-C16-N2 <sup>i</sup>	107.5(3)	110.17	C11-Rh1-C15-C14	−148.5(2)	−150.05
C12-C12 <sup>i</sup>	1.382(5)	1.345	C16-N2-C17	113.5(2)	110.23	C11-Rh1-C15-C15 <sup>j</sup>	90.50(18)	89.59
C15-C15 <sup>i</sup>	1.358(4)	1.341	N2-C17-C17 <sup>i</sup>	102.6(3)	104.63	C12-Rh1-C15-C14	13.2(2)	10.08
C12-C13A/B	1.50(2)/1.57(2)	1.450	C1-C2-C7	122.5(3)	122.38	C12-Rh1-C15-C15 <sup>j</sup>	−107.7(2)	−110.28
C13A/B-C14	1.471(18)/1.443(18)	1.464	N2-C1-C2	120.7(2)	122.79	C12 <sup>j</sup> -Rh1-C15-C14	50.2(2)	46.64
C14-C15	1.503(5)	1.452	N1-C8-C9	109.7(4)	116.18	C15 <sup>j</sup> -Rh1-C15-C14	121.0(3)	120.36
N2-C1	1.440(3)	1.406	C8-N1-C10	116.9(3)	117.35	C11-Rh1-C16-N2	88.3(3)	92.10
N1-C4	1.390(4)	1.391	N1-C10-C11	113.9(4)	115.98	C12-Rh1-C16-N2 <sup>j</sup>	111.1(3)	106.48



Total energy [kcal/mol]	-208320.373
Total energy (a.u.)	-331.973
Binding energy [kcal/mol]	-27666.488
Isolated atomic energy [kcal/mol]	-180653.885
Electronic energy [kcal/mol]	-1944804.692
Core-core interaction [kcal/mol]	1736484.318
Heat of formation [kcal/mol]	-18912.232
Molecular point group	C <sub>1</sub>
Point charge dipole (debye)	6.922
sp hybrid dipole (debye)	2.752
pd hybrid dipole (debye)	0.069
Total dipole (debye)	9.486

the same C9...Cg distance, C9---H23c...Cg16 [sym. code:  $-x, -y, -z$ ], the H23c...Cg16 distances and the C9---H23c...Cg16 angle are 3.2244 Å and 107.78° respectively.

Although the optimized geometry of the molecule is in  $C_1$  molecular point symmetry group, the crystallographic structure is in  $C_s$  point symmetry group. Except for this difference, no considerable difference is found in the study. Some geometrical parameters obtained by the different methods are compared in Table 3, and energy parameters are given in Table 4. The calculated energy profile from ZINDO/1 versus the torsion angle  $T(C17-N2-C1-C6)$  is given in Fig. 4. In this profile, the prominent peak near to  $0^\circ$  is due to steric hindrance between the methyl group linked to C2 and the COD ring, especially the rhodium atom. The other

peaks are also primarily due to the rhodium atom and COD, not due to the position or orientation of the chlorine atom.

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