

Neutral and Cationic Rhodium(III) Complexes with Tridentate Bis(benzimidazole)amine Ligands

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The X-ray crystal structures of bis(benzimidazol-2-ylmethyl)methylamine (L) and *N,N*-bis(1-methylbenzimidazol-2-ylmethyl)methylamine (Me₂L) are described; mono- and bis-ligand rhodium(III) complexes of L and Me₂L are prepared and characterized by elemental analysis, conductometric measurements, NMR and IR spectroscopy.

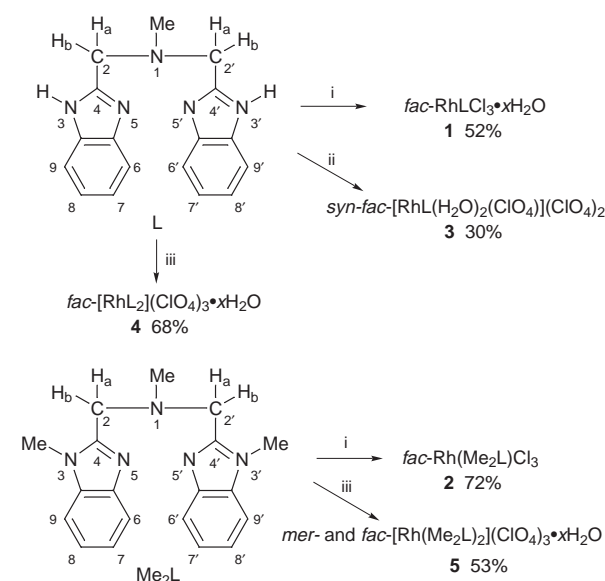
It has been demonstrated that different rhodium(III) substrates, such as RhCl₃·3H₂O and [Rh(H₂O)₆](ClO₄)₃ used as starting materials for syntheses of rhodium compounds, affect the stoichiometry of the substitution products.^{24b,28}

Here, we present the synthesis and structural characterization of rhodium complexes with bis(benzimidazol-2-ylmethyl)methylamine (L) and *N,N*-bis(1-methylbenzimidazol-2-ylmethyl)methylamine (Me₂L) using RhCl₃·H₂O and [Rh(H₂O)₆](ClO₄)₃ as starting reagents. The molecular structures of L and Me₂L have been determined by single-crystal X-ray analysis. The most relevant result of the measurements is establishing the effect of the substituents R on the molecular structure of the ligands. For ligand L the C(2) atom is disordered between two symmetry related positions while the C(1) carbon atom is disordered between two sites [the other position is marked as C(1')] with occupancy factors for these two positions set to 0.5. Overall ligand L is planar (Fig. 1). The presence of two methyl groups at N(2) and N(4) atoms in the ligand Me₂L results in distortion of the benzimidazole planes. The angle between the planes C(11)N(3)C(17)C(16)C(15)C(14)C(13)C(12)N(2) and C(21)N(5)C(27)C(26)C(25)C(24)C(23)C(22)N(4) is 66.24(4)° (Fig. 2).

Reaction of rhodium trichloride with L and Me₂L produced complexes of formulae *fac*-RhLCl₃·xH₂O **1** and *fac*-Rh(Me₂L)Cl₃ **2**, independently of the substrate ratio used (Scheme A).

[Rh(H₂O)₆](ClO₄)₃ in acidic water-ethanolic solution reacts with L in 1:1 molar ratio to give *syn*-[RhL(ClO₄)(H₂O)₂](ClO₄)₂ **3**, while *fac*-[RhL₂](ClO₄)₃·3H₂O **4** was formed when a 1:2 metal:ligand molar ratio was applied.

The reaction of [Rh(H₂O)₆]³⁺ with Me₂L in 1:2 ratio gives a mixture of isomers of [Rh(Me₂L)₂](ClO₄)₃·H₂O **5** with the ligands coordinated facially and **5'** involving a meridional arrangement of the Me₂L groups. The structures



Scheme A Reagents and conditions: i, RhCl₃·3H₂O, EtOH and/or HClO₄, N₂, 75 °C, Rh:L (or Me₂L) = 1:1 or 1:2; ii, [Rh(H₂O)₆]³⁺, HClO₄-EtOH, Rh:L = 1:1; iii, [Rh(H₂O)₆]³⁺, Rh:L (or Me₂L) = 1:2.

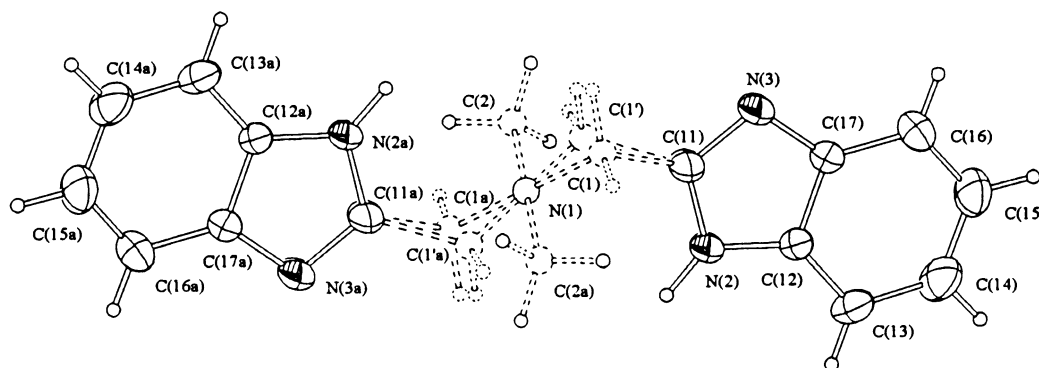


Fig. 1 The molecular structure of bis(benzimidazol-2-ylmethyl)-methylamine L with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. The second positions of the disordered atoms are denoted by dashed lines. Symmetry transformations used to generate equivalent atoms: (a) $-x + 1, -y, -z + 1$.

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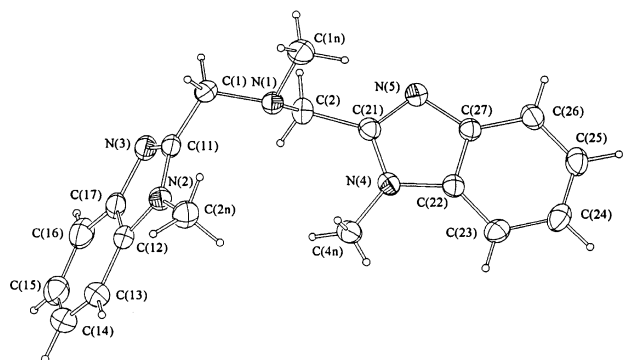


Fig. 2 The molecular structure of *N,N*-bis(1-methylbenzimidazol-2-ylmethyl)methylamine Me_2L with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

of compounds **1–5'** were determined from their analytical data and spectral properties. The ligand geometry (*fac* or *mer*) has been readily distinguished on the basis of $^1\text{H NMR}$ spectral observation (Fig. 3, see full text). The methylene hydrogens produce AB-type spectra in *fac* isomers, while a singlet methylene proton resonance was characteristic for *mer* isomer **5'** (Fig. 6, see full text). Surprisingly, the $^1\text{H NMR}$ spectrum of **3** indicated that not only was ligand L coordinated facially but that the two halves of the ligand were magnetically distinguishable. Consequently, the remaining coordination sites must be occupied by two different ligands, *i.e.* water molecules and perchlorate anion as oxygen donors. This is supported by the 1:2 electrolytic behavior of the complex in DMF. One water molecule and one perchlorate anion are coordinated *syn* with respect to the $\text{N}(1)\text{--CH}_3$ group of L, rendering the two halves of the ligand magnetically inequivalent. These facts together suggest that the ligands in **3** are coordinated in a *syn-fac* mode (Fig. 3, see full text). Similarly in complexes **4** and **5** the ligands are arranged a *syn-fac* mode (Fig. 5, see full text).

In conclusion, the data obtained demonstrate the effect of substituents R on the molecular structure of tridentate bis(benzimidazole)amine ligands L and Me_2L . The reaction

of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with both L and Me_2L leads to facially coordinated mono-ligand products. However, when $[\text{Rh}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ is used as a metal ion source both mono- and bis-substituted complexes are formed, the structure of which strongly depends on the substrate molar ratio as well as on the ligand employed. The steric congestion of methyl groups of Me_2L results in formation of the *mer* isomer, whereas for L only *fac* isomers were isolated.

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Techniques used: $^1\text{H NMR}$, $^1\text{H}\text{--}^1\text{H NMR}$ 2-D COSY, IR, conductometric measurements, X-ray diffraction.

References: 37

Scheme 1: The formulae and numbering scheme of the ligands used.

Fig. 3: Schematic projection of a molecule of complex **3**.

Fig. 4: The $^1\text{H NMR}$ spectrum of complex **4** in acetonitrile- d_3 at 293 K. The relevant fragments of the 2-D $^1\text{H NMR}$ COSY spectrum are shown below the 1-D spectrum. The labelling of resonances in this and Fig. 6 is in accordance with the numbering shown in Scheme 1.

Fig. 5: Schematic projection of a molecule of complex **4**.

Fig. 6: The $^1\text{H NMR}$ spectrum of complexes **5** and **5'** in acetonitrile- d_3 at 293 K.

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