ORGANOMETALLICS
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Direct Synthesis of Iron(0) N-Heterocyclic Carbene Complexes by Using $Fe_3(CO)_{12}$ and Their Application in Reduction of Carbonyl Groups

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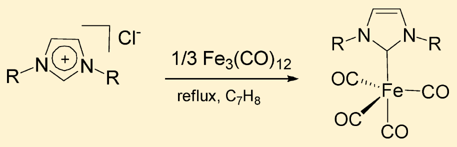
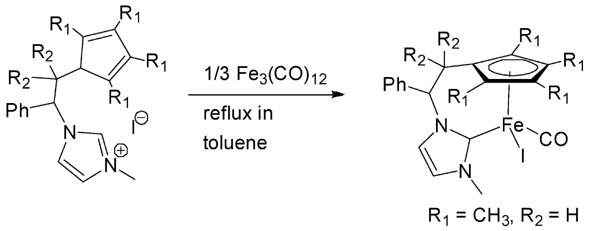
Ⓢ *Supporting Information*

ABSTRACT: Iron $Fe(NHC)(CO)_4$ complexes were formed by direct reaction of $Fe_3(CO)_{12}$ with equimolecular amounts of NHC imidazolium halide precursors; addition of base was not needed in this reaction. When excess (9:1 ratio) 1,3-dimesitylimidazolium chloride is reacted with the iron cluster $Fe_3(CO)_{12}$, a mixture of $Fe(IMes)(CO)_4$ and $Fe(IMes)_2(CO)_3$ is obtained. Single crystals of $Fe(IMes)(CO)_4$ and crystals resulting from the cocrystallization of $Fe(IMes)(CO)_4$ and $Fe(IMes)_2(CO)_3$ have been studied by X-ray diffraction. These iron(0) complexes were found to catalyze the reduction of benzaldehydes.



N-Heterocyclic carbene (NHC) ligands have gained enormous popularity in organometallic chemistry for their strong σ-donating characteristics and ability to bind and stabilize a range of transition-metal complexes.[1,2] In recent years, the use of N-heterocyclic carbenes in the chemistry of iron is attracting considerable attention due to the potential applications of Fe-NHC complexes in homogeneous catalysis[3−8] and biomimetic chemistry.[9] In general, iron-NHC complexes are prepared via free carbenes generated from deprotonation of imidazolium salts by a strong base[7,10] or by metalation reactions where the imidazolium salt is deprotonated by the basic amide $Fe[(N(SiMe_3)_2]_2$.[11] Recently, we disclosed the unprecedented synthesis of bidentate cyclopentadienyl-functionalized NHC iron(II) complexes by direct reaction of the corresponding imidazolium proligands with commercially available $Fe_3(CO)_{12}$ (Scheme 1).[12] This synthetic approach precludes the requirement for strong bases previously employed in the synthesis of these half-sandwich iron carbonyl complexes.[13] The formation of (Cp-NHC)Fe(CO)I complexes implies the C−H activation of the C−H bond of imidazolium to Fe(0) and constitutes a rare example of Fe-NHC complexes prepared by direct reaction of the corresponding imidazolium salts.[14]

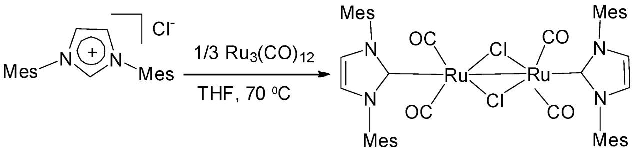
Scheme 1. Synthesis of Iron Complexes Containing Cyclopentadienyl-Functionalized NHCs



$R_1 = CH_3$, $R_2 = H$
$R_1 = H$, $R_2 = Ph$

Encouraged by these results, we became interested in exploring the reactivity of NHCs and their imidazolium precursors with $Fe_3(CO)_{12}$. The reactivity of the related ruthenium carbonyl cluster $Ru_3(CO)_{12}$ with NHCs has been recently investigated by the research groups of Cabeza,[15] Whittlesey,[16,17] Cole,[18] and Wang.[19] They described the successful C−H activation of NHCs at N-alkyl and heterocyclic C−H positions when coordinated to triruthenium undecacarbonyl complexes $Ru_3(NHC)(CO)_{11}$, which are prepared by reaction of the corresponding NHCs with $Ru_3(CO)_{12}$ in 1:1 mol ratio. When the reaction of $Ru_3(CO)_{12}$ is carried out with an excess of NHC, the cluster cleavage products $Ru(NHC)_2(CO)_3$[17] and $Ru(NHC)(CO)_4$[18] are isolated. In 2008, Cole and co-workers described the uncommon C−H activation of 1,3-dimesitylimidazolium chloride (IMes·HCl) by $Ru_3(CO)_{12}$.[18] Equimolecular reaction of the NHC precursor IMes·HCl with $Ru_3(CO)_{12}$ affords the dinuclear $Ru_2(\mu\text{-}Cl)_2(IMes)_2(CO)_4$ complex (Scheme 2), which represents an unusual example of a ruthenium−ruthenium-bonded Ru(I) dimer. Intrigued by the former reaction and taking into account our findings on the C−H activation of imidazolium proligands by $Fe_3(CO)_{12}$, we decided to investigate the reactivity of $Fe_3(CO)_{12}$ with simple monodentate imidazolium salts.

Scheme 2. Reaction of an NHC Precursor with $Ru_3(CO)_{12}$ Reported by Cole[18]



Received: December 14, 2012
Published: January 29, 2013

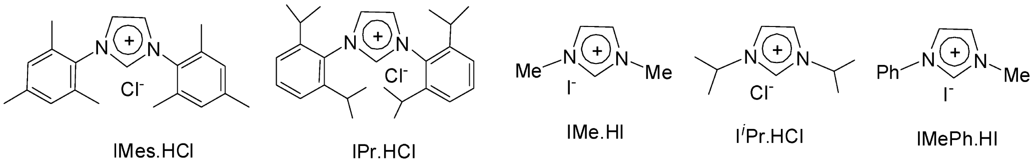
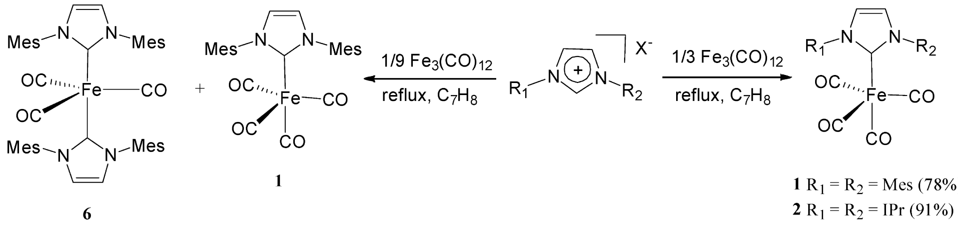


Figure 1. NHC Precursors Studied in this Work.

Scheme 3. Reaction of NHC Precursors with $Fe_3(CO)_{12}$



1 $R_1 = R_2$ = Mes (78%)
2 $R_1 = R_2$ = IPr (91%)
3 $R_1 = R_2$ = Me (30%)
4 $R_1 = R_2$ = ^{i}Pr (30%)
5 R_1 = Me, R_2 = Ph (45%)

Here we describe the reactivity of $Fe_3(CO)_{12}$ with a variety of NHC precursors, NHC·HX (X = Cl, I) (Figure 1), which led to the formation of the mononuclear iron(0) carbonyl complexes $Fe(NHC)(CO)_4$ (**1**–**5**) and $Fe(IMes)_2(CO)_3$ (**6**) [NHC = 1,3-dimesitylimidazol-2-ylidene (IMes), **1**; 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), **2**; 1,3-dimethylimidazol-2-ylidene (IMe), **3**; 1,3-diisopropylimidazol-2-ylidene (I^{i}Pr), **4**; and 1-phenyl-3-methylimidazol-2-ylidene (IPhMe), **5**], and their catalytic application in the hydrosilylation of carbonyl groups. Remarkably, addition of base is not needed to generate the NHC ligands.

As shown in Scheme 3, the reaction of $Fe_3(CO)_{12}$ with 3 equiv of 1,3-dimesitylimidazolium chloride in toluene under reflux afforded the mononuclear tetracarbonyl complex $Fe(IMes)(CO)_4$ (**1**) in good yield (78%). Similar reaction of $Fe_3(CO)_{12}$ with 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride gave the corresponding complex $Fe(IPr)(CO)_4$ (**2**) in 91% yield. Iron tetracarbonyl complexes $Fe(NHC)(CO)_4$ containing 1,3-dialkyl-substituted imidazol-2-ylidenes could also be prepared by this route, although lower yields were obtained, $Fe(IMe)(CO)_4$ (**3**) in 30% and $Fe(I^iPr)(CO)_4$ (**4**) in 30%; the unsymmetrically substituted imidazolium salt 1-phenyl-3-methylimidazolium iodide reacted with $Fe_3(CO)_{12}$ (ratio 3:1) to give $Fe(CO)_4(IMePh)$ (**5**) in 45% yield. Along with the formation of $Fe(NHC)(CO)_4$ complexes, unidentified species were formed in these reactions. In all cases, a black residue insoluble in most common organic solvents (THF, acetonitrile, toluene, dichloromethane) was formed. The IR spectrum of the black residue did not display any carbonyl stretching absorptions. Further characterization attempts of the byproducts formed in the reaction were unsuccessful due to their insolubility. The HX (X = halide) lost during Fe-NHC formation might form some iron halide byproducts, although the high yields isolated when NHC·HCl (NHC = IMes and IPr) are reacted with $Fe_3(CO)_{12}$ do not suggest formation of large amounts of any iron halides. Further reactivity studies are carried out in our group in order to understand the mechanism operating in these reactions.

The iron complexes **1**–**5** were isolated as yellow crystalline powders and were fully characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscropy, and elemental analysis. The ^{13}C NMR spectra confirm that coordination of NHC has occurred. Signals ranging from 181 to 196 ppm, indicative of an $Fe-C_{carbene}$, are in the region of previously reported Fe-NHC complexes.[10,11] The IR spectra of complexes **1**–**5** show the characteristic strong carbonyl stretching absorptions (at 2035, 1949, and 1915 cm^{-1} for $Fe(IMes)(CO)_4$; see Experimental Section) consistent with trigonal bipyramidal $Ru(NHC)(CO)_4$[18] and $Fe(SIMe)(CO)_4$ (SIMe = 1,3-dimethylimidazolinylidene) complexes.[20] The structure of compound **1** was determined by X-ray diffraction methods. The molecular structure and selected bond lengths and angles are depicted in Figure 2. The molecule can be described as a distorted trigonal bipyramid, with the NHC ligand occupying an axial position. The $Fe-C_{carbene}$ distance of 1.992(2) Å is comparable to the value reported for the $Fe-C_{carbene}$ distance in $Fe(IMe)(CO)_4$, 2.007(5) Å.[21] The $C_{NHC}-Fe-C_{CO}$ angle with a value of 175.36(8)° presents a similar deviation to that observed in the molecular structure of $Ru(IMes)(CO)_4$ [176.5(2)°].[18] One of the O–C–Fe angles deviated from the linear disposition with a value of 170.82(16)°.

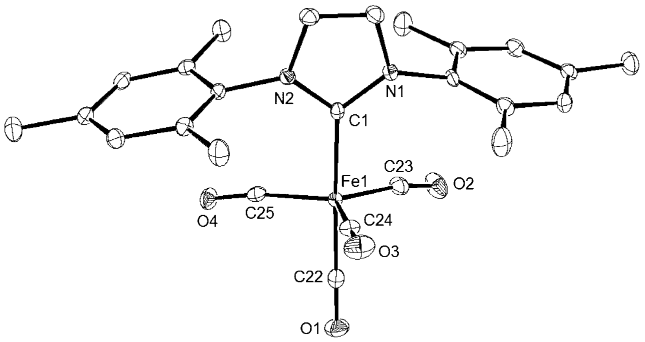


Figure 2. ORTEP of $Fe(IMes)(CO)_4$ (**1**). Ellipsoids are at 50% probability. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1–C1 1.992(2), Fe1–C22 1.783(2), Fe1–C23 1.7971(19), Fe1–C24 1.797(2), Fe1–C25 1.807(2), C22–O1 1.147(2), C23–O2 1.152(2), C24–O3 1.149(2), C25–O4 1.149(2), N1–C1 1.373(2), N2–C1 1.366(2), C24–Fe1–C23 119.01(9), C22–Fe–C25 86.34(9), C22–Fe1–C23 87.36(8), C23–Fe1–C25 120.30(9), C22–Fe–C1 175.36(8), C24–Fe1–C1 84.41(8), C23–Fe1–C1 95.68(8), C25–Fe–C1 95.10(8), N2–C1–N1 103.02(15).

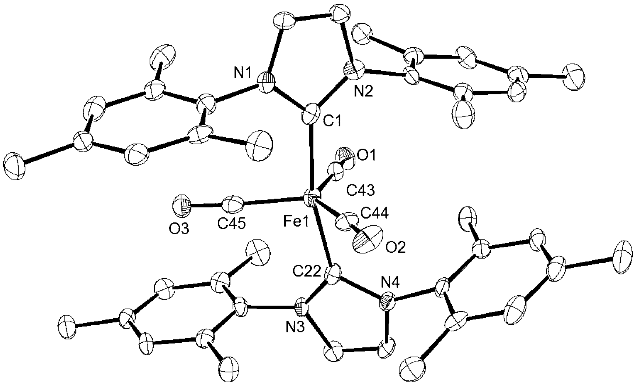
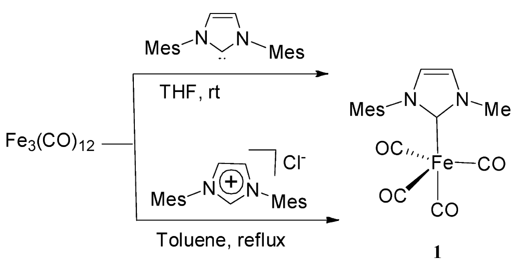


Figure 3. ORTEP of $Fe(IMes)_2(CO)_3$ (**6**). Ellipsoids are at 50% probability. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1−C1 1.982(4), Fe1−C22 1.976(4), Fe1−C43 1.758(5), Fe1−C44 1.775(5), Fe1−C45 1.781(5), C43−O1 1.173(5), C44−O2 1.163(5), C45−O3 1.151(5), C1−Fe1−C22 167.19(17), C45−Fe1−C44 116.1(2), C43−Fe1−C45 106.1(2), C43−Fe1−C44 137.7(2), C43−Fe−C1 91.68(19), C44−Fe1−C1 86.75(18), C45−Fe1−C1 95.07(18), N1−C1−Fe1 130.8(3), N2−C1−Fe1 127.6(3), N3−C22−Fe1 130.5(3), N4−C22−Fe1 127.6(3).

The 1:6 stoichiometric reaction of $Fe_3(CO)_{12}$ with IMes·HCl afforded a mixture of $Fe(IMes)(CO)_4$ (**1**) and $Fe(IMes)_2(CO)_3$ (**6**) in ca. 1:1 ratio. Due to the similar solubilities of complexes **1** and **6**, their separation proved difficult. A mixture of both complexes **1** and **6** was obtained even when a considerably larger excess of NHC precursor was reacted with $Fe_3(CO)_{12}$. From this mixture, a crystal that resulted from the cocrystallization of complexes **1** and **6** was isolated and studied by X-ray diffraction, confirming the identity of this species. Figure 3 shows the independent structure of **6**, with salient bond lengths and angles provided in the figure caption. The molecular structure consists of a distorted trigonal bipyramid with the NHC ligands located in a *trans*-axial arrangement [C_{NHC}−Fe−C_{NHC} angle of 167.9(17)°]. Similar *trans*-donor ligand disposition has been found in $Fe(CO)_3(PPh_3)_2$.[22] The bulk of the NHC ligands leads to discrepancy in the equatorial angles, one of which is considerably larger than the other two C_{CO}−Fe−C_{CO} angles, with a value of 137.7(2)°. The Fe−C−O angles deviated from a linear disposition, with angles ranging from 172.6(4)° to 176.5(4)°. The Fe−C_{NHC} distances of 1.976(4) and 1.982(4) Å are slightly shorter than the Fe−C_{NHC} distance found in complex **1**. As observed in the structures of $Ru(NHC)_2(CO)_3$ complexes,[17] the structure of **6** showed an NHC tilting,[23] which is reflected in the N−$C_{carbene}$−Fe angles [N1−C1−Fe1, 130.8(3)°; N2−C1−Fe1, 127.6(3)°; N3−C22−Fe1, 130.5(3)°; N4−C22−Fe1, 127.6(3)°].

We have also attempted the synthesis of an iron trinuclear NHC derivative analogous to [$Ru_3(NHC)(CO)_{11}$] with the idea of exploring the capability of iron in promoting C−H activation of NHCs at N-alkyl or aryl positions and resembling the reactivity of the ruthenium undecacarbonyl. In contrast to the reactivity described for the ruthenium cluster $Ru_3(CO)_{12}$, the reaction of 1 equiv of 1,3-dimethylimidazol-2-ylidene with $Fe_3(CO)_{12}$ in THF afforded $Fe(IMes)(CO)_4$ (**1**) as the only isolable product. A similar result is obtained when the reaction is carried out with 1 equiv of the imidazolium salt IMes·HCl (Scheme 4).

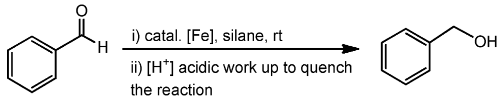
Scheme 4. Reaction of 1,3-Dimesitylimidazol-2-ylidene and Its Precursor with $Fe_3(CO)_{12}$



With these complexes in hand, we set out to examine their potential in the reduction of carbonyl groups. Recent works on iron chemistry have demonstrated the capability of this metal to efficiently catalyze the reduction of carbonyl groups.[24] However, reports on Fe-NHC complexes are relatively scarce. Recently, we[13] and others[4,5,8] have described iron(II) NHC complexes catalyzing the hydrogenation and hydrosilylation of carbonyl compounds. To the best of our knowledge, iron(0) NHC complexes have not been applied as catalysts in this catalytic reaction. Notice that reduction of amides and carboxamides has been successfully achieved using the iron carbonyl $Fe_3(CO)_{12}$.[25]

We examined the catalytic activity of complexes **1**−**4** in the reduction of benzaldehyde. The results are summarized in Table 1. The reduction of benzaldehyde with $PhSiH_3$ took place in the presence of a catalytic amount (2 mol %) of complex **1** at room temperature in THF (entry 1). The reaction also proceeded in NCMe, although longer reaction times (24 h, entry 2) were needed to achieve quantitative yields. Diphenylsilane can also be used as reducing agent in this catalytic reaction (entry 3), but $(EtO)_2MeSiH$ and $(EtO)_3SiH$ are not applicable. The amount of catalyst could be decreased to 1 mol % without decreasing the yield (entry 4); if decreased to 0.5 mol %, the yield of the isolated alcohol drops to 57% (entry 5). In order to explore the effect of the NHC in the performance of the catalyst, complexes **1**−**4** were applied in the reduction of benzaldehyde. As shown in Table 1, entries 4 and 6−8, the best catalysts are complexes **1** and **2**, containing the bulkier IMes and IPr ligands. To further investigate the scope

Table 1. Hydrosilylation of Benzaldehyde Catalyzed by $Fe(NHC)(CO)_4$ Complexes[a]

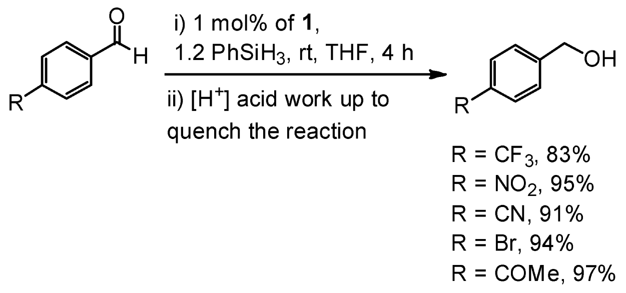


entry	cat(mol %)	silane	solv	*t* (h)	conv,[b] yield (%)[c]
1	$Fe(IMes)(CO)_4$ (2)	$PhSiH_3$	THF	4	>99 (94)
2	$Fe(IMes)(CO)_4$ (2)	$PhSiH_3$	NCMe	24	>99 (96)
3	$Fe(IMes)(CO)_4$ (2)	Ph_2SiH_2	THF	24	80 (77)
4	$Fe(IMes)(CO)_4$ (1)	$PhSiH_3$	THF	4	>99 (94)
5	$Fe(IMes)(CO)_4$ (0.5)	$PhSiH_3$	THF	4	60 (57)
6	$Fe(IPr)(CO)_4$ (1)	$PhSiH_3$	THF	4	90 (87)
7	$Fe(IMe)(CO)_4$ (1)	$PhSiH_3$	THF	4	45 (43)
8	$Fe(I^{i}Pr)(CO)_4$ (1)	$PhSiH_3$	THF	4	50 (48)

[a] All reactions were carried out with 1.0 equiv of aldehyde, 1.2 equiv of silane in the presence of the Fe-NHC catalysts at room temperature. [b] Yield determined by ^1H NMR spectroscopy. [c] Isolated yield after treatment with *p*-toluenesulfonic acid.

of the reaction, benzaldehyde substrates containing halo, cyano, nitro, and acyl functionalities were reduced, giving the corresponding alcohols in high yields (isolated yields 83−97%, Scheme 5). The ketone 3-(trifluoromethyl)acetophenone can also be reduced using **1** (2 mol %) as catalyst and $PhSiH_3$ as reducing agent, but heating to 70 °C is needed to achieve good conversion of the corresponding alcohol (78% yield in 4 h). The catalytic performance of **1** in the reduction of carbonyl groups compares well with those of reported Fe(II)-NHC catalysts.[4,5,8,13]

Scheme 5. Scope of the Reduction of Benzaldehyde Derivatives Catalyzed by Fe(IMes)(CO)$_4$



In conclusion, we have described here the reactivity of $Fe_3(CO)_{12}$ with NHCs and their precursors. We have proved that Fe(0) carbonyl complexes are capable of promoting C−H activation of simple monodentate imidazolium salts. We believe that the direct reaction of iron(0) with imidazolium salts can be a useful reaction for the preparation of Fe-NHC complexes, avoiding the use of strong bases such as KO^{t}Bu or BuLi generally required for the *in situ* generation of free NHCs. The iron(0) NHC carbonyl complexes prepared in this work catalyzed the reduction of benzaldehyde and acetophenone, giving high yields of the corresponding alcohols.

■ EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were carried out under dry, oxygen-free nitrogen standard Schlenk techniques, and solvents were purified from appropriate drying agents and distilled prior to use. The imidazolium salts NHC·HX (Figure 1) were prepared according to the published procedures.[26] All other reagents were purchased from commercial suppliers and used without further purification.

Synthesis of Fe(IMes)(CO)$_4$ (1). A mixture of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (0.20 g, 0.58 mmol) and $Fe_3(CO)_{12}$ (0.09 g, 0.19 mmol) in toluene (15 mL) was heated under reflux for 14 h. The suspension was filtered through Celite, and the filtrate was evaporated to dryness, yielding complex **1** as a crystalline yellow solid. Yield: 0.21 g (78%). Crystallization from THF−hexane leads to yellow crystals suitable for X-ray diffraction studies. ^{1}H NMR (400 MHz, C_6D_6): 6.78 (s, 4H, CH_{Ph}), 6.16 (s, 2H, CH_{Imid}), 2.11 (s, 6H, *Me*), 2.05 (s, 12H, *Me*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 217.0 (Fe-CO), 187.7 (Fe-C_{Carbene}), 139.4 (C_{iPh}), 137.2 (C_{iPh}), 135.9 (CH_{Ph}), 124.6 (CH_{Imid}), 21.1 (*Me*), 18.1 (*Me*). Anal. Calc for $C_{25}H_{24}N_2FeO_4$ (472.31): C, 63.51; H, 5.08; N, 5.93. Found: C, 63.70; H, 5.30; N, 6.29. IR (KBr): ν(CO) 2035, 1949, 1915 cm^{-1}. MS (ESI-TOF, toluene): *m*/*z* [M − 4CO + toluene]$^+$ calcd for $C_{28}H_{32}N_2Fe$ 452, found 452 [Fe(IMes)(toluene)]$^+$.

Synthesis of Fe(IPr)(CO)$_4$ (2). A procedure similar to that used for the preparation of **1** was applied by using 3 equiv of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.25 g, 0.58 mmol) and 1 equiv of $Fe_3(CO)_{12}$ (0.09 g, 0.19 mmol) Yield: 0.30 g (91%). ^{1}H NMR (C_6D_6): 7.28 (t, 2H, *J* = 7.7 Hz, CH_{Ph}), 7.13 (d, 4H, *J* = 7.7 Hz, CH_{Ph}) 6.59 (s, 2H, CH_{Imid}), 2.72 (q, 4H, *J* = 6.8 Hz, CH_{iPr}), 1.43 (d, 12H, *J* = 6.8 Hz, *Me*), 1.00 (d, 12H, *J* = 6.8 Hz, *Me*). ^{13}C NMR (C_6D_6): 215.8 (Fe-CO), 191.7 (Fe-C_{Carbene}), 146.6 (C_{iPh}), 137.0 (C_{iPh}), 130.9 (CH_{Ph}), 125.7 (CH_{Ph}), 124.6 (CH_{Imid}), 28.9 (CH_{iPr}), 25.8 (*Me*), 22.7 (*Me*). Anal. Calc for $C_{31}H_{36}N_2FeO_4$ (556.47): C, 66.91; H, 6.52; N, 5.04. Found: C, 67.29; H, 6.68; N, 5.43. IR (KBr): ν(CO) 2035, 1947, 1928, 1919 cm^{-1}.

Synthesis of Fe(IMe)(CO)$_4$ (3). A procedure similar to that used for the preparation of **1** was applied by using 3 equiv of 1,3-bis(methylimidazolium) iodide (0.40 g, 1.78 mmol) and 1 equiv of $Fe_3(CO)_{12}$ (0.30 g, 0.59 mmol). Yield: 0.14 g (30%). ^{1}H NMR (C_6D_6): 5.74 (s, 2H, CH_{Imid}), 3.05 (s, 6H, *Me*). ^{13}C NMR (C_6D_6): 216.9 (Fe-CO), 181.2 (Fe-C_{Carbene}), 123.2 CH_{Imid}), 39.2 (*Me*). IR (KBr): ν(CO) 2036, 1938, 1924 cm^{-1}. Anal. Calc for $C_9H_8N_2FeO_4$ (264.02): C, 40.94; H, 3.05; N, 10.61. Found: C, 40.70; H, 2.92; N, 10.52. MS (ESI-TOF, MeOH): *m*/*z* [M − 4CO]$^+$ calcd for $C_5H_8N_2Fe$ 152, found 152 [Fe(IMe)]$^+$.

Synthesis of Fe(I^{i}Pr)(CO)$_4$ (4). A procedure similar to that used for the preparation of **1** was applied by using 3 equiv of 1,3-bis(isopropylimidazolium) chloride (0.20 g, 1.05 mmol) and 1 equiv of $Fe_3(CO)_{12}$ (0.18 g, 0.35 mmol). Yield: 0.10 g (30%). ^{1}H NMR (C_6D_6): 6.46 (s, 2H, CH_{Imid}), 5.24 (q, 2H, CH_{iPr}), 0.99 (d, 12H, *J* = 6.8 Hz, *Me*). ^{13}C NMR (C_6D_6): 218.5 (Fe-CO), 177.6 (Fe-C_{Carbene}), 119.3 (CH_{Imid}), 52.4 (CH_{iPr}), 22.7 (*Me*). IR (KBr): ν(CO) 2023, 1998, 1942 cm^{-1}. Anal. Calc for $C_{13}H_{16}N_2FeO_4$ (320.19): C, 48.77; H, 5.04; N, 8.75. Found: C, 48.40; H, 5.32: N, 9.12.

Synthesis of Fe(IPhMe)(CO)$_4$ (5). A procedure similar to that used for the preparation of **1** was applied by using 3 equiv of 1-phenyl-3-methylimidazolium iodide (0.50 g, 1.78 mmol) and 1 equiv of $Fe_3(CO)_{12}$ (0.29 g, 0.59 mmol). Yield: 0.09 g (45%). ^{1}H NMR (400 MHz, C_6D_6): 7.00 (m, 5H, CH_{Ph}), 6.13 (d, 1H, *J* = 3.1 Hz, CH_{Imid}), 5.89 (d, 1H, *J* = 3.1 Hz, CH_{Imid}), 3.23 (s, 3 H, *Me*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 216.1 (Fe-CO), 184.2 (Fe-C_{Carbene}), 141.5 (C_{iPh}), 129.5 (CH_{Ph}), 124.1 (CH_{Imid}), 123.4 (CH_{Imid}), 39.1 (*Me*). IR (KBr): ν(CO) 2034, 1950, 1925, 1896 cm^{-1}. Anal. Calc for $C_{14}H_{10}N_2FeO_4$ (326.00): C, 51.57; H, 3.09; N, 8.59. Found: C, 51.28; H, 3.37; N, 8.21.

Reaction of $Fe_3(CO)_{12}$ with One Equivalent of IMes. IMes (0.20 g, 0.58 mmol) was added to a THF solution of $Fe_3(CO)_{12}$ (0.09 g, 0.19 mmol), and the mixture was stirred at room temperature for 16 h. Volatiles were removed under vacuum, and the resulting crude was extracted with toluene (10 mL). Removal of the toluene afforded an orange solid, which was recrystallized from THF−hexane to yield Fe(IMes)(CO)$_4$. Yield: 0.08 g (30%).

Reaction of $Fe_3(CO)_{12}$ with Excess IMes·HCl. A mixture of 6 equiv of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (0.39 g, 1.14 mmol) and 1 equiv of $Fe_3(CO)_{12}$ (0.09 g, 0.19 mmol) in toluene (15 mL) was heated under reflux for 14 h. The suspension was filtered through Celite, and the filtrate was evaporated to dryness, yielding a mixture of complexes **1** and **6** in ca. 1:1 ratio. Crystallization from THF−hexane solutions led to yellow crystals suitable for X-ray diffraction studies. NMR data for **6**: ^{1}H NMR (400 MHz, C_6D_6): 6.77 (s, 4H, CH_{Ph}), 6.11 (s, 2H, CH_{Imid}), 2.19 (s, 6H, *Me*), 2.10 (s, 12H, *Me*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 222.3 (Fe-CO), 196.9 (Fe-C_{Carbene}), 138.4 (C_{iPh}), 137.4 (C_{iPh}), 135.0 (C_{Ph}), 125.7 (CH_{Imid}), 21.2 (*Me*), 18.8 (*Me*).

Typical Procedure for the Reduction of Carbonyls. A dried J. Young tube equipped with a Teflon screw cap was flushed with nitrogen and charged with the appropriate amount of catalyst in 0.5 mL of the corresponding solvent. Then, neat silane (1.20 mmol) and the corresponding substrate (1.0 mmol) were added. The samples were monitored periodically by ^{1}H NMR. When the reaction was completed, the mixture was treated with 1 mL of a 1% solution of *p*-toluenesulfonic acid in MeOH for 2 h. The solvent was removed under vacuum, and the alcohol was extracted in diethyl ether (5 mL). This solution was filtered through silica, and the filtrate was concentrated under vacuum to yield the corresponding alcohol. Reaction times and temperatures are indicated in Table 1.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving X-ray crystallographic data for complexes **1** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support by FCT (Fundação para a Ciência e a Tecnologia) through projects PTDC/QUI-QUI/110349/2009, REDE/1517/RMN/2005, and REDE/1504/REM/2005 is gratefully acknowledged. S.W. is grateful to the Leonardo da Vinci Programme.

REFERENCES

(1) (a) Díez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (b) Drögue, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940. (c) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687. (d) Glorius, F. N-Heterocyclic Carbenes in Transition-Metal Catalysis. In *Topics in Organometallic Chemistry*; Springer: Berlin, Germany, 2007; Vol. *21*.

(2) (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (b) Jahnke, M. C.; Hahn, F. E. *Top Organomet. Chem.* **2010**, *30*, 95. (c) Crabtree, R. H. *Coord. Chem. Rev.* **2007**, *251*, 595.

(3) A recent review on Fe-NHCs: Ingleson, M. J.; Layfield, R. A. *Chem. Commun.* **2012**, *48*, 3579.

(4) (a) Hashimoto, T.; Urban, S.; Hoshino, R.; Ohki, Y.; Tatsumi, K.; Glorius, F. *Organometallics* **2012**, *31*, 4474. (b) Grohmann, C.; Hashimoto, T.; Fröhlich, R.; Ohki, Y.; Tatsumi, K.; Glorius, F. *Organometallics* **2012**, *31*, 8047.

(5) (a) Buitrago, E.; Zani, L.; Adolfsson, H. *Appl. Organomet. Chem.* **2011**, *25*, 748. (b) Buitrago, E.; Tinnis, F.; Adolfsson, H. *Adv. Synth. Catal.* **2012**, *354*, 217.

(6) Meyer, S.; Orben, C. M.; Demeshko, S.; Dechert, S.; Meyer, F. *Organometallics* **2011**, *30*, 6692.

(7) Gao, H.; Yan, C.-H.; Tao, X.-P.; Xia, Y.; Sun, H.-M.; Shen, Q.; Zhang, Y. *Organometallics* **2010**, *29*, 4189.

(8) (a) Jiang, F.; Bézier, D.; Sortais, J.-B.; Darcel, C. *Adv. Synth. Catal.* **2011**, *353*, 239. (b) Bézier, D.; Jiang, F.; Roisnel, T.; Sortais, J.-B.; Darcel, C. *Eur. J. Inorg. Chem.* **2012**, 1333. (c) Castro, L. C. M.; Sortais, J.-B.; Darcel, C. *Chem. Commun.* **2012**, *48*, 151. (d) Bézier, D.; Venkanna, G. T.; Sortais, J.-B.; Darcel, C. *ChemCatChem.* **2011**, *11*, 1747. (e) Bézier, D.; Venkanna, G. T.; Castro, L. C. M.; Zheng, J.; Roisnel, T.; Sortais, J.-B.; Darcel, C. *Adv. Synth. Catal.* **2012**, *354*, 1879.

(9) (a) Capon, J.-F.; El-Hassnaoui, S.; Gloaguen, F.; Schollhammer, P.; Talarmin, J. *Organometallics* **2005**, *24*, 2020. (b) Hess, J. L.; Hsieh, C.-H.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **2011**, *50*, 8541. (c) Hsieh, C.-H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2010**, *132*, 14119.

(10) Selected references: (a) McGuinness, D. S.; Gibson, V. C.; Steed, J. W. *Organometallics* **2004**, *23*, 6288. (b) Lavallo, V.; Grubbs, R. H. *Science* **2009**, *326*, 559. (c) Xiang, L.; Xiao, J.; Deng, L. *Organometallics* **2011**, *30*, 2018. (d) Przyojski, J. A.; Arman, H. D.; Tonzetich, Z. J. *Organometallics* **2012**, *31*, 3264.

(11) Selected references: (a) Danopoulos, A. A.; Braunstein, P.; Stylianides, N.; Wesolek, M. *Organometallics* **2011**, *30*, 6514. (b) Layfield, R. A.; McDouall, J. J. W.; Scheer, M.; Schwarzmaier, C.; Tuna, F. *Chem. Commun.* **2011**, *47*, 10623. (c) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* **2004**, *23*, 166. (d) Danopoulos, A. A.; Pugh, D.; Smith, H.; Saßmannshausen, J. *Chem.—Eur. J.* **2009**, *15*, 5491. (e) Zlatogorsky, S.; Muryn, C. A.; Tuna, F.; Evans, D. J.; Ingleson, M. J. *Organometallics* **2011**, *30*, 4974.

(12) Cardoso, J. M. S.; Royo, B. *Chem. Commun.* **2012**, *48*, 4944.

(13) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Peris, E.; Royo, B. *Organometallics* **2010**, *29*, 2777.

(14) (a) Liu, B.; Xia, Q.; Chen, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 5513. (b) Liu, B.; Zhang, Y.; Xu, D.; Chen, W. *Chem. Commun.* **2011**, *47*, 2883.

(15) (a) A recent review on NHC chemistry of transition metal carbonyl clusters: Cabeza, J. A.; García-Alvarez, P. *Chem. Soc. Rev.* **2011**, *40*, 5389. (b) Cabeza, J. A.; del Río, I.; Miguel, D.; Sánchez-Vega, M. G. *Chem. Commun.* **2005**, 3956. (c) Cabeza, J. A.; del Río, I.; Miguel, D.; Pérez-Carreño, E.; Sánchez-Vega, M. G. *Dalton Trans.* **2008**, 1937. (d) Cabeza, J. A.; Pérez-Carreño, E. *Organometallics* **2008**, *27*, 4697. (e) Cabeza, J. A.; del Río, I.; Miguel, D.; Pérez-Carreño, E.; Sánchez-Vega, M. G. *Organometallics* **2008**, *27*, 211.

(16) (a) Ellul, C. E.; Mahon, M. F.; Saker, O.; Whittlesey, M. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6343. (b) Critall, M. R.; Ellul, C. E.; Mahon, M. F.; Saker, O.; Whittlesey, M. K. *Dalton Trans.* **2008**, 4209.

(17) Ellul, C. E.; Saker, O.; Mahon, M. F.; Apperley, D. C.; Whittlesey, M. K. *Organometallics* **2008**, *27*, 100.

(18) Bruce, M. I.; Cole, M. L.; Fung, R. S. C.; Forsyth, C. M.; Hilder, M.; Junk, P. C.; Konstas, K. *Dalton Trans.* **2008**, 4118.

(19) (a) Zhang, C.; Li, B.; Song, H.; Xu, S.; Wang, B. *Dalton Trans.* **2009**, 7230. (b) Zhang, C.; Li, B.; Song, H.; Xu, S.; Wang, B. *Organometallics* **2011**, *30*, 3029.

(20) (a) Çetinkaya, B.; Dixneuf, P.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, *74*, 1827. (b) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172.

(21) Huttner, G.; Gartzke, W. *Chem. Ber.* **1972**, *105*, 2714.

(22) Glaser, R.; Yoo, Y.-H.; Chen, G. S.; Barnes, C. L. *Organometallics* **1994**, *13*, 2578.

(23) Leung, C.-H.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2006**, *25*, 6099.

(24) Selected references: (a) Junge, K.; Schröder, K.; Beller, M. *Chem. Commun.* **2011**, *47*, 4849. (b) Chakraborty, S.; Guan, H. *Dalton. Trans.* **2010**, *39*, 7427. (c) Le Bailly, B. A. F.; Thomas, S. P. *RSC Adv.* **2011**, *1*, 1435. (d) Yang, J.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2010**, *49*, 10186.

(25) (a) Zhou, S.; Junge, K.; Addis, D.; Das, S.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9507. (b) Das, S.; Li, Y.; Junge, K.; Beller, M. *Chem. Commun.* **2012**, *48*, 10742.

(26) (a) Arduengo, A. J.; Krafcyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523. (b) Zoller, U. *Tetrahedron* **1988**, *44*, 7413. (c) Berding, J.; van Paridon, J. A.; van Rixel, V. H. S.; Bouwman, E. *Dalton Trans* **2011**, 2450. (d) Herrmann, W. A.; Köcher, C.; Gooßen, L. J.; Artus, R. J. *Chem.—Eur. J.* **1996**, *2*, 1627.