Cationic Half-Sandwich Iron(II) and Iron(III) Complexes with N-Heterocyclic Carbene Ligands

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Supporting Information

ABSTRACT: The cationic piano-stool iron complexes containing the N-heterocyclic carbene ligand tethered to a tetramethylcyclopentadienyl ring [(Cp*-NHC)Fe(CO)(L)][X] (L = NCMe, DMSO; X = BF4, OTf) have been prepared and analyzed by spectroscopic, electrochemical, and crystallographic methods. Oxidation reactions of the cationic complex [(Cp*-NHC)Fe(CO)(NCMe)][BF4] (2) with silver tetrafluoroborate and tert-butyl hydroperoxide in acetonitrile yield the dicaticionic iron(III) complexes [(Cp*-NHC)Fe(NCMe)2][BF4]+ and [(Cp*-NHC)Fe(H2O)][BF4]+, respectively. When the reaction of 2 with AgBF4 is performed in dichloromethane, the cationic complex [(Cp*-NHC)FeCl][BF4] is obtained. These new iron(III) complexes have been characterized by Mössbauer spectroscopy and in one case by X-ray diffraction studies. DFT calculations were used to rationalize experimental results. The cationic complex [(Cp*-NHC)Fe(CO)(NCMe)][OTf]− is catalytically active toward the reduction of benzaldehyde and acetophenone using phenylsilane under neat conditions and in the absence of visible light irradiation.

INTRODUCTION

In recent years, the use of N-heterocyclic carbene (NHC) ligands in the chemistry of iron has attracted considerable attention due to the potential application of Fe-NHC complexes in homogeneous catalysis and in biomimetic chemistry.1–3 The strong σ-donor properties and the easy accessibility of NHCs are responsible for their extensive use as supporting ligands in coordination chemistry and catalysis.4–9

In the last 10 years, the chemistry of piano-stool iron-NHC complexes has been the subject of intense research,10–25 including their successful application in catalytic reduction reactions, e.g. hydrosilylation,14–23 and hydrogen transfer14 and in C–H activation and borylation reactions.24,25 Most of these studies were performed with complexes bearing the cyclopentadienyl (Cp = η5-C5H5) ligand, while complexes with Cp* (Cp* = η5-C5Me5) are less common. It is worth noting the coordinatively unsaturated Cp* iron-NHC complexes reported by Oki, Tatsumi, and co-workers and their application in C–H bond activation, borylation, and hydrogenation reactions.24,25

We recently disclosed the unprecedented synthesis of cyclopentadienyl-functionalized iron(II)-NHC complexes by direct reaction of the corresponding imidazolium proligands with commercially available Fe2(CO)9.18 This convenient synthetic route avoids the use of strong bases previously needed in the preparation of (Cp*-NHC)Fe(CO)I complexes. Later, we demonstrated that this straightforward pathway could be successfully applied to the preparation of iron(0) complexes containing monodentate NHCs.26

As a part of our ongoing research on iron-NHC chemistry,14,18,22,26 we sought to explore further the reactivity of our Cp*-NHC iron complexes. Here we describe the synthesis and characterization of cationic piano-stool Fe(II)-NHCs and their oxidation to Fe(III) complexes, complemented by DFT calculations.

RESULTS AND DISCUSSION

Synthesis of Fe(II) and Fe(III) Complexes. The cationic iron(II) carbonyl complex [(Cp*-NHC)Fe(CO)(NCMe)]- [BF4]− (2; Cp* = η5-C5Me5) was prepared by the stoichiometric reaction of (Cp*-NHC)Fe(CO)I (1) with silver tetrafluoroborate (AgBF4) in acetonitrile, as shown in Scheme 1. Complex 2 was isolated as a crystalline orange solid in high yield (95%), and it has been fully characterized by NMR and IR spectroscopy and HRMS-ESI spectrometry. NMR characterization of complex 2 revealed the presence of two diastereomers in a 2:1 ratio. The presence of diastereomers was rationalized by the existence of two stereogenic centers in the molecule: at the metal and at the aliphatic linker between...
the NHC and the cyclopentadienyl ring. Therefore, two sets of signals corresponding to the coordinated cyclopentadienyl-NHC ligand were observed in the NMR spectra. Its $^{13}$C NMR spectrum shows the characteristic carbene signal at 187 ppm for the major isomer (minor isomer at 186 ppm), shifted upward in comparison to the neutral complex ($\text{Cp}^*\text{-NHC})\text{Fe(CO)}\text{I}$ (195 ppm). Related cationic piano-stool iron-NHC complexes containing the unsubstituted Cp ligand display resonances for the carbene signal shifted to higher field (182–174 ppm).10,13

The infrared vibrational spectrum of 2 shows an intense absorption band at 1937 cm$^{-1}$, indicative of the terminal carbonyl ligand. As expected, the carbonyl stretching band is shifted to higher wavenumber in comparison to the band for the neutral complex 1 ($\nu_{\text{CO}}$ 1906 cm$^{-1}$), indicating less $\pi$ back-donation from iron and thus higher Lewis acidity. The presence of the carbonyl ligand is further verified by the carbonyl signal at 222 ppm (for the major isomer) in the $^{13}$C NMR spectrum.

In an attempt to obtain single crystals of 2, complex 1 was treated with AgBF$_4$ in acetonitrile for 16 h, and the acetonitrile solution was filtered and layered with ether. In this way, dark red crystals suitable for X-ray diffraction studies were isolated after several days. Surprisingly, the crystals turned out to be the dicationic Fe(III)-NHC complex $[(\text{Cp}^*-\text{NHC})\text{Fe(NCMe)}\text{2}]^2$-$[\text{BF}_4]^2$ (3). The molecular structure of 3 and selected bond lengths and angles are depicted in Figure 1. The structure can be described as a distorted three-legged piano stool with the tetramethylcyclopentadienyl ring bonded in a $\eta^5$ fashion with distances between iron and cyclopentadienyl ring carbon varying from 2.0301(16) to 2.1872(16) Å. The Fe–C$_{\text{carbene}}$ bond distance of 1.9870(4) Å is in good agreement with the Fe–C$_{\text{carbene}}$ bond distances reported for related complexes, which are in the range 1.98–2.085 Å.10,11,14,24 Two acetonitrile molecules complete the coordination sphere of iron, with Fe–N distances of 1.9645 and 1.9696 Å. As far as we know, this is the first piano-stool Fe(III) NHC complex reported in the literature.

This result indicates that the silver salt AgBF$_4$ behaves as a noninnocent one-electron oxidant capable of oxidizing the cationic complex 2 to give 3 (Scheme 2). The oxidation process is accompanied by the release of the carbonyl ligand. An excess of AgBF$_4$ present in the acetonitrile solution might be responsible for the oxidation process. In fact, the presence of AgBF$_4$ was corroborated by the concomitant formation of colorless crystals, which were isolated and studied by X-ray diffraction. The acetonitrile complex $[\text{Ag(NCMe)}4][\text{BF}_4]$ was present in the solution along with the red crystals of 3.27 Oxidation reactions of Fe(0) to Fe(I) complexes conducted by AgBF$_4$ were reported by Lappert with mono- and bis-NHC iron carbonyl complexes.28 In those examples, the resulting Fe(I) complexes maintained the iron environment intact.

We therefore decided to examine the cyclic voltammetry (CV) of the iron(II) compounds 1 and 2 in order to characterize the Fe$^{II}$/Fe$^{III}$ couple. The CVs of complexes 1 and 2 in CH$_2$Cl$_2$ are displayed in Figure 2. The neutral compound 1 shows a reversible one-electron oxidation at 0.53 V (vs ferrocene/ferrocenium). This value compares well with those of related cyclopentadienyl Fe-NHC complexes.10,11 The cationic complex 2 displays almost reversible one-electron oxidation at 0.68 V corresponding to the Fe$^{II}$/Fe$^{III}$ couple. As expected, the higher oxidation potential of the cationic complex reflects the higher Lewis acidity of the metal center in 2 in comparison with 1.

\[\text{Scheme 1. Synthesis of the Cationic Fe(II)-NHC Complexes 2, 5, and 6*}\]

\[\text{Scheme 2. Single-Electron Oxidation of 2 by AgBF$_4$ in Acetonitrile and in Dichloromethane}\]

\[\text{Figure 1. ORTEP drawing of } [(\text{Cp}^*-\text{NHC})\text{Fe(NCMe)}\text{2}]^2 \text{BF}_4^2 (3). \text{Ellipsoids are given at the 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1−C(1) 1.9870(17), Fe(1−N(3) 1.9645(15), Fe(1−N(4) 1.9696(15), Fe(1−Cp* centroid 2.1089; C(1−Fe(1−N(3) 95.29(6), C(1−Fe(1−N(4) 98.37(6), N(3)−Fe(1−N(4) 88.14(6), Cp* centroid−Fe(1−C(1) 121.634, Cp* centroid−Fe(1−N(3) 116.504, Cp* centroid−Fe(1−N(4) 117.29.}\]
We performed DFT calculations\textsuperscript{29} (see Computational Details) to optimize the geometries of complexes (Cp*-NHC)Fe(CO)I (1) and [(Cp*-NHC)Fe(CO)(NCMe)][BF$_4$] (2) and their one-electron-oxidized products 1$^+$ and 2$^+$, both in the gas phase and in solvent (dichloromethane), in order to estimate the oxidation potentials. The calculated oxidation potential for complex 1, $E^\ddagger$(1$\rightarrow$1$^+$) is 0.78 V, on the basis of the gas-phase Gibbs free energy differences between 1$^+$ and 1, in relatively good agreement with the experimental value 0.53 V (relative to Fe/CFe$^\ddagger$). The same calculation for complex 2 leads to an estimate of 4.12 V for $E^\ddagger$(2$\rightarrow$2$^+$). Although it is higher than the oxidation potential of 1, this value is too high in comparison with the experimental value. The calculation taking into account the solvent (dichloromethane) did not lead to improved values, probably because the charges on the two complexes are different (0, +1 in 1 and +1, +2 in 2). The oxidation potentials follow the same trend as the energy of the HOMO of 1 can be assigned to the high Fe-I antibonding character, while the HOMO of 2 is only slightly Fe-C(NHC) antibonding (Figure 3). Both are bonding to the Cp* ring and almost nonbonding to the CO (and NCMe in 2). The different compositions may be associated with the processes following oxidation.

Complex 3 was obtained serendipitously in the crystallization process. Attempts to develop a controlled oxidation reaction of 2 with AgBF$_4$ in acetonitrile were unfruitful. It seems that the concentration of the Ag$^+$ salt plays a crucial role in the successful isolation of 3. The strength of the silver(I) ion as an abstractor of electrons is 0.78 kcal mol$^{-1}$ higher than that of the Fe$^+$ ion (\textit{vide infra}). The presence of HS Fe(II) in the Mössbauer spectrum indicates that the oxidation reaction was not complete and traces of uncharacterized paramagnetic iron(II) species remained in the reaction mixture. The $^{57}$Fe Mössbauer parameters were calculated for complex 4 with a DFT approach (using ORCA\textsuperscript{33}, see the Experimental Section). The electronic density at the nucleus ($\rho(0)$) was converted to isomer shifts ($\delta$), using the approach of Vanko\textsuperscript{33}, and the quadrupole splitting ($\Delta E_Q$) was obtained directly. The $\delta$ and $\Delta E_Q$ values were calculated as 0.37 and $-1.02$ mm s$^{-1}$, respectively, for complex 4, assuming $S = \frac{1}{2}$. The energy of this state is only 0.7 kcal mol$^{-1}$ higher than that of the $S = \frac{5}{2}$ state, and the agreement with experimental values is much better (for $S = \frac{5}{2}$, $\delta$ and $\Delta E_Q$ are 0.59 and 2.77 mm s$^{-1}$).

Figure 2. Cyclic voltammograms of (Cp*-NHC)Fe(CO)I (1) (in red) and [(Cp*-NHC)Fe(CO)(NCMe)][BF$_4$] (2) (in blue) in CH$_2$Cl$_2$/0.1 M [Bu$_4$N][PF$_6$] and at the voltage sweep rate $\nu$ = 100 mV s$^{-1}$.

Figure 3. HOMOs of (left) (Cp*-NHC)Fe(CO)I (1) and (right) [(Cp*-NHC)Fe(CO)(NCMe)][BF$_4$] (2).

Figure 4. $^{57}$Fe Mössbauer spectrum (78 K) of the solid isolated from the reaction of 2 with AgBF$_4$ in dichloromethane (complex 4).

The use of thallium trifluoromethanesulfonate as a halide abstractor of 1 allowed us to prepare the pure cationic species [(Cp*-NHC)Fe(CO)L][OTf] ($L =$ NCMe (5), DMSO (6); DMSO = dimethyl sulfoxide, OTf = SO$_3$CF$_3$), avoiding the oxidation processes promoted by AgBF$_4$. Reaction of 1 with a stochiometric amount of TlOTf in dichloromethane/L (L = NCMe, DMSO) afforded complexes 5 and 6, which were isolated as crystalline orange solids in high yields (Scheme 1). Attempts to prepare the corresponding aqua complex [(Cp*-NHC)Fe(CO)(H$_2$O)][OTf] following a similar reaction, by treatment of 1 with TlOTf in CH$_2$Cl$_2$/H$_2$O, led to an intractable mixture of complexes. The diamagnetic complexes revealed the presence of three different iron sites. The major site (73.5%), with an isomer shift ($\delta$) of 0.444(5) mm s$^{-1}$ and quadrupole splitting ($\Delta E_Q$) of 0.99(1) mm s$^{-1}$, is consistent with Fe(III), by comparison with spectra of other Cp*Fe derivatives, which were also shown to be low-spin Fe(III) from EPR measurements.\textsuperscript{31} The two minor doublets (7.1 and 19.4%), with $\delta = 1.15(4)$, $\Delta E_Q = 3.89(5)$ and $\delta = 1.32(2)$, $\Delta E_Q = 3.26(3)$, respectively, were assigned to high-spin (HS) Fe(II).

On the basis of these results, we propose the formation of the Fe(III) complex [(Cp*-NHC)FeCl][BF$_4$] (4) by chemical oxidation of the cationic complex 2 with AgBF$_4$ in dichloromethane (Scheme 2). We believe that the chloride atom present in 4 might originate from the solvent, CH$_2$Cl$_2$. The presence of HS Fe(II) in the Mössbauer spectrum indicates that the oxidation reaction was not complete and traces of uncharacterized paramagnetic iron(II) species remained in the reaction mixture. The $^{57}$Fe Mössbauer parameters were calculated for complex 4 with a DFT approach (using ORCA\textsuperscript{33}, see the Experimental Section). The electronic density at the nucleus ($\rho(0)$) was converted to isomer shifts ($\delta$), using the approach of Vanko\textsuperscript{33}, and the quadrupole splitting ($\Delta E_Q$) was obtained directly. The $\delta$ and $\Delta E_Q$ values were calculated as 0.37 and $-1.02$ mm s$^{-1}$, respectively, for complex 4, assuming $S = \frac{1}{2}$. The energy of this state is only 0.7 kcal mol$^{-1}$ higher than that of the $S = \frac{5}{2}$ state, and the agreement with experimental values is much better (for $S = \frac{5}{2}$, $\delta$ and $\Delta E_Q$ are 0.59 and 2.77 mm s$^{-1}$). The use of thallium trifluoromethanesulfonate as a halide abstractor of 1 allowed us to prepare the pure cationic species [(Cp*-NHC)Fe(CO)L][OTf] ($L =$ NCMe (5), DMSO (6); DMSO = dimethyl sulfoxide, OTf = SO$_3$CF$_3$), avoiding the oxidation processes promoted by AgBF$_4$. Reaction of 1 with a stochiometric amount of TlOTf in dichloromethane/L (L = NCMe, DMSO) afforded complexes 5 and 6, which were isolated as crystalline orange solids in high yields (Scheme 1). Attempts to prepare the corresponding aqua complex [(Cp*-NHC)Fe(CO)(H$_2$O)][OTf] following a similar reaction, by treatment of 1 with TlOTf in CH$_2$Cl$_2$/H$_2$O, led to an intractable mixture of complexes. The diamagnetic complexes revealed the presence of three different iron sites. The major site (73.5%), with an isomer shift ($\delta$) of 0.444(5) mm s$^{-1}$ and quadrupole splitting ($\Delta E_Q$) of 0.99(1) mm s$^{-1}$, is consistent with Fe(III), by comparison with spectra of other Cp*Fe derivatives, which were also shown to be low-spin Fe(III) from EPR measurements.\textsuperscript{31} The two minor doublets (7.1 and 19.4%), with $\delta = 1.15(4)$, $\Delta E_Q = 3.89(5)$ and $\delta = 1.32(2)$, $\Delta E_Q = 3.26(3)$, respectively, were assigned to high-spin (HS) Fe(II).

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5 and 6 were characterized by NMR and IR spectroscopy, HRMS-ESI spectrometry, and elemental analyses. Complex 6 was also measured by Mössbauer spectroscopy and studied by single crystal X-ray diffraction.

The triflate complex 5 gave NMR spectra identical with those described for the corresponding BF₄ complex 2. In contrast, complex 6 displayed a single set of resonances corresponding to the Cp⁺-NHC ligand. The dimethyl sulfoxide ligand displayed two resonances at 3.23 and 2.62 ppm for the nonequivalent methyl groups, indicating that the rotation of the methyl groups around the Fe–S axis is restricted. The structure of 6 was determined by X-ray diffraction studies. The molecular structure and selected bond lengths and angles are depicted in Figure 5. The iron center adopts a conventional three-legged piano-stool geometry with the cyclopentadienyl group of a pendant NHC ligand chelating the metal center. Interestingly, the dimethyl sulfoxide ligand coordinates through the sulfur atom with a distance of 2.1778 Å, which falls in the range of Fe–S distances reported for the limited number of known S-bonded sulfoxide iron compounds (2.101–2.308 Å). The carbonyl ligand completes the coordination sphere of the iron, with an Fe–CO distance of 1.752 Å, which is in the range of Fe–C(carbonyl) distances in piano-stool complexes (1.71–1.76 Å). The SO₂CF₃ counteranion does not coordinate with the metal center.

The Mössbauer spectrum of complex 6 collected at 290 K is illustrated in Figure 6. As can be seen, the experimental data are well reproduced by a doublet, the obtained hyperfine parameters being well ascribed to Fe(II) in a low-spin oxidation state (δ = 0.076(3) mm s⁻¹ and ΔE₀ = 2.122(5) mm s⁻¹). The calculated parameters are δ = 0.16 and ΔE₀ = 2.03 mm s⁻¹, in good agreement with experiment. These values are comparable to those reported for the piano-stool iron complex Cp⁺Fe(CO)₂I (δ = 0.124 mm s⁻¹ and ΔE₀ = 1.954 mm s⁻¹). The lower isomer shift value of complex 6 should reflect a higher s electron density at the iron nucleus in 6 in comparison to Cp⁺Fe(CO)₂I. The ν(CO) frequency is observed at 1935 cm⁻¹ in 6 and at 1957 and 2007 cm⁻¹ for Cp⁺Fe(CO)₂I, suggesting more π back-donation to CO in 6, but they cannot be directly compared, due to the different numbers of carbonyls.

The cationic complexes 5 and 6 do not release the CO ligand upon UV irradiation of their acetonitrile solutions. This behavior is in agreement with the chemistry described by Guerchais for the related complex [CpFe(NHC)(CO)-(NCMe)]³⁺ [PF₆]⁻ (Cp = η⁵-C₅H₅; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene). The strong metal–CO π back-donation of the carbonyl ligand due to the presence of the NHC ligand may inhibit complete decarbonylation.

We have also explored the oxidation reaction of the cationic complex 2 with tert-butyl hydroperoxide (TBHP). Treatment of 2 with 2 equiv of TBHP (5.5 M in decane) in acetonitrile afforded a paramagnetic orange solid. Its ⁵⁷Fe Mössbauer spectra (recorded at 290 and 78 K; Figure 7) were well fitted using a doublet with δ = 0.368(1) mm s⁻¹ (290 K) and δ = 0.476(2) mm s⁻¹ (78 K) and a distribution of quadrupole splittings with mean value (ΔE₀) = 0.87(1) mm s⁻¹. These values are consistent with those of Fe(III) species, namely [FeCp⁺(dppe)(CH₃)][PF₆]⁻, with δ = 0.35 and ΔE₀ = 0.76 mm s⁻¹, and an EPR signal typical of S = 1/₂ (LS). A residual impurity (<7%) is clearly observed in the 78 K spectrum. The hyperfine parameters characterizing this impurity (δ = 0.07(2) mm s⁻¹ and ΔE₀ = 1.95(2) mm s⁻¹) are similar to those obtained for the cationic complex 6, allowing us to consider the presence of a residual fraction of the starting material 2.
The IR spectrum of this solid displayed a strong resonance at 1061 cm$^{-1}$ characteristic of the $\nu_{BF}$ band. Carbonyl, oxo, and peroxy resonances were not observed in its IR spectrum. Elemental analysis is in accord with the formulation of the iron(III) dicaticionic species $[\{\text{Cp}^*\text{-NHC}\}\text{Fe}(\text{H}_2\text{O})\}][\text{BF}_4]_2$ (7) (Scheme 3). The isomer shift value found for this compound

(0.476(2) mm s$^{-1}$ at 78 K) is slightly higher than that obtained for complex 4 (0.444(5) mm s$^{-1}$), which is consistent with the lower s electron density at the iron metal in complex 7. Confirmation of the formulation of 7 by X-ray diffraction studies would be desirable. However, its poor solubility in most common organic solvents, e.g. NCMe, CH$_2$Cl$_2$, and THF, hindered its full characterization. DFT calculations were also performed on the model complex $[\{\text{Cp}^*\text{-NHC}\}\text{Fe}(\text{H}_2\text{O})\}][\text{BF}_4]_2$, which was optimized for spin states $S = 1/2$ and $S = 3/2$, $S = 1/2$ being the lowest energy state by 4.2 kcal mol$^{-1}$. The calculated $\delta$ value for this species was 0.52 mm s$^{-1}$, not too far from the 0.48 mm s$^{-1}$ value obtained at low temperature, while the $\Delta E_1$ value was 1.41 mm s$^{-1}$, higher than the experimental value of 0.87 mm s$^{-1}$. Although these values are not in perfect agreement with the experimentally determined ones, the model did not include the effects of the counterion, which may be relevant since the presence of O--H--F hydrogen bonds cannot be discarded. Note that no such effects were expected in complex 4 above and the agreement was much better. We therefore believe that these calculations provide further support for the proposed formulation of complex 7.

**Catalytic Activity of Complex 5 in the Hydrosilylation of Carbonyl Groups.** Recently, we$^{14,18,22}$ and the group of Darcel and Sortais$^{15,17,19,21,23}$ explored the catalytic activity of iron piano-stool NHC complexes in the reduction of organic functionalities through hydrosilylation processes. Most of these studies have been performed with complexes containing the unsubstituted cyclopentadienyl ring. The only report using an iron complex bearing a Cp* group was reported by us in 2010.$^{14}$ The coordinatively unsaturated species (Cp*-NHC)-FeCl displayed good catalytic activity in the reduction of aldehydes with silanes, but it was inactive in the reduction of ketones. We decided to explore the catalytic activity of the caticionic complex 5 with the model substrates benzaldehyde and acetophenone, in order to compare with previously reported results. We found that 5 catalyzes the reduction of benzaldehyde with phenylsilane under neat conditions, yielding quantitative conversion in 1.5 h at 60 °C (Table 1, entry 1). Comparable activity was previously reported by us with (Cp*-NHC)FeCl (100% yield of alcohol in 2 h at 80 °C)$^{14}$ Notably, complex 5 displayed good activity toward the reduction of ketones; full conversion of acetophenone was obtained in 4 h at 100 °C (Table 1, entry 3). Moreover, the catalyst amount can be reduced to 0.5 mol % and similar catalytic activity is maintained (Table 1, entries 2 and 4). This result contrasts with that obtained for (Cp*-NHC)FeCl, which was totally inactive toward reduction of ketones, and it demonstrates the improved efficiency of catalyst 5 in comparison to the previously reported (Cp*-NHC)FeCl.

The group of Darcel, Sortais, and co-workers have extensively studied the catalytic efficiency of the related cationic species $[\{\text{Cp}(\text{IMes})\text{Fe}(\text{CO})_3\}][\text{BF}_4]$.$^{1}$ The best catalytic performances in the reduction of carbonyl groups were obtained by carrying out the catalytic reaction under neat conditions with light irradiation, whereas no reaction occurred in the absence of light.$^{15,16}$ Last year, they, in collaboration with the Özdemir group, reported an improved catalyst, the complex $[\text{Cp}(\text{NHC})\text{Fe}(\text{CO})_3]^+$ containing benzyl-substituted imidazolin-2-ylidine, which was able to catalyze the reduction of carbonyl groups in the absence of light by heating to 100 °C.$^{23}$ Comparable catalytic activity was obtained with complex 5, which was active in the absence of visible light. These results demonstrate that smooth changes in the coordination sphere of the iron center have some implications on the catalytic activity of the complex.

### CONCLUSIONS

The results presented above open up new perspectives for the development of iron(III)-NHC chemistry. The half-sandwich iron(III) complexes described in this work are rather stable in the solid state and can be handled in air. Preliminary catalytic studies indicate that these new iron(III)-NHC complexes might find interesting applications in catalysis. Investigation of their potential in different catalytic reactions is ongoing in our group.

### EXPERIMENTAL SECTION

**General Comments.** All manipulations, unless otherwise stated, were performed under an atmosphere of nitrogen gas using standard Schlenk techniques. All solvents were purified by using the appropriate drying agents and were distilled and stored in molecular sieves prior to use. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 400 MHz instrument. Infrared (IR) spectra was recorded on samples as KBr pellets using a Bruker IFS 66/S ATR-FTIR spectrometer. Electrospray mass spectra (MS-ES) were recorded on a Bruker Daltonics esquire 3000 plus instrument. A QTOFI (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, U.K.) was used for high-resolution mass spectrometry (HRMS). The drying gas as well as the nebulizing gas was nitrogen at a flow rate of 400 L h$^{-1}$, respectively. Electrochemical studies were carried out by using an Autolab Model PGSTAT101 potentiostat, with a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver-wire reference electrode. In all experiments, $\text{[NaBu$_4$][PF$_6$]}$ (0.1 M in dry CH$_2$Cl$_2$) was used as the supporting electrolyte with an analyte concentration of approximately 1 mM. Measurements were performed at a scan rate of 100 mV s$^{-1}$. All redox potentials were referenced to the Fe$^0$/Fe$^+$ couple as an internal standard with $E_{1/2}(\text{Fe}^+/\text{Fe}^0)$ vs SCE = +0.44 V.

### Table 1. Reduction of Benzaldehyde and Acetophenone by 5 with Phenylsilane$	ext{a}$

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$^a$Typical procedure: substrate (1.0 mmol), phenylsilane (1.2 mmol), catalyst 5 under neat conditions. $^b$Conversion determined by $^1$H NMR spectroscopy.
Organometallics

**Materials.** Complex 1 was synthesized according to a method previously described by us. All reagents were used as received from commercial suppliers and used without further purification.

**Mössbauer Spectroscopy.** The $^{57}$Fe Mössbauer spectra were recorded in transmission mode at 290 and 78 K using a conventional constant-acceleration spectrometer and a 50 mCi $^{57}$Co source in a Rh matrix. The low-temperature measurements were performed using a liquid nitrogen flow cryostat with a temperature stability of ±0.5 K. The velocity scale was calibrated using α-Fe foil. The spectra were fitted using the WinNormos software program, and the isomer shifts reported are relative to metallic α-Fe at room temperature.

**X-ray Data Collection and Structure Solution Refinement.** Data collection was carried out with a Bruker Apex-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. 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 S1 (Supporting Information). The diffraction frames were integrated using the SAINT package.

**Synthesis of $[\text{Cp}^{+}\text{-NHImFe(OCOMe)}][\text{BF}_4]$ (2).** To a solution of 1 (0.13 g, 0.25 mmol) in NCMe (10 mL) was added AgBF$_4$ (0.06 g, 0.26 mmol), and the reaction mixture was stirred for 15 min at room temperature. The solution was washed with diethyl ether and dried under vacuum to afford 0.12 g (95% yield) of an orange solid. NMR showed two sets of signals in a 2:1 ratio. Data for the major isomer are as follows. $^1$H NMR (400 MHz, δ in ppm, CD$_2$Cl$_2$): δ 7.50–7.55 (m, 3H, CH$_{phenyl}$), 7.07 (s, 1H, CH$_{methyl}$), 6.57 (s, 1H, CH$_{methyl}$), 4.94–4.91 (dd, J = 4.96 Hz, 1H, CH$_{methyl}$), 3.59 (s, 3H, NCH$_3$), 2.82–2.64 (m, 4H, CH$_2$Imid), 2.32 (s, 3H, CH$_3SO$), 1.87 (s, 3H, CH$_3Cp$), 1.63 (s, 3H, CH$_3Cp$), 1.58 (s, 3H, CH$_3Cp$), 1.51 (s, 3H, CH$_3Cp$), 1.25 (Cp$^*$) (NMR (100 MHz, CD$_2$Cl$_2$): δ 8.22, 8.20 (CH$_{methyl}$), 124.92 (C$_{methyl}$), 389.13 (NCCH)).

**Analytical Data.** For C$_{25}$H$_{31}$N$_2$FeO$_5$S$_2$F$_3$ (616.49): C, 48.71; H, 5.07; N, 4.54; S, 10.40. Found: C, 49.2; H, 5.33; N, 4.65; S, 10.5. Similar calculations were made for the minor isomer.

**Synthesis of $[\text{Cp}^{+}-\text{NHImFe(OCOMe)}][\text{OsF}_6] (6).** To a solution of 1 (0.13 g, 0.25 mmol) in CD$_2$Cl$_2$ (10 mL) was added TiOTf (0.09 mg, 0.26 mmol), and the reaction mixture was stirred for 15 min at room temperature. Then, a few drops of DMSO were added and the mixture was stirred for further 16 h. The solution was filtered, and the filtrate was evaporated under vacuum to dryness. The residue was washed first with toluene and then with hexane to give 0.12 g (94% yield) of a crystalline orange solid. Crystals suitable for X-ray diffraction studies were grown by vapor diffusion of diethyl ether into a saturated dichloromethane solution of the complex. $^1$H NMR (400 MHz, δ in ppm, CD$_2$Cl$_2$): δ 7.54–7.49 (m, 3H, CH$_{phenyl}$), 7.15 (s, 1H, CH$_{methyl}$), 6.63 (s, 1H, CH$_{methyl}$), 6.05–6.01 (dd, J = 5.95 Hz, 1H, CH$_{methyl}$, 3.86 (s, 3H, NCH$_3$), 3.23 (s, 3H, CH$_3SO$), 2.90–2.75 (m, 2H, CH$_2$Imid), 2.62 (s, 3H, CH$_3SO$), 2.09 (s, 3H, CH$_3Cp$), 1.94 (s, 3H, CH$_3Cp$), 1.88 (s, 3H, CH$_3Cp$), 1.03 (s, 3H, CH$_3Cp$), 1.25 (Cp$^*$) (NMR (100 MHz, CD$_2$Cl$_2$): δ 219.26 (CO), 181.86 (NCN), 153.99–158.28 (6 × CH$_3$Ph), 152.70 (C$_{methyl}$), 107.02, 100.05, 95.32, 95.00, 87.24 (5 × CH$_3$Ph), 66.02 (CH$_3SO$), 52.62 (CH$_3SO$), 51.27 (CH$_3SO$C), 39.92 (NCCH), 28.13 (CH$_3$Ph)).

**Analytical Data.** For C$_{33}$H$_{34}$FeO$_4$F$_6$ (616.49): C, 48.71; H, 5.07; N, 4.65; S, 10.5. Found: C, 48.00; H, 5.05; N, 4.48; S, 10.4. The discrepancy between calculated and experimental values of the elemental analysis might be due to retention of fractional amount of water. IR (KBr): $v_{max}$ 1647 (vs) cm$^{-1}$, $v_{max}$ 1095 (vs) cm$^{-1}$.

**Reaction of 2 with TBHP in NCMe.** To a solution of 2 (0.16 g, 0.31 mmol) in NCMe (10 mL) was added TBHP (0.45 g, 0.23 mmol), and the reaction mixture was stirred for 6 h at room temperature. The solution was filtered, and the filtrate was concentrated to dryness under vacuum. The residue was washed with diethyl ether and dried under vacuum to afford 0.12 g of an orange solid of 7 (68% yield). Anal. Calc. for C$_{33}$H$_{34}$FeO$_4$F$_6$ (579.11): C, 51.82; H, 4.87; N, 7.25; S, 5.53. Found: C, 51.47; H, 4.72; N, 6.93; S, 5.29. MS (ESI$^+$): $m/z$ 430.1$^{[M] +}$ calculated for C$_{22}$H$_{25}$FeO$_3$ 389.13. $^{13}$C NMR, calculated for C$_{22}$H$_{25}$FeO$_3$.

**Synthesis of $[\text{Cp}^{+}-\text{NHImFe(OCOMe)}][\text{DMSO}] (5).** A typical procedure was performed as follows. A dried J. Young tube was equipped with a Teflon screw cap was flushed with nitrogen and charged with catalyst. The substrate and phenylsilane were added to the NMR tube. Deuterol solvent was added at the end of the reaction, and the NMR spectrum was recorded.

**Hydrosilylation of Benzaldehyde and Acetophenone.** The substrate was washed with diethyl ether and dried under vacuum to afford 0.12 g of an orange solid of 7 (68% yield). Anal. Calc. for C$_{33}$H$_{34}$FeO$_4$F$_6$ (579.11): C, 45.61; H, 4.92; N, 5.07. Found: C, 45.60; H, 5.54; N, 4.43. The optimized geometries were obtained with the Stuttgart/Dresden ESP (SDD) basis set to...
describe the electrons of the iron atom, the LANL2DZdp ECP basis set, obtained from the EMSL basis set exchange Web site for iodine, and a standard 6-31G(d,p) set for the remaining elements (H, C, N, O, S, Cl). The single-crystal X-ray structures described in this work were used to build the models for geometry optimizations. No symmetry constraints were considered, and frequency calculations showed the structures to be true minima. Open-shell calculations were performed whenever $S \neq 0$. Some geometry optimizations and frequency calculations were performed by taking into account solvent effects using the integral equation formalism polarizable continuum model (IEFPCM) in Truhlar’s SMD solvent model.66

The Mössbauer parameters (quadrupole splitting, $\Delta E_Q$, and electron density at the nucleus, $\rho(0)$) were calculated with the methodology developed by Vanko in his recent benchmark study.33 Single-point calculations at the RIPE82 level of theory with the ORCA software (version 2.9.0)32 were performed on the optimized geometries. Fe was described by the triply polarized core properties basis set CP(PPP),66 and the other atoms (H, C, N, O, S, Cl) were described by the TZVP.66 In order to gain accuracy on core properties, the integral equation formalism was used to build the models for geometry optimizations. No frequency calculations were performed by taking into account solvent effects using the electron density at the Fe nucleus, using a linear dielectric constant for methanol ($\varepsilon = 32.7$).33

Relativistic effects were not included, since their contribution was shown to be minor and contraction of inner $s$ functions was kept.33 The $\Delta E_Q$ value is obtained directly by the program when an electric field gradient (EFG) calculation is performed. The isomer shift was obtained from the electron density at the Fe nucleus, using a linear fit function as proposed by Vanko:66 $\delta = \alpha(\rho(0) - \zeta) + \beta$. For the methodology described here, $\alpha = -0.459$ au $^{-1}$ mm s$^{-1}$, $\beta = 12.91$ mm s$^{-1}$, and $\zeta = 11800$ au$^{-1}$.33

The 3D orbital representations were obtained with Molekel.51

### ASSOCIATED CONTENT

#### Supporting Information

Figures, a table, and CIF and xyz files giving NMR (1, 5, 6) and HRMS spectra (1, 4–6), crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for complexes 3 and 6, and coordinates of optimized structures (1, 2, 1’, 2’, 4, 6, 7). This material is available free of charge via the Internet at http://pubs.acs.org.

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### REFERENCES


(48) (a) The ORCA basis set “CoreProp” was used. This basis is based on the TurboMole DZ basis developed by Ahlrichs and co-workers and obtained from the basis set library under ftp.chemie.uni- karlsruhe.de/pub/basen. (b) The Ahlrichs (2d2f,3p2d) polarization functions were obtained from the Turbomole basis set library under ftp.chemie.uni-karlsruhe.de/pub/basen Sc-Zn. 2p functions from: Wachters, J. Chem. Phys. 1970, 52, 1033 plus one f function from the TurboMole library.


(53) SAINT, version 5.0; Bruker AXS, Madison, WI, 1998.