ORGANOMETALLICS

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Preparation, Hydrogen Bonds, and Catalytic Activity in Metal-Promoted Addition of Arylboronic Acids to Enones of a Rhodium Complex Containing an NHC Ligand with an Alcohol Function

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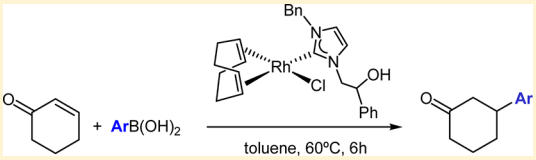
Supporting Information

ABSTRACT: The complex RhCl(COD){3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazol-2-ylidene} has been prepared by reaction of the dimer [Rh(μ-OMe)(COD)]$_2$ with 3-benzyl-1-(2-hydroxy-2-phenylethyl)-imidazolium chloride and characterized by X-ray diffraction analysis. The structure reveals that 75% of the molecules are associated through intermolecular O−H···Cl hydrogen bonds between the OH group of the NHC substituent of one molecule and the chloride ligand of the adjacent molecule. This complex catalyzes the addition of arylboronic acids to cyclic and acyclic enones in anhydrous toluene. The alcohol function of the substituent of the NHC ligand plays the role assigned to water in previous cases.



INTRODUCTION

The chemistry of N-heterocyclic carbenes (NHCs) is a field of great current interest due to the transversal applications of the NHC complexes, including homogeneous catalysis,[1] antimicrobial and cytotoxic agents,[2] photoactive sites in luminescent materials for self-assembly into liquid crystalline materials and metallosupramolecular structures, and synthons for molecular switches and conducting polymeric materials.[3] Although several methods have been developed for the preparation of complexes containing these ligands, deprotonation of imidazolium salts is the most used synthetic pathway.[4]

The vast majority of reported NHC ligands are substituted at nitrogens by alkyl or aryl groups. Imidazolium salts with carbonyl,[5] pyridyl,[6] pyrazolyl,[7] amine,[8] and phosphine[9] substituents are also known. They can be deprotonated and are thus suitable for the preparation of metal complexes.

The catalytic transformations usually take place at the metal center. However, there is an increasing number of reactions involving both the metal center and an acidic hydrogen atom of the ligands,[10] which can further form hydrogen bonds. It has been found that processes involving passive diffusion depend primarily on the hydrogen-bonding capacity or polar surface area of a drug solute.[11] Intermolecular hydrogen bonds also play an important role in the design and engineering of architectures of many polymeric materials. Hydrogen bonding can affect the chain length, chain packing, rigidity, and molecular order.[12] In addition, the induction and stabilization of liquid crystallinity by hydrogen bonding has been shown.[13] As a consequence of these observations, the preparation of transition-metal complexes with N-heterocyclic carbenes bearing acidic substituents, such as alcohols, at the N center constitutes a special challenge.

Alcohol-functionalized imidazolium salts are readily accessible by the nucleophilic opening of epoxides.[14] However, alcohol-functionalized imidazolylidene transition-metal complexes are scarce.[15] In order to justify this, it has been argued that the alcohol function is more acidic than the heterocycle. Thus, the single deprotonation leads to zwitterionic alcoholate imidazolium derivatives.[16]

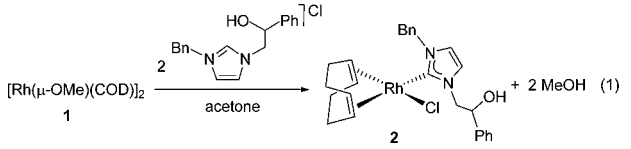
The hexahydride complex $OsH_6(P^iPr_3)_2$ is basic enough to produce the deprotonation of imidazolium salts, generating families of osmium polyhydride derivatives containing both normal and abnormal imidazolylidene complexes.[6e,17] Furthermore, it shows a marked tendency to dehydrogenate alcohols.[18] In agreement with both properties, the hexahydride reacts with alcohol-functionalized imidazolium salts to give NHC-keto derivatives.[19] In the search for new transition-metal compounds with NHC ligands bearing an alcohol function, we are investigating the use of basic transition-metal precursors without capacity for dehydrogenating alcohols. Thus, we have recently reported that the reaction of $Pd(OAc)_2$ with 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium chloride affords *trans*-$PdCl_2$\{3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazol-2-ylidene\}$_2$, which is an efficient catalyst for the Hiyama cross-coupling reaction between arylsiloxanes and aryl halides.[20] Now, we show that the dimer [Rh(μ-OMe)(COD)]$_2$ affords a related rhodium derivative, which catalyzes the 1,4-addition of arylboronic acids to enones, in the absence of water.

Received: June 5, 2012
Published: August 15, 2012

   dx.doi.org/10.1021/om300498e | *Organometallics* 2012, 31, 6154−6161

RESULTS AND DISCUSSION

1. Preparation and Characterization of the Hydroxyalkyl-Functionalized NHC-Rh Complex. Treatment of $[Rh(\mu\text{-OMe})(COD)]_2$ (**1**) with 2.0 equiv of 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium chloride in acetone, at room temperature, for 3 h leads to RhCl(COD){3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazol-2-ylidene} (**2**) as a result of the selective deprotonation of the imidazolium ring in the presence of the alcohol function, the release of methanol from the metal centers, and the coordination of the resulting hydroxyalkyl-functionalized NHC ligand and the chloride anion to the rhodium atoms of **1**. Complex **2** was isolated as a yellow solid in 75% yield, according to eq 1.



Complex **2** has been characterized by X-ray diffraction analysis. Figure 1 gives a view of the structure. The

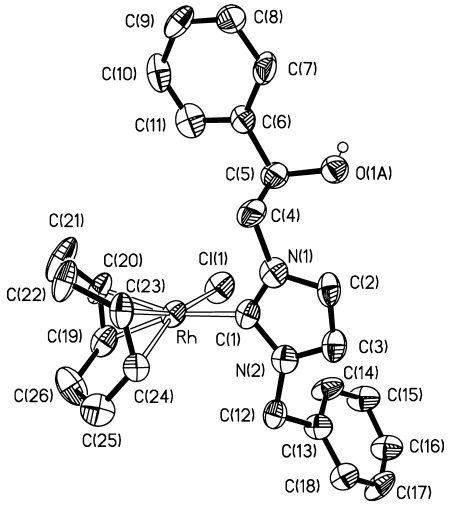


Figure 1. Molecular diagram of complex **2**. Selected bond lengths (Å) and angles (deg): Rh−Cl(1) = 2.3795(19), Rh−C(1) = 2.004(9), Rh−C(19) = 2.167(12), Rh−C(20) = 2.174(7), Rh−C(23) = 2.134(6), Rh−C(24) = 2.095(7), C(19)−C(20) = 1.336(12), C(23)−C(24) = 1.387(9); Cl(1)−Rh-C(1) = 89.6(2).

coordination geometry around the rhodium atom is almost square planar with the imidazolylidene ring perpendicular to the coordination plane, forming a dihedral angle of 89.20°. The greatest deviation from the best plane through the Rh, Cl(1), and C(1) atoms and the midpoints of the coordinated C−C double bonds of the diene is 0.0051 Å for the metal. The Rh−C(1) bond length of 2.004(9) Å compares well with those reported for other Rh-NHC complexes.[21] Due to the different trans influences of the NHC and the chloride ligands, a slight difference in the rhodium to carbon distances of the coordinated olefin is observed. While the carbon atoms C(23) and C(24) (trans to Cl(1)) are located at 2.134(6) and 2.095(7) Å from the metal center, the Rh−C bond lengths for C(19) and C(20) (trans to C(1)) are 2.167(12) and 2.174(7) Å. As expected, owing to the coordination to the metal center, the distances between the sp^2 carbon atoms C(23), C(24) and C(19), C(20) are increased to 1.387(9) and 1.336(12) Å, respectively. An extended view of the structure (Figure 2) reveals that 75% of the molecules of complex are

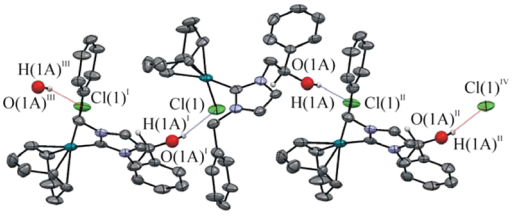


Figure 2. View of the intermolecular interactions via hydrogen bonding in the structure of complex **2**. Symmetry codes: (I) $-{}^1/_2 + x$, ${}^1/_2 + y$, ${}^1/_2 + z$; (II) ${}^1/_2 + x$, ${}^1/_2 - y$, ${}^1/_2 + z$; (III) $-1 + x$, y, $-1 + z$; (IV) $1 + x$, y, $1 + z$.

associated through intermolecular O−H···Cl hydrogen bonds between the OH group of one molecule and the chloride ligand of the adjacent molecule. In agreement with this, the separation H(1A)−Cl(1) of 2.449(2) Å is shorther than the sum of the van der Waals radii of hydrogen and chloride (r_{vdw}(H) = 1.20 Å, r_{vdw}(Cl) = 1.75 Å).[22] Furthermore, the O(1A)···Cl(1) separation is 3.263(6) Å and the angle O(1A)−H(1A)−Cl(1) is almost linear at 163.3(5)°. The remaining 25% of the molecules form an intramolecular O(1B)−H(1B)−Cl(1) hydrogen bond with H(1B)···Cl(1) and O(1B)−Cl(1) separations of 2.004(3) and 2.83(2) Å, respectively, and an O(1B)−H(1B)−Cl(1) angle of 179.11(4)°.

The ^{1}H and ^{13}C{^{1}H} NMR spectra reveal that in solution complex **2** exists as a 63:37 mixture of the two pairs of diastereoisomers, resulting from the chirality of C(5) and the fact that the molecular square plane is not a symmetry plane: i.e., as a mixture of S,R_a and S,S_a along with their respective enantiomers R,S_a and R,R_a. The 63:37 mixture of the pair of diastereoisomers R,R_a and R,S_a was prepared by the reaction of **1** with (*R*)-3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium chloride as shown in eq 1. As expected for the presence of an alcohol function in the NHC ligand, the ^{1}H NMR spectra of the mixtures contain two OH resonances at 3.88 (major) and 4.31 ppm (minor). In agreement with the presence of four inequivalent C(sp^2) atoms in the coordinated olefin, the ^{13}C{^{1}H} NMR spectra show four olefin resonances at 67.8, 69.8, 98.3, and 98.5 ppm for the major diastereoisomer and three signals at 69.3 (two carbons), 98.8, and 99.4 ppm for the minor species. The NHC Rh−C resonances appear at 182.2 (major) and 183.4 ppm (minor), as doublets with Rh−C coupling constants of 50.5 and 51.0 Hz, respectively.

2. Addition of Organoborons to α,β-Unsaturated Ketones. The rhodium-catalyzed conjugated addition of organoboron reagents to α,β-unsaturated carbonyl compounds is paramount in organic chemistry.[23] This reaction is generally performed in the presence of water, which appears to have two functions:[24] to hydrolyze the enolate intermediate that generates the addition product and to facilitate the transmetalation from the organoboron compound to the metal center through a hydroxorhodium intermediate. With the well-established complex **2** in hand, we reasoned that the alcohol function of the NHC ligand could perform the roles of the water, and in this way, the reaction should work in anhydrous solvent.

The addition of phenylboronic acid (**3a**) to cyclohex-2-enone (**4**) in the presence of 1 mol % of **2** was chosen in order to

dx.doi.org/10.1021/om300498e | Organometallics 2012, 31, 6154−6161

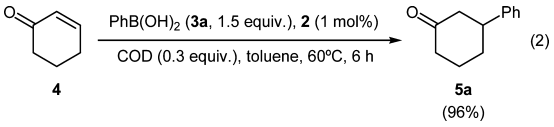
study the optimal reaction conditions.[25] Thus, a design of experiments (DOE) was used to plan a minimum set of assays to check the maximum range of variables that would determine the maximum information about which were the critical factors and what was the best combination of variables to obtain the highest yield of 3-phenylcyclohexanone (**5a**). The DOE was performed for five parameters with an average of two levels each. They were as follows: (i) temperature, (ii) the use of cycloocta-1,5-diene as additive, (iii) base, (iv) solvent, and (v) conventional heating (6 h) versus microwave heating (1 h). The selection of experiments was carried out according to a Taguchi L15 array. Table 1 collects the obtained results. The

Table 1. Addition of Phenylboronic Acid to Cyclohex-2-enone

heating	temp (°C)	additive	solvent	base	yield (%)[a]
conventional 6 h	40	none	toluene	NaOH	80
conventional 6 h	40	none	water	none	68
conventional 6 h	40	none	THF	KOH	8
conventional 6 h	60	COD	toluene	none	98
MW 1 h	60	COD	THF	none	42
conventional 6 h	40	none	toluene	none	53
conventional 6 h	60	none	toluene	none	86
conventional 6 h	60	none	water	none	75
MW 1 h	40	none	water	none	0
MW 1 h	60	none	water	none	23
MW 1 h	60	none	toluene	none	14
conventional 6 h	60	COD	toluene	none	95
conventional 6 h	60	none	toluene	NaOH	78
conventional 6 h	60	COD	water	none	80
conventional 6 h	60	none	water	NaOH	48

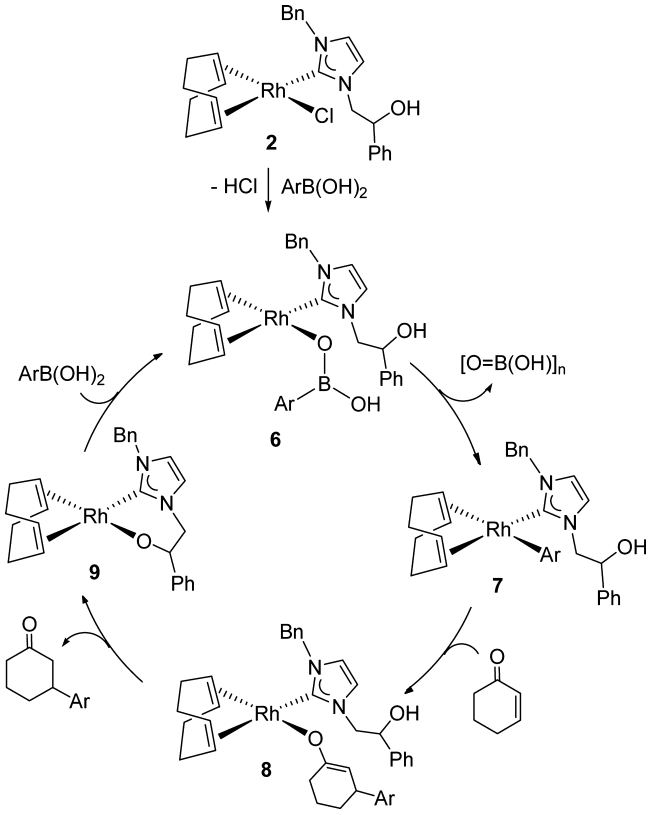
[a]The yield was calculated by GLC analysis by employing tridecane as an internal standard.

reaction is better performed at 60 °C by conventional heating in anhydrous toluene and in the presence of cycloocta-1,5-diene as an additive. Under these conditions, **5a** is obtained in 96% isolated yield (eq 2).



The reaction certainly works in the absence of water, in agreement with our initial hypothesis. Thus, **5a** is also formed by using triphenylboroxine instead of phenylboronic acid,[26] although the bigger steric hindrance of the boroxine gives rise to a slower reaction (24% conversion after 6 h). On the basis of the Hayashi mechanism,[24a,b] this fact can be rationalized according to Scheme 1. The catalytically active species is generated by transmetalation from the organoboron compound.[23c,27] Thus, the reaction of **2** with the arylboronic acid should give the boronate **6** and HCl. Then the key intermediate **6** could undergo intramolecular transfer of the aryl group from boron to rhodium to afford the square-planar aryl species **7**, by a β-aryl elimination pathway. In this context, it should be noted that Hartwig and co-workers have previously reported that the silylamido precursor $Rh[N(SiMe_3)_2](PEt_3)_2$ reacts with arylboronic acids, in the presence of PEt_3, to yield $Rh[OB(OH)Ph](PEt_3)_3$, which evolves into $Rh(Ar)(PEt_3)_3$ and $[O{=}B(OH)]_n$ in C_6D_{12} at 70 °C.[28] The subsequent coordination of the α,β-unsaturated ketone to the rhodium atom, followed by the regioselective 1,4-insertion of the coordinated substrate into the Rh−Ar bond of **7**, should lead to **8** via oxallyl or hydroxoallyl intermediates.[29] Thus, the intramolecular protonolysis of the alcoholated group of **8** by the alcohol substituent of the NHC ligand could afford the catalytic product and **9**, containing a chelate NHC-alcoholate group, which should regenerate the boronate **6** by reaction with the arylboronic acid. The role of the hydroxyl group is strongly supported by the fact that the complex RhCl(COD){3-benzyl-1-(2-phenylethyl)-imidazol-2-ylidene}, which does not bear an alcohol function, does not catalyze the reaction under anhydrous conditions, while **5a** is formed in 78% yield, after 6 h, in the presence of an aqueous 2.5 M NaOH solution.

Scheme 1



The presence of free cycloocta-1,5-diene during the catalysis prevents the dissociation of the coordinated olefin, increasing the stability of the catalytic system and the yield of the reaction (Figure 3a). The reaction works well in the absence of base. However, in the presence of 1.0 equiv of NaOH, the reproducibility of the assays is better (Figure 3b). This appears to be related to the neutralization of the generated HCl during the activation of the catalytic precursor, which could degrade the catalyst and/or the substrate.[30]

The versatility of the catalyst has been corroborated by using a variety of arylboronic acids (**3a**−**g**) bearing electron-donating and electron-withdrawing groups (Table 2). The addition of 1-naphthylboronic acid to cyclohexen-2-one gives the expected product **5b** in good yield, both in the presence and in the absence of NaOH. The corresponding 3-substituted cyclohexanones **5c**−**g** are also obtained in high yields. No reaction was observed when employing a more congested boron derivative such as 2,6-dimethoxyphenylboronic acid. The use

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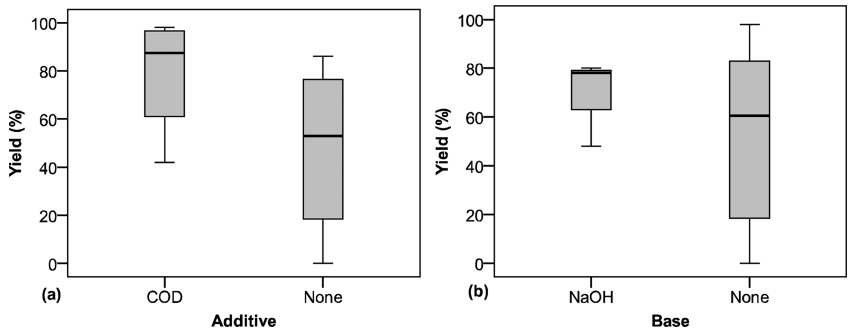
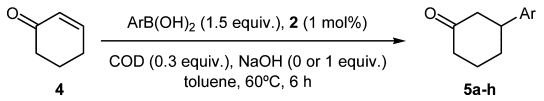


Figure 3. (a) Boxplot of experimental data with and without additive. (b) Boxplot of experimental data with and without base.

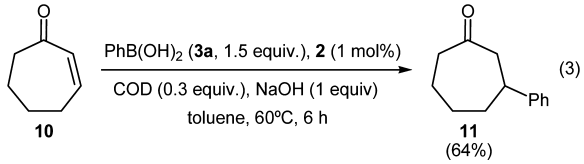
Table 2. Conjugate Addition of Arylboronic Acids to Cyclohex-2-enone[a]



entry	Ar	boronic acid	base[b]	product	yield (%)[c]
1	Ph	**3a**	none	**5a**	96
2	1-naphthyl	**3b**	none	**5b**	89
3	1-naphthyl	**3b**	NaOH	**5b**	86
4	4-$(CF_3)C_6H_4$	**3c**	none	**5c**	77
5	4-$(CF_3)C_6H_4$	**3c**	NaOH	**5c**	89
6	4-BrC_6H_4	**3d**	none	**5d**	57
7	4-BrC_6H_4	**3d**	NaOH	**5d**	88
8	4-$(MeO)C_6H_4$	**3e**	NaOH	**5e**	92
9	2-MeC_6H_4	**3f**	none	**5f**	53
10	2-MeC_6H_4	**3f**	NaOH	**5f**	64
11	3-ClC_6H_4	**3g**	NaOH	**5g**	74
12	2,6-$(MeO)_2C_6H_3$	**3h**	NaOH	**5h**	

[a]Reaction performed with cyclohex-2-enone (0.5 mmol) and arylboronic acid (0.7 mmol) in the presence of complex **2** (0.005 mmol) and cycloocta-1,5-diene (0.075 mmol), at 60 °C in toluene over 6 h. [b]The reaction was performed in the absence of a base or with NaOH (0.2 mL, 2.5 M aqueous solution). [c]Isolated yield of pure product after purification by chromatography (preparative TLC, hexane/ethyl acetate mixtures).

of the 63:37 mixture of the pair of diastereoisomers R,R_a and R,S_a produces the expected products **5** with similar yields and enantioselectivities of about 10%. Additionally, it should be mentioned that the addition of **3a** to cyclohepten-2-one (**10**) is less effective than the addition to cyclohexen-2-one. Thus, under basic conditions, 3-phenylcycloheptanone (**11**) is only isolated in 64% yield (eq 3).



Complex **2** also catalyzes the addition of arylboronic acids to acyclic enones such as methyl vinyl ketone (**12** in eq 4 and

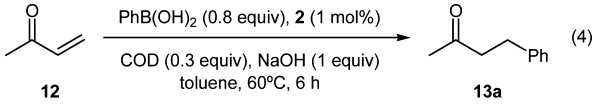
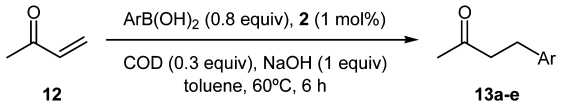


Table 3). The addition of phenylboronic acid in the absence of NaOH gives 4-phenylbutan-2-one (**13a**) as the only addition

Table 3. Conjugate Addition of Arylboronic Acids to Methyl Vinyl Ketone[a]



entry	Ar	boronic acid	product	yield (%)[b]
1	Ph	**3a**	**13a**	89
2	1-naphthyl	**3b**	**13b**	84
3	4-$(CF_3)C_6H_4$	**3c**	**13c**	66
4	4-BrC_6H_4	**3d**	**13d**	70
5	4-$(MeO)C_6H_4$	**3e**	**13e**	80

[a]Reaction performed with methyl vinyl ketone (0.5 mmol) and arylboronic acid (0.4 mmol) in the presence of complex **2** (0.005 mmol), cycloocta-1,5-diene (0.075 mmol), and NaOH (0.2 mL, 2.5 M aqueous solution) at 60 °C in a sealed tube with toluene over 6 h. [b]Isolated yield of pure product after purification by chromatography (preparative TLC, hexane/ethyl acetate mixtures).

product detected by GC. The amount of saturated ketone isolated after the disappearance of the substrate is, however, lower than 59%. The presence of 1.0 equiv of NaOH during the catalysis increases the isolated yield to 89%. This is consistent with the neutralization of the HCl generated in the formation of **6**, which prevents the partial subtraction of the substrate as a nondetected polymer. The polymerization of methyl vinyl ketone promoted by H^+ is a well-known process. In the presence of NaOH, 1-naphthyl- and 4-methoxyphenyl boronic acids give the corresponding products **13b,e** with yields over 80%, whereas the use of boron reagents with electron-withdrawing groups such as 4-trifluoromethylphenyl- and 4-bromophenylboronic acids produces the expected compounds **13c,d** in 66% and 70% yields, respectively.

■ CONCLUDING REMARKS

The complex RhCl(COD){3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazol-2-ylidene}, bearing an alcohol function, has been prepared by direct metalation of 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium chloride with the dimer $[Rh(\mu\text{-OMe})(COD)]_2$. In the solid state, 75% of the molecules of the complex are associated through intermolecular O−H···Cl hydrogen bonds between the OH group of one molecule and the chloride ligand of the adjacent molecule. In anhydrous toluene, it catalyzes the addition of arylboronic acids to cyclic and acyclic enones. The alcohol substituent of the NHC ligand

dx.doi.org/10.1021/om300498e | Organometallics 2012, 31, 6154−6161

appears to play the role assigned to water in this interesting reaction.

EXPERIMENTAL SECTION

General Information. The organometallic syntheses were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except for acetone, which was dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, and Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks. Coupling constants J are given in hertz. Infrared spectra were recorded on 400D, Jasco 4100LE (Pike MIRacle ATR), and Perkin-Elmer Spectrum 100 spectrophotometers. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). Mass spectra (EI) were obtained at 70 eV on an Agilent 5973 spectrometer; fragment ions are given in m/z units with relative intensities (%) in parentheses. [Rh(μ-OMe)(COD)]$_2$[31] and 3-benzyl-1-(2-hydroxy-2-phenylethyl)-imidazolium chloride[19] were prepared by published methods. All commercially available reagents (Acros, Aldrich, Fluka) were used without further purification. Melting points were determined with a Reichert Thermovar hot plate apparatus and are uncorrected. Analytical TLC was performed on Merck aluminum sheets with silica gel 60 F254. Silica gel 60 (0.04−0.06 mm) was employed for flash chromatography.

Preparation of 3-Benzyl-1-(2-phenylethyl)imidazolium Chloride. 1-Chloro-2-phenylethane (5.5 mmol, 0.75 mL) was added at room temperature to a solution of 1-benzylimidazole (5 mmol, 0.79 g) in acetonitrile (10 mL), and the resulting mixture was stirred at 85 °C for 16 h, in a sealed tube. The solution was concentrated to dryness, and diethyl ether was added to the residue to afford a yellow oil. The mixture was sonicated for 15 min, and the ethereal phase was decanted. The product was dried in vacuo. Yield: 0.94 g (63%). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.63 (s, 1H), 7.36−7.30 (m, 6H), 7.28−7.27 (m, 1H), 7.22−7.20 (m, 3H), 7.14−7.12 (m, 2H), 5.43 (s, 2H), 4.58 (t, J_{H-H} = 7.0, 2H), 3.19 (t, J_{H-H} = 7.0, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ 136.2, 135.1, 132.9, 129.2, 128.8, 128.6, 127.1, 122.5, 121.7, 53.1, 51.0, 36.1. MS: m/z (%) 263 (M^+ − Cl, 2), 261 (7), 173 (7), 172 (60), 105 (9), 104 (15), 103 (7), 92 (11), 91 (100), 81 (35), 65 (17).

Preparation of RhCl(COD){3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazol-2-ylidene} (2). A mixture of [Rh(μ-OMe)(COD)]$_2$ (**1**; 100 mg, 0.206 mmol) and 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium chloride (130 mg, 0.413 mmol) was dissolved in acetone (5 mL). The reaction mixture was stirred at room temperature for 3 h, during which time the formation of a yellow precipitate was observed. The yellow solid thus formed was washed with acetone and dried in vacuo. Yield: 162 mg (75%). Anal. Calcd for $C_{26}H_{30}ClN_2ORh$: C, 59.33; H, 5.77; N, 5.34. Found: C, 59.65; H, 5.36; N, 5.00. IR (cm^{-1}): ν(O−H) 3406 (w); ν(C−O) 1099 (m). HRMS (electrospray, m/z): calcd for $C_{26}H_{30}N_2ORh$ [M − Cl]$^+$ 489.1408; found 489.1455. ^{1}H and ^{13}C{^{1}H} NMR spectroscopy shows the presence of two pairs of diastereoisomers in the ratio 63:37.

Major Diastereoisomer. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.62−7.34 (m, 10H, Ph), 6.78 (d, J_{H-H} = 2.1, 1H, C*H* im), 6.68 (d, J_{H-H} = 2.1, 1H, C*H* im), 6.58 (m, 1H, −C*H*(OH)−), 5.87 (AB spin system, J_{A-B} = 15, $\Delta\nu$ = 58, 2H, −CH_2Ph), 5.07−4.95 (m, 2H, =C*H* COD), 4.86 (dd, J_{H-H} = 13.5, J_{H-H} = 3.1, 1H, −CH_2CH(OH)−), 3.94 (dd, J_{H-H} = 13.5, J_{H-H} = 9.6, 1H, −CH_2CH(OH)−), 3.88 (d, J_{H-H} = 4.8, 1H, −OH), 3.45−3.32 (m, 2H, =C*H* COD), 2.46−1.91 (m, 8H, CH_2 COD). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 293 K, plus apt): δ 182.2 (d, J_{Rh-C} = 50.5, Rh−*C*), 142.3, 137.0 (both s, C_{ipso} Ph), 129.1, 128.8, 128.5, 128.4, 128.2, 126.1 (all s, *C*H Ph), 124.4, 120.0 (both s, *C*H im), 98.5 (d, J_{Rh-C} = 6.9, =*C*H COD), 98.3 (d, J_{Rh-C} = 7.0, =*C*H COD), 72.3 (s, −*C*H(OH)−), 69.8 (d, J_{Rh-C} = 14.6, =*C*H COD), 67.8 (d, J_{Rh-C} = 14.6, =*C*H COD), 59.0 (s, −CH_2−), 54.8 (s, −CH_2−), 33.6, 33.0, 29.6, 28.7 (all s, −CH_2− COD).

Minor Diastereoisomer. ^{1}H NMR (300 MHz, CD_2Cl_2, 293K, plus COSY): δ 7.62−7.34 (m, 10H, Ph), 7.03 (d, J_{H-H} = 1.8, 1H, C*H* im), 6.79 (d, J_{H-H} = 1.8, 1H, C*H* im), 6.58 (m, 1H, −C*H*(OH)−), 5.81 (AB spin system, J_{A-B} = 15, $\Delta\nu$ = 127, 2H, −CH_2Ph), 5.35 (dd, J_{H-H} = 10.5, J_{H-H} = 13.8, 1H, −CH_2CH(OH)−), 5.07−4.95 (m, 3H, 2 =C*H* COD + −C*H*(OH)−), 4.32 (dd, J_{H-H} = 13.8, J_{H-H} = 3.4, 1H, −CH_2CH(OH)−), 4.31 (br, 1H, -O*H*), 3.45−3.32 (m, 2H, =C*H* COD), 2.46−1.91 (m, 8H, CH_2 COD). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 293 K, plus apt): δ 183.4 (d, J_{Rh-C} = 51, Rh−*C*), 142.7, 136.9 (both s, C_{ipso} Ph), 129.1, 128.9, 128.4, 128.2, 127.9, 126.5 (all s, *C*H Ph), 121.7, 121.4 (both s, *C*H im), 99.4 (d, J_{Rh-C} = 6.8, =*C*H COD), 98.8 (d, J_{Rh-C} = 6.9, =*C*H COD), 73.9 (s, −*C*H(OH)−), 69.3 (d, J_{Rh-C} = 14.5, =*C*H COD), 58.5 (s, −CH_2−), 55.5 (s, −CH_2−), 33.2, 33.1, 29.3, 29.0 (all s, −CH_2− COD).

Preparation of RhCl(COD){(*R*)-3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazol-2-ylidene} (2). A mixture of [Rh(μ-OMe)(COD)]$_2$ (**1**; 100 mg, 0.206 mmol) and (*R*)-3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium chloride (130 mg, 0.413 mmol) was dissolved in acetone (5 mL). The reaction mixture was stirred at room temperature for 3 h, during which time the formation of a yellow precipitate was observed. The yellow solid thus formed was washed with acetone and dried in vacuo. Yield: 125 mg (58%). ^{1}H NMR spectroscopy show the presence of a pair of diastereoisomers in the ratio 63:37.

Preparation of RhCl(COD){3-benzyl-1-(2-phenylethyl)-imidazol-2-ylidene}. A mixture of [Rh(μ-OMe)(COD)]$_2$ (**1**; 100 mg, 0.206 mmol) and 3-benzyl-1-(2-phenylethyl)imidazolium chloride (123 mg, 0.413 mmol) was dissolved in acetone (5 mL). The reaction mixture was stirred at room temperature for 5 h, during which time the formation of a yellow precipitate was observed. The yellow solid thus formed was washed with acetone and dried in vacuo. Yield: 148 mg (72%). Anal. Calcd for $C_{26}H_{31}ClN_2Rh$: C, 61.24; H, 6.13; N, 5.49. Found: C, 60.85; H, 5.77; N, 5.12. IR (cm^{-1}): ν(C=C) 1602 (d). HRMS (electrospray, m/z): calcd for $C_{26}H_{31}N_2Rh$ [M − Cl]$^+$ 473.1459; found 489.1512. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.42−7.25 (m, 10H, Ph), 6.72 (d, J_{H-H} = 2, 1H, C*H* im), 6.55 (d, J_{H-H} = 2, 1H, C*H* im), 5.77 (AB spin system, J_{A-B} = 14.8, $\Delta\nu$ = 105, 2H, −CH_2Ph), 5.10−4.98 (m, 2H, =C*H* COD), 4.89 (ddd, J_{H-H} = 15, J_{H-H} = 9.5, J_{H-H} = 5, 1H, −CH_2CH$_2$Ph), 4.57 (ddd, J_{H-H} = 15, J_{H-H} = 9, J_{H-H} = 7.6, 1H, −CH_2CH$_2$Ph), 3.41 (ddd, J_{H-H} = 13.5, J_{H-H} = 5, J_{H-H} = 9, 1H, −CH$_2$CH_2Ph), 3.35−3.28 (m, 2H, =C*H* COD), 3.41 (ddd, J_{H-H} = 13.5, J_{H-H} = 9.5, J_{H-H} = 7.6, 1H, −CH$_2$CH_2Ph), 2.38−2.28 (m, 4H, CH_2 COD), 1.98−1.83 (m, 4H, CH_2 COD). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 293 K, plus apt): δ 183.2 (d, J_{Rh-C} = 50.5, Rh−*C*), 138.9, 137.1 (both s, C_{ipso} Ph), 129.4, 129.1, 129.0, 128.6, 128.4, 127.0 (all s, *C*H Ph), 121.6, 120.7 (both s, *C*H im), 98.2 (d, J_{Rh-C} = 6.9, =*C*H COD), 98.0 (d, J_{Rh-C} = 6.9, =*C*H COD), 70.0 (d, J_{Rh-C} = 14.4, =*C*H COD), 69.3 (d, J_{Rh-C} = 14.4, =*C*H COD), 54.8 (s, NCH_2Ph), 52.8 (s, NCH_2CH$_2$Ph), 34.5 (s, NCH_2CH$_2$Ph), 33.3, 32.8, 29.7, 29.1 (all s, −CH_2− COD).

General Procedure for the Conjugate Addition of Arylboronic Acids to Enones. In a 10 mL vessel containing a solution of complex **2** (0.005 mmol, 2.62 mg) and the corresponding arylboronic acid (0.7 mmol) in toluene (1 mL), the enone (0.5 mmol) and cycloocta-1,5-diene (0.075 mmol, 9.2 μL) were added. Then, if necessary, 0.2 mL of an aqueous solution of NaOH (2.5 M) was added dropwise. The vessel was sealed with a septum, and the mixture was heated at 60 °C for 6 h. The reaction mixture was hydrolyzed at room temperature with H_2O (5 mL). The organic phase was separated, and the resulting aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic phases were filtered over a plug of Celite and silica, dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by chromatography (preparative TLC plates, hexane/ethyl acetate) to give the corresponding final products **5** and **13**. Yields are given in Tables 2 and 3.

Physical and Spectroscopic Data of the Addition Products. *3-Phenylcyclohexanone (**5a**).*[32] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.34 (m, 2H), 7.28−7.24 (m, 3H), 3.06−2.95 (m,

dx.doi.org/10.1021/om300498e | *Organometallics* 2012, 31, 6154−6161

1H), 2.59−2.37 (m, 2H), 2.16−2.06 (m, 2H), 1.92−1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 144.6, 128.6, 126.6, 126.5, 48.9, 44.7, 41.1, 32.7, 25.5. MS: *m/z* (%) 174 (46) [M^+], 131 (74), 118 (27), 117 (91), 115 (20), 105 (16), 104 (70), 103 (26), 91 (31).

*3-(Naphth-1-yl)cyclohexanone (**5b**).*[33] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J_{H-H} = 8.0, 1H), 7.87−7.85 (m, 1H), 7.54 (d, J_{H-H} = 8.0, 1H), 7.54−7−47 (m, 4H), 3.9−3.8 (m, 1H), 2.89−2.39 (m, 4H), 2.30−2.10 (m, 2H), 2.04−1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.2, 139.9, 133.9, 130.8, 129.0, 127.2, 126.1, 125.6, 125.5, 122.6, 122.4, 48.5, 41.4, 39.3, 32.2, 25.5. MS: *m/z* (%) 224 (88) [M^+], 181 (17), 168 (17), 167 (100), 165 (26), 154 (36), 153 (53), 152 (40), 141 (25), 128 (12).

*3-[4-(Trifluoromethyl)phenyl]cyclohexanone (**5c**).*[34] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, J_{H-H} = 7.9, 2H), 7.34 (d, J_{H-H} = 7.9, 2H), 3.12−3.04 (m, 1H), 2.59−2.38 (m, 4H), 2.19−2.08 (m, 2H), 1.90−1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 150.5, 148.2, 127.0, 125.7, 77.2, 48.5, 44.5, 41.1, 32.5, 25.4. MS: *m/z* (%) 242 (54) [M^+], 223 (12), 200 (11), 199 (100), 186 (34), 185 (18), 172 (41), 171 (13), 145 (13), 103 (13).

*3-(4-Bromophenyl)cyclohexanone (**5d**).*[35] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.43 (m, 2H), 7.12−7.07 (m, 2H), 3.01−2.93 (m, 1H), 2.61−2.32 (m, 4H), 2.19−2.05 (m, 2H), 1.88−1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 139.9, 131.4, 130.0, 119.8, 44.7, 30.0, 29.0. MS: *m/z* (%) 254 (98) [M^+ + 2], 252 (100) [M^+], 209 (40), 198 (19), 197 (55), 196 (20), 195 (55), 184 (47), 183 (12), 182 (48), 173 (15), 171 (12), 145 (15), 117 (15), 116 (67), 115 (29), 103 (23), 102 (19), 77 (23).

*3-(4-Methoxyphenyl)cyclohexanone (**5e**).*[32] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J_{H-H} = 8.7, 2H), 6.93 (d, J_{H-H} = 8.7, 2H), 3.85 (s, 3H), 3.09−2.97 (m, 1H), 2.62−2.42 (m, 4H), 2.23−2.09 (m, 2H), 1.90−1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1, 158.2, 136.5, 127.4, 113.9, 55.2, 49.2, 43.9, 41.1, 32.9, 25.4. MS: *m/z* (%) 204 (63) [M^+], 147 (100), 134 (31), 121 (16), 119 (12), 91 (19).

*3-(o-Tolyl)cyclohexanone (**5f**).*[33] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.04 (m, 5H), 3.25−3.16 (m, 1H), 2.53−2.34 (m, 4H), 2.32 (s, 3H), 2.18−2.17 (m, 1H), 2.02−1.99 (m, 1H), 1.89−1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.3, 142.3, 135.1, 130.7, 126.5, 126.4, 125.1, 48.4, 41.3, 40.4, 32.0, 25.8, 19.3. MS: *m/z* (%) 188 (72) [M^+], 173 (17), 146 (17), 145 (100), 132 (12), 131 (86), 129 (14), 118(43), 117 (55), 115 (34), 105 (24), 91 (31).

*3-(3-Chlorophenyl)cyclohexanone (**5g**).*[33] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.24 (m, 4H), 3.07−2.99 (m, 1H), 2.69−2.34 (m, 4H), 2.24−2.05 (m, 2H), 2.93−1.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5, 146.2, 134.4, 129.9, 128.7, 126.9, 124.8, 48.6, 44.3, 41.0, 32.5, 25.4. MS: *m/z* (%) 208 (26) [M^+ + 2], 210 (83) [M^+], 167 (35), 166 (13), 165 (100), 153 (15), 152 (28), 151 (37), 145(21), 140 (20), 139 (19), 138 (55), 129 (14), 125 (18), 117 (18), 116 (17), 115 (32), 103 (37), 102 (16), 101 (11), 77 (23).

*3-Phenylcycloheptanone (**11**).*[33] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.26 (m, 2H), 7.23−7.16 (m, 3H), 2.98−2.89 (m, 2H), 2.67−2.57 (m, 3H), 2.11−1.96 (m, 3H), 1.80−1.62 (m, 2H), 1.56−1.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.4, 146.9, 128.6, 126.4, 126.3, 51.2, 43.9, 42.7, 39.2, 29.2, 24.1. MS: *m/z* (%) 188 (100) [M^+], 145 (13), 131 (62), 130 (60), 129 (24), 118 (16), 117 (42), 115 (24), 105 (20), 104 (90), 103 (22), 97 (18), 91 (51), 78 (17), 77 (17).

*4-Phenylbutan-2-one (**13a**).*[32] White solid. Mp: 78−80 °C (acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.26 (m, 2H), 7.21−7.17 (m, 3H), 2.90 (dt, J_{H-H} = 6.4, 2.4, 2H), 2.76 (d, J_{H-H} = 8.2, 2.4, 2H), 2.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 140.5, 128.1, 127.8, 125.7, 44.7, 29.6, 29.3. MS: *m/z* (%) 148 (100) [M^+], 133 (19), 105 (98), 91 (69), 79 (15), 78 (14), 77 (23), 65 (12), 51 (13).

*4-(Naphth-1-yl)butan-2-one (**13b**).*[36] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J_{H-H} = 8.1, 1H), 7.83−7.81 (m, 1H), 7.69 (d, J_{H-H} = 8.1, 1H), 7.51−7.44 (m, 2H), 7.43−7.42 (m, 1H), 7.38−7.28 (m, 1H),), 3.33 (t, J_{H-H} = 7.5, 2H), 2.83 (t, J_{H-H} = 7.5, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 136.9, 133.8, 131.5, 128.8, 126.8, 125.9, 125.8, 125.5, 123.3, 44.3, 29.9, 26.6. MS: *m/z* (%) 199 (12) [M^+], 198 (75), 155 (66), 154 (13), 153 (22), 152 (15), 142 (12), 141 (100), 128 (21), 115 (24).

*4-[4-(Trifluoromethyl)phenyl]butan-2-one (**13c**).*[37] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J_{H-H} = 8.1, 2H), 7.30 (d, J_{H-H} = 8.1, 2H), 2.95 (t, J_{H-H} = 7.5, 2H), 2.78 (t, J_{H-H} = 7.5, 2H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 140.5, 128.1, 127.8, 125.7, 44.7, 29.6, 29.3. MS: *m/z* (%) 216 (100) [M^+], 197 (21), 1173 (37), 159 (40), 153 (18),133 (23), 109 (12).

*4-(4-Bromophenyl)butan-2-one (**13d**).*[38] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J_{H-H} = 8.3, 2H), 7.05 (d, J_{H-H} = 8.3, 2H), 2.84 (t, J_{H-H} = 7.2, 2H), 2.73 (t, J_{H-H} = 7.2, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 139.9, 131.4, 130.0, 119.8, 44.7, 30.0, 29.0. MS: *m/z* (%) 228 (98) [M^+ + 2], 226 (100) [M^+], 213 (23), 211 (24), 185 (30), 183 (31), 171 (85), 169 (87), 147 (79), 132 (17), 104 (76), 103 (36), 102 (17), 90 (25), 89 (24), 78 (19), 77 (38).

*4-(4-Methoxyphenyl)butan-2-one (**13e**).*[36] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10−7.08 (m, 2H), 6.82−6.80 (m, 2H), 3.77 (s, 3H), 2.83 (t, J_{H-H} = 7.5, 2H), 2.71 (t, J_{H-H} = 7.5, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 157.8, 132.9, 129.1, 133.8, 55.1, 45.3, 30.0, 28.8. MS: *m/z* (%) 178 (40) [M^+], 121 (100), 91 (11).

Structural Analysis of Complex 2. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated solution of **2** in dichloromethane. X-ray data were collected on a Bruker Smart APEX CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube source (Mo radiation, λ = 0.710 73 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s, covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[39] The structure was solved by Patterson (Rh atom) and conventional Fourier techniques and refined by full-matrix least squares on F^2 with SHELXL97.[40] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms (except those corresponding to the olefinic carbon atoms and that of the OH, which were observed in the difference Fourier maps and refined as free isotropic atoms) were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. All the highest electronic residuals were observed in the close proximity of the Rh center and make no chemical sense.

*Crystal data for **2**:* $C_{26}H_{30}ClN_2ORh$, mol wt 524.88, yellow, prism (0.08 × 0.06 × 0.02), monoclinic, space group *Cc*, *a* = 13.521(6) Å, *b* = 21.920(9) Å, *c* = 7.978(3) Å, α = 90.00°, β = 103.597(7)°, γ = 90.00°, *V* = 2298.3(17) Å^3, *Z* = 4, D_{calcd} = 1.517 g cm^{-3}, *F*(000) = 1080, *T* = 100(2) K, μ = 0.880 mm^{-1}, 13 163 measured reflections (2θ = 3−58°, ω scans 0.3°), 5437 unique reflections (R_{int} = 0.1045), minimum/maximum transmission factors 0.703/0.967, final agreement factors R1 = 0.0564 (3320 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.1037, 5437/2/286 data/restraints/parameters, GOF = 0.856, largest peak and hole 0.975 and −1.008 e/Å^3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A CIF file giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Ministerio de Ciencia e Innovación (MICINN) of Spain (Projects CTQ2007-65218, CTQ2011-23459, CTQ2011-24165, Consolider Ingenio 2010 CSD2007-

00006), the Generalitat Valenciana (PROMETEO/2009/0349 and FEDER), the Diputación General de Aragón (E35), and the European Social Fund is acknowledged. I.P. thanks the MICINN for a predoctoral fellowship.

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