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New Rh(I) and Rh(III) Bisimidazol-2-ylidene Complexes: Synthesis, Reactivity, and Molecular Structures

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New chelate bis-heterocyclic-carbene complexes of Rh(I) and Rh(III) have been obtained and fully characterized. The molecular structures of the new species have been determined. The synthesis of the compounds starts from the bisimidazolium precursors, which are deprotonated with NEt_3 under mild reaction conditions, leading to coordination to the Rh complex. The Rh(III) compounds are generated from Rh(I) and $[Rh(II)]_2$ species, although there is no apparent oxidizing agent in the reaction media.

N-Heterocyclic carbenes are very interesting ligands because of their many synthetic and catalytic applications.[1−3] The use of chelate and pincer coordination of these ligands has opened a new dimension in the preparation of new catalysts because it yields complexes with unusually high thermal and air stabilities, widening their potential applications. Although most of the previous chelate biscarbene complexes were restricted to Pd,[4−11] during the past 2 years there have been several Ru,[12,13] Rh,[14−16] and Ir[17,18] complexes whose catalytic properties were explored (hydrogen transfer, olefin oxidation, hydrosilylation, hydroformylation, etc).

Despite their potential applications, N-heterocyclic carbenes are far from being as widely used as phosphines in catalyst design, probably because synthetic high-yielding methods constitute the bottleneck for the preparation of a more varied library of catalysts. For example, phosphines can be used as purchased in the synthesis of new compounds, but imidazolyl carbenes are often prepared from imidazolium salts, which need to be activated (deprotonated) prior to their coordination. In most of the occasions, the coordination of the imidazolyl ligands requires harsh reaction conditions such as the use of strong bases (need of an air- and moisture-free atmosphere) and high temperatures. In just a few cases reported in the literature, the reaction conditions for the coordination of the carbene need the use of a weak base (NaOAc, NEt_3), which can be added to the reaction mixture or be present as a ligand of the starting metal complex [$Pd(OAc)_2$,[5−7] $Rh_2(OAc)_4$].[14]

Despite the relatively few examples leading to satisfactory yields of chelate biscarbene complexes, the mechanism of metalation is still unclear. In some cases, the metalation of the imidazolium precursor occurs without the use of a base

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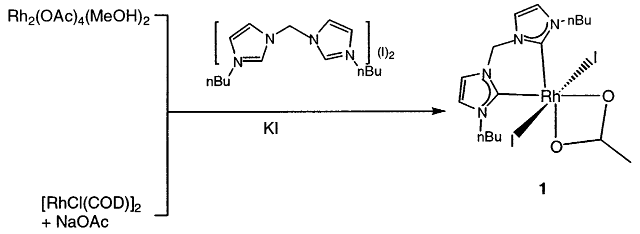
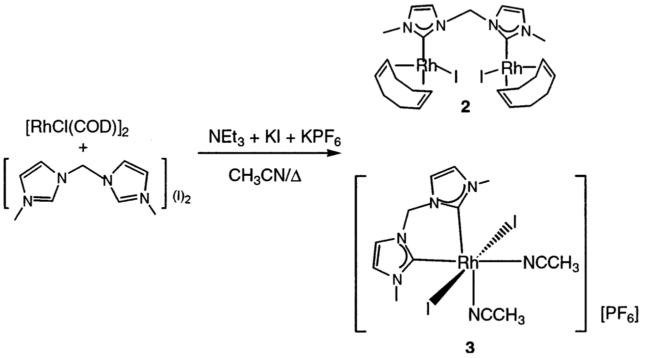
Scheme 1



Scheme 2



via the oxidative addition of the C−H bond to a low-valence metal complex.[19] In some other cases, the metal suffers a two-electron-oxidation process upon coordination of the ligand without any apparent oxidative addition or other process justifying the oxidation.[14,18,20]

On the basis of our previous experience, we now report the synthesis and reactivity of new chelate biscarbenes of Rh(I) and Rh(III). The synthetic route to these compounds is milder than those previously reported, allowing high yields of the desired complexes. We also discuss the oxidation of the metal in the metalation process.

Results and Discussion

Synthesis and Characterization of the Compounds. According to our previously reported results,[14−16] we designed three different routes to obtain the desired chelate carbene complexes: (i) deprotonation of the imidazolium precursor with NaOAc, (ii) use of $Rh_2(OAc)_4$ without any other base added, and (iii) deprotonation with NEt_3. We used methylenebis(*N*-methylimidazolium) iodide and methylenebis(*N*-*n*-butylimidazolium) iodide as biscarbene precursors.

For methods i and ii, we observed that the reactions yielded the same compound in high yield (**1** in Scheme 1). For the reaction starting with $[RhCl(COD)]_2$, the metalation of the carbene proceeds via a two-electron oxidation of the metal, while the reaction from $Rh_2(OAc)_4$ is a dinuclear two-electron-oxidation process, with both reactions leading to **1** as the only isolable Rh species. We first thought that the production of the Rh(III) complex could be due to a dismutation process of the Rh(I) and $[Rh(II)]_2$ starting species, but we did not observe the appearance of any black mirrors. Besides, the high yield obtained based on Rh (>60%) made us discard the possibility that the production of any other Rh(0) species justifies the oxidation because of obvious stoichiometric reasons. Under the reaction conditions used, we were unable to detect any intermediate Rh(I) species, even when we carried out the reaction at lower temperatures and with different amounts of imidazolium precursor and NaOAc.

Compound **1** was fully characterized by NMR spectroscopy and elemental analysis. ^1H and ^{13}C NMR spectra reveal that the imidazol-2-ylidene rings are symmetry-related. The ^1H NMR spectrum shows one set of signals for the *n*-Bu fragment and one sharp signal for the methylene bridge at δ 6.0. Evidence of metalation comes from the ^{13}C NMR spectrum, which shows a doublet at δ 154.7 ($J_{Rh-C} = 43$ Hz), which is diagnostic of a Rh−C binding.

As we have previously reported, **1** is an effective hydrogen-transfer catalyst,[14] and further catalytic applications are under study.

As an alternative to the use of NaOAc, we previously observed[13,15] that NEt_3 gives very good results under mild conditions. Besides, its coordination capability, lower than that of acetate, affords its easy elimination after the reaction has finished. The p*K*'s of the species involved should make one think that NEt_3 is not strong enough to deprotonate the bisimidazolium salt. However, the addition of an excess of the base (20:1), together with the rapid coordination of the carbene to the metal, displaces the equilibrium of deprotonation to the formation of the desired products. Scheme 2 shows the general synthetic procedure for two new Rh(I) (**2**) and Rh(III) (**3**) complexes. The Rh(I)/Rh(III) ratio clearly depends on the reaction conditions used. When the reaction is carried out in the presence of air without previously degassed solvent, **3** is the major product obtained. The reaction is quasi-quantitative on **3** (yield > 80%) when carried out in acetonitrile at 45 °C for 1 h. Only for the reactions run at room temperature for 1 h is **2** produced in moderate yield (30%), together with **3** (61%), with both compounds being easily separated by gradient column chromatography. When the reaction is performed under inert conditions with degassed acetonitrile, we mainly obtained compound **2**, confirming that the oxidation step of the process is clearly dependent on the oxygen present in the reaction medium. In any case, these data confirm that, in contrast to other synthetic procedures to bis-heterocyclic carbenes, the reaction is very fast even under these mild conditions.

Compounds **2** and **3** were fully characterized by NMR spectroscopy and elemental analysis. The ^1H NMR spectrum of **2** shows the typical pattern of the coordinated COD fragment. The methylene bridge appears as a singlet at δ 7.38, and the equivalency of the imidazolyl rings confirms the twofold symmetry of the ligand. The more relevant feature of the ^{13}C NMR spectrum of **2** is the doublet at δ 183 ($^1J_{Rh-C} = 48.3$ Hz), confirming that the Rh−C bond has been formed.

The neat aliphatic region in the ^1H NMR spectrum of **3** reveals that the COD fragment has been lost. The only signal in this region is that due to CH_3CN (δ 2.51) and the *N*-methyl

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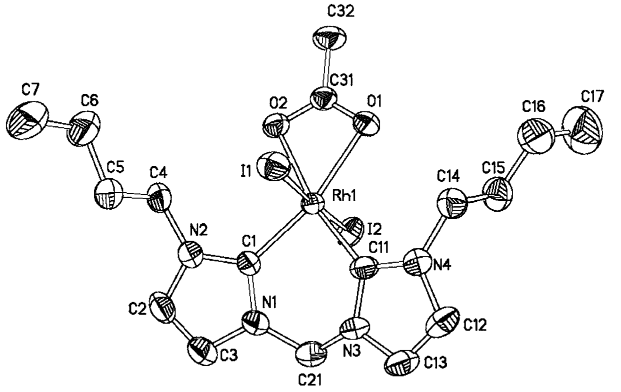


Figure 1. Molecular diagram of compound **1** (50% probability; hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−C(11) 1.976(5), Rh(1)−C(1) 1.978(5), Rh(1)−O(1) 2.177(3), Rh(1)−O(2) 2.178(4), Rh(1)−I(1) 2.6576(8), Rh(1)−I(2) 2.6489(8); C(11)−Rh(1)−C(1) 87.3(2).

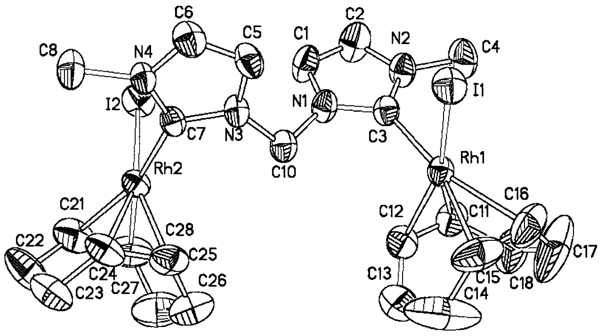


Figure 2. Molecular diagram of compound **2** (50% probability; hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−Rh(2) 6.6376(14), Rh(1)−C(3) 2.014(4), Rh(2)−C(7) 2.023(4), Rh(1)−I(1) 2.6720(6), Rh(2)−I(2) 2.6618(6); N(1)−C(10)−N(3) 112.1(3).

groups (δ 4.06). Again, the imidazolyl signals indicate that the ligand is symmetry-related. The metalation of the ligand is confirmed by the ^{13}C NMR spectrum, which shows the typical doublet at δ 147.1 ($^{1}J_{Rh-C} = 44$ Hz).

To unequivocally confirm the molecular structures of **1**−**3**, we obtained crystals of these compounds (slow evaporation from MeOH solutions) suitable for X-ray diffraction.

The molecular structure of **1** (Figure 1) confirms the pseudo-octahedral coordination of the Rh atom. The biscarbene is chelating, with a bite angle C(1)−Rh(1)−C(11) of 87.3(2)°, smaller than that shown for our previously reported bisimidazol-2-ylidene−phenylene-bridged related complex (C−Rh−C, 92.2°),[14] obviously due to the substitution of the phenylene by the methylene bridge. The sum of the angles in the equatorial plane containing the acetate and biscarbene ligand is 360.03°, indicating a highly coplanar arrangement. The Rh−C distances (1.976 and 1.978 Å) are a little shorter than that shown for the phenylene-bridged complex,[14] probably because of steric reasons. The distances are, however, still typical for σ-character bonds, indicating that the back-donation is negligible for this compound. The high trans influence produced by the carbenes is evident in the rather long Rh−O distances in the acetate ligand, Rh−O of 2.177 Å.

Figure 2 shows the molecular structure of **2**. The dimetallic structure consists of two rhodium atoms bridged by the methylene−imidazolyl ligand. One iodine atom and the COD ligand complete the coordination sphere of each pseudo-square-planar rhodium atom. The Rh−Rh distance discards any possible bonding interaction ($d_{Rh-Rh} = 6.6376$ Å). The Rh−C distances for the carbene ligand are 2.023 and 2.014 Å, again typical for Rh−C σ bonds with very little back-donation. We have found that there is a preference of the bisimidazolyl carbenes to act as bridges when coordinated to Rh(I) species.[15,16] In fact, there is only one example, reported by us, of a Rh(I) chelate bisimidazolyl carbene.[16]

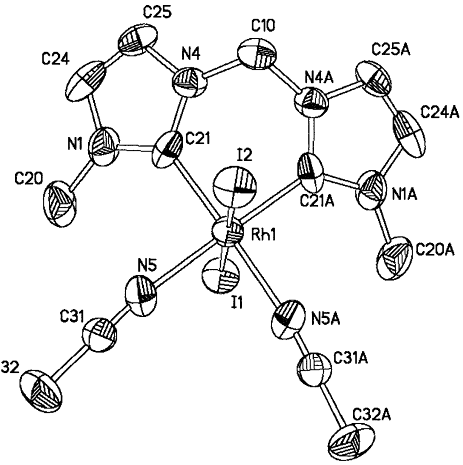


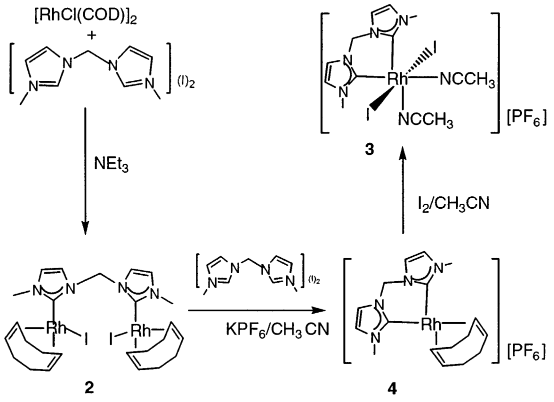
Figure 3. Molecular diagram of compound **3** (50% probability; hydrogen atoms and PF_6 have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−C(21) 2.025(12), Rh(1)−N(5) 2.079(12), Rh(1)−I(2) 2.672(2), Rh(1)−I(1) 2.682(2); C(21)−Rh(1)−C(21A) 87.8(8).

The molecular structure of **3** is shown in Figure 3. The Rh atom is coordinated to two iodine atoms, two acetonitrile ligands, and the chelating biscarbene in a pseudo-octahedral disposition. The chelating biscarbene bite angle is 87.8(8)°, very similar to that shown in compound **1**. The sum of the angles in the equatorial plane containing the two acetonitrile ligands and the biscarbene is 359.9°, indicating high coplanarity. The Rh−C distance is 2.025 Å, very similar to that shown for **2** and, again, indicative of very little back-donation.

One question that remained unanswered in the synthesis of our compounds was the oxidation from Rh(I) and Rh(II) to Rh(III) in the formation of the chelate biscarbene complexes. As we mentioned above, the oxidation step depends on the amount of oxygen present in the reaction medium. We believe that the oxygen may be an indirect oxidant in this reaction, which may occur by the previous oxidation of I^- to I_2, which oxidatively adds to the Rh(I) compound (Scheme 3).

We did not detect the formation of **4** in our reaction, but we recently reported a similar chelate biscarbene Rh(I) complex with an *o*-xylylene bridge,[16] so we believe that it may be a reaction intermediate in the formation of **3**. The proposed mechanism is supported by the fact that, for reactions performed in the presence of air, the formation of biscarbene Rh(III) species is favored when imidazolium iodide precursors are used,[14,16] while the Rh(I) species are obtained when chlorides are used. The use of imidazolium bromide precursors results in the formation of both Rh(I)

Scheme 3



and Rh(III) species.[15] In any case, the high donor abilities of the di-heteroatom-stabilized carbene ligands clearly favor a high-valent metal for bonding, justifying in our case why compound **4** is not detected under the reaction conditions used.[21,22]

Experimental Section

General. NMR spectra were recorded on a Varian Innova 300 and 500 MHz spectrometer, using $CDCl_3$ and DMSO-d_6 as solvents. The ligand precursors methylenebis(*N*-methylimidazolium) iodide and methylenebis(*N*-*n*-butylimidazolium) iodide were prepared according to literature methods.[14] All of the other reagents were used as received from commercial suppliers.

Synthesis of 1. Method a. A mixture of $[RhCl(COD)]_2$ (243 mg, 0.5 mmol), methylene-bis(*N*-*n*-butylimidazolium) iodide (516 mg, 1 mmol), KI (332 mg, 2.0 mmol), and NaOAc (328 mg, 4.0 mmol) was stirred in CH_3CN (20 mL) at reflux for 16 h. After cooling, the solvent was removed under reduced pressure. The crude solid was then redissolved and added to a column (1.2 × 30 cm) for chromatography. Elution with CH_2Cl_2 separated a minor yellow fraction containing $[RhCl(COD)]_2$. Subsequent elution with CH_2Cl_2−acetone (3:1) separated **1** as an orange solid (yield 74%).

Method b. A mixture of $Rh_2(OAc)_4$ (200 mg, 0.4 mmol) and methylenebis(*N*-*n*-butylimidazolium) iodide (420 mg, 0.81 mmol) was stirred in DMSO at 100 °C for 30 min followed by 165 °C for 90 min. After cooling, the solvent was removed under reduced pressure and the residue purified by gradient column chromatography following the procedure described above (yield 62%).

1. ^1H NMR (DMSO-d_6, 300 MHz): δ 7.10 (d, 2H, $^3J_{HH} = 2.1$ Hz, imidazole−*H*), 7.08 (d, 2H, $^3J_{HH} = 2.1$ Hz, pyridine−*H*), 6.03 (s, 2H, NCH_2N), 4.48 (t, 4H, $NCH_2CH_2CH_2CH_3$), 1.89 (quintet, 4H, $NCH_2CH_2CH_2CH_3$), 2.00 (s, 3H, acetate−CH_3), 1.48 (sextet, 4H, $NCH_2CH_2CH_2CH_3$), 0.98 (t, 6H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (DMSO-d_6, 300 MHz): δ 188.61 (acetate), 154.74 (d, $^1J_{Rh-C} =$ 42.5 Hz, N*C*N), 123.09 (imidazole−*C*), 120.46 (imidazole−*C*), 63.54 (acetate−CH_3), 51.00 ($CH_2CH_2CH_2CH_3$), 33.25 ($CH_2CH_2CH_2CH_3$), 20.28 ($CH_2CH_2CH_2CH_3$), 14.23 ($CH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{17}H_{27}I_2N_4O_2Rh$: C, 30.17; H, 3.99; N, 8.28. Found: C, 29.82; H, 4.21; N, 8.13.

Synthesis of 2. A mixture of $[RhCl(COD)]_2$ (200 mg, 0.41 mmol), methylenebis(*N*-methylimidazolium) iodide (350 mg, 0.81 mmol), and NEt_3 (0.5 mL, 3.5 mmol) was stirred at room temperature under inert conditions in CH_3CN (15 mL) for 1 h. **2** appeared as a yellow precipitate, which was filtered and washed with cold CH_3CN (yield 30%).

Table 1. Crystallographic Data

	1	**2**	**3**
empirical formula	$C_{17}H_{27}I_2N_4O_2Rh$	$C_{25}H_{36}I_2N_4Rh_2$	$C_{13}H_{16}F_6I_2N_6PRh$
fw	676.14	852.20	758.00
λ (Å)	0.710 73	0.710 73	0.710 73
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	*Pbca*	$C2/m$
a (Å)	8.032(2)	14.208(4)	20.607(6)
b (Å)	19.584(5)	16.727(5)	11.779(4)
c (Å)	14.648(4)	24.192(7)	11.662(4)
α (deg)	90	90	90
β (deg)	98.497(6)	90	120.138(7)
γ (deg)	90	90	90
V (Å^3)	2278.8(11)	5749(3)	2447.9(13)
Z	4	8	4
density$_{calcd}$ (mg/m^3)	1.971	1.969	2.057
abs coeff (mm^{-1})	3.477	3.316	3.341
reflns collected	18 941	45 970	10 302
GOF on F^2	1.052	0.996	0.936
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0575 wR2 = 0.1524	R1 = 0.0340 wR2 = 0.0711	R1 = 0.0684 wR2 = 0.2024

2. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, 2H, $^3J_{HH} = 1.8$ Hz, imidazole−*H*), 7.38 (s, 2H, NCH_2N), 6.82 (d, 2H, $^3J_{HH} = 1.8$ Hz, imidazole−*H*), 3.97 (s, 6H, NCH_3). ^{13}C NMR (DMSO-d_6, 300 MHz): δ 183 (d, $^1J_{Rh-C} = 48.3$ Hz, N*C*N), 123.83 (imidazole−*C*), 121.39 (imidazole−*C*), 62.45 (NCH_2N), 38.43 (NCH_3). Anal. Calcd for $C_{25}H_{36}I_2N_4Rh_2$: C, 35.20; H, 4.22; N, 6.57. Found: C, 34.91; H, 4.15; N, 6.72.

Synthesis of 3. A mixture of $[RhCl(COD)]_2$ (200 mg, 0.41 mmol), methylenebis(*N*-methylimidazolium) iodide (350 mg, 0.81 mmol), NaI (400 mg), and NEt_3 (0.5 mL, 3.6 mmol) was heated at 45 °C in CH_3CN (15 mL) for 1 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The crude solid was redissolved in CH_2Cl_2, and the solution was transferred to a column for chromatography. The solution was eluted with CH_2Cl_2 and then with gradient CH_2Cl_2−acetone starting with a 10:1 (v/v) ratio. Small amounts of KPF_6 were added to the column to provide the counterion and facilitate the elution of the cationic complex. This method afforded the separation of only an orange band that contained **3** (yield 80%).

3. ^1H NMR (DMSO, 300 MHz): δ 7.62 (imidazole−*H*), 7.56 (imidazole−*H*), 6.37 (s, NCH_2N), 4.06 (s, 6H, NCH_3), 2.51 (s, 6H, CH_3CN). ^{13}C NMR (DMSO-d_6, 300 MHz): δ 172.35 (CH_3CN), 147.08 (d, $^1J_{Rh-C} = 44.1$ Hz, N*C*N), 126.32 (imidazole−*C*), 123.14 (imidazole−*C*), 64.24 (NCH_2N), 22.3 (CH_3CN). Anal. Calcd for $C_{13}H_{16}F_6I_2N_6PRh$: C, 20.58; H, 2.11; N, 11.08. Found: C, 20.67; H, 2.41; N, 10.85.

X-ray Diffraction Studies. Single crystals of **1**−**3** were grown by slow evaporation from MeOH solutions and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart charge-coupled device diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was collected on the basis of three ω-scan runs (starting at $\omega = -28°$) at values of $\phi = 0$, 90, and 180° with the detector at $2\theta = 28°$. Space-group assignments are based on systematic absences, E statistics, and the successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogens were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 1.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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