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Synthesis of new iron–NHC complexes as catalysts for hydrosilylation reactions

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A series of new piano-stool iron(II) complexes comprising *N*-heterocyclic carbene ligands [Fe(Cp)(CO)$_2$(NHC)]I (NHC = 1,3-disubstituted imidazolidin-2-ylidene) have been synthesized and analyzed by ^{1}H NMR, ^{13}C NMR, IR, elemental analysis and mass spectrometric techniques. These compounds were easily prepared from the reaction of disubstituted imidazolidin-2-ylidene with [FeI(Cp)(CO)$_2$] in toluene at room temperature. These complexes were tested in the catalytic hydrosilylation reaction of aldehydes and ketones with phenylsilane in solvent-free conditions. After a basic hydrolysis step, the corresponding alcohols were obtained in good yields. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: iron; NHC ligands; hydrosilylation; aldehydes; ketones

Introduction

The development and application of efficient, convenient, selective and environmentally friendly synthetic methods are highly desirable in organic chemisrty. In light of this, transition-metal-catalyzed processes have been developed in the synthesis of organic compounds. In the last few decades, late transition metal catalysts based on Pd, Ru, Rh, Ir, Au and Pt have exhibited powerful catalytic ability.[1–6] However, the limited availability of these metals as well as their high price and significant toxicity make it more desirable to search for more economical and environmentally friendly alternatives. The application of inexpensive, non-toxic, commercially available and environmentally friendly iron complexes as catalysts in chemical synthesis has attracted much attention.[7] To date, the use of iron is becoming a highly attractive and challenging area of research, with special significance focused on homogeneous catalysis, and various organic transformations catalysed by iron have been achieved, including C-C cross-coupling reactions,[8] substitutions,[9] reductions,[10] oxidations,[11] C-H functionalizations,[12] cycloadditions[13] as well as polymerization.[14] Ligands also play a pivotal role in the modulation of the metal center reactivity. During the past decade, *N*-heterocyclic carbenes (NHCs) have received increasing attention as alternative ligands for the development of homogeneous catalyst based on last transition metals.[15] A large number of well-defined NHC complexes of Pd, Ru, Rh and Ir have been found to show outstanding catalytic activity for cross-coupling reactions and related transformations. As a result, iron complexes containing NHC ligands have been prepared and characterized[16]; however, they are seldom used in catalysis.[17] The first use of NHCs in homogeneous iron catalysis was reported by Grubbs and co-workers in 2000 in atom transfer radical polymerization of styrene and methyl methacrylate using well-defined [(NHC)$_2$FeX$_2$] complexes as catalysts.[18] To date, only a few kinds of well-defined iron NHC complexes have been reported, which include hexacarbene,[19] tetracarbene,[20] tricarbene,[21] biscarbene[16,18,22] and piano-stool monocarbene complexes that are co-ligated with cyclopentadienyl and CO ligands.[23] Piano-stool Fe(II) complexes of the type [CpFe(CO)$_2$(NHC)]X[23,24] and pincer Fe(II)/Fe(III) complexes of Fe(2,6-bis(NHC)pyridine)X$_n$ (n = 2 or 3)[20] were reported by Siebert, Guerchais and Gibson *et al*., respectively.

On the another hand, the catalytic reduction of carbonyl compounds is most frequently performed using hydrogenation with molecular hydrogen, or via transfer hydrogenation in isopropanol or formic acid.[25] An interesting alternative to these methods for mild and selective reduction is the use of the combined catalytic hydrosilylation/hydrolysis protocol.[26] Indeed, Brunner first reported the iron-catalyzed hydrosilylation of carbonyl compounds in the early 1990s.[27] After the renewal of this research area by Beller[28] and Nishiyama[29] in 2007, hydrosilylation using iron as the catalyst is now well exemplified for the hydrosilylation of aldehydes and ketones.[30] Interestingly, well-defined NHC–iron complexes such as tethered (Cp-NHC)FeCl[31] are also efficient catalysts for hydrosilylation of activated aldehydes. Furthermore, cationic and neutral piano-stool complexes [Cp(IMes)Fe(CO)$_2$][I] and [Cp(IMes)Fe(CO)(I)], respectively, are efficient catalysts not only for aldehydes and ketones[32] hydrosilylations, but also for imines[33] and amides.[34] When generated *in situ* from iron salts and NHC ligands, the resulting catalysts are also able to promote the reduction of aldehydes, ketones and amides.[35] Based on these studies, which demonstrate that iron complexes with NHC ligands play a beneficial role in hydrosilylation catalysis, we report herein the preparation of cationic piano-stool iron(II) complexes containing saturated imidazolidin-2-ylidene NHC ligands and

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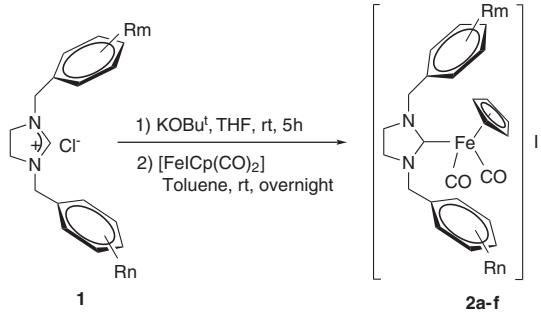
their use in reduction of aldehydes and ketones by hydrosilylation/hydrolysis reaction.

Results and Discussion

Synthesis of NHC–Iron(II) Complexes

Iron–NHC complexes are generally prepared via free carbenes (generated from deprotonation of imidazolium salts by a strong base)[18,20,36] or by using iron amides.[22,37] Recently, Chen and colleages have have elucidated new approaches to Fe–NHC complexes: (i) the electrochemical synthesis using imidazolium salts and metal plates[38] and (ii) direct reaction of metal powders with imidazolium salts or silver–NHC complexes.[39] Another synthetic route is also template-controlled formation of iron complex as described by Hahn.[40]

In this work, we have chosen the free carbene reaction methodology to synthesize the iron complexes. According to the procedure described by Guerchais,[23] we have prepared cationic NHC–Fe complexes with iodide as the counterion. The deprotonation of the imidazolidinium salts **1** with KOBu^t as a base took place at room temperature for 5 h, leading to the corresponding carbene, which was metalated *in situ* with [FeI(Cp)(CO)$_2$] as iron(II) precursor in toluene at room temperature overnight in the dark (Scheme 1 and Fig. 1). Complexes **2a–f** were then obtained in 51–67% isolated yields. All the new complexes were characterized by spectral data (IR, NMR spectroscopy, mass spectral data and elemental analysis). The characterization data of the new compounds are consistent with the assigned formula.



Scheme 1. Preparation of NHC–iron complexes (**2a-f**).

Notably, the mass spectra showed a peak which can be assigned to the cation [CpFe(NHC)(CO)$_2$]$^+$, which confirmed the proposed structures and the coordination of the NHC ligand to the iron center. Moreover, the IR spectra clearly indicate that the expected two CO ligands are coordinated to the metal centre which can be observed as two peaks for CO stretching mode in the IR spectrum of all complexes ($\nu_{s(CO)}$ = 2026–2036 and $\nu_{as(CO)}$ = 1964–1987 cm^{-1}). These values are in good agreement with previously reported values for piano-stool iron complexes bearing an NHC ligand.[23] Interestingly, CO vibrations in such monocarbene complexes are slightly lower than those described for the similar SIMes imidazolin-2-ylidene iron complex [CpFe(CO)$_2$(SIMes)][I] ($\nu_{s(CO)}$ = 2043 and $\nu_{as(CO)}$ = 2005 cm^{-1}), illustrating that the benzyl-substituted imidazolin-2-ylidene ligands **1a–f** are stronger donating carbenes than aryl-substituted ones such as SIMes. ^{13}C NMR spectra indicated that the resonance characteristics of the carbene were located at δ 199.3, 199.6, 199.7, 199.4, 199.3 and 199.7 ppm for **2a–f**, respectively. Carbonyl signals were observed at δ 211.5, 211.4, 211.4, 211.5, 211.9 and 211.6 pm for **2a–2f**, respectively. During the time that the cationic complexes were stirred in dichlorometane at room temperature under visible light irradiation, no neutral complex were obtained, which contrasts with the results obtained with IMes or SIMes NHC iron complexes but showed the bulkier character of the present NHC.[32]

Catalytic Hydrosilylation of Aldehydes and Ketones

The catalytic activities of the new [Fe(Cp)(CO)$_2$(NHC)]I cationic complexes **2a–f** have been studied for the hydrosilylation reaction of aldehydes and ketones (Scheme 2).

Optimization of the hydrosilylation reaction was carried out with benzadehyde and acetophenone as model carbonyl compounds. Using complex **2a** as the model catalyst (1 mol%), we first surveyed different silanes as hydride sources (1.2 equiv.)

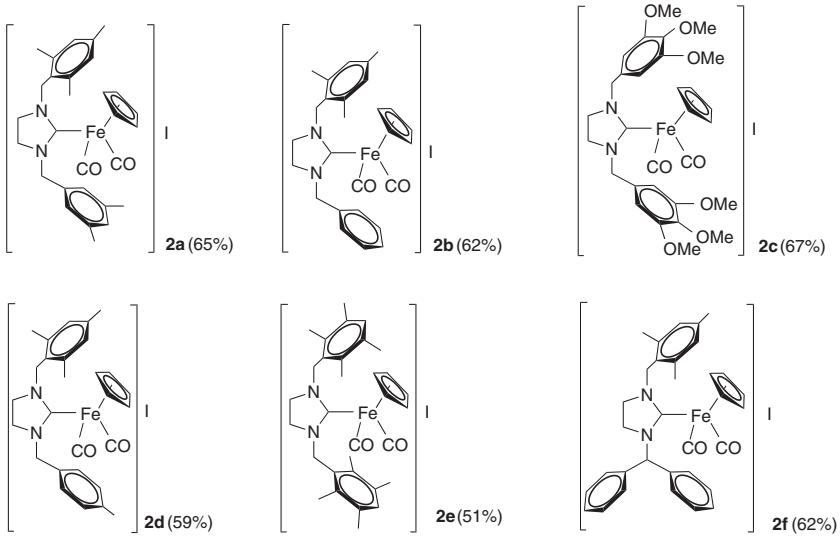
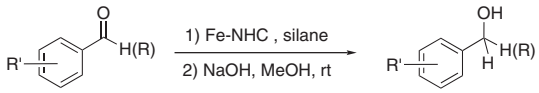


Figure 1. Cationic iron piano-stool cyclopentadienyl complexes bearing saturated NHC carbene ligands (in parentheses: isolated yields).



Scheme 2. Fe–NHC-catalyzed hydrosilylation reaction.

and found that phenylsilane exhibited the best activity as full conversion of benzaldehyde was observed after 1 h of reaction at 100°C in neat conditions (Table 1, entry 4). Interestingly, a low loading of 0.5 mol% **2a** was also permitted to reached full conversion under similar conditions (Table 1, entry 5). The reaction was then performed with various silanes, including polymethylhydrosiloxane and tetramethyldisiloxane, and only phenylsilane was able to obtain good conversions. (Table 1, entries 1–4). Notably, the catalytic activity of the cationic complex **2a** was examined in toluene, THF and without solvent, and only solvent-free conditions were able to obtain good conversions.

Encouraged by the efficiency of the hydrosilylation of benzaldehyde with complex **2a** (1 mol%) (1.2 equiv. phenylsilane, neat condition, 100°C, 1 h), we then investigated the activities of different NHC–iron catalysts **2b–f** bearing different NHC ligands and the scope of the reaction under these optimized conditions (Table 2).

Evaluation of the activity of complexes **2b–f** was used as the catalyst (1 mol%) at 100°C under solvent-free conditions; using 1.2 equiv. phenylsilane revealed that the best catalyst of the series was complex **2a**, which was able to obtain 94% conversion in 1 h, whereas all the other complexes reached a maximum of 90% (range 80–90% conversion).

Using 1 mol% of complex **2a** as the catalyst and 1.2 equiv. phenylsilane under neat conditions, various methoxy-substituted benzaldehyde derivatives were efficiently reduced under the optimized conditions (conversion 85–98% at 100°C in 5 min to 1 h). Notably, with 2,5-dimethoxybenzaldehyde, a very short reaction time (5 min) was necessary to reach full conversion. In this case, complexes **2b**, **2c** and **2e** also gave quite full conversions (>96%) in only 5 min of reaction at 100°C. 4-*tert*-Butylbenzaldehyde was converted into 4-*tert*-butylbenzyl alcohol in only 30 min of reaction at 100 °C, complexes **2a** and **2b** being the most effective catalysts.

The reduction of ketones such as acetophenone and 4-bromoacetophenone can also be achieved by hydrosilylation using such complexes as catalysts, but a longer reaction time (4 h) was necessary at 100°C to obtain the corresponding secondary alcohols. Notably, catalyst **2a** once again showed the best activity.

Of notable interest, and incontrast to the previous results reported with simple IMes NHC ligands,[32] using this type of benzyl-substituted imidazolidin-2-ylidene NHC–iron complexes, no visible light activation was necessary to peform the reduction reaction.

Experimental

General Procedures

All synthesis were carried out under an inert atmosphere using Schlenk line techniques. Chemicals and solvents were acquired from Sigma Aldrich Co. (Poole, UK). Imidazolidinium salts were

Table 1. Optimization for the hydrosilylation of benzaldehyde and acetophenone with the catalyst **2a**[a]

Entry		**2a** (mol%)	Silane	Time (h)	Temp. (°C)	Conv. (%)[b]
1	Benzaldehyde	1	Ph_3SiH	6	100	—
2		1	Ph_2SiH_2	6	100	—
3		1	$(MeO)_2PhSiH$	6	100	—
4		1	$PhSiH_3$	1	100	>97
5		0.5	$PhSiH_3$	1	100	>97
6	Acetophenone	1	$PhSiH_3$	24	50	66
7		1	$PhSiH_3$	4	100	86

[a]Reaction conditions: (i) benzaldehyde or acetophenone (1.0 mmol), silane (1.2 mmol), Fe–NHC complex (1.0 mol%) under neat conditions; (ii) MeOH (1 ml), then NaOH (2M, 10 ml), room temperature, 1 h.
[b]Conversion determined by GC after methanolysis.

Table 2. Hydrosilylation of carbonyl compounds by iron catalysts **2a–f**[a]

Carbonyl compound	Yield (%)[b]					
	2a	2b	2c	2d	2e	2f
C_6H_5-CHO	94 (1 h)	85 (1 h)	80 (1 h)	80 (1 h)	89 (1 h)	90 (1 h)
p-MeO-C_6H_4-CHO	85 (1 h)	88 (1 h)	71 (1 h)	70 (1 h)	79 (1 h)	72 (1 h)
2,5-$(OMe)_2$-C_6H_3-CHO	> 8 (5 min)	98 (5 min)	97 (5 min)	75 (5 min)	96 (5 min)	78 (5 min)
3,4,5-$(OMe)_3$-C_6H_2-CHO	>98 (30 min)	90 (30 min)	>98 (30 min)	81 (30 min)	98 (30 min)	>98 (30′)
p-$(CH_3)_3C$-C_6H_4-CHO	98 (30 min)	>98 (30 min)	86 (30 min)	96 (30 min)	95 (30 min)	93 (30′)
C_6H_5-$COCH_3$	86 (4 h)	75 (4 h)	65 (4 h)	81 (4 h)	71 (4 h)	68 (4 h)
p-Br-C_6H_4-$COCH_3$	96 (2 h)	89 (2 h)	73 (2 h)	87 (2 h)	71 (2 h)	84 (2 h)

[a]Reaction conditions: (i) aldehyde or ketone (1.0 mmol), phenylsilane (1.2 mmol), Fe–NHC complex (1.0 mol%) in neat conditions at 100°C; (ii) MeOH (1 ml) then NaOH (2 M, 10 ml), room temperature, 1 h.
[b]Yield determined by GC after methanolysis. In parentheses: time of reaction.

synthesized in our laboratory according to the literature.[41] Solvents were dried with standard methods and freshly distilled prior to use. Elemental analyses were performed by LECO CHNS-932 elemental analyzer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a PerkinElmer Spectrum 100. ^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (J values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. HR mass spectra and elemental analysis were recorded on a Bruker MicrO-Tof-Q 2 spectrometer at the CRMPO (Centre Régional de Mesure Physiques de l'Ouest), University of Rennes 1. All catalytic reactions were monitored on a Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70-230 mesh). Solvent ratios are given as v/v.

General Experimental Procedure for the Preparation of the Iron–NHC Complexes

A mixture of freshly sublimed KO^{t}Bu and the NHC precursor in THF was stirred at room temperature for 5 h. After evaporation of the solvent, toluene was added in the Schlenk tube and the solution was subsequently filtered. [CpFe(CO)$_2$I] complex was then added to the bright light-yellow solution at room temperature. The Schlenk tube was wrapped with aluminium foil and the solution was stirred overnight at room temperature. The solvent was removed under vacuum and the crude product washed several times diethyl ether to remove starting iron complex.

Dicarbonyl-[1-(2,4,6-trimethylbenzyl)-3-(3,5-dimethylbenzyl)imidazolin-2-ylidene] cyclopentadienyliron(II) iodide, ***2a***

0.40 g; yield 65%; m.p.: decomposition temperature 190°C. IR (KBr, cm^{-1}): $\nu_{(CN)}$ = 1498, $\nu_{(CO)}$ = 2036 and 1985. ^1H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 2.32 (s, 6H, $CH_2C_6H_3(CH_3)_2$-3,5); 2.44 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 3.68–3.35 (m, 4H, NCH_2CH_2N); 4.84 (s, 2H, $CH_2C_6H_3(CH_3)_2$-3,5); 5.00 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 5.67 (s, 5H, Cp); 6.90 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_3(CH_3)_2$-3,5); 6.95 (s, 1H, $CH_2C_6H_3(CH_3)_2$-3,5).$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 20.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 21.3 ($CH_2C_6H_3(CH_3)_2$-3,5); 49.5 and 49.2 (NCH_2CH_2N); 50.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 56.1 ($CH_2C_6H_3(CH_3)_2$-3,5); 87.7 (Cp); 125.3, 127.2, 129.7, 129.8, 134.4, 137.9 and 138.6 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_3(CH_3)_2$-3,5); 199.3 (Fe-$C_{carbene}$); 211.5 (CO). HR-MS: *m/z* 497.1893 [M+] calculated for $C_{29}H_{33}N_2O_2Fe$ 497.1892. Anal. Calcd for $C_{29}H_{33}N_2O_2FeI$: C, 55.79; H, 5.33; N, 4.49; Found: C, 55.73; H, 5.38; N, 4.45%.

Dicarbonyl-[1-(2,4,6-trimethylbenzyl)-3-(benzyl)imidazolin-2-ylidene] cyclopentadienyl iron(II) iodide, ***2b***

0.37 g; yield 62%. m.p.: decomposition temperature 120°C. IR (KBr, cm^{-1}): $\nu_{(CN)}$ = 1593, $\nu_{(CO)}$ = 2034 and 1987. ^1H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 2.43 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 3.66–3.34 (m, 4H, NCH_2CH_2N); 4.84 (s, 2H, $CH_2C_6H_5$); 5.10 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 5.68 (s, 5H, Cp); 6.90 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 7.33–7.37 (m, 5H, $CH_2C_6H_5$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 20.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 49.6 and 49.3 (NCH_2CH_2N); 50.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 56.2 ($CH_2C_6H_5$); 87.8 (Cp); 127.2, 127.5, 128.2, 129.0, 129.7, 134.6, 137.9 and 138.7 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_5$); 199.6 (Fe-$C_{carbene}$); 211.4 (CO). HR-MS: *m/z* 469.1579 [M+] calculated for $C_{27}H_{29}N_2O_2Fe$ 469.1578. Anal. Calcd for $C_{27}H_{29}N_2O_2FeI$: C, 54.39; H, 4.90; N, 4.70, Found: C, 54.35; H, 4.92; N, 4.66%.

Dicarbonyl-[1,3-bis(3,4,5-trimethoxybenzyl)imidazolin-2-ylidene]cyclopentadienyl iron(II) iodide, ***2c***

0.49 g; yield 67%; m.p.: decomposition temperature 230°C. IR (KBr, cm^{-1}): $\nu_{(CN)}$ = 1590, $\nu_{(CO)}$ = 2026 and 1977. ^1H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 18H, $CH_2C_6H_2(OCH_3)_2$-3,4,5); 3.91 (s, 4H, NCH_2CH_2N); 4.97 (s, 4H, $CH_2C_6H_2(OCH_3)_2$-3,4,5); 5.64 (s, 5H, Cp); 6.58 (s, 4H, $CH_2C_6H_2(OCH_3)_2$-3,4,5). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 50.2 (NCH_2CH_2N); 56.8 ($CH_2C_6H_2(OCH_3)_2$-3,4,5); 60.9 ($CH_2C_6H_2(OCH_3)_2$-3,4,5); 87.9 (Cp); 104.9, 129.8, 138.1 and 153.8 ($CH_2C_6H_2(OCH_3)_2$-3,4,5); 199.7 (Fe-$C_{carbene}$); 211.4 (CO). HR-MS: *m/z* 607.1718 [M+] calculated for $C_{30}H_{35}N_2O_8Fe$ 607.1719. Anal. Calcd for $C_{30}H_{35}N_2O_8FeI$: C, 49.07; H, 4.80; N, 3.81, Found: C, 49.05; H, 4.78; N, 3.87%.

Dicarbonyl-[1-(2,4,6-trimethylbenzyl)-3-(4-methylbenzyl)imidazolin-2-ylidene] cyclopentadienyliron(II) iodide, ***2d***

0.36 g; yield 59%; m.p.: decomposition temperature 170°C, IR (KBr, cm^{-1}): $\nu_{(CN)}$ = 1493, $\nu_{(CO)}$ = 2034 and 1982. ^1H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 2.35 (s, 3H, $CH_2C_6H_4(CH_3)$-4); 2.43 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 3.66-3.33 (m, 4H, NCH_2CH_2N); 4.83 (s, 2H, $CH_2C_6H_4(CH_3)$-4); 5.05 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 5.67 (s, 5H, Cp); 6.90 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 7.19 (s, 4H, $CH_2C_6H_4(CH_3)$-4). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 20.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 21.1 ($CH_2C_6H_4(CH_3)$-4); 49.5 and 49.2 (NCH_2CH_2N); 50.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 55.9 ($CH_2C_6H_4(CH_3)$-4); 87.8 (Cp); 127.2, 127.5, 129.6, 129.7, 129.8, 131.4, 137.9 and 138.6 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_4(CH_3)$-4); 199.4 (Fe-C_{cabene}); 211.5 (CO). HR-MS: m/z 483.1734 [M+] calculated for $C_{28}H_{31}N_2O_2Fe$ 483.1735. Anal. Calcd for $C_{28}H_{31}N_2O_2FeI$: C, 55.10; H, 5.12; N, 4.59, Found: C, 55.13; H, 5.17; N, 4.56%.

Dicarbonyl-[1,3-bis(2,3,5,6-tetramethylbenzyl)imidazolin-2-ylidene] cyclopentadienyl iron(II) iodide, ***2e***

0.34 g; yield: 51%; m.p.: decomposition temperature 200°C. IR (KBr, cm^{-1}): $\nu_{(CN)}$ = 1426, $\nu_{(CO)}$ = 2036 and 1968. ^1H NMR (300 MHz, $CDCl_3$): δ 2.25, (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 2.33 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 3.28 (s, 4H, NCH_2CH_2N); 4.91 (s, 4H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 5.76 (s, 5H, Cp); 6.99 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 16.7($CH_2C_6H(CH_3)_4$-2,3,5,6), 20.5 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 48.7 (NCH_2CH_2N); 50.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 87.7 (Cp); 130.2, 132.4, 134.1, and 134.4 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 199.3 (Fe-C_{cabene}); 211.9 (CO). HR-MS: *m/z* 539.2357 [M+] calculated for $C_{32}H_{39}N_2O_2Fe$ 539.2361. Anal. Calcd for $C_{32}H_{39}N_2O_2FeI$: C, 57.67; H,5.90; N, 4.20, Found: C, 57.65; H, 5.92; N, 4.17%.

Dicarbonyl-[1-(2,4,6-trimethylbenzyl)-3-(benzhydryl)imidazolin-2-ylidene] cyclopenta dienyliron(II) iodide, ***2f***

0.42 g; yield: 62%; m.p.: decomposition temperature 220°C. IR (KBr, cm^{-1}): $\nu_{(CN)}$ = 1417, $\nu_{(CO)}$ = 2036 and 1964. ^1H NMR (300 MHz, $CDCl_3$): δ 2.28, (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 2.45 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 3.51–3.37 (m, 4H, NCH_2CH_2N); 5.05 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 5.44 (s, 5H, Cp); 6.89 (s, 2H, $CH_2C_6H_2$

$(CH_3)_3$-2,4,6); 6.82 (s 1H, $CH(C_6H_5)_2$); 7.29-7.43 (m, 10H, $CH(C_6H_5)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 20.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 20.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 49.1 (NCH_2CH_2N); 51.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 67.1 ($CH(C_6H_5)_2$); 87.6 (Cp); 127.3, 128.5, 128.6, 129.1, 129.4, 129.8, 137.8 and 138.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH(C_6H_5)_2$); 199.7 (Fe-C_{cabene}); 211.6 (CO). HR-MS: *m/z* 545.1928 [M+] calculated for $C_{33}H_{33}N_2O_2Fe$ 545.1931. Anal. Calcd for $C_{33}H_{33}N_2O_2FeI$: C, 58.95; H, 4.95; N, 4.17, Found: C, 58.91; H, 4.97; N, 4.21%.

General Procedure for the Hydrosilylation of Carbonyl Compound-Catalyzed Fe-NHC

Under a nitrogen atmosphere, carbonyl compound (1.0 mmol), silane (1.2 mmol) and Fe-NHC complex (1.0 mol%) were added in an oven-dried Schlenk tube. The reaction was stirred at 100°C for 5 min to 4 h. The reaction mixture was then cooled to room temperature and MeOH (1 ml) was added, followed by aqueous NaOH (2 M, 10 ml). The resulting mixture was stirred for 1 h and subsequently extracted with diethyl ether (2 × 10 ml). The combined organic layer was dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The conversion was determined by GC and NMR spectroscopy and compared to the corresponding known substances. The NMR result of the products was identical to data published literature.[42]

Conclusions

A novel series of cationic piano-stool iron complexes bearing benzyl-substituted imidazolidin-2-ylidene NHC ligand was synthesized from *in situ* generated carbene ligand and $[CpFe(CO)_2I]$ iron precursor, and characterized by NMR, IR, high-resolution mass spectrometry and elemental analysis. The catalytic activity of the new complexes was evaluated in the hydrosilylation of aldehydes and ketones, which proceeded in a short reaction time (up to 5 min at 100°C). Further investigation into the activity of *in situ* NHC/iron salt catalytic system is currently underway in our laboratory.

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