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Ruthenium(II) Picolyl-NHC Complexes: Synthesis, Characterization, and Catalytic Activity in Amine N-alkylation and Transfer Hydrogenation Reactions

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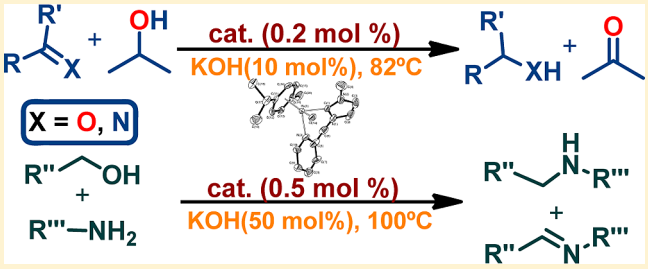
Supporting Information

ABSTRACT: Ruthenium(II) *p*-cymene complexes with picolyl-functionalized N-heterocyclic carbenes [(η^6-*p*-cymene)Ru(**L**)(Cl)][PF_6] (**L** = 3-methyl-1-(2-picolyl)imidazol-2-ylidene (**1a**), 3-isopropyl-1-(2-picolyl)imidazol-2-ylidene (**1b**), 3,4,5-trimethyl-1-(2-picolyl)imidazol-2-ylidene (**1c**), 3-mesityl-1-(2-picolyl)-imidazol-2-ylidene (**1d**), 3-methyl-1-(2-picolyl)benzoimidazol-2-ylidene (**1e**), 3-methyl-1-(2-picolyl)-4,5-dichloroimidazol-2-ylidene (**1f**), 3-phenyl-1-(2-picolyl)imidazol-2-ylidene (**1g**)) have been synthesized and characterized. Compounds **1a**−**g** were recrystallized, and X-ray crystal structures are reported for **1a**,**f**. Furthermore, compounds **1a**−**f** show catalytic activity in transfer hydrogenation of ketones and N-alkylation of amines. Notably, complexes **1a**,**c**,**f** were found to be very efficient and versatile catalysts toward transfer hydrogenation of a wide range of ketones and imines in addition to N-alkylation of several amines.



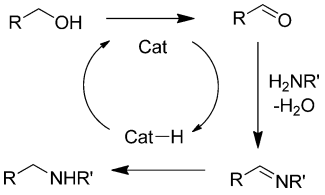
INTRODUCTION

Amines and alcohols are key building blocks in organic synthesis. The use of catalytic transformations for the generation of those products is one of the means toward sustainable industrial processes. Transfer hydrogenation reactions of C═O and C═N groups is a source of amines and alcohols using transition-metal complexes as catalysts. This reaction has been widely studied and continues to attract special interest, given its simplicity and readily availability of substrates.[1] The alkylation reaction of amines is usually completed using alkyl halides. However, the procedure frequently leads to overalkylation and, considering the necessity for environmentally friendly processes, the high toxicity of many alkylating agents is a major disadvantage.[2] The use of alcohols as alkylating agents for amines has proven to be less efficient, given their low electrophilicity. Nevertheless, the use of transition-metal complexes as catalysts via a borrowing hydrogen mechanism (Scheme 1) makes the N-alkylation using alcohols a potentially less hazardous and more atom-economical process.[3]

Several transition-metal complexes have been used as catalysts in transfer hydrogenation and N-alkylation reactions. Recently, N-heterocyclic carbenes (NHCs) have been widely used in organometallic chemistry as an alternative to well-known phosphine ligands for the synthesis of homogeneous catalysts.[4] Particularly, NHCs functionalized with an additional donor group have become an important group of ligands due to the potential hemilability of the new donor group, capable of reversible dissociation from the metal center.[5] Several donor groups such as phosphine,[6] pyrimidine,[7] ether,[8] thioether,[9] carboxylate,[10] indenyl,[11] oxazoline,[12] and pyridine[13] have been reported to functionalize NHCs. Ligands bearing nitrogen donors have attracted a great deal of attention. Particularly, metal complexes of Ir,[14] Ag,[15] Pd,[16] Ru,[17] and Ni[18] containing pyridine-functionalized NHCs have been synthesized. Among nitrogen donors, picoline has been used to generate *N*-picolyl-NHC ligands which can be easily synthesized with different substitution patterns on the picoline ring and the NHC.[19]

NHC complexes of iridium,[7b,20] rhodium,[21] and ruthenium[22] have demonstrated good activity in transfer hydrogenation reactions, mainly showing significant applications in asymmetric reductions[23] and racemization of chiral alcohols.[24] Recently, we have reported the synthesis of Cp* ruthenium complexes (Cp* = pentamethylcyclopentadienyl) bearing picolyl-NHCs, which showed excellent catalytic activity in transfer hydrogenation reactions of C═O and C═N groups (Figure 1).[25] In contrast, to the best of our knowledge only Crabtree and co-workers have described the use of chelating NHC complexes

Scheme 1. Representative Reaction Using the Borrowing Hydrogen Mechanism



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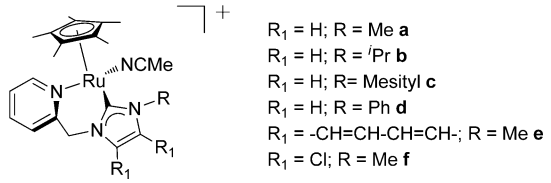


Figure 1. $[(Cp^*)Ru(picolyl\text{-}NHC)(CH_3CN)]PF_6$.[25]

of iridium and ruthenium for N-alkylation of amines.[7b] In addition, Peris et al. described an efficient catalytic system of iridium with NHCs, $[IrCl_2Cp^*(NHC)]$, for the cross-coupling of amines and alcohols.[26] However, several ruthenium and iridium catalytic systems bearing phosphine ligands have been reported to complete the N-alkylation of amines with alcohols with good yields and selectivity.[27]

The permanent search for new homogeneous catalytic systems led us toward the continuation of our recent work on the synthesis of $[Cp^*Ru(picolyl\text{-}NHC)(CH_3CN)][PF_6]$. Here we report the synthesis of a series of $[(p\text{-cymene})Ru(picolyl\text{-}NHC)Cl]PF_6$ complexes. Picolyl-NHC ligands have been varied systematically to study the influence on the catalytic activity of the wingtip substituent as well as the substituents at the C-4 and C-5 carbons of the imidazole ring. The new ruthenium compounds have shown excellent activity toward transfer hydrogenation of a wide variety of ketones and imines with high conversions. Additionally, the compounds have proved to catalyze amine N-alkylation reactions.

RESULTS AND DISCUSSION

Synthesis of (η^6-*p*-cymene)Ru^{II}(picolyl-NHC) Complexes. Picolyl imidazolium salts were obtained as previously described in the literature and used as picolyl-NHC precursors.[25,28−31] At first, in situ generation of the free picolyl-NHCs by treatment of the imidazolium salts **a**−**g** with a strong base (i.e., KO^{t}Bu or Li^{n}Bu) in THF followed by the addition of the metal precursor was attempted, but the products were not obtained quantitatively; in most attempts unreacted $[(\eta^6\text{-}p\text{-cym})RuCl_2]_2$ was observed in the ^{1}H NMR spectrum of the reaction mixture. Hence, the transmetalation method was the route of choice to afford the new Ru(II) cationic complexes **1a**−**g** (Scheme 2). Previously, Jin et al. synthesized a half-sandwich ruthenium containing 1,2-dichalcogenolato 1,2-dicarba-*closo*-dodecarborane and a picolyl-NHC ligand noncoordinated by the pyridyl arm using the transmetalation path.[32] Silver carbene complexes were prepared in situ upon treatment of the appropriate picolyl imidazolium salts **a**−**g** with silver oxide in dichloromethane. The metal precursor $[(\eta^6\text{-}p\text{-cymene})Ru(Cl)_2]_2$ and an excess of $NaPF_6$ were added to the corresponding silver carbene solution, generating the new ruthenium picolyl-NHC complexes **1a**−**g** in high yields (over 83%) in all cases. The reaction is complete after 3 h at room temperature. The new Ru(II) compounds were characterized by ^{1}H and $^{13}C\{^1H\}$ NMR and elemental analysis. All the ruthenium picolyl-NHC complexes are very soluble in THF, acetone, and chlorinated solvents but insoluble in other solvents such as hexane, diethyl ether, and petroleum ether.

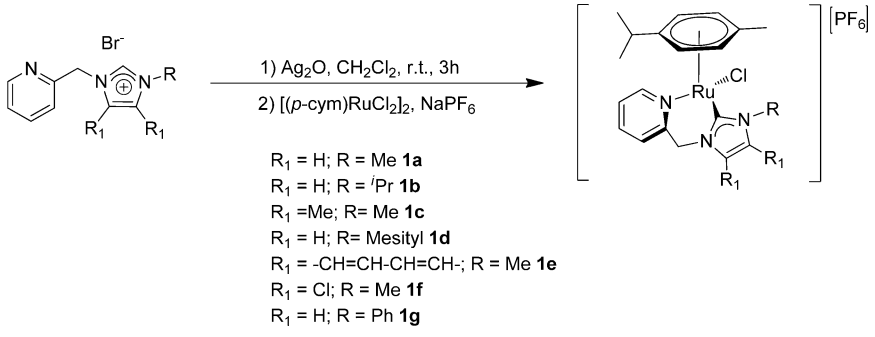
^{1}H NMR spectra of compounds **1a**−**g** do not show the NC*H*N proton resonance signals at 10−12 ppm, as expected after the coordination of the C_2 carbene carbon to the metal center. Also, ^{1}H NMR spectra show two characteristic AB doublet signals at 5−6 ppm with coupling constants of 15−16 Hz corresponding to the methylene bridge protons, which become diastereotopic after coordination of the ligands to the Ru atom, particularly in κ^2C,N coordination. Furthermore, analogous NMR features for $(\eta^5\text{-}C_5Me_5)Ru$ chelating κ^2C,N-picolyl-NHC ligands and chelating κ^2P,N-phosphinopicoline ligands have been observed.[25,33] Also, this pattern has been reported by Xue and co-workers, in the synthesis of Ru(II) carbonyl Py-NHC complexes.[34] The $^{13}C\{^1H\}$ NMR signals of the carbene carbon atoms of **1a**−**g** (170−190 ppm) are located as expected for (*p*-cymene)Ru(NHC) compounds.[22d,32,33,35] It is interesting to note the displacement to lower field, up to 190 ppm, of the NMR resonance of the C_2 carbon atom corresponding to the benzoimidazol analogue **1e**. The lower electron density in the C_2 carbon due to the destabilization of the imidazolium ring conjugation caused by the benzene ring could explain this observation. Also, this behavior was evidenced in the previous synthesis of the $(\eta^5\text{-}C_5Me_5)Ru$ picolyl-NHC analogues.[25]

Crystals suitable for X-ray diffraction of **1a**,**f** were obtained after layering the recrystallization solution on a mixture of dichloromethane and hexane (1/2). ORTEP diagrams of the two Ru(II) cationic complexes are displayed in Figures 2 and 3, along with selected interatomic distances and angles.

In these structures the ruthenium(II) metal centers adopt a pseudo-octahedral coordination geometry with all the Cl−Ru−$C_{carbene}$, Cl−Ru−N, and N−Ru−$C_{carbene}$ angles in the range 83.7(2)−87.7(1)°.

In both cases η^6-π-*p*-cymene and Cl ligands coordinate to a slightly distorted octahedral metal center that is also chelated by one NHC ligand. The interatomic distances in the coordination sphere of ruthenium are all comparable with those found in closely related chloro *p*-cymene NHC ruthenium complexes[13f,35] or chloro η^6-mesitylene NHC ruthenium complexes.[36] Dihedral angles between pyridyl and imidazolyl rings were found to be 55.3(3)° for **1a** and 58.8(1)° for **1f**.

Scheme 2



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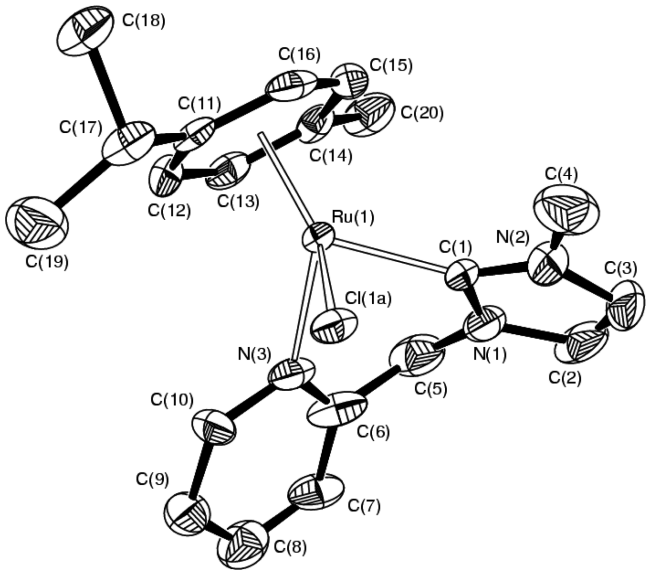

Figure 2. ORTEP diagram for the complex cation in [RuCl(η^6-*p*-cymene)(NHC-κ^2*C*,*N*)][PF_6] (**1a**; NHC = 3-methyl-1-(2-picolyl)-imidazol-2-ylidene). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru(1)–phenylidene (centroid) = 1.710(3), Ru(1)–Cl(1a) = 2.389(2), Ru(1)–N(3) = 2.095(6), Ru(1)–C(1) = 2.035(7); Cl(1a)–Ru(1)–N(3) = 86.32(18), Cl(1a)–Ru(1)–C(1) = 84.8(3), N(3)–Ru(1)–C(1) = 84.2(3).

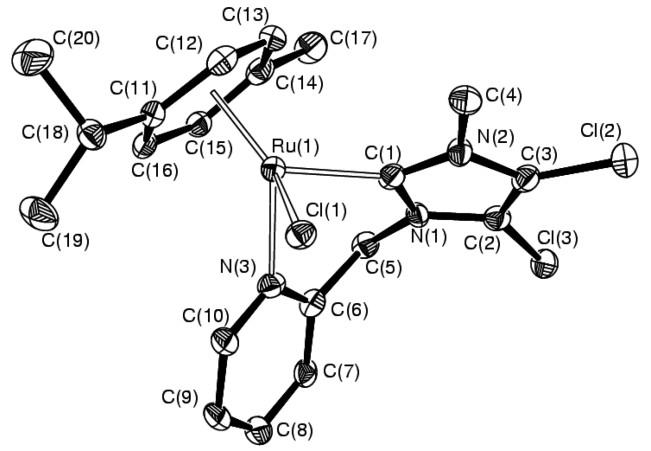

Figure 3. ORTEP diagram for the complex cation in [RuCl(η^6-*p*-cymene)(NHC-κ^2*C*,*N*)] [PF_6] (**1f**; NHC = 3-methyl-1-(2-picolyl)-4,5-dichloroimidazol-2-ylidene). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru(1)–phenylidene (centroid) = 1.696 (2), Ru(1)–Cl(1) = 2.448(1), Ru(1)–N(3) = 2.111(4), Ru(1)–C(1) = 2.023(5); Cl(1)–Ru(1)–N(3) = 86.75(12), Cl(1)–Ru(1)–C(1) = 87.69(14), N(3)–Ru(1)–C(1) = 83.70(18).

Catalytic N-Alkylation of Amines with Alcohols. Nitrogen-containing compounds as amines are very important due to the wide applications they have in several industrial processes and the key role they play in the synthesis of several pharmaceutically and biologically significant molecules.[37] Ruthenium complexes have been commonly used as catalysts for the N-alkylation of amines via a hydrogen autotransfer process, particularly $RuCl_2(PPh_3)_3$ and its derivatives.[3,27] It is interesting that, considering the wide amount of work published on ruthenium-NHC complexes, Albretch et al. just recently described the use of ruthenium triazolylidene complexes as catalysts for oxidative coupling of alcohols and amines.[38] In addition, Crabtree and co-workers have reported the use of a ruthenium pyrimidine-NHC complex as a catalyst for the N-alkylation of amines.[7b] However, many examples with transition-metal complexes used as catalysts for this transformation have been described recently.[3b,27a,39,40] Therefore, complexes **1a**–**f** were tested as catalysts for this transformation.

Optimization of Reaction Conditions. The generation of N-benzylaniline from benzyl alcohol and aniline was used as a representative reaction to optimize the reaction conditions (Scheme 3). The results given in Table 1 show the screening of

Table 1. Optimization of Conditions[a]

entry	base	amt of base (mol %)	yield (%)[b]	amine (%)[c]
1			0	
2	$NaHCO_3$	15	0	
3	$NaHCO_3$	50	0	
4	$NaHCO_3$	100	0	
5	KO^{t}Bu	15	85	72
6	KO^{t}Bu	20	86	80
7	KO^{t}Bu	50	97	97
8	KO^{t}Bu	100	>99	>99
9	K_2CO_3	15	0	
10	K_2CO_3	50	0	
11	K_2CO_3	100	0	
12	KOH	15	90	85
13	KOH	20	88	88
14	KOH	50	>99	>99
15	KOH	100	>99	>99

[a]N-alkylation reaction conditions: 2.00 mmol of aniline, 2.00 mmol of benzyl alcohol, **1a** (0.5 mol %) in 2 mL of toluene at 100 °C for 24 h. [b]Product yield determined by GC-MS using 1,3,5-trimethoxybenzene as an internal standard. [c]Conversions determined by GC-MS. The formation of the corresponding imine as a byproduct accounts for the difference in conversion.

bases as initiators of the catalytic reaction. Weak bases such as $NaHCO_3$ and K_2CO_3 were not effective (entries 2–4 and 9–11). However, the use of strong bases such as KO^{t}Bu and KOH lead to high yields of the desired product, *N*-benzylaniline (entries 5–8 and 12–15). In addition, to obtain almost quantitative yields and avoid the presence of the imine as a secondary product, from lack of hydrogenation of the condensation product, at least 50 mol % of base is needed.

We continued the N-alkylation reaction optimization process after finding the need for a strong base to activate the ruthenium complex **1a**. The following step was to study the

Scheme 3

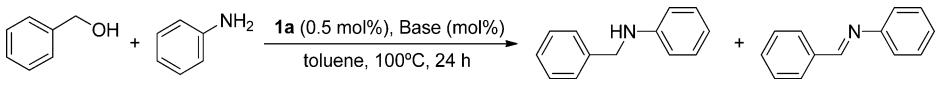

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Table 2. Influence of Wingtips, Backbone Substituents, and Catalyst Loading on the Catalytic Activity of Ru(picolyl-carbene) Complexes[a]

entry	cat.	amt of cat. (mol %)	time (h)	TON[b]	yield (%)[c]	amine (%)[d]
1	**1a**	0.15	72	360	54	43
2	**1b**	0.15	72	480	72	62
3	**1c**	0.15	72	360	54	42
4	**1d**	0.15	72	373	56	46
5	**1e**	0.15	72	406	61	45
6	**1f**	0.15	72	480	72	65
7	**1a**	0.25	72	252	63	55
8	**1b**	0.25	72	296	74	64
9	**1c**	0.25	72	284	71	65
10	**1d**	0.25	72	248	62	55
11	**1e**	0.25	72	328	82	79
12	**1f**	0.25	72	288	72	61
13	**1a**	0.50	15	184	92	92
14	**1b**	0.50	15	154	77	72
15	**1c**	0.50	15	186	93	93
16	**1d**	0.50	15	164	82	78
17	**1e**	0.50	15	184	92	90
18	**1f**	0.50	15	160	80	75

[a]N-alkylation reaction conditions: 2.00 mmol of aniline, 2.00 mmol of benzyl alcohol, KOH (50 mol %), catalyst (mol %) in 2 mL of toluene at 100 °C. [b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time *t*. [c]Product yield determined by GC-MS using 1,3,5-trimethoxybenzene as an internal standard. [d]Conversions determined by GC-MS. Formation of the corresponding imine as a byproduct accounts for the difference in conversion.

influence of the wingtip, backbone substituents, and catalyst loadings on the catalytic activity. The results given in Table 2 indicate that lower catalyst loadings lead to moderate yields and longer reaction times are required to achieve maximum TONs (entries 1−12). Also, as expected, higher catalyst loadings led to higher yields and higher amine content in the product distribution (entries 1−12). Furthermore, considering the results when 0.5 mol % of catalyst was used, it is clear that ruthenium complexes containing Me (entries 13, 15, 17, and 18) as a wingtip substituent lead to higher yields than those containing isopropyl or mesityl (entries 2 and 4) and significantly shorter reaction times are needed to complete the N-alkylation process. This behavior indicates that steric effects may be playing an important role in the catalytic activity. In addition, **1b,d** showed good activity at lower catalyst loadings, but when the catalyst concentration was increased, it was not possible to obtain yields as high as those with their analogues. However, it is important to note that, among complexes with methyl substituents in the wingtip, those containing methyl groups, **1c**, in the imidazole backbone or a benzimidazole ring, **1e**, showed the best selectivity toward the synthesis of the amine (entries 9, 11, 15, and 17). Also, to consider possible electronic effects on the catalytic activity, **1f** with chloro substituents on the imidazole backbone was tested and yields and selectivity lower than those with its analogues **1c,e** were obtained under the same reaction conditions. Thus, electronic properties may also account for the catalytic activity, although not as much as steric effects.

The optimization process led us toward the determination of the best reaction conditions to analyze the substrate scope. Catalysts **1a,c,e** proved to be the most efficient complexes for the N-alkylation of aniline in terms of yield and selectivity, and 0.5 mol % catalyst loading was chosen, given the high yields and shorter reaction times needed to complete the process.

Substrate Scope. Several amines and alcohols were chosen to explore the range of application of the catalysts for the hydrogen autotransfer N-alkylation of amines (Scheme 4). The

Scheme 4

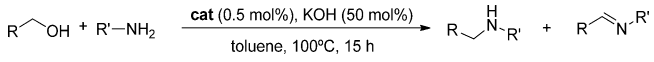

Table 3. Catalytic Aromatic Amine N-alkylation[a]

entry	R	R′	cat.	yield (%)[b]	amine (%)[c]
1	Ph	Ph	**1a**	92	92
2			**1c**	93	93
3			**1e**	92	92
4	Ph	4-MePh	**1a**	95	95
5			**1c**	94	94
6			**1e**	90	86
7	Ph	4-OMePh	**1a**	93	93
8			**1c**	94	94
9			**1e**	89	80
10	Ph	4-ClPh	**1a**	92	92
11			**1c**	96	96
12			**1e**	>99	>99
13	Ph	2-NH_2Py	**1a**	85	85
14			**1c**	75	75
15	4-MePh	Ph	**1a**	89	83
16			**1c**	93	91
17			**1e**	81	73
18	4-OMePh	Ph	**1a**	92	92
19			**1c**	97	92
20			**1e**	84	75
21	4-ClPh	Ph	**1a**	94	94
22			**1c**	94	94
23			**1e**	80	75
24	1-naphthalene	Ph	**1a**	88	88
25			**1c**	86	86
26			**1e**	77	77
27	^{i}Pr	Ph	**1a**	67	67
28			**1c**	69	69
29			**1e**	61	61

[a]N-alkylation reaction conditions: 2.00 mmol of amine, 2.00 mmol of alcohol, KOH (50 mol %), catalyst (0.5 mol %) in 2 mL of toluene at 100 °C for 15 h. [b]Product yield determined by GC-MS and ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Conversions determined by GC-MS. Formation of the corresponding imine as a byproduct accounts for the difference in conversion.

results shown in Table 3 summarize the effect of the substrates on the yield and selectivity of the catalytic reaction after 15 h. The use of donor or electron-withdrawing groups in the aniline ring does not affect the catalyst performance. In all cases the corresponding amine was generated with almost quantitative yields and high selectivity (entries 1−12). However, when 2-aminopyridine was used as substrate, lower yields were obtained, indicating that when a heteroaromatic amine is used the catalytic reaction is less efficient (entries 13 and 14). In addition, in that case **1a** leads to higher yields than **1c**.

Alcohols are the source of the alkyl groups for the generation of the new amines. Thus, the tolerance to different substituents in benzyl alcohol derivatives toward the synthesis of amines was investigated. The use of electron-donor substituents

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(entries 15–20) indicates that the reaction yields are comparable to those when benzyl alcohol was used as substrate, but there was a small selectivity loss, evidenced by the generation of small amounts of the corresponding imine. Nonetheless, when an electron-withdrawing group such as a halogen (entries 21–23) is present, the yields and selectivity are very high. Also, the use of a bulky alcohol such as 1-naphthalene methanol (entries 24 and 25) or an alkyl alcohol such as isobutanol (entries 27–29) does not affect the selectivity of the reaction but leads to lower yields. In general, **1a,c** show high tolerance to different alcohols. However, **1e** showed a decrease in reaction yield in comparison with its analogues.

It is very important to note that the use of a nonaromatic amine as substrate (Table 4) generated mostly the corresponding imine as the reaction product. The use of lower amounts of base (entries 2, 4, and 6) led to higher selectivity toward the imine when benzylamine was used as substrate. Also, several experiments were conducted by increasing the base loading up to 200 mol %, catalyst loading up to 5%, and reaction temperatures up to 150 °C and in no case an evident improvement toward the amine synthesis was observed. These results indicate that the late stage of the hydrogen autotransfer mechanism is disrupted.

Table 4. Catalytic Nonaromatic Amines N-alkylation[a]

entry	R	R′	cat.	amt of KOH (mol %)	yield (%)[b]	imine (%)[c]
1	Ph	$PhCH_2$	**1a**	50	99	57
2			**1a**	20	98	98
3			**1c**	50	81	62
4			**1c**	20	84	84
5			**1e**	50	85	73
6			**1e**	20	88	88
7	Ph	Cy	**1a**	50	56	56
8			**1c**	50	67	65
9			**1e**	50	71	71
10	Ph	$PhCH_2CH_2$	**1e**	50	75	69

[a]N-alkylation reaction conditions: 2.00 mmol of amine, 2.00 mmol of alcohol, KOH (mol %), catalyst (0.5 mol %) in 2 mL of toluene at 100 °C for 24 h. [b]Product yield determined by GC-MS and ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Conversions determined by GC-MS. Formation of the corresponding amine as a byproduct accounts for the difference in conversion.

Usually, imines are obtained during the preparation of amines, but as a side product in small yields or as species detected as reaction intermediates. Just a few examples of catalysts used for selective imine synthesis are known.[27a,39] Particularly, Milstein and co-workers reported selective imine synthesis of imines with a ruthenium PNP pincer complex.[27a] However, this is the first example of selective imine synthesis using ruthenium NHC complexes as catalysts. Catalysts **1a,c,e** performed better than previously reported catalytic systems,[39] although the most efficient catalysts reported to date for the selective synthesis of imines is Milstein's ruthenium PNP pincer complex.[27a] In addition, **1a,c,e** to the best of our knowledge are the most effective ruthenium catalysts reported for the N-alkylation of aromatic amines, given the high yields and low catalyst loadings needed to complete the transformation in comparison to other ruthenium systems.[3b,27d–f,41]

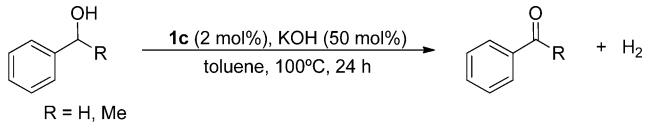
Mechanistic Study. To gain further understanding of the N-alkylation process, considering it follows the "borrowing hydrogen" pathway, we conducted two experiments using benzyl alcohol and 1-phenylethanol as substrates (Table 5). The aim was to assess if the corresponding oxidation reaction was completed (Scheme 5).[7b,26,38] No aldehyde was observed in the reaction mixture after 24 h when benzyl alcohol was used as a substrate. Thus, the aldehyde should be a short-lived intermediate or it does not dissociate from the metal center before being condensed with the corresponding amine in the N-alkylation reaction. However, in the case of 1-phenylethanol, acetophenone was observed as a product. No further experiments for optimization of the oxidation reaction were completed. Nonetheless, this result indicates that catalysts **1a–f** may be used in a wider range of reactions. We will further investigate the β-alkylation of alcohols and secondary alcohol oxidation reactions.

Table 5. Dehydrogenation of Aromatic Alcohols[a]

entry	substrate	time (h)	yield[b] (%)
1	benzyl alcohol	24	<2
2	1-phenylethanol	24	38

[a]Dehydrogenation reaction conditions: 2.00 mmol of alcohol, KOH (50 mol %), catalyst (2 mol %) in 2 mL of toluene at 100 °C. [b]Product yield determined by GC-MS and ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Scheme 5



Also, to gain more insight into the reaction mechanism and intermediates, we conducted NMR reactions in toluene-d_8 with higher catalyst loadings (6 mol % of **1c**) to be able to detect intermediates, using aniline and benzyl alcohol as substrates, and 50% KO^{t}Bu. Immediately, after the addition of substrates and base the ^{1}H NMR spectrum recorded at room temperature showed the formation of two ruthenium hydride species, as evidenced by the appearance of two singlets, at −8.2 ppm (minor) and −9.4 ppm (major). This indicates a quick exchange of the chloride with the alkoxide, as an initiation step that does not require heating. The reaction mixture was heated at 100 °C for 15 h in an oil bath, and while the formation of *N*-benzylamine progressed, the initial hydride peaks disappeared and many weak peaks appeared in the ^{1}H NMR spectrum between −11 and −25 ppm. Furthermore, to confirm the initial formation of the ruthenium hydride alkoxide specie as the initial step, an NMR experiment on toluene-d_8 with a 1:4:4 ratio of **1c**, KO^{t}Bu, and benzyl alcohol was conducted. At first, at room temperature two hydride peaks at −9.4 and −8.6 ppm were observed, which disappeared after prolonged heating of the sample at 100 °C. The catalyst decomposition was confirmed by the disappearance of the characteristic π-bound *p*-cymene protons and the doublets corresponding to the κ^2C,N-picolylimidazolidene close to 4–6 ppm. The hydride peak at −9.4 ppm in the ^{1}H NMR spectrum confirms the formation of species similar to that formed in the previous N-alkylation experiment. Finally, to complete our study, when the experiment was ran without the presence of a base, with only a 1/4 ratio of **1c** and benzyl alcohol, no hydride peaks were observed in the ^{1}H NMR spectrum.

In addition, to obtain further information concerning the reaction mechanism, the reaction of aniline with an equimolar amount of benzaldehyde and a catalytic amount of benzyl

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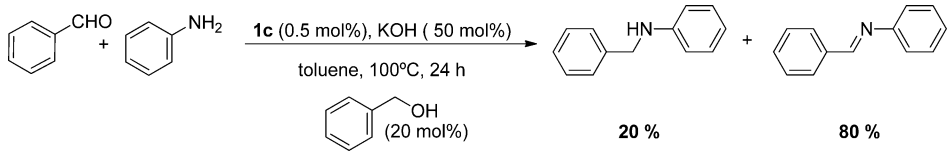
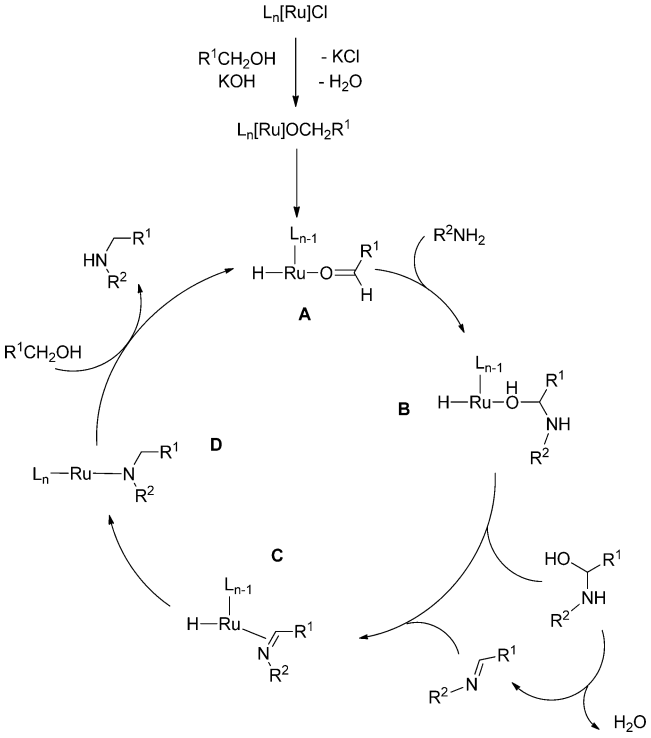
Scheme 6



alcohol, **1c**, and KOH was conducted (Scheme 6). The reaction was completed after heating the mixture for 24 h at 100 °C. However, the product distribution was 20/80 amine/imine. The presence of amine in the reaction mixture indicates that part of the generated imine has been hydrogenated, in contrast to results reported by Madsen and co-workers.[42] Also, the completion of the reaction with benzaldehyde confirms that the reaction proceeds through an aldehyde intermediate. The presence of the imine implies the formation of an hemiaminal intermediate that is released from the catalyst, and the consequent water loss leads to the imine. In addition, a non free hemiaminal intermediate would have produced an amide, as has been reported for several ruthenium(II) catalysts.[43]

On the basis of the above results and the known chemistry of N-alkylation,[7,3a] transfer hydrogenation,[8,44a,c] and amide synthesis[3,35c,43,44b] reactions with ruthenium complexes, we propose the mechanism illustrated in Scheme 7. The initial step

Scheme 7. Proposed Mechanism

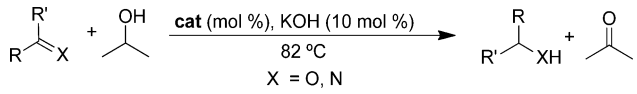


is alkoxide formation and subsequent oxidation to the aldehyde with the generation of a ruthenium hydride intermediate (**A**). Given that no free aldehyde is observed in the reaction mixture, we suggest the formation of a hemiaminal by condensation of the aldehyde and the amine (**B**) while the aldehyde is coordinated to the metal center. The following step is the hemiaminal release and water elimination, leading to the imine. This pathway diverges from other reported ruthenium systems, where the hemiaminal is coordinated to the metal and undergoes β-hydrogen loss, generating the amide.[35,42−44] However, in our case, amide has not been observed as a product in any reaction. The proposed mechanism indicates that the imine is subsequently hydrogenated by hydrogen transfer to generate the secondary amine (**C**−**D**). Nonetheless, this mechanism does not explain the disruption of the late hydrogenation step to generate secondary amines when nonaromatic amines are used as substrates. Further experiments are ongoing to explain these results.

Our catalyst system has proven to be very effective toward a wide range of amines and alcohols for the synthesis of amines with high yields and selectivity when aromatic amines are used as substrates. Also, **1a,c,e** have proven to be an alternative for the selective synthesis of imines, which are key intermediates for the manufacture of commercially important compounds such as agrochemicals, dyes, and medicines.[39] Furthermore, **1a,c,e** proved to be an alternative to widely used ruthenium phosphine complexes in the advance toward the generation of more environmentally friendly processes.

Catalytic Transfer Hydrogenation. Some ruthenium-NHC complexes have been reported as catalysts for the transfer hydrogenation of ketones,[8b,45,46] including our recently reported pentamethylcyclopentadienyl Ru-(picolylcarbene) analogues.[25] Thus, ruthenium-(picolylcarbene) complexes **1a−f** were tested as catalysts for this transformation. The ruthenium-(picolylcarbene) complexes catalyze the transfer hydrogenation of ketones and imines from ^{i}PrOH with KOH as the initiator (Scheme 8).

Scheme 8



The generation of 1-phenylethanol from acetophenone was used as a representative reaction to screen the performance of Ru-(picolylcarbene) catalysts. The results given in Table 6

Table 6. Influence of Wingtips and Backbone Substituents on the Catalytic Activity of Ru(picolyl-carbene) Complexes[a]

entry	cat.	cat. R wingtip group	cat. R_1 backbone group	t (h)	TON[b]	yield (%)[c]
1	**1a**	Me	H	2	184	92
2	**1b**	^{i}Pr	H	2	174	87
3	**1c**	Me	Me	2	166	83
4	**1d**	mesityl	H	2 (4)	34 (148)	17 (74)
5	**1e**	Me	−CH═CHCH═CH−	2	178	89
6	**1f**	Me	Cl	2	180	90

[a]Transfer hydrogenation reaction conditions: 2.00 mmol of acetophenone, KOH (10 mol %), catalyst (0.5 mol %) in 4 mL of ^{i}PrOH at 82 °C. [b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t. [c]Product yield determined by GC-MS using 1,3,5-trimethoxybenzene as an internal standard.

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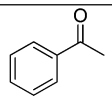
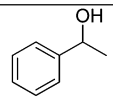
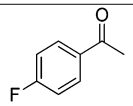
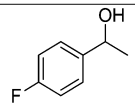
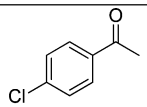
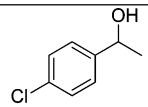
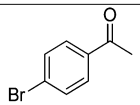
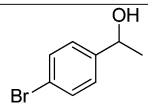
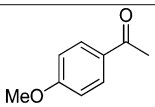
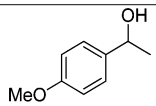
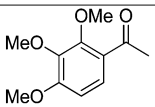
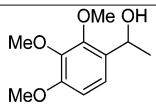
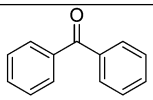
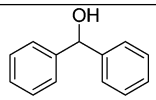
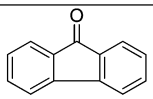
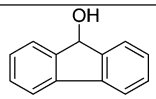
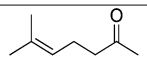
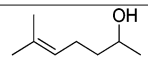
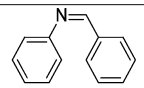
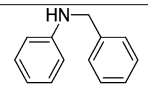
Table 7. Catalytic Transfer Hydrogenation

Entry	Substrate	Product	Catalyst	t (h)	TON[b]	Yield (%)[c]
1			**1a**	15	445	89
2			**1f**	15	460	92
3			**1a**	15	460	92
4			**1f**	15	430	86
5			**1a**	15	495	> 99
6			**1f**	15	445	89
7			**1a**	15	490	98
8			**1f**	15	465	93
9			**1a**	24	385	77
10			**1f**	24	320	64
11			**1a**	15	470	94
12			**1f**	15	400	80
13			**1a**	6	490	97
14			**1f**	8	440	88
15			**1a**	6	495	> 99
16			**1f**	6	495	> 99
17			**1a**	6	495	> 99
18			**1f**	6	495	> 99
19			**1a**	6	465	93
20			**1f**	8	375	75
21			**1a**	15	495	> 99
22			**1f**	15	495	> 99

[a]Transfer hydrogenation reaction conditions: 2.00 mmol of substrate, KOH (10 mol %), catalyst (0.2 mol %) in 4 mL of ^{i}PrOH at 82 °C. [b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t. [c]Product yield determined by GC-MS using 1,3,5-trimethoxybenzene as an internal standard.

show the influence of the wingtip and imidazole backbone substituents on the catalytic activity. Catalysts containing a bulky mesityl (**1d**) or isopropyl group (**1b**) (entries 2 and 4) as a wingtip substituent are less active than those containing methyl groups (entries 1, 5, and 6). Also, when electron-donor methyl substituents were introduced in the imidazole backbone (entry 3), lower yields were obtained in comparison with the electron-withdrawing analogue containing chloro substituents in the imidazole backbone (entry 6). However, it is important to note that steric effects may play a greater role in the catalytic activity than electronic effects, as evidenced by the lower yields obtained when bulkier groups were used as wingtip substituents. This behavior is in line with our previously synthesized pentamethylcyclopentadienyl ruthenium(picolyl-carbene) analogues.[25]

Catalysts **1a**,**f** proved to be very efficient complexes in the transfer hydrogenation of acetophenone. Hence, several aromatic and aliphatic ketones as well as imines were chosen to explore the activity of **1a**,**f** toward transfer hydrogenations (Table 7). Aromatic halo substituents in para positions have an enhancing effect on the catalytic activity, showing almost quantitative results on the formation of the corresponding alcohols (entries 1−8). On the other hand, the presence of a methoxy group at the para position led to lower reaction yields for acetophenones (entries 9 and 10), indicating a less efficient hydrogenation process. However, when three methoxy groups were introduced in the aromatic ring, the yields obtained were higher (entries 11 and 12), indicating that the initial deactivating effect of a single methoxy group was overcome

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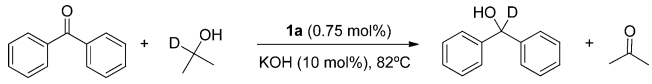
by the presence of two additional donor groups. Thus, electron-withdrawing groups at the para position of acetophenones benefit the catalytic activity, while electron donating groups decrease it, unless more than one donating group is present in the aromatic ring. Also, bulkier aromatic ketones were tested. Among them, benzophenone generated 1,1-diphenylmethanol in high yields (entries 13 and 14). Also, when the more rigid ketone 9-fluorenone was used, the yields were almost quantitative (entries 15 and 16).

Complexes **1a,f** were shown to be very active toward alkyl ketones. Particularly, cyclohexanone was reduced to cyclohexanol almost quantitatively (entries 17 and 18). Unsaturated ketones are interesting substrates for transfer hydrogenation reactions, because they may undergo reduction on the carbonyl and/or olefin moiety. However, **1a,f** proved to selectively reduce the carbonyl moiety on 6-methylhept-5-en-2-one (entries 19 and 20). Moreover, complexes **1a,f** work as efficient catalysts in the hydrogenation of *N*-benzylideneaniline (entries 21 and 22), demonstrating the versatility of the new catalyst toward the hydrogenation of ketones and imines. In addition, it is clear that on comparison of the performances of **1a** and **1f**, **1a** is a better catalyst for this transformation, as evidenced by the higher yields obtained in comparison to its analogue in the cases where the reactions were not completed quantitatively. In addition, higher catalyst loadings up to 0.75 mol % allowed significant shortening of reaction times (see the Supporting Information for details). In comparison with previously reported ruthenium(II) complexes bearing chelating NHCs, our catalytic system led to better yields and lower catalyst loadings were needed to complete the hydrogenation of a wide range of ketones and imines.[45b−e,g−i] However, during the preparation of this work, Ohara and co-workers reported the synthesis of ruthenium(II) complexes bearing primary amino-NHC ligands and their activity as catalysts in the transfer hydrogenation of ketones, showing that using lower catalyst loadings up to 0.08 mol % can lead to moderate to good yields on many cases, but their catalyst lack of selectivity when α,β-unsaturated ketones were used as substrates.[45]

Transition-metal-catalyzed hydrogen transfer reactions usually follow a "hydride" mechanism which may proceed via either a monohydride or dihydride intermediate species in the catalytic cycle. Labeling protocols reported by Pàmes and Bäckvall[47] and by Crabtree et al.[20e] allowed us to distinguish between the two possible catalytic pathways. The main characteristic of the monohydride route is that the C−H bond from the hydrogen donor ends up as a C−H bond on the carbinol carbon of the product. On the other hand, when the dihydride route is observed, the C−H from the donor is scrambled between the C−H and O−H in the product. Hence, when a hydrogen donor deuterated in the carbinol carbon is used, and the reaction proceeds via a monohydride pathway, deuterium incorporation will be only observed in the carbinol carbon of the product. However, if the reaction follows the dihydride mechanism, deuterium is observed in the carbinol carbon and oxygen. Commercially available 2-propanol-2-*d* was used to study the transfer hydrogenation of benzophenone using **1a** as catalyst (Scheme 9).

After 2 h of reaction time NMR and GC-MS analysis showed that mostly monodeuterated 1,1-diphenylmethanol-1-*d* was observed as a product with 84% of deuterium incorporation in the carbinol position. Furthermore, longer reaction times did not increase the reaction yields or the deuterium incorporation rates. This results are in line with a monohydride mechanism,

Scheme 9



84 % D incorporation

as has also been reported for other ruthenium arene complexes such as [(*p*-cymeme)Ru(dppp)Cl]Cl (dppp = 1,3-bis-(diphenylphosphino)propane) and [(*p*-cymene)Ru(bipy)Cl]Cl analogues (bipy = bipyridine).[48]

CONCLUSION

We have reported the synthesis and characterization of the novel air-stable complexes [(*p*-cymene)Ru(picolyl-NHC)-(Cl)][PF_6] (**1a−g**), in which the substituents on the NHC backbone and wingtip have been modified. The crystal structures of two of the complexes prepared, **1a,f**, have been described. The catalytic study of [(*p*-cymene)Ru(picolyl-NHC)(Cl)][PF_6] complexes **1a−f** toward amine N-alkylation and transfer hydrogenation reactions was completed, showing that all catalysts are active toward catalytic transformations. The results also showed that steric effects in the ligands play a more important role than electronic effects in the catalytic activity of the new complexes.

In the N-alkylation process complexes **1a,c,e** have been proven to be versatile and efficient catalysts under mild conditions in comparison to its analogues and other ruthenium and iridium complexes.[3,39] Also, **1a,c** have shown high tolerance to functional groups in the amine and alcohol moieties. Furthermore, **1a,c,e** have been proven to selectively catalyze the synthesis of imines when nonaromatic amines are used as substrates. Several experiments allowed the detection of reaction intermediates and the proposal of a reaction mechanism which implies the imine generation after water elimination from the hemiaminal, as key steps to generate secondary amines.

On the other hand, **1a,f** have been proven to be very efficient and versatile in transfer hydrogenation reactions of a wide variety of ketones and imines. Moreover, a monohydride transfer hydrogenation mechanism is proposed after deuterium labeling experiments.

EXPERIMENTAL SECTION

General Methods. Unless otherwise stated, all manipulations were carried out under dry nitrogen or argon using conventional Schlenk techniques. Dichloromethane, hexane, toluene, and isopropyl alcohol were of anhydrous quality and were used as received. All solvents were degassed immediately prior to use. 3-methyl-1-(2-picolyl)imidazolium bromide (**a**),[28] 3-isopropyl-1-(2-picolyl)imidazolium bromide (**b**),[29] 3-mesityl-1-(2-picolyl)imidazolium bromide (**d**),[30] 3-methyl-1-(2-picolyl)-benzoimidazolium bromide (**e**),[31] 3-phenyl-1-(2-picolyl)imidazolium bromide,[25] 3-methyl-1-(2-picolyl)-4,5-dichloroimidazolium bromide,[25] 3,4,5-trimethyl-1-(2-picolyl)imidazolium bromide,[25] [(*p*-cymene)-$RuCl_2]_2$,[49] and $NaBAr^F_4$[50] were prepared using slightly modified versions of the published procedures. All other reagents were purchased from commercial sources and used without further purification.

NMR spectra were recorded using a Varian INOVA 400 MHz spectrometer, and chemical shifts are reported relative to TMS for ^1H and $^{13}C\{^1H\}$. Assignments of ^1H and $^{13}C\{^1H\}$ NMR spectra were made on the basis of 2D NMR experiments. Microanalyses were performed with a LECO CHNS-932 elemental analyzer by Servicios Centrales de Ciencia y Tecnología, Universidad de Cádiz. GC-MS analyses were recorded in an Agilent 6890N device equipped with an HP-5 column.

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Representative Procedure for Synthesis of Metal Complexes. A suspension of the appropriate imidazolium bromide (**a**–**g**) and silver oxide (0.5 equiv) was stirred at room temperature in the dark for 3 h. The mixture was then filtered through a pad of Celite into $[(p\text{-cymene})RuCl_2)]_2$ and $NaPF_6$ (2.1 equiv) and stirred at room temperature for 3 h. The suspension was filtered through Celite to remove silver salts, and the solvent was removed under reduced pressure. The resulting solid was washed with ether, dried under vacuum, and recrystallized from CH_2Cl_2/hexane.

Chloro(η^6-*p*-cymene)(κ^2*C*,*N*-3-methyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (1a). Transmetalation was carried out in CH_2Cl_2 (30 mL) with 3-methyl-1-(2-picolyl)imidazolium bromide (**a**; 254.1 mg, 1 mmol), Ag_2O (115.9 mg, 0.5 mmol), $[(p\text{-cymene})RuCl_2)]_x$ (306.2 mg, 1 mmol), and $NaPF_6$ (352.7 mg, 2.1 mmol). The product was a yellow microcrystalline solid. Yield: 506.47 mg, 86%. ^{1}H NMR ($CDCl_3$, 400 MHz, $SiMe_4$): δ 9.14 (d, $^3J_{HH}$ = 5.86 Hz, 1H, $H_{pyridine}$), 7.77 (t, 1H, $^3J_{HH}$ = 8.11 Hz, 1H, $H_{pyridine}$), 7.68 (d, $^3J_{HH}$ = 7.03 Hz, 1H, $H_{pyridine}$), 7.45 (d, $^3J_{HH}$ = 1.75 Hz, 1H, H_{imid}), 7.29 (t, $^3J_{HH}$ = 7.32 Hz, 1H, $H_{pyridine}$), 7.03 (d, $^3J_{HH}$ = 1.46 Hz, 1H, H_{imid}), 5.66 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.63 (d, $^2J_{HH}$ = 15.94 Hz, 1H, H_{bridge}), 5.62 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.58 (d, $^3J_{HH}$ = 6.16 Hz, 1H, H_{arom}), 5.51 (d, $^3J_{HH}$ = 5.86 Hz, 1H, H_{arom}), 5.08 (d, $^2J_{HH}$ = 14.82 Hz, 1H, H_{bridge}), 3.91 (s, 3H, NCH_3), 2.76 (m, $^3J_{HH}$ = 6.88, 1H, $CH(CH_3)_2$), 2.12 (s, 3H, CH_3), 1.19 (d, $^3J_{HH}$ = 7.03 Hz, 3H, $CHCH_3$), 1.15 (d, $^3J_{HH}$ = 7.03 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, $SiMe_4$): δ 173.29 ($C_{imid}Ru$), 157.52 ($C_{pyridine}$), 156.60 ($C_{pyridine}$), 139.41 ($C_{pyridine}$), 125.78 ($C_{pyridine}$), 124.47 ($C_{pyridine}$), 123.62 (C_{imid}), 123.12 (C_{imid}), 111.91 (C_{arom}), 101.79 (C_{arom}), 87.83 (C_{arom}), 85.68 (C_{arom}), 85.31 (C_{arom}), 84.86 (C_{arom}), 54.79 (CH_2), 37.75 (NCH_3), 31.26 (CH), 23.30 ($CHCH_3$), 21.47 ($CHCH_3$), 19.91 (CH_3). Anal. Calcd for $C_{20}H_{25}ClF_6N_3PRu$: C, 40.79; H, 4.28; N, 7.14. Found: C, 40.54; H, 4.17; N, 7.17.

Chloro(η^6-*p*-cymene)(κ^2*C*,*N*-3-isopropyl-1-(2-picolyl)-imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (1b). Transmetalation was carried out in CH_2Cl_2 (30 mL) with 3-isopropyl-1-(2-picolyl)imidazolium bromide (**b**; 283.2 mg, 1 mmol), Ag_2O (115.9 mg, 0.5 mmol), $[(p\text{-cymene})RuCl_2)]_x$ (306.2 mg, 1 mmol), and $NaPF_6$ (352.7 mg, 2.1 mmol). The product was an orange microcrystalline solid. Yield: 549.1 mg, 89%. ^{1}H NMR (acetone-d_6, 400 MHz, $SiMe_4$): δ 9.30 (d, $^3J_{HH}$ = 5.72 Hz, 1H, $H_{pyridine}$), 7.97 (t, 1H, $^3J_{HH}$ = 7.61 Hz, 1H, $H_{pyridine}$), 7.65 (d, $^3J_{HH}$ = 7.91 Hz, 1H, $H_{pyridine}$), 7.60 (d, $^3J_{HH}$ = 2.05 Hz, 1H, H_{imid}), 7.59 (d, $^3J_{HH}$ = 2.05 Hz, 1H, H_{imid}), 7.47 (t, $^3J_{HH}$ = 6.74 Hz, 1H, $H_{pyridine}$), 5.94 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.88 (d, $^3J_{HH}$ = 5.72 Hz, 1H, H_{arom}), 5.75 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.61 (d, $^2J_{HH}$ = 15.81 Hz, 1H, H_{bridge}), 5.58 (d, $^3J_{HH}$ = 6.16 Hz, 1H, H_{arom}), 5.08 (d, $^2J_{HH}$ = 15.53 Hz, 1H, H_{bridge}), 5.03 (m, $^3J_{HH}$ = 6.74, 1H, NCH), 2.85 (m, $^3J_{HH}$ = 6.74 Hz, 1H, $CH(CH_3)_2$), 2.19 (s, 3H, CH_3), 1.64 (d, $^3J_{HH}$ = 6.73 Hz, 3H, $NCHCH_3$), 1.38 (d, $^3J_{HH}$ = 6.44 Hz, 3H, $NCHCH_3$), 1.20 (d, $^3J_{HH}$ = 7.03 Hz, 3H, $CHCH_3$), 1.18 (d, $^3J_{HH}$ = 6.74 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100 MHz, $SiMe_4$): δ 174.09 ($C_{imid}Ru$), 159.52 ($C_{pyridine}$), 157.30 ($C_{pyridine}$), 140.31 ($C_{pyridine}$), 125.59 ($C_{pyridine}$), 125.26 ($C_{pyridine}$), 124.10 (C_{imid}), 119.78 (C_{imid}), 111.14 (C_{arom}), 103.46 (C_{arom}), 89.95 (C_{arom}), 86.88 (C_{arom}), 85.53 (C_{arom}), 85.32 (C_{arom}), 54.61 (CH_2), 53.21 (NCH), 32.30 (CH), 24.39 ($NCHCH_3$), 24.16 ($CHCH_3$), 24.04 ($NCHCH_3$), 21.07 ($CHCH_3$), 18.53 (CH_3). Anal. Calcd for $C_{22}H_{29}ClF_6N_3PRu$: C, 42.83; H, 4.74; N, 6.81. Found: C, 42.71; H, 4.58; N, 7.01.

Chloro(η^6-*p*-cymene)(κ^2*C*,*N*-3,4,5-trimethyl-1-(2-picolyl)-imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (1c). Transmetalation was carried out in CH_2Cl_2 (30 mL) with 3,4,5-trimethyl-1-(2-picolyl)imidazolium bromide (**c**; 282.18 mg, 1 mmol), Ag_2O (115.9 mg, 0.5 mmol), $[(p\text{-cymene})RuCl_2)]_x$ (306.2 mg, 1 mmol), and $NaPF_6$ (352.7 mg, 2.1 mmol). The product was an orange microcrystaline solid. Yield: 573.8 mg, 93%. ^{1}H NMR (acetone-d_6, 400 MHz, $SiMe_4$): δ 9.32 (d, $^3J_{HH}$ = 5.90 Hz, 1H, $H_{pyridine}$), 8.01 (t, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{pyridine}$), 7.81 (d, $^3J_{HH}$ = 7.82 Hz, 1H, $H_{pyridine}$), 7.50 (t, 1H, $^3J_{HH}$ = 6.69 Hz, 1H, $H_{pyridine}$), 5.93 (d, $^3J_{HH}$ = 5.89 Hz, 1H, H_{arom}), 5.89 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.74 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.59 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.52 (d, $^2J_{HH}$ = 15.63 Hz, 1H, H_{bridge}), 4.93 (d, $^2J_{HH}$ = 15.64 Hz, 1H, H_{bridge}), 3.85 (s, 3H, NCH_3), 2.84 (m, $^3J_{HH}$ = 6.92 Hz, 1H, CH), 2.34 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 1.23 (d, $^3J_{HH}$ = 7.02 Hz, 3H, $CHCH_3$), 1.21 (d, $^3J_{HH}$ = 6.79 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100 MHz, $SiMe_4$): δ 172.80 ($C_{imid}Ru$), 159.56 ($C_{pyridine}$), 157.58 ($C_{pyridine}$), 140.31 ($C_{pyridine}$), 128.07 (C_{imid}), 126.49 (C_{imid}), 125.80 ($C_{pyridine}$), 125.28 ($C_{pyridine}$), 112.26 (C_{arom}), 102.75 (C_{arom}), 89.73 (C_{arom}), 86.71 (C_{arom}), 85.62 (C_{arom}), 85.47 (C_{arom}), 51.64 (CH_2), 35.50 (NCH_3), 32.13 (CH), 23.80 (CH_3), 21.37 (CH_3), 18.56 (CH_3), 9.13 (CH_3), 8.79 (CH_3). Anal. Calcd for $C_{22}H_{29}ClF_6N_3PRu$: C, 42.83; H, 4.74; N, 6.81. Found: C, 42.92; H, 4.65; N, 6.74.

Chloro(η^6-*p*-cymene)(κ^2*C*,*N*-3-mesityl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (1d). Transmetalation was carried out in CH_2Cl_2 (30 mL) with 3-mesityl-1-(2-picolyl)imidazolium bromide (**d**; 328.3 mg, 1 mmol), Ag_2O (115.9 mg, 0.5 mmol), $[(p\text{-cymene})RuCl_2)]_x$ (306.2 mg, 1 mmol), and $NaPF_6$ (352.7 mg, 2.1 mmol). The product was an orange microcrystaline solid. Yield: 630.71 mg, 91%. ^{1}H NMR (acetone-d_6, 400 MHz, $SiMe_4$): δ 9.47 (d, $^3J_{HH}$ = 5.80 Hz, 1H, $H_{pyridine}$), 8.06 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{pyridine}$), 7.82 (d, 1H, $^3J_{HH}$ = 1.83 Hz, H_{imid}), 7.76 (d, $^3J_{HH}$ = 7.32 Hz, 1H, $H_{pyridine}$), 7.50 (t, 1H, $^3J_{HH}$ = 6.71 Hz, 1H, $H_{pyridine}$), 7.34 (d, 1H, $^3J_{HH}$ = 1.83 Hz, H_{imid}), 7.15 (s, 1H, $H_{mesityl}$), 6.97 (s, 1H, $H_{mesityl}$), 5.94 (d, $^3J_{HH}$ = 6.10 Hz, 2H, H_{arom}), 5.87 (d, $^3J_{HH}$ = 5.64 Hz, 1H, H_{arom}), 5.78 (d, $^2J_{HH}$ = 15.56 Hz, 1H, H_{bridge}), 5.56 (d, $^3J_{HH}$ = 5.80 Hz, 1H, H_{arom}), 5.51 (d, $^3J_{HH}$ = 5.19 Hz, 1H, H_{arom}), 5.26 (d, $^2J_{HH}$ = 15.57 Hz, 1H, H_{bridge}), 2.81 (m, 1H, $^3J_{HH}$ = 7.02 Hz, CH), 2.34 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.14 (d, $^3J_{HH}$ = 7.02 Hz, 3H, $CHCH_3$), 0.58 (d, $^3J_{HH}$ = 7.02 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100 MHz, $SiMe_4$): δ 176.68 ($C_{imid}Ru$), 160.62 ($C_{pyridine}$), 156.93 ($C_{pyridine}$), 140.50 ($C_{pyridine}$), 140.03 ($NC_{mesityl}$), 138.74 ($C_{mesityl}$), 136.57 ($C_{mesityl}$), 135.52 ($C_{mesityl}$), 130.21 ($C_{mesityl}$), 129.03 ($C_{mesityl}$), 126.17 (C_{imid}), 125.75 ($C_{pyridine}$), 125.27 ($C_{pyridine}$), 124.31 (C_{imid}), 109.14 (C_{arom}), 97.02 (C_{arom}), 90.93 (C_{arom}), 90.38 (C_{arom}), 88.66 (C_{arom}), 84.36 (C_{arom}), 55.19 (CH_2), 31.92 (CH), 24.19 (CH_3), 20.92 (CH_3), 20.13 (CH_3), 19.82 (CH_3), 18.30 (CH_3), 18.22 (CH_3). Anal. Calcd for $C_{28}H_{33}ClF_6N_3PRu$: C, 48.52; H, 4.80; N, 6.06. Found: C, 48.43; H, 4.86; N, 6.15.

Chloro(η^6-*p*-cymene)(κ^2*C*,*N*-3-methyl-1-(2-picolyl)-benzimidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (1e). Transmetalation was carried out in CH_2Cl_2 (30 mL) with 3-methyl-1-(2-picolyl)benzimidazolium bromide (**e**; 304.2 mg, 1 mmol), Ag_2O (115.9 mg, 0.5 mmol), $[(p\text{-cymene})RuCl_2)]_x$ (306.2 mg, 1 mmol), and $NaPF_6$ (352.7 mg, 2.1 mmol). The product was an orange microcrystaline solid. Yield: 549.5 mg, 86%. ^{1}H NMR (acetone-d_6, 400 MHz, $SiMe_4$): δ 9.34 (d, $^3J_{HH}$ = 5.86 Hz, 1H, $H_{pyridine}$), 8.04 (t, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{pyridine}$), 7.90 (d, $^3J_{HH}$ = 7.68 Hz, 1H, $H_{pyridine}$), 7.89 (m, 1H, $H_{benzimid}$), 7.68 (m, 1H, $H_{benzimid}$), 7.53 (t, 1H, $^3J_{HH}$ = 6.86 Hz, 1H, $H_{pyridine}$), 7.37 (m, 2H, $H_{benzimid}$), 6.13 (d, $^2J_{HH}$ = 16.11 Hz, 1H, H_{bridge}), 6.10 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 6.07 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.91 (d, $^3J_{HH}$ = 6.30 Hz, 1H, H_{arom}), 5.77 (d, $^3J_{HH}$ = 6.01 Hz, 1H, H_{arom}), 5.22 (d, $^2J_{HH}$ = 15.82 Hz, 1H, H_{bridge}), 4.22 (s, 3H, NCH_3), 2.91 (m, $^3J_{HH}$ = 7.03 Hz, 1H, CH), 2.23 (s, 3H, CH_3), 1.22 (d, $^3J_{HH}$ = 7.03 Hz, 3H, $CHCH_3$), 1.19 (d, $^3J_{HH}$ = 6.74 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100 MHz, $SiMe_4$): δ 190.45 ($C_{imid}Ru$), 158.59 ($C_{pyridine}$), 156.38 ($C_{pyridine}$), 140.56 ($C_{pyridine}$), 136.31 ($C_{benzimid}$), 134.61 ($C_{benzimid}$), 125.99 ($C_{pyridine}$), 125.59 ($C_{pyridine}$), 124.38 ($C_{benzimid}$), 124.36 ($C_{benzimid}$), 113.56 (C_{arom}), 111.44 ($C_{benzimid}$), 110.99 ($C_{benzimid}$), 103.29 (C_{arom}), 90.57 (C_{arom}), 87.64 (C_{arom}), 86.53 (C_{arom}), 51.16 (CH_2), 35.32 (NCH_3), 32.18 (CH), 23.58 (CH_3), 21.53 (CH_3), 18.64 (CH_3). Anal. Calcd for $C_{24}H_{27}ClF_6N_3PRu$: C, 45.11; H, 4.26; N, 6.58. Found: C, 45.02; H, 4.31; N, 6.64.

Chloro(η^6-*p*-cymene)(κ^2*C*,*N*-3-methyl-1-(2-picolyl)-4,5-dichloroimidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (1f). Transmetalation was carried out in CH_2Cl_2 (30 mL) with 3-methyl-1-(2-picolyl)-4,5-dichloroimidazolium bromide (**f**; 323.0 mg, 1 mmol), Ag_2O (115.9 mg, 0.5 mmol), $[(p\text{-cymene})RuCl_2)]_x$ (306.2 mg, 1 mmol), and $NaPF_6$ (352.7 mg, 2.1 mmol). The product was a yellow microcrystaline solid. Yield: 605.2 mg, 92%. ^{1}H NMR (acetone-d_6, 400 MHz, $SiMe_4$): δ 9.32 (d, $^3J_{HH}$ = 5.76 Hz, 1H, $H_{pyridine}$), 8.08 (t, $^3J_{HH}$ = 7.63 Hz, 1H, $H_{pyridine}$), 7.90 (d, $^3J_{HH}$ = 7.76 Hz, 1H, $H_{pyridine}$), 7.57 (t, 1H,

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$^3J_{HH}$ = 6.70 Hz, 1H, $H_{pyridine}$), 6.07 (d, $^3J_{HH}$ = 6.17 Hz, 1H, H_{arom}), 6.02 (d, $^3J_{HH}$ = 6.16 Hz, 1H, H_{arom}), 5.90 (d, $^3J_{HH}$ = 6.29 Hz, 1H, H_{arom}), 5.77 (d, $^3J_{HH}$ = 5.89 Hz, 1H, H_{arom}), 5.76 (d, $^2J_{HH}$ = 16.07 Hz, 1H, H_{bridge}), 5.08 (d, $^2J_{HH}$ = 16.08 Hz, 1H, H_{bridge}), 4.00 (s, 3H, NCH_3), 2.90 (m, $^3J_{HH}$ = 6.88 Hz, 1H, CH), 2.22 (s, 3H, CH_3), 1.27 (d, $^3J_{HH}$ = 6.70 Hz, 3H, $CHCH_3$), 1.21 (d, $^3J_{HH}$ = 6.96 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100 MHz, $SiMe_4$): δ 178.39 ($C_{imid}Ru$), 159.84 ($C_{pyridine}$), 156.10 ($C_{pyridine}$), 140.72 ($C_{pyridine}$), 126.37 ($C_{pyridine}$), 125.88 ($C_{pyridine}$), 118.10 (C_{imid}), 117.42 (C_{imid}), 113.77 (C_{arom}), 102.23 (C_{arom}), 89.77 (C_{arom}), 87.67 (C_{arom}), 86.62 (C_{arom}), 86.37 (C_{arom}), 52.62 (CH_2), 36.93 (NCH_3), 32.05 (CH), 23.24 (CH_3), 21.79 (CH_3), 18.62 (CH_3). Anal. Calcd for $C_{20}H_{23}Cl_3F_6N_3PRu$: C, 36.52; H, 3.52; N, 6.39. Found: C, 36.48; H, 3.55; N, 6.31.

Chloro(η^6-*p*-cymene)(κ^2C,N-3-phenyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (1g). Transmetalation was carried out in CH_2Cl_2 (30 mL) with 3-phenyl-1-(2-picolyl)imidazolium bromide (**g**; 317.2 mg, 1 mmol), Ag_2O (115.9 mg, 0.5 mmol), $[(p\text{-cymene})RuCl_2)]_x$ (306.2 mg, 1 mmol), and $NaPF_6$ (352.7 mg, 2.1 mmol). The product was an orange microcrystaline solid. Yield: 540.32 mg, 83%. ^1H NMR (acetone-d_6, 400 MHz, $SiMe_4$): δ 9.42 (d, $^3J_{HH}$ = 5.72 Hz, 1H, $H_{pyridine}$), 8.03 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{pyridine}$), 7.91 (m, 2H, H_{arom}), 7.71 (d, $^3J_{HH}$ = 1.76 Hz, 1H, H_{imid}), 7.69 (d, $^3J_{HH}$ = 7.50 Hz, 1H, $H_{pyridine}$), 7.57 (m, 3H, H_{arom}), 7.56 (d, $^3J_{HH}$ = 1.76 Hz, 1H, H_{imid}), 7.49 (t, $^3J_{HH}$ = 6.74 Hz, 1H, $H_{pyridine}$), 5.73 (d, $^2J_{HH}$ = 15.53 Hz, 1H, H_{bridge}), 5.68 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.60 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.36 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 5.16 (d, $^2J_{HH}$ = 15.52 Hz, 1H, H_{bridge}), 5.04 (d, $^3J_{HH}$ = 6.15 Hz, 1H, H_{arom}), 2.45 (m, $^3J_{HH}$ = 7.03 Hz, 1H, CH), 1.92 (s, 3H, CH_3), 1.10 (d, $^3J_{HH}$ = 7.03 Hz, 3H, $CHCH_3$), 0.95 (d, $^3J_{HH}$ = 7.03 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, $SiMe_4$): δ 175.10 ($C_{imid}Ru$), 158.74 ($C_{pyridine}$), 155.38 ($C_{pyridine}$), 139.56 ($C_{pyridine}$), 139.26 (C_{NPh}), 129.59 (C_{Ph}), 128.99 (C_{Ph}), 128.10 (C_{Ph}), 125.28 ($C_{pyridine}$), 125.19 ($C_{pyridine}$), 124.66 (C_{imid}), 123.08 (C_{imid}), 109.52 (C_{arom}), 101.50 (C_{arom}), 89.97 (C_{arom}), 86.24 (C_{arom}), 85.09 (C_{arom}), 84.30 (C_{arom}), 54.51 (CH_2), 31.21 (CH), 22.98 ($CHCH_3$), 21.72 ($CHCH_3$), 18.37 (CH_3). Anal. Calcd for $C_{25}H_{27}ClF_6N_3PRu$: C, 46.12; H, 4.18; N, 6.45. Found: C, 46.07; H, 4.22; N, 6.49.

Crystal Structure Analysis. Crystals of **1a**,**f** suitable for X-ray structural determination were mounted on glass fibers and then transferred to the cold nitrogen gas stream of a Bruker Smart APEX CCD three-circle diffractometer (T = 100 K) with a sealed-tube source and graphite-monochromated Mo Kα radiation (α = 0.710 73 Å) at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Four sets of frames were recorded over a hemisphere of the reciprocal space by ω scans with $\delta(\omega)$ = 0.30 and an exposure of 10 s per frame. Correction for absorption was applied by scans of equivalents using the SADABS program.[51] An insignificant crystal decay correction was also applied. The structures were solved by direct methods and refined on F^2 by full-matrix least squares (SHELX97) by using all unique data.[52] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions and treated as riding atoms. For **1a** the PF_6 anion and the chlorido ligand were found to be disordered. The PF_6 anion was refined over two different orientations with complementary occupancies (the final values at convergence were 0.89 and 0.11). In the cation, the chloride ligand was refined in two positions with complementary occupancy factors (the final values were 0.90 and 0.10). The program ORTEP-3 was used for plotting.[53] In the Supporting Information, Table S2 summarizes the crystal data and data collection and refinement details for **1a**,**f**. CCDC 888193 and 888194 contain supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Typical Procedure for Catalytic Transfer Hydrogenation. Ketone or imine (2.0 mmol), catalyst 0.2 mol % (0.004 mmol) KOH (0.2 mmol), 1,3,5-trimethoxybenzene (0.5 mmol), and ^{i}PrOH (4 mL) were placed in a 10 mL vial and stirred on a preheated oil bath (82 °C). Aliquots (0.2 mL) were taken at fixed times, and the reaction mixture was quenched with Et_2O (3 mL) and filtered through a short pad of SiO_2. The filtrate was subjected to GC-MS and ^1H NMR analysis. All data reported are an average of at least two runs.

Typical Procedure for Catalytic N-alkylation of Amines with Alcohols. Amine (2.0 mmol), alcohol (2.0 mmol), catalyst 0.5 mol % (0.01 mmol), KOH (1 mmol), 1,3,5-trimethoxybenzene (0.5 mmol), and toluene (2 mL) were placed in a 10 mL vial and stirred on a preheated oil bath (100 °C) for 15 h. Aliquots (0.2 mL) were taken at fixed times, and the reaction mixture was quenched in Et_2O (3 mL) and filtered through a short pad of SiO_2. The filtrate was subjected to GC-MS and ^1H NMR analysis. All data reported are an average of at least two runs.

■ ASSOCIATED CONTENT

Supporting Information

A table detailing catalytic transfer hydrogenation with higher catalyst loadings and a table and CIF files giving crystallographic data for compounds **1a**,**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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