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# Half-Sandwich Ruthenium(II) Picolyl-NHC Complexes: Synthesis, Characterization, and Catalytic Activity in Transfer Hydrogenation Reactions

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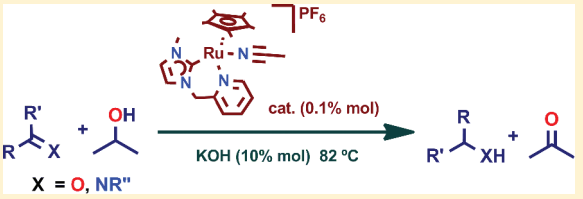
Supporting Information

**ABSTRACT:** Pentamethylcyclopentadienyl ruthenium(II) complexes with picolyl-functionalized N-heterocyclic carbenes [($\eta^5$-$C_5Me_5$)Ru(L)($CH_3CN$)][$PF_6$] (L = 3-methyl-1-(2-picolyl)imidazol-2-ylidene (**1a**), 3-isopropyl-1-(2-picolyl)imidazol-2-ylidene (**1b**), 3-phenyl-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**)) have been synthesized and characterized. Compounds **1a**,**b** were recrystallized as $BAr_4^F$ salts (anion $BAr_4^{F-}$ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), giving **2a**,**b**. X-ray crystal structures of the acetonitrile adduct **2a** and the dioxygen compound **2b** are also reported. Furthermore, carbonyl derivatives **3a**−**f** have been prepared, characterized, and used to study the donor properties of the picolylcarbene ligands (L) via infrared spectroscopy. Compounds **1a**−**f** show catalytic activity in transfer hydrogenation of ketones. Notably, complex **1a** was found to be a very efficient and versatile catalyst toward transfer hydrogenation of a wide range of ketones and imines.




## INTRODUCTION

In recent years, 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.[1] Many efforts have been placed in the design of new NHC ligands to tune their steric and electronic properties toward enhancing the catalytic activity of their complexes. 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. Many reports have been published with phosphine,[2] pyrimidine,[3] ether,[4] thioether,[5] carboxylate,[6] indenyl,[7] oxazoline,[8] and pyridine[9] as donor groups. Ligands with nitrogen donors have attracted the most attention; particularly, metal complexes bearing pyridine-functionalized NHCs of Ir,[10] Ag,[11] Pd,[12] Ru,[13] and Ni[14] have been synthesized. Those complexes have shown catalytic activity in olefin polymerization reactions,[15] C−C coupling reactions,[16] transfer hydrogenation of ketones,[17] hydrosilylation reactions,[18] and reduction of nitroarenes.[19] 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.[20] This leads to a versatile ligand group for the study of coordination properties.

Ruthenium compounds with cyclopentadienyl type ligands have been greatly studied because they are able to give rise to metastable 16-electron species with many potential catalytic applications.[21] Nolan and co-workers have synthesized half-sandwich ruthenium complexes bearing monodentate NHCs proven to be active toward olefin metathesis and racemization of chiral alcohols.[22] In addition, the synthesis of Cp ruthenium complexes (Cp = cyclopentadienyl) with NHCs which showed catalytic activity for alkyne dimerization has been reported.[23] Recently, Peris reported the synthesis and catalytic activity of two complexes of ruthenium with Cp-NHC-functionalized ligands.[24] 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 (Figure 1).[25] However, to the best of our knowledge there are no reports of cyclopentadienyl Ru picolyl-NHC complexes.

Transfer hydrogenation reactions of C═O and C═NR groups using metal complexes as catalysts have been extensively studied and continue to generate a high degree of interest, given the need to develop environmentally friendly and simple processes.[26] NHC complexes of iridium,[27] rhodium,[28] and ruthenium[29] have demonstrated good activity in those reactions, particularly showing significant applications in asymmetric reductions[30] and racemization of chiral alcohols.[31] Recently, Morris and co-workers reported the hydrogenation of substituted acetophenones using a pentamethylcyclopentadienyl ruthenium(II) NHC complex.[32]

Our group has broad experience with the stoichiometric chemistry of pentamethylcyclopentadienyl ruthenium complexes bearing P,P and P,N ligands.[33,34] We aim to replace the

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phosphine fragment by an NHC, pursuing less toxic complexes toward greener chemistry. Here we report a series of novel half-sandwich ruthenium(II) picolyl-NHC complexes in which the ligands have been varied systematically to study the influence of the wingtip substituent as well as the substituents at the C-4 and C-5 carbons of the imidazole ring on the steric and electronic properties of the metal center. To obtain further information on the donor strength of the carbene ligands, CO analogues were synthesized and analyzed by infrared spectroscopy. The new ruthenium compounds are active toward transfer hydrogenation of a wide variety of ketones and imines under mild conditions with almost quantitative conversions and short reaction times.

## RESULTS AND DISCUSSION

**Synthesis of Precursors of Picolyl-NHC Ligands.** A series of picolylimidazolium salts (**a**−**f**, Scheme 1) have been prepared as ligand precursors following literature procedures[35−38] and, in the case of 3-(phenyl)-1-(2-picolyl)imidazolium bromide and 3-(methyl)-1-(2-picolyl)-4,5-dichloroimidazolium bromide, by reaction of the alkyl imidazolium and picolyl bromide in a nonpolar solvent. The salts were isolated in high yields and characterized by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy. The $^1$H NMR spectra of **c** and **f** in DMSO-$d_6$ showed a characteristic low-field resonance for the $C_2$ imidazolium proton at 10.95 and 10.81 ppm, respectively.

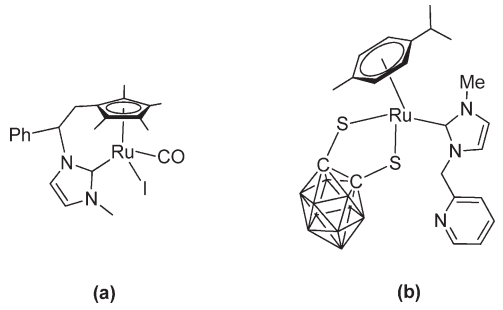
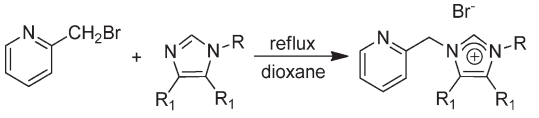



**Figure 1.** (a) [Ru(Cp-NHC)(CO)I][24] and (b) [(*p*-cymene)Ru-(Cab$^{S,S}$)(3-methyl-1-picolylimidazolin-2-ylidene)].[25]

**Scheme 1**

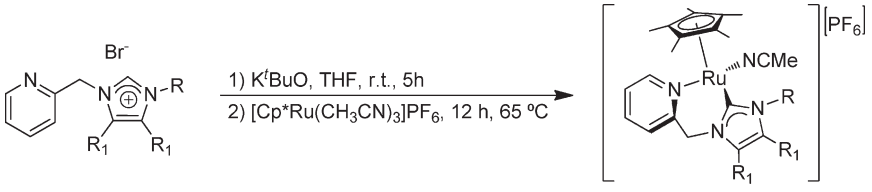



**Synthesis of $\eta^5$-Pentamethylcyclopentadienyl Picolyl-NHC Ru(II) Complexes.** The Ru(II) cationic complexes **1a**−**f** (Scheme 2) have been prepared as hexafluorophosphate salts upon treatment of the metal precursor $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ with a THF solution of the appropriate ligand, generated in situ by the reaction of the picolylimidazolium bromide **a**−**f** and an excess of K$^t$BuO. The reaction is complete after 12 h at 65 °C. All products were purified by column chromatography on $Al_2O_3$, with $CH_3CN$ as eluent, and isolated in good yields. The new Ru(II) compounds were characterized by $^1$H and $^{13}$C{$^1$H} NMR and elemental analysis. All the ruthenium picolyl-NHC complexes are very soluble in THF, acetone, and chlorinated solvents but insoluble in nonpolar solvents such as hexane, $Et_2O$, and petroleum ether.

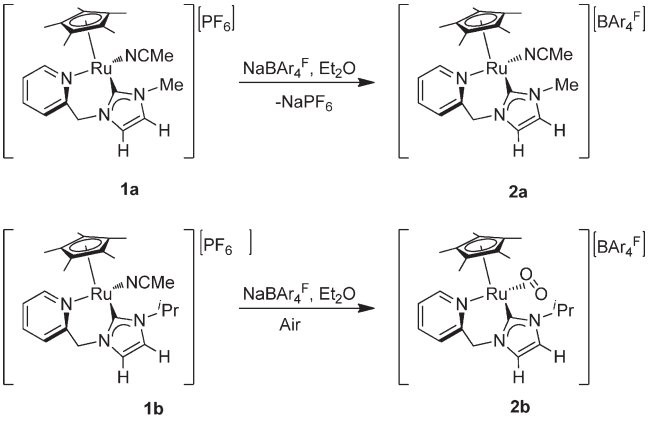
$^1$H NMR spectra of compounds **1a**−**f** lack the $C_2$ imidazolium proton resonance signals at 10−12 ppm, indicating the coordination of the $C_2$ carbene carbon to the metal center. Also, there are two characteristic AB doublet signals at 5−6 ppm with coupling constants of 14−15 Hz corresponding to the methylene bridge protons, which become diastereotopic after coordination of the ligands to the Ru atom, given the $\kappa^2$-C,N coordination. Similar NMR features for $(\eta^5\text{-}C_5Me_5)Ru$ complexes with $\kappa^2$-P,N chelating phosphinopicoline ligands have been observed.[34b] Furthermore, this behavior has been reported by Xue and co-workers in the synthesis of Ru(II) carbonyl Py-NHC complexes.[39] The $^{13}$C{$^1$H} NMR signals of the carbene carbons atoms of **1a**−**f** (191−209 ppm) are located as expected for $(\eta^5\text{-}C_5Me_5)Ru(NHC)$ compounds.[22,23,32] It is interesting to note the displacement to lower field, up to 209 ppm, of the NMR resonance of the $C_2$ carbon atom corresponding to the benzoimidazole analogue **1e**. It is possible to explain this observation due to destabilization in the imidazolium ring conjugation produced by the attached benzene ring, which leads to a lower electron density at the $C_2$ carbon.

Many attempts to crystallize compounds **1a**−**f** were made in different solvent combinations. However, it was not possible to

**Scheme 2**



**Scheme 3**



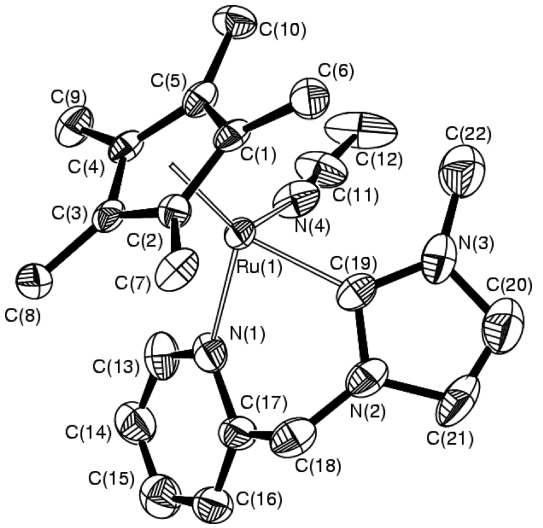




**Figure 2.** ORTEP view of the cationic complex in **2a**, $[Ru(\eta^5\text{-}C_5Me_5)(NHC\text{-}\kappa^2C,N)(NCCH_3\text{-}\kappa^1N)][B(Ar^F)_4]$ (NHC = 3-methyl-1-(2-picolyl)imidazol-2-ylidene). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−cyclopentadienyl (centroid) = 1.811(2), Ru(1)−C(19) = 2.059(5), Ru(1)−N(1) = 2.106(4), Ru(1)−N(4) = 2.047(5), C(19)−N(2) = 1.343(7), C(19)−N(3) = 1.356(7); N(4)−C(11) = 1.128(7); C(19)−Ru(1)−N(1) = 84.3(2), C(19)−Ru(1)−N(4) = 86.9(2), N(1)−Ru(1)−N(4) = 91.8(2), N(2)−C(19)−N(3) = 105.3(5); N(4)−C(11)−C(12) = 172.4(8).

obtain crystals suitable for X-ray diffraction. Hence, an anion exchange process of compounds **1a,b** from $PF_6$ to $BAr_4^F$ ($Ar^F$ = 3,5-bis(trifluoromethyl)phenyl) was completed. The anion exchange was accomplished quantitatively by stirring an ether solution of **1a** and $NaBAr_4^F$ under argon for 24 h at room temperature. The product **2a** was then filtered through Celite to remove $NaPF_6$ to yield a brown-red solid. After recrystallization on $Et_2O$/petroleum (1/2) crystals that allowed us to unambiguously determine the molecular structure of **2a** by X-ray diffraction were obtained. On the other hand, with complex **1b** the anion exchange process was completed in air, and after following an experimental procedure similar to that previously mentioned the $\eta^2$-dioxygen complex **2b** was obtained. Crystals of **2b** suitable for

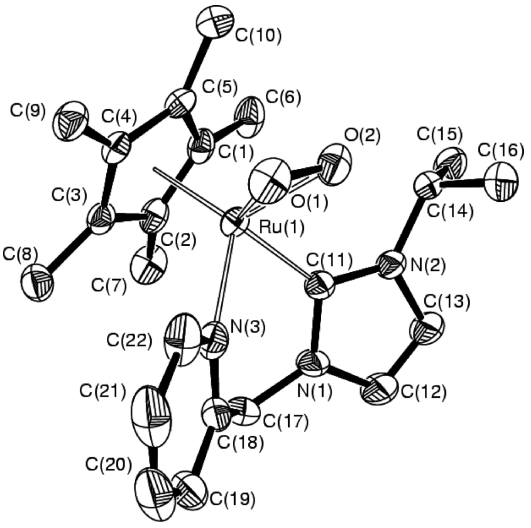



**Figure 3.** ORTEP view of the cationic complex in **3b**, $[Ru(\eta^5\text{-}C_5Me_5)(NHC\text{-}\kappa^2C,N)(\eta^2\text{-}O_2)][B(Ar^F)_4]$ (NHC = 3-isopropyl-1-(2-picolyl)imidazol-2-ylidene). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−cyclopentadienyl (centroid) = 1.863(2), Ru(1)−C(11) = 2.051(3), Ru(1)−N(3) = 2.155(3), Ru(1)−O(1) = 1.995(2), Ru(1)−O(2) = 2.029(3), O(1)−O(2) = 1.390(4), C(11)−N(1) = 1.349(4), C(11)−N(2) = 1.347(4); O(1)−Ru(1)−O(2) = 40.41(11), O(1)−Ru(1)−C(11) = 115.81(12), O(2)−Ru(1)−C(11) = 85.68(12), O(1)−Ru(1)−N(3) = 83.54(12), O(2)−Ru(1)−N(3) = 107.20(11), C(11)−Ru(1)−N(3) = 84.33(12), N(1)−C(11)−N(2) = 104.6(3).

X-ray diffraction were obtained after recrystallization on $Et_2O$/petroleum (1/2) (Scheme 3).

The $\eta^2$-dioxygen complex **2b** is stable in the solid state as well as in solutions of $Et_2O$ and $CH_2Cl_2$. In previous work our group reported dioxygen compounds containing the fragment $\{(\eta^5\text{-}C_5Me_5)Ru\}$, but in those cases the dissolution of the complexes was unstable and led to transfer of dioxygen to the phosphino ligand.[40a] However, oxygen transfer to the imidazolidene was not observed, giving the possibility to explore in the future the oxygen transfer capabilities of **2b** to other substrates. The stability of **2b** is remarkable, as it is inverse to that of other reported dioxygen complexes containing imidazolidene ligands that easily undergo oxidation on the metal center.[40b]

Complexes **2a,b** were unambiguously characterized by X-ray diffraction studies (Figures 2 and 3).

Both complexes adopt a piano stool geometry about the ruthenium center, with the corresponding chelating NHC and acetonitrile (**2a**) or $\eta^2$-dioxygen ligands (**2b**). The $Ru-C_{carbene}$ bonds, 2.059(5) Å in **2a** and 2.051(3) Å in **2b**, are slightly larger than that of the complex $[Ru(\eta^5\text{-}C_5Me_5)(C-NH_2)(py)]PF_6$, 2.03(1) Å,[32] the only previously reported structure of a $(\eta^5\text{-}C_5Me_5)Ru$ cationic complex containing a chelating NHC ligand, but it is in the expected range of other $Ru(\eta^5\text{-}C_5Me_5)(NHC)L_2$ complexes.[6a,23b,24] The $Ru-N_{pyridyl}$ lengths found in **2a,b**, 2.106(4) and 2.155(3) Å, respectively, are also comparable to the 2.156(8) Å found for $Ru(\eta^5\text{-}C_5Me_5)(C-NH_2)(py)]PF_6$.[32] The acetonitrile ligand in **2a** bonds linearly with characteristics similar to those found for other $Ru(\eta^5\text{-}C_5Me_5)$ acetonitrile complexes such as $[(\eta^5\text{-}C_5Me_5)Ru(MeCN)(\kappa^2\text{-}3\text{-}Ph_2P\text{-}2\text{-}Me_2N\text{-}indene)][SO_3CF_3]$[41a] and $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)(^{Me}Tpm)][PF_6]$ ($^{Me}Tpm$ = tris(3,5-dimethylpyrazolyl)methane).[41b]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**Scheme 4**

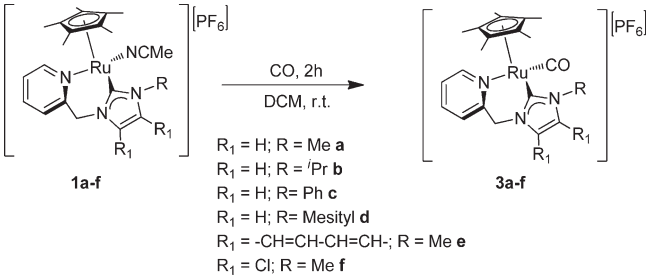



**Table 1. Selected IR Data (Nujol, $cm^{-1}$) for Compounds 3a−f and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(^iPr_2PCH_2Py)]BPh_4$**

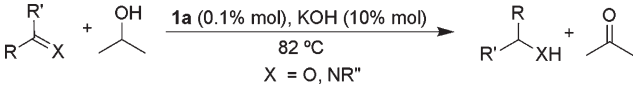
| | $\nu$(C═O) |
|---|---|
| **3a** | 1925 |
| **3b** | 1920 |
| **3c** | 1929 |
| **3d** | 1928 |
| **3e** | 1929 |
| **3f** | 1937 |
| $[(\eta^5\text{-}C_5Me_5)Ru(CO)(^iPr_2PCH_2Py)]BPh_4$[44] | 1937 |

Parameters for the dioxygen ligand in **2b** indicate a $\eta^2$-symmetrical disposition. Also, the $O_1-O_2$ bond distance is intermediate between those of free dioxygen and peroxide ligand, as well as close to those found in $Ru(\eta^5\text{-}C_5Me_5)$ complexes containing bidentate phosphines such as $[Ru(\eta^5\text{-}C_5Me_5)(O_2)(dippe)][BPh_4]$ (dippe = 1,2-bis(diisopropylphosphino)ethane),[42a] $[Ru(\eta^5\text{-}C_5Me_5)(O_2)(dppm)][BPh_4]$ (dppm = 1,1-bis(diphenylphosphino)methane),[42b] and $[Ru(\eta^5\text{-}C_5Me_5)(O_2)(\kappa^2\text{-}P,N\text{-}^iPr_2PCH_2Quin)][BAr'_4]$.[42c]

**Synthesis of Carbonyl Derivatives.** Several attempts have been made to establish the donor properties of NHCs,[43] and the carbonyl derivatives of pentamethylcyclopentadienyl Ru(II) complexes provide the opportunity to assess the basicity of NHCs via infrared and NMR spectroscopy. The new carbonyl complexes **3a**−**f** can be easily synthesized by bubbling CO through a DCM solution of the acetonitrile precursors **1a**−**f** (Scheme 4).

Infrared absorption energies corresponding to CO stretching from compounds **3a**−**f** provide valuable information regarding the donor strength of the picolyl-NHC ligands (Table 1). The difference in wingtip substituent does not significantly affect the CO absorption energies. On the other hand, compound **3f** exhibits the highest stretching frequency, indicative of less back-donation to CO from the metal center and a less electron donating ligand set; this is consistent with the inclusion of Cl on the NHC. It is interesting to note that compounds **3a**−**e** show significantly lower stretching frequencies on comparison with those of **3f** and the $[(\eta^5\text{-}C_5Me_5)Ru(CO)(^iPr_2PCH_2Py)]BPh_4$ analogue; this experimental evidence reinforces the fact that NHCs are stronger $\sigma$ donors in comparison to phosphines. It is necessary to modify the NHC backbone via the inclusion of a chloride atom on the NHC, as observed for **3f**, to diminish the donating power of the ligand up to being comparable with phosphines.

**Scheme 5**




**Catalytic Transfer Hydrogenation.** A few ruthenium NHC complexes have been reported as catalysts for the transfer hydrogenation of ketones.[3b,45] Therefore, complexes **1a**,**b**,**e**,**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 5).

The reduction of acetophenone to 1-phenylethanol was used as a representative reaction to screen the performance of Ru picolylcarbene catalysts. The results given in Table 2 show the influence of the wingtip and imidazole backbone substituents on the catalytic activity. Catalysts containing a Me (entries 1, 5, and 6) as a wingtip substituent are more active than those containing isopropyl or mesityl (entries 3 and 4). This behavior indicates that steric effects may be playing an important role in the catalytic activity. However, it is important to note that the lower donor character of the ligand with the chloro substituents on the imidazole backbone in compound **1f** (entry 6) shows a significantly lower activity than its analogue **1a** (entry 1) under the same reaction conditions. Thus, electronic properties may also account for the catalytic activity, although not as much as steric effects. Compound **1a** showed the best activity even with catalyst loadings as low as 0.1 mol %, giving a TOF up 100 $min^{-1}$.

Catalyst **1a** proved to be the most efficient of these 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** toward transfer hydrogenations (Table 3). Aromatic halo substituents have an enhancing effect on the catalytic activity, showing quantitative results on the formation of the corresponding alcohols (entries 2 and 3). However, MeO-substituted acetophenones showed lower yields (entries 4−6), indicating a less efficient hydrogenation process. Thus, electron-withdrawing groups on acetophenones benefit the catalytic activity while electron donating groups decrease it. On the other hand, benzophenone is quantitatively reduced to 1,1-diphenylmethanol (entry 7).

Complex **1a** was demonstrated to be very active toward a variety of alkyl ketones. Particularly, cyclohexanone was reduced to cyclohexanol almost quantitatively (entry 8). Also **1a** showed activity for the synthesis of 2-(1-hydroxyethyl)cyclohexanol (entry 9), which is an important building block in organic chemistry. However, the presence of two ketone groups diminishes the reaction yields, even with an increased reaction time. Unsaturated ketones are interesting substrates for TH reactions because they may undergo reduction on the carbonyl and/or olefin moiety. Nonetheless, **1a** proved to selectively reduce the carbonyl moiety on 6-methylhept-5-en-2-one (entry 10). Moreover, 2-acetylpyridine is efficiently hydrogenated (entry 11) almost quantitatively with an increased reaction time of 3 h. Furthermore, complex **1a** works as an efficient catalyst in the hydrogenation of *N*-benzylideneaniline (entry 12), demonstrating the versatility of the new catalyst toward the hydrogenation of ketones and imines. Our catalyst system has exhibited much better catalytic activity and works on a wider scope of substrates than do previously reported ruthenium pyridyl-NHC

**Table 2. Influence of Wingtips and Backbone Substituents on the Catalytic Activity of Ru Picolylcarbene Complexes[a]**

| entry | catalyst | cat. R wingtip group | cat. $R_1$ backbone group | $t$ (min)[b] | $TOF_{50}$ ($min^{-1}$)[c] |
|---|---|---|---|---|---|
| 1 | **1a** | Me | H | 10 | 62 |
| 2 | **1a** | Me | H | 60 | 100[d] |
| 3 | **1b** | $^i$Pr | H | 40 | 16 |
| 4 | **1d** | mesityl | H | >1000 | 0.38 |
| 5 | **1e** | Me | −CH═CH−CH═CH− | 30 | 16 |
| 6 | **1f** | Me | Cl | 15 | 20 |

[a] Transfer hydrogenation of acetophenone reaction conditions: 2.00 mmol of acetophenone, KOH (10 mol %), catalyst (1 mol %) in 4 mL of *i*PrOH. [b] Reaction time required for conversions >90%. [c] Turnover frequency at 50% conversion. [d] 0.1 mol % of catalyst loading.

complexes.[46] Furthermore, compound **1a** has shown better performance when compared with $(C_5Me_5)Ir(NHC)$ complexes, as evidenced in the lower reaction times and catalyst loadings needed to complete the reactions.[47] It is reasonable to assume that catalytic transfer hydrogenation reaction of **1a** occurs via a monohydride mechanism, as has been reported for other ruthenium Cp analogues.[48]

## CONCLUSION

We have reported the synthesis and characterization of novel $[(\eta^5\text{-}C_5Me_5)Ru(picolyl\text{-}NHC)(CH_3CN)][PF_6]$ (**1a**−**f**) complexes in which the substituents on the NHC backbone and wingtip have been modified. The crystal structures of two of the complexes prepared (**2a**,**b**) after completing an anion exchange process have been described. The reactivity of such complexes toward CO led to the production of carbonyl derivatives **3a**−**f**. An infrared spectroscopy study of the CO stretching frequencies of carbonyl complexes **3a**−**f** has shown that picolyl-NHC ligands **a**−**d** are stronger donors than the analogous picolyl-phosphine ligand. Furthermore, the inclusion of chloride on the NHC backbone is needed to obtain a less donating ligand (**f**) comparable to phosphines.

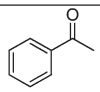
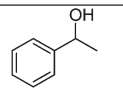
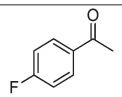
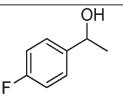
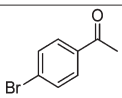
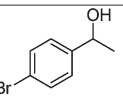
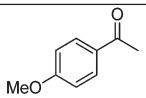
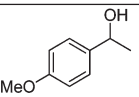
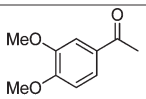
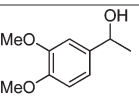
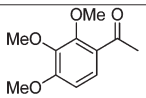
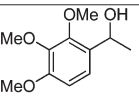
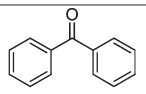
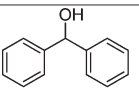
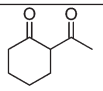
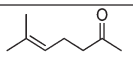
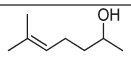
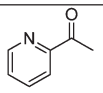
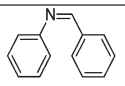
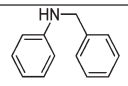
The catalytic study of $[(\eta^5\text{-}C_5Me_5)Ru(picolyl\text{-}NHC)(CH_3CN)][PF_6]$ complexes **1a**−**f** toward transfer hydrogenation reactions of acetophenone was completed, showing high activity in most cases. The results also showed that picolylcarbenes are tunable ligands that with small changes can lead to an increase of catalytic activity. Particularly, complex **1a** has proved to be a versatile and efficient transfer hydrogenation catalyst with outstanding activity in comparison to its analogues and other ruthenium and iridium complexes.[46,47] Furthermore, **1a** has shown high tolerance to functional groups on the reduction of a wide range of ketones and imines.

## EXPERIMENTAL SECTION

**General Methods.** Unless otherwise stated, all manipulations were carried out under dry nitrogen or argon using conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling range 40−60 °C) were obtained free of oxygen and water with an Innovative Technology Inc. solvent purification system. Acetonitrile and dichloromethane were of anhydrous quality and used as received. All solvents were degassed immediately prior to use. 3-Methyl-1-(2-picolyl)imidazolium bromide (**a**),[35] 3-isopropyl-1-(2-picolyl)imidazolium bromide (**b**),[36] 3-mesityl-1-(2-picolyl)imidazolium bromide (**d**),[37] 3-methyl-1-(2-picolyl)benzoimidazolium bromide (**e**),[38] $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$,[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 Varian INOVA 400 MHz and Varian Inova 600 MHz spectrometers, and chemical shifts are reported relative to TMS for $^1H$ and $^{13}C\{^1H\}$ and 85% $H_3PO_4$ for $^{31}P\{^1H\}$. Assignments of $^1H$ and $^{13}C\{^1H\}$ NMR spectra were made on the basis of 2D NMR experiments. IR spectra were recorded in Nujol mulls with a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. Microanalyses were performed with a LECO CHNS-932 elemental

**Table 3. Catalytic Transfer Hydrogenation**

| Entry | Substrate | Product | t (h) | TON | % yield |
|---|---|---|---|---|---|
| 1 |  |  | 1 | 930 | 93 |
| 2 |  |  | 1 | 1000 | > 99 |
| 3 |  |  | 1 | 1000 | > 99 |
| 4 |  |  | 1 | 740 | 74 |
| 5 |  |  | 1 | 820 | 82 |
| 6 |  |  | 1 | 830 | 83 |
| 7 |  |  | 1 | 1000 | > 99 |
| 8 |  |  | 1 | 1000 | > 99 |
| 9 |  |  | 1 (3) | 100 (270) | 10 (27) |
| 10 |  |  | 1 | 950 | 95 |
| 11 |  |  | 1 (3) | 740 (> 990) | 74 (> 99) |
| 12 |  |  | 1 | 1000 | > 99 |

[a] Transfer hydrogenation reaction conditions: 2.00 mmol of substrate, KOH (10 mol %), catalyst (0.1 mol %) in 4 mL of $^i$PrOH at 82 °C. [c] Product yield determined by GC-MS using 1,3,5-trimethoxybenzene as an internal standard. Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time *t*.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analyzer by Servicios Centrales de Ciencia y Tecnología, Universidad de Cádiz. GC-MS analyses were recorded in an Agilent 6890N device.

**3-Phenyl-1-(2-picolyl)imidazolium Bromide (c).** 2-(Bromomethyl)pyridine hydrobromide (1.01 g, 4 mmol) was neutralized using a saturated aqueous solution of $Na_2CO_3$. The released 2-(bromomethyl)pyridine was extracted using ice-cold diethyl ether (3 × 30 mL). The solution was dried with $Na_2SO_4$ and filtered into a dissolution of 1-phenylimidazole (0.58 g, 4 mmol) in 1,4-dioxane (30 mL). Diethyl ether was removed under reduced pressure and the reaction mixture refluxed for 12 h. The volatiles were removed under reduced pressure, and the oily residue was purified by repetitive precipitation from $CH_2Cl_2/Et_2O$. The resulting light brown solid was dried in vacuo. Yield: 0.76 g, 60%. $^1$H NMR (DMSO-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 10.95 (s, 1H, NCHN), 8.45 (d, $^3J_{HH}$ = 4.69 Hz, 1H, $H_{py}$), 7.85 (s, 1H, $H_{imid\ backbone}$), 7.82 (d, 1H, $^3J_{HH}$ = 7.97 Hz, 1H, $H_{py}$), 7.78 (s, 1H, $H_{imid\ backbone}$), 7.68 (m, 2H, $H_{Ph}$), 7.65 (t, $^3J_{HH}$ = 7.76 Hz, 1H, $H_{py}$), 7.46 (m, 3H, $H_{Ph}$), 7.21 (m, 1H, $H_{py}$), 5.92 (s, 2H, $H_{bridge}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, $SiMe_4$): $\delta$ 152.25 ($C_{py}$), 149.64 ($C_{py}$), 137.50 ($C_{py}$), 135.76 ($C_{imid}$), 134.27 ($C_{Ph}$), 130.42 ($C_{Ph}$), 130.09 ($C_{py}$), 124.11 ($C_{py}$), 123.88 ($C_{imid}$), 123.7289 ($C_{imid}$),, 121.62 ($C_{Ph}$), 120.28 ($C_{Ph}$), 53.91 ($CH_2$). Anal. Calcd for $C_{15}H_{14}BrN_3$: C, 56.98; H, 4.46; N, 13.29. Found: C, 56.95; H, 4.41; N, 13.33.

**3-Methyl-1-(2-picolyl)-4,5-dichloroimidazolium Bromide (f).** 2-(Bromomethyl)pyridine hydrobromide (1.01 g, 4 mmol) was neutralized using a saturated aqueous solution of $Na_2CO_3$. The liberated 2-(bromomethyl)pyridine was extracted using ice-cold diethyl ether (3 × 30 mL). The solution was dried with $Na_2SO_4$ and filtered into a dissolution of 1-methyl-4,5-dichloroimidazole (0.60 g, 4 mmol) in $CH_3CN$ (30 mL). Diethyl ether was removed under reduced pressure and the reaction mixture refluxed for 3 days. The reaction mixture was filtered, and the solvent was evaporated under reduced pressure. The resulting yellow solid was washed with $Et_2O$ (3 × 10 mL) and dried in vacuo. Yield: 0.52 g, 40%. $^1$H NMR (DMSO-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 10.81 (s, 1H, NCHN), 8.33 (d, $^3J_{HH}$ = 4.10 Hz, 1H, $H_{py}$), 7.63 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.48 (d, $^3J_{HH}$ = 7.61 Hz, 1H, $H_{py}$), 7.14 (t, $^3J_{HH}$ = 4.10 Hz, 1H, $H_{py}$), 5.71 (s, 2H, $CH_2$), 3.94 (s, 3H, $NCH_3$). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 150.68 ($C_{py}$), 149.48 ($C_{py}$), 138.42 ($C_{imid}$), 137.90 ($C_{py}$), 124.01 ($C_{py}$), 123.02 ($C_{py}$), 119.92 ($C_{imid}$), 119.57 ($C_{imid}$), 52.56 ($CH_2$), 35.57 ($NCH_3$). Anal. Calcd for $C_{10}H_{10}BrCl_2N_3$: C, 37.18; H, 3.12; N, 13.01. Found: C, 37.16; H, 3.08; N, 13.02.

**Representative Procedure for the Synthesis of Metal Complexes (1a−f).** A suspension of the appropriate picolylimidazolium bromide (**a**−**f**) and potassium *tert*-butoxide in THF was stirred at room temperature for 5 h. $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ was added to the mixture and stirred under reflux for 12 h. The suspension was filtered through a pad of $Na_2SO_4$ to remove the bromide salt and the solvent evaporated under reduced pressure. The resulting solid was dissolved in acetonitrile and eluted through a neutral $Al_2O_3$ column with $CH_3CN$ as a solvent. The solvent was removed under reduced pressure and the solid washed with petroleum ether and dried under vacuum.

*Acetonitrile($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-methyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**1a**).* The reaction was carried out with 3-methyl-1-(2-picolyl)imidazolium bromide (**a**; 0.25 g, 1 mmol) and potassium *tert*-butoxide (0.33 g, 3 mmol) in THF (30 mL) followed by the addition of $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ (0.40 g, 0.8 mmol). The product was a yellowish microcrystalline solid. Yield: 0.31 g, 66%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.97 (d, $^3J_{HH}$ = 5.57 Hz, 1H, $H_{py}$), 7.89 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.64 (d, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.47 (d, $^3J_{HH}$ = 1.76 Hz, 1H, $H_{imid\ backbone}$), 7.39 (t, $^3J_{HH}$ = 6.41 Hz, 1H, $H_{py}$), 7.31 (d, $^3J_{HH}$ = 1.76 Hz, 1H, $H_{imid\ backbone}$), 5.58 (d, $^2J_{HH}$ = 15.23 Hz, 1H, $H_{bridge}$), 4.75 (d, $^2J_{HH}$ = 15.23 Hz, 1H, $H_{bridge}$), 3.92 (s, 3H, $NCH_3$), 2.45 (s, 3H, $CH_3$), 1.61 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 193.28 ($C_{imid}Ru$), 158.61 ($C_{py}$), 157.79 ($C_{py}$), 138.00 ($C_{py}$), 125.25 ($C_{py}$), 125.14 ($C_{py}$), 122.70 ($C_{imid}$), 122.56 ($C_{imid}$), 83.10 ($C_5$-$(CH_3)_5$), 55.07 ($CH_2$), 36.97 ($NCH_3$), 10.31 ($C_5(CH_3)_5$), 3.57 ($CH_3$). IR (Nujol, $cm^{-1}$): $\nu$ 1590, 1458, 1402, 1377, 1301, 1246, 1222, 1180, 1107, 1075, 1027, 947, 843, 762, 724, 687. Anal. Calcd for $C_{22}H_{29}F_6N_4PRu$: C, 44.37; H, 4.91; N, 9.41. Found: C, 44.35; H, 4.94; N, 9.38.

*Acetonitrile($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-isopropyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**1b**).* The reaction was carried out with 3-isopropyl-1-(2-picolyl)imidazolium bromide (**b**; 0.30 g, 1.1 mmol) and potassium *tert*-butoxide (0.35 g, 3.2 mmol) in THF (30 mL) followed by the addition of $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ (0.45 g, 0.9 mmol). The product was a reddish microcrystalline solid. Yield: 0.41 g, 73%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.98 (d, $^3J_{HH}$ = 5.27 Hz, 1H, $H_{py}$), 7.88 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.65 (d, $^3J_{HH}$ = 7.61 Hz, 1H, $H_{py}$), 7.51 (d, $^3J_{HH}$ = 2.05 Hz, 1H, $H_{imid\ backbone}$), 7.42 (d, $^3J_{HH}$ = 1.76 Hz, 1H, $H_{imid\ backbone}$), 7.40 (t, $^3J_{HH}$ = 7.03 Hz, 1H, $H_{py}$), 5.48 (d, $^2J_{HH}$ = 14.94 Hz, 1H, $H_{bridge}$), 5.07 (m, $^3J_{HH}$ = 6.74 Hz, 1H, $NCH(CH_3)_2$), 4.81 (d, $^2J_{HH}$ = 14.64 Hz, 1H, $H_{bridge}$), 2.48 (s, 3H, $CH_3$), 1.64 (d, $^3J_{HH}$ = 6.74 Hz, 3H, $NCH(CH_3)_2$), 1.59 (s, 15H, $(C_5$-$(CH_3)_5)$, 1.38 (d, $^3J_{HH}$ = 6.74 Hz, 3H, $NCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 191.42 ($C_{imid}Ru$), 158.45 ($C_{py}$), 157.44 ($C_{py}$), 137.76 ($C_{py}$), 124.97 ($C_{py}$), 124.93 ($C_{imid}$), 122.96 ($C_{imid}$), 117.46 ($C_{py}$), 95.64 ($NCCH_3$), 82.85 ($C_5(CH_3)_5$), 54.77 ($CH_2$), 51.52 ($NCH(CH_3)_2$), 24.70 ($NCH(CH_3)_2$), 23.46 ($NCH(CH_3)_2$), 10.09 ($C_5(CH_3)_5$), 3.54 ($NCCH_3$). IR (Nujol, $cm^{-1}$): $\nu$ 1732, 1644, 1602, 1590, 1566, 937. Anal. Calcd for $C_{24}H_{33}F_6N_4PRu$: C, 46.23; H, 5.33; N, 8.98. Found: C, 46.19; H, 5.36; N, 8.96.

*Acetonitrile($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-phenyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**1c**).* The reaction was carried out with 3-phenyl-1-(2-picolyl)imidazolium bromide (**c**; 0.35 g, 1.1 mmol) and potassium *tert*-butoxide (0.35 g, 3.2 mmol) in THF (30 mL) followed by the addition of $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ (0.50 g, 1 mmol). The product was a reddish microcrystalline solid. Yield: 0.44 g, 67%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.98 (d, $^3J_{HH}$ = 5.58 Hz, 1H, $H_{py}$), 7.93 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.70 (d, $^3J_{HH}$ = 7.71 Hz, 1H, $H_{py}$), 7.69 (d, $^3J_{HH}$ = 1.96 Hz, 1H, $H_{imid\ backbone}$), 7.68 (d, $^3J_{HH}$ = 8.84 Hz, 2H, $H_{Ph}$), 7.61 (t, $^3J_{HH}$ = 7.86 Hz, 2H, $H_{Ph}$), 7.50 (m, 1H, $H_{Ph}$), 7.51 (d, $^3J_{HH}$ = 1.96 Hz, 1H, $H_{imid\ backbone}$), 7.44 (t, $^3J_{HH}$ = 6.44 Hz, 1H, $H_{py}$), 5.61 (d, $^2J_{HH}$ = 14.88 Hz, 1H, $H_{bridge}$), 4.94 (d, $^2J_{HH}$ = 14.69 Hz, 1H, $H_{bridge}$), 2.50 (s, 3H, $CH_3$), 1.35 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 193.62 ($C_{imid}Ru$), 158.20 ($C_{py}$), 157.28 ($C_{py}$), 141.57 ($NC_{Ph}$), 137.91 ($C_{py}$), 129.44 ($C_{Ph}$), 128.74 ($C_{Ph}$), 127.38 ($C_{Ph}$), 125.20 ($C_{py}$), 125.03 ($C_{py}$), 123.80 ($C_{imid}$), 123.21 ($C_{imid}$), 83.21 ($C_5(CH_3)_5$), 55.49 ($CH_2$), 9.91 ($C_5(CH_3)_5$), 4.91 ($NCCH_3$). Anal. Calcd for $C_{27}H_{31}F_6N_4PRu$: C, 49.31; H, 4.75; N, 8.52. Found: C, 49.27; H, 4.74; N, 8.55.

*Acetonitrile($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-mesityl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**1d**).* The reaction was carried out with 3-mesityl-1-(2-picolyl)imidazolium bromide (**d**; 0.39 g, 1.1 mmol) and potassium *tert*-butoxide (0.35 g, 3.2 mmol) in THF (30 mL) followed by the addition of $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ (0.50 g, 1 mmol). The product was a reddish microcrystalline solid. Yield: 0.58 g, 84%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.91 (d, $^3J_{HH}$ = 5.57 Hz, 1H, $H_{py}$), 7.91 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.75 (d, $^3J_{HH}$ = 8.19 Hz, 1H, $H_{py}$), 7.74 (d, $^3J_{HH}$ = 2.05 Hz, 1H, $H_{imid\ backbone}$), 7.38 (t, $^3J_{HH}$ = 7.03 Hz, 1H, $H_{py}$), 7.13 (d, $^3J_{HH}$ = 2.05 Hz, 1H, $H_{imid\ backbone}$), 7.09 (s, 1H, $H_{mes}$), 7.01 (s, 1H, $H_{mes}$), 5.65 (d, $^2J_{HH}$ = 14.94 Hz, 1H, $H_{bridge}$), 4.87 (d, $^2J_{HH}$ = 14.64 Hz, 1H, $H_{bridge}$), 2.35 (s, 3H, $CH_3$), 2.33 (s, 3H, $CH_3$), 2.08 (s, 3H, $CH_3$), 1.51 (s, 3H, $CH_3$), 1.41 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 193.25 ($C_{imid}Ru$), 158.97 ($C_{py}$),

157.18 ($C_{py}$), 139.27 ($NC_{mes}$), 138.01 ($C_{py}$), 137.70 ($C_{mes}$), 137.29 ($C_{mes}$), 135.75 ($C_{mes}$), 129.27 ($C_{mes}$), 128.69 ($C_{mes}$), 125.41 ($C_{py}$), 124.99 ($C_{py}$), 124.27 ($C_{imid}$), 123.40 ($C_{imid}$), 83.10 ($C_5(CH_3)_5$), 56.08 ($CH_2$), 21.01 ($CH_3$), 19.17 ($CH_3$), 18.04 ($CH_3$), 10.15 ($C_5(CH_3)_5$), 4.44 ($NCCH_3$). IR (Nujol, $cm^{-1}$): $\nu$ 2258, 2177, 1592, 1452, 1371, 1021, 837. Anal. Calcd for $C_{30}H_{37}F_6N_4PRu$: C, 51.50; H, 5.33; N, 8.01. Found: C, 51.54; H, 5.29; N, 7.98.

*Acetonitrile($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-methyl-1-(2-picolyl)benzoimidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**1e**).* The reaction was carried out with 3-methyl-1-(2-picolyl)benzoimidazolium bromide (**e**; 0.33 g, 1.1 mmol) and potassium *tert*-butoxide (0.35 g, 3.2 mmol) in THF (30 mL) followed by the addition of $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ (0.50 g, 1 mmol). The product was a yellowish orange microcrystalline solid. Yield: 0.49 g, 75%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.95 (d, $^3J_{HH}$ = 5.60 Hz, 1H, $H_{py}$), 7.89 (t, 1H, $^3J_{HH}$ = 7.60 Hz, 1H, $H_{py}$), 7.82 (d, $^3J_{HH}$ = 7.60 Hz, 1H, $H_{py}$), 7.74 (m, 1H, $H_{benzimid}$), 7.51 (m, 1H, $H_{benzimid}$), 7.41 (t, $^3J_{HH}$ = 6.44 Hz, 1H, $H_{py}$), 7.27 (m, 2H, $H_{benzimid}$), 5.94 (d, $^2J_{HH}$ = 15.23 Hz, 1H, $H_{bridge}$), 4.92 (d, $^2J_{HH}$ = 15.23 Hz, 1H, $H_{bridge}$), 4.13 (s, 3H, $NCH_3$), 2.42 (s, 3H, $CH_3$), 1.63 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 208.65 ($C_{imid}Ru$), 158.27 ($C_{py}$), 157.74 ($C_{py}$), 138.28 ($C_{py}$), 136.57 ($C_{benzimid}$), 135.62 ($C_{benzimid}$), 125.46 ($C_{py}$), 125.43 ($C_{py}$), 123.09 ($C_{benzimid}$), 122.98 ($C_{benzimid}$), 110.40 ($C_{benzimid}$), 109.78 ($C_{benzimid}$), 84.27 ($C_5(CH_3)_5$), 68.00 (NC), 51.20 ($CH_2$), 34.23 ($NCH_3$), 10.28 ($C_5(CH_3)_5$), 3.60 ($NCCH_3$). IR (Nujol, $cm^{-1}$): $\nu$ 2256, 2199, 2062, 1951, 1593, 1451, 1368. Anal. Calcd for $C_{26}H_{31}F_6N_4PRu$: C, 48.37; H, 4.84; N, 8.68. Found: C, 48.40; H, 4.86; N, 8.71.

*Acetonitrile($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-methyl-1-(2-picolyl)-4,5-dichloroimidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**1f**).* The reaction was carried out with 3-methyl-1-(2-picolyl)-4,5-dichloroimidazolium bromide (**f**; 0.36 g, 1.1 mmol) and potassium *tert*-butoxide (0.35 g, 3.2 mmol) in THF (30 mL) followed by the addition of $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3][PF_6]$ (0.50 g, 1 mmol). The product was a yellowish microcrystalline solid. Yield: 0.51 g, 77%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.98 (d, $^3J_{HH}$ = 5.13 Hz, 1H, $H_{py}$), 7.94 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.79 (d, $^3J_{HH}$ = 7.61 Hz, 1H, $H_{py}$), 7.45 (t, $^3J_{HH}$ = 6.52 Hz, 1H, $H_{py}$), 5.58 (d, $^2J_{HH}$ = 15.23 Hz, 1H, $H_{bridge}$), 4.75 (d, $^2J_{HH}$ = 15.23 Hz, 1H, $H_{bridge}$), 3.97 (s, 3H, $NCH_3$), 2.45 (s, 3H, $CH_3$), 1.63 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 196.52 ($C_{imid}Ru$), 157.61 ($C_{py}$), 156.91 ($C_{py}$), 138.21 ($C_{py}$), 125.46 ($C_{py}$), 124.88 ($C_{py}$), 116.60 ($C_{imid}$), 115.65 ($C_{imid}$), 83.65 ($C_5(CH_3)_5$), 52.45 ($CH_2$), 35.71 ($NCH_3$), 9.96 ($C_5(CH_3)_5$), 3.38 ($NCCH_3$). IR (Nujol, $cm^{-1}$): $\nu$ 2255, 2188, 2079, 2044, 1944, 1594, 1456, 1376, 722. Anal. Calcd for $C_{22}H_{27}Cl_2F_6N_4PRu$: C, 39.77; H, 4.10; N, 8.43. Found: C, 39.79; H, 4.06; N, 8.40.

**Procedure for Anion Exchange Reactions (2a,b).** A suspension of the appropriate metal complex **1a,b** and 1 equiv of $NaBAr_4^F$ in ether was stirred at room temperature for 24 h. The suspension was filtered through a pad of Celite and the solvent evaporated under reduced pressure. The resulting solid was washed with petroleum ether and dried under vacuum.

*($\eta^2$-$O_2$)($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-isopropyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) $BAr_4^F$ (**2b**).* A suspension of **1b** (0.19 g, 0.3 mmol) and $NaBAr_4^F$ (0.26 g, 0.3 mmol) was stirred in air at room temperature for 24 h. The suspension was filtered through a pad of Celite and the solvent evaporated under reduced pressure. The product was obtained as a brown microcrystalline solid. Yield: 0.29 g, 73%. $^1$H NMR ($CD_2Cl_2$, 400 MHz, $SiMe_4$): $\delta$ 9.22 (d, $^3J_{HH}$ = 5.85 Hz, 1H, $H_{py}$), 7.85 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.72 (br s, 8H, $B(C_6H_3C_2F_6)_4$), 7.56 (br s, 4H, $B(C_6H_3C_2F_6)_4$), 7.49 (t, $^3J_{HH}$ = 6.45 Hz, 1H, $H_{py}$), 7.45 (d, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.32 (m, 2H, $H_{imid\ backbone}$), 5.15 (d, $^2J_{HH}$ = 15.82 Hz, 1H, $H_{bridge}$), 4.73 (m, $^3J_{HH}$ = 6.66 Hz, 1H, $NCH(CH_3)_2$), 4.41 (d, $^2J_{HH}$ = 15.82 Hz, 1H, $H_{bridge}$), 1.70 (d, $^3J_{HH}$ = 6.45 Hz, 3H, $NCH(CH_3)_2$), 1.60 (d, $^3J_{HH}$ = 7.03 Hz, 3H, $NCH(CH_3)_2$), 1.44 (s, 15H, $(C_5(CH_3)_5)$, $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 100 MHz, $SiMe_4$): $\delta$ 180.22 ($C_{imid}Ru$), 162.11 (q, $^1J_{B-C}$ = 49.72 Hz, $B(C_6H_3C_2F_6)_4$), 154.42 ($C_{py}$), 152.51 ($C_{py}$), 140.31 ($C_{py}$), 135.17 ($B(C_6H_3C_2F_6)_4$), 129.26 (q, $^2J_{C-F}$ = 31.60 Hz, $B(C_6H_3C_2F_6)_4$), 125.87 ($C_{py}$), 125.83 ($C_{imid}$), 124.96 (q, $^1J_{C-F}$ = 272.24 Hz, $B(C_6H_3C_2F_6)_4$), 124.24 ($C_{py}$), 121.16 ($C_{imid}$), 104.15 ($C_5(CH_3)_5$), 54.39 ($CH_2$), 53.29 ($NCH(CH_3)_2$), 26.08 ($NCH(CH_3)_2$), 24.10 ($NCH(CH_3)_2$), 9.16 ($C_5(CH_3)_5$). Anal. Calcd for $C_{54}H_{42}BF_{24}N_3O_2Ru$: C, 48.66; H, 3.18; N, 3.15. Found: C, 48.63; H, 3.22; N, 3.21.

**Representative Procedure for the Synthesis of Carbonyl Metal Complexes (3a−f).** A solution of the metal complex **1a−f** in $CH_2Cl_2$ was stirred under CO (1 atm) for 2 h. The solvent was removed under reduced pressure; the resulting solid was washed with petroleum ether and dried under vacuum.

*Carbonyl($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-methyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**3a**).* The reaction was carried out with **1a** (60 mg, 0.1 mmol). The product was a brownish microcrystalline solid. Yield: 55 mg, 97%. $^1$H NMR ($CDCl_3$, 400 MHz, $SiMe_4$): $\delta$ 8.52 (d, $^3J_{HH}$ = 5.85 Hz, 1H, $H_{py}$), 7.77 (t, 1H, $^3J_{HH}$ = 7.62 Hz, 1H, $H_{py}$), 7.72 (d, $^3J_{HH}$ = 7.03 Hz, 1H, $H_{py}$), 7.42 (d, $^3J_{HH}$ = 2.05 Hz, 1H, $H_{imid\ backbone}$), 7.17 (t, $^3J_{HH}$ = 6.44 Hz, 1H, $H_{py}$), 7.00 (d, $^3J_{HH}$ = 2.05 Hz, 1H, $H_{imid\ backbone}$), 5.52 (d, $^2J_{HH}$ = 15.82 Hz, 1H, $H_{bridge}$), 4.51 (d, $^2J_{HH}$ = 15.82 Hz, 1H, $H_{bridge}$), 3.68 (s, 3H, $NCH_3$), 1.61 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, $SiMe_4$): $\delta$ 203.86 (CO), 178.93 ($C_{imid}Ru$), 158.44 ($C_{py}$), 156.51 ($C_{py}$), 139.54 ($C_{py}$), 127.02 ($C_{py}$), 124.72 ($C_{py}$), 123.65 ($C_{imid}$), 122.99 ($C_{imid}$), 94.78 ($C_5(CH_3)_5$), 54.19 ($CH_2$), 37.21 ($NCH_3$), 10.18 ($C_5(CH_3)_5$). IR (Nujol, $cm^{-1}$): $\nu$ 1925 (CO). Anal. Calcd for $C_{21}H_{26}F_6N_3OPRu$: C, 43.30; H, 4.50; N, 7.21. Found: C, 43.32; H, 4.47; N, 7.17.

*Carbonyl($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-isopropyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**3b**).* The reaction was carried out with **1b** (63 mg, 0.1 mmol). The product was a brownish microcrystalline solid. Yield: 61 mg, 99%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.90 (d, $^3J_{HH}$ = 5.54 Hz, 1H, $H_{py}$), 8.07 (t, 1H, $^3J_{HH}$ = 7.66 Hz, 1H, $H_{py}$), 7.83 (d, $^3J_{HH}$ = 7.66 Hz, 1H, $H_{py}$), 7.68 (d, $^3J_{HH}$ = 2.12 Hz, 1H, $H_{imid\ backbone}$), 7.58 (d, $^3J_{HH}$ = 1.85 Hz, 1H, $H_{imid\ backbone}$), 7.47 (t, $^3J_{HH}$ = 6.61 Hz, 1H, $H_{py}$), 5.69 (d, $^2J_{HH}$ = 15.58 Hz, 1H, $H_{bridge}$), 4.82 (d, $^2J_{HH}$ = 15.58 Hz, 1H, $H_{bridge}$) 4.75 (m, $^3J_{HH}$ = 6.74 Hz, 1H, $NCH(CH_3)_2$), 1.77 (s, 15H, $(C_5(CH_3)_5)$, 1.60 (d, $^3J_{HH}$ = 6.87 Hz, 3H, $NCH(CH_3)_2$), 1.41 (d, $^3J_{HH}$ = 6.60 Hz, 3H, $NCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 205.06 (CO), 177.96 ($C_{imid}Ru$), 159.88 ($C_{py}$), 157.34 ($C_{py}$), 140.31 ($C_{py}$), 127.15 ($C_{py}$), 125.72 ($C_{py}$), 124.55 ($C_{imid}$), 119.07 ($C_{imid}$), 95.58 ($C_5(CH_3)_5$), 54.61 ($CH_2$), 52.54 ($NCH(CH_3)_2$), 24.07 ($NCH(CH_3)_2$), 23.23 ($NCH(CH_3)_2$), 9.87 ($C_5(CH_3)_5$). IR (Nujol, $cm^{-1}$): $\nu$ 1920 (CO). Anal. Calcd for $C_{23}H_{30}F_6N_3OPRu$: C, 45.25; H, 4.95; N, 6.88. Found: C, 45.21; H, 4.92; N, 6.91.

*Carbonyl($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-phenyl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**3c**).* The reaction was carried out with **1c** (66 mg, 0.1 mmol). The product was a brownish microcrystalline solid. Yield: 62 mg, 95%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.89 (d, $^3J_{HH}$ = 5.62 Hz, 1H, $H_{py}$), 8.11 (t, 1H, $^3J_{HH}$ = 7.69 Hz, 1H, $H_{py}$), 7.88 (d, $^3J_{HH}$ = 7.10 Hz, 1H, $H_{py}$), 7.82 (d, $^3J_{HH}$ = 1.97 Hz, 1H, $H_{imid\ backbone}$), 7.60 (d, $^3J_{HH}$ = 4.34 Hz, 2H, $H_{Ph}$), 7.57 (m, 3H, $H_{Ph}$), 7.55 (d, $^3J_{HH}$ = 1.78 Hz, 1H, $H_{imid\ backbone}$), 7.50 (t, $^3J_{HH}$ = 6.30 Hz, 1H, $H_{py}$), 5.82 (d, $^2J_{HH}$ = 15.57 Hz, 1H, $H_{bridge}$), 4.99 (d, $^2J_{HH}$ = 15.58 Hz, 1H, $H_{bridge}$), 1.56 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 206.27 (CO), 180.01 ($C_{imid}Ru$), 160.08 ($C_{py}$), 159.98 ($C_{Ph}$), 157.39 ($C_{py}$), 140.60 ($C_{py}$), 129.75 ($C_{Ph}$), 128.38 ($C_{Ph}$), 127.2 ($C_{py}$), 125.99 ($C_{imid}$), 124.26 ($C_{imid}$), 95.43 ($C_5(CH_3)_5$), 55.32 ($CH_2$), 9.79 ($C_5(CH_3)_5$. IR (Nujol, $cm^{-1}$): $\nu$ 1929 (CO). Anal. Calcd for $C_{26}H_{28}F_6N_3OPRu$: C, 48.45; H, 4.38; N, 6.52. Found: C, 48.44; H, 4.35; N, 6.54.

**Table 4. Summary of Crystallographic Data for 2a,b**

| | 2a | 2b |
|---|---|---|
| formula | $C_{54}H_{41}BF_{24}N_4Ru$ | $C_{56.32}H_{47.53}BC_{l11.12}F_{24}N_3O_{2.44}Ru$ |
| fw | 1313.79 | 1412.93 |
| $T$ (K) | 100 | 100 |
| cryst size (mm) | | 0.53 × 0.36 × 0.11 |
| cryst syst | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| cell params | | |
| $a$ (Å) | 12.427(3) | 12.498(3) |
| $b$ (Å) | 12.814(3) | 17.896(4) |
| $c$ (Å) | 17.884(4) | 26.458(5) |
| $\alpha$ (deg) | 91.85(3) | 90.00 |
| $\beta$ (deg) | 100.30(3) | 90.67(3) |
| $\gamma$ (deg) | 104.44(3) | 90.00 |
| $V$ (Å$^3$) | 2704.5(9) | 5917(2) |
| $Z$ | 2 | 4 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.613 | 1.585 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 0.415 | 0.436 |
| $F$(000) | 1316 | 2840.8 |
| max−min transmission factors | 0.955−0.788 | 1.000−0.792 |
| $\theta$ range for data collection (deg) | 1.16 < $\theta$ < 25.09 | 1.91 < $\theta$ < 25.04 |
| no. of rflns collected | 18 176 | 12 034 |
| no. of unique rflns | 9179 ($R_{int}$ = 0.0437) | 10 356 ($R_{int}$ = 0.0363) |
| no. of obsd rflns ($I > 2\sigma_I$) | 7324 | 9256 |
| no. of params | 784 | 876 |
| final R1, wR2 values ($I > 2\sigma_I$) | 0.0671, 0.1670 | 0.0497, 0.1196 |
| final R1, wR2 values (all data) | 0.0843, 0.1783 | 0.0570, 0.1242 |
| residual electron density peaks (e Å$^{-3}$) | +0.341, −0.634 | +1.110, −0.863 |

*Carbonyl($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-mesityl-1-(2-picolyl)imidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**3d**).* The reaction was carried out with **1d** (70 mg, 0.1 mmol). The product was a brownish microcrystalline solid. Yield: 65 mg, 96%. $^1$H NMR ($CD_2Cl_2$, 400 MHz, $SiMe_4$): $\delta$ 8.59 (d, $^3J_{HH}$ = 5.57 Hz, 1H, $H_{py}$), 7.94 (t, 1H, $^3J_{HH}$ = 7.69 Hz, 1H, $H_{py}$), 7.85 (d, $^3J_{HH}$ = 7.61 Hz, 1H, $H_{py}$), 7.68 (d, $^3J_{HH}$ = 2.06 Hz, 1H, $H_{imid\ backbone}$), 7.27 (t, $^3J_{HH}$ = 6.51 Hz, 1H, $H_{py}$), 7.06 (s, 1H, $H_{mes}$), 6.97 (s, 1H, $H_{mes}$), 6.95 (d, $^3J_{HH}$ = 1.76 Hz, 1H, $H_{imid\ backbone}$), 5.63 (d, $^2J_{HH}$ = 15.53 Hz, 1H, $H_{bridge}$), 4.73 (d, $^2J_{HH}$ = 15.23 Hz, 1H, $H_{bridge}$), 2.35 (s, 3H, $CH_3$), 2.13 (s, 3H, $CH_3$), 6.68 (s, 3H, $CH_3$), 1.57 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 100 MHz, $SiMe_4$): $\delta$ 205.19 (CO), 182.07 ($C_{imid}$Ru), 159.07 ($C_{py}$), 156.88 ($C_{py}$), 139.910 ($C_{py}$), 139.88 ($NC_{mes}$), 136.91 ($C_{mes}$), 135.78 ($C_{mes}$), 134.69 ($C_{mes}$), 129.55 ($C_{mes}$), 128.94 ($C_{mes}$), 127.17 ($C_{py}$), 125.25 ($C_{py}$), 124.47 ($C_{imid}$), 124.16 ($C_{imid}$), 95.23 ($C_5(CH_3)_5$), 55.54 ($CH_2$), 21.19 ($CH_3$), 18.84 ($CH_3$), 18.62 ($CH_3$), 10.16 ($C_5(CH_3)_5$). IR (Nujol, cm$^{-1}$): $\nu$ 1928 (CO). Anal. Calcd for $C_{29}H_{34}F_6N_3OPRu$: C, 50.73; H, 4.99; N, 6.12. Found: C, 50.70; H, 5.02; N, 6.15.

*Carbonyl($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-methyl-1-(2-picolyl)benzoimidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**3e**).* The reaction was carried out with **1e** (65 mg, 0.1 mmol). The product was a brownish microcrystalline solid. Yield: 62 mg, 99%. $^1$H NMR (acetone-$d_6$, 400 MHz, $SiMe_4$): $\delta$ 8.95 (d, $^3J_{HH}$ = 5.57 Hz, 1H, $H_{py}$), 8.12 (t, 1H, $^3J_{HH}$ = 7.61 Hz, 1H, $H_{py}$), 8.04 (d, $^3J_{HH}$ = 7.91 Hz, 1H, $H_{py}$), 7.91 (m, 1H, $H_{benzimid}$), 7.69 (m, 1H, $H_{benzimid}$), 7.51 (t, $^3J_{HH}$ = 6.15 Hz, 1H, $H_{py}$), 7.41 (m, 2H, $H_{benzimid}$), 6.19 (d, $^2J_{HH}$ = 15.81 Hz, 1H, $H_{bridge}$), 5.00 (d, $^2J_{HH}$ = 15.81 Hz, 1H, $H_{bridge}$), 4.13 (s, 3H, $NCH_3$), 1.85 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 100 MHz, $SiMe_4$): $\delta$ 204.61 (CO), 194.70 ($C_{benzimid}$Ru), 160.24 ($C_{py}$), 157.41 ($C_{py}$), 140. 75 ($C_{py}$), 136.39 ($NC_{benzimid}$), 135.48 ($NC_{benzimid}$), 127.60 ($C_{py}$), 126.21 ($C_{py}$), 124.28 ($C_{benzimid}$), 124.12 ($C_{benzimid}$), 111.59 ($C_{benzimid}$), 110.89 ($C_{benzimid}$), 96.29 ($C_5(CH_3)_5$), 51.44 ($CH_2$), 34.95 ($NCH_3$), 10.18 ($C_5(CH_3)_5$), 4.91 ($NCCH_3$). IR (Nujol, cm$^{-1}$): $\nu$ 1929 (CO). Anal. Calcd for $C_{25}H_{28}F_6N_3OPRu$: C, 47.47; H, 4.46; N, 6.64. Found: C, 47.45; H, 4.49; N, 6.67.

*Carbonyl($\eta^5$-pentamethylcyclopentadienyl)($\kappa^2$-C,N-3-methyl-1-(2-picolyl)-4,5-dichloroimidazol-2-ylidene)ruthenium(II) Hexafluorophosphate (**3f**).* The reaction was carried out with **1f** (65 mg, 0.1 mmol). The product was a brownish microcrystalline solid. Yield: 61 mg, 98%. $^1$H NMR (acetone-$d_6$, 600 MHz, $SiMe_4$): $\delta$ 8.92 (d, $^3J_{HH}$ = 5.48 Hz, 1H, $H_{py}$), 8.12 (t, 1H, $^3J_{HH}$ = 7.74 Hz, 1H, $H_{py}$), 7.99 (d, $^3J_{HH}$ = 7.63 Hz, 1H, $H_{py}$), 7.52 (t, $^3J_{HH}$ = 6.55 Hz, 1H, $H_{py}$), 5.77 (d, $^2J_{HH}$ = 15.96 Hz, 1H, $H_{bridge}$), 4.79 (d, $^2J_{HH}$ = 15.72 Hz, 1H, $H_{bridge}$), 3.92 (s, 3H, $NCH_3$), 1.83 (s, 15H, $(C_5(CH_3)_5)$. $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 150 MHz, $SiMe_4$): $\delta$ 204.34 (CO), 183.34 ($C_{imid}$Ru); 160.27 ($C_{py}$), 156.31 ($C_{py}$), 140.87 ($C_{py}$), 127.86 ($C_{py}$), 126.43 ($C_{py}$), 118.51 ($C_{imid}$), 117.68 ($C_{imid}$), 96.16 ($C_5(CH_3)_5$), 52.88 ($CH_2$), 36.76 ($NCH_3$), 10.08 ($C_5(CH_3)_5$). IR (Nujol, cm$^{-1}$): $\nu$ 1937 (CO). Anal. Calcd for $C_{21}H_{24}Cl_2F_6N_3OPRu$: C, 38.72; H, 3.71; N, 6.45. Found: C, 38.76; H, 3.68; N, 6.49.

**Crystal Structure Analysis.** Crystals of **2a,b** 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 K$\alpha$ radiation ($\alpha$ = 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 $\omega$ 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 with hydrogen atoms included in calculated positions (riding model). In each case two disordered $CF_3$ groups in the anion were refined split into two complementary orientations using displacement parameter restraints. For **2b** dichloromethane (56%) and diethyl ether (44%) solvates were found disordered with complementary occupation factors. The program ORTEP-3 was used for plotting.[53] Table 4 summarizes the crystal data and data collection and refinement details for **2a,b**. CCDC 833091−833092 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Typical Procedure for Catalytic Transfer Hydrogenation.** Ketone or imine (2.0 mmol), catalyst 0.1% (0.002 mmol), KOH (0.2 mmol), 1,3,5-trimethoxybenzene (0.5 mmol), and $^i$PrOH (5 mL) were placed in a 10 mL vial and stirred on a prehetaed oil bath (82 °C). Aliquots (0.2 mL) were taken at fixed times, quenched in $Et_2O$ (3 mL), and filtered through a short pad of $SiO_2$. The filtrate was subjected to GC-MS and $^1$H NMR analysis. For $TOF_{50}$ measurements the catalyst

loading was 1% (0.02 mmol). The substrate was preheated at 82 °C for 5 min before catalyst and base were added. All data reported are averages of at least two runs.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Table giving catalytic screening results and CIF files giving crystallographic data for compounds **2a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) Work in progress. Relevant spectral data are as follows. $^{1}$H NMR ($CDCl_3$, 400 MHz, $SiMe_4$): $\delta$ 8.00 (d, $^{3}J_{HH}$ = 5.27 Hz, 1H, $H_{py}$), 7.45 (br s, 8H, $BPh_4$), 7.27 (t, $^{3}J_{HH}$ = 7.32 Hz, 1H, $H_{py}$), 7.00 (t, $^{3}J_{HH}$ = 7.32 Hz, 8H, $BPh_4$), 6.87 (t, $^{3}J_{HH}$ = 7.17 Hz, 4H, $BPh_4$), 6.82 (t, $^{3}J_{HH}$ = 6.59 Hz, 1H, $H_{py}$), 6.69 (d, $^{3}J_{HH}$ = 7.91 Hz, 1H, $H_{py}$), 2.83, 2.69 (m, 1H each, $PCH_2$), 2.29, 2.21 (m, 1H each, $P(CH(CH_3)_2)_2$), 1.73 (d, 15 H, $^{4}J_{HP}$ = 1.46 Hz, $C_5(CH_3)_5$), 1.12 (m, 6H, $P(CH(CH_3)_2)_2$), 0.97 (m, 3H, $P(CH(CH_3)_2)_2$), 0.60 (m, 3H, $P(CH(CH_3)_2)_2$). $^{31}P\{^{1}H\}$ NMR (161.89 MHz, $CDCl_3$): $\delta$ 78.51 (s). $^{13}$C NMR ($CDCl_3$, 100 MHz, $SiMe_4$): $\delta$ 205.30 (d, $^{2}J_{CP}$ = 15.61 Hz, CO), 164.08 (q, $^{1}J_{BC}$ = 49.37 Hz, $BPh_4$), 162.12 ($C_{py}$), 154.31 ($C_{py}$), 138.88 ($C_{py}$), 136.20 ($BPh_4$), 125.46 ($BPh_4$), 124.60 ($C_{py}$), 124.05 ($C_{py}$), 121.63 ($BPh_4$), 96.38 ($C_5(CH_3)_5$), 35.74 (d, $^{1}J_{CP}$ = 24.47 Hz, $PCH_2$), 25.68 (d, $^{1}J_{CP}$ = 27.43 Hz, $P(CH(CH_3)_2)_2$), 23.79 (d, $^{1}J_{CP}$ = 19.84 Hz, $P(CH(CH_3)_2)_2$), 18.70, 18.01, 17.71, 16.74 (s, $P(CH(CH_3)_2)_2$), 10.38 ($C_5(CH_3)_5$) . IR (Nujol, $cm^{-1}$): $\nu$ 1937 (CO).

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