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A New Rhodium(III) Complex with a Tripodal Bis(imidazolylidene) Ligand. Synthesis and Catalytic Properties

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Summary: A new bis(imidazolylidene) tripodal ligand has been obtained by a simple method. The coordination of this ligand to Rh provides the first Rh(III) complex with a bis(carbene) ligand in a tripodal coordination, and its catalytic properties toward hydrogen transfer have been examined.

N-heterocyclic carbenes (NHCs) have emerged as new types of ligands in homogeneous catalysis.[1,2] The combination of chelate and pincer effects on such carbenes have provided a new type of catalyst whose properties can be easily modulated by changing the topology and electronic properties of the ligands.[2,3] In many cases, the coordination of NHCs results in an improvement in the catalytic properties and stability of the compounds. A large number of the N-heterocyclic chelate complexes reported so far have been η^2-bis(carbene) species or CNC-pincer (*mer*) compounds of Pd, Rh, Ir, and Ru. However, the design of such ligands with a tripodal (*fac*) topology has been restricted to a few articles describing their coordination to Fe,[4] Ag,[5] and Tl[6] and the recently described nitrogen-anchored tris(carbene) complexes of Cu(I) and Cu(II) reported by Meyer et al.[7] The preparation of other tris(carbene) tripodal ligands has resulted in their coordination in η^2-chelate or bridging forms.[8]

Most of the non-phosphine tripodal heterocyclic ligands reported so far have been restricted to N-donor compounds such as poly(pyrazolyl)borates[9] and triamidoamine[10] compounds. On the basis of the topology of these compounds, we have now prepared a new precursor of a tripodal bis(carbene) ligand, by reaction of salicylaldehyde and bis(imidazolyl) ketone at 80 °C in the presence of $CoCl_2 \cdot 6H_2O$ as catalyst (Scheme 1). The synthesis of this compound is similar to that reported by Higgs et al. for the preparation of the bis(pyrazolyl) analogue.[11] The reaction of (2-hydroxyphenyl)bis(imidazolyl)methane (**1**) with MeI gives the corresponding methylated bis(imidazolium) salt (2-hydroxyphenyl)bis(3-methylimidazolium-1-yl)methane diiodide (**2**; BIPHOH-H_2) in high yield.[12]

In the presence of a weak base such as NEt_3, **2** reacted with $[(COD)RhCl]_2$ in refluxing MeCN to give [(BIPHO)(*N*-methylimidazole)$_2$RhI]I (**3**)[13] in good yield, as shown in Scheme 2. The metalation and the chelating character of the BIPHO ligand can be deduced by NMR spectroscopy. The three protic hydrogen atoms of the precursor BIPHOH-H_2 (**2**) disappear upon coordination, and the imidazolylidene rings are symmetry-related. The more direct evidence of the metalation of the ligand comes from ^{13}C NMR spectroscopy, which shows the carbene signal at δ 156.8 and a coupling constant that is diagnostic of direct Rh binding ($^1J_{C-Rh} = 40.3$ Hz). The signals due to the three hydrogens in the two methylimidazole ligands appear at frequencies higher than those due to the imidazolylidene rings of the tripodal ligand. The methylimidazole rings are N-bound, since

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(12) Synthesis of (2-hydroxyphenyl)bis(imidazolyl)methane (**1**): bis(imidazolyl) ketone (4.57 g, 28.2 mmol), salicylaldehyde (3 mL, 28.2 mmol), and $CoCl_2 \cdot 6H_2O$ (31 mg, 0.13 mmol) were stirred and heated to 80 °C for 2 h. The mixture was cooled to room temperature, 30 mL of CH_2Cl_2 was added, and a white solid appeared. The white solid was filtered and recrystallized with acetone/CH_3OH. Yield: 6.26 g (92%). Synthesis of (2-hydroxyphenyl)bis(3-methylimidazolium-1-yl)methane diiodide (BIPHOH-H_2) (**2**): a mixture of **1** (0.5 g, 2.1 mmol) and iodomethane (3 mL, 48.2 mmol) was refluxed in CH_3OH overnight. The solvent was evaporated, and the product was precipitated with CH_3OH/ether, giving a light yellow solid. Yield: 870 mg (80%).

(13) Synthesis of [(BIPHO)(*N*-methylimidazole)$_2$RhI]I (**3**): a mixture of $[(COD)RhCl]_2$ (150 mg, 0.30 mmol), **2** (345 mg, 0.66 mmol), and NEt_3 (0.3 mL, 2.0 mmol) was refluxed in CH_3CN overnight. A brown solid appeared and was filtered off. The solvent was eliminated under vacuum, the crude solid was redissolved in CH_2Cl_2, and the solution was transferred to a column chromatograph. Elution with CH_2Cl_2 separated a minor yellow band that contained $[(COD)RhCl]_2$. Further elution with gradient CH_2Cl_2/acetone afforded the separation of a major orange-yellow band that contained **3**. The product was precipitated with CH_2Cl_2/hexane. Yield: 144 mg (30%). Crystal data for **3**: $C_{23}H_{27}I_2N_8ORh$, $M_w = 788.24$, orange crystal, monoclinic, space group $Pna2_1$, $a = 17.340(5)$ Å, $b = 12.394(3)$ Å, $c = 13.206(3)$ Å, $\beta = 90.00°$, $V = 2838.3(13)$ Å^3, $Z = 4$, $D_c = 1.845$ g cm^{-3}, $\mu = 2.807$ mm, Mo Kα radiation ($\lambda = 0.710\,73$ Å), 22 427 reflections measured, 8415 unique ($R_{int} = 0.3460$). The final wR2 value was 0.1878 (all data) and R1 = 0.0772 ($I > 2\sigma(I)$).

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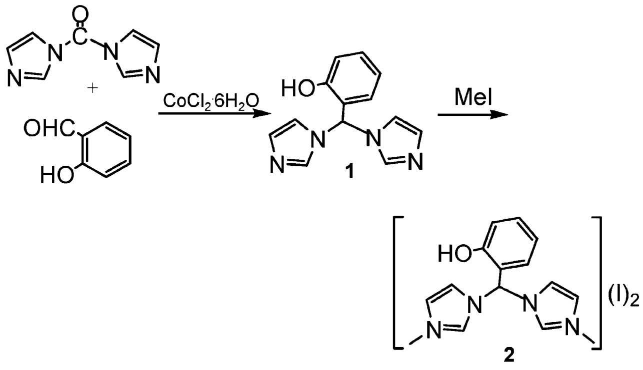
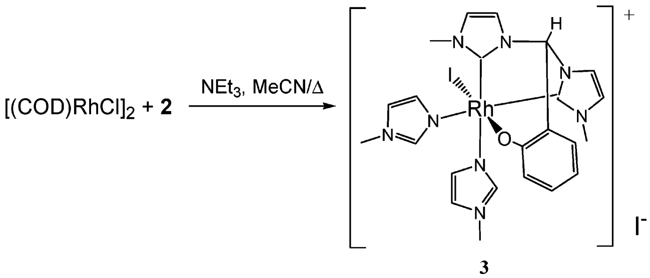
Scheme 1



Scheme 2



we did not detect any C−Rh coupling in the ^{13}C NMR for these two ligands. We were slightly concerned that the compound obtained could contain the ligand in a bridging form, yielding a dimetallic species, since we have observed that these species can be readily formed with some bis(carbene) ligands,[14−16] but this possibility was eliminated by elemental analysis and mass spectroscopy.

The oxidation of Rh(I) to Rh(III) in the reaction process is still a matter of discussion, although it has been observed for the reaction of other bis(carbene) ligands with Rh(I),[14,16,17] and a possible mechanism has been proposed.[16] The two coordinated *N*-methylimidazole ligands come from the cleavage of the ligand precursor **2**; we have observed that under mild reaction conditions some bis-N-heterocyclic carbene precursors can break their C−N bonds, yielding the *N*-alkylimidazole fragments.[8]

The structure of **3** was unequivocally determined by single-crystal X-ray crystallography. Figure 1 shows the molecular structure of **3**. The Rh is octahedral, with a metal−bis(carbene) (CRhC) bite angle of 87.1(8)°. The Rh−C distances for the NHCs are usually near 2 Å for Rh complexes; in our case they are 2.00(2) Å, suggesting that the bond has mainly σ-character. The high trans influence of the carbenes is reflected in the long Rh−N distances of 2.10 and 2.17 Å.

Complex **3** catalyzes the hydrogenation of C═O and C═N groups via hydrogen transfer from i-PrOH/KOH at 82 °C. As shown in Table 1, aryl and alkyl ketones are converted to the corresponding alcohols in good yields with a catalyst loading of 0.1 mol %. Under these conditions the reactions are almost complete in 2 h, except for ethyl methyl ketone, which only reaches full conversion after 24 h. **3** also catalyzes the reduction of imines to the corresponding amines, although the reactions are slower.

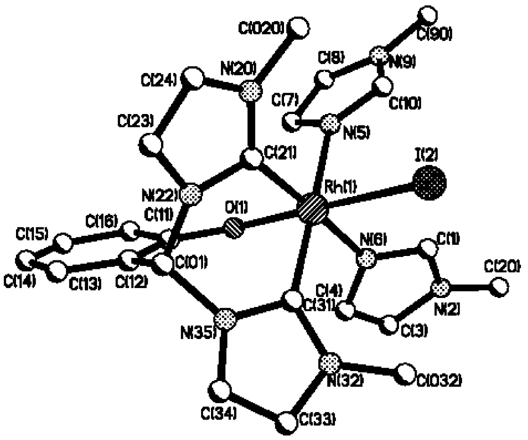


Figure 1. X-ray molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Rh(1)−C(31) = 2.00(2), Rh(1)−C(21) = 2.00(2), Rh(1)−O(1) = 2.030(12), Rh(1)−N(6) = 2.10(2), Rh(1)−N(5) = 2.170(15), Rh(1)−I(2) = 2.671(19); C(31)−Rh(1)−C(21) = 87.2(8), C(31)−Rh(1)−O(1) = 89.1(7), C(21)−Rh(1)−O(1) = 93.6(7).

Table 1. Catalytic Transfer Hydrogenation Using Compound 3 as Catalyst[a]

entry	substrate	amt of cat. (mol %)	time (h)	yield (%)	TON	TOF
1	cyclohexanone	0.1	1	97	970	970
2	cyclohexanone	0.1	2	>99	1000	500
3	benzophenone	0.1	0.5	70	700	1400
4	benzophenone	0.1	1	79	790	790
5	benzophenone	0.1	5	>98	1000	200
6	acetophenone	0.1	0.5	86	860	1720
7	acetophenone	0.1	1	91	910	910
8	acetophenone	0.1	2	>98	1000	500
9	ethyl methyl ketone	0.1	7	65	650	93
10	ethyl methyl ketone	0.1	24	90	900	38
11	*N*-benzylideneaniline	0.1	0.5	55	550	1100
12	*N*-benzylideneaniline	0.1	1	65	650	650
13	*N*-benzylideneaniline	0.1	24	85	850	35
14	*N*-benzylidenemethylamine	0.1	0.5	60	600	1200
15	*N*-benzylidenemethylamine	0.1	1	72	720	720
16	*N*-benzylidenemethylamine	0.1	24	>98	1000	42
17	cyclohexanone	0.001	6	50	50000	8333
18	cyclohexanone	0.001	24	70	70000	2917
19	benzophenone	0.001	6	60	60000	10000
20	benzophenone	0.001	24	68	68000	2833
21	acetophenone	0.001	6	20	20000	3333
22	acetophenone	0.001	24	50	50000	2083

[a] Conditions: 10 mL of 0.1 M KOH in i-PrOH, reflux temperature 82 °C. Yields were determined by ^{1}H NMR. TON is given in units of (mol of product)/(mol of catalyst) and TOF in units of (mol of product)/((mol of catalyst) h).

Interestingly, lower catalyst loadings of **3**, such as 10^{-3} mol %, still are efficient enough to catalyze the reduction of the ketones in high yields. TOFs as high as 8300 and 10 000 are achieved for the cyclohexanone and benzophenone cases (entries 17 and 19), which show a higher activity toward reduction under all the condi-

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tions used. The TONs of 50 000–70 000 observed for the benzophenone and cyclohexanone cases (entries 17–22) are considerably larger than those reported for other Rh(III) carbene complexes described by us[14,17] and are among the highest reported for this reaction using a Rh catalyst.

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Supporting Information Available: Text giving spectroscopic data of compounds **2** and **3** and complete listings of structural parameters for **3** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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