Preparation of a Series of "Ru(*p*-cymene)" Complexes with Different N-Heterocyclic Carbene Ligands for the Catalytic *β*-Alkylation of Secondary Alcohols and Dimerization of Phenylacetylene

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A series of five different "(*p*-cymene)Ru(NHC)" complexes (NHC = imidazolin-2-ylidene, imidazolin-4-ylidene, and pyrazolin-3-ylidene) have been obtained and fully characterized. The crystal structure of two of the new complexes has been determined by X-ray diffraction methods. All five complexes have been tested in the catalytic *β*-alkylation of secondary alcohols with primary alcohols and the dimerization of phenylacetylene, showing an excellent activity in both processes. A clear improvement on the catalytic activity of the complexes is observed when the more basic NHC ligands are used. The pyrazolylidene-Ru complex lies among the best catalysts for the *β*-alkylation of secondary alcohols reported to date.

Introduction

The use of N-heterocyclic carbene ligands (NHCs) for the preparation of homogeneous catalysts has now become one of the most productive fields in organometallic chemistry. Since 1995, when Herrmann reported the first use of a NHC ligand in the preparation of a homogeneous catalyst,[1] there has been an enourmous development of NHC chemistry, which has been triggered by the search for enhanced or even new catalytic processes.[2] Probably, one of the main benefits of NHCs is that their preparation is simple and that the coordination methodologies that are now available allow the preparation of NHC complexes of almost any transition metal in a variety of oxidation states, affording a wide set of potential catalytic applications.

When talking about Ru-NHC chemistry, it is inevitable to mention the enourmous applications that these compounds have achieved in the development of highly effective catalysts for the metathesis of olefins,[3,4] probably the most important achievement of any of the M-NHC complexes known to date. Other interesting catalytic applications of Ru-NHC complexes have also been described, and the effects of a full set of NHC ligands with different topologies have been studied.[5]

With the rapid development of Ru-NHC chemistry, it is strange that some of the simplest NHCs have not been tested in Ru-catalyzed reactions. For example, since the description of the *abnormal* coordination of NHCs (*a*NHCs) by Crabtree and co-workers,[6] there has been an increasing number of complexes with *a*NHCs,[7,8] but this type of carbene has not been used yet in the development of a Grubbs-type catalyst. In fact, the only Ru(*a*NHC) complexes known so far are those recently reported by Whittlesey and co-workers in a Ru_3 cluster,[9] with the interesting feature that one of them is a doubly bound *abnormal*-NHC that is bridging two Ru atoms.

Although the coordination of pyrazole-based carbenes (pyrazolylidenes) has been known since 1997,[10] only a few examples regarding Rh-,[10] Cr-,[11] and Pd-pyrazolylidenes[12] have been published, probably because the lower C−H acidity of the pyrazolium ion makes its deprotonation more difficult than in other azolium ions. The search for cheap, simple, and accessible methods for the preparation of homogeneous catalysts with improved efficiencies is a continuous demand in chemistry, and pyrazolylidenes are known to be stronger *σ*-donors than

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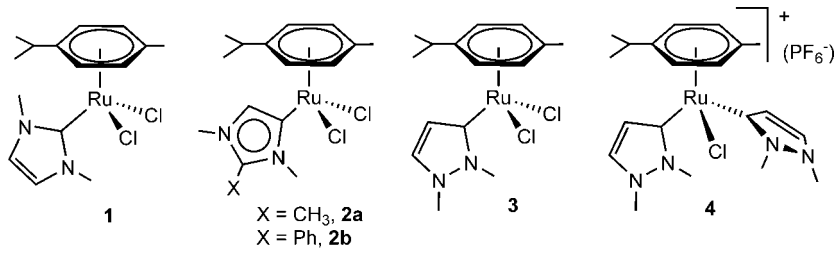
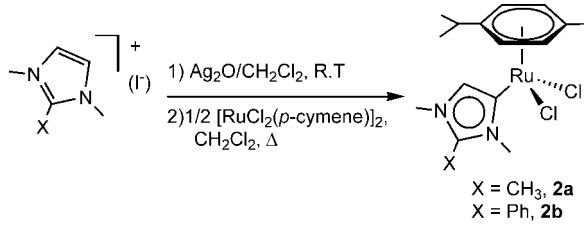
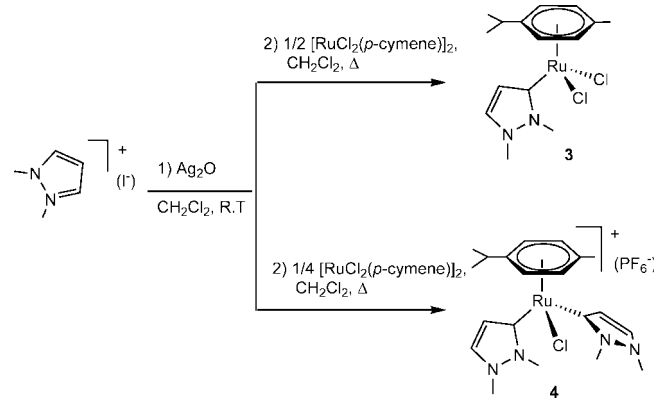
Scheme 1



Scheme 2



Scheme 3



imidazolylidenes, thus making them a good choice for the preparation of C−H activation catalysts.

We now report the preparation of a series of "(*p*-cymene)Ru(NHC)" complexes (NHC = imidazolin-2-ylidene, imidazolin-4-ylidene, and pyrazolin-3-ylidene; **1**−**4**, Scheme 1), not only aiming to fulfill the gap in the chemistry of *a*NHCs and pyrazolylidenes of ruthenium but also trying to have a wide set of topologically similar ligands with different electron-donor properties and study their effect in catalysis. For this purpose we have studied the catalytic activity of our new compounds in the β-alkylation of secondary alcohols with primary alcohols and in the dimerization of phenylacetylene.

Results and Discussion

To selectively prepare *a*NHC complexes, one of the most convenient methods is to block the imidazolium ligand precursors by substitution at C2 with alkyl or aryl groups.[7,13] The coordination of 1,2,3-trimethylimidazolium iodide to $[RuCl_2(p\text{-cymene})]_2$ was performed by transmetalation of the previously obtained (not isolated) silver-carbene in CH_2Cl_2, as shown in Scheme 2. The reaction product, **2a**, was obtained in moderate yield (40%). Compound **2b** (X = Ph) was obtained by a similar procedure using 1,3-dimethyl-2-phenylimidazolium iodide (yield 65%). Under the reaction conditions used, we did not see the formation of cationic biscarbene complexes, not even using an excess of the imidazolium salt.

The transmetalation from a preformed silver carbene was also effective for the coordination of the pyrazolylidene ligand to $[RuCl_2(p\text{-cymene})]_2$. The reaction of 1,2-dimethylpyrazolium iodide with Ag_2O in CH_2Cl_2 afforded the correponding Ag-NHC complex, which was used *in situ* for the transmetalation of the carbene to $[RuCl_2(p\text{-cymene})]_2$. Depending on the Ru/pyrazolium molar ratio used, the monocarbene compound **3** (60% yield) or the cationic bis-carbene complex **4** (35% yield) was obtained, as shown in Scheme 3.

Compounds **2a**, **2b**, **3**, and **4** were characterized by spectroscopic techniques and elemental analysis. The most significant ^{1}H NMR signal for the *a*NHC complexes **2a** and **2b** is the one corresponding to the proton at the backbone of the abnormal coordinated azole, at δ 6.6 (**2a**) and 6.9 (**2b**). The ^{13}C NMR spectra show the characteristic signals due to the abnormal coordinated carbene carbons at 152.2 (**2a**) and 154.3 (**2b**) ppm.

The ^{1}H NMR spectrum of the pyrazolylidene complex **3** shows two representative doublets due to the protons of the azole ring at δ 7.2 and 6.5 ($^3J_{H-H}$ = 2.2 Hz). The signals due to the protons of the N−Me groups appear at different chemical shifts as a consequence of the loss of symmetry of the ligand upon coordination (4.0 and 3.8 ppm). The ^{13}C NMR spectrum shows a signal at 180.3 ppm due to the metalated carbon. The ^{1}H NMR spectrum of **4** is qualitatively similar to that shown by **3**, although the comparison of the integrals of the signals assigned to the pyrazolylidene and the *p*-cymene ligands allowed us to determine the number of azoles bound to the metal. The ^{13}C NMR spectrum shows a signal at 175.1 ppm due to the $C_{carbene}$ atom.

The molecular structures of **2b** and **3** were unequivocally determined by means of X-ray diffraction studies. Figure 1 and 2 show the ORTEP diagrams of **2b** and **3**, respectively.

Both structures can be regarded as three-legged piano stools. Together with the azolylidene ligand, two chloro ligands and the *p*-cymene ring complete the coordination sphere about the

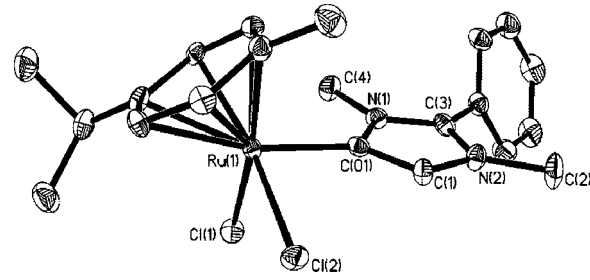


Figure 1. Molecular diagram of compound **2b**. Hydrogen atoms have been omitted for clarity. Ellipsoids are at 30% probability. Selected bond distances (Å) and angles (deg): Ru(1)−C(01) 2.084(7), Ru(1)−Cl(1) 2.4212(16), Ru(1)−Cl(2) 2.4465(14), Ru(1)−$C_{centroid}$ 1.688, C(01)−Ru(1)−Cl(1) 85.14(19), C(01)−Ru(1)−Cl(2) 85.73(19), Cl(1)−Ru(1)−Cl(2) 89.55(5).

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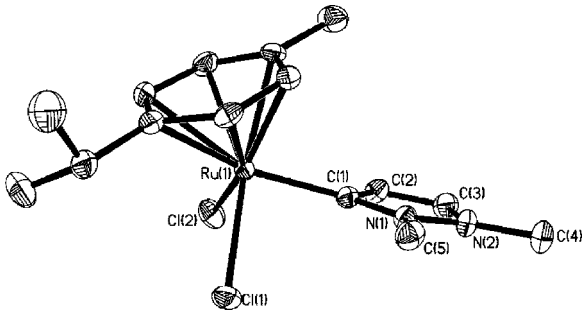


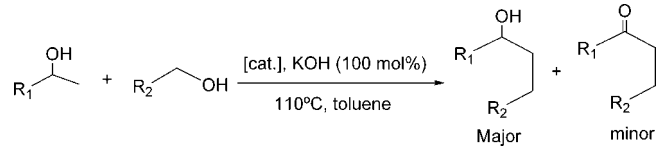
Figure 2. Molecular diagram of compound **3**. Hydrogen atoms have been omitted for clarity. Ellipsoids are at 30% probability. Selected bond distances (Å) and angles (deg): Ru(1)−C(1) 2.044(5), Ru(1)−Cl(1) 2.4295(13), Ru(1)−Cl(2) 2.4201(14), Ru(1)−$C_{centroid}$ 1.695, C(1)−Ru(1)−Cl(1) 88.54(13), C(1)−Ru(1)−Cl(2) 86.47 (14), Cl(2)−Ru(1)−Cl(1) 87.31(5).

metal atoms. The molecular structure of compound **2b** confirms that the carbene ligand is bound in an *abnormal* coordination mode. The Ru−$C_{carbene}$ distance is 2.084 Å, in the range of other (*p*-cymene)Ru(NHC) complexes.[14,15] The Ru−$C_{carbene}$ distance in compound **3** is 2.044 Å, very similar to the analogous distance found for **2b**. All other distances and angles are unexceptional.

Compounds **2a**, **2b**, **3**, and **4** and the previously reported complex **1**[15] contain three different types of N-heterocyclic carbenes with similar topological frameworks but different electron-donor power. Pyrazolin-3-ylidenes[11] and *a*NHCs[7] are known to be better σ-donors than imidazolin-2-ylidenes, so the use of **1**−**4** in different catalytic reactions under the same reaction conditions can provide useful information in the design of future catalysts.

We have recently studied the catalytic β-alkylation of secondary alcohols with primary alcohols.[16,17] Despite the important benefits of this process, apart from our two works, we found only a few pioneering examples of this catalytic reaction described in the literature, referring to Ru[18,19] and to Ir[20] complexes. This reaction is believed to involve oxidation of both alcohols to form a ketone and an aldehyde, which undergo an aldol condensation, giving an α,β-unsaturated ketone, which is further reduced to give the saturated alcohol.[20,21] Taking this into account, we thought that complexes **1**−**4** could be good candidates for this reaction, because Ru-NHC complexes have proven to be excellent catalysts for the transfer hydrogenation reactions between alcohols and ketones.[22] NHC ligands have also been shown to be efficient catalysts toward C−H activation processes.[4,23]

Table 1. β-Alkylation of Secondary Alcohols with Primary Alcohols[a]



entry	cat.	R1	R2	*t* (h)	yield (%)	alcohol:ketone
1	**1**	Ph	Pr	22	60	78:22
2	**2a**	Ph	Pr	22	>95	90:10
3	**2b**	Ph	Pr	22	86	91:9
4	**3**	Ph	Pr	13	>95	90:10
5	**4**	Ph	Pr	10	95	90:10
6	**1**	Ph	3-Cl(C_6H_4)	24	95	92:8
7	**2a**	Ph	3-Cl(C_6H_4)	24	94	81:19
8	**2b**	Ph	3-Cl(C_6H_4)	24	86	100:0
9	**3**	Ph	3-Cl(C_6H_4)	10	>95	100:0
10	**4**	Ph	3-Cl(C_6H_4)	8	>95	85:15
11	**1**	Ph	Ph	24	57	100:0
12	**2a**	Ph	Ph	24	>95	88:12
13	**2b**	Ph	Ph	8	>95	93:7
14	**3**	Ph	Ph	8	>95	97:3
15	**4**	Ph	Ph	8	>95	88:12
16	**1**	Ph	4-Cl(C_6H_4)	24	87	92:8
17	**2a**	Ph	4-Cl(C_6H_4)	8	>95	90:10
18	**2b**	Ph	4-Cl(C_6H_4)	24	90	83:17
19	**3**	Ph	4-Cl(C_6H_4)	8	>95	77:23
20	**4**	Ph	4-Cl(C_6H_4)	8	>95	96:4
21	**1**	C_5H_{11}	Ph	20	>95	100:0
22	**2a**	C_5H_{11}	Ph	14	>95	100:0
23	**2b**	C_5H_{11}	Ph	20	>95	100:0
24	**3**	C_5H_{11}	Ph	10	>95	100:0
25	**4**	C_5H_{11}	Ph	8	>95	100:0

[a] Reaction conditions: 1 mmol of primary alcohol, 1 mmol of secondary alcohol, 1 mmol of KOH, and 0.01 mmol of catalyst in 0.3 mL of toluene at 110 °C. Yields and ratios were determinad by ^{1}H NMR.

The reactions were carried out under atom-economic conditions, using an equimolecular amount of the primary and secondary alcohols. A fixed catalyst loading of 1 mol % was used in the presence of KOH in toluene at a temperature of 110 °C. The reaction was performed using 2-phenylethanol and 2-heptanol as secondary alcohols and four different primary alcohols (*n*-butanol, benzyl alcohol, 3-chlorobenzyl alcohol, and 4-chlorobenzyl alcohol). Table 1 shows the catalytic results for this process, and the reaction times correspond to the maximum conversions achieved by each catalyst. All catalysts **1**−**4** show good catalytic activities in this reaction, although significant differences are observed between them. The cationic compound **4** invariably shows the best catalytic activity, achieving full conversions in short reaction times (8−10 h). The monopyrazolylidene complex **3** also shows an excellent activity in all the reactions tested, although slightly longer reaction times are needed for completion (8−13 h). The *normal*-NHC complex **1** shows lower activity than the rest of the catalysts, providing

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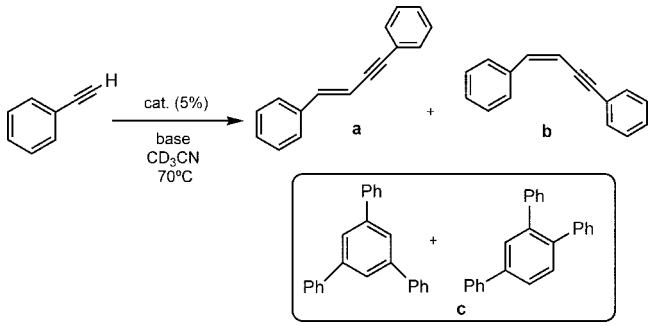
Table 2. Dimerization and Cyclotrimerization Reaction of Phenylacetylene[a]



entry	catalyst	conversion (%)	ratio a:b:c
1	**1**	97	33:9:58
2	**2a**	88	14:5:81
3	**2b**	79	26:10:64
4	**3**	95	21:8:71
5	**4**	81	28:9:63
6	$[RuCl_2(p\text{-cym})]_2$	56	0:0:100

[a] Reaction conditions: 0.3 mmol of phenylacetylene, 0.075 mmol of NEt_3, and 0.015 mmol of catalyst in 0.3 mL of CD_3CN at 70 °C for 8 h. Yields and ratios were determinad by ^1H NMR.

Table 3. Crystallographic Data

	2b	**3**
empirical formula	$C_{21}H_{26}Cl_2N_2Ru$	$C_{15}H_{22}Cl_2N_2Ru$
fw	478.41	402.32
wavelength (Å)	0.71073	0.71073
temperature (K)	273(2)	273(2)
cryst syst	orthorhombic	monoclinic
space group	*Pna*2 (1)	*P*2(1)/*c*
a (Å)	14.5949(5)	14.2961(17)
b (Å)	10.8530(4)	7.0647(9)
c (Å)	26.1994(9)	16.3109(19)
α (deg)	90	90
β (deg)	90	92.052(3)
γ (deg)	90	90
V (Å)^3	4149.9 (3)	1646.3 (3)
Z	8	4
density (calcd) (Mg/m^3)	1.531	1.623
absorp coeff (mm^{-1})	1.020	1.040
no. of reflns collected	32 497	10 295
goodness-of-fit on F^2	1.006	1.002
R indices (all data)	R1 = 0.0495	R1 = 0.0448
	wR2 = 0.1030	wR2 = 0.0973

only moderate yields in rather long reaction times (20−24 h). The *abnormally*-bound NHC complexes **2a** and **2b** show good activity in terms of conversions achieved, but longer reaction times are needed than those for **3** and **4**. The phenyl-substituted NHC complex (**2b**) shows lower efficiency than **2a**, probably because of the higher steric crowding around the metal center. For most of the reactions, the process is very selective in the production of the alkylated alcohols, although in some cases small amounts of the alkylated ketones were obtained as secondary products.

It is worth mentioning that compound **4** lies among the most efficient catalysts for this type of reaction, taking into account the short reaction times needed and the low catalyst loadings used. To our knowledge, only an iridium compound reported by us displays a similar activity for this type of reaction,[16] but among ruthenium complexes **4** seems to be the most active reported to date.

An interesting feature about the comparison of the results that we present in Table 1 is that the different types of NHC ligands are providing different activities in a quite rational way. It seems that the more *σ*-donating NHCs (*a*NHCs and pyrazolylidene) are providing the best activities, and among these, the pyrazole-based NHC seems to be the most active one. Since there are no studies yet comparing the *σ*-donating powers of *a*NHCs and pyrazolylidenes, we cannot fully attribute the differences in activity to the electronic differences between the ligands, but it seems clear that the pyrazolylidenes should be considered as a good choice for catalyst design.

Compounds **1**−**4** were also tested in the catalytic dimerization of phenylacetylene to provide the corresponding enynes. The direct coupling of two terminal alkynes is an interesting process because enynes may serve as building blocks for the synthesis of natural products. One of the main challenges in this type of reaction is the preparation of highly effective catalysts capable of affording good selectivities in the formation of the *E*-dimers, for which commercially available metal precursors do not seem to give the desired results, and the preparation of more sophisticated organometallic species is needed. Several reports have appeared in which ruthenium complexes have provided good *E*-selectivities in this reaction,[24,25] but still the reactions fail to give high yields and long reaction times are needed.

The reactions were carried out with phenylacetylene and a fixed amount of catalyst (5 mol %) in acetonitrile-d_3 at 70 °C, in the presence of NEt_3. The dimer $[RuCl_2(p\text{-cymene})]_2$ was also tested for comparison. Table 2 shows the catalytic results for the process. As observed, high conversions are achieved in all cases, although the dimerization competes with the trimerization of the acetylene, generating two possible trisubstituted benzenes. Catalysts **1**−**4** provide yields in the range 20−42% in the dimerization products with a moderate *E*-selectivity, while $[RuCl_2(p\text{-cymene})]_2$ affords only the cyclotrimerization compounds under the same reaction conditions. The results obtained for compounds **1**−**4** compare well with the activities shown by other ruthenium catalysts recently reported.[24,26] For this reaction we did not find any substantial differences in the catalytic activities of **1**−**4**, although it becames clear that the introduction of the basic NHC ligand provides an inversion of the catalytic behavior compared to $[RuCl_2(p\text{-cymene})]_2$.

Conclusions

We have prepared a set of simple "(*p*-cymene)Ru(NHC)" complexes, with the NHC ligands being of the type *normal*-NHC, *abnormal*-NHC, and pyrazolin-3-ylidene. All complexes were obtained by the transmetalation from the corresponding silver-carbene preformed complexes. While we found that there is only one publication describing Ru-*a*NHC complexes in the literature, our Ru-pyrazolylidene complex is the first one to coordinate such a ligand to ruthenium and one of the few examples known for transition metal compounds,[10–12,26] a fact that is even more remarkable if we take into account that three of the five examples reported to date refer to remote pyrazolylidenes (pyrazolin-4-ylidenes).[12,27]

The "(*p*-cymene)Ru(NHC)" complexes were tested in two catalytic reactions, namely, the *β*-alkylation of secondary alcohols with primary alcohols and the dimerization of phenylacetylene, showing good activities in both of them. The results

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obtained for the β-alkylation of secondary alcohols lie among the best reported to date and allowed a clear comparison of the activities provided by the different ligands, the pyrazolylidene being the best one. In the dimerization of phenylacetylene, we have observed that the introduction of the NHC ligand affords a clear improvement to the formation of the dimerization products compared to the results provided by $[RuCl_2(p\text{-cymene})]_2$ under the same reaction conditions.

Our results prove that pyrazolylidene ligands are an excellent choice for the design of simple and highly effective catalysts. Studies on the modification of the topologies of this type of ligands and their coordination to other potential catalytically active metal fragments are underway.

Experimental Section

NMR spectra were recorded on Varian Innova 300 and 500 MHz spectrometers, using $CDCl_3$ and DMSO-d_6 as solvents. Elemental analyses were carried out in an EA 1108 CHNS-O Carlo Erba analyzer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument, and nitrogen was employed as drying and nebulizing gas. 1,2,3-Trimethylimidazolium iodide,[28] 1,2-dimethylpyrazolium iodide,[10] $[RuCl_2(p\text{-cymene})]_2$,[29] and **1**[15] were prepared according to literature procedures. All other reagents are commercially available and were used as received.

Synthesis of 1,3-Trimethyl-2-phenylimidazolium Iodide. To a round-bottomed flask were added 2-phenylimidazolium (1 g, 6.9 mmol), NaOH (416 mg, 10.4 mmol), TBABr (50 mg, 0.15 mmol), and a few drops of water. The mixture was stirred at room temperature for 1 h, and then iodomethane (650 μL, 10.40 mmol) was added. After being stirred for 48 h at room temperature, the reaction mixture was extracted with CH_2Cl_2/H_2O and the organic extracts were collected and dried over Na_2SO_4. Evaporation of the solvent under vacuum gave an oil. The oil was redissolved in CH_3CN (10 mL), and iodomethane (650 μL, 10.40 mmol) was added. The mixture was refluxed overnight. The volatile components were removed under vacuum, and the product was washed with CH_2Cl_2 to give the desired product. Yield: 80%. ^{1}H NMR (500 MHz, DMSO-d_6): 7.88 (s, 2H, CH_{imid}), 7.77−7.69 (m, 5H, CH_{Ph}), 3.69 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): 144.8 (Cq), 133.0 (Cq_{Ph}), 131.3 (CH_{imid}), 130.1, 123.8, 121.8 (CH_{Ph}), 36.5 (NCH_3). Electrospray MS: m/z 173.3 [M^+].

Synthesis of 2a. A suspension of 1,2,3-trimethylimidazolium iodide (93 mg, 0.39 mmol) and silver oxide (136 mg, 0.59 mmol) in CH_2Cl_2 was stirred at room temperature for 2 h. The product mixture was filtered through Celite, and then $[RuCl_2(p\text{-cymene})]_2$ (100 mg, 0.16 mmol) was added to the solution. The mixture was refluxed for 3 h and then was filtered through Celite. The solvent was evaporated and the crude solid purified by column chromatography using silica gel. Elution with CH_2Cl_2/MeOH (9:1) afforded the separation of an orange band that contained **2a**. Complex **2a** was obtained as a brown solid by precipitation from CH_2Cl_2/Et_2O solution. Yield: 53 mg, 40%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.59, (s, 1H, CH_{imid}), 5.22 (d, $^3J_{H-H}$ = 5.70 Hz, 2H, CH_{pcym}), 5.08 (d, $^3J_{H-H}$ = 5.70 Hz, 2H, CH_{pcym}), 3.81 (s, 3H, NCH_3), 3.55 (s, 3H, NCH_3), 2.75−2.66 (m, 1H, $CH_{isop\ pcym}$), 2.47 (s, 3H, CCH_3), 2.09 (s, 3H, CH_{3pcym}), 1.18 (d, $^3J_{H-H}$= 6.90 Hz, 6H, $CH_{3isop\ pcym}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 152.2 (C-Ru), 141.0 (Cq_{imid}), 125.1 (CH_{imid}), 103.1, 99.1 (Cq_{pcym}), 83.9, 83.8 (CH_{pcym}), 37.1, 34.3 (NCH_3), 30.8 ($CH_{isop\ pcym}$), 22.6 ($CH_{3isop\ pcym}$), 18.6 (CH_{3pcym}), 10.7 (CCH_3). Electrospray MS (25 V, m/z): 381.3 [$M - Cl]^+$. Anal. Calcd for $C_{16}N_2RuCl_2H_{24}$ (mol wt 416.04): C, 46.16; H, 5.81; N, 5.73. Found: C, 45.96; H, 5.95; N, 5.75.

Synthesis of 2b. A suspension of 1,3-dimethyl-2-phenylimidazolium iodide (176 mg, 0.59 mmol) and silver oxide (204 mg, 0.88 mmol) in CH_2Cl_2 was stirred at room temperature for 2 h. The mixture was filtered through Celite, and then $[RuCl_2(p\text{-cymene})]_2$ (150 mg, 0.25 mmol) was added. The mixture was refluxed for 3 h, and the white precipitate formed (silver halide) was separated by filtration through Celite. The solvent was evaporated, and the crude solid was purified by column chromatography using silica gel. Elution with CH_2Cl_2/acetone (4:1) afforded the separation of an orange band that contained **2b**. Complex **2b** was obtained as a brown solid by precipitation from CH_2Cl_2/Et_2O solution (yield: 155 mg, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61−7.58 (m, 3H, CH_{Ph}), 7.38−7.35 (m, 2H, CH_{Ph}), 6.91 (s, 1H, CH_{imid}), 5.30 (d, $^3J_{H-H}$ = 5.70 Hz, 2H, CH_{pcym}), 5.17 (d, $^3J_{H-H}$ = 5.70 Hz, 2H, CH_{pcym}), 3.81 (s, 3H, NCH_3), 3.51 (s, 3H, NCH_3), 2.86−2.74 (m, 1H, $CH_{isop\ pcym}$), 2.15 (s, 3H, CH_{3pcym}), 1.23 (d, $^3J_{H-H}$ = 6.90 Hz, 6H, $CH_{3isop\ pcym}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 154.3 (C-Ru), 143.6 (Cq_{imid}), 131.5 (CH_{imid}), 130.2, 129.8, 126.4 (CH_{Ph}), 124.6 (Cq_{Ph}), 102.8, 99.3 (Cq_{pcym}), 84.1, 84.0 (CH_{pcym}), 34.8 ($CH_{isop\ pcym}$), 31.1, 30.9 (NCH_3), 22.6 ($CH_{3isop\ pcym}$), 18.6 (CH_{3pcym}). Electrospray MS (20 V, m/z): 443.1 [$M - Cl]^+$. Anal. Calcd for $C_{21}N_2RuCl_2H_{26}$ (mol wt 478.42): C, 52.72; H, 5.48; N, 5.86. Found: C, 52.78; H, 5.60; N, 5.71.

Synthesis of 3. Silver oxide (174 mg, 0.75 mmol) was added to a solution of 1,2,-dimethylpyrazolium iodide (110 mg, 0.50 mmol) in CH_2Cl_2, and the mixture was stirred at room temperature for 2 h. Then $[RuCl_2(p\text{-cymene})]_2$ (150 mg, 0.25 mmol) was added. The mixture was refluxed for 3 h. The suspension was filtered through Celite, and the solvent was evaporated under reduced pressure. The crude solid was purified by column chromatography. Elution with a mixture of CH_2Cl_2/MeOH (9:1) afforded a yellow band that contained compound **3**. The pure compound was precipitated from a mixture of CH_2Cl_2/hexanes (yield: 120 mg, 60%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (d, $^3J_{H-H}$ = 2.50 Hz, 1H, $CH_{pyrazole}$), 6.51 (d, $^3J_{H-H}$ = 2.00 Hz, 1H, $CH_{pyrazole}$), 5.19 (d, $^3J_{H-H}$ = 5.99 Hz, 2H, CH_{pcym}), 5.03 (d, $^3J_{H-H}$ = 5.99 Hz, 2H, CH_{pcym}), 4.01 (s, 3H, NCH_3), 3.78 (s, 3H, NCH_3), 2.70−2.65 (m, 1H, $CH_{isop\ pcym}$), 2.02 (s, 3H, CH_{3pcym}), 1.14 (d, $^3J_{H-H}$ = 6.50 Hz, 6H, $CH_{3\ isop\ pcym}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 180.3 (C-Ru), 133.0, 117.1 ($CH_{pyrazole}$), 104.8, 99.3 (Cq_{pcym}), 84.5, 84.1 (CH_{pcym}), 31.8 (NCH_3), 30.7 ($CH_{isop\ pcym}$), 22.8 ($CH_{3isop\ pcym}$), 14.3 (CH_{3pcym}). Electrospray MS (15 V, m/z): 367.0 [$M - Cl]^+$. Anal. Calcd for $C_{15}N_2RuCl_2H_{22}$ (mol wt 402.3): C, 44.78; H, 5.51; N, 6.96. Found: C, 44.65; H, 5.62; N, 6.88.

Synthesis of 4. In an analogous manner to the preparation of **3**, the transmetalation was carried out in dichloromethane with 1,2,-dimethylpyrazolium iodide (172 mg, 0.78 mmol), silver oxide (274 mg, 1.18 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (120 mg, 0.20 mmol). Elution with 20 mL of CH_2Cl_2/acetone (1:1) with 30 mg of KPF_6 afforded the separation of a yellow band that contained compound **4** and residual KPF_6, which was filtered off. Complex **4** was obtained as a green solid by precipitation from a CH_2Cl_2/Et_2O solution (yield: 85 mg, 35%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (d, $^3J_{H-H}$ = 3.00 Hz, 2H, $CH_{pyrazole}$), 6.55 (d, $^3J_{H-H}$ = 2.70 Hz, 2H, $CH_{pyrazole}$), 5.44 (d, $^3J_{H-H}$ = 6.00 Hz, 2H, CH_{pcym}), 5.16 (d, $^3J_{H-H}$ = 6.00 Hz, 2H, CH_{pcym}), 3.90 (s, 6H, NCH_3), 3.53 (s, 6H, NCH_3), 2.70−2.60 (m, 1H, $CH_{isop\ pcym}$), 1.88 (s, 3H, CH_{3pcym}), 1.16 (d, $^3J_{H-H}$ = 6.90 Hz, 6H, $CH_{3isop\ pcym}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 175.1 (C-Ru), 133.6, 118.4 ($CH_{pyrazole}$), 112.2, 100.9 (Cq_{pcym}), 92.0, 88.8 (CH_{pcym}), 37.2, 36.8 (NCH_3), 30.6 ($CH_{isop\ pcym}$), 22.6 ($CH_{3isop\ pcym}$), 18.5 (CH_{3pcym}). Electrospray MS (15 V, m/z): 463.1 [$M]^+$. Anal. Calcd for $C_{20}N_4RuClH_{30}PF_6$ (mol wt 607.97): C, 39.51; H, 4.97; N, 9.22. Found: C, 39.35; H, 5.27; N, 5.90.

β-Alkylation of Secondary Alcohols with Primary Alcohols. Standard Procedure. The reaction was carried out with secondary alcohol (1 mmol), primary alcohol (1 mmol), 1 mol % of catalyst, and base, KOH (1 mmol), in toluene (0.3 mL) at 110 °C. The

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reaction was monitored by ^{1}H NMR spectroscopy, by introducing aliquots of the reacting solution inside an NMR tube with 0.5 mL of $CDCl_3$. The evolution was determined by integration. The signals due to reagents and products were taken from the literature.[19]

Dimerization of Phenylacetylene. Standard Procedure. The reaction was carried out with phenylacetylene (0.3 mmol), 5 mol % of catalyst, and base, Et_3N (0.075 mmol), in acetonitrile-d_3 (0.3 mL) at 70 °C. The reaction was monitored by ^{1}H NMR spectroscopy, by introducing aliquots of the reacting solution inside an NMR tube with 0.5 mL of $CDCl_3$. The evolution was determined by integration, using ferrocene as internal standard. The signals due to reagents and products were taken from the literature.[26]

X-ray Diffraction Studies. Crystals for X-ray diffraction of **2b** and **3** were obtained by slow diffusion of pentane in a concentrated solution of the compound in dichloromethane. Crystal data are summarized in Table 3. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the SAINT package.[30]

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.[31] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were assigned to ideal positions and refined using a riding model.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2b** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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