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Cationic Iron(II) Complexes of the Mixed Cyclopentadienyl (Cp) and the Nheterocyclic Carbene (NHC) Ligands as Effective Precatalysts for the Hydrosilylation of Carbonyl Compounds

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Abstract

A series of iron(II) complexes of N-heterocyclic carbene ligands were synthesized and fully structurally characterized. Specifically, the benzimidazole based {Cp[1,3-*di*-R-benzimidazol-2-ylidene]-Fe(CO)₂}I [R = Et (**1b**), *i*-Pr (**2b**) and *n*-Bu (**3b**)] and the imidazole based {Cp[1-benzyl-3-R-imidazol-2-ylidene]Fe(CO)₂}PF₆ [R = Me (**4b**) and Et (**5b**)] type of complexes were synthesized from their respective benzimidazolium iodide (**1–3**)**a** and their imidazolium hexafluorophosphate (**4–5**)**a** salts by the reaction with CpFe(CO)₂I in the presence of MN(SiMe₃)₂ (M = Li or K) as a base. The molecular structures of the (**1–5**)**b** complexes reveal that the metal center display a conventional piano stool structure. More importantly, the (**1–5**)**b** complexes, when irradiated with visible light, effectively catalyzed the hydrosilylation reaction of carbonyl compounds namely, of the aldehyde and ketone substrates, using organosilane reagents. Specifically, the (**1–5**)**b** complexes performed the hydrosilylation of a representative benzaldehyde substrate using phenylsilane in ambient conditions at 30 °C while that of the representative acetophenone substrate at a more elevated temperature of 70 °C. The benzimidazole derived complexes (**1–3**)**b** displayed superior activity than the imidazole derived (**4–5**)**b** complexes.

1. Introduction

Iron, being the second most abundant metal and also the fourth most abundant element on the earth's crust,^[1] the need for its gainful utilization in various commercial and non-commercial application purposes is easily discernible.^[2] The metal, for its non-toxic nature, ready availability and economic viability, arises enormous interest in the academic and industrial worlds alike as potential catalysts for many useful transformations of contemporary organic synthesis. Consequently, in the recent years, a rich chemistry of iron catalysis has been developed in C–H bond activation reactions,^[3] reductions,^[4] in selective carboxylic acid derivatives hydrosilylation,^[5] in C–C^[6] and C–O^[7] cross-coupling reactions,^[8] olefin isomerization reactions^[9] and etc.^[10] including a few in the asymmetric synthesis.^[11]

Owing to our long standing interest in the catalytic applications of iron^[12] along with that of the N-heterocyclic carbenes (NHC),^[13,14] we hypothesized that the iron complexes of the much famed and also catalytically relevant N-heterocyclic carbene ligands would be of considerable interest.^[15,16] In light of the fact that a few cyclopentadienyl ligand derived iron complexes of the N-heterocyclic carbene

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ACCEPTED MANUSCRIPT ligands have indeed been catalytically active for the borylation of heteroarenes,¹¹⁷¹ the hydrosilylation and the hydrogen transfer reactions,^[18] we rationalized the related type $\{Cp(NHC)Fe(CO)_2\}X$ (X = anion), bearing both cyclopentadienyl (Cp) and the Nheterocyclic carbene (NHC) ligands, would thus be worth examining further for their catalytic potentials. More interestingly so, we observed that of the limited examples of the $\{Cp(NHC)Fe(CO)_2\}X(X = anion)$ type of iron complexes that exist in the literature, ^[19] only a handful for them have been structurally characterized,^[20] and because of which we became interested in developing the chemistry of these type of complexes. In this regard it is worth mentioning that for the hydrosilylation reaction as catalyzed by the molecularly defined Cp-NHC iron complexes, the reduction of aldehydes, ketones,^[21] imines^[22] and amides^[23] were performed using organosilane reagents like the phenylsilane and diphenylsilane.

Based on these findings, which suggest that the heteroleptic iron complexes of the mixed NHC and the Cp ligands form efficient catalysts for the hydrosilylation reaction, herein, we report a series of iron complexes of the type $\{Cp(NHC)Fe(CO)_{2}\}X$ (X = I, PF₆) that are supported over benzimidazole (1-3)b and imidazole (4-5)b derived unsymmetrical N-heterocyclic carbene ligands (Figure 1) for application in the catalysis of the hydrosilylation reaction.

2. Results and Discussion

2.1. Synthesis and characterization of the iron-NHC complexes

A series of new iron complexes of two different families of the N-heterocyclic carbene ligands were synthesized (Figure 1).



Figure 1. Prepared iron complexes (1-5)b.

In particular, the benzimidazole derived N-heterocyclic carbene complexes, $\{Cp[1,3-di-R-benzimidazol-2-y|idene]Fe(CO)_2\}I[R = Et$ (1b), *i*-Pr (2b) and *n*-Bu (3b)], were synthesized in moderate yields from the respective benzimidazolium iodide (1–3)a salts, which were deprotonated at 0 °C in the presence of LiN(SiMe₃)₂ as a base, by the reaction with CpFe(CO)₂I at room temperature for 16 hours (Scheme 1).



Scheme 1. Synthesis of the complexes (1-3)b

The unsymmetrical imidazole based N-heterocyclic carbene complexes, $\{Cp[1-benzyl-3-R-imidazol-2-y|idene]Fe(CO)_{2}\}PF_{6}$ [R = Me (4b) and Et (5b)], were similarly synthesized from the corresponding imidazolium hexafluorophosphate (4-5)a salts, which were deprotonated at -20 °C in the presence of KN(SiMe₃)₂, by the reaction with CpFe(CO)₂I in the presence of 1.1 equiv. of AgPF₆ at room temperature for 10 hours (Scheme 2).



Scheme 2. Synthesis of the complexes (4-5)b

All of the (1–5)**b** complexes are diamagnetic and hence have been appropriately characterized by various NMR spectroscopies. For example, the characteristic cyclopentadienyl (Cp) resonance appeared as a singlet in the range 5.39–5.62 ppm in ¹H NMR and in the range 87.3–88.1 ppm in the ¹³C NMR spectrum. As expected, the infrared spectrum of the (1–5)**b** complexes exhibited two carbonyl stretching frequencies (v_{CO}) at 2037–2039 cm⁻¹ and 1985–1993 cm⁻¹ and is consistent with the presence of two CO ligands attached to the iron center, which are in the range of the v_{CO} of the previous described NHC cyclopentadienyl complexes.^[18-19] These carbonyl moieties appeared at its characteristic highly downfield region 210.7–211.1 ppm in the ¹³C{¹H} NMR spectrum. Furthermore, in concurrence with the values reported in the literature, the characteristic carbene resonance of the NHC ligand for benzimidazole derived (1-3)**b** complexes appeared in the range 178.7–180.5 ppm in the ¹³C{¹H} NMR^[18a] while that for the imidazole based (4-5)**b** complexes appeared at 165.1 and 164.4 ppm respectively.^[18b,19b] Additionally, the presence of PF₆⁻ counter anion in the (4–5)**b** complexes were confirmed by the observation of a septet at *ca.* –144.3 ppm in ³¹P NMR and a corresponding doublet at *ca.* –72.6 ppm in ¹⁹F NMR exhibiting a ¹J_{FP} coupling of *ca* 711 Hz.

The molecular structures of all of the (1-5)b complexes as determined by the X-ray single crystal diffraction studies reveal that the iron center adopt a conventional "piano stool" geometry with the cyclopentadienyl (Cp) moiety representing the seat of the stool and the *N*-heterocyclic carbene ligands along with two CO ligands forming its legs (Figures 2–3 and Tables 1–2). Quite interestingly, in the (1-5)b complexes, the Cp ligand was found to be located relatively more close to the iron center than its other ligands, as observed in a shorter Cp_(centroid)•••Fe distance [1.7200(3)–1.7331(7) Å] in comparison to the Fe–NHC bond [1.965(5)–1.9777(4) Å] and the other two Fe–CO bond [1.765(5)–1.783(5) Å and 1.770(5)–1.780(5) Å] distances. The iodide and the PF₆⁻ counter anions were seen to be non-coordinating in the (1–3)b and (4–5)b complexes respectively.



Figure 2. ORTEP views of the complexes **1b**, **2b** and **3b**. For **1b**: Selected bond lengths (Å) and angles (°): Fe1-C18 1.765(5), Fe1-C17 1.780(5), Fe1-C1 1.972(5), O1-C17 1.143(5), O2-C18 1.165(5), N1-C1 1.375(5), N2-C1 1.363(5), C18-Fe1-C17 91.0(2), C18-Fe1-C1 96.28(17), C17-Fe1-C1 95.90(19), N2-C1-Fe1 127.4(3), N1-C1-Fe1 126.4(3), N2-C1-N1 105.8(3). For **2b**: Selected bond lengths (Å) and angles (°): Fe1-C1 1.972(4), Fe1-C19 1.780(4), Fe1-C20 1.770(4), C1-N2 1.371(4), C1-N1 1.353(5), O2-C20 1.147(4), O1-C19 1.145(4), C20-Fe1-C19 89.2(16), C20-Fe1-C1 92.93(16), C19-Fe1-C1 95.75(16), N1-C1-N2 106.7(3), N1-C1-Fe1 127.8(2), N2-C1-Fe1 125.6(3). For **3b**: (hydrogen atoms and one molecule of H₂O are omitted for clarity); Selected bond lengths (Å) and angles (°): Fe1-C1 1.976(4), Fe1-C22 1.765(5), Fe1-C21 1.762(6), O2-C21 1.149(7), O1-C22 1.153(6), N1-C1 1.361(6), N2-C1 1.354(6), C21-Fe1-C22 90.3(2), C21-Fe1-C1 95.1(2), C22-Fe1-C1 97.1(2), N1-C1-N2 106.4(4), N2-C1-Fe1 126.8(3), N1-C1-Fe1 126.4(3)

		81	- / -
compound	1b	2b	3b
lattice	Monoclinic	Triclinic	Monoclinic
formula	$C_{18}H_{21}FeIN_2O_3$	$C_{20}H_{25}FeIN_2O_4$	$C_{22}H_{27}FeIN_2O_3$
formula weight	496.12	540.17	552.22
space group	P 21	P -1	$P2_1/c$
a/Å	9.23(2)	9.711(7)	18.436(6)
b/Å	10.80(7)	9.931(7)	10.789(3)
c/Å	9.95(2)	12.229(7)	25.125(9)
$\alpha/^{\circ}$	90.00	92.058(9)	90.00
$\beta/^{\circ}$	107.16(4)	90.989(14)	109.085(5)
γ/°	90.00	110.688(14)	90.00
$V/Å^3$	948(3)	1102.0(13)	4723(3)
Z	2	2	8
temperature (K)	100(2)	100(2)	150(2)
radiation (λ,Å)	0.71075	0.71075	0.71075
ρ (calcd.), g cm ⁻³	1.738	1.628	1.553
μ(Mo Ka), mm ⁻¹	2.442	2.112	1.970
θ max, deg.	25.33	25.36	25.00
no. of data	3413	3937	8283
no. of parameters	235	262	523
R ₁	0.0288	0.0364	0.0525
wR_2	0.0503	0.0861	0.1217
GOF	1.007	1.062	1.167

ACCEPTED MANUSCRIPT **Table 1.** X-ray crystallographic data (1–3)b



Figure 3. ORTEP views of the complexes 4b and 5b. (hydrogen atoms are omitted for clarity) For 4b: Selected bond lengths (Å) and angles (°): Fe1-C21 1.9753(19), Fe1-C1 1.777(2), Fe1-C3 1.777(2), C1-O2 1.136(3), C3-O4 1.140(3), C23-C24 1.336(3), C21-N22 1.360(2), C21-N25 1.361(2), C21-Fe1-C1 94.19(9), C21-Fe1-C3 97.57(8), C1-Fe1-C3 93.86(9), N22-C21-N25 103.57(16), N22-C21-Fe1 125.96(14), N25-C21-Fe1 130.40(14). For 5b: Selected bond lengths (Å) and angles (°): Fe1-C1 1.977(4), Fe1-C18 1.782(4), Fe1-C19 1.777(4), C18-O1 1.141(5), C19-O2 1.138(5), C2-C3 1.339(5), C1-N1 1.363(4), C1-N2 1.367(5), C1-Fe1-C18 96.51(16), C1-Fe1-C19 92.16(16), C18-Fe1-C19 90.67(18), N1-C1-N2 104.1(3), N1-C1-Fe1 129.6(3), N2-C1-Fe1 126.2(3)

compound	4b	5b
lattice	Monoclinic	Monoclinic
formula	$C_{18}H_{17}FeN_2O_2PF_6$	$C_{19}H_{19}FeN_2O_2PF_6$
formula weight	494.16	508.18
space group	$P2_1/c$	$P2_1/c$
a/Å	12.1755(10)	13.584(6)
b/Å	10.4387(6)	10.517(4)
c/Å	15.5426(12)	15.681(8)
α/°	90.00	90.00
β/°	97.841(3)	114.645(7)
γ/°	90.00	90.00
$V/Å^3$	1956.9(2)	2036.2(16)
Z	4	4
temperature (K)	150(2)	100(2)
radiation (λ,Å)	0.71073	0.71073
ρ(calcd.), g cm ⁻³	1.677	1.658
μ(Mo Kα), mm ⁻¹	0.926	0.893
θ max, deg.	27.48	25.35
no. of data	4437	3736
no. of parameters	272	281
R ₁	0.0345	0.0458
wR_2	0.0911	0.1239
GOF	1.029	1.182

ACCEPTED MANUSCRIPT Table 2. X-ray crystallographic data (4–5)b

2.2. Catalytic evaluation of the prepared NHC-Fe complexes

The catalytic activities of these new molecularly defined iron NHC complexes (1-5)b were evaluated on hydrosilylation of carbonyl derivatives such as of the aldehydes and ketones. Based on our previous observations with the { $Cp[1,3-di-R-imidazol-2-ylidene]Fe(CO)_2$ }I [R = Mes and i-Pr]^[21b] complexes, that required activation by visible light, we chose to study the hydrosilylation of benzaldehyde (6) and acetophenone (7) as two representative benchmark test reactions for the aldehyde and ketone substrates using the newly synthesized (1-5)b complexes under analogous photo-activation conditions with the aim of comparing their catalytic activities. The catalysis results along with the reaction conditions are reported in the Table 3

For example, in case of the reduction of benzaldehyde, the hydrosilylation reaction was performed at 30 °C for 3 hours in the presence of 1.2 equiv. of phenylsilane and 2 mol% of a Fe–NHC complex as the pre-catalyst. The benzimidazole derived iron complex **1b** yielded 68% conversion after 3 hours of reaction time, whereas only 15% and 6% conversions were observed in case of the complexes **2b** and **3b**, thus showing the crucial influence of substituents on the benzimidazole moiety (Entries 1, 4 and 7). Nevertheless, by extending the reaction time to 17 hours, full conversions were achieved in each case (Entries 2, 5 and 8).

In case of the imidazole based iron complexes, **4b** led to 90% conversion after 3 hours at 30 °C, whereas **5b** gave only 44% conversion (Entries 10 and 13). Notably, using 1 mol% of **4b** under similar conditions, the same conversion was observed. Benzyl substituents on the imidazole-based NHC ligand seems to have a positive influence on the catalytic activity than the *i*-propyl moiety in our earlier reported complex {Cp[1,3-*di*-(*i*-Pr)-imidazol-2-ylidene]Fe(CO)₂}I that showed 28% conversion after 3 hours at 30 °C, while the best performance was seen the mesityl substituted imidazole-based Fe–NHC complex {Cp[1,3-*di*-(IMes)-imidazol-2-ylidene]Fe(CO)₂}I^[21b] that resulted full conversion in 3 hours at 30 °C. However, after a prolonged reaction time of 17 hours at 30 °C, the **4b** and **5b** complexes resulted in full conversions (entries 11 and 14). Notably, when the reaction were performed in solvent free conditions for 3 h at 30 °C using 2 mol% of the complexes (**1-5)b**, full conversions were obtained (Entries 3, 6, 9, 12 and 15).

R' = H(6), Me (7)	R R R R CO R	R N Fe CO Ph
	R = Et (1b), i-Pr (2b), n-Bu (3b)	R = Me(4b). Et (5b)

Table 3. Hydrosilylation of benzaldehyde and acetophenone as catalyzed by the Fe–NHC complexes (1-5)b

Entry	Catalyst	Benzaldehy	/de	Ace	tophenone
	(2 mol%)	Conditions	Conv. (%) ^[b]	Conditions	Conv. (%) ^[b]
1	1b	THF, 30 °C, 3 h	68	neat, 70 °C, 17 h	90
2		17 h	> 98		
<mark>3</mark>		Neat, 30 °C, 3 h	<mark>> 98</mark>		
4	2 h	THE 20 °C 2 h	15	nost 70 °C 17 h	75
5	20	1111, 50°C, 511	> 08	licat, 70°C, 17 li	15
		17 II Neet 20 %C 2 h	> 98		
0		Neat, 50°C, 5 II	<mark>> 90</mark>		
<mark>7</mark>	3b	THF, 30 °C, 3 h	6	neat, 70 °C, 17 h	> 98
<mark>8</mark>		17 h	90		
<mark>9</mark>		Neat, 30 °C, 3 h	<mark>> 98</mark>		
10	46	THE 20 °C 2 h		next 70 °C 17 h	79
10	40	1HF, 50°C, 5 II	90 <mark>(90°*)</mark>	neat, 70°C, 17 n	78
11		1/h	> 98		
12		Neat, 30 °C, 3 h	<mark>> 98</mark>		
<mark>13</mark>	5b	THF, 30 °C, 3 h	44	neat, 70 °C, 17 h	72
<mark>14</mark>		17 h	> 98		
15		Neat, 30 °C, 3 h	> 98		

[a]Aldehyde or ketone (1 mmol), phenylsilane (1.2 mmol), [CpFe(CO)₂(NHC)][X] (2 mol%), THF (4 mL) or neat, 30-70 °C, 17 h under visible light irradiation. (ii) quench with NaOH 2M (2 mL) and MeOH (2 mL) at rt for 2 h. [b] Conversion determined by ¹H-NMR analysis. [c] Reaction performed with 1 mol% of the complex **4b** in THF at 30 °C for 3 h.

In case of the hydrosilylation of acetophenone by the (1-5)b complexes, it was necessary to heat the reaction at 70 °C under solvent free conditions in order to obtain good conversions (72-98%). Notably, the benzimidazole-derived Fe–NHC complexes 1b and 3b gave encouraging 90–98% conversions after 17 hours of reaction time, whereas the remaining three 2b, 4b and 5b complexes gave satisfactory 72–78% conversions (Entries 1, 7 *versus* 4, 10 and 13). Thus, overall, the benzimidazole-based Fe–NHC complexes (1-3)b seem to be interesting precatalysts for the hydrosilylation of carbonyl compounds. Additionally, the complexes 1b and 4b were able to quantitatively transform an activated acetophenone, namely 4-trifluoromethylacetophenone into the corresponding alcohol at 70 °C for 17 hours.

3. Conclusions

In summary, several ionic $\{Cp(NHC)Fe(CO)_2\}X$ (X = I, PF₆) type of iron *N*-heterocyclic carbene complexes derived from the benzimidazole (1–3)b and the imidazole (4–5)b motifs were synthesized and fully structurally characterized. These iron complexes were found to be active catalyst precursors for the hydrosilylation of carbonyl derivatives. Further investigations on the reactivity of such benzimidazole-derived iron complexes are under investigations in both of our groups.

4. Experimental Section

4.1. General Procedures.

All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. $KN(SiMe_3)_2$, $LiN(SiMe_3)_2$ and $AgPF_6$, were purchased from Sigma Aldrich (USA) and used without any further purification. **1a**,^[24] **2a**,^[25] **3a**,^[26] **4a**,^[27] **5a**^[28] and $CpFe(CO)_2I^{[29]}$ were synthesized according to modified literature procedures. ¹H,

 ${}^{13}C{}^{1}H$ and ${}^{19}F{}^{1}H$ NMR spectra were recorded on a Varian and Bruker 400 MHz NMR spectrometer. ¹H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-T of spectrometer. Elemental Analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. X-ray diffraction data for compounds (**1–3**)**b** were collected on a Rigaku Hg 724+ diffractometer and for the compounds (**4–5**)**b** were collected on APEXII, Bruker-AXS diffractometer equipped with a CCD detector, using graphite-monochromated Mo Ka radiation (k = 0.71073 Å) at T = 150(2) K, and crystal data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by fullmatrix least-squares procedures on F^2 with SHELXTL (Version 6.10).^[30]

4.2. Synthesis of the NHC-Fe comples

4.2.1. Synthesis of {Cp[1,3-di-ethyl-benzimidazol-2-ylidene]Fe(CO)₂}I (1b)

To a solution of 1,3-*di*-ethyl-benzimidazolium iodide (**1a**) (0.501 g, 1.66 mmol) in THF (*ca.* 10 mL), a solution of LiN(SiMe₃)₂ (0.552 g, 3.30 mmol) in THF (*ca.* 10 mL) was added dropwise and the resulting mixture was stirred for 1 hour at 0 °C under N₂ atmosphere. A solution of CpFe(CO)₂I (0.861 g, 2.83 mmol) in THF (*ca.* 10 mL) was added to it and the resultant mixture was stirred for another 16 hours at room temperature. All volatiles were then removed under *vacuum* to give the crude product as a brown residue which was purified by column chromatography using 230–400 mesh silica gel as a stationary phase and by eluting it with a CHCl₃/MeOH mixture (95 : 5 v/v) to give the product **1b** as a brown solid (0.293 g, 37%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.53–7.52 (m, 2H, C₇<u>H</u>₄N₂), 7.4–17.39 (m, 2H, C₇<u>H</u>₄N₂), 5.59 (s, 5H, C₅<u>H</u>₅), 4.71 (q, 4H, ³J_{HH} = 7 Hz, C<u>H</u>₂CH₃), 1.64–1.58 (m, 6H, CH₂C<u>H</u>₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 210.8 (<u>C</u>O), 178.9 (Fe–N<u>C</u>N of C₇H₄N₂), 135.4 (<u>C</u>₇H₄N₂), 124.2 (<u>C</u>₇H₄N₂), 111.2 (<u>C</u>₇H₄N₂), 87.9 (<u>C</u>₅H₅), 45.6 (<u>C</u>H₂CH₃), 14.7 (CH₂<u>C</u>H₃). IR data (cm⁻¹) KBr pellet (v_{CO}): 2039 (s) and 1993 (s). HRMS (ES): m/z 351.0793 [M–I]⁺, calcd 351.0796. Anal. Calcd. for C₁₈H₁₉FeIN₂O₂: C, 45.22; H, 4.01; N, 5.86; Found: C, 44.52; H, 4.39; N, 5.68%.

4.2.2. Synthesis of {Cp[1,3-*di-i*-propyl-benzimidazol-2-ylidene]Fe(CO)₂}I (2b) To a solution of 1,3-di-*i*-propyl-benzimidazolium iodide (2a) (0.401 g, 1.21 mmol) in THF (*ca.* 10 mL), a solution of LiN(SiMe₃)₂ (0.482 g, 2.88 mmol) in THF (*ca.* 10 mL) was added dropwise and the resulting mixture was stirred for 1 hour at 0 °C under N₂ atmosphere. A solution of CpFe(CO)₂I (0.738 g, 2.42 mmol) in THF (*ca.* 10 mL) was added and the reaction mixture was allowed to stir for another 16 hours at room temperature. All volatiles were then removed under *vacuum* to give the crude product as a brown residue which was purified by column chromatography using 230–400 mesh silica gel as a stationary phase and by eluting it with a CHCl₃/MeOH mixture (94 : 6 *v/v*) to give the product **2b** as a yellow solid (0.251 g, 41%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.99-7.97 (m, 2H, C₇<u>H</u>₄N₂), 7.37–7.33 (m, 2H, C₇<u>H</u>₄N₂), 5.62 (s, 5H, C₅<u>H</u>₅), 5.53 (sept, 2H, ³J_{HH} = 7 Hz, CH[CH₃]₂), 1.82 (d, 12H, ³J_{HH} = 7 Hz, CH[C<u>H</u>₃]₂). ¹³C{¹H} NMR (DMSO-d₆, 100 MHz, 25 °C): δ 211.0 (<u>C</u>O), 180.5 (Fe–N<u>C</u>N of C₇H₄N₂), 134.3 (<u>C</u>₇H₄N₂), 122.8 (<u>C</u>₇H₄N₂), 113.2 (<u>C</u>₇H₄N₂), 87.9 (<u>C</u>₅H₅) 54.3 (<u>C</u>H[CH₃]₂), 20.1 (CH[<u>C</u>H₃]₂). IR data (cm⁻¹) KBr pellet (v_{CO}): 2039 (s) and 1994 (s). HRMS (ES): m/z 379.1102 [M–I]⁺, calcd 399.1104. Anal. calcd. for C₂₀H₂₃FeIN₂O₂•1/3H₂O: C, 46.90; H, 4.66; N, 5.47; Found: C, 47.56; H, 4.41; N, 5.35%.

4.2.3. Synthesis of {Cp[1,3-di-n-butyl-benzimidazol-2-ylidene]Fe(CO)₂}I (3b)

To a solution of 1,3-di-*n*-butyl-benzimidazolium iodide (**3a**) (0.674 g, 1.88 mmol) in THF (*ca.* 10 mL), a solution of LiN(SiMe₃)₂ (0.610 g, 3.65 mmol) in THF (*ca.* 10 mL) was added dropwise and the resulting mixture was stirred for 1 hour at 0 °C under N₂ atmosphere. A solution of CpFe(CO)₂I (1.00 g, 3.29 mmol) in THF (*ca.* 10 mL) was added to it and the resultant mixture was stirred for another 16 hours at room temperature. All volatiles were then removed under *vacuum* to give the crude product as a brown residue which was purified by column chromatography using 230–400 mesh silica gel as a stationary phase and by eluting it with a CHCl₃/MeOH mixture (95 : 5 ν/ν) to give the product **1b** as a brown solid (0.278 g, 28%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.50–7.48 (m, 2H, C₇<u>H</u>₄N₂), 7.40–7.38 (m, 2H, C₇<u>H</u>₄N₂), 5.58 (s, 5H, C₅<u>H</u>₅), 4.58–4.53 (m, 4H, [C<u>H</u>₂]₃CH₃), 1.88 (br, 4H, [C<u>H</u>₂]₃CH₃), 1.65 (m, 4H, ([C<u>H</u>₂]₃CH₃), 1.06 (t, 6H, ³J_{HH} = 7 Hz, [CH₂]₃C<u>H</u>₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 210.7 (<u>C</u>O), 178.7 (Fe–N<u>C</u>N of C₇H₄N₂), 135.6 (<u>C</u>₇H₄N₂), 124.2 (<u>C</u>₇H₄N₂), 111.3 (<u>C</u>₇H₄N₂), 88.1 (<u>C</u>₅H₅) 50.3 ([<u>C</u>H₂]₃CH₃), 31.8 ([<u>C</u>H₂]₃CH₃), 20.2 ([<u>C</u>H₂]₃CH₃), 13.9 ([CH₂]₃<u>C</u>H₃). IR data (cm⁻¹) KBr pellet (v_{CO}): 2039 (s) and 1986 (s). HRMS (ES): m/z 407.1416 [M–I]⁺, calcd 407.1422. Anal. Calcd. for C₂₂H₂₇FeIN₂O₂: C, 49.46; H, 5.09; N, 5.24; Found: C, 49.89, H, 5.24, N, 4.80%.

4.2.4. Synthesis of {Cp[1-benzyl-3-methyl-imidazol-2-ylidene]Fe(CO)₂}PF₆ (4b)

To a solution of 1-benzyl-3-methyl-imidazolium hexafluorophosphate (**4a**) (0.300 g, 0.943 mmol) in dry THF (*ca.* 10 mL) at $-20 \,^{\circ}$ C, a solution of KN(SiMe₃)₂ (0.376 g, 1.89 mmol) was added dropwise while stirring. The resultant yellow solution was vigorously stirred for 1 hour at $-20 \,^{\circ}$ C and then allowed to attain room temperature while stirring. The reaction mixture was again cooled to $-20 \,^{\circ}$ C, and to which a solution of CpFe(CO)₂I (0.487 g, 1.60 mmol) in dry THF (*ca.* 10 mL) was added dropwise. The reaction mixture was stirred for 1 hour and AgPF₆ (0.446 g, 1.76 mmol) was added and further stirred at room temperature for another 10 hours. The solvent was then removed under vacuum and the residue was purified by 230–400 mesh silica gel column chromatography by elution with MeOH/CHCl₃ (1:9 *v*/*v*) mixed medium to get the product (**4b**) as a dark green solid (0.184 g, 39% yield). ¹H NMR (CDCl₃, 400 MHz, 25 $\,^{\circ}$ C): δ ppm, 7.43–7.37 (m, 4H, C₆<u>H</u>₅), 7.19–7.17 (m, 2H, C₆<u>H</u>₅ and NCHC<u>H</u>N), 7.11 (s, 1H, NC<u>H</u>CHN), 5.49 (s, 2H, C<u>H</u>₂), 5.42 (s, 5H, C₅<u>H</u>₅), 4.05 (s, 3H, C<u>H</u>₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 $\,^{\circ}$ C): δ ppm, 211.1 2(CO), 165.1 (N<u>C</u>(2)N), 134.9 *ipso*-(<u>C</u>₆H₅), 129.2 (<u>C</u>₆H₅), 128.5 (<u>C</u>₆H₅), 127.6 (N<u>C</u>HCHN), 127.1 (<u>C</u>₆H₅), 125.9 (NCH<u>C</u>HN), 87.3 (<u>C</u>₅H₅), 55.5 (<u>C</u>H₂), 41.0 (<u>C</u>H₃). ³¹P{¹H</sup> NMR (CDCl₃, 162 MHz, 25 $\,^{\circ}$ C): δ ppm, -144.4 (sept, ¹J_{PF} = 712 Hz). ¹⁹F{¹H} NMR (CDCl₃, 376 MHz, 25 $\,^{\circ}$ C): δ ppm, -72.6 (d, ¹J_{FP} = 711 Hz). IR data (cm⁻¹) KBr pellet (v_{CO}): 2038 (s) and 1989 (s). HRMS (ES): m/z 349.0634 [M-PF₆]⁺, calcd 349.0639. Anal. calcd. for C₁₈H₁₇FeN₂O₂PF₆: C, 43.75; H, 3.47; N, 5.67; Found: C, 43.60; H, 3.70; N, 5.55\%.

4.2.5. Synthesis of ${Cp[1-benzyl-3-ethyl-imidazol-2-ylidene]Fe(CO)_2}PF_6(5b)$

To a solution of 1-benzyl-3-ethyl-imidazolium hexafluorophosphate (**5a**) (0.330 g, 0.993 mmol) in dry THF (*ca.* 10 mL) at -20 °C, a solution of KN(SiMe₃)₂ (0.396 g, 1.99 mmol) was added dropwise while stirring. The resultant yellow solution was vigorously stirred for 1 hour at -20 °C and then allowed to attain room temperature while stirring. The reaction mixture was again cooled to -20 °C, and to which a solution of CpFe(CO)₂I (0.528 g, 1.74 mmol) in dry THF (*ca.* 10 mL) was added dropwise. The reaction mixture was stirred for 1 hour and AgPF₆ (0.483 g, 1.91 mmol) was added and further stirred at room temperature for another 10 hours. The solvent was then removed under vacuum and the residue was purified by 230–400 mesh silica gel column chromatography by elution with MeOH/CHCl₃ (1:9 *v*/*v*) mixed medium to get the product (**5b**) as a dark green solid (0.144 g, 29% yield). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ ppm, 7.42–7.34 (m, 5H, C₆<u>H</u>₅), 7.18 (s, 1H, NCHC<u>H</u>N), 7.15 (s, 1H, NC<u>H</u>CHN), 5.50 (s, 2H, C<u>H</u>₂), 5.39 (s, 5H, C₅<u>H</u>₅), 4.40 (q, 2H, ³_J_{HH} = 7 Hz, C<u>H</u>₂CH₃), 1.55 (t, 3H, ³_J_{HH} = 7 Hz, CH₂C<u>H</u>₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ ppm, 211.1 1(CO), 164.4 (N<u>C</u>(2)N), 134.9 *ipso*-(<u>C</u>₆H₅), 129.3 (<u>C</u>₆H₅), 128.5 (<u>C</u>₆H₅), 126.7 (N<u>C</u>HCHN), 124.8 (NCH<u>C</u>HN), 87.4 (<u>C</u>₅H₅), 55.6 (<u>C</u>_H₂), 47.6 (<u>C</u>H₂CH₃), 16.2 (<u>C</u>H₃). ³¹P{¹H} NMR (CDCl₃, 162 MHz, 25 °C): δ ppm, -144.2 (sept, ¹J_{PF} = 711 Hz). ¹⁹F{¹H} NMR (CDCl₃, 376 MHz, 25 °C): δ ppm, -26.1 (d, ¹J_{FP} = 726 Hz). IR data (cm⁻¹) KBr pellet (v_{CO}): 2037 (s) and 1987 (s). HRMS (ES): m/z 363.0796 [M-PF₆]⁺, calcd 363.0791. Anal. calcd. for C₁₉H₁₉Fe₂O₂PF₆: C, 44.91; H, 3.77; N, 5.51; Found: C, 44.57; H, 3.68; N, 6.43%.

4.3. General procedure for the hydrosilylation of benzaldehyde and acetophenone catalyzed by the Fe–NHC complexes

A 10 mL oven dried Schlenk tube containing a stirring bar, was charged with one of the (1-5)b, 8 or 9 complex (0.01 mmol, 2 mol%). After purging with argon (argon-vacuum three cycles) benzaldehyde or acetophenone (0.5 mmol) was added followed by PhSiH₃ (68 μ L, 0.6 mmol, 1.2 equiv.). The reaction mixture was stirred in a preheated oil bath at 30 °C (for benzaldehyde) or 70 °C (for acetophenone) for 17 hours under light irradiation (24 W fluocompact bulb-light). Then 1 mL of MeOH was added followed by 1 mL of 2M NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 1 hour at room temperature and was extracted with diethyl ether (2×10 mL). The combined organic layers were washed with brine (3×10 mL), dried over anhydrous MgSO4, filtered and concentrated under vacuum. The conversion was determined by ¹H NMR. The residue can be then purified by silica gel column chromatography using ethyl acetate-petroleum ether mixture (10 to 50%) to afford the desired product

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Supplementary Material Available: CCDC-940393 (for 1b), CCDC-940172 (for 2b), CCDC-935844 (for 3b), CCDC-910399 (for 4b) and CCDC-926830 (for 5b) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or [from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: <u>deposit@ccdc.cam.ac.uk</u> ¹H NMR, ¹³C{¹H} NMR, ¹⁹F NMR, ³¹P NMR, IR, HRMS, elemental analysis and the CIF file giving X-ray crystallographic data of (1–5)b are available free of charge via the internet at <u>doi:XXXXXXXXXX</u>.

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Table of Contents

A series of cationic iron(II) complexes of the mixed cyclopentadienyl (Cp) and the benzimidazole- and imidazole-derived N-heterocyclic carbene (NHC) ligands effectively catalyze the hydrosilylation of aldehyde and ketone compounds.



Cationic Iron(II) Complexes of the Mixed Cyclopentadienyl (Cp) and the Nheterocyclic Carbene (NHC) Ligands as Effective Precatalysts for the Hydrosilylation of Carbonyl Compounds

Dharmendra Kumar,^a A. P. Prakasham,^a Linus Paulin Bheeter,^b Jean-Baptiste Sortais,^b Manoj Gangwar,^a Thierry Roisnel,^c Alok Kalita,^a Christophe Darcel^{*b} and Prasenjit Ghosh^{*a}

Research Highlights

Three new {Cp[1,3-*di*-R-benzimidazol-2-ylidene]-Fe(CO)₂}I complexes were prepared Two new {Cp[1-benzyl-3-R-imidazol-2-ylidene]Fe(CO)₂}PF₆ complexes were synthesized Full structural characterizations including X-ray of these 5 complexes were done. Evaluation of their activities was performed in hydrosilylation of carbonyl compounds Benzimidazole based complexes displayed superior activity than the imidazole ones

Supplementary Material Available

Cationic Iron(II) Complexes of the Mixed Cyclopentadienyl (Cp) and the N-heterocyclic Carbene (NHC) Ligands as Effective Precatalysts for the Hydrosilylation of Carbonyl Compounds

Dharmendra Kumar,^a A. P. Prakasham,^a Linus Paulin Bheeter,^b Jean-Baptiste Sortais,^b Manoj Gangwar,^a Thierry Roisnel,^c Alok Kalita,^a Christophe Darcel^{*,b} and Prasenjit Ghosh^{*,a}

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Figure S2. Expanded ¹H NMR spectrum of 1b in CDCl₃.



Figure S3. ¹³C{¹H} NMR spectrum of 1b in CDCl₃.



Figure S4. IR spectrum of 1b in KBr pellet.



rdb e Conf mSigma #Sigma Score N-Rule err [ppm] Meas. m/z # Ion Formula m/z -0.7 7.8 100.00 10.5 even ok 351.0793 1 C18H19FeN2O2 351.0791 1

Figure S5. High resolution mass spectrum of 1b.

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Method File : D:	\CHNS2012\SP	-150713.m	th			
Chromatogram : PG	-DK-2-26-2					
Operator ID : MN	RAO		Company Na	me :	C.E. Instru	ments
Analysed : 07	/15/2013 14	:03	Printed	:	7/15/2013	18:02
Sample ID : PG	-DK-2-26-2 (# 15) 🔅	Instrument 1	N. :	Instrument	#1
Analysis Type : Un	kNown (Area)		Sample weig	ht :	1.368	
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Element Name	8	Ret.Time	Area	BC	Area ratio	K factor
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Carbon	44.5217	66	1642871	RS	1.000000	.269224E+07
Hydrogen	4.3941	178	437881	RS	3.751866	.686357E+07
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Totals	01.0002					



Figure S7. ¹H NMR spectrum of **2b** in CDCl₃.



Figure S8. Expanded ¹H NMR spectrum of 2b in CDCl₃.







Figure S10. IR spectrum of 2b in KBr pellet.

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- 48089 m/	600 n #1-16, 100%*	500 +M5, 0.0-0.3m	400	323.1203 300	203.1548 200	(2b)	4 3 2 1 0 10 10 10
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Figure S11. High resolution mass spectrum of 2b.

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Figure S12. Elemental analysis data of **2b**.



Figure S13. ¹H NMR spectrum of **3b** in CDCl₃..



Figure S14. Expanded ¹H NMR spectrum of **3b** in CDCl₃.





Figure S16. IR spectrum of 3b in KBr pellet.



Figure S17. High resolution mass spectrum of 3b.



Figure S18. Elemental analysis of compound 3b.





















Figure S25. High resolution mass spectrum of 4b.



Figure S26. Elemental analysis data of 4b.













	Ir	idian Institute o	f Technol	ogy (B)			11
Analysis Info Analysis Name Method Sample Name Comment	D:\Data\MAR-13\P Tune_pos_Standar PG-APP-2-169-2 C19H19N2FeO2	G-APP-2-169-2 .d d_NAi-1000.m		Acquisition Date Operator Instrument	3/6/201 IIT-B maXis imp	3 11:47:08 A dct 282001.	M 00081
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Meas. m/z # Ion Formula m/z err [ppm] mSigma Score rdb e Conf N-Rule 363.0796 1 C19H19FeN2O2 363.0791 -1.4 24.4 1 100.00 11.5 even ok

Figure S32. High resolution mass spectrum of 5b.



Figure S33. Elemental analysis data of 5b.