

A new pyridine-bis-*N*-heterocyclic carbene ligand and its coordination to Rh: Synthesis and characterization

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Received 31 May 2005; received in revised form 27 June 2005; accepted 4 July 2005

Available online 11 August 2005

Abstract

The new bis(imidazolylidene) tripodal ligand precursor (2-pyridine)bis(3-methylimidazolium-1-yl)methane diiodide, [H₂PYBI-M^{Me}]₂, has been obtained by a simple method. The molecular structure of this new ligand precursor has been determined by means of X-ray diffraction. The coordination of this ligand to Rh, provides a Rh(III) complex with very low solubility in most solvents, which we attributed to the polymeric nature of the species. Solution of this polymer in DMSO provided a biscarbene Rh(III) complex in which the pyridine fragment remained unbound.

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Keywords: Rhodium; Carbene; *N*-heterocyclic; Tripodal

1. Introduction

N-heterocyclic carbene (NHC) ligands have shown as efficient components in the design of homogeneous catalysts [1–4]. Probably, one of the main reasons why these ligands have been so widely used in catalyst design in the last decade, is that their steric and electronic properties can be easily modulated, mainly due to their relatively simple preparation methodology and the extraordinary high variety of cheap commercial precursors that we can find from the ordinary chemical suppliers. A large number of mono- [1,5], bis- [3,4] and tris-carbene [3,4,6–11] ligands have been described, and their topological versatilities have afforded a large number of metal complexes with many different geometries. Regarding chelate–carbene ligands, the first biscarbene complexes described were Pd-based [12], but soon the use of chelate and pincer carbene ligands were extended to Rh [3,13–15], Ir [10,16,17], Ag [18], Cu [7,8,19], Fe

[20,21], and even early transition metals such as Cr [22] and Ti [23], the latter ones challenging the idea that NHCs are only stable when coordinated to late transition metals.

Despite the large variety of NHC ligands described, the number of such compounds displaying a tripodal geometry is still relatively scarce [7–11,15,19,21,24], and among these, the number of ‘true’ tripodal coordination of the ligand is even lower [7,15,21,24,25]. The design of tripodal NHC ligands is important because the *fac* tricoordinate geometry should determine the catalytic properties of the metal complex, especially when the stability of the ligand–metal bond is high, and the catalytic activity of the complex must rely on the lability of the other co-ligands, and the relative geometry of the potential vacant sites.

With these ideas in mind, we recently described the coordination of the potentially tripodal ligands [1,1,1-tris(3-butylimidazolium-1-yl)methyl]ethane trichloride, [H₃TIME^{Bu}]₃Cl₃, and tris-[2-(3-isopropylimidazolium-1-yl)ethyl]amine hexafluorophosphate [H₃TIMEN^{iPr}]₃(PF₆)₃, to Rh and Ir [10,11], but in all the cases the

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ligand adopted a η^2 -chelating or bridging form, and the tripodal coordination fashion remained elusive. In contrast, the preparation of the precursor (2-hydroxyphenyl)bis(3-methylimidazolium-1-yl)methane diiodide, provided a new Rh(III) biscarbene complex with the ligand in a tripod conformation, that showed high catalytic activity towards hydrogenation transfer from alcohols to ketones [15].

We now report the synthesis of the biscarbene ligand precursor (2-pyridine)bis(3-methylimidazolium-1-yl)methane diiodide, $[\text{H}_2\text{PYBIM}^{\text{Me}}]\text{I}_2$, and its coordination to rhodium. The crystal structure of the bisimidazolium precursor is also described.

2. Results and discussion

The reaction of 1,1-carbonyldiimidazole and 2-pyridinecarboxaldehyde at 80 °C in the presence of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ as catalyst, affords the preparation of (2-pyridine)bis(imidazolyl)methane (**1**), which had been previously obtained by a different method [26]. The reaction of **1** with MeI gives the corresponding methylated compound, (2-pyridine)bis(3-methylimidazolium-1-yl)methane diiodide, $[\text{H}_2\text{PYBIM}^{\text{Me}}]\text{I}_2$ (**2**), in high yield (Scheme 1). This procedure is similar to the one that we reported for the preparation of (2-hydroxyphenyl)bis(3-methylimidazolium-1-yl)methane diiodide, and, in fact, provides an easy method to access to a new type of tripodal biscarbene ligands.

Compounds **1** and **2** were fully characterized by NMR and elemental analysis, and the molecular structure of a hexafluorophosphate salt of **2** was confirmed by means of X-ray crystallography. Fig. 1 shows the molecular structure of **2**. As expected, the molecule consists of two methylimidazolium fragments and a pyridyl ring bound to a CH central group. The distances and angles of this carbene precursor lie in the expected range.

In the presence of a weak base as NEt_3 , **2** reacted with $[\text{Rh}(\text{COD})_2](\text{BF}_4)$ yielding a pale brown highly insoluble species that we could hardly analyse. The product showed very little solubility in most organic solvents (CH_2Cl_2 , THF, acetone, acetonitrile, methanol) and H_2O , which we attributed to a polymeric nature of the compound (**3** in Scheme 2). The exchange of the BF_4 counter-anion by PF_6 or BPh_4 did not improve the sol-

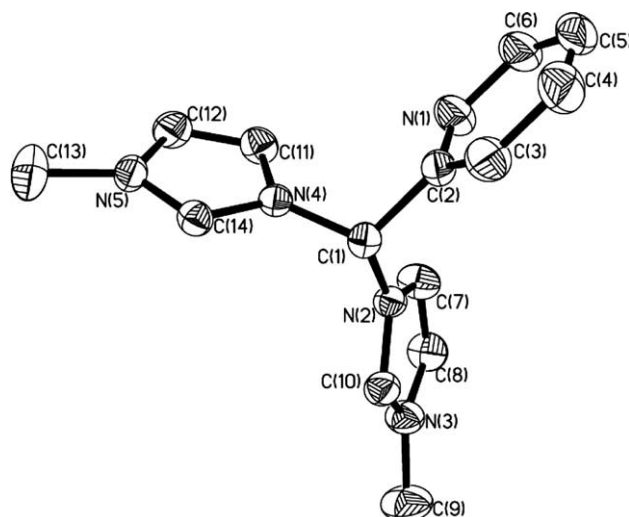
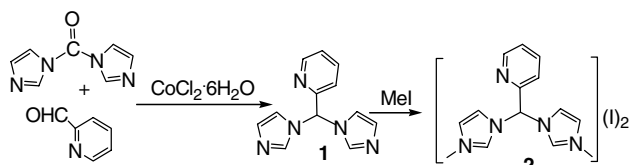


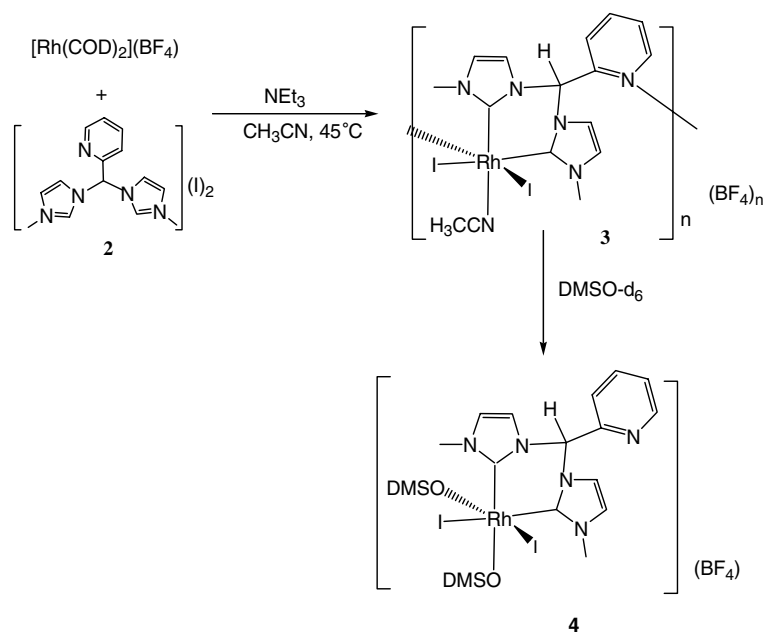
Fig. 1. Molecular diagram of compound **2**. (Hydrogen atoms and counter-anions have been omitted for clarity). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.505(8), C(1)–N(2) 1.470(7), C(1)–N(4) 1.461(7), N(2)–C(1)–N(4) 109.2(4), N(4)–C(1)–C(2) 111.9(4).

ubility of the complex at all. The compound could only be dissolved in DMSO, yielding compound **4** (Scheme 2). The ^1H NMR spectrum of **4** in $\text{DMSO}-d_6$ shows that the twofold symmetry of the ligand was lost upon coordination. The two downfield signals of the protic hydrogens in the precursor **2** disappeared, suggesting that the coordination has taken place. The signal due to the pyridine *hypo*-hydrogen appears at $\delta = 9.2$, suggesting that the pyridine remains unbound. The two methyl groups of the imidazolium fragments appear as two different signals at 4.09 and 4.03 ppm. The ^{13}C NMR spectrum shows two doublets at 159.18 and 151.09 ppm ($^1J_{\text{C-Rh}} = 42.9$ and 44.1 Hz, respectively) in the region where Rh(III)–NHC compounds appear, thus confirming that the metallation has occurred. The pattern of the signals due to the imidazolylidene and pyridine rings, as well as the two different methyl groups observed, confirm the loss of the binary symmetry of the ligand in the complex. In order to confirm that the pyridine is not bound to the Rh atom, we performed a ^1H – ^{15}N correlation of the metal complex, observing that the signal due to the nitrogen atom of the pyridine appears in the region typical for unbound pyridine fragments. ($\delta = -110$) and we did not observe any ^{105}Rh – ^{15}N coupling (Fig. 2). The signals due to the nitrogen atoms of the imidazolylidene rings appear between -64 and -70 ppm. A ^1H – ^{13}C correlation was also performed in order to assign all the signals of the ^1H and ^{13}C NMR spectra (see ESI).

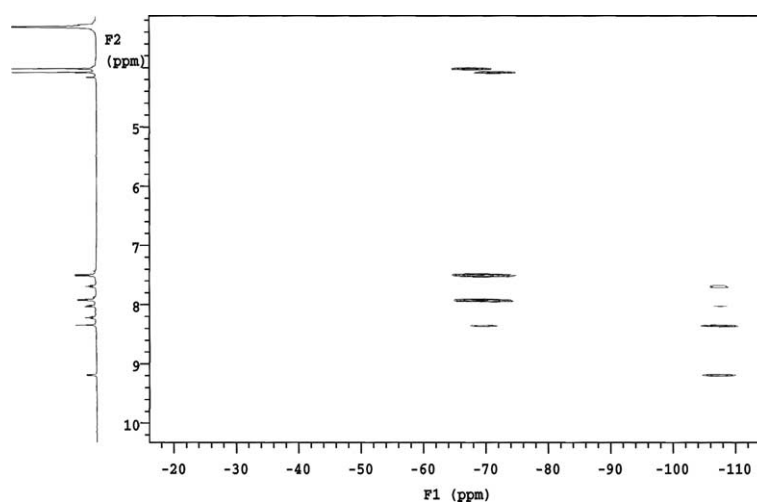
The mass spectroscopy analysis for a solution of the complex in CH_3CN , showed peaks (m/z) at 693.6 $[(\text{PYBIM}^{\text{Me}})\text{I}_2\text{Rh}(\text{CH}_3\text{CN})_2]^+$, 650.9 $[(\text{PYBIM}^{\text{Me}})\text{I}_2\text{Rh}(\text{CH}_3\text{CN})]^+$, and 609.9 $[(\text{PYBIM}^{\text{Me}})\text{I}_2\text{Rh}]^+$, whereas a solution of the complex in DMSO showed peaks at 687.2 $[(\text{PYBIM}^{\text{Me}})\text{I}_2\text{Rh}(\text{DMSO})]^+$ and 609.9



Scheme 1.



Scheme 2.

Fig. 2. ^1H - ^{15}N GHMBC spectrum of compound **4**.

$[(\text{PYBIM}^{\text{Me}})_2\text{Rh}]^+$. According to these results, we have tentatively assigned a polymeric structure such as that shown in Scheme 2 (compound **3**), for the polymeric compound obtained from the reaction of **2** and $[\text{Rh}(\text{COD})_2](\text{BF}_4)$. In DMSO, the pyridine is displaced by a molecule of solvent forming **4**, thus facilitating the solution of the complex. The same effect is observed in CH_3CN forming compound $[(\text{PYBIM}^{\text{Me}})_2\text{Rh}(\text{CH}_3\text{CN})_2](\text{BF}_4)$ (**5**), although the lower coordination capability of this solvent may be responsible for the lower solubility of the compound, which could only be detected by Mass Spectroscopy analysis, and no NMR spectrum in CD_3CN could be recorded.

As observed for the coordination of other imidazolium-based biscarbene ligands [14,17,27], the Rh(I) starting compound $[\text{Rh}(\text{COD})_2](\text{BF}_4)$ oxidized to Rh(III) upon coordination of the ligand. We recently proposed that an oxidative addition of the C2–H bond of the imidazolium precursor may help to explain this observation [17], and further experimental evidences to support this proposal will be published soon.

We believe that the failure of the ligand $[\text{PYBIM}^{\text{Me}}]$ to coordinate in a tripodal form is mainly due to topologic restrictions of the ligand. Iodide removal from the coordination sphere of **3** and **4** with AgBF_4 always resulted in decomposition of the product, and changing

the conditions of the reaction only resulted in a reduction of the reaction yield. In fact, the η^2 -coordination of the bis-NHC rings may be pushing the pyridine ring out of the coordination sphere of the complex, thus releasing the steric constrain about the CH linker. In any case, we are carrying out further experiments with other metals such as Cu(I) and Fe(III) for which we believe that the tripodal coordination of the ligand may be possible, and may provide interesting catalytic performances.

3. Experimental

NMR spectra were recorded on a Varian Innova 300 and 500 MHz instruments, using CDCl_3 and $\text{DMSO-}d_6$. Elemental analyses were carried out in an EA 1108 CHNS-O Carlo Erba Analyser. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quattro LC instrument, nitrogen was employed as drying and nebulizing gas. The $[\text{Rh}(\text{COD})_2]\text{BF}_4$ precursor was obtained according to the literature methods [28]. All the other reagents are commercially available and were used as received.

3.1. Synthesis of (2-pyridine)bis(imidazolyl)methane (**1**)

A mixture of 1,1-carbonyldiimidazole (4.40 g, 27.14 mmol), 2-pyridinecarboxaldehyde (2.58 mL, 27.14 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (31 mg, 0.13 mmol) was stirred at 80 °C for 12 h. The mixture was allowed to cool to room temperature, dissolved in 30 mL of CH_2Cl_2 and extracted with water. Then the organic layer was dry under Na_2SO_4 . The product was purified by column chromatography; elution with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (9:1) afforded the desired compound **1** as a brown oil. Yield: 5.19 g (85%). ^1H NMR (CDCl_3 , 500 MHz): 8.68 (d, $^3J_{\text{H-H}} = 4.0$ Hz, 1H, pyridine-*H*), 7.78 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 1H, pyridine-*H*), 7.56 (s, 1H C-*H*), 7.38 (m, 1H, pyridine-*H*), 7.36 (s, 2H, NCH N), 7.14 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 1H, pyridine-*H*), 7.10 (s, 2H, imidazole-*H*), 7.00 (s, 2H, imidazole-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 500 MHz): 151.59 (C, pyridine), 150.60 (C-*H*, pyridine), 138.06 (C-*H*, pyridine), 136.79 (2C, NCHN), 130.48 (2C, imidazole-*C*), 125.08 (C-*H*, pyridine), 122.27 (C-*H*, pyridine), 118.36 (2C, imidazole-*C*), 71.08 (C-*H*). Anal. Calc. for $\text{C}_{12}\text{H}_{11}\text{N}_5$ (225.10): C, 63.99; H, 4.92; N, 31.09. Found: C, 64.25; H, 5.00; N, 29.99%.

3.2. Synthesis of (2-pyridine)bis(3-methylimidazolium-1-yl)methane diiodide (**2**)

A mixture of **1** (0.5 g, 2.2 mmol) and iodomethane (3 mL, 48.2 mmol) was refluxed in CH_3OH overnight. The solvent was evaporated and the product was washed

with ether, precipitated with CH_3OH /ether and dry under vacuum, giving a brown solid. Yield: 0.90 g (80%). ^1H NMR ($\text{DMSO-}d_6$, 500 MHz): 9.44 (s, 2H, NCHN), 8.76 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 1H, pyridine-*H*), 8.55 (s, 1H, C-*H*), 8.10 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 1H, pyridine-*H*), 8.03 (s, 2H, imidazole-*H*), 7.90 (s, 2H, imidazole-*H*), 7.78 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 1H, pyridine-*H*), 7.67 (m, 1H, pyridine-*H*), 3.91 (s, 6H, CH_3 -N). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO-}d_6$, 500 MHz): 150.98 (C-*H*, pyridine), 149.42 (C, pyridine), 139.39 (C-*H*, pyridine), 138.27 (2C, NCHN), 126.87 (C-*H*, pyridine), 125.23 (2C, imidazole-*C*), 122.26 (2C, imidazole-*C*), 71.37 (C-*H*), 37.24 (2C, CH_3 -N). Anal. Calc. for $\text{C}_{14}\text{H}_{17}\text{I}_2\text{N}_5$ (509.13): C, 33.03; H, 3.37; N, 13.76. Found: C, 33.45; H, 3.29; N, 13.98%.

3.3. X-ray diffraction studies of compound **2**

A single crystal of a hexafluorophosphate salt of **2** was mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the SAINT package.

Space group assignment was based on systematic absences, *E* statistics and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were assigned to ideal positions and refined using a riding model.

3.4. Syntheses of complexes **3** and **4**

A mixture of $[\text{Rh}(\text{COD})_2](\text{BF}_4)$ (200 mg, 0.49 mmol), **2** (251 mg, 0.49 mmol), and $\text{N}(\text{Et})_3$ (250 μL , 1.8 mmol) was heated at 45 °C in CH_3CN overnight. During this time, a pale brown solid appeared. The solid containing **3** was filtered and washed with CH_2Cl_2 . Yield: 190 mg (52%). Compound **4** was obtained dissolving **3** in $\text{DMSO-}d_6$. ^1H NMR for complex **4** ($\text{DMSO-}d_6$, 500 MHz): 9.20 (d, $^3J_{\text{H-H}} = 3.5$ Hz, 1H, pyridine-*H*), 8.36 (s, 1H, C-*H*), 8.23 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 1H, pyridine-*H*), 8.03 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 1H, pyridine-*H*), 7.93 (d, $^3J_{\text{H-H}} = 1.5$ Hz, 1H, imidazole-*H*), 7.92 (d, $^3J_{\text{H-H}} = 1.5$ Hz, 1H, imidazole-*H*), 7.70 (t, $^3J_{\text{H-H}} = 6.5$ Hz, 1H, pyridine-*H*), 7.52 (d, $^3J_{\text{H-H}} = 1.5$ Hz, 1H, imidazole-*H*), 7.51 (d, $^3J_{\text{H-H}} = 1.5$ Hz, 1H, imidazole-*H*), 4.09 (s, 3H, CH_3 -N), 4.03 (s, 3H, CH_3 -N). $^{13}\text{C}\{^1\text{H}\}$ NMR of complex **4** ($\text{DMSO-}d_6$, 500 MHz): 159.18 (d, $^1J_{\text{C-Rh}} = 42.9$ Hz, C-*Rh*), 156.96 (pyridine-*C*), 151.15 (pyridine-*C*), 151.09 (d, $^1J_{\text{C-Rh}} = 44.1$ Hz, C-*Rh*), 141.73 (pyridine-*C*), 127.54 (pyridine-*C*), 126.05 (2C, imidazole-*C*), 125.00 (pyridine-*C*), 122.76 (imidazole-*C*),

121.75 (imidazole-C), 71.96 (C–H), 43.67 (CH₃–N), 39.90 (CH₃–N). Anal. Calc. for C₁₆H₁₈BF₄N₆I₂Rh (complex **3**) (737.87): C, 26.04; H, 2.46; N, 11.39. Found: C, 26.48; H, 2.47; N, 10.80%. Electrospray MS. Cone 30V. *m/z* (fragments) for **3** in DMSO (complex **4**): 687.2 [(PYBIM^{Me})₂Rh(DMSO)]⁺ and 609.9 [(PYBIM^{Me})₂Rh]⁺. Electrospray MS. Cone 30V. *m/z* (fragments) for **3** in CH₃CN (complex **5**): 693.9 [(PYBIM^{Me})₂Rh(CH₃CN)₂]⁺ 650.9 [(PYBIM^{Me})₂Rh(CH₃CN)]⁺ and 609.9 [(PYBIM^{Me})₂Rh]⁺.

Acknowledgements

We gratefully acknowledge financial support from CICYT(MAT2002-04421-C02-01). We thank the Spanish MEC for a fellowship to E.M.-M. We thank Dr. Cristian Vicent (SCIC) for his helpful comments on the ¹H–¹⁵N NMR interpretations.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.04.060](https://doi.org/10.1016/j.jorganchem.2005.04.060).

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