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Synthesis and Reactivity of New Chelate-N-Heterocyclic Biscarbene Complexes of Ruthenium

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The carbene-ligand precursors methylenebis(*N*-alkylimidazolium) iodide (alkyl = methyl, *neo*-pentyl) and ethylenebis-(*N*-methylimidazolium) chloride have been used in the preparation of several new Ru(II)-*p*-cymene complexes where the ligand behaves as mono- and bidentate. The molecular structures of the two biscarbene-complexes are reported. From the data reported, we can conclude that steric reasons (mainly the bisimidazolium linkers, methylene/ethylene) are the main factors determining both reactivity and synthetic difficulties of the products reported.

N-Heterocyclic carbenes derived from imidazolium ions[1] have attracted greatly increased attention since they have proven to act as efficient spectator ligands in homogeneous catalysis.[2,3] Among organometallic catalysts, only phosphines are currently more versatile, and only because the design of carbene ligands is much less developed. Despite the application of N-heterocyclic ligands (NHCs) in the design of homogeneous catalysts being relatively recent (mid-1990s), the area has grown so much that we can now find efficient NHC-based catalysts in a wide range of reactions such as hydrogenation,[4] hydroformylation,[5,6] Heck, Suzuki, and Stille couplings,[7−10] olefin methatesis,[11] hydrosilylation,[12] and hydroamination,[13] among many others.[2]

As observed for phosphines, the introduction of the chelate effect in carbenes confers the ligand an additional stabilizing character that may have interesting applications in the design of stable complexes. The first chelate biscarbene complexes described were Pd-based,[7,8,14−16] showing good catalytic activity in C−C coupling reactions such as Heck,[7,8,14] Suzuki, and Sonogashira,[8] and the stability of the compounds

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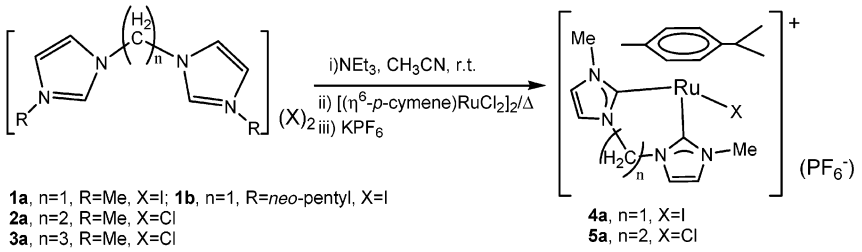
Scheme 1



1a, n=1, R=Me, X=I; **1b**, n=1, R=*neo*-pentyl, X=I
2a, n=2, R=Me, X=Cl
3a, n=3, R=Me, X=Cl

4a, n=1, X=I
5a, n=2, X=Cl

obtained allowed the design of methods for catalyst recycling, such as immobilization on solid surfaces.[9,17] Then, the use of chelate and pincer carbene ligands was extended to Rh[3,5,18,19] and Ir,[20] thus widening the range of catalytic applications.

Despite the rich catalytic applications of ruthenium, the number of chelate-carbene complexes of this metal is restricted to two pincer complexes reported by Danopoulos[21] and us,[22] which showed very good catalytic activity in transfer hydrogenation reactions[21,22] and oxidation of olefins.[22] Some mono-carbene η^6-arene−ruthenium complexes have been recently described and have shown interesting applications in homogeneous catalysis,[23] but we did not find in the literature a single example where a chelate biscarbene is coordinated to this metal fragment. We have now considered the possibility of coordinating bis-carbene ligands to η^6-arene-ruthenium complexes, since there is an increasing interest in incorporating substituted imidazol-2-ylidenes to this metal fragment, in view of the interesting reactivity that can be derived.[23,24]

On the basis of our previous experience in the coordination of chelate bis-imidazol-2-ylidenes, we now report the synthesis and reactivity of several new η^6-arene-ruthenium complexes with chelating bis-N-heterocyclic-carbene ligands. The molecular structure of two of the complexes is also described.

Results and Discussion

Synthesis and Characterization of the Compounds. According to our previously reported results, we decided to use NEt_3 as deprotonating agent to generate the biscarbene ligands from the bisimidazolium precursors. Other weak bases such as NaOAc or Na_2CO_3 did not yield the desired compounds and only gave mixtures, which we were not able to identify. We have found that NEt_3 is a good deprotonating agent of bisimidazolium salts, although we do not believe that free biscarbenes are generated in situ by such a weak base. In fact, we believe that the deprotonation of the precursor is favored by its fast coordination to the metal, thus deplacing the equilibrium to the biscarbene formation. The formation of HN^+Et_3 as a byproduct of the reaction confirms that NEt_3 is behaving as the true proton acceptor. As biscarbene precursors, we used the bisimidazolium salts shown in Scheme 1, aiming to evaluate the effect of the linker length in the reactivity of the products obtained. In a recent work, we described the different coordination capabilities of these ligands when coordinated to rhodium and iridium, and we observed that the relative orientation of the azole rings is strongly dependent on the number of carbon atoms (*n*) in the linker, thus affecting the reactivity of the complexes and coordination type (chelate, bridge) of the ligand. We believe that the steric hindrance of the ligand could also play an important role in the coordination of the biscarbene, so we decided to use the crowded *N*-*neo*-pentyl precursor **1b** to compare the reactivity with the less hindered imidazolium ions, **1a**−**3a**.

The reaction products of the reaction with $[(\eta^6$-*p*-cymene)-$RuCl_2]_2$ depend on the precursor (**1a**, **1b**, **2a**, and **3a**) used. While **1a** and **2a** yielded the expected biscarbene complexes (**4a** and **5a**, respectively), the sterically crowded precursor **1b** and the propylene-linked **3a** did not yield the desired biscarbene compounds under the same reaction conditions (12 h reflux, CH_3CN). It is important to point out that **4a** was obtained in a much higher yield than **5a** (45% vs 21%, respectively). For the methylene-bridged-bisimidazolium salts, **1a** and **1b**, we prepared the iodide derivatives. The reaction of these precursors with $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ results in the substitution of the halogen ligand from the coordination sphere of the Ru atom. In order to avoid mixtures of the Cl/I products, in those reactions where we used **1a** and **1b**, we added an excess of KI aiming to obtain the fully iodinated complexes. All the compounds were separated by column chromatography eluting with gradient acetone/dichloromethane. In order to facilitate the elution of the cationic complexes obtained, we added KPF_6 to the eluent, thus obtaining the final products as PF_6^- salts.

For the more sterically demanding imidazolium salt **1b**, the only reaction product which we could isolate under the same conditions was the monocarbene complex **6b** (Scheme

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Scheme 2

1a, R=Me; **1b**, R=*neo*-pentyl

6a, R=Me
6b, R=*neo*-pentyl

2). Compound **6b** did not evolve to the corresponding chelate biscarbene complex, even under harsher reaction conditions such as addition of an excess of NEt_3 or use of a stronger base such as NaH or *t*-BuOK. In this sense, we also performed reactions directed to generate the corresponding free biscarbene in situ in order to determine whether, once generated, their coordination would be favored compared to the use of NEt_3. Addition of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ to a 0 °C THF solution of the ligand precursor (**1b**) treated with NaH or *t*-BuOK did not yield the desired carbene complex, and only the initial Ru precursor was recovered. The same result was reproduced when the reaction was carried out leaving the reaction to warm at room temperature and react for 24−48 h and even after refluxing the mixture for long reaction times. We also have to point out that none of the other ligand precursors (**1a**−**3a**) yielded any of the carbene coordinated species that we describe in the present work under the harsher reaction conditions that we just described. In the case of the compound **1b**, we believe that the steric hindrance of the *neo*-pentyl wingtips of the ligand is preventing the chelation of the ligand. A similar monocarbene compound can be obtained with **1a**, when the reaction is performed at 50 °C in CH_3CN. Using the same ligands, Herrmann and co-workers have described a series of complexes of Pd(II) where the mono-carbene coordination of the ligand is also observed.[16] The precursor with the longer linker length, **3a** ($n = 3$), did not give any of the biscarbene nor monocarbene complexes. We believe that the larger bite angle imposed by the linker (see below the comments regarding the molecular structures of **4a** and **5a**) may prevent the ligand to coordinate in a bidentate form due to higher sterically demanding reasons. Attempts to coordinate the longer-linked precursor *o*-xylylenebis(*N*-methylimidazolium)chloride did not afford any of the mono- or biscarbene complexes either. This unsatisfactory result may not be so surprising since these two precursors have always coordinated to square planar complexes, and failed to coordinate to pseudo-octahedral metal complexes.[18,25] We have very recently reported that the coordination of long-linked bisimidazol-2-ylidene ligands favors the azole rings to orient perpendicular to the sterically crowded coordination plane in square planar tetracoordinated complexes, thus preventing the formation of octahedral species due to the steric hindrance induced along the perpendicular axis.[25] In our case, the pseudo-octahedral coordination around the Ru atom may be suffering the same effect, avoiding the chelate coordination of the ligand. This effect may also explain the different reaction yields in the synthesis of **4a** and **5a**, the latter one being clearly disfavored due to the more sterically demanding ligand. However, for **3a** we would expect to obtain a monocarbene complex such as **6**, but the reaction of **3a** with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ did not yield any more isolable species than the starting ligand precursor and metal complex.

All new compounds reported in the present work (**4a**, **5a**, **6a**, and **6b**) were characterized by NMR and mass spectroscopy and gave satisfactory elemental analyses.

The equivalency of the two imidazol rings in the ^1H NMR spectra of **4a** and **5a** confirms the 2-fold symmetry of the chelate ligands. The signals due to the *p*-cymene ligand appear in the usual pattern. It is interesting to point out that the two hydrogen atoms of the CH_2 linker in **4a** are geometrically unequivalent, one of them pointing at the η^6-arene ligand, while the other is closer to the iodine atom. This effect is observed in the ^1H NMR spectrum, where the two hydrogen atoms of the CH_2 linker show two separate doublets ($^2J_{H-H} = 13.2$ Hz). The same effect is observed for **5a**, showing two multiplets for the unequivalent two pairs of hydrogens of the ethylene bridge. The more relevant feature in the ^{13}C NMR spectra of these two complexes is the signal due to the metalated carbon atom, in the typical high-frequency region ($\delta = 172.5$, **4a**; 169.2, **5a**).

Both ^1H and ^{13}C NMR spectra of **6a** and **6b** reveal the loss of the 2-fold symmetry of the ligand upon coordination. The downfield signal of the proton in the 2′-position of the imidazolium functionality ($\delta = 9.0$, **6a**; 8.8, **6b**) reveals that one of the rings remains unbound. The bound imidazolylidene ring appears at higher field compared to the unbound azole. The ^{1}HNMR signals due to the hydrogen atoms in the linker appear as broad signals, probably due to the fluxional behavior of the ligand about the linker chain. These signals were unequivocally assigned by HETCOR and COSY experiments. The metalated C resonances appear in the ^{13}C NMR spectra at 177.1 (**6a**) and 174.6 (**6b**) ppm, while the signals due to the protonated N*C*HN carbon atom appear at 137.5 (**6a**) and 136.5 (**6b**) ppm.

Positive ion ESMS analyses of the isolated chelate products **4a** and **5a** in MeOH showed a peak at *m*/*z* [M^+] (539) for **4a** and [M^+] (461) for **5a**. For the monocarbene complex **6a**, we observed a major peak at *m*/*z* [M^+] (667). For the *neo*-pentyl derivative **6b**, the most intense peak appeared at *m*/*z* [$M^+ - I$] (652), and a weaker peak at *m*/*z*

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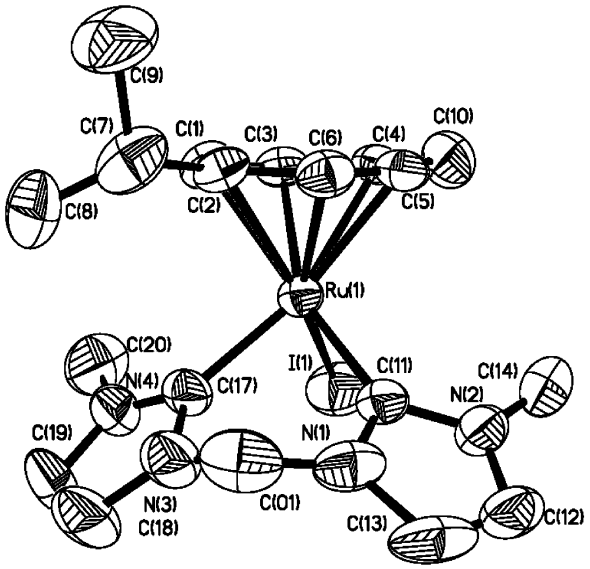

Figure 1. X-ray molecular structure of **4a**. Selected bond lengths (Å) and angles (deg): Ru(1)−C(17) 2.053(7), Ru(1)−C(11) 2.061(7), Ru(1)−I(1) 2.6775(11), C(17)−Ru(1)−C(11) 83.6(3).

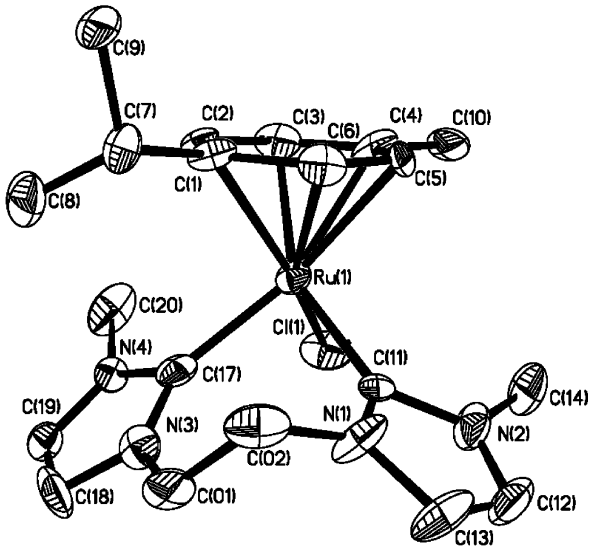

Figure 2. X-ray molecular structure of **5a**. Selected bond lengths (Å) and angles (deg): Ru(1)−C(11) 2.033(15), Ru(1)−C(17) 2.049(15), Ru(1)−Cl(1) 2.436(4), C(17)−Ru(1)−C(11) 87.2(6).

[M^+] (779). All the spectra showed the characteristic isotopic distribution for one ruthenium atom.

X-ray Crystal Structures of Complexes 4a and 5a. To unequivocally confirm the molecular structures of **4a** and **5a**, we obtained crystals of these compounds by slow evaporation from MeOH solutions. We were unable to obtain crystals suitable for X-ray diffraction for the monocarbene complexes **6a** and **6b**.

The molecular structure of **4a** is shown in Figure 1. The biscarbene chelating, bite angle C(11)−Ru(1)−C(17) of 83.6°, lies among the lower angles reported for this ligand (83.2−87.8°),[13,18,19,25,26] probably due to the highly sterically demanding situation of the metal fragment to which it is bound. The CH_2 linker of the biscarbene ligand is pointing out of the coordination sphere of the metal atom thus minimizing its repulsion with the iodine ligand. The average dihedral angle between the plane defined by C(11)−Ru(1)−C(17) and the imidazol rings is 32.14° (higher than the same angle observed for other pseudo-octahedral complexes; range 19.7−26.3°).[18,19,25,27] The dihedral angle C_t−Ru(1)−C(11)−N(1) (C_t is the central point of the *p*-cymene ring) is 103.9°, thus minimizing the repulsion between the *p*-cymene and the imidazole rings. The Ru−C distances for the imidazol-2-ylidene ligand are 2.053 and 2.061 Å, typical for Ru−C σ-bonds, indicating that the back-donation is negligible for this compound, a situation that has become typical for this an other related NHC−metal complexes. The Ru−C distances for the *p*-cymene ligand lie in the usual range.

Figure 2 shows the molecular structure of **5a**. The biscarbene ligand is chelating the metal with a bite angle of 87.2°, bigger than that shown in **4a** as a consequence of the longer linker between the azole rings. The average dihedral angle between the plane defined by C(17)−Ru(1)−C(11) and the imidazol rings is 34.9° which indicates that this angle is not depending on the length of the linker, conversely to our previous findings in Rh and Ir complexes. The dihedral angle C_t−Ru(1)−C(11)−N(1) is 83.7°. As we have previously reported, the dihedral angle between the *xy* plane of a series Rh(I) complexes and the NHC ring is ca. 20° for the methylene linker, ca. 60° for ethylene, and ca. 90° for propylene, thus clearly depending on the linker length. For our two complexes, this angle is also modified by replacing the methylene-bridged ligands by the ethylene-bridged ligands (dihedral angles 103.9° vs 83.7°). We believe that, in our case, the *p*-cymene ligand is highly sterically demanding, forcing the azole rings to orient their slim angle in the bulky axis of the complex. For the propylene-bridged ligand (which we were unable to coordinate), a similar effect would force the azole rings to orientate far from its natural orientation (orthogonal to the C−Ru−C plane), thus yielding a highly unstable structure. However, we are aware that the structures of these two compounds may well be more complex than suggested by the static structures, since correlated motion of the NHC may be possible.[25,28] The Ru−C distances for the imidazol-2-ylidene are 2.033 and 2.049 Å, again typical for Ru−C σ-bonds.

Conclusions

The present work describes the synthesis and properties of a series of ruthenium−arene−monocarbene and biscarbene complexes. The synthesis of the chelate-biscarbene complexes is highly influenced by the nature of the ligand, especially concerning the length of the linker between the azole rings. The crystal structures of the two biscarbenes described indicate that the different reactivity of the ligands with the metal precursor may be due to the different sterically

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demanding situations of the two ligands, especially concerning the relative orientation of the two azole rings with their coordination plane. The results that we describe in this work are in agreement with previously reported papers, where a clear dependence of the biscarbene ligand on its linker length seems to operate. For pseudo-octahedral metal complexes, we did not find in the literature any chelate biscarbene compound with a linker longer than two carbon atoms. For these ligands, pseudo-square-planar complexes of the ligands are highly preferred, while shorter linkers (two or one carbon atoms) tend to give pseudo-octahedral or bimetallic complexes.

We are currently exploring the catalytic application of these complexes, although our initial attempts in reactions such as hydrosilylation of terminal alkynes, hydrogen transfer between alcohols and ketones, and intramolecular hydroamination were unsuccessful. We believe that this result is in fact confirming the high coordination abilities of the ligand, which prevents the complex from opening a coordination vacant site needed for catalytic activity. We are currently modifying the compounds in order to obtain catalytic results.

Experimental Section

General Details. NMR spectra were recorded on Varian Innova 300 and 500 MHz instruments, using $CDCl_3$, DMSO-d_6, and CD_3OD. The bis-imidazolium ligand precursors **1a**, **1b**, **2a**, and **3a**[19,25,27] and the metal complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$[29] were prepared according to literature methods. All other reagents were used as received from commercial suppliers. All reactions were carried out under inert conditions, the solvent was degassed prior to use, and the NEt_3 was distilled under potassium hydroxide.

Synthesis of Compounds. Synthesis of 4a. A mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (100 mg, 0.16 mmol), methylenebis(*N*-methylimidazolium) iodide (**1a**) (117 mg, 0.32 mmol), KI (200 mg, 1,2 mmol), and NEt_3 (250 μL, 1.66 mmol) was stirred in CH_3CN (10 mL) at reflux for 12 h. After cooling, the solvent was removed under reduced pressure. The crude solid was then redissolved in CH_2Cl_2 and added to a column for chromatography. Elution with CH_2Cl_2/acetone (9/1) separated a minor red band containing $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$. Subsequent elution with CH_2Cl_2/acetone (1/1) and KPF_6, afforded the separation of **4a** as a yellow band. Compound **4a** was recrystallized from methanol as an orange crystalline solid. Yield: 45%. ^{1}H NMR (DMSO-d_6, 300 MHz): 7.50−7.54 (m, 4H, CH_{imid}), 6.29 (d, 1H, $^2J_{H-H}$ = 13.2 Hz, $NCH_{2\ linker}$), 5.78−5.94 (m, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 5.52 (d, 1H,$^2J_{H-H}$ = 13.2, $NCH_{2,linker}$), 3.32 (s, 6H, NCH_3), 3.08 (m, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.05 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 0.91 (d, 6H, $^3J_{H-H}$ = 6.9 Hz, $(CH_3)_2CHC_6H_4(CH_3)$-*p*). ^{13}C{^{1}H} NMR (DMSO-d_6, 300 MHz): 172.54 (1C, C−Ru), 124.55, 122.09 (4C, CH_{imid}), 109.75, 104.00, 92.43, 86.48 (6C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 61.47 (1C, $NCH_{2,linker}$), 46.43 (2C, NCH_3), 32.16 (1C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 22.93 (2C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 19.59 (1C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*). Anal. Calcd for $C_{19}H_{26}F_6IN_4PRu$ (683.38): C, 33.39; H, 3.83; N, 8.20. Found: C, 33.43; H, 3.80; N, 8.22. Electrospray MS. Cone 20 V. *m*/*z* (fragment): 539 $[M]^+$.

Synthesis of 5a. A mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (100 mg, 0.16 mmol), ethylenebis(*N*-methylimidazolium) chloride (**2a**) (172 mg, 0.65 mmol), and NEt_3 (250 μL, 1.66 mmol) was stirred in CH_3CN (10 mL) for 12 h. After cooling, the solvent was removed under vacuum. Then the crude solid was redissolved in CH_2Cl_2 and purified by column chromatography; elution with CH_2Cl_2/CH_3OH (9/1) and KPF_6 afforded the separation of **5a** as an orange band. Compound **5a** was precipitated from a CH_2Cl_2/hexane solution. Yield: 21%. ^{1}H NMR (CD_3OD, 300 MHz): 7.37, 7.26 (d, 4H, CH_{imid}), 5.74, 5.64 (d, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 4.56, 4.30 (m, 4H, $NCH_{2\ linker}$), 4.02 (s, 6H, NCH_3), 3.21 (m, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.23 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.02 (d, 6H, $^3J_{H-H}$ = 6.9 Hz, $(CH_3)_2CHC_6H_4(CH_3)$-*p*). ^{13}C{^{1}H} NMR (CD_3OD, 500 MHz): 169.17 (1C, C−Ru), 125.37, 123.23 (4C, CH_{imid}), 106.64, 105.64, 92.70, 86.64 (6C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 54.88, 49.25 (2C, $NCH_{2\ linker}$), 38.96 (2C, NCH_3), 31.69 (1C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 21.84 (2C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 17.22 ($(CH_3)_2CHC_6H_4(CH_3)$-*p*). Anal. Calcd for $C_{20}H_{28}ClF_6N_4PRu$ (605.95): C, 39.64; H, 4.66; N, 9.25. Found: C, 39.60; H, 4.69; N, 9.22. Electrospray MS. Cone 30V. *m*/*z* (fragment): 461 $[M]^+$.

Synthesis of 6a. A mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (100 mg, 0.16 mmol), methylenebis(*N*-methylimidazolium) iodide (**1a**) (117 mg, 0.32 mmol), NEt_3 (250 μL, 1.66 mmol), and KI (100 mg, 0.6 mmol) was stirred in CH_3CN (10 mL) at 50 °C for 12 h and at 90 °C for 4 h. The solvent was eliminated under vacuum. The compound was purified by column chromatography**.** Elution with CH_2Cl_2/acetone (1/1) and KPF_6 gave compound **6a** as an orange band. The product was precipitated from a CH_2Cl_2/ether solution. Yield: 15%. ^{1}H NMR (CD_3OD, 300 MHz): 9.00 (s, 1H, NCHN), 7.78, 7.52 (s, 2H, free CH_{imid}), 7.48, 7.41 (d, 2H, coord CH_{imid}), 5.63, 5.35 (d, 4H,$^3J_{H-H}$ = 6 Hz, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 4.04 (s, 3H, free NCH_3), 3.88 (s, 3H, coord. NCH_3), 2.98 (m, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.00 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.28 (d, 6H, $^3J_{H-H}$ = 3.3 Hz, $(CH_3)_2CHC_6H_4(CH_3)$-*p*). ^{13}C{^{1}H} NMR (CD_3OD, 300 MHz): 177.13 (1C, C−Ru), 137.48 (1C, NCHN), 126.78, 123.56 (2C, free CH_{imid}), 122.12 (2C, coord.CH_{imid}), 110.85, 99.42 86.56, 82.19 (6C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 62.41 (1C, $NCH_{2\ linker}$), 39.05 (1C, free NCH_3), 35.57 (1C, coord. NCH_3), 30.97 (1C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 21.43 (2C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 17.47 (1C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*). Anal. Calcd for $C_{19}H_{27}F_6I_2N_4PRu$ (811.29): C, 34.25; H, 4.08; N, 8.41. Found: C, 34.28; H, 4.10; N, 8.38. Electrospray MS. Cone 30 V. *m*/*z* (fragment): 667 $[M]^+$.

Synthesis of 6b. A mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (100 mg, 0.16 mmol), methylenebis(*N-neo*-pentylimidazolium) iodide (**1b**) (356 mg, 0.65 mmol), NEt_3 (150 μL, 1.00 mmol), and KI (100 mg, 0.6 mmol) was stirred in CH_3CN (10 mL) at 50 °C for 12 h and at 90 °C for 4 h. This compound was purified by a method similar to that described above. Elution with CH_2Cl_2/acetone (1/1) and KPF_6 afforded the separation of a major red band that contained **6b**. The product was precipitated with CH_2Cl_2/ether. Yield: 45%. ^{1}H NMR (CD_3OD, 500 MHz): 8.77 (s, 1H, NCHN), 7.73, 7.61 (s, 2H, free CH_{imid}), 7.54, 6.90 (d, 2H, coord. CH_{imid}), 5.22, 5.43 (d, 4H,$^3J_{H-H}$ = 6 Hz, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 4.05 (s, 2H, free NCH_2-*t*-Bu), 3.92 (s, 2H, coord NCH_2-*t*-Bu), 5.62 (s, 2H, $NCH_{2\ linker}$), 2.82 (m, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.20 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.31 (d, 6H, $^3J_{H-H}$ = 7 Hz, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 0.998 (s, 9H, coord *t*-Bu), 0.976 (s, 9H, free *t*-Bu). ^{13}C{^{1}H} NMR (CD_3OD, 500 MHz): 174.58 (1C, C−Ru), 136.50 (1C, NCHN), 124.71, 123.47 (2C, free CH_{imid}), 122.98, 122.46 (2C, coord. CH_{imid}), 110.32, 101.68, 88.08, 83.55 (6C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 64.66 (1C, $NCH_{2,linker}$), 63.76 (1C, free NCH_2-*t*-Bu), 62.15 (1C, coord NCH_2-*t*-Bu), 31.74 (1C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 29.41 (1C, free *C*-$(CH_3)_3$), 29.01 (3C, free C−$(CH_3)_3$), 27.75 (1C, coord *C*-$(CH_3)_3$), 27.45 (3C, coord *C*-$(CH_3)_3$), 23.70 (2C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 19.61 (1C, $(CH_3)_2CHC_6H_4(CH_3)$-*p*). Anal. Calcd for $C_{27}H_{43}I_2F_6N_4PRu$ (923.50): C, 35.12; H, 4.69; N, 6.07. Found: C, 35.15; H,

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Table 1. Crystallographic Data

	4a	**5a**
empirical formula	$C_{19}H_{26}IN_4RuPF_6$	$C_{20}H_{28}ClN_4RuPF_6$
fw	683.38	605.95
wavelength (Å)	0.71073	0.71073
cryst syst	orthorhombic	monoclinic
space group	$Pna2_1$	$P1c1$
a (Å)	12.111(2)	11.897(2)
b (Å)	13.081(3)	10.797(2)
c (Å)	15.513(3)	19.355(4)
α	90.00°	90.00°
β	90.00°	100.017(5)°
γ	90.00°	90.00°
V (Å^3)	2457.7(8)	2448.3(8)
Z	4	2
D (calcd)	1.847 Mg/m^3	1.644 Mg/m^3
abs coeff	2.018 mm^{-1}	0.876 mm^{-1}
reflns collected	15742	16480
GOF on F^2	1.055	0.957
final R indices [$I > 2\sigma(I)$]	R1 = 0.0519 wR2 = 0.1627	R1 = 0.0703 wR2 = 0.1910

4.66; N, 6.03. Electrospray MS. Cone 20 V. m/z (fragment): 779 $[M]^+$, 652 $[M - I]^+$.

X-ray Diffraction Studies. Single crystals of **4a** and **5a** were mounted on a glass fiber in a random orientation. Crystal data are summarized in Table 1. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. An hemisphere of data was collected based on three ω-scan runs (starting $\omega = -28°$) at values $\phi = 0°$, 90°, and 180° with the detector at $2\theta = 28°$ At each of these runs, frames (606, 435 and 230) were collected at 0.3° intervals and 30 s per frame. Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and was refined using the SHELXTL 5.1 software package.[30] All non-hydrogens were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 1. The diffraction frames were integrated using the SAINT package.[31]

Electrospray Mass Spectrometry. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument using CH_3OH as the mobile phase solvent. Nitrogen was employed as drying and nebulizing gas. Isotope experimental patterns were compared with theoretical patterns obtained using the Masslynx 3.5 program. In all cases there was good agreement between the experimental and calculated isotopic mass distributions.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035307O

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