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Syntheses, Properties, and X-ray Crystal Structures of Piano-Stool Iron Complexes Bearing an N-Heterocyclic Carbene Ligand

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*Summary: Piano-stool iron complexes containing the C−C unsaturated IMes or saturated H_2-IMes ligand are readily synthesized from $[CpFe(CO)_2(I)]$. Substitution of the iodide ligand affords the cationic species $[CpFe(CO)_2(L)][I]$ (**$1a^+I^-$**) and (**$1b^+I^-$**) (**a**, L = IMes, **b**, L = H_2-IMes), subsequent decarbonylation of which yields the neutral iodo derivatives **2a**,**b**. Cyclic voltammetry studies of **2a**,**b** show a reversible one-electron oxidation to the corresponding 17-electron radical cation. The mono(acetonitrile) complexes **3a**,**b** are obtained from UV irradiation of **$1a,b^+PF_6^-$** in CH_3CN, but displacement of the second CO ligand is inhibited by strong metal−CO π-back-donation.*

Introduction

Nucleophilic N-heterocyclic carbene ligands (NHC) constitute an important class of ligands that have proven to be exceptionally useful in catalysis.[1] These ligands, bulkier and more basic than the ubiquitous phosphines,[2] are promising candidates as alternative ligands for organometallic chemistry; their use for stabilization of reactive intermediates has become significant.[3] As a part of ongoing research on iron−carbene complexes,[4] we sought to develop a convenient route to complexes containing an NHC ligand for their intrinsic interest in stabilizing reactive moieties.

NHC-containing metal complexes are generally accessible by ligand exchange reactions using either the free carbene ligand or protected derivatives. For example, ruthenium alkylidene complexes are available by this route via phosphine substitution reactions.[5] Ligand exchange reactions are also operative for "piano-stool" C_5R_5-ruthenium (R = H, Me) complexes; one or two NHC ligands can be bonded.[6,7] The coordinatively unsaturated species $Cp^*Ru(L)Cl$ (L = NHC) are quantitatively obtained by treatment of $[Cp^*RuCl]_4$ with the appropriate carbene ligand or from $[Cp^*Ru(OMe)]_2$ by direct reaction with the imidazolium chloride.[6,7a] These reactions open up a convenient entry to Cp*Ru derivatives. A few Cp-iron complexes containing different heterocyclic carbene ligands—symmetrically substituted or otherwise—have been reported.[8−11] It has been shown that the dithiocarbene complex $[CpFe(CO)_2\{C(SMe)_2\}][PF_6]$ reacts with appropriate diamines to afford the cyclic diaminocarbene complexes.[9] Another approach consists of multicomponent cycloadditions starting from mono- or dicyano derivatives leading to complexes containing one and two carbene ligands, respectively.[10] Addition of lithium 3-borane-1,4,5-trimethylimidazol-2-ylidene to the bromo derivative $[CpFe(CO)_2Br]$ allows the formation of the corresponding carbene complex; the yield, however, is low due to side electron-transfer reactions.[11] No general and straightforward route to piano-stool iron complexes bearing an NHC ligand has been developed so far. This led us to investigate a convenient access to iron complexes containing the sterically demanding carbene ligands 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and 1,3-bis-

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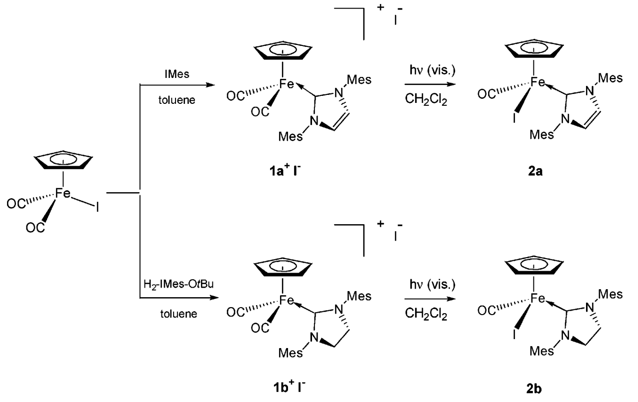
Scheme 1



(2,4,6-trimethylphenyl)imidazolin-2-ylidene (H_2-IMes), starting directly from the isolated carbene or a protected form.[5b,12] We report herein the isolation and characterization of both cationic and neutral derivatives; the availability of such complexes allows us to compare their behavior with the related phosphine-substituted complexes.

Results and Discussion

Treatment of the iodo derivative [$CpFe(CO)_2(I)$] with a solution of IMes in toluene allows precipitation of [$CpFe(CO)_2(L)$][I] (**1a**$^+$**I**$^-$) (**a**, L = IMes), the iodide ligand being displaced by the IMes ligand (Scheme 1). Compound **1a**$^+$**I**$^-$ was readily isolated as a yellow powder in 76% yield after stirring overnight. The alternative route starting from the mono(acetonitrile) complex [$CpFe(CO)_2(CH_3CN)$][PF_6][13] in the presence of 1 equiv of IMes in THF (−80 °C) gives the expected monosubstituted derivative **1a**$^+$**PF**$_6^-$. However, the reaction product is contaminated with the corresponding imidazolium salt, and attempts to separate these two cations were unsuccessful. Similarly, the related complex **1b**$^+$**I**$^-$ (**b**, L = H_2-IMes) containing the CC-saturated ligand H_2-IMes is prepared by using the *tert*-butoxy adduct H_2-IMes-O*t*Bu, a protected carbene form[5b] (Scheme 1). The ^1H NMR spectra of **1a,b**$^+$**I**$^-$ ($CDCl_3$) show the 2-fold equivalence for the NHC signals, indicative of fast rotation about the Fe−C bond. The low-field ^{13}C resonances characteristic of the carbene ligand are located at δ 171.3. and 205.9 for **1a**$^+$**I**$^-$ and **1b**$^+$**I**$^-$, respectively. In the IR spectra of **1a**$^+$**I**$^-$ and **1b**$^+$**I**$^-$, the CO stretching bands are strikingly identical (two bands in each case, at 2050, 2005 cm^{-1}), although the CC-saturated ligand is expected to be a better donor than the CC-unsaturated one.[14] It is noteworthy that these CO bands appear at a slightly lower frequency than those of the phosphine complex [$(C_5H_5)Fe(CO)_2(PPh_3)$][PF_6] (2055, 2010 cm^{-1}).[13]

The neutral iodo derivatives **2a**,**b** are then obtained by irradiation of **1a**,**b** for 3 h in a noncoordinating solvent such as CH_2Cl_2, during which, the iodide counteranion replaces a carbonyl ligand (Scheme 1). Compounds **2a**,**b** are thus obtained in 76% yield as green microcrystals. The carbene ^{13}C ($CDCl_3$) signals were found at 192.9 and 228.7 for **2a** and **2b**, respectively. Again, the N*C*N signal of the carbene ligand of **2b** is ca. 36 ppm downfield from that of **2a**. In both cases, the magnetic inequivalence of the ^1H and ^{13}C for the *o*-Me and mesityl *meta*-CH moieties may be due to the stereogenic iron center. However, a hindered rotation of the mesityl group cannot be ruled out. The free rotation around the Fe−C bond is indicated by the magnetic equivalence of the im-$C^{4,5}$ carbons. The CO stretching frequencies of these two complexes are similar and surprisingly appear as the same frequency as those of the neutral phosphine complex [$(C_5H_5)Fe(CO)(I)(PPh_3)$].[13]

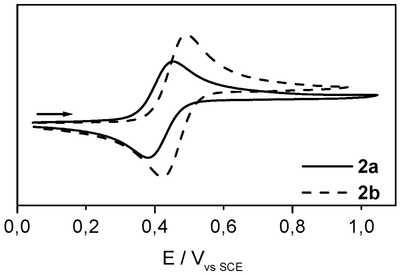


Figure 1. Cyclic voltammograms of [Cp(CO)(I)IMesFe] (**2a**) and [Cp(CO)(I)H_2-IMesFe] (**2b**) in CH_2Cl_2/0.1 M [Bu_4N][PF_6] at 295 K and a voltage sweep rate v = 100 mV s^{-1}.

Cyclic voltammetric studies (Figure 1) reveal that **2a**,**b** undergo reversible one-electron oxidations to the corresponding 17-electron radical cation. These oxidations occur at +0.41 and +0.45 V vs SCE for **2a** and **2b**, respectively. For comparison, the oxidation potential of the phosphine complex [$(C_5H_5)Fe(CO)(I)(PPh_3)$] is observed at +0.69 V vs SCE under the same conditions. These potential values reflect the higher electron density at the iron center provided by the NHC ligand. No significant difference is, however, observed for the saturated and unsaturated complexes as one would expect.[14] Attempts to isolate the Fe(III) complex **2b**$^{+\bullet}$ by chemical oxidation of **2b** using $Cp_2Fe^+PF_6^-$ were unsuccessful. Examples of isolated Fe(III) complexes containing a carbonyl ligand are scarce.[15,16]

The structures of the iodo derivatives **2a**,**b** have been determined by X-ray analyses (Table 1). The ORTEP drawings are depicted in Figures 2 and 3. Selected bond lengths and bond angles are reported in Table 2. The Fe−C bond distances are similar in **2a** (1.980(5) Å) and **2b** (1.977(4) Å), and they compare well with that of other heterocyclic iron carbene complexes, such as [CpFe-$(CO)_2$(CCH=CHNHNPh)][OTf] (1.969(5) Å).[8a,b] The Fe−C bond distances in Fischer-carbene complexes are typically in the range 1.82−1.97 Å.[4] In both complexes, the orientation of the carbene ligand is twisted with respect to the Cp ligand [Cp(c)−Fe−C(17) 126.2° (**2a**), 128.7 °-(**2b**)], probably as a result of steric factors.[7b] The Fe−CO bond lengths in **2a**,**b** are significantly shortened

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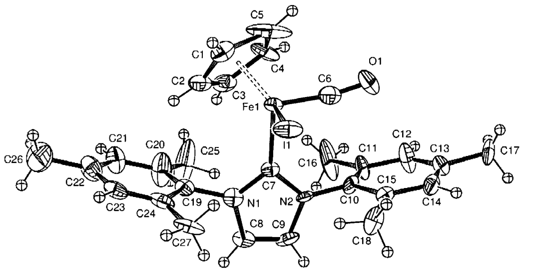


Figure 2. ORTEP representation of compound **2a**. The unit cell contains one molecule of toluene, which is omitted for clarity.

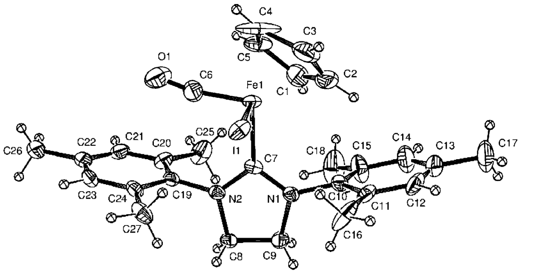


Figure 3. ORTEP representation of compound **2b**.

Table 1. Crystallographic Data and Refinement for Complexes 2a,b

	2a	2b
formula	$C_{27}H_{29}IN_2OFe{-}C_7H_8$	$C_{27}H_{31}IN_2OFe$
fw	672.41	582.29
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1/a$
a, Å	8.3759(1)	8.7125(1)
b, Å	23.8868(3)	17.4639(3)
c, Å	8.5664(1)	17.1934(2)
β, deg	118.454(1)	103.409(1)
V, Å^3	1506.87(3)	2544.73(6)
Z	2	4
D_{calcd}, g/cm^3	1.482	1.520
$F(000)$	684	1176
λ(Mo Kα), Å	0.71073	0.71073
θ range, deg	2.7−27.48	2.63−27.51
no.of reflns collected	3524	5840
no. of unique reflns	3524	5840
no. of obsd reflns ($I > 2\sigma(I)$)	3071	5301
no. of params	352	290
goodness of fit on F^2	1.035	1.017
final R, R_w	0.042, 0.115	0.058, 0.1582
$\Delta\rho_{\max,\min}$/e A^{-3}	1.556,−0.976	2.8, −1.572

(Table 2), the average Fe−C(carbonyl) distances in piano-stool iron complexes falling in the range 1.71−1.76 Å.[4,8,17] These values are indicative of the enhanced Fe−CO π-back-donation due to the presence of the NHC ligand, a feature that is not reflected by the IR data. Moreover, this could explain the observed reactivity (see below).

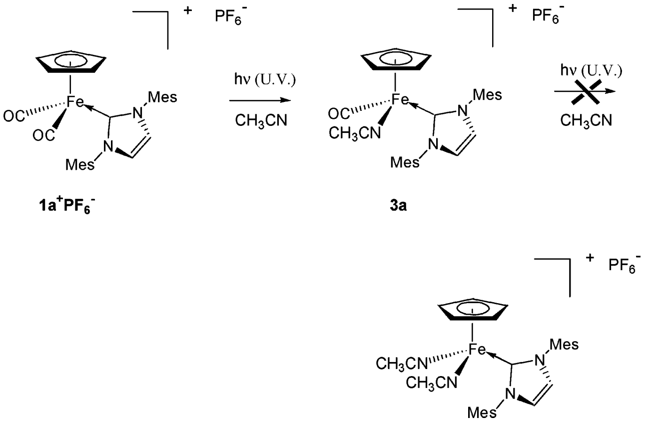
Complexes $\mathbf{1a,b^+PF_6^-}$ are converted under UV irradiation in CH_3CN into the mono(acetonitrile) complexes $[CpFe(CO)(L)(CH_3CN)][PF_6]$ (**3a**,**b**) (**a**, L = IMes; **b**, L = H_2-IMes) (Scheme 2). The expected bis(acetonitrile) complex $[CpFe(L)(CH_3CN)_2][PF_6]$ is not formed: the second CO ligand is resistant to dissociation. The presence of the NHC ligand inhibits complete decarbonylation. It may be due to increased metal−carbonyl π-donation, as a result of the σ-donor properties of the carbene ligand. This behavior contrasts with that of the phosphine complexes $[(C_5R_5)Fe(PR'_3)(CO)_2]^+$ (R = H, Me; R′ = Me, Ph), which undergo complete CO dissocation under the same conditions.[18]

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2a,b[a]

complex **2a**		complex **2b**	
	Bond Lengths		
Fe−C(6)	1.641(9)	Fe−C(6)	1.712(7)
C(6)−O(1)	1.187(11)	C(6)−O(1)	1.077(8)
Fe−I	2.6445(8)	Fe−I	2.6311(8)
Fe−C(7)	1.980(5)	Fe−C(7)	1.977(4)
Fe−Cp(c)	1.742	Fe−Cp(c)	1.752
N(1)−C(7)	1.363(16)	N(1)−C(7)	1.355(6)
N(2)−C(7)	1.387(15)	N(2)−C(7)	1.350(6)
N(1)−C(19)	1.471(17)	N(1)−C(10)	1.445(6)
N(2)−C(10)	1.424(17)	N(2)−C(19)	1.429(6)
C(8)−C(9)	1.319(9)	C(8)−C(9)	1.510(7)
	Bond Angles		
N(2)−C(7)−N(1)	101.7(4)	N(2)−C(7)−N(1)	106.3(4)
C(6)−Fe−C(7)	101.2(5)	C(6)−Fe−C(7)	99.5(3)
Fe−C(6)−O(1)	170.5(7)	Fe−C(6)−O(1)	168.3(6)
Fe−C(7)−N(1)	129.7(10)	Fe−C(7)−N(1)	127.6(3)
Fe−C(7)−N(2)	128.6(9)	Fe−C(7)−N(2)	126.0(3)
C(7)−N(1)−C(8)	113.8(10)	C(7)−N(1)−C9)	114.1(4)
C(7)−N(2)−C(9)	110.6(9)	C(7)−N(2)−C(8)	113.6(4)
C(6)−Fe−I	86.5(3)	C(6)−Fe−I	91.4(3)

[a] Estimated standard deviations are given in parentheses.

Scheme 2



Conclusion

These reactions represent a new entry to iron(II) piano-stool complexes containing an NHC ligand, including neutral and cationic derivatives. Moreover, the presence of the NHC ligand inhibits the complete decarbonylation reaction, due to increased metal−carbonyl π-back-donation. The oxidation potentials of the iodo derivatives clearly illustrate the enhanced electron density at the metal center provided by the nucleophilic carbene ligand, which on the other hand is not reflected in their IR or NMR data. This study opens up new perspectives for the development of iron(III) carbene chemistry.

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Experimental Section

All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. Photolysis experiments were done using a Hanovia lamp (450 W, 258 nm). NMR spectra were recorded on Bruker DPX-200, AV 300, or AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Attribution of carbon atoms was based on HMBC and HMQC experiments. High-resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed by the CRMPO. IR spectra were recorded on a Bruker IFS 28 spectrometer. Cyclic voltammograms were recording using a PAR model 273 Autolab. The working electrode was polished Pt, the counter-electrode was a Pt wire, and a saturated calomel electrode (SCE) was used as the reference electrode. The decamethylferrocene/decamethylferrocenium couple was used as an internal calibrant for the potential measurements.[19]

Structural Determination of 2a,b. Single crystals for X-ray diffraction studies were grown from a concentrated solution of **2a**,**b** in toluene at −20 °C. The samples were studied on a NONIUS Kappa CCD with graphite-monochromatized Mo Kα radiation. The data collection and refinement parameters are presented in Table 1. The structures were solved with SIR-97,[20a] which reveals the non-hydrogen atoms of the molecules. The whole structures were refined by full-matrix least-squares techniques on F^2, with hydrogens refined using the riding mode. Structures were solved by Patterson or direct methods. The structures were completed by subsequent difference Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-97) with initial isotropic parameters.[20] The absolute configuration of **2a** was unambiguously determined with the refinement of the Flack parameter: −0.12(5).

Synthesis of [CpFe(CO)$_2$(IMes)][I] (1a$^+$I$^-$). A mixture of *t*-BuOK (530 mg, 4.73 mmol) and IMes·HCl (1.35 g, 3.97 mmol) in THF (10 mL) was stirred for 30 min. After evaporation of the solvent, the free carbene was extracted in warm toluene (2 × 30 mL) and to this solution was added [CpFe(CO)$_2$(I)] (1.32 g, 4.34 mmol). Overnight stirring allows precipation of **1a$^+$I$^-$**, and the solid was filtered. Crystallization in CH_2Cl_2/Et_2O gave yellow microcrystals. Yield: 76% (1.83 g). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 7.44 (s, 2H, im-H^{4,5}), 7.11 (s, 4H, mes-H^{3}), 4.90 (s, 5H, Cp), 2.41 (s, 6H, *p*-CH_3), 2.07 (s, 12H, *o*-CH_3). ^{13}C[^{1}H] NMR (75.47 MHz, $CDCl_3$): δ 209.4 (CO), 171.3 (im-C^{2}), 141.3 (mes-C^{4}), 135.4 (mes-C^{2}), 135.3 (mes-C^{1}), 130.1 (mes-C^{3}), 128.2 (im-C^{4,5}), 86.2 (Cp), 21.2 (*p*-CH_3), 18.3 (*o*-CH_3). IR (CH_2Cl_2, cm^{-1}): 2050, 2006 ν(CO). HRMS: *m*/*z* 481.1578 [M$^+$] calcd for $C_{28}H_{29}N_2O_2{}^{56}Fe$ 481.15784.

Synthesis of [CpFe(CO)$_2$(H$_2$-IMes)][I] (1b$^+$I$^-$). A mixture of *t*-BuOK (414 mg, 3.7 mmol) and H$_2$-IMes·HCl (1.09 g, 3.2 mmol) in THF (15 mL) was stirred for 30 min. The obtained white suspension was transferred to a solution of [CpFe(CO)$_2$(I)] (1.14 g, 3.75 mmol) in toluene (60 mL). Overnight stirring allows precipation of **1b**, and filtration gave a yellow powder. Yield: 61% (1.19 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (s, 4H, mes-H^{3}), 4.94 (s, 5H, Cp), 4.28 (s, 4H, im-H^{4,5}), 2.40 (s, 12H, mes-*o*-CH_3), 2.38 (s, 6H, mes-*p*-CH_3). ^{13}C [^{1}H] NMR (75.47 MHz, $CDCl_3$): δ 209.3 (CO), 205.9 (im-C^{2}), 140.1 (mes-C^{4}), 136.4 (mes-C^{2}), 136.1 (mes-C^{1}), 130.2, (mes-C^{3}), 86.3 (Cp), 53.4 (im-C^{4,5}), 21.1 (*p*-CH_3), 19.0 (*o*-CH_3). IR (CH_2Cl_2, cm^{-1}): 2049, 2005 ν(CO) HRMS: *m*/*z* 483.1739 [M$^+$] calcd for $C_{28}H_{31}N_2O_2{}^{56}Fe$ 483.17349.

Synthesis of [CpFe(CO)(IMes)(I)] (2a). A Schlenk tube was charged with **1a** (222 mg, 0.36 mmol) and CH_2Cl_2 (20 mL). The solution was irradiated under visible light for 3 h. After evaporation of the solvent, **2a** was extracted with toluene (2 × 10 mL). Concentration of the solution to ca. 5 mL gave green microcrystals. Yield: 76% (161 mg). IR (CH_2Cl_2, cm^{-1}): 1938 ν(CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (s, 2H, mes-CH), 7.08 (s, 4H, mes-CH and im-H^{4,5}), 4.04 (s, 5H, Cp), 2.45 (s, 6H, *p*-CH_3), 2.20 (s, 6H, *o*-CH_3), 2.16 (s, 6H, *o*-CH_3). ^{13}C[^{1}H] NMR (75.47 MHz, $CDCl_3$): δ 219.5 (CO), 192.9 (im-C^{2}), 139.4 (mes-C^{4}), 138.0 (mes-C^{1}), 137.0, 136.3 (mes-C^{2}), 129.6, 129.5 (mes-C^{3}), 125.6 (im-C^{4,5}), 79.2 (Cp), 21.2 (*p*-CH_3), 20.2 (*o*-CH_3), 19.0 (*o*-CH_3). Anal. Calcd for $C_{27}H_{29}IN_2OFe$: C, 55.89; H, 5.04; N, 4.83. Found: C, 55.06; H, 4.99; N, 4.95.

Synthesis of [CpFe(CO)(H$_2$-IMes)(I)] (2b). Compound **2b** was prepared following the above procedure, starting from **1b** (224 mg, 0.37 mmol). Crystallization in toluene gave green microcrystals. Yield: 58% (123 mg). IR (CH_2Cl_2, cm^{-1}): 1939 ν(CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (s, 2H, mes-CH), 7.06 (s, 2H, mes-CH), 4.01 (s, 5H, Cp), 3.95 (s, 4H, im-CH_2), 2.42 (s, 6H, *o*-CH_3), 2.40 (s, 12H, *o*-CH_3 and *p*-CH_3). ^{13}C[^{1}H] NMR (75.47 MHz, $CDCl_3$): δ 228.7 (im-C^{2}), 218.8 (CO), 138.8 (mes-C^{1}), 138.6 (mes-C^{4}), 137.7, 137.0 (mes-C^{2}), 129.9, 129.8 (mes-C^{3}), 79.8 (Cp), 52.1 (im-CH_2), 21.1 (*p*-CH_3), 20.5 (*o*-CH_3), 19.1 (*o*-CH_3). Anal. Calcd for $C_{27}H_{31}IN_2OFe$: C, 55.69; H, 5.37. Found: C, 55.25; H, 5.40.

Synthesis of [CpFe(CO)(CH$_3$CN)(L)][PF$_6$] (3a,b) (a, L = IMes; b, L = H$_2$-IMes). Complex **1$^+$PF$_6$$^-$** was prepared from **1$^+I^-$** in the presence of 1 equiv of $AgPF_6$ in CH_2Cl_2 (10 mL). The solution was stirred for 1 h and filtered. After evaporation of the solvent, the residue was dissolved in CH_3CN (10 mL) and irradiated under UV overnight. Crystallization in CH_3CN/Et_2O gave red microcrystals. Complex **3a**: Yield: 36%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 2H, im-H^{4,5}), 7.15 (s, 2H, mes-CH), 7.04 (s, 2H, mes-CH), 4.32 (s, 5H, Cp), 2.42 (s, 3H, *p*-CH_3), 2.17 (s, 3H, *o*-CH_3), 2.06 (s, 3H, CH_3CN), 1.91 (s, 3H, *o*-CH_3). ^{13}C[^{1}H] NMR (125.7 MHz, $CDCl_3$): δ 217.1 (CO), 181.8 (im-C^{2}), 140.3 (mes-C^{4}), 136.6 (mes-C^{1}), 135.6 (mes-C^{3}), 135.4 (mes-C^{3}), 133.7 (CN), 129.8 (mes-C^{2}), 129.2 (mes-C^{2}), 127.1 (im-C^{4,5}), 81.8 (Cp), 21.1 (*p*-CH_3), 18.1 (*o*-CH_3), 17.7 (*o*-CH_3), 4.6 (CH_3CN). IR (CH_2Cl_2, cm^{-1}): 1984 ν(CO). Anal. Calcd for $C_{29}H_{32}N_3F_6OFeP$: C, 54.48; H, 5.04; N, 6.57. Found: C, 54.24; H, 5.10; N, 6.52. Complex **3b**: Yield: 40%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (s, 2H, mes-CH), 6.98 (s, 2H, mes-CH), 4.34 (s, 5H, Cp), 4.05 (s, 4H, im-CH_2), 2.42 (s, 3H, *o*-CH_3), 2.38 (s, 3H, *p*-CH_3), 2.08 (s, 3H, CH_3CN), 2.15 (s, 3H, *o*-CH_3). ^{13}C[^{1}H] NMR (125.7 MHz, $CDCl_3$): δ 216.8 (im-C^{2}), 216.1 (CO), 139.4 (mes-C^{4}), 136.8 (mes-C^{1}), 136.3 (mes-C^{3}), 136.0 (mes-C^{3}), 133.6 (CN), 130.2 (mes-C^{2}), 129.4 (mes-C^{2}), 82.2 (Cp), 52.5 (im-C^{4,5}), 21.0 (*p*-CH_3), 18.2 (*o*-CH_3), 17.9 (*o*-CH_3), 4.7 (CH_3CN). IR (CH_2Cl_2, cm^{-1}): 1985 ν(CO). HRMS: *m*/*z* 496.2062 [M$^+$] calcd for $C_{29}H_{34}N_3O^{56}Fe$ 496.20513.

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Supporting Information Available: Full details of the crystallographic analysis. This material is available free of charge via the Internet at http://pubs.ac.org.

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