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Iron(II) Complexes Bearing Chelating Cyclopentadienyl-N-Heterocyclic Carbene Ligands as Catalysts for Hydrosilylation and Hydrogen Transfer Reactions

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A series of piano-stool iron(II) complexes bearing bidentate cyclopentadienyl-functionalized N-heterocyclic carbene ligands (Cp-NHC)Fe(CO)I (Cp = substituted and unsubstituted cyclopentadienyl) have been prepared upon reaction with $Fe(CO)_4I_2$ and characterized by spectroscopic and crystallographic methods. The 16-electron half-sandwich compound (Cp*-NHC)FeCl (Cp* = η^5-C_5Me_4) has been synthesized by using $FeCl_2$ as precursor material. The new iron complexes displayed good catalytic activity in catalytic transfer hydrogenation of ketones and hydrosilylation reactions.

Introduction

We recently disclosed a simple synthetic pathway for the preparation of cyclopentadienyl-functionalized N-heterocyclic carbene (NHC) ligands that allowed us to independently vary their structural components, namely, the substitution of the cyclopentadienyl ring, the spacer, and the NHC fragment.[1] Following this method, we prepared a series of unsubstituted and sterically demanding cyclopentadienyl-NHCs that we coordinated to a variety of metal centers, e.g., Ir,[1] Rh,[2] Ru,[3] and Mo.[4] As a part of our ongoing research on cyclopentadienyl-functionalized N-heterocyclic carbene ligands, we sought to synthesize iron complexes of general formula (Cp-NHC)Fe(CO)X and (Cp-NHC)FeX in an attempt to extend the poorly developed NHC-iron chemistry. Iron offers significant advantages compared to transition metals typically used in catalysis; iron is cheap, nontoxic, environmentally friendly, and abundant.[5] During the last years an increasing number of catalytic applications in organic synthesis have demonstrated the versatility of this metal.[6] However, catalytic applications of iron complexes containing NHC ligands are scarce.[7] The first use of NHCs in homogeneous iron catalysis was reported by Grubbs and co-workers in 2000.[8] They described the catalytic activity of well-defined $[(NHC)_2FeX_2]$ complexes in atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate. Latter on, Gibson, Shen, and co-workers developed several NHC-based iron catalysts for polymerization reactions.[9,10] Other catalytic applications of Fe-NHCs embrace C−C bond forming and cyclization reactions.[11] Furthermore, stable NHCs can mediate unusual transformations of organometallic iron complexes.[12] The use of Fe-NHCs in homogeneous catalysis is an emerging field that represents an opportunity to develop new sustainable catalytic systems.

Half-sandwich iron complexes containing NHCs are known.[13−15] Recently, Tatsumi and co-workers described the activation of C−H bonds of thiophenes, furans, and pyridine, promoted by a coordinatively unsaturated half-sandwich iron complex containing a metallacycle derived

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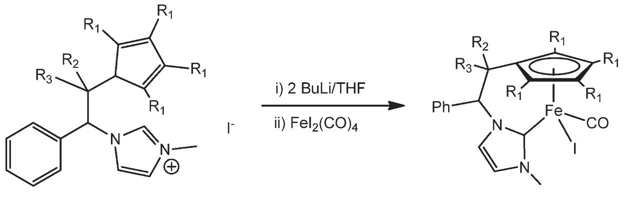
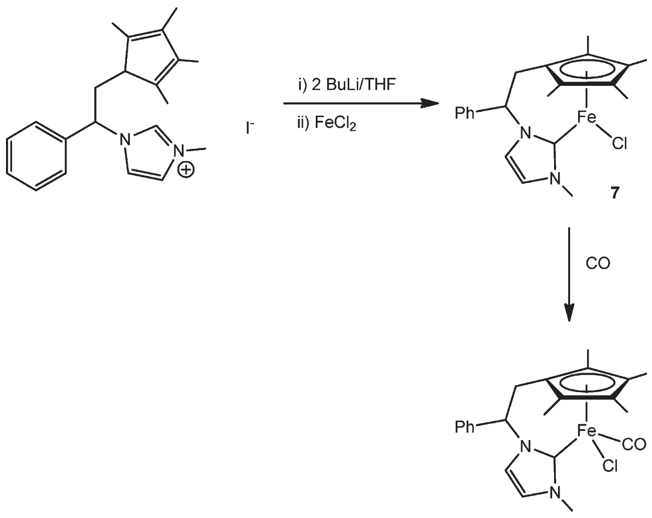
Scheme 1



1 $R_1 = CH_3$, R_2, $R_3 = H$
2 $R_1 = H$, R_2, $R_3 = Ph$
3 $R_1 = CH_2Ph$, $R_2 = Ph$, $R_3 = H$

4 $R_1 = CH_3$, R_2, $R_3 = H$
5 $R_1 = H$, R_2, $R_3 = Ph$
6 $R_1 = CH_2Ph$, $R_2 = Ph$, $R_3 = H$

Scheme 2



from an NHC.[15] We believe that the presence of a tethered Cp-NHC system may help to stabilize species not reachable by combination of other monodentate ligands and also provide interesting catalytic applications. In this work, we have prepared a series of piano-stool iron(II) complexes bearing bidentate cyclopentadienyl-functionalized N-heterocyclic carbene ligands of general type (Cp-NHC)Fe(CO)I, and we have explored their catalytic applications in the reduction of carbonyl groups, namely, in hydrosilylation of aldehydes and hydrogen transfer of ketones.

Results and Discussion

The iron(II) carbonyl compounds (Cp^x-NHC)Fe(CO)I [Cp^x = Cp*(η^5-C_5Me_4) (**4**); Cp (η^5-C_5H_4) (**5**); Cp^{Bz} (η^5-$C_5(CH_2Ph)_4$) (**6**)] were synthesized as shown in Scheme 1. The *in situ* reaction at low temperature (−60 °C) of proligands **1**−**3** with two equivalents of *n*-butyllithium followed by addition of $FeI_2(CO)_4$ affords complexes **4**−**6** as green crystalline solids in high yield. All complexes are stable in the solid state and can be handled in air. Complexes **4**−**6** exhibited characteristic ^{13}C NMR shifts at δ 195 (for **4**), δ 188 (for **5**), and δ 193 (for **6**) for the carbene carbon, confirming the coordination of NHC fragments to the metal center. These resonances appeared in the same range of related Fe-NHC complexes.[13,15]

The IR spectra of **4**−**6** show the CO stretching bands at 1906 (**4**), 1949 (**5**), and 1920 cm^{-1} (**6**). The shift to lower frequency in compound **4** is a consequence of the stronger donor capacity of the tetramethylcyclopentadienyl ring compared to the unsubstituted-Cp and tetrabenzyl-cyclopentadienyl ligand. The less electron-donating capacity of the benzyl-substituted cyclopentadienyl ligand compared to the Cp* ligand has been already observed in complexes containing the [Fe(C_5Bz_5)] fragment.[16]

The coordinatively and electronically unsaturated iron(II) species (Cp*-NHC)FeCl (**7**) was prepared by addition of $FeCl_2$ to a THF solution of proligand **1**, previously treated with two equivalents of *n*-butyllithium, as shown in Scheme 2. Complex **7** was isolated in 67% yield as a crystalline red solid. This complex is highly sensitive to air and moisture and needs to be handled under inert conditions. Compound **7** is paramagnetic, and its ^1H NMR spectrum displays broad signals. The high-resolution mass spectrum of **7** gave the molecular peak corresponding to $[M - Cl]^+$ at m/z = 396.1056. Complex **7** was converted under CO atmosphere in dichloromethane into the corresponding carbonyl compound, which displayed a CO stretching band at 1911 cm^{-1} in its IR spectrum, Scheme 2.

The crystal structures of **5** and **6** were unequivocally determined by single-crystal X-ray diffraction analysis. Quality crystals were obtained by cooling ether solutions to −10 °C. The molecular structures and selected bond lengths and angles are depicted in Figure 1 (for **5**) and Figure 2 (for **6**). The structures can be described as a distorted four-legged piano stool with the cyclopentadienyl-NHC ligand chelating the iron center. The cyclopentadienyl ligands are bonded in pentahapto fashion with metal ring carbon distances ranging from 2.107(4) to 2.69(4) Å for **5** and 2.149(4) to 2.050(5) Å for **6**. The Fe−$C_{carbene}$ bond distances of 1.942(4) Å (for both compounds **5** and **6**) are in good agreement with the Fe−$C_{carbene}$ bond distances reported for related complexes, which are in the range 1.98−1.968 Å.[13−15]

For complex **6**, three of the phenyls of the benzyl groups are situated above the cyclopentadienyl ring and directed away from the metal center, while the other phenyl group of the fourth benzyl group is situated below the cyclopentadienyl ring and approaches the metal center atom. The same disposition of the phenyl rings about the metal center has been observed in other metal complexes containing the η^5-C_5Bz_5 ligand.[17,18]

Preliminary studies of the catalytic activity of the novel iron complexes **4**−**7** were performed to explore their potential in the reduction of organic molecules. We studied the hydrosilylation of carbonyl groups and hydrogen transfer hydrogenation.

The use of well-defined organometallic and coordination complexes of iron as catalysts for the reduction of carbonyl groups has been recently explored by several groups. Casey and co-workers, inspired by the bifunctional, ionic hydrogenation catalysis known for ruthenium, recently disclosed the catalytic activity of related iron-cyclopentadienyl complexes.[19,20] Their catalysts showed high activity in the hydrogenation of several

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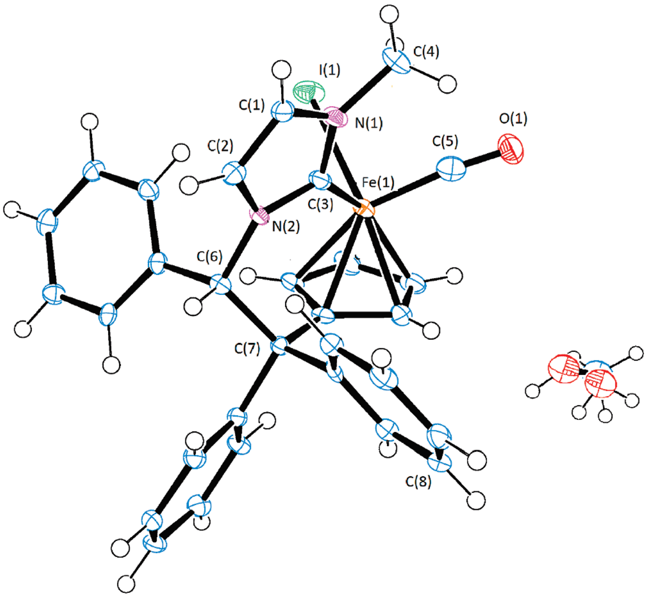

Figure 1. Molecular diagram of compound **5**. Selected bond distances (Å) and angles (deg): Fe(1)−C(3) 1.942(4), Fe(1)−I(1) 2.6452(6), Fe(1)−C(5) 1.759(5), C(5)−O(1) 1.134(5), Fe(1)−Cp$_{\text{centroid}}$ 2.0972, C(3)−Fe(1)−I(1) 90.69(11), C(3)−Fe(1)−C(5) 97.46(18), C(5)−Fe(1)−I(1) 94.06(14), Cp$_{\text{centroid}}$−Fe(1)−C(3) 120.538, Cp$_{\text{centroid}}$−Fe(1)−I(1) 118.462, Cp$_{\text{centroid}}$−Fe(1)−C(5) 117.06.

ketones, aldehydes, and imines using H_2 as a reducing agent and also displayed activity in transfer hydrogenation reaction using 2-propanol as hydrogen source. Recently, Morris and co-workers reported the first version of an enantioselective reduction of prochiral ketones in the presence of iron complexes containing P,N,P,N-tetradentate ligands.[21−24,6b] In addition, Chirik and co-workers developed iron catalysts with bis(imino)pyridine ligands that are active in the hydrosilylation of aldehydes and ketones.[25] They also recently described enantiopure pyridine bis(oxazoline) and bis(oxazoline) iron dialkyl complexes as efficient catalysts for hydrosilylation of various ketones.[26] So far, no reports on a [(NHC)Fe]-based catalyst for hydrogen transfer and hydrosilylation of carbonyl groups are found in the literature. On the basis of our findings on the use of (Cp-NHC)IrX_2 as catalyst for hydrogen transfer reactions,[1] we decided to explore the capability of related iron complexes as catalysts for reduction of carbonyl groups.

We have investigated the catalytic activity of (Cp*-NHC)FeCl (**7**) in the hydrosilylation of aldehydes using a catalyst loading of 1 mol % with 1.2 equiv (based on substrate) of $(EtO)_2MeSiH$ at 80 °C. The progress of each reaction was monitored by ^{1}H NMR. As shown in Table 1, the hydrosilylation reaction proceeds faster in acetonitrile (quantitative conversion in 2 h, Table 1, entry 1) than in benzene and tetrahydrofuran (24 h was needed to achieve quantitative conversions). No reaction takes place in chlorinated solvents such as dichloromethane and chloroform. Dimethylphenylsilane was ineffective as stoichiometric reductant, while $PhSiH_3$ and Ph_2SiH_2 worked well in the reduction of aldehyhdes, although a mixture of the corresponding silylated ether and alcohol was obtained for Ph_2SiH_2 (Table 1, entry 7). Benzaldehyde derivatives containing functional groups such as halo (Table 1, entries 9 and 10), cyano (Table 1, entry 8), nitro (Table 1, entry 1), and ester (Table 1, entry 11) were well tolerated. Aliphatic aldehydes and ketones were not reduced under the conditions used in these reactions. When the catalytic hydrosilylation reaction is performed at room temperature, longer reaction times are needed to achieve quantitative conversions (30 h was required for the hydrosilylation of 4-nitrobenzaldehyde with $(EtO)_2MeSiH$ at 25 °C). The carbonyl complexes of general formula (Cp^x-NHC)Fe(CO)I were inactive with respect to catalyzing the hydrosilylation of carbonyl groups.

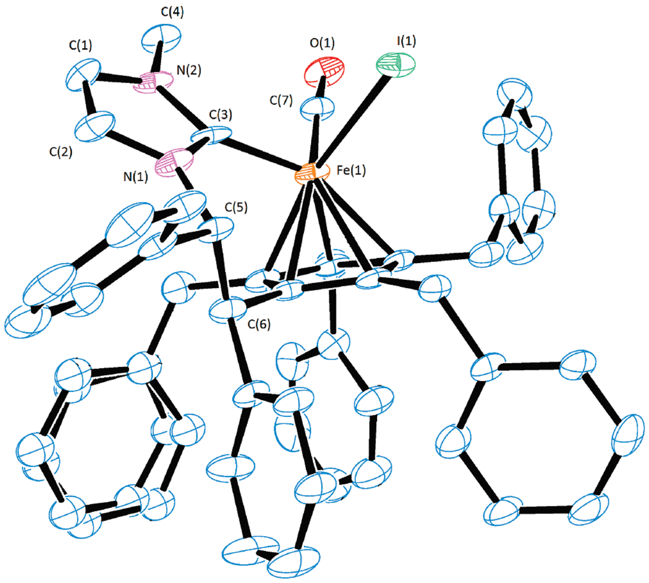

Figure 2. Molecular diagram of compound **6**. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)−C(3) 1.942(5), Fe(1)−I(1) 2.6208(8), Fe(1)−C(7) 1750(5), C(7)−O(1) 1.148(6), Fe(1)−Cp$^{\text{Bz}}{}_{\text{centroid}}$ 2.0992, C(3)−Fe(1)−I(1) 88.64(15), C(3)−Fe(1)−C(7) 100.1(2), C(7)−Fe(1)−I(1) 89.62(17), Cp$^{\text{Bz}}{}_{\text{centroid}}$−Fe(1)−C(3) 116.24, Cp$^{\text{Bz}}{}_{\text{centroid}}$−Fe(1)−I(1) 122.29, Cp$^{\text{Bz}}{}_{\text{centroid}}$−Fe(1)−C(7) 119.86.

The catalytic transfer hydrogenation of ketones was carried out in 2-propanol, serving as a hydrogen source. All complexes **4**−**7** catalyzed the hydrogenation of C=O via hydrogen transfer from *i*-PrOH/KOH at 80 °C. From the data shown in Table 2, aryl ketones were converted into the corresponding alcohols in good yields with a catalyst loading of 1 mol %. Under these conditions, the reactions were almost complete in 6 h. As shown in Table 2, the catalytic activity of complexes **4**−**7** is very similar. Interestingly, the different substitution on the cyclopentadienyl ring does not seem to affect the catalytic performance in the hydrogen transfer reaction (Table 2, entries 1, 4, and 5). Furthermore,

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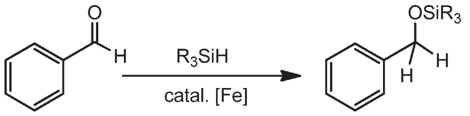
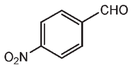
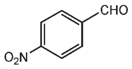
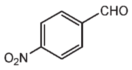
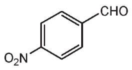
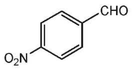
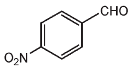
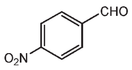
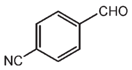
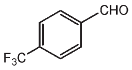
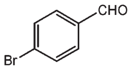
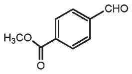
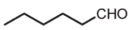
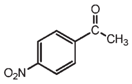
Table 1. Hydrosilylation of Aldehydes Catalyzed by 7[a]

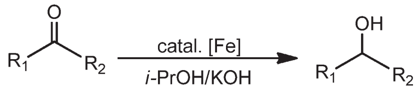


Entry	Substrate	Silane	Solv.	T (°C)	t (h)	Yield (%)[b,c]
1		$(EtO)_2MeSiH$	NCMe	80	2	100
2		$(EtO)_2MeSiH$	CH_2Cl_2	40	24	0
3		$(EtO)_2MeSiH$	C_6H_6	80	24	81
4		$(EtO)_2MeSiH$	THF	65	24	100
5		Me_2PhSiH	NCMe	80	24	0
6		$PhSiH_3$	NCMe	80	2	100
7		Ph_2SiH_2	NCMe	80	18	100 (42)
8		$(EtO)_2MeSiH$	NCMe	80	4	100
9		$(EtO)_2MeSiH$	NCMe	80	6	100
10		$(EtO)_2MeSiH$	NCMe	80	17	98
11		$(EtO)_2MeSiH$	NCMe	80	1	100
12		$(EtO)_2MeSiH$	NCMe	80	26	0
13		$(EtO)_2MeSiH$	NCMe	80	24	0

[a] All reactions were carried out with 1.0 equiv of aldehyde, 1.2 equiv of silane using 1 mol % of catalyst. [b] Yield determined by ^1H NMR spectroscopy. [c] The corresponding silylated ether is obtained accompanied by desilylated alcohol; yield indicated in parentheses.

the coordinatively unsaturated species (Cp*-NHC)FeCl displayed comparable activity to the corresponding carbonyl complex **4** (Table 2, entries 1 and 6). We therefore investigated the scope of the catalytic transfer hydrogenation of ketones with catalyst **4**, which proved to be fairly stable under air atmosphere, since these reactions could be carried out without any special attention to keep inert conditions. The conversion rates in hydrogen transfer of complex **4** are comparable with those of our related (Cp*-NHC)IrI_2 complex, although the amount of catalyst **4** (1 mol %) used in the reaction was higher compared to the iridium complex (0.1 mol %); decreasing the amount of catalyst to 0.5 mol % diminished the yield of the corresponding alcohol (75%, Table 2, entry 6). However, the potentially low cost of the iron catalyst is a great advantage.[6c]

Table 2. Catalytic Transfer Hydrogenation Catalyzed by Complexes 4, 6, and 7[a]



entry	substrate	catalyst	*t* (h)	yield (%)[b]
1	acetophenone	(Cp*-NHC)Fe(CO)I (**4**)	6	86
2	cyclohexanone	(Cp*-NHC)Fe(CO)I (**4**)	2	100
3	benzophenone	(Cp*-NHC)Fe(CO)I (**4**)	18	85
4	acetophenone	(Cp-NHC)Fe(CO)I (**5**)	6	85
5	acetophenone	(Cp^{Bz}-NHC)Fe(CO)I(**6**)	6	84
6	acetophenone	(Cp*-NHC)FeCl (**7**)	6	80
7	acetophenone	(Cp*-NHC)Fe(CO)I (**4**)[c]	6	75

[a] Reactions carried out with 2 mmol of ketone, KOH (10 mL, 0.2 M in *i*-PrOH), and 1 mol % of catalyst. Temperature 80 °C. [b] Yield determined by ^{1}H NMR spectroscopy. [c] Reaction carried out with 0.5 mol % of catalyst.

Conclusion

We synthesized new Fe(II) complexes containing cyclopentadienyl-functionalized N-heterocyclic carbene ligands of the general type (Cp^x-NHC)Fe(CO)I. The molecular structures of (Cp-NHC)Fe(CO)I and (Cp^{Bz}-NHC)Fe(CO)I showed the cyclopentadienyl-NHC ligand chelating the iron center in a four-legged piano-stool geometry. The catalytic activity of the new complexes was tested in hydrosilylation and hydrogen transfer reactions, revealing the efficient activity of (Cp*-NHC)FeCl in the hydrosilylation of aldehydes and the good activity of (Cp^x-NHC)Fe(CO)I complexes in catalytic transfer hydrogenation of ketones using 2-propanol as hydrogen source.

Experimental Section

General Procedures. Ligands **1**[1] and **3**[4] were synthesized according to the method described by us. Ligand **2** has been synthesized following a similar method to that described for **1** and **3** (see Experimental Section). $FeI_2(CO)_4$[27] and 6,6-diphenylfulvene[28] were prepared following literature procedures. $FeCl_2$ was used as purchased. All other reagents were used as received from commercial suppliers without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz. Infrared (IR) spectra were recorded on samples as KBr pellets using a Mattson 7000 FT-IR spectrometer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. A QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used for high-resolution mass spectrometry (HRMS). The drying gas as well as nebulizing gas was nitrogen at a flow of 400 and 80 L/h, respectively. Complexes **4**−**7** did not give reproducible elemental analyses due to the retention of fractional amounts of solvent. In lieu of acceptable elemental analyses for compounds **4**−**7** HRMS (ESI-TOF) were recorded.

Synthesis of [Cp-CPh$_2$-CHPh-NHC^{Me}]I (2). A hexane solution of *n*-BuLi (11.86 mL of 1.6 M in hexane, 18.97 mmol) was added dropwise to a solution of benzylimidazole (2.50 g, 15.80 mmol) in dried THF (20 mL) at −60 °C. The solution was stirred for 20 min, 6,6-diphenylfulvene (3.60 mg, 15.80 mmol) was added, and the reaction mixture was allowed to reach room temperature and stirred for 1 h. Methanol was then added, and the volatiles were evaporated. The crude oil was purified by flash chromatography (hexane/ethyl acetate, 1:4), affording a yellow oil of Cp-CPh$_2$-CHPh-NHC (3.67 g, 60%). Iodomethane (353 mg, 1.2 mmol) was added to a solution of Cp-CPh$_2$-CHPh-NHC (467 mg, 1.2 mmol) in 5 mL of acetone. The reaction was stirred at room temperature for 12 h, and all the volatiles were evaporated, affording a white solid, which was washed several times with dried diethyl ether to yield the title compound **2** in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 1H, NC*H*N), 7.39−7.16 (m, 16H, CH_{Ph}+CH_{Imid}), 6.71 (s, 1H, CH_{Imid}), 6.32 (m, 2H, CH_{Cp}), 6.25 (s, 1H, C*H*Ph$_{linker}$), 6.01 (m, 2H, CH_{Cp}), 3.87 (s, 3H, NCH_3), 3.04 (s, 1H, CH_{Cp}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$,): δ 147.9 (C_{phenyl}), 140.2 (C_{phenyl}), 139.7 (C_{phenyl}), 135.0 (*C*Ph$_{2linker}$), 132.8 (N*C*N), 128.9−127.6 (*C*H$_{Ph}$ + *C*H$_{Cp}$), 122.8 (*C*H$_{Imid}$), 122.1 (*C*H$_{Imid}$), 69.4 (*C*H$_{Cp}$), 36.9 (N*C*H$_3$). MS (ESI): *m*/*z* 403 (100, M + H$^+$).

Synthesis of 4. A solution of **1** (400 mg, 0.93 mmol) in THF (30 mL) was treated with two equivalents of *n*-BuLi (1.16 mL of 1.6 M in hexane, 1.86 mmol) at −60 °C. The mixture was stirred for 15 min followed by warming to room temperature. To the resulting mixture was added at once a solution of $FeI_2(CO)_4$ (0.39 g, 0.93 mmol) in THF (5 mL), and the reaction mixture was stirred overnight. All volatiles were then removed under vacuum, and the remaining solid was extracted with diethyl ether, yielding the iron complex **4** (369 mg, 0.71 mmol, 77%) as a green solid. ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.62−7.51 (m, 5H, Ph), 7.13 (s, 1H, CH_{Imid}), 6.44 (s, 1H, CH_{Imid}), 6.00−5.97 (dd, 1H, C*H*Ph$_{linker}$), 3.79 (s, 3H, NCH_3), 2.98−2.96 (m, 2H, C*H*$_{2linker}$), 2.36 (s, 3H, C*H*$_{3Cp*}$), 1.81 (s, 3H, C*H*$_{3Cp*}$), 1.74 (s, 3H, C*H*$_{3Cp*}$), 0.96 (s, 3H, C*H*$_{3Cp*}$). ^{13}C{^{1}H} NMR (100 MHz, acetone-*d*$_6$): δ 226.5 (CO), 195.5 ($C_{carbene}$-Fe), 138.3 ($C_{ipso phenyl}$), 129.7−128.7 (*C*H$_{phenyl}$), 123.8 (*C*H$_{Imid}$), 120.3 (*C*H$_{Imid}$), 103.7 (C_{Cp*}), 91.8 (C_{Cp*}), 90.4 (C_{Cp*}), 83.0 (C_{Cp*}), 81.6 (C_{Cp*}), 66.6 (*C*HPh$_{linker}$), 38.7 (N*C*H$_3$), 28.9 (*C*H$_{2linker}$), 12.9 (*C*H$_{3Cp*}$), 10.2 (*C*H$_{3Cp*}$), 9.5 (*C*H$_{3Cp*}$), 9.2 (*C*H$_{3Cp*}$). HRMS (ESI-TOF): *m*/*z* [M − I + NCMe]$^+$ calcd for $C_{22}H_{25}N_2OFeNCCH_3$, 430.1588; found, 430.1582; [M − I]$^+$ calcd for $C_{22}H_{25}N_2OFe$, 389.1317; found, 389.1323. IR (KBr): ν(Fe−CO) 1906 (vs) cm^{-1}.

Synthesis of 5. A solution of **2** (150 mg, 2.8 mmol) in THF (15 mL) was treated with two equivalents of *n*-BuLi (3.50 mL of 1.6 M in hexane, 5.60 mmol) at −60 °C. The mixture was stirred for 15 min followed by warming to room temperature. To the resulting mixture was added at once a solution of $FeI_2(CO)_4$ (118 mg, 2.8 mmol) in THF (15 mL), and the reaction mixture was stirred overnight. All volatiles were then removed under vacuum, and the remaining solid was extracted with diethyl ether, yielding the iron complex **5** (616 mg, 1.0 mmol, 36%) as a green solid. ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 8.01 (s, 1H, CH_{Imid}), 7.56 (s, 1H, CH_{Imid}), 7.37−6.85 (m, 15H, Ph), 5.28 (s, 1H, CH_{Cp}), 4.93 (s, 1H, CH_{Cp}), 4.55 (s, 2H, CH_{Cp}) 4.42 (s, 1H, C*H*Ph$_{linker}$), 3.76 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (100 MHz, acetone-*d*$_6$): δ 224.3 (CO), 188.2 ($C_{carbene}$-Fe), 146.5 (C_{phenyl}), 146.4 (C_{phenyl}) 139.5 (C_{phenyl}), 132.0−125.2 (*C*H$_{phenyl}$ + *C*H$_{Imid}$), 105.2 (C_{Cp}), 95.6 (CH_{Cp}), 85.8 (CH_{Cp}), 78.2 (CH_{Cp}), 72.1 (CH_{Cp}), 65.9 (*C*HPh$_{linker}$), 41.0 (N*C*H$_3$), 26.4 (*C*Ph$_{2linker}$). HRMS (ESI-TOF): *m*/*z* [M − I]$^+$ calcd for $C_{30}H_{25}N_2OFe$, 485.1317; found, 485.1320; [M − I + NCCH$_3$]$^+$ calcd for $C_{30}H_{25}N_2OFeNCCH_3$, 526.1582; found, 526.1581. IR (KBr): ν(Fe−CO) 1949 cm^{-1}.

Synthesis of 6. A solution of **3** (450 mg, 0.55 mmol) in 20 mL of THF was was treated with two equivalents of *n*-BuLi (0.69 mL of 1.6 M in hexane, 1.11 mmol) at −60 °C. The mixture was stirred for 15 min followed by warming to room temperature. To the resulting mixture was added at once a solution of $FeI_2(CO)_4$ (230 mg, 0.55 mmol) in THF (5 mL), and the reaction mixture was stirred overnight. All volatiles were then removed under vacuum, and the remaining solid was extracted with diethyl ether, yielding the iron complex **6** (409 mg, 0.45 mmol, 83%) as a green solid. ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.22−6.28 (m, 33H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 5.7 Hz, 1H), 3.9

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(s, 3H), 3.66 (s, 1H), 3.48 (d, J = 7.4 Hz, 3H), 3.32 (d, J = 3.3 Hz, 1H), 3.26 (d, J = 3.7 Hz, 1H), 2.42 (d, J = 16.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 225.9, 193, 140.6, 140.0, 139.9, 139.1, 138.4, 137.6, 130.49−125.35, 124.2, 122, 105.2, 96.5, 94.8, 88.2, 87.7, 69.0, 45.1, 39.32, 36.1, 32.1, 31.7, 30.9. HRMS (ESI-TOF): m/z $[M]^+$ calcd for $C_{52}H_{45}N_2FeO$, 769.2883; found, 769.2878. IR (KBr): ν(Fe−CO) 1920 (vs) cm^{-1}.

Synthesis of 7. A solution of **1** (260 mg, 0.61 mmol) in THF (15 mL) was treated with two equivalents of *n*-BuLi (0.76 mL of 1.6 M in hexane, 1.23 mmol) at −60 °C. The mixture was stirred for 15 min followed by warming to room temperature. To the resulting mixture was added at once a solution of $FeCl_2$ (700 mg, 0.61 mmol) in THF (5 mL), and the reaction mixture was stirred overnight. All volatiles were then removed under vacuum, and the remaining solid was washed with diethyl ether and extracted with dichloromethane, yielding the iron complex **7** (176 mg, 0.40 mmol, 67%) as a red solid. HRMS (ESI-TOF): m/z $[M - Cl]^+$ calcd for $C_{21}H_{25}N_2FeCl$, 396.1068; found, 396.1056. UV−vis (CH_2Cl_2): absorption 360 nm (Supporting Information).

Hydrosilylation of Aldehydes. A typical procedure was performed as follows. A dried J. Young tube equipped with a Teflon screw cap was flushed with nitrogen and charged with catalyst (0.010 mmol). The appropriate solvent (0.4 mL) followed by the corresponding aldehyde (1.01 mmol) and neat silane (1.24 mmol) were added. The samples were monitored periodically by ^{1}H NMR. Reaction times and temperatures are indicated in Table 1.

Hydrogen Transfer. A mixture of the appropriate ketone (2 mmol), KOH (10 mL, 0.2 M in *i*-PrOH), and catalyst was refluxed. The reaction was monitored by ^{1}H NMR spectroscopy by introducing aliquots of the reacting solution inside an NMR tube with 0.5 mL of $CDCl_3$. The evolution of the reaction was determined by integration.

X-ray Diffraction Studies. Data collection was carried out in a Bruker Appex-II CCD diffractometer at 100 K. Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package (Sheldrick, G. M. *SHELXTL*, version 6.1; Bruker AXS, Inc.: Madison, WI, 2000). All non-hydrogen atoms 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 3 (Supporting Information). The diffraction frames were integrated using the SAINT package (*SAINT*, version 5.0; Bruker Analytical X-ray System: Madison, WI, 1998).

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Supporting Information Available: Full crystallographic data as CIF files and NMR and HRMS spectra of compounds are available free of charge via the Internet at http://pubs.acs.org.