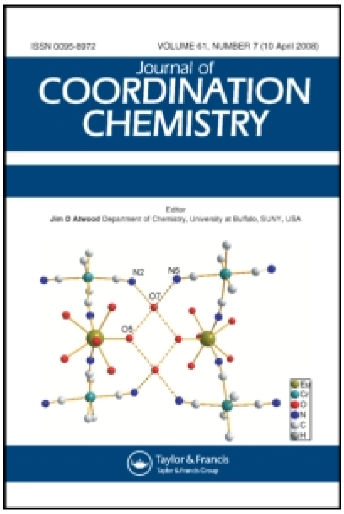

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Synthesis and structural characterization of two novel <i>N</i>-heterocyclic carbene complexes of Rh(I)

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Synthesis and structural characterization of two novel *N*-heterocyclic carbene complexes of Rh(I)

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Two new *N*-heterocyclic carbene (NHC) ligands with *p*-methylphenyl and *p*-methoxyphenyl substituents on 4,5-positions and methoxyethyl pendants on N atoms of the imidazole ring were complexed together with cyclooctadiene and an iodide ion to Rh(I) to give **4a** and **4b**, respectively. The complexes were characterized by elemental analyses, NMR and IR spectroscopy. In addition, molecular and crystal structure of **4a** was determined by single-crystal X-ray methods. In **4a** the rhodium ion has distorted square planar coordination geometry chelating with cyclooctadiene (COD) ligand. Molecules of **4a** form polymeric chains along the *c* axis through C–H $\cdots$ I hydrogen bonds.

Keywords: Crystal structure; *N*-heterocyclic carbene; Iodide; Rh(I) complex; Hydrogen bond

1. Introduction

Because of their extraordinary properties, *N*-heterocyclic carbenes (NHCs) have found application in a great variety of catalytic processes which include C–C coupling reactions [1–3], formation of furans [4–6], cyclopropanation [7], olefin metathesis [8–11], hydroformylation [12], polymerization [13] and hydrosilylation reactions [14–16]. These useful catalytic reactions attract interest in the search of new catalysts with high activity. The nature of the *N*-substituents of the carbene ligand have pronounced effects upon catalytic activity [4, 7]. Complexes containing NHCs, which are neutral two-electron-donor ligands with negligible π-backbonding, are thermally rather stable. This feature represents an essential prerequisite for the synthesis of highly efficient catalysts.

NHCs, particularly five-membered heterocycles, have emerged as a predominant ligand class in organometallic chemistry. Much work has focused on the study of structure-reactivity relationships in NHCs. Thus, useful information has been collected

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about the influence of several structural factors, including steric bulkiness around the carbene carbon, the presence of electron-withdrawing groups in the imidazole backbone or the presence or absence of unsaturation at the C_4–C_5 bond in the imidazole/dihydroimidazole series [17–21]. On the other hand, in catalytic transformations, a stabilizing ligand must coordinate and uncoordinate as many times as possible. In this, hemilabile chelate ligands are ideal. This concept has been applied to NHC ligands where neutral donors with N, P, O or S atoms are attached to the 5-membered ring by a suitable spacer [7]. Here, we describe Rh–NHC complexes bearing *p*-methylphenyl and *p*-methoxyphenyl groups at C_4–C_5 positions and incorporate 2-methoxyethyl substituents on N atoms.

2. Experimental

2.1. *Materials and methods*

Synthesis of imidazolinium salts **3a**,**b** and the rhodium complexes **4a**,**b** were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were of analytical grade and distilled after drying. NMR spectra were recorded at 297 K on Varian spectrometer operating at 400 MHz (^{1}H) or 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 TÜBİTAK with a Carlo Erba 1106 apparatus. Crystallographic data related to single crystal X-ray diffraction were measured with a STOE-IPDS 2 diffractometer.

2.2. *Synthesis*

2.2.1. Preparation of 4a. A mixture of 1,3-bis(methoxyethyl)-4,5-bis(4-methylphenyl) imidazolinium iodide (0.25 g, 0.50 mmol) and $[Rh(\mu\text{-OMe})(1,5\text{-COD})]_2$ (0.12 g, 0.25 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 2 h and hexane (15 cm^3) was added. The resulting brown precipitate was filtered off and recrystallized from CH_2Cl_2/EtOH (1 : 3, v/v). Yield: 0.296 g, 84%; m.p.: 185–187°C. Anal. Calcd for $RhIC_{31}H_{42}N_2O_2$ (%): C, 52.85; H, 6.01; N, 3.98. Found: C, 53.12; H, 6.10; N, 4.09. ^{1}H NMR (δ, $CDCl_3$): 1.82 [t, 2H, $J = 8.4$ Hz, COD–CH_2]; 1.96 [t, 2H, $J = 8.4$ Hz, COD–CH_2]; 2.15 [s, 6H, 4-$CH_3C_6H_4$]; 2.29 [d, 4H, $J = 6.4$ Hz, COD–CH_2]; 3.25 [s, 6H, $NCH_2CH_2OCH_3$]; 3.38 [t, 2H, $J = 4.8$ Hz, $NCH_2CH_2OCH_3$]; 3.41 [t, 2H, $J = 3.8$ Hz, $NCH_2CH_2OCH_3$]; 3.46–3.49 [m, 2H, $NCH_2CH_2OCH_3$]; 3.93 [s, 2H, COD–CH]; 5.14–5.18 [m, 2H, $NCH_2CH_2OCH_3$]; 5.20 [s, 2H, COD–CH]; 5.22 [s, 2H, NCHCHN]; 6.84 [d, 4H, $J = 7.6$ Hz, 4-$CH_3C_6H_4$]; 6.95 [d, 4H, $J = 6.0$ Hz, 4-$CH_3C_6H_4$]. ^{13}C NMR (δ, $CDCl_3$): 21.3 [4-$CH_3C_6H_4$]; 29.7 [COD–CH_2]; 32.7 [COD–CH_2]; 47.2 [$NCH_2CH_2OCH_3$]; 58.9 [$NCH_2CH_2OCH_3$]; 69.1 [NCHCHN]; 70.2 [$NCH_2CH_2OCH_3$]; 72.2 [d, $J = 13.78$ Hz, COD–CH]; 97.8 [d, $J = 6.13$ Hz, COD–CH]; 128.3, 129.2, 131.7, 137.5 [4-$CH_3C_6H_4$]; 215.5 [d, $J = 44.45$ Hz, C_{carb} Rh].

2.2.2. Preparation of 4b. The compound was prepared in the same manner as **4a** using 1,3-bis(methoxyethyl)-4,5-bis(4-methoxylphenyl)imidazolinium iodide

(0.26 g, 0.50 mmol) and $[Rh(\mu\text{-OMe})(1,5\text{-COD})]_2$ (0.12 g, 0.25 mmol). Brown crystals were obtained. Yield: 0.473 g, 88%; m.p.: 187–189°C. Anal. Calcd for $RhIC_{31}H_{42}N_2O_4$ (%): C, 50.56; H, 5.75; N, 3.80. Found: C, 50.67; H, 4.94; N, 4.26. ^{1}H NMR (δ, $CDCl_3$): 1.78 [t, 2H, $J = 5.6$ Hz, COD–CH_2]; 1.88 [t, 2H, $J = 5.4$ Hz, COD–CH_2]; 2.29 [d, 4H, $J = 6.4$ Hz, COD–CH_2]; 3.25 [s, 6H, $NCH_2CH_2OCH_3$]; 3.28–3.39 [m, 2H, $NCH_2CH_2OCH_3$]; 3.40–3.42 [m, 2H, $NCH_2CH_2OCH_3$]; 3.46–3.51 [m, 2H, $NCH_2CH_2OCH_3$]; 3.66 [s, 6H, 4-$OCH_3C_6H_4$]; 3.93 [s, 2H, COD–CH]; 5.13–5.17 [m, 2H, $NCH_2CH_2OCH_3$]; 5.18 [s, 2H, COD–CH]; 5.20 [s, 2H, NCHCHN]; 6.59 [d, 4H, $J = 9.2$ Hz, 4-$OCH_3C_6H_4$]; 6.99 [s, 4H, 4-$OCH_3C_6H_4$]. ^{13}C NMR (δ, $CDCl_3$): 29.6 [COD–CH_2]; 32.4 [COD–CH_2]; 47.2 [$NCH_2CH_2OCH_3$]; 55.3 [4-$OCH_3C_6H_4$]; 58.9 [$NCH_2CH_2OCH_3$]; 69.9 [NCHCHN]; 71.7 [$NCH_2CH_2OCH_3$]; 72.2 [d, $J = 14.58$ Hz, COD–CH]; 97.8 [d, $J = 6.94$ Hz, COD–CH]; 113.7, 126.9, 129.5, 159.2 [4-$OCH_3C_6H_4$]; 215.5 [d, $J = 45.25$ Hz, C_{carb} Rh].

2.3. *X-ray crystallography*

A suitable crystal of **4a** with dimensions $0.380 \times 0.317 \times 0.280$ mm^3 was mounted on a STOE IPDS 2 diffractometer employing plane graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å), and crystallographic data were recorded at room temperature. A summary of crystallographic data and details of the structure refinement are listed in table 1. Cell parameters were determined by using X-AREA software [22] from the setting angles of 41574 reflections [$1.36° < \theta < 26.11°$]. Absorption correction was achieved by the integration method via X-RED software [22]. For determining the crystal structure, a total of 29895 reflections (6105 unique, 4087 observed [$I > 2\sigma(I)$]

Table 1. Crystal data and details of the structure refinement for **4a**.

Chemical formula	$C_{31}H_{42}N_2O_2RhI$
Colour/Shape	Brown/Prism
Formula weight	704.50
Crystal system	Monoclinic
$F(000)$	1424
Space group	$P2_1/c$
Cell constants (Å, °)	
a	10.3851(5)
b	19.8826(12)
c	15.6972(8)
β	107.303(4)
Cell volume (Å^3)	3094.5(3)
Formula units/unit cell	4
Density (g cm^{-3})	1.512
μ (Mo-Kα) mm^{-1}	1.578
Calculated T_{min}/T_{max}	0.554/0.643
Temperature (K)	293(2)
Unique reflections measured	6105
Data/restraints/parameters	4087/0/343
Final R indices [$I > 2\sigma(I)$]	$R = 0.0379$, $R_w = 0.0973$
R indices (all data)	$R = 0.0577$, $R_w = 0.1029$
Goodness-of-fit (GoF) on F^2	0.932
Highest peak (e Å^{-3})	0.40
Deepest hole (e Å^{-3})	−1.09
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$ where $P = [F_o^2 + 2F_c^2]/3$

were collected with $R_{\text{int}} = 0.0881$. The structure was solved by SHELXS-97 [23] and refined by full-matrix least-square techniques on F^2 using the SHELXL-97 program [24] with anisotropic temperature parameters for the non-hydrogen atoms. Hydrogen atoms were located geometrically and refined as riding with respective C–H distances of 0.93, 0.96, 0.97 and 0.98 Å corresponding to the aromatic, methyl, methylene and methine C–H bonds. Their isotropic displacement parameters were constrained as $1.5U_{\text{eq}}$(C) for methyl carbon atoms and $1.2U_{\text{eq}}$(C) for the other types of carbon. Further details are available in supplementary material, deposited at the CCDC (see below).

3. Results and discussion

Proligands **3a**,**b** derived were prepared by treatment of **2a**,**b** with $(EtO)_3CH/NH_4I$ as shown in figure 1. Their subsequent treatment with $[Rh(\mu\text{-OMe})(1,5\text{-COD})]_2$ afforded the complexes **4a** and **4b**. The formulations of both complexes are consistent with analytical and spectroscopic data. Generation of NHC complex was confirmed by the disappearance of the low field shifted C2-H of **3** and detection of the ^{13}C NMR resonance of C_{carb} at δ 215.5 ppm ($J = 44.45$ Hz for **4a**, 45.25 Hz for **4b**). IR spectra of **4a**,**b** show a strong band at 1473 cm^{-1} attributable to $\nu(CN_2)$. Absorption bands in the 1400–1620 cm^{-1} region arise from skeletal vibrations of the aromatic rings of the ligand.

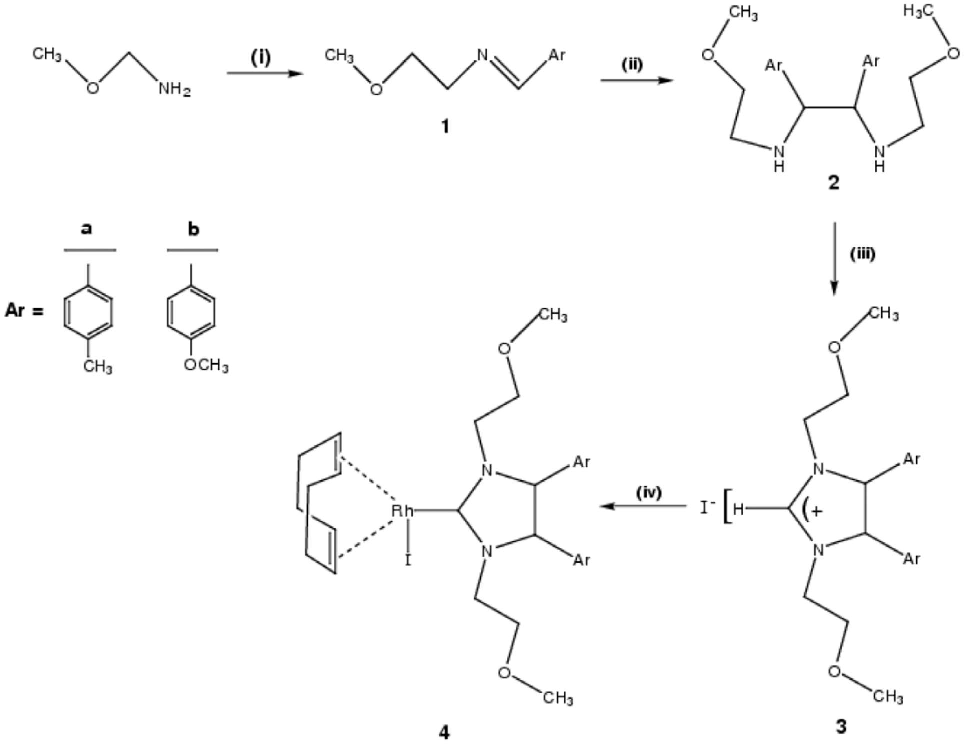

Figure 1. Synthesis scheme for **4a** and **4b**; (i) 4-$CH_3C_6H_4$–CHO or 4-$CH_3OC_6H_4$–CHO, RT; (ii) Al(Hg), H_2O, Et_2O, RT; (iii) $CH(OEt)_3$, NH_4I, 140°C; (iv) $[Rh(\mu\text{-OMe})(1,5\text{-COD})]_2$, CH_2Cl_2, RT.

3.1. *Structure of 4a*

An ORTEP [25] view of **4a** is shown in figure 2. The asymmetric unit contains one neutral mononuclear complex. Selected bond distances, bond angles and torsion angles are listed in table 2. The molecular structure proves that in the solid state the pendant 2-methoxyethyl group is not coordinated to the metal centre of **4a**. The NHC ring of which the weighted average ring bond distance is 1.4389 Å adopts a nearly planar conformation. The maximum deviation from the average ring plane of NHC involves C2 atom (−0.033(3) Å). As with similar carbene complexes [26–30], it is remarkable that C–N bond lengths in the NHC ring are different, although all C–N bonds are of single bond character. C1–N1 and C1–N2 bonds are shorter than C2–N1 and C3–N2 (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(π) orbital of the carbene carbon (C1) [26, 30]. For this reason, $C_{carbene}$–N bonds are shortened in NHC complexes. The distance between Rh and the midpoint of the double bond of the COD ligand which is *trans* to NHC is longer than that *trans* to the iodide with respective distances of 2.103 and 2.005 Å. When midpoints of C28–C29 and C24–C25 are considered, it can be stated that the complex **4a** has a *cis* arrangement.

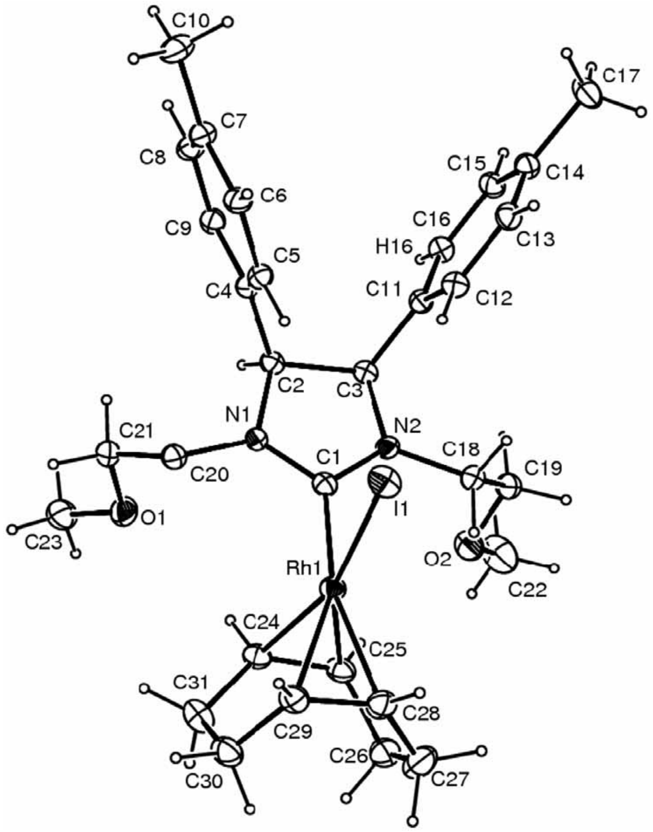

Figure 2. An ORTEP view of the complex **4a** indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 10% probability level.

Table 2. Selected geometrical parameters (Å, °) for **4a**.

Bond lengths			
C24–Rh1	2.125(4)	C25–Rh1	2.118(4)
C28–Rh1	2.206(4)	C29–Rh1	2.216(4)
I1–Rh1	2.6774(4)	Rh1–C1	2.014(4)
C1–N2	1.332(5)	C1–N1	1.337(5)
C2–N1	1.472(5)	N2–C3	1.471(5)
C11–C3	1.506(5)	C2–C4	1.518(5)
C2–C3	1.566(5)	C29–C28	1.365(7)
C24–C25	1.386(6)	C25–C26	1.549(7)
C24–C31	1.496(7)	C30–C31	1.493(7)
Bond angles			
C1–Rh1–I1	85.43(9)	N2–C1–N1	108.1(3)
C1–N1–C2	114.0(3)	C1–N2–C3	114.4(3)
C28–Rh1–C29	35.95(18)	C25–Rh1–C24	38.12(17)
C1–Rh1–C25	94.75(16)	C1–Rh1–C24	91.78(15)
C29–Rh1–I1	95.80(12)	C28–Rh1–I1	91.97(16)
Torsion angles			
C18–N2–C3–C11	−48.0(5)	C4–C2–N1–C20	52.8(5)
N1–C2–C3–N2	−5.1(3)	N2–C1–N1–C2	−4.3(4)
C25–C26–C27–C28	21.5(9)	C24–C25–C26–C27	−84.2(7)
C29–C30–C31–C24	20.7(7)	C25–C24–C31–C30	53.0(7)
I1–Rh1–C1–N1	−94.5(3)	I1–Rh1–C1–N2	80.6(3)

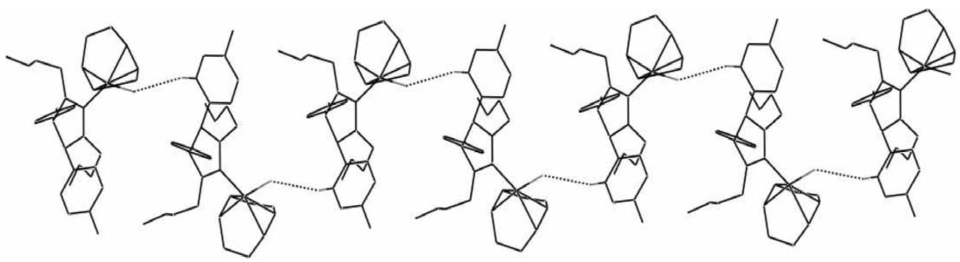

Figure 3. Polymeric chain of **4a** along the *c* axis constituted by means of C–H $\cdots$ I hydrogen bonds shown by dashed lines.

These midpoints, the iodide ion and C1 exhibit slight distortion from exact planarity around the rhodium atom (table 2). As expected for a 16e Rh(I) complex, the coordination geometry is distorted square planar. C2 and C3 atoms have *S* and *R* absolute configurations, respectively. The COD ring adopts the distorted boat conformation with the total puckering amplitude $Q_T = 1.4643(58)$ Å [31].

There is C–H $\cdots$ I intermolecular hydrogen bonding associated with the C16, H16 and I1 atoms in the crystal structure. Neutral complexes of **4a** form a one-dimensional polymeric array along the [001] direction (figure 3). Distances between H16 and I1, and the angle C16–H16 $\cdots$ I1 are 3.04 Å and 164°, respectively. The symmetry code to generate the positions of the equivalent atoms for the intermolecular hydrogen bond is defined as x, $1/2 - y$, $-1/2 + z$. The C–H $\cdots$ I hydrogen bond is presumably responsible for the distortion from purely square planar coordination geometry.

Supplementary data

Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 600355. 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; Email: deposit@ccdc.cam.ac.uk).

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