# Ferrocenyl-Imidazolylidene Ligand for Redox-Switchable Gold-Based Catalysis. A Detailed Study on the Redox-Switching Abilities of the Ligand

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S *Supporting Information*
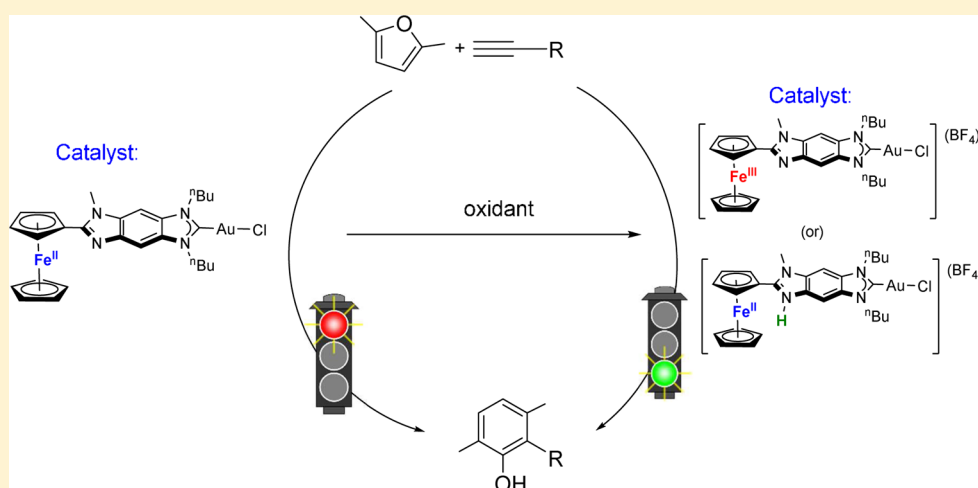
ABSTRACT: An imidazolium salt with a fused benzoferrocenyl was synthesized. This compound was used as an N-heterocyclic carbene (NHC) precursor, and the related ferrocenyl-imidazolylidene complexes Fc-NHC-ML$_n$ (ML$_n$ = IrCl(COD), IrCl(CO)$_2$, AuCl) were synthesized and fully characterized, including the crystallographic characterization of some of the key structures. The oxidation of the iridium carbonyl compound Fc-NHC-IrCl(CO)$_2$ with acetylferrocenium tetrafluoroborate afforded the oxidized ferrocenium-NHC-IrCl(CO)$_2$ (Fe(III)) species; however the isolated product contained a byproduct resulting from the protonation of the starting Fe(II) complex. The analysis of the electron-donating character of the neutral ligand and the ligand resulting from the oxidation was carried out by studying the variation of the ν(CO) stretching frequencies of Fc-NHC-IrCl(CO)$_2$ and its oxidized analogue, revealing that this shift is 2.9 cm^{-1}, which is consistent with a decrease of the electron-donating character of the ligand produced by the generation of a positively charged metal complex. DFT calculations were carried out in order to rationalize these results. The effects of the oxidation of the ligand in homogeneous catalysis were tested by using a related ferrocenyl-imidazolylidene-gold(I) complex. In the hydroamination of terminal alkynes, the results indicated that the oxidation of the ligand produced a moderate increase of the activity of the gold catalyst. In the cyclization of alkynes with furans, the neutral complex was not active, while the product resulting from its oxidation produced moderate to good yields in the formation of the final products.

■ INTRODUCTION

In the traditional design of homogeneous catalysts, the choice of a ligand is based on the notion that the ligand plays a spectator role. However, some properties of a metal complex may be influenced by essentially ligand-based reactivity.[1] For example, the introduction of a *redox-active* functionality within a ligand framework potentially allows the reactivity and selectivity of complexed metal centers to be modulated through the electrochemical switching of the redox center.[2] The redox-active ligand can modify the Lewis acidity/basicity of the metal or influence the catalytic process by acting as an electron reservoir.[3]

In a typical reaction, a redox-switchable catalyst facilitates a given transformation at a given rate, when the ligand is in the neutral form. However, upon oxidation (or reduction), the activity or selectivity of the catalyst changes, or the catalyst can facilitate a new transformation.[3b] Such redox-switchable events frequently use a metallocene (most often ferrocene) to influence the ligand's electron-donating power and, consequently, the catalytic activity of a metal complex may change. Among the known N-heterocyclic carbene ligands containing

ferrocenyl substituents,[4] few have been used in redox-switchable catalysts, but they all revealed that the redox event has important consequences in their catalytic activities.[4i−l] Interestingly, most ferrocenyl-containing NHC-based complexes that have been used as redox-switchable catalysts possess ferrocenyl fragments electronically disconnected from the active catalytic sites (Scheme 1). Therefore, there is the risk that the

Scheme 1
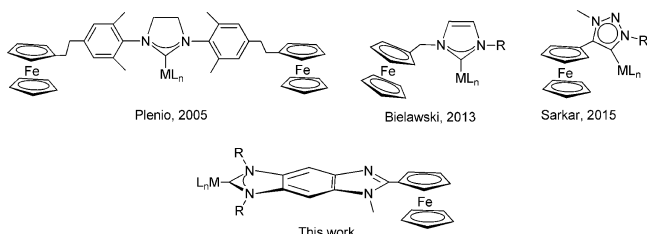
changes in the chemical properties suffered by the active metal fragment may not be due to the modification of the electronic properties of the ligand, but for other reasons, e.g., change in solubility, decomposition of the catalyst, interaction of the oxidants with the substrates, etc.

We have been recently interested in studying the influence of additives on the electronic properties of a series of polyaromatic NHC ligands[5] and observed that using additives produced important changes in the catalytic activities of the NHC complexes.[6] In this context, we thought that connecting a ferrocenyl fragment with a polyaromatic backbone of an N-heterocyclic carbene (NHC) ligand might afford a new family of NHC ligands whose electronic properties could undergo subtle electronic changes upon application of redox stimuli and, therefore, could allow tuning the catalytic activity of the metal complexes.

On the basis of all these precedents, herein we report the preparation of an imidazolium salt with a fused ferrocenyl-benzimidazole, which we used for the preparation of the corresponding ferrocenyl-NHC metal complexes (Scheme 1, ML_n = [IrCl(COD)], [IrCl(CO)$_2$], and [AuCl]). This ferrocenyl monocarbene mimics the topological features of the ubiquitous benzobis(imidazolylidene) ligand,[7] whose electronic properties were extensively studied.[8] Together with the full characterization of the new metal complexes, we studied the catalytic properties of the gold complex in the hydroamination of alkynes and in the cyclization of 2,5-dimethylfuran with terminal alkynes. For both processes, the addition of an oxidant produced an improvement of the activity of the catalyst.

■ RESULTS AND DISCUSSION

a. Synthesis and Characterization of the Compounds. The reactions displayed in Schemes 2, 3, and 4 summarize all the synthetic procedures performed in this work. The ferrocenyl-imidazolium salt **1** was quasi-quantitatively prepared
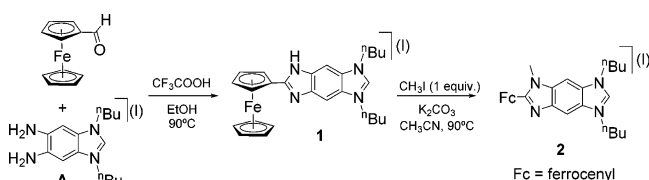
(yield 95%) by the cyclization of the diaminobenzimidazolium iodide **A** with ferrocenecarboxaldehyde, in the presence of trifluoroacetic acid. Subsequent reaction with methyl iodide in the presence of potassium carbonate afforded the imidazolium **2**, in which the N−H proton of **1** was replaced by a methyl group (yield 68%). The ferrocenyl-imidazolium salt **2** was used for the preparation of the NHC-metal complexes by following the procedures displayed in Scheme 3. In all cases, the NHC metal complexes were synthesized by the transmetalation from the *in situ* prepared NHC-Ag complex **3**, which we also isolated for its full characterization. The reaction of **2** with Ag$_2$O in CH$_2$Cl$_2$, followed by the addition of [IrCl(COD)]$_2$, afforded the Ir(I) complex **4** in 60% yield. The iridium−carbonyl compound **5** was obtained by bubbling carbon monoxide over a CH$_2$Cl$_2$ solution of **4**. The gold complex **7** was obtained in 61% yield by the reaction of the *in situ* prepared complex **3** with [AuCl(SMe$_2$)].

All new complexes were characterized by NMR spectroscopy and electrospray mass spectrometry (ESI-MS) and gave satisfactory elemental analyses. As a diagnostic of the formation of the NHC-metal complexes, the ^{13}C NMR spectra of **3**, **4**, **5**, and **7**, displayed the distinctive signals due to the metalated carbene carbons at 192.8, 192.0, 182.8, and 178.3 ppm, respectively.

In order to oxidize the ferrocenyl-imidazolylidene complexes **5** and **7**, these were reacted with acetylferrocenium tetrafluoroborate in dry dichloromethane at room temperature. The reaction quantitatively produced acetylferrocene, which was separated by washing the evaporated reaction crude with dry diethyl ether. As a result of the analysis of the bulk solids obtained, we concluded that they contained mixtures of the oxidized ferrocenium complexes **6/8** together with the protonated Fe(II) species **6**-H/ **8**-H, respectively. The presence of the protonated species was confirmed by their mass spectra (ESI-MS), which showed intense peaks assigned to **6**-H (m/z = 753.1) and **8**-H (m/z = 701.3). In order to determine the source of the hydrogen atom, we repeated the oxidation of **5** in deuterated solvents (CD$_2$Cl$_2$ and CD$_3$CN). **6**-H was again detected, although with a much lower intensity. When the reaction was carried out using the same deuterated solvents but in the presence of small amounts of D$_2$O, the deuterated species **6**-D (m/z = 754.1) was observed. These results suggest that water might be responsible for the formation of **6**-H and **8**-H, although the details about their formation are not clear.

The slow crystallization of the products in a mixture of dichloromethane/hexane afforded crystals of **6**-H and **8**-H, which gave satisfactory elemental analysis and whose structures were determined by X-ray crystallography (see below for details). Unfortunately, all our attempts to obtain **6**-H and **8**-H by protonation of **5** and **7** with stoichiometric amounts of HBF$_4$ or CF$_3$COOH were unsuccessful. Similarly, the reaction of **6**-H or **8**-H with Cs$_2$CO$_3$ in CH$_2$Cl$_2$ did not afford **5** and **7**, therefore suggesting that **6**-H and **8**-H are not simply protonated species.

The comparison of the infrared spectra of **5** and **6**-H allowed quantifying the modification of the electron-donating character of the ferrocenyl-NHC ligand upon protonation. The infrared spectrum of **6**-H showed two CO stretching bands at 2071.2 and 1989.2 cm^{-1}. These values may be compared with the two CO stretching bands shown by **5**, at 2068.3 and 1986.3 cm^{-1}, thus indicating that the oxidation of the Fc-NHC ligand affords an increase of the average stretching frequency $\Delta\nu_{av}$(CO) by 2.9 cm^{-1}, in agreement with the lower electron-donating power

Scheme 2
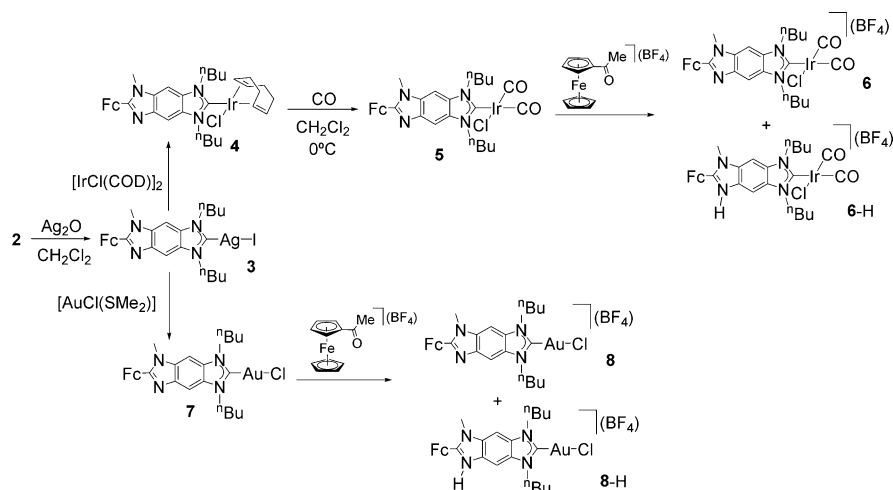
Scheme 3

Scheme 4
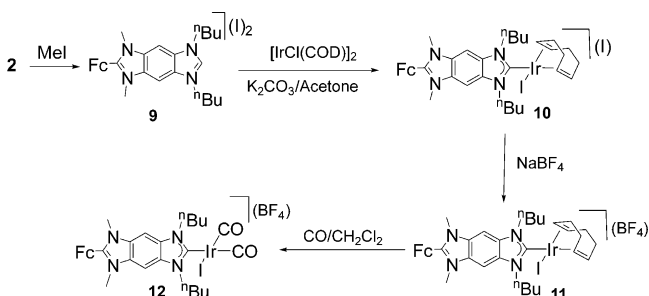
of the protonated ligand. As a reference for comparing the magnitude of the modification of the electron-donating character of the ligand, it may be taken into account that a similar shift (based on the shift of the Tolman electronic parameter, TEP) is found between N,N'-dimethylimidazolylidene (IMe) and N,N'-dimethylbenzimidazolylidene (two NHCs that are considered electronically different). However, this shift is much smaller than 9 cm^{-1}, observed by Bielawski and co-workers upon the oxidation of their ferrocenyl-NHC ligand (see Scheme 1).[4i]

In order to determine if the $\Delta\nu_{av}(CO)$ value that we obtained upon the protonation of **5** is consistent with the generation of a positively charged ferrocenyl-NHC ligand, we

decided to introduce a positive charge in the ferrocenyl-NHC ligand by methylating the unalkylated nitrogen in the ferrocenyl-imidazolium compound **2**. The resulting dicationic ferrocenyl-imidazolium, **9**, allowed us to obtain the cationic complex [Fc-NHC-IrI(CO)$_2$](BF$_4$), **12**, by following the procedure described in Scheme 4 (more details about the synthetic procedure and the characterization of the compounds may be found in the Experimental Section).

The average of the two CO stretching bands of **12** was only 1.8 cm^{-1} higher than the average $\nu(CO)$ of the analogue neutral compound **13** (see Scheme 5), thus indicating that the introduction of a positive charge in the ferrocenyl-NHC ligand, by either protonation or methylation, has a small (although not negligible) influence on the electron-donating character of the carbene ligand. Complex **12** can be further oxidized in dichloromethane by addition of acetylferrocenium tetrafluoroborate, which is quantitatively transformed into acetylferrocene. The IR spectrum of an *in situ* prepared solution of the resulting Fe(III) complex **14** showed two CO stretching bands at 2068.0 and 1991.4 cm^{-1}; thus the average $\nu(CO)$ is 2.4 cm^{-1} higher than that shown by **12** and 4.2 cm^{-1} higher than the average $\nu(CO)$ shown by **13** (Scheme 5). Unfortunately, all attempts to isolate a pure form of **14** were unsuccessful.

The study of the electronic properties of the complexes was also carried out by means of electrochemical studies. The cyclic voltammetries were conducted in CH$_2$Cl$_2$, with [NBu$_4$][PF$_6$] as

Scheme 5
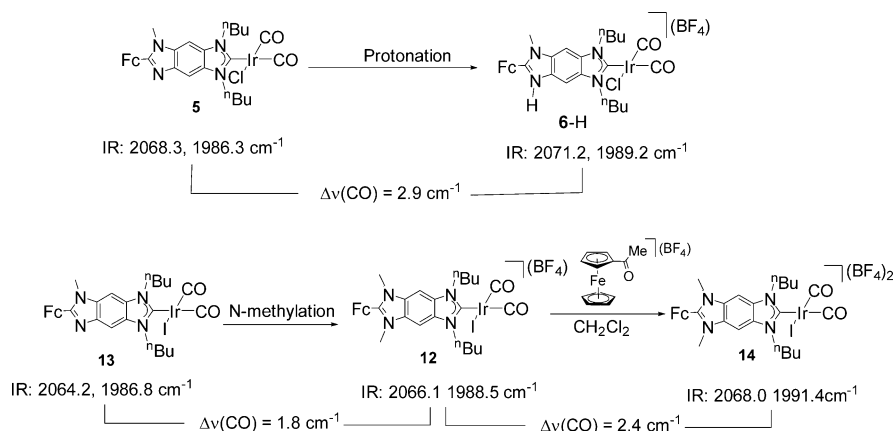
the electrolyte. The cyclic voltammograms (CV) of compounds **1** and **2** showed a complicated set of bands that could be tentatively assigned to the successive Fe^{2+}/Fe^{3+} and $2I^{-}/I_2$ redox couples and the oxidation of the polyaromatic system containing the imidazolium ion.[9] It has been previously reported that the presence of iodide (or bromide) counteranions in ferrocenylimidazolium salts induces the appearance of additional peaks due to the increased electroactivity shown by the imidazolium in close proximity to the iodide.[10] In both complexes, the band attributed to the oxidation of Fe^{2+}/Fe^{3+} was measured at 0.76 and 0.84 V (versus saturated calomel electrode, SCE) for **1** and **2**, respectively (see Figures S1–S4 in the Supporting Information). The cyclic voltammograms of complexes **4**, **5**, and **7** are displayed in Figure 1. Complex **4**,
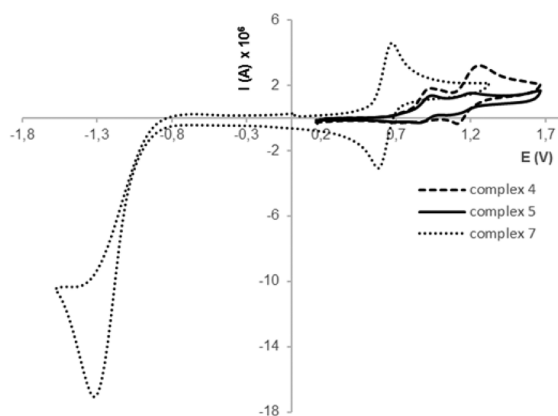

Figure 1. Cyclic voltammetry (CV) plot of complexes **4**, **5**, and **7**. Measurements were performed on a 1 mM solution of the analyte in dry CH_2Cl_2 with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte, 100 mV/s scan rate, Fc/Fc^+ used as standard with $E_{1/2}(Fc/Fc^+) = 0.46$ V vs SCE.

with a ferrocenyl-imidazolylidene ligand bound to [IrCl(COD)], exhibited two quasireversible redox events at 0.87 and 1.18 V, which were attributed to the Fe^{2+}/Fe^{3+} and Ir^{+}/Ir^{2+} redox couples, respectively. Given that the redox potentials for [IrCl(NHC)(COD)] (NHC = unsaturated N-heterocyclic carbene) are known to range between 0.59 and 0.91 V,[11] it can be concluded that the oxidation of the ferrocenyl fragment in **4** has a strong influence on the value of the redox potential of the Ir^{+}/Ir^{2+} couple. Complex **5**, consisting of a ferrocenylimidazolylidene ligand bound to $[IrCl(CO)_2]$, shows two quasi-irreversible oxidation processes at 0.88 and 1.17 V, again attributed to the oxidations occurring at the Fe and Ir centers, respectively. The value of the redox potential for the Ir^{+}/Ir^{2+} couple in **4** and **5** is virtually identical, indicating that the presence of the electron-withdrawing carbonyl ligands has negligible influence on the redox potential of the iridium center.

Complex **7**, in which the ferrocenyl-imidazolylidene is bound to a Au(I) center, showed one reversible oxidation process at 0.63 V assigned to the ferrocenyl fragment and an irreversible reduction event due to the reduction of Au(I) to Au(0).

In order to confirm that complexes **5** and **7** were oxidized to their Fe(III) analogues in the presence of acetylferrocenium tetrafluoroborate, we decided to measure the ^{57}Fe Mössbauer spectra of complexes **5** and **7** and of the bulk solids that we isolated from their reactions with the oxidant. Figure 2 shows the spectra recorded at 77 K. The spectra of complexes **5** and **7** (Figure 2a and c, respectively) are fully consistent with the

complexes containing a Fe^{2+} center, as shown by the isomer shifts at 0.54 and 0.53 mm s^{-1} and quadrupole splittings of 2.21 and 2.37 mm s^{-1}, respectively. The spectrum of the bulk solid resulting from the oxidation of **5** (Figure 2b) reveals two signals of equal intensity. The outer doublet reflects the presence of a Fe^{2+} center, while the inner singlet is consistent with Fe^{3+} (singlet, isomer shift at 0.51 mm s^{-1}). This result suggests that this solid contains **6** (Fe^{3+}) and **6**-H (Fe^{2+}) in a 1:1 ratio. The spectrum of the bulk solid resulting from the oxidation of **7** (Figure 2d) also reveals the presence of two oxidation states for the iron centers (the Fe^{3+} center is observed as a doublet at 0.50 mm s^{-1}, with a quadrupole splitting of 0.67 mm s^{-1}). In this case the relative integrals of the two signals indicate that the bulk solid contains **8** (Fe^{3+}) and **8**-H (Fe^{2+}) in a 1:2 molar ratio.

The molecular structures of complexes **6**-H, **7**, **8**-H, and **11** were determined by means of X-ray diffraction studies.

The molecular structure of complex **6**-H in Figure 3 consists of a ferrocenyl moiety connected to an iridium chloride dicarbonyl fragment through a planar benzimidazolium-imidazolylidene ligand. The cationic nature of the complex is confirmed by the presence of a tetrafluoroborate counteranion. The $Ir-C_{carbene}$ distance is 2.064(9) Å, and the $Ir-CO$ distances are 1.916(13) and 1.89(2) Å, for the *trans* and *cis* carbonyl groups, respectively, which are consistent with the high *trans* influence of the carbene ligand. The coordination plane of the Ir(I) fragment is quasi-perpendicular with respect to the carbene-tricyclic ligand (86.4°). The substituted cyclopentadienyl fragment of the ferrocenyl group is almost coplanar with the tricyclic polyaromatic linker, establishing an angle between them of 4.12°. The distances between the iron atom and the Cp centroids are 1.677 and 1.640 Å for the unsubstituted and substituted cyclopentadienyls, in agreement with the presence of a Fe(II) center.[12] The N–C distances of the methyl imidazole bound to the ferrocenyl fragment are similar, 1.342(11) and 1.323(11) Å, indicating a high degree of delocalization, rather than showing the difference expected for a single and double bonds, expected for a structure without a proton at N3. The presence of the N3–H3 proton is also supported by the close contact with the BF_4 counteranion (H3···F3 distance = 1.949 Å), which reflects a hydrogen-bonding interaction.

The molecular structures of **7** and its protonated analogue **8**-H (*vide infra*) allow the comparison of the structural changes produced by the protonation of the ligand.

The molecular structures of complex **7** and **8**-H are displayed in Figures 4 and 5, respectively. The cationic nature of complex **8**-H is confirmed by the presence of the BF_4 counteranion. One of the main differences between the two structures is that the cyclopentadienyl-substituted ring in **7** deviates from the plane of the tricyclic polyaromatic fragment by 18.64°, while in **8**-H the two planes are almost coplanar (angle 3.11(19)°). The Au–$C_{carbene}$ distance in **7** is slightly shorter than in **8**-H (1.989 vs 1.953(6) Å), maybe as a consequence of the lower electron-donating character of the ligand (in **8**-H), which is reflected in a weaker σ-bond. The metric parameters of the ferrocenyl fragments of these two structures are almost identical. For example, the dihedral angles between the cyclopentadienyl rings are 0.73° and 0.8(3)° for **7** and **8**-H, respectively. The average distances between the Fe atom and the Cp(centroids) are 1.640 (for **7**) and 1.643 Å (for **8**-H), which are suggestive of the presence of a Fe(II) center.[12] As in the case of the molecular structure of **6**-H, in the case of **8**-H, the two N–C
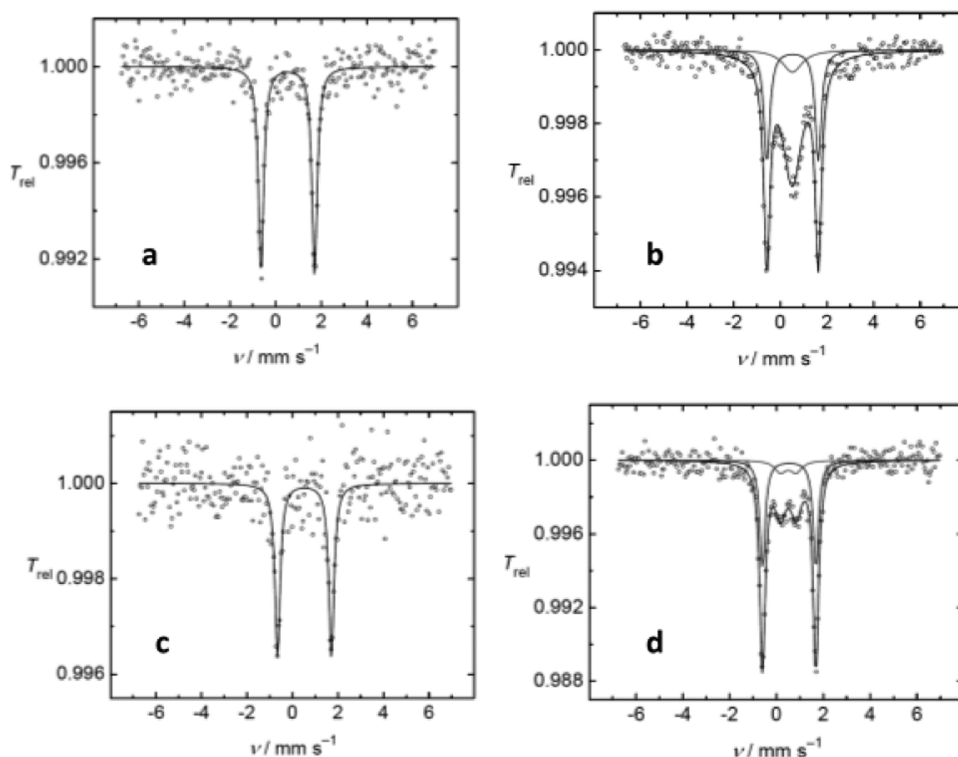
Figure 2. ^{57}Fe Mössbauer spectra (recorded at 77 K) of (a) **5**, (b) bulk solid resulting from oxidation of **5**, (c) **7**, and (d) bulk solid resulting from the oxidation of **7**. Open circles are the experimental data, and solid lines are the corresponding spectral fits.
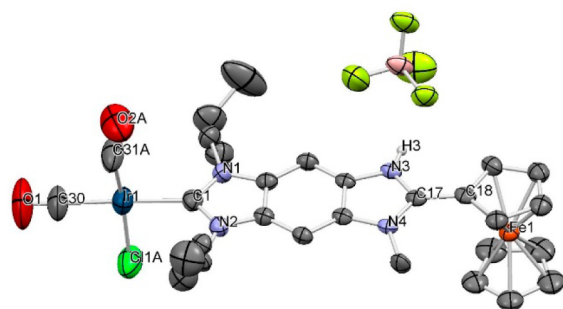

Figure 3. Molecular diagram of complex **6**-H. Ellipsoids are at 50% probability. Hydrogen atoms (except H3), minor disorder components, and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1−C1 2.064(9), Ir1−C31A 1.89(2), Ir1−C30 1.916(13), Ir1−Cl1 2.329(6), C30−O1 1.088(16), C31A−O2A 1.13(3), N3−C17 1.342(11), N4−C17 1.323(11), C17−C18 1.449(12), C1−Ir1−C30 178.1(6), C1−Ir1−Cl1 87.7(3).

Figure 4. Molecular structure of complex **7**. Hydrogen atoms and solvent (CHCl$_3$) have been omitted for clarity. Ellipsoids are at 50% probability. Selected bond distances (Å) and angles (deg): Au1−C1 1.989(5), Au1−Cl1 2.2823(13), N4−C17 1.382(6), N3−C17 1.326(6), C1−Au1−Cl1 179.58(15).

distances of the imidazolyl ring bound to the ferrocenyl fragment are identical within standard uncertainties (N4−C17 1.351(7), N3−C17 1.340(7) Å), indicating a high degree of delocalization, while in the neutral molecule **7** the analogous distances are more consistent with the presence of a single and a double bond (N3−C17 1.326, N4−C17 1.462 Å). The proton bound to the nitrogen of the ligand (H3) is at a distance of 1.94(2) Å to one of the fluorine atoms of the BF$_4$ counteranion, thus strongly suggesting a hydrogen-bonding interaction.

Figure 6 shows the molecular structure of complex **11**. The molecule contains a ferrocenyl group connected to an iridium cyclooctadiene iodide fragment via a benzimidazolium imidazolylidene 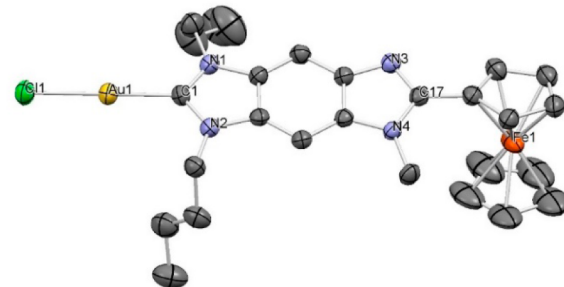ligand. The cationic nature of the molecule is confirmed by the presence of a tetrafluoroborate counteranion. The Ir−C$_{carbene}$ bond distance is 1.9887 Å. The coordination plane of the Ir(I) fragment is oriented quasi-perpendicular with respect to the plane of the tricyclic ligand (87.33°), and the plane of the substituted Cp ring deviates from the plane of the tricyclic ligand by 41.29°. The distances between the Fe(II) center and the centroids of the cyclopentadienyl rings are 1.637 and 1.657 Å for the substituted and unsubstituted Cp rings, respectively. The two N−C distances of the imidazolyl bound to the ferrocenyl fragment are quasi-identical (N4−C17 1.350, N3−C17 1.345), thus indicating a delocalized π-bond between the three atoms involved.

Complexes **5**, **6**, and **6**-H were studied computationally, using a local M06L DFT functional and a hybrid ωB97XD functional with the good-quality def2TZVP basis set (QZVP for Ir). Both functionals are modern methods suitable for modeling transition-metal complexes. A search for the lowest
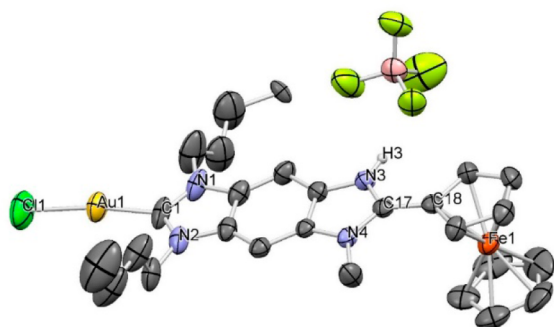
Figure 5. Molecular structure of complex **8**-H. Hydrogen atoms (except H3), minor disorder components, and lattice solvent have been omitted for clarity. Ellipsoids are at 50% probability. Selected bond distances (Å) and angles (deg): Au1−C1 1.953(6), Au1−Cl1 2.270(8), N4−C17 1.351(7), N3−C17 1.340(7), C17−C18 1.449(8), C1−Au1−Cl1 173.0(4).
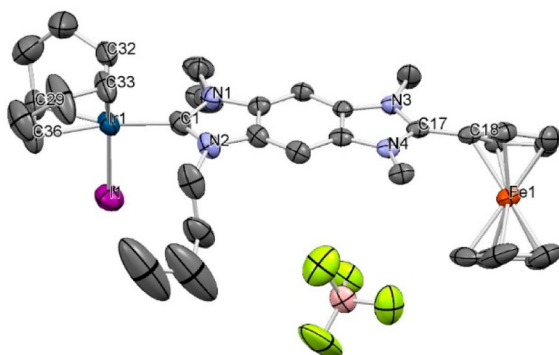

Figure 6. Molecular structure of complex **11**. Hydrogen atoms have been omitted for clarity. Ellipsoids are at 50% probability. Selected bond distances (Å) and angles (deg): Ir1−C1 1.9887(7), Ir1−I1 2.6558(6), Ir1−C33 2.101(8), Ir1−C32 2.089(8), Ir1−C36 2.201(8), Ir1−C29 2.192(8), N4−C17 1.350(8), N3−C17 1.345(9), C7−C18 1.531(12), I1−Ir1−C1 91.4(2).

energy structures returned the optimized geometries presented in Figure 7; the selected structural information is collected in Table 1.

The data of Table 1 show minor structural changes upon oxidation or protonation of **5**; overall, the three structures of Figure 7 are similar. Among the salient features are the C17−N distances that are different by ca. 0.07 Å in **5** and **6** and by ca. 0.03 Å in **6**-H; the latter is in reasonable agreement with the experiment. Unlike the crystal structures of this work, the calculated gas-phase structures all exhibit some degree of rotation of the metal fragments with respect to the NHC ligand backbone that is obvious when looking at Figure 7. We believe that these molecules do not benefit by conjugation between the Cp$_2$Fe fragment and the rest of the NHC ligand. The experimental structures of **6**-H, **7**, and **8**-H, where the FeCp$_2$ fragment appears to be in conjugation with the rest of the NHC ligand, might be influenced by packing.

One question that we wanted to answer with the help of the calculations was about the location of the unpaired electron in **6**. The α-electron density, associated with the unpaired electron, was found exclusively on iron in **6** by the ωB97XD calculation. The M06L calculation found most (0.81) α-spin density on iron, but suggested some probability (0.26) of finding the α-spin on iridium as well. The M06L calculation of
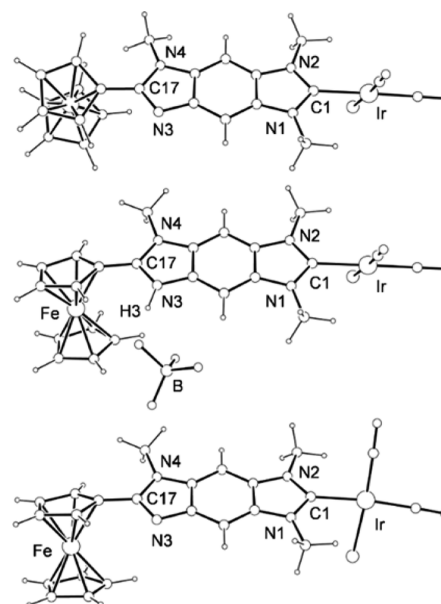

Figure 7. DFT (M06L)-optimized geometries of complexes **5** (top), **6**-H (center), and **6**.

Table 1. Bond Distances (Å) in 5, 6-H, and 6

system	C1−Ir	C1−N1	C17−N3	C17−N4	Fe−X1[a]	Fe−X2[a]
5, M06L	2.10	1.35	1.31	1.38	1.62	1.63
5, ωB97XD	2.09	1.34	1.31	1.38	1.67	1.67
6, M06L	2.09	1.35	1.32	1.38	1.66	1.67
6, ωB97XD	2.08	1.35	1.31	1.37	1.68	1.68
6-H, M06L	2.10	1.35	1.33	1.36	1.62	1.64
6-H, ωB97XD	2.08	1.35	1.32	1.35	1.66	1.67
6-H, expt	2.06	1.37	1.33	1.34	1.64	1.67

[a]X1 and X2 denote the centroids of the C$_5$H$_4$ and C$_5$H$_5$ rings in Figure 7.

the singlet **5** placed the two highest occupied molecular orbitals on iron (d$_{xy}$ and d$_{x^2-y^2}$, HOMO and HOMO−1, at −0.181 06 and −0.182 15 hartree), while the next two MOs were combinations of the d$_{z^2}$ orbitals of both metals (HOMO−2 and HOMO−3, at −0.192 00 and −0.192 24 hartree). These observations qualitatively agree with the CV data of Figure 1, showing two quasireversible oxidation processes at 0.88 and 1.17 V for **5**, attributed to the successive oxidations occurring first at the iron center and next on iridium.

The final piece of computational data concerns the stretching vibrations of the carbonyls in the complexes of Figure 7. The averaged calculated harmonic C−O stretching frequencies of **5** (M06L: 2087.2, ωB97XD: 2141.2 cm^{-1}) and [**6**-H]BF$_4$ (M06L: 2091.7, ωB97XD: 2144.8 cm^{-1}) are exaggerated compared to the experimental average ν(CO) = 2027.3 (**5**) and 2030.2 (**6**-H) values, as expected. The changes from **5** to [**6**-H]BF$_4$ upon protonation are small (M06L: 4.5, ωB97XD: 3.6 cm^{-1}) and comparable to the experimental value of 2.9 cm^{-1} in Scheme 5. We noticed a peculiar influence of the counterion, BF$_4^-$, on the calculated frequencies of **6**-H. When the cation **6**-H was optimized without BF$_4^-$ using the M06L functional, the average ν(CO) increased to 2106.6 cm^{-1}, and thus the difference versus **5** increased to 19.4 cm^{-1}. The C−O stretching frequencies (M06L: 2112.7, ωB97XD: 2155.2 cm^{-1}) of the radical cation **6**, calculated without BF$_4^-$, are also

significantly shifted versus **5** by 25.5 (M06L) and 14.0 cm^{-1} (ωB97XD), in disagreement with the small experimental difference observed upon oxidation of the related complex **12** in Scheme 5. The DFT results suggest that **6** and **6**-H might exist (and should be treated) as tight ion pairs with BF$_4^-$ in solution.

b. Catalytic Studies. For the study of the catalytic effects produced upon the oxidation of the ferrocenyl-imidazolylidene ligand, we decided to test the Fc-NHC-Au complexes **7** and **8** in two benchmark gold-catalyzed reactions. During the past few years, gold catalysis has become a hot topic in chemistry, especially regarding reactions proceeding by activation of unsaturated carbon−carbon bonds.[13] Among homogeneous Au-based catalysts, those containing NHC ligands are becoming increasingly visible, probably due to the steric and electronic stabilization of the complexes imparted by the NHC ligands.[14e,f] Because the activity of the gold-based catalysts has often been related to the tendency of the Au center to behave as an electrophile, we thought that the decrease of the electron-donating character of the NHC ligand produced upon oxidation (or protonation) of **7** could yield some improvement of the catalytic efficiency.

We first studied the hydroamination of terminal alkynes, a process for which several Au-NHC complexes have proved very active.[14] For this same reaction, Gabbai and co-workers recently described that the activity of a Au(III)-based catalyst could be improved by oxidizing a redox-switchable ligand, which consequently featured a more Lewis acidic gold center.[15] Table 2 summarizes the results that we obtained for the

Table 2. Activity of Complex 7 (with and without Oxidant) in the Hydroamination of Phenylacetylene with Arylamines[a]

Ar-NH$_2$ + ≡≡Ph →

entry	Ar	cat.	additives[b]	yield (%)[c]
1	Ph	7	AgBF$_4$	89
2	Ph	7	AgBF$_4$, oxidant	91
3	Ph		oxidant	0
4	4-MeC$_6$H$_4$	7	AgBF$_4$	88
5	4-MeC$_6$H$_4$	7	AgBF$_4$, oxidant	90
6	2,4,6-Me$_3$C$_6$H$_2$	7	AgBF$_4$	82
7	2,4,6-Me$_3$C$_6$H$_2$	7	AgBF$_4$, oxidant	90

[a]Reaction conditions: 0.5 mmol of phenylacetylene, 0.55 mmol of aryl amine, 1 mol % of the catalyst **7**, 1 mL of CH$_3$CN at 90 °C, 3 h. [b]2 mol % of AgBF$_4$ and/or 1 mol % of acetylferrocenium tetrafluoroborate (oxidant) was added to the reaction mixture. [c]Yields calculated by GC using anisole (0.5 mmol) as internal standard.

hydroamination of phenylacetylene with three different arylamines (aniline, 4-tolylamine, and mesitylamine). The reactions were carried out at 90 °C in acetonitrile, using a catalyst loading of 1 mol %. Complex **8** was generated *in situ*, by addition of acetylferrocenium tetrafluoroborate to a reaction containing catalyst **7**. With this we intended to minimize the production of **8**-H by abstraction of a hydrogen from the solvents used in the isolation. The potential activity of the oxidant alone was discarded by a blank experiment in which the reaction was carried out in the absence of complex **7** (entry 3). As can be seen from the results shown, the activity of the catalyst with and without the oxidant is very similar, although the addition of the

oxidant apparently produces a slight increase of the activity. This increase is more significant for the case of the hydroamination of phenylacetylene with mesitylamine, for which 90% and 82% yield of the product is obtained, depending on whether the oxidant is added or not, respectively (entries 6 and 7).

In order to have a more detailed insight into the possible improvement of the catalytic process by oxidizing the ligand, we monitored the reaction and studied the time-dependent reaction profile of the process for the hydroamination of phenylacetylene using aniline and mesitylamine. As can be observed from the profiles shown in Figure 8, the addition of
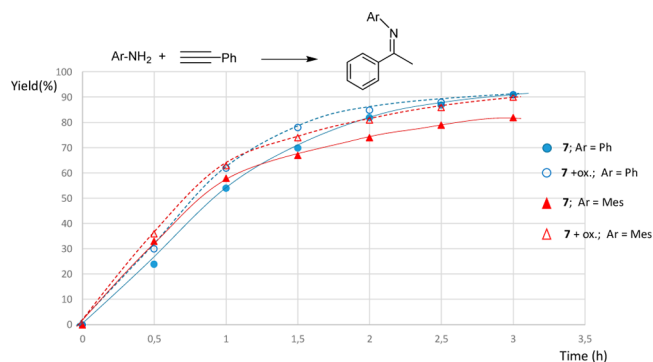

Figure 8. Time-dependent reaction profile of the hydroamination of phenylacetylene with aniline and mesitylamine. All reactions were carried out under the same conditions described in Table 2 (Ox. = oxidant = acetylferrocenium tetrafluoroborate). Lines are only to guide the eye.
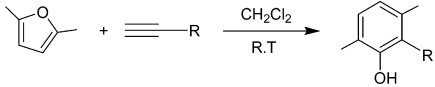
the catalyst not only produces a slightly higher yield of the product but also accelerates the reaction, hence indicating that the higher efficiency of the oxidized catalyst is due to inherent catalytic (kinetic) enhancement, rather than reasons related to thermodynamic factors (i.e., stability of the catalyst). At this point it is important that we checked that the reaction is homogeneously catalyzed, not only because the reaction mixtures did not show any trace of formation of solid all along the reaction course but also because the reactions carried out in the presence of a drop of Hg did not yield any variation in the reaction yields with respect to those reactions for which Hg was not added.

A plausible explanation that may justify the small effect observed in the hydroamination of phenylacetylene is that the aniline substrate deprotonates **8**-H (if formed) and regenerates the unoxidized catalyst **7**. In order to circumvent this, we decided to test a new catalytic reaction not involving basic substrates.

We wanted to see if we could provide an example of a catalytic reaction for which the addition of the oxidant afforded a more significant improvement. The gold-catalyzed synthesis of phenols by cyclization of alkynes with furans developed by Hashmi in 2006 is one of the most important gold-facilitated transformations.[16] Recently, cationic Au-NHC complexes proved to be excellent catalysts for this type of reaction.[17] For this reason, we thought that our two Fc-Au complexes **7** and **8** might be good candidates for catalyzing the cyclization of alkynes with furans. The reactions were carried out following the method previously described,[17] by reacting the alkyne with 2,5-dimethylfuran in dichloromethane, at room temperature in the presence of 3 mol % of catalyst and an equal amount of

NaBARF (BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate]. As can be seen from the results shown in Table 3,

Table 3. Intermolecular Gold(I)-Catalyzed Cyclization of 2,5-Dimethylfuran with Terminal Alkynes[a]


entry	R	catalyst	yield (%)[b]
1	Ph	7	0
2	Ph	8 + 8-H	62[c]
3	Ph	7 + oxidant	60[c]
4	1-butyl	7	0
5	1-butyl	7 + oxidant	53
6	1-hexyl	7	0
7	1-hexyl	7 + oxidant	66
8	m-Tol	7	0
9	m-Tol	7 + oxidant	75

[a]Reaction conditions: 2 mmol of 2,5-dimethylfuran, 1 mmol of alkyne, 0.03 mmol of NaBARF, 3 mol % of the catalyst, 2.5 mL of CH_2Cl_2 at room temperature, 24 h. [b]Yields of the isolated products. [c]Hydroarylated product was also observed.

complex **7** is completely inactive in the reaction, while the oxidized complex **8** (or **7** + oxidant) produces moderate to good yields of the final phenols. Interestingly, when we used a mixture of **8** and **8**-H from the precipitation of the bulk material resulting from the oxidation of **7**, we observed that the yield obtained was the same as that obtained for the *in situ* preparation of **8** (compare entries 2 and 3). The results are particularly interesting because, contrary to what we observed for the hydroamination of alkynes, in this reaction the oxidation of the ligand is able to "switch on" the activity of the gold catalyst.

Under the same reaction conditions, catalyst **7** in the presence of acetylferrocenium tetrafluoroborate facilitated the cyclization of 1,4-diethynylbenzene with 2,5-dimethylfuran, affording the corresponding terphenylene in 45% isolated yield (Scheme 6). The yield of this reaction is slightly lower

Scheme 6
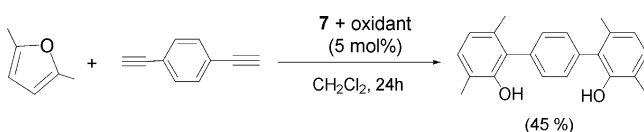
than the best result reported to date with the same substrate (55% production of the terphenylene),[17] but illustrates the scope of this catalyst in this reaction.

■ CONCLUSIONS

In summary, this work describes the preparation of a ferrocenyl-imidazolylidene ligand, which was coordinated to iridium(I) and gold(I). The electronic properties of the ligand were analyzed by means of IR spectroscopy of the corresponding $[IrCl(Fc-NHC)(CO)_2]$ complex **5** and were compared to those shown by its oxidized analogue **6**. The comparison of the IR spectra revealed an unexpected low modification of the electron-donating power of the ligand upon oxidation. A more detailed analysis of the nature of the "oxidized" species revealed that, contrary to our expectations,

the isolated species contained the protonated ferrocenyl-imidazolylidene-iridium complex (**6**-H, Fe^{2+}), together with the ferrocenium-imidazolylidene iridium compound (**6**, Fe^{3+}) resulting from the oxidation of the ferrocenyl fragment. These findings were supported by experimental results, based on the mass spectrometry of the compounds, X-ray-diffraction studies, and Mössbauer spectroscopy. Interestingly, DFT calculations on both the oxidized and protonated species (**6** and **6**-H, according to Scheme 3) reveal that large $\nu(CO)$ shifts should be expected for their IR spectra, compared to those calculated for the neutral parent compound **5**, when the calculations are carried out for the cation alone. However, for the case of the protonated species **6**-H, a much lower $\nu(CO)$ shift is obtained if the molecule is calculated with a BF_4 counteranion, because the ion pair formed by the N−H and one of the fluorine atoms of the anion is apparently reducing the effect of the positive charge on the ligand.

These results are of significant importance because they reveal that special caution has to be taken when redox-switchable ligands are used. The modification (or switch) of the electron-donating nature of the ligand may be wrongly ascribed to a redox event, while a "protonation" is the real process happening. In any case, such protonation should be understood as a consequence of the oxidation of the ligand followed by a hydrogen abstraction.

The effects of the oxidation of the ligand in homogeneous catalysis were tested by using the ferrocenyl-imidazolylidene-gold(I) complex (**7**, Scheme 3). This compound was tested in two typical gold-catalyzed reactions. In the hydroamination of terminal alkynes, the results made us conclude that the oxidation of the ligand produced a moderate increase of the activity of the gold catalyst. In the cyclization of alkynes with furans, the results were more remarkable, because the neutral complex (**7**) was not active at all, while the product resulting from its oxidation (regardless whether this is the oxidized or the protonated species, **8** or **8**-H) produced moderate to good yields in the formation of the final products. This result indicates that for this latter reaction the addition of the oxidant switches the activity of the catalyst on. For both catalytic reactions, the enhancement of the activity upon oxidation is interpreted as a consequence of the higher electrophilicity of the gold center produced by the generation of a cationic ligand upon its oxidation.

■ EXPERIMENTAL SECTION

General Considerations. 1,3-Dibutyl-5,6-diaminobenzimidazolium iodide (**A**)[18] and acetylferrocenium tetrafluoroborate, [Fe(η^5-C_5H_4COMe)Cp][BF_4],[19] were prepared according to literature methods. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 300 and 500 MHz or on a Bruker 400 MHz, using $CDCl_3$, CD_2Cl_2, and DMSO-d_6 as solvents. Electrospray mass spectra were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series. Infrared spectra (FTIR) were performed on a Bruker EQUINOX 55 spectrometer with a spectral window of 4000−600 cm^{-1}. The resolution of the IR experiments is 0.5 cm^{-1}. ^{57}Fe Mössbauer spectra were recorded at the Departament Chemie and Pharmazie of the University of Erlangen−Nürnberg on a WissEl Mössbauer spectrometer (MRG-500) at 77 K in constant acceleration mode. ^{57}Co/Rh was used as the radiation source. WinNormosfor Igor Pro software has been used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.20 mm s^{-1}. The temperature of the samples was controlled by an MBBC-HE0106

Mössbauer He/N$_2$ cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to α-iron at 298 K. Electrochemical studies were carried out by using an Autolab Potentiostat (model PGSTAT101) using a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver wire reference electrode. In all experiments, [NBu$_4$][PF$_6$] (0.1 M in dry CH$_2$Cl$_2$) was used as the supporting electrolyte with analyte concentration of approximately 1 mM. Unless otherwise stated, measurements were performed at 100 mV s^{-1} scan rates. All redox potentials were referenced to the Fc$^+$/Fc couple as internal standard with $E_{1/2}$(Fc/Fc$^+$) versus the SCE = +0.46 V.

Synthesis and Characterization of the Precursors of the Ligands and the Metal Complexes. *Synthesis of Compound 1.* Ferrocenecarboxaldehyde (337.5 mg, 1.54 mmol) and 6 drops of trifluoroacetic acid were subsequently added to a solution of compound **A** (600 mg, 1.54 mmol) in ethanol (100 mL). The resulting mixture was heated at reflux for 24 h under aerobic conditions. After removal of the volatiles, compound **1** was isolated as a dark brown solid and was used in the following step without further purification. Yield: 960.8 mg, 95%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.80 (s, 1H, NC*H*N), 8.13 (s, 2H, C*H*$_{Ph}$), 5.25 (s, 2H, C*H*$_{Cp}$), 4.64 (s, 2H, C*H*$_{Cp}$), 4.55 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.16 (s, 5H, C*H*$_{Cp}$), 1.99−1.90 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.41−1.31 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.04 (t, $^3J_{H-H}$ = 15 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.95 (t, $^3J_{H-H}$ = 15 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 159.4 (NCN), 139.4 (NCHN), 138.7 (C$_{q\,Ph}$), 128.0 (C$_{q\,Ph}$), 97.2 (CH$_{Ph}$), 71.8 (CH$_{Cp}$), 70.4 (CH$_{Cp}$), 69.3 (C$_{q\,Cp}$), 68.7 (CH$_{Cp}$), 47.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 30.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.5 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (20 V, *m/z*): 455.3 [M − I]$^+$. Anal. Calcd for C$_{26}$H$_{31}$N$_4$FeI·4H$_2$O (654.36): C, 47.72; H, 6.01; N, 8.56. Found: C, 47.33; H, 6.19; N, 8.20.

Synthesis of Compound 2. A solution of compound **1** (300 mg, 0.51 mmol) and K$_2$CO$_3$ (142.4 mg, 1.03 mmol) in dry acetonitrile (10 mL) was stirred at 90 °C for 1 h. After this time, methyl iodide was added (33 μL, 0.51 mmol) and the resulting mixture was heated at 90 °C overnight. After this time, the solvent was removed under vacuum. The solid residue was dissolved in dichloromethane and filtered through a pad of Celite to remove insoluble salts. The resulting residue was taken up in the minimum amount of dichloromethane, diethyl ether (5 mL) was added, and the precipitated solid was collected by filtration. Compound **2** was isolated as a light brown solid. Yield: 220.5 mg, 68%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 10.71 (s, 1H, NC*H*N), 8.02 (s, 1H, C*H*$_{Ph}$), 7.85 (s, 1H, C*H*$_{Ph}$), 4.99 (s, 2H, C*H*$_{Cp}$), 4.77 (s, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.55 (s, 4H; 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$; and 2H, C*H*$_{Cp}$), 4.20 (s, 8H; 5H, C*H*$_{Cp}$; and 3H, NC*H*$_3$), 2.12−2.01 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.55−1.36 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.97 (t, $^3J_{H-H}$ = 20 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ = 159.1 (NCN), 143.3 (C$_{q\,Ph}$), 141.1 (NCHN), 137.4 (C$_{q\,Ph}$), 128.2 (C$_{q\,Ph}$), 127.9 (C$_{q\,Ph}$), 101.0 (CH$_{Ph}$), 93.0 (CH$_{Ph}$), 72.4 (C$_{q\,Cp}$), 71.1 (CH$_{Cp}$), 70.0 (CH$_{Cp}$), 69.7 (CH$_{Cp}$), 47.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 47.7 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.7 (NCH$_3$), 31.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.2 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.7 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (20 V, *m/z*): 469.3 [M − I]$^+$ and 235.2 [M − I + H]$^{2+}$. Anal. Calcd for C$_{27}$H$_{33}$N$_4$FeI·2H$_2$O (632.36): C, 51.28; H, 5.90; N, 8.86. Found: C, 51.37; H, 5.67; N, 8.72.

Synthesis of Complex 3. A mixture of compound **2** (200 mg, 0.33 mmol) and silver oxide (39.25 mg, 0.17 mmol) in CH$_2$Cl$_2$ (15 mL) was stirred at room temperature overnight. After this time, the mixture was filtered through a pad of Celite to remove insoluble salts. The solvent was removed nearly to dryness, and diethyl ether (5 mL) was added. The precipitate so formed was collected by filtration and washed with diethyl ether (5 mL). Complex **3** was isolated as an orange solid. Yield: 129.5 mg, 55%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.70 (s, 1H, C*H*$_{Ph}$), 7.23 (s, 1H, C*H*$_{Ph}$), 4.96 (s, 2H, C*H*$_{Cp}$), 4.55−4.47 (m, 6H; 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$; and 2H, C*H*$_{Cp}$), 4.21 (s, 5H, C*H*$_{Cp}$), 4.06 (s, 3H, NC*H*$_3$), 2.01−1.89 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.51−

1.44 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.98 (t, $^3J_{H-H}$ = 20 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.95 (t, $^3J_{H-H}$ = 20 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ = 192.8 (Ag-C$_{carbene}$), 156.3 (NCN), 141.0 (C$_{q\,Ph}$), 135.2 (C$_{q\,Ph}$), 131.2 (C$_{q\,Ph}$), 130.9 (C$_{q\,Ph}$), 100.0 (CH$_{Ph}$), 90.3 (CH$_{Ph}$), 73.5 (C$_{q\,Cp}$), 70.6 (CH$_{Cp}$), 69.9 (CH$_{Cp}$), 69.3 (CH$_{Cp}$), 49.6 (NCH$_2$CH$_2$CH$_2$CH$_3$), 49.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.2 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.0 (NCH$_3$), 20.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.1 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.0 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (20 V, *m/z*): 469.3 [M − AgI + H]$^+$. Anal. Calcd for C$_{27}$H$_{32}$N$_4$AgFeI (703.2): C, 46.12; H, 4.59; N, 7.97. Found: C, 46.71; H, 4.86; N, 7.80.

Synthesis of Complex 4. A suspension of the ferrocene-based imidazolium salt **2** (200 mg, 0.33 mmol) and Ag$_2$O (39.25 mg, 0.17 mmol) in CH$_2$Cl$_2$ was stirred at room temperature overnight. Then, [IrCl(COD)]$_2$ (112.6 mg, 0.17 mmol) was added. Immediately, the formation of a white precipitate was observed. To complete the reaction, the suspension was stirred at room temperature for 6 h. The suspension was filtered through a pad of Celite to remove unreacted Ag$_2$O and other insoluble salts. The solution was concentrated nearly to dryness, and diethyl ether (5 mL) was added to precipitate the complex, which was collected by filtration and further washed with diethyl ether. Complex **4** was isolated as a brown solid. Yield: 160 mg, 60%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.60 (s, 1H, C*H*$_{Ph}$), 7.08 (s, 1H, C*H*$_{Ph}$), 4.97 (s, 2H, C*H*$_{Cp}$), 4.83−4.60 (m, 6H; 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$; and 2H, C*H*$_{cod}$), 4.51 (s, 2H, C*H*$_{Cp}$), 4.22 (s, 5H, C*H*$_{Cp}$), 4.08 (s, 3H, NC*H*$_3$), 3.03−3.00 (m, 2H, C*H*$_{cod}$), 2.33−2.23 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.65−1.52 (m, 12H; 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$; and 8H, C*H*$_{2\,cod}$), 1.11 (t, $^3J_{H-H}$ = 10 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.07 (t, 6H, $^3J_{H-H}$ = 10 Hz, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ = 192.0 (Ir-C$_{carbene}$), 155.0 (NCN), 139.7 (C$_{q\,Ph}$), 133.9 (C$_{q\,Ph}$), 132.4 (C$_{q\,Ph}$), 132.1 (C$_{q\,Ph}$), 99.1 (CH$_{Ph}$), 89.2 (CH$_{Ph}$), 86.1 (CH$_{cod}$), 74.0 (C$_{q\,Cp}$), 70.4 (CH$_{Cp}$), 69.8 (CH$_{Cp}$), 69.2 (CH$_{Cp}$), 52.5 (CH$_{cod}$), 52.2 (CH$_{cod}$), 48.6 (NCH$_2$CH$_2$CH$_2$CH$_3$), 48.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 33.8 (CH$_{2\,cod}$), 33.7 (CH$_{2\,cod}$), 31.8 (NCH$_3$), 31.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 29.7 (CH$_{2\,cod}$), 29.5 (CH$_{2\,cod}$), 20.7 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.9 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (20 V, *m/z*): 805.2 [M + H]$^+$ and 405.8 [M + H − Cl + CH$_3$CN]$^{2+}$. Anal. Calcd for C$_{35}$H$_{44}$N$_4$ClFeIr (804.27): C, 52.27; H, 5.51; N, 6.97. Found: C, 52.36; H, 5.57; N, 7.17.

Synthesis of Complex 5. CO gas was bubbled through a solution of complex **4** (100 mg, 0.05 mmol) in CH$_2$Cl$_2$ (20 mL) for 1 h at 0 °C. The solution was then concentrated nearly to dryness. The crude solid was washed three times with hexane to remove the released 1,5-cyclooctadiene. The pure complex **5** was collected by filtration. Yield: 55.6 mg, 60%. IR (CH$_2$Cl$_2$): 2068.3 and 1986.3 cm^{-1} (ν_{CO}). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.72 (s, 1H, C*H*$_{Ph}$), 7.22 (s, 1H, C*H*$_{Ph}$), 4.98 (s, 2H, C*H*$_{Cp}$), 4.87−4.63 (m, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.53 (s, 4H, 2H, C*H*$_{Cp}$ and 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.22 (s, 5H, C*H*$_{Cp}$), 4.09 (s, 3H, NC*H*$_3$), 2.16−1.87 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.62−1.39 (m, 12H; 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.07−0.99 (m, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 182.8 (Ir-C$_{carbene}$), 181.6 (Ir-CO), 168.4 (Ir-CO), 156.4 (NCN), 140.9 (C$_{q\,Ph}$), 135.1 (C$_{q\,Ph}$), 131.5 (C$_{q\,Ph}$), 131.2 (C$_{q\,Ph}$), 100.0 (CH$_{Ph}$), 90.1 (CH$_{Ph}$), 73.5 (C$_{q\,Cp}$), 70.6 (CH$_{Cp}$), 69.8 (CH$_{Cp}$), 69.4 (CH$_{Cp}$), 49.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 48.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.9 (NCH$_3$), 31.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.9 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (20 V, *m/z*): 753.2 [M + H]$^+$. Anal. Calcd for C$_{29}$H$_{32}$N$_4$ClFeIrO$_2$ (752.10): C, 46.31; H, 4.29; N, 7.45. Found: C, 46.70; H, 4.62; N, 7.47.

Synthesis of Complex 6. Complex **5** (20 mg, 0.03 mmol) and acetylferrocenium tetrafluoroborate (8.37 mg, 0.03 mmol) were placed together in a Schleck tube. The tube was evacuated and filled with nitrogen three times. The solids were dissolved in dry CH$_2$Cl$_2$ (10 mL), and the resulting mixture was stirred at room temperature for 1 h. The solution was then concentrated nearly to dryness, and dry diethyl ether (5 mL) was added. The brown solid so formed was

washed three times with dry diethyl ether in order to remove the formed acetylferrocene, which is soluble in diethyl ether. Complex **6** was isolated, along with **6**-H, as a brown solid. Yield: 20.2 mg, 88%. IR (CH$_2$Cl$_2$): 2071.2 and 1989.2 cm^{-1} (ν_{CO}). Anal. Calcd for C$_{29}$H$_{32}$N$_4$ClFeIrO$_2$BF$_4$ (838.9): C, 41.52; H, 3.85; N, 6.68. Found: C, 41.48; H, 3.80; N, 6.66. Electrospray MS (20 V, m/z): 753.1 [M − BF$_4$ + H]$^+$. Electrospray MS negative mode (20 V, m/z): 87.3 [BF$_4$]$^-$.

Synthesis of Complex 7. A suspension of the ferrocene-based imidazolium salt **2** (100 mg, 0.17 mmol) and Ag$_2$O (19.63 mg, 0.08 mmol) in CH$_2$Cl$_2$ was stirred at room temperature overnight. Then, [AuCl(SMe$_2$)] (50.05 mg, 0.17 mmol) was added. Immediately, the formation of a white precipitate was observed. To complete the reaction, the suspension was stirred at room temperature for 7 h and then filtered through a pad of Celite. The solution was concentrated nearly to dryness, and hexane (5 mL) was added to precipitate the complex, which was collected by filtration and further washed with hexane. Complex **7** was isolated as an orange solid. Yield: 76.5 mg, 61%. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 7.70 (s, 1H, C*H*$_{Ph}$), 7.29 (s, 1H, C*H*$_{Ph}$), 4.96 (s, 2H, C*H*$_{Cp}$), 4.56−4.51 (m, 6H; 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$ and 2H, C*H*$_{Cp}$), 4.21 (s, 5H, C*H*$_{Cp}$), 4.08 (s, 3H, NC*H*$_3$), 2.03−1.95 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.53−1.42 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.00 (t, $^3J_{H-H}$ = 20 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.98 (t, $^3J_{H-H}$ = 20 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$): δ = 178.3 (Au-*C*$_{carbene}$), 156.6 (NCN), 141.6 (*C*$_{q\ Ph}$), 135.8 (*C*$_{q\ Ph}$), 130.5 (*C*$_{q\ Ph}$), 130.2 (*C*$_{q\ Ph}$), 100.2 (*C*H$_{Ph}$), 90.7 (*C*H$_{Ph}$), 70.8 (*C*$_{q\ Cp}$), 69.9 (*C*H$_{Cp}$), 69.5 (*C*H$_{Cp}$), 49.2 (*N*CH$_2$CH$_2$CH$_2$CH$_3$), 32.1 (N*C*H$_3$), 32.0 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.5 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, m/z): 701.2 [M + H]$^+$. Anal. Calcd for C$_{27}$H$_{32}$N$_4$AuClFe (700.8): C, 46.27; H, 4.60; N, 7.99. Found: C, 46.25; H, 4.60; N, 7.98.

Synthesis of Complex 8. As described for the oxidation of complex **5**, complex **7** (150 mg, 0.21 mmol) was reacted with acetylferrocenium tetrafluoroborate (67.4 mg, 0.21 mmol) in dry CH$_2$Cl$_2$ (20 mL). The resulting mixture was stirred at room temperature for 1 h. Upon mixing, a color change from orange to red occurred immediately. The solution was then concentrated nearly to dryness and dry diethyl ether (20 mL) was added. After three subsequent washings with dry diethyl ether, complex **8** was isolated, along with **8**-H, as a red solid. Yield: 130.0 mg, 77%. Anal. Calcd for C$_{27}$H$_{32}$N$_4$AuClFeBF$_4$ (789.6): C, 41.17; H, 4.09; N, 7.11. Found: C, 41.09; H, 4.21; N, 7.11. Electrospray MS (20 V, m/z): 701.3 [M − BF$_4$]$^+$. Electrospray MS negative mode (20 V, m/z): 87.3 [BF$_4$]$^-$.

Synthesis of Compound 9. An excess of methyl iodide (5.62 mL, 89.40 mmol) was added to a solution of compound **2** (200 mg, 0.33 mmol) in dry acetonitrile (10 mL), and the resulting mixture was heated at 90 °C overnight. After this time, the solvent was removed nearly to dryness and diethyl ether (5 mL) was added. The brown precipitate so formed was filtrated and washed with diethyl ether (5 mL). Compound **9** was isolated as a dark brown and highly insoluble solid. Yield: 200.7 mg, 81%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.05 (s, 1H, NC*H*N), 8.85 (s, 1H, C*H*$_{Ph}$), 5.33 (s, 2H, C*H*$_{Cp}$), 5.04 (s, 2H, C*H*$_{Cp}$), 4.62−4.57 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.53 (s, 3H, NC*H*$_3$), 4.29 (s, 3H, NC*H*$_3$), 4.10 (s, 5H, C*H*$_{Cp}$), 2.02−1.97 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.43−1.36 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.96 (t, $^3J_{H-H}$ = 15 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 155.2 (NCN), 144.7 (*C*$_{q\ Ph}$), 137.6 (N*C*HN), 131.6 (*C*$_{q\ Ph}$), 129.7 (*C*$_{q\ Ph}$), 113.1 (*C*$_{q\ Ph}$), 104.3 (*C*H$_{Ph}$), 97.6 (*C*H$_{Ph}$), 72.9 (*C*H$_{Cp}$), 71.9 (*C*H$_{Cp}$), 70.7 (*C*H$_{Cp}$), 64.0 (*C*$_{q\ Cp}$), 47.1 (*N*CH$_2$CH$_2$CH$_2$CH$_3$), 34.5 (N*C*H$_3$), 30.2 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 19.0 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.4 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, m/z): 242.3 [M − 2I]$^{2+}$. Anal. Calcd for C$_{28}$H$_{36}$N$_4$FeI$_2$ (738.4): C, 45.55; H, 4.91; N, 7.59. Found: C, 45.51; H, 5.00; N, 7.54.

Synthesis of Complex 10. A mixture of compound **9** (100 mg, 0.13 mmol), [IrCl(COD)]$_2$ (45.5 mg, 0.07 mmol), K$_2$CO$_3$ (112.3 mg, 0.81 mmol), and KI (134.9 mg, 0.81 mmol) in acetone (15 mL) was stirred at reflux overnight. After removal of the volatiles, the crude solid was suspended in CH$_2$Cl$_2$ and filtered through a pad of Celite to remove insoluble salts. The solvent was removed nearly to dryness, and diethyl ether (5 mL) was added, yielding a brown solid, which was collected by filtration. Yield: 49.7 mg, 36%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.79 (s, 2H, C*H*$_{Ph}$), 5.01 (s, 2H, C*H*$_{Cp}$), 4.94 (br s, 4H; 2H, C*H*$_{cod}$; and 2H, C*H*$_{Cp}$), 4.82 (s, 5H, C*H*$_{Cp}$), 4.79−4.67 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.38 (s, 3H, NC*H*$_3$), 4.36 (s, 3H, NC*H*$_3$), 3.03 (br s, 2H, C*H*$_{cod}$), 1.94−1.81 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.66−1.53 (m, 12H; 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$; and 8H, C*H*$_{2\ cod}$), 1.05 (t, $^3J_{H-H}$ = 16 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 198.2 (Ir-*C*$_{carbene}$), 152.5 (NCN $_{Cp}$), 135.1 (*C*$_{q\ Ph}$), 128.9 (*C*$_{q\ Ph}$), 93.6 (*C*H$_{Ph}$), 86.1 (*C*H$_{cod}$), 72.8 (*C*$_{q\ Cp}$), 72.0 (*C*H$_{Cp}$), 71.2 (*C*H$_{Cp}$), 69.1 (*C*H$_{Cp}$), 56.7 (*C*H$_{cod}$), 48.8 (*N*CH$_2$CH$_2$CH$_2$CH$_3$), 35.3 (N*C*H$_3$), 33.1 (*C*H$_{2\ cod}$), 30.8 (*C*H$_{2\ cod}$), 30.3 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.6 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.0 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, m/z): 911.1 [M − I]$^+$. Electrospray MS negative mode (20 V, m/z): 126.9 [I]$^-$. Anal. Calcd for C$_{36}$H$_{47}$N$_4$I$_2$FeIr (1037.66): C, 41.67; H, 4.56; N, 5.40. Found: C, 41.66; H, 4.57; N, 5.44.

Synthesis of Complex 11. Complex **11** was isolated by anion exchange starting from complex **10** using NaBF$_4$. Complex **10** was dissolved in CH$_2$Cl$_2$ and introduced in a chromatography column packed with silica gel saturated with CH$_2$Cl$_2$. Elution with 1:1 CH$_2$Cl$_2$/acetone containing NaBF$_4$, gave compound **11** as a tetrafluoroborate salt. Yield: 125.3 mg, 37%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.56 (s, 2H, C*H*$_{Ph}$), 4.95 (s, 4H; 2H, C*H*$_{Cp}$ and 2H, C*H*$_{cod}$), 4.80 (s, 2H, C*H*$_{Cp}$), 4.77−4.59 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.29 (s, 8H; 5H, C*H*$_{Cp}$ and 3H, NC*H*$_3$), 4.25 (s, 3H, NC*H*$_3$), 3.04 (br s, 2H, C*H*$_{cod}$), 2.26−2.10 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.94−1.81 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.66−1.53 (m, 8H, C*H*$_{2\ cod}$), 1.07 (t, $^3J_{H-H}$ = 12 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{19}F NMR (376.5 MHz, CDCl$_3$): δ = −152.2. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 197.8 (Ir-*C*$_{carbene}$), 152.6 (NCN), 134.9 (*C*$_{q\ Ph}$), 128.9 (*C*$_{q\ Ph}$), 93.1 (*C*H$_{Ph}$), 85.9 (*C*H$_{cod}$), 72.9 (*C*$_{q\ Cp}$), 71.7 (*C*H$_{Cp}$), 71.0 (*C*H$_{Cp}$), 69.8 (*C*H$_{Cp}$), 56.5 (*C*H$_{cod}$), 48.6 (*N*CH$_2$CH$_2$CH$_2$CH$_3$), 34.1 (N*C*H$_3$), 33.1 (*C*H$_{2\ cod}$), 30.7 (*C*H$_{2\ cod}$), 30.3 (*C*H$_{2\ cod}$), 29.4 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.5 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, m/z): 911.1 [M − BF$_4$]$^+$. Electrospray MS negative mode (20 V, m/z): 87.1 [BF$_4$]$^-$. Anal. Calcd for C$_{36}$H$_{47}$N$_4$IFeIrBF$_4$ (997.56): C, 43.34; H, 4.75; N, 5.62. Found: C, 43.39; H, 4.72; N, 5.63.

Synthesis of Complex 12. CO gas was bubbled through a solution of complex **11** (120 mg, 0.12 mmol) in CH$_2$Cl$_2$ (10 mL) for 2 h at 0 °C. The solution was then concentrated nearly to dryness. The crude solid was washed three times with hexane to remove the released 1,5-cyclooctadiene. The pure complex **12** was collected by filtration. Yield: 94.0 mg, 83%. IR (CH$_2$Cl$_2$): 2066.1 and 1988.5 cm^{-1} (ν_{CO}). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.99 (s, 1H, C*H*$_{Ph}$), 4.99 (s, 2H, C*H*$_{Cp}$), 4.91−4.70 (m, 6H; 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$ and 2H, C*H*$_{Cp}$), 4.55 (s, 5H, C*H*$_{Cp}$), 4.35 (s, 6H, NC*H*$_3$), 2.13−1.83 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.60−1.36 (m, 12H; 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.12−0.91 (m, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{19}F NMR (376.5 MHz, CDCl$_3$): δ = −151.5. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 186.5 (Ir-*C*$_{carbene}$), 181.7 (Ir-CO), 167.7 (Ir-CO), 154.2 (NCN), 134.1 (*C*$_{q\ Ph}$), 129.9 (*C*$_{q\ Ph}$), 128.8 (*C*$_{q\ Ph}$), 95.0 (*C*H$_{Ph}$), 73.2 (*C*$_{q\ Cp}$), 72.0 (*C*H$_{Cp}$), 71.2 (*C*H$_{Cp}$), 69.0 (*C*H$_{Cp}$), 49.4 (*N*CH$_2$CH$_2$CH$_2$CH$_3$), 34.9 (N*C*H$_3$), 30.8 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.3 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, m/z): 859.2 [M − BF$_4$]$^+$. Electrospray MS negative mode (20 V, m/z): 87.2 [BF$_4$]$^-$. Anal. Calcd for C$_{30}$H$_{35}$N$_4$O$_2$IFeIrBF$_4$ (945.4): C, 38.11; H, 3.73; N, 5.93. Found: C, 38.24; H, 3.78; N, 5.92.

Synthesis of Complex 15. A mixture of compound **2** (250 mg, 0.43 mmol), K$_2$CO$_3$ (360 mg, 2.60 mmol), [IrCl(COD)]$_2$ (114 mg, 0.21 mmol), and KI (429 mg, 2.60 mmol) in acetone (40 mL) was stirred at reflux overnight. After removal of the volatiles, the crude solid was suspended in CH$_2$Cl$_2$ and filtered through a pad of Celite to remove insoluble salts. The crude solid was purified by column chromatography eluting with CH$_2$Cl$_2$. Yield: 130 mg, 34%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.56 (s, 1H, C*H*$_{Ph}$), 7.08 (s, 1H, C*H*$_{Ph}$), 4.93 (s, 2H, C*H*$_{Cp}$), 4.87 (br s, 2H, C*H*$_{cod}$), 4.73−4.69 (m, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.69−4.53 (m, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.48 (s, 2H, C*H*$_{Cp}$), 4.17 (s, 5H, C*H*$_{Cp}$), 4.05 (s, 3H, NC*H*$_3$), 3.01 (br s, 2H, C*H*$_{cod}$), 2.14 (br s, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.59−1.50 (m, 12H;

4H, $NCH_2CH_2CH_2CH_3$; and 8H, $CH_{2\ cod}$), 1.07 (t, $^3J_{H-H}$ = 15 Hz, 6H, $NCH_2CH_2CH_2CH_3$), 1.03 (t, $^3J_{H-H}$ = 15 Hz, 6H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 191.9 (Ir-$C_{carbene}$), 155.0 (NCN), 139.6 ($C_{q\ Ph}$), 133.8 ($C_{q\ Ph}$), 132.5 ($C_{q\ Ph}$), 132.3 ($C_{q\ Ph}$), 99.1 (CH_{Ph}), 89.3 (CH_{Ph}), 84.2 (CH_{cod}), 74.0 ($C_{q\ Cp}$), 70.4 (CH_{Cp}), 69.8 (CH_{Cp}), 69.2 (CH_{Cp}), 55.8 (CH_{cod}), 55.5 (CH_{cod}), 48.4 ($NCH_2CH_2CH_2CH_3$), 33.2 ($CH_{2\ cod}$), 33.0 ($CH_{2\ cod}$), 31.9 (NCH_3), 31.0 ($NCH_2CH_2CH_2CH_3$), 30.5 ($CH_{2\ cod}$), 30.3 ($CH_{2\ cod}$), 20.7 ($NCH_2CH_2CH_2CH_3$), 14.0 ($NCH_2CH_2CH_2CH_3$). Electrospray MS (20 V, m/z): 897.2 [M + H]$^+$. Anal. Calcd for $C_{35}H_{44}N_4IFeIr$ (895.72): C, 46.92; H, 4.95; N, 6.25. Found: C, 46.90; H, 4.93; N, 6.25.

Synthesis of Complex 13. CO gas was bubbled through a solution of complex **15** (100 mg, 0.05 mmol) in CH_2Cl_2 (20 mL) for 2 h at 0 °C. The solution was then concentrated nearly to dryness. The crude solid was washed three times with hexane to remove the released 1,5-cylooctadiene. The corresponding carbonyl derivative was collected by filtration as a brown solid. Yield: 58.8 mg, 62%. IR (CH_2Cl_2): 2064.2 and 1986.8 cm^{-1} (ν_{CO}). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (s, 1H, CH_{Ph}), 7.22 (s, 1H, CH_{Ph}), 4.99 (s, 2H, CH_{Cp}), 4.76–4.65 (m, 2H, $NCH_2CH_2CH_2CH_3$), 4.54 (s, 2H, CH_{Cp}), 4.49–4.42 (m, 2H, $NCH_2CH_2CH_2CH_3$), 4.22 (s, 5H, CH_{Cp}), 4.10 (s, 3H, NCH_3), 2.06–1.94 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.56–1.46 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.02 (t, $^3J_{H-H}$ = 20 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.01 (t, $^3J_{H-H}$ = 20 Hz, 3H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 182.2 (Ir-$C_{carbene}$), 180.8 (Ir-CO), 168.0 (Ir-CO), 156.4 (NCN), 140.8 ($C_{q\ Ph}$), 134.9 ($C_{q\ Ph}$), 131.9 ($C_{q\ Ph}$), 128.8 ($C_{q\ Ph}$), 99.9 (CH_{Ph}), 90.0 (CH_{Ph}), 73.5 ($C_{q\ Cp}$), 70.6 (CH_{Cp}), 69.9 (CH_{Cp}), 69.4 (CH_{Cp}), 49.0 ($NCH_2CH_2CH_2CH_3$), 48.9 ($NCH_2CH_2CH_2CH_3$), 31.9 (NCH_3), 30.8 ($NCH_2CH_2CH_2CH_3$), 30.7 ($NCH_2CH_2CH_2CH_3$), 20.4 ($NCH_2CH_2CH_2CH_3$), 14.0 ($NCH_2CH_2CH_2CH_3$), 13.9 ($NCH_2CH_2CH_2CH_3$). Electrospray MS (20 V, m/z): 845.1 [M + H]$^+$. Anal. Calcd for $C_{29}H_{32}N_4FeIrO_2$ (843.56): C, 41.29; H, 3.82; N, 6.64. Found: C, 41.42; H, 3.84; N, 6.57.

Synthesis of Complex 14. Complex **12** (20 mg, 0.02 mmol) and acetylferrocenium tetrafluoroborate (6.66 mg, 0.02 mmol) were dissolved in dry CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 2 h. The solvent was removed nearly to dryness, and diethyl ether (20 mL) was added. The supernatant ether was removed with a syringe. This was repeated three times to remove all acetylferrocene. Yield: 19.0 mg, 87%. IR (CH_2Cl_2): 2068.0 and 1991.4 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{30}H_{35}N_4FeIrO_2B_2F_8$ (1032.2): C, 34.91; H, 3.42; N, 5.43. Found: C, 34.89; H, 3.45; N, 5.47. Electrospray MS (20 V, m/z): 859.0 [M − 2BF$_4$]$^+$. Electrospray MS negative mode (20 V, m/z): 87.3 [BF$_4$]$^-$.

General Procedure for the Intermolecular Au(I)-Catalyzed Cyclization of 2,5-Dimethylfuran with Different Terminal Alkynes. A solution of the alkyne (1 mmol), 2,5-dimethylfuran (2 mmol), the gold(I) catalyst (3 mol %), and NaBARF (3 mol %) in dry dichloromethane (2.5 mL) was stirred at room temperature for 24 h. Then, a drop of trimethylamine was added, and the solvent was removed under vacuum. The crude was purified by flash column chromatography using different gradients of hexane, ethyl acetate, and dichloromethane to obtain the desired products. The products were identified by comparison to previously reported data.[16,17]

General Procedure for the Au(I)-Catalyzed Hydroamination of Phenylacetylene with Aryl Amines. The gold(I) catalyst (1 mol % based on metal) and AgBF$_4$ (2 mol %, 0.01 mmol) were placed together in a thick-walled Schlenk tube fitted with a Teflon cap. The tube was then evacuated and filled with nitrogen three times. Afterward, 1 mL of CH_3CN was added, and the reaction mixture was stirred at room temperature for 5 min. After this time, the corresponding arylamine (0.55 mmol), phenylacetylene (0.5 mmol), and anisole as internal reference (0.5 mmol) were subsequently added. The resulting mixture was stirred at 90 °C for the appropriate time. The evolution of the reactions, yields, and conversions were determined by GC analysis. The products were identified by comparison to previously reported data.[14f]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00517.

     NMR spectra of complexes of the new complexes, cyclic voltammograms of complexes **1**, **2**, **4**, **5**, and **7**, and computational details, including atomic coordinates of optimized structures (PDF)

     Crystallographic data for **6**-H (CIF)

     Crystallographic data for **7** (CIF)

     Crystallographic data for **8**-H (CIF)

     Crystallographic data for **11** (CIF)

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Notes

The authors declare no competing financial interest.

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