1832 *Organometallics* **2010,** *29,* 1832–1838
DOI: 10.1021/om100090c

ORGANOMETALLICS
Article

Preparation of Cp-Functionalized N-Heterocyclic Carbene Complexes of Ruthenium. Resolution of Chiral Complexes and Catalytic Studies

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Received February 4, 2010

A series of piano-stool ruthenium(II) complexes bearing bidentate cyclopentadienyl-functionalized N-heterocyclic carbene ligands Ru(Cp^X-NHC)(CO)I [Cp = tetramethylcyclopentadienyl (Cp*) and tetrabenzylcyclopentadienyl (Cp^{Bz})] have been prepared by the diastereoselective reaction of the imidazolium Cp^X-NHC proligands with $[Ru_3(CO)_{12}]$. The new complexes have been characterized by spectroscopic techniques and X-ray diffraction methods. The enantiopure complexes have been separated by preparative thin-layer chromatography of the diastereomeric mixtures resulting from the reaction of the Ru(Cp^X-NHC)(CO)I compounds with an auxiliary chiral amine. Ru(Cp*-NHC)(CO)I is an efficient catalyst for the isomerization of allylic alcohols both in water and in THF.

Introduction

Some of the reasons that may justify the rich chemistry of ruthenium are its ability to afford a wide range of stable oxidation states and coordination geometries and also to provide electronically unsaturated species. These properties have turned this metal into one of the richest sources of catalysts for a wide variety of organic transformations.[1] Among Ru-complexes, those containing the cyclopentadienyl-type ligands have constituted an interesting class of complexes because they can provide stable 16-electron species that can have important catalytic applications.[2] An interesting subclass of such complexes is formed by those species containing cyclopentadienyl-tethered ligands.[3] The chelating coordination of the ligand may have important implications because it affords an "extra" stabilization of the metal complex and can potentially provide desired properties such as hemilability or chirality.

With the ubiquitous use of N-heterocyclic carbenes (NHC) in catalyst design,[4] there has been an enormous number of new NHC-based ligands that have been coordinated to almost every metal in the periodic table. As Cp-related ligands, some indenyl- and fluorenyl-NHC ligands have been coordinated to a variety of transition and f-block metals,[5] although their coordination to ruthenium remained elusive until Wang and co-workers recently described their first indenyl-imidazolylidene ruthenium complexes.[6]

We recently described a series of Cp-NHC-functionalized ligands that we coordinated to Ir,[7,8] Rh,[8] and Mo.[9] However, we did not resolve the enantiomeric mixtures generated.

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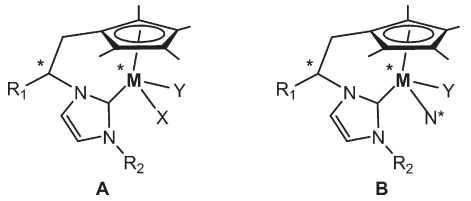
 Published on Web 03/05/2010

Scheme 1



With this in mind, we pursued a double aim for this new work: first, to extend the coordination of Cp-functionalized NHC ligands to ruthenium and study the catalytic activities of the resultant compounds and, second, to establish a suitable method for the preparation of enantiomeric pure compounds in order to widen the scope of the catalytic applications of the resulting products to asymmetric processes.

In this work we report the preparation of two new η^5-Cp-NHC complexes of ruthenium that contain two stereogenic centers, at the linker between the azole ring and the cyclopentadienyl ring and at the metal (A, Scheme 1). The coordination of an enantiomerically pure amine to the metal center afforded a mixture of diastereoisomers that could be resolved by chromatography, and the enantiomerically pure complexes have been characterized by spectroscopic techniques (B, Scheme 1).

Results and Discussion

Synthesis and Characterization of New Compounds. The direct reaction of the Cp*-NHC^{Me} and Cp^{Bz}-NHC^{Me} imidazolium proligands **1** and **2** with $[Ru_3(CO)_{12}]$ in refluxing toluene followed by treatment of the resulting residue (evaporation of volatiles and purification by column chromatography) afforded the corresponding Cp^X-NHC-ruthenium (X = Me, Bz) complexes **3** and **4** in high yield (65−70%), as shown in Scheme 2. The presence of the stereogenic centers at the aliphatic linker between the NHC and Cp^X rings and at the metal center suggested that four stereoisomers (two diasteromers) are expected.[10] However, the NMR characterization of the products revealed that only one diasteromer had been formed as a racemic mixture of the two possible enantiomers. In order to confirm that only one of the diastereomers was formed, we performed the NMR spectrum of the species in different solvents, and also VT NMR experiments, so that we could discard the existence of a dynamic equilibrium implying the interconversion of the two possible diasteromers.[11] The reasons that justify the diastereoselectivity of this reaction will be discussed below.

Compounds **3** and **4** were characterized by means of NMR spectroscopy and mass spectrometry. NMR spectroscopy allows the confirmation that both reactions leading to **3** and **4** are diastereoselective. The ^{1}H NMR spectrum of **3** shows two doublets at δ 6.68 and 6.25, due to the protons of the imidazolylidene ring. The four methyl groups of the cyclopentadienyl ring display four signals at 2.29, 2.02, 1.96, and 1.47 ppm, as a consequence of the asymmetry of the molecule. The ^{13}C NMR confirms the coordination of both the Cp* and NHC fragments of the ligand, with a signal at 184.1 ppm attributed to the Ru−C$_{carbene}$ and five distinctive signals due to the Cp ring. The ^{1}H NMR spectrum of **4** shows the signals due to the protons of the imidazolylidene ring at δ 6.63 and 5.90. The two protons at the aliphatic C$_2$ linker between the Cp and NHC rings appear as two doublets at 3.56 and 3.40 ppm, with the characteristic J_{H-H} value of a relative *anti* disposition (16 Hz). The ^{13}C NMR shows the signal due to the Ru−C$_{carbene}$ carbon at 182.2 ppm.

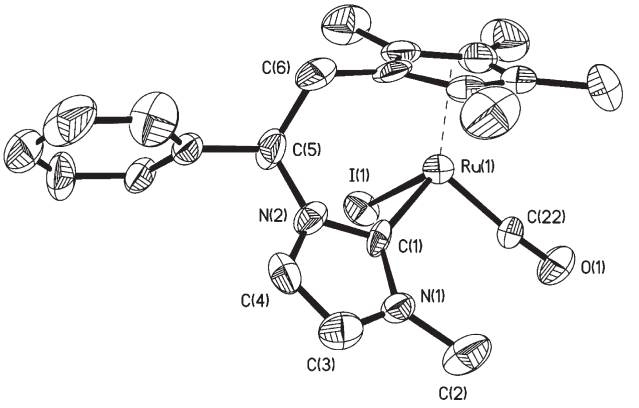
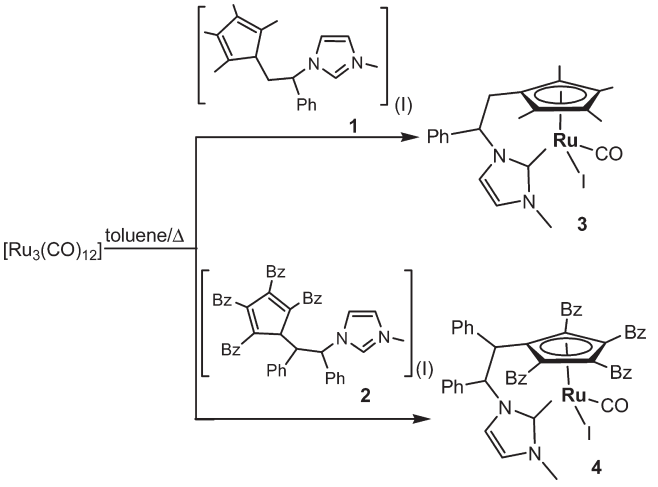


Figure 1. Molecular diagram of compound **3**. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−C(1) 2.050(12), Ru(1)−I(1) 2.7377(13), Ru(1)−C(22) 1.863(13), C(22)−O(1) 1.139(13), Ru(1)−Cp*$_{centroid}$ 1.877, C(1)−Ru(1)−I(1) 92.2(3), C(1)−Ru(1)−C(22) 99.8(5), C(22)−Ru(1)−I(1) 90.0(4), Cp*$_{centroid}$−Ru(1)−C(1) 116.46, Cp*$_{centroid}$−Ru(1)−I(1) 124.07, Cp*$_{centroid}$−Ru(1)−C(22) 126.50.

Scheme 2



The IR spectra of **3** and **4** show the CO stretching bands at 1910 (**3**) and 1923 cm^{-1} (**4**), which suggests the more electron-donating character of the Cp*-NHC ligand in **3**.

The molecular structures of complexes **3** and **4** were confirmed by means of X-ray diffraction. The crystals of both compounds contained a racemic mixture of the two enantiomers. Figures 1 and 2 illustrate one of the enantiomers of **3** and **4**, respectively.

The molecular structure of **3** (Figure 1) shows that the η^5-(tetramethylcyclopentadienyl)-NHC ligand is chelating the ruthenium center, generating a pseudo-three-legged piano-stool structure. One carbonyl and one iodide ligand complete the coordination sphere about the metal. The Ru−C$_{carbene}$ distance is 2.050 Å, similar to other

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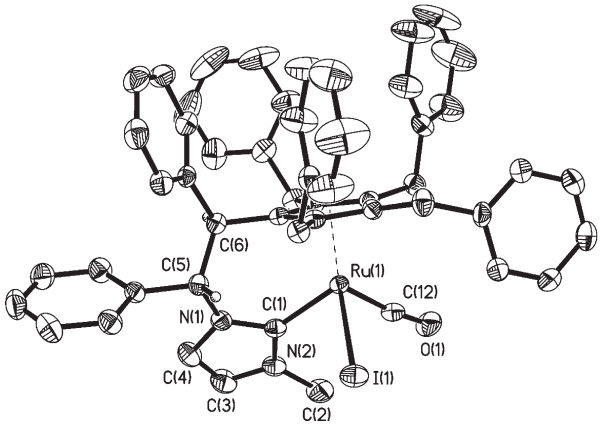

Figure 2. Molecular diagram of compound **4**. All hydrogen atoms have been omitted for clarity, except H(5) and H(6). Selected bond distances (Å) and angles (deg): Ru(1)−C(1) 2.046(3), Ru(1)−I(1) 2.7173(4), Ru(1)−C(12) 1.849(3), C(2)−O(1) 1.159(3), Ru(1)−$Cp^{Bz}_{centroid}$ 1.858, C(1)−Ru(1)−I(1) 84.90(7), C(1)−Ru(1)−C(12) 98.72(11), C(12)−Ru(1)−I(1) 89.00(8), $Cp^{Bz}_{centroid}$−Ru(1)−C(1) 119.90, $Cp^{Bz}_{centroid}$−Ru(1)−I(1) 127.70, $Cp^{Bz}_{centroid}$−Ru(1)−C(12) 126.00.

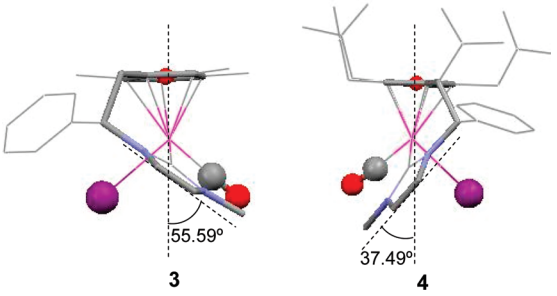

Figure 3. Schematic views of compounds **3** (left) and **4** (right), with the deviation angle of the azole planes with respect to the vertical axis of the molecule. Some of the atoms of the phenyl rings of the molecule **4** have been removed for clarity.

[Cp*RuX(NHC)(CO)] species.[12] The two Cp* carbons *trans* to the NHC ligand display slightly larger Ru−C distances than those shown for the other carbon atoms (see Supporting Information), as a consequence of the *trans* influence of the NHC ligand.

The molecular structure of **4** confirms that the Cp^{Bz}-NHC ligand is coordinated through the tetrabenzylcyclopentadienyl and NHC functionalities. The coordination sphere about the metal center is completed with carbonyl and iodide ligands. The Ru−$C_{carbene}$ distance is 2.046 Å, very similar to the related distance shown for compound **3**. The phenyl rings at the ethylene Cp^{Bz}-NHC linker have a relative *anti* configuration.

The molecular structures of these two molecules provide a suitable explanation for the diastereoselectivity of the reactions. Figure 3 shows a schematic view of compounds **3** and **4** with the angle between the azole (taken as the axis of the backbone) with respect to the vertical axis of the molecule. The deviation from an ideal parallel alignment of the azole plane and the vertical axis is forced by the asymmetry of the ethylene linker between the azole and the cyclopentadienyl

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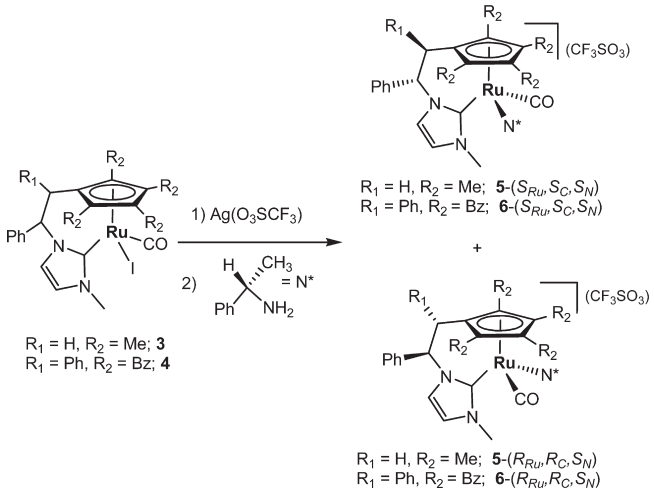
Scheme 3



functionalities. As can be seen, this deviation locates the N-methyl groups of both **3** and **4** close to the carbonyl groups, avoiding the more bulky iodine ligand. The other diastereomers (not observed and not depicted in Figure 3) would consist of the reverse situation in which the N-methyl group is close to the iodine, affording a sterically strained situation.

In order to check if the separation of the two enantiomers contained in **3** and **4** was possible, we decided to coordinate a chiral amine to **3** and **4** in order to afford the formation of the corresponding two separable diastereomers. The reaction proceeded as shown in Scheme 3, with the addition of $Ag(O_3SCF_3)$ for the removal of the iodide prior to the addition of the (*S*)-(−)-α-methylbenzylamine.

For the reaction with **3**, both enantiomers **5**-(R_{Ru},R_C,S_N) and **5**-(S_{Ru},S_C,S_N) (from now on **5A** and **5B**) were separated by preparative thin-layer chromatography. Figure 4 shows the region of the imidazolylidene and the C*H*Ph protons of three ^{1}H NMR spectra of compound **3** before and after addition of the chiral amine and after purification of both enantiomers. We characterized both species by NMR spectroscopy and mass spectrometry. Unfortunately, we could not obtain crystals suitable for X-ray diffraction, so we were not able to determine the absolute configuration of the enantiomers. The ^{1}H NMR spectrum of **5A** show the signals due to the protons of the imidazolylidene at δ 6.52 and 6.26 (6.73 and 6.33 in **5B**). The characteristic doublet of doublets assigned to the C*H*Ph proton of the Cp*-NHC linker appears at 5.21 ppm (5.13 in **5B**). The ^{13}C NMR spectrum of **5A** shows the characteristic signals due to the carbonyl group at 208.2 ppm (209.7 in **5B**) and to the Ru−$C_{carbene}$ at 179.5 ppm (180.3 in **5B**).

For the reaction with **4** (Scheme 3), the separation was performed by preparative thin-layer chromatography, which afforded the isolation of the pure **6**-(R_{Ru},R_C,S_N) and **6**-(S_{Ru}, S_C,S_N) in moderate yields (≈30%). Both species were fully characterized by NMR spectroscopy and ESI-MS, but we were unable to obtain suitable crystals for X-ray diffraction; therefore, we could not determine the absolute configuration of each of the enantiomers. Thus the NMR spectra could not be assigned to each enantiomer. The ^{1}H NMR spectra of **6**-(R_{Ru},R_C,S_N) and **6**-(S_{Ru},S_C,S_N) (**6A** and **6B** from now on) show the signals due to the N-methyl groups at the imidazole rings at 3.04 (**6A**) and 3.75 (**6B**) ppm. The signals due to the imidazolylidene protons appear at δ 6.67 and 6.42 (**6A**) and

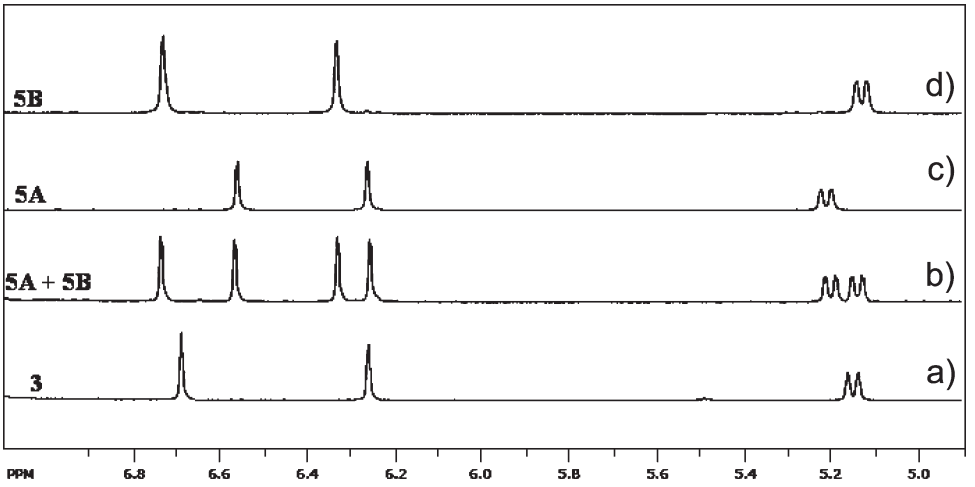


Figure 4. Region of the imidazolylidene and C*H*Ph protons of the ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of (a) **3**, (b) **5A** and **5B**, (c) **5A**, and (d) **5B**. **5A** and **5B** correspond to either **5**-(R_{Ru},R_C,S_N) or **5**-(S_{Ru},S_C,S_N). The definitive assignation has not been made.

6.51 and 6.38 (**6B**). Each of the isomers display eight distinctive doublets attributed to the diastereotopic methylene protons at the four benzyl groups, between 4.2 and 3.1 ppm. The ^{13}C NMR spectra show the signals due to the carbonyl groups at δ 209.7 (**6A**) and 209.6 (**6B**) and to the metalated Ru−$C_{carbene}$ carbons at δ 180.2 (**6A**) and 181.2 (**6B**). Again, the IR spectra of **5A**, **5B**, **6A**, and **6B** suggest the higher electron-donating character of the Cp* ligand in **5A** and **5B**, as shown by the CO stretching frequencies at 1918(**5A**), 1919 (**5B**), 1925 (**6A**) and 1924 cm^{-1} (**6B**).

Catalytic Studies. The catalytic isomerization of allylic alcohols allows the direct preparation of the corresponding carbonyl compounds, thus simplifying the conventional two-step organic procedures.[13] Several ruthenium complexes have been reported to show high activities in this catalytic reaction,[14−17] but the most recent studies are focused on the asymmetric version of the process, where rhodium,[18] iridium,[19,20] and ruthenium[16] have demonstrated very good performances. We thought that **3** and **4** may possess the structural and electronic requirements to be efficient catalysts for this reaction, so we decided to study their activity with the aim of extending the study to their enantiomerically pure derivatives in a future work. The catalytic results are summarized in Table 1.

The reactions were carried out using a catalyst loading of 1 or 0.2 mol %. Prior to the addition of the substrates, compounds **3** and **4** were dissolved in the reaction solvent (THF or H_2O) together with 3 equiv of AgOTf as halide abstractor, in order to activate the catalysts. Also, it is noteworthy that the addition of AgOTf facilitates the solubility of the two compounds in H_2O, probably via the formation of the corresponding [$Cp^XRu(CO)(H_2O)$](OTf) species. As can be seen from the data shown in Table 1, compound **3** is far more active than **4**. Considering the electronic differences between these two complexes (based on the CO stretching frequencies obtained by IR spectroscopy), it seems that the complex with the stronger σ-donor ligand is the one to provide better catalytic outcomes. On the other hand the difference in activities may also be attributed to the different steric environments shown by the two metal centers, with the metal at **4** being highly sterically hindered due to the presence of the bulky benzyl groups. Catalyst **3** shows to be an excellent catalyst for a wide variety of allylic alcohols (Scheme 4), with activities that compare well with previously reported data for other ruthenium catalysts.[14,17] Remarkably, in contrast with other known ruthenium catalysts,[17] **3** does not need the addition of base in order to possess good activity, thus simplifying the reaction procedure and widening its scope to allylic alcohols that transform into aldehydes and base-sensitive ketones. The activity of the catalyst in H_2O was high, although we needed to increase the temperature to 75 °C (reactions in THF are performed at 55 °C), for which full conversions were achieved even with catalyst loadings as low as 0.2 mol % (entries 2, 7, 10, 11, and 12).

Some mechanistic studies on this reaction have been performed using deuterium-labeled alcohols of the type R-CD_2OH[20,21] and also examples in which O-deuterated alcohols were used.[22] The isomerization of 3-buten-1-ol in D_2O in the presence of **3** (0.2 mol %) afforded the corresponding ketone, in which the deuterium atom is quantitatively and selectively incorporated at the α-carbon (Scheme 5). This observation is similar to that previously observed by Grubbs and co-workers.[22] The monitoring of the reaction of isomerization of 3-buten-1-ol in D_2O and H_2O shows that both reactions occur at the same reaction rates, which indicates that the isotopic effect is negligible ($k_D/k_H \approx 1$).

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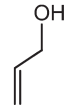
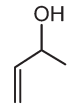
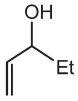
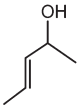
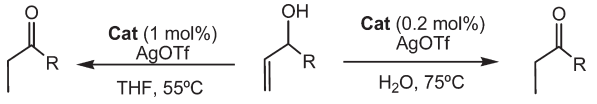
Table 1. Isomerization of Allylic Alcohols Catalyzed by 3 and 4[a]

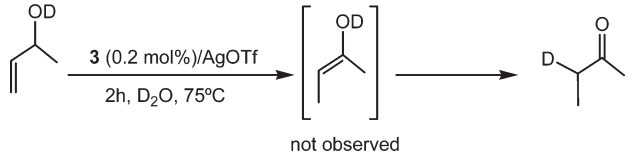
Entry	Substrate	Cat.[b]	Cat. Load (mol%)	Solv.	T (°C)	t (h)	Yield (%)[c]
1		**3**	1	THF	55	1	99
2		**3**	0.2	H_2O	75	2	99
3		**3**	1	THF	rt	6	99
4		**3**	1	THF	55	3	99
5		**3**	1	THF	75	0.33	99
6		**4**	1	THF	55	24	20
7		**3**	0.2	H_2O	75	4	99
8		**3**	1	THF	55	3	99
9		**4**	1	THF	55	24	25
10		**3**	0.2	H_2O	75	4	99
11		**3**	0.2	H_2O	75	4	99
12		**3**	0.2	H_2O	75	24	20
13		**3**	1	THF	55	24	60

[a] Reactions carried out with 0.4 mmol of substrate dissolved in 0.5 (THF) or 4 (H_2O) mL of solvent. [b] Activated by AgOTf, 10 min at rt. [c] Yield determined by ^1H NMR.

Scheme 4



Scheme 5



This observation is indicative that the activation of the O−H bond proceeds rapidly.

Conclusion

In this work we have described the convenient synthesis of two ruthenium complexes with Cp-functionalized N-heterocyclic carbenes. The synthetic procedure consists of the direct reaction of the corresponding imidazolium Cp-NHC proligands[7,8] and $[Ru_3(CO)_{12}]$, which affords the diastereoselective formation of the reaction products in high yield. The coordination of the ligand may be a consequence of the oxidative addition of the C−H bond of the imidazolium to the Ru(0), followed by reductive elimination of hydrogen from the Ru−H and a proton from the cyclopentadiene group, which coordinates to the metal as a cyclopentadienyl ligand. This mechanism was previously suggested by Wang and co-workers for the coordination of an indenyl-functionalized NHC,[6] but in that case the yields of the reaction products were very low.

The two compounds obtained have been fully characterized, both by spectroscopic techniques and by X-ray diffraction. Interestingly, both species present stereogenic centers at the metal and at the linker between the azole and the cyclopentadienyl rings. The diastereomeric resolution of the two enantiomers has been performed by addition of a chiral amine, which allows the NMR detection of the mixture of the two enantiomers. The separation of the enantiomers has been made by thin-layer chromatography, allowing the spectroscopic characterization of each enantiomerically pure chiral complex.

Compounds **3** and **4** have been tested in the catalytic isomerization of allylic alcohols. The more sterically crowded complex, **4**, shows very low activity, while **3** is very active in THF and H_2O. The isomerization of a O-deuterated allylic alcohol provides the corresponding ketone with the deuterium at the α-carbon, in agreement with previously reported results by Grubbs and co-workers.[22] The negligible

isotopic effect ($k_D/k_H \approx 1$) indicates thet the O−H(D) bond activation proceeds rapidly.

Further studies in order to determine the asymmetric catalytic behavior of the enantiomerically pure metal complexes are underway.

Experimental Section

General Procedures. Ligands **1**[7] and **2**[9] were synthesized according to literature procedures. All other reagents were used as received from commercial suppliers and used without further purification. NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using $CDCl_3$ as solvent. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. A QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used for high-resolution mass spectrometry (HRMS). The drying gas as well as nebulizing gas was nitrogen at a flow of 400 L/h and 80 L/h, respectively.

Synthesis of 3. A solution of **1** (300 mg, 0.69 mmol) and triruthenium dodecarbonyl (147 mg, 0.23 mmol) is refluxed in toluene (10 mL) overnight. The resulting red solution with black precipitate is evaporated to dryness and purified by column chromatography (dichloromethane/acetone), yielding the ruthenium complex **3** (220 mg, 0.39 mmol, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (m, 5H), 6.68 (d, J = 2.1 Hz, 1H), 6.25 (d, J = 2.1 Hz, 1H), 5.15 (dd, J = 2.7 Hz J = 11.4 Hz, 1H), 3.75 (s, 3H), 2,76 (m, 2H), 2.29 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.47 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 209.1, 184.1, 137.8, 129.4, 129.0, 121.6, 119.6, 104.4, 99.1, 95.1, 89.8, 83.2, 67.7, 39.8, 29.1, 11.9, 11.1, 10.97, 10.52. MS (ESI): m/z [M − I]$^+$ calcd for $C_{22}H_{25}N_2ORu$, 435.1; found, 435.0, [M + Na]$^+$ calcd for $C_{22}H_{25}N_2NaORu$, 585.0; found, 484.9. HRMS (ESI-TOF): m/z [M]$^+$ calcd for $C_{22}H_{25}N_2ORu$, 435.1017; found, 435.1017. IR (KBr): ν(CO) 1910 cm^{-1}.

Synthesis of 4. A solution of **2** (158 mg, 0.19 mmol) and triruthenium dodecarbonyl (41 mg, 0.06 mmol) is refluxed in toluene (10 mL) overnight. The resulting red solution with black precipitate is evaporated to dryness and purified by column chromatography (dichloromethane/acetone), yielding the ruthenium complex **4** (100 mg, 0.11 mmol, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17−6.30 (m, 30H), 6.63 (m, 1H), 5.94 (m, 1H), 5.90 (d, J = 11.1 Hz, 1H), 4.39 (d, J = 17.4 Hz, 1H), 4.36 (d, J = 11.1 Hz, 1H), 4.08 (d, J = 17.1 Hz, 1H), 3.56 (d, J = 15.9 Hz, 1H), 3.40 (d, J = 16.8 Hz, 1H), 3.34 (d, J = 17.7 Hz, 1H), 3.17 (d, J = 16.8 Hz, 1H), 3.11 (d, J = 15.9 Hz, 1H), 2.86 (d, J = 16.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 208.0, 182.2, 140.0, 139.7, 139.2, 138.9, 138.2, 137.0, 130.6, 129.6, 129.0−127.4, 126.4−126.2, 125.7, 125.3, 121.7, 121.3, 107.5, 102.5, 99.2, 96.2, 89.1, 70.6, 44.4, 40.2, 34.4, 31.9, 31.5, 31.25. MS (ESI): m/z [M − I]$^+$ calcd for $C_{52}H_{45}N_2ORu$, 815.26; found, 815.2; [M − I + CH_3CN]$^+$ calcd for $C_{54}H_{48}N_3ORu$, 856.28; found, 856.2; [M + Na]$^+$ calcd for $C_{52}H_{45}IN_2NaORu$, 865.15; found, 965.1. HRMS (ESI-TOF): m/z [M]$^+$ calcd for $C_{52}H_{45}N_2ORu$, 815.2590; found, 815.2590. IR (KBr): ν(CO) 1923 cm^{-1}.

Synthesis of 5A and 5B. A solution of **3** (30 mg, 0.053 mmol) and AgOTf (17 mg, 0.064 mmol) in 5 mL of dichloroethane was stirred at room temperature for 10 min. Then (*S*)-(−)-α-methylbenzylamine (8 μL, 0.064 mmol) was added, the reaction mixture was heated at 70 °C for 20 min, the yellow solution was filtered through Celite, and the volatiles were removed under vacuum. The crude was applied in a preparative TLC and eluted several times with diethyl ether/hexane (8:2). Both diastereoisomers were characterized:

5A (6 mg, 0.0085 mmol, 16%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 7 Hz, 2H), 7.44−7.36 (m, 3H), 7.24−7.18 (m, 5H), 6.52 (s, 1H), 6.26 (s, 1H), 5.21 (dd, J = 12.5 Hz J = 2 Hz, 1H), 3.62 (m, 1H), 3.42 (m, 2H), 3.20 (s, 3H), 2.78−2.63 (m, 2H), 1.97 (s, 3H), 1.95 (s, 3H), 1.77 (s, 3H), 1.51 (d, J = 6.8 Hz, 3H), 1.16 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 208.2, 179.5, 142.2, 136.4, 129.0, 128.9, 128.5, 127.6, 126.2, 121.7, 120.6, 103.4, 99.8, 96.5, 89.0, 80.4, 66.7, 66.2, 38.5, 28.3, 26.4, 10.2, 9.7, 9.6, 8.9. HRMS (ESI-TOF): m/z [M]$^+$ calcd for $C_{30}H_{36}N_3ORu$, 556.1910; found, 556.1910. IR (KBr): ν(CO) 1919 cm^{-1}.

5B (6 mg, 0.0085 mmol, 16%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 7.2 Hz, 2H), 7.44−7.36 (m, 5H), 7.30 (t, J = 7.5 Hz, 2H), 7.20 (d, J = 7 Hz, 1H), 6.73 (br, 1H), 6.33 (s, 1H), 5.13 (dd, J = 12.2 Hz J = 2.2 Hz, 1H), 3.74 (br, 2H), 3.63 (s, 3H), 2.76−2.64 (m, 3H), 1.81 (s, 3H), 1.72 (s, 3H), 1.46 (d, J = 6.5 Hz, 3H), 1.41 (s, 3H), 1.16 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 209.7, 180.3, 143.3, 136.8, 129.7, 129.5, 129.3, 129.2, 128.2, 127.1, 122.7, 121.3, 104.5, 99.9, 96.6, 90.4, 81.4, 67.7, 62.7, 39.5, 28.7, 24.2, 10.7, 10.3, 9.6, 9.2. HRMS (ESI-TOF): m/z [M]$^+$ calcd for $C_{30}H_{36}N_3ORu$, 556.1910; found, 556.1904. IR (KBr): ν(CO) 1918 cm^{-1}.

Synthesis of 6A and 6B. A solution of **4** (35 mg, 0.037 mmol) and AgOTf (12 mg, 0.045 mmol) in 5 mL of dichloroethane was stirred at room temperature for 10 min. Then (*S*)-(−)-α-methylbenzylamine (6 μL, 0.045 mmol) was added, the reaction mixture was heated at 70 °C for 1 h, the yellow solution was filtered through Celite, and the volatiles were removed under vacuum. The crude was applied in a preparative TLC and eluted several times with diethyl ether. Both diastereoisomers were characterized:

6A (5 mg, 0.0046 mmol, 12.5%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 7 Hz, 1H), 7.42 (t, J = 7.5 Hz, 3H), 7.31−6.92 (m, 23H), 6.67 (d, J = 8 Hz, 1H), 6.63 (br, 2H), 6.42 (d, J = 7.5 Hz, 2H), 6.32 (m, 3H), 6.26 (t, J = 7.5 Hz, 1H), 6.16 (d, J = 11 Hz, 1H), 6.10 (br, 2H), 6.03 (br, 1H), 4.32 (d, J = 18 Hz, 1H), 4.29 (t, J = 6.5 Hz, 1H), 4.20 (d, J = 16.5 Hz, 1H), 4.05 (d, J = 11 Hz, 1H), 3.53 (d, J = 16.5 Hz, 1H), 4.45 (d, J = 14.5 Hz, 1H), 4.41 (d, J = 18.5 Hz, 1H), 3.04 (s, 3H), 1.99 (d, J = 15.5 Hz, 1H), 1.14 (d, 6.5 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 209.7, 180.2, 142.3, 142.1, 138.5, 138.4, 136.4, 136.0, 135.3, 132.9, 130.0−125.3, 122.5, 121.3, 113.0, 102.3, 100.5, 95.7, 87.1, 70.0, 62.3, 44.4, 39.2, 32.0, 31.7, 30.11, 29.8, 29.7, 28.4. MS (ESI-TOF): m/z [M]$^+$ calcd for $C_{60}H_{56}N_3ORu$, 936.3484; found, 936.3507. IR (KBr): ν(CO) 1925 cm^{-1}.

6B (5 mg, 0.0046 mmol, 12.5%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 8 Hz, 1H), 7.39−7.25 (m, 5H), 7.19−7.13 (m, 8H), 7.10−6.97 (m, 8H), 7.0−6.77 (m, 6H), 6.58 (br, 2H), 6.51 (d, J = 8 Hz, 2H), 6.38 (t, J = 7.5 Hz, 2H), 6.31 (t, J = 6.5 Hz, 1H), 6.25−6.20 (m, 3H), 4.29 (d, J = 14.5 Hz, 1H), 4.25 (d, J = 11.5 Hz, 1H), 4.13 (d, J = 16.5 Hz, 1H), 3.80 (m, 1H), 3.75 (s, 3H), 3.58 (d, J = 16.5 Hz, 1H), 3.35−3.20 (m, 3H), 3.08 (d, J = 14.5 Hz, 1H), 3.39 (d, J = 16 Hz, 1H), 2.39 (d, J = 16.5 Hz, 1H), 0.94 (d, J = 6.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 209.6, 181.2, 144.1, 141.4, 138.8, 138.5, 136.6, 136.0, 133.0, 130−126.9, 122.75, 112.5, 101.4, 96.2, 87.0, 71.1 63.8, 44.8, 40.0, 32.2, 30.3, 22.3. HRMS (ESI-TOF): m/z [M]$^+$ calcd for $C_{60}H_{56}N_3ORu$, 936.3484; found, 936.3518. IR (KBr): ν(CO) 1924 cm^{-1}.

Catalytic Experiments. In THF. A solution of catalyst (1 mol %) in 0.5 mL of THF is treated with AgOTf (1−2 mol %) and stirred at room temperature for 10 min. Then 0.8 mmol of substrate is added and the reaction heated to 55 °C followed by ^{1}H NMR.

In H_2O. A solution of catalyst (0.2 mol %) in 4 mL of H_2O is treated with AgOTf (0.2 mol %) and stirred at room temperature for 10 min. Then 0.4 mmol of substrate is added and the reaction heated to 75 °C followed by ^{1}H NMR.

Kinetic Isotopic Effect. A solution of **1** (0.9 mg, 0.2 mol %) in 4 mL of H_2O/D_2O is treated with AgOTf (0.3 mg, 0.2 mol %) and stirred at room temperature for 10 min. Then 3-buten-1-ol (43 μL, 0.4 mmol) is added and the reaction heated to 75 °C. Aliquots (50 μL) are taken and dissolved in D_2O, and the ^{1}H NMR spectra recorded.

Table 2. Crystallographic Data for Complexes 3 and 4

	3	4
empirical formula	$C_{22}H_{25}IN_2ORu$	$C_{52}H_{45}IN_2ORu$
mol wt	561.41	941.87
radiation	Mo Kα (monochr); 0.71073 λ (Å)	
T (K)	273	273
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	8.9778(6)	16.601(3)
b (Å)	15.7073(9)	14.227(2)
c (Å)	31.0292(18)	19.133(3)
α (deg)	90	90
β (deg)	95.163(2)	111.765(3)
γ (deg)	90	90
V (Å^3)	4357.9(5)	4196.8(12)
Z	8	4
D_{calcd} (Mg m^{-3})	1.711	1.491
μ(Mo Kα) (mm^{-1})	2.150	1.150
total, unique no. of rflns	24 764, 7445	35 730, 9637
R_{int}	0.1078	0.0424
no. of params, restrictions	497, 0	515, 0
R, R_w ($I > 2\sigma$)[a]	0.0677, 0.1467	0.0322, 0.0482
GOF	0.999	1.085
min., max. resid dens (e Å^{-3})	−0.85, 1.48	−0.52, 0.37

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

X-ray Diffraction Studies. Single crystals of **3** and **4** were 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 Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 4.0 cm. 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 refined using the SHELXTL 6.1 software package.[23] All non-hydrogen atoms 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 2. The diffraction frames were integrated using the SAINT package.[24]

Acknowledgment. We gratefully acknowledge financial support from FCT of Portugal, POCI 2010, and FEDER through project PTDC/QUI/64458/2006. From the Spanish side we gratefully acknowledge financial support from the MEC of Spain (CTQ2008-04460) and Bancaixa (P1.1B2007-04). A.P.d.C. thanks the FCT for a grant (SFRH/BD/28490/2006). The authors are grateful to the Serveis Centrals d'Instrumentació Científica (SCIC) of the Universitat Jaume I for providing spectroscopic and X-ray facilities.

Supporting Information Available: Full crystallographic data as CIF files and NMR and HRMS spectra of compounds are available free of charge via the Internet at http://pubs.acs.org.

(23) Sheldrick, G. M. *SHELXTL*, version 6.1; Bruker AXS, Inc.: Madison, WI, 2000.

(24) *SAINT*, version 5.0; Bruker Analytical X-ray System: Madison, WI, 1998.