ORGANOMETALLICS

Knölker-Type Iron Complexes Bearing an N-Heterocyclic Carbene Ligand: Synthesis, Characterization, and Catalytic Dehydration of **Primary Amides**

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Supporting Information

ABSTRACT: A family of iron Knölker-type complexes bearing an N-heterocyclic carbene (NHC) ligand has been synthesized from the corresponding tricarbonyl(η^4 -cyclopentadienone)iron complex by reaction with the in situ generated NHC ligand, under UV irradiation (350 nm) at room temperature. The six complexes, obtained in good yields (64-84%) after purification on column chromatography, were fully characterized, including



X-ray diffraction and electrochemical studies. The activity of these complexes in catalysis has been demonstrated for the dehydration of primary benzamides into benzonitriles under hydrosilylation conditions using inexpensive polymethylhydrosiloxane (PMHS) as the hydrosilane at 100 °C.

INTRODUCTION

Since the discovery of the potential of tricarbonyl(η^4 cyclopentadienone)iron complexes in catalysis by Casey in 2007,¹ especially in the reduction area, this family of complexes has gained a renewal of interest over the last few years.² Tricarbonyl(η^4 -cyclopentadienone)iron complexes were synthesized in the 1950s³ and studied in depth by Knölker in the 1990s,⁴ including the synthesis of the (hydroxycyclopentadienyl)iron hydride complex in 1999,^{4e} which is the iron structural analogue of Shvo's complex with ruthenium.⁵ Knölker-type complexes are attractive due to their versatile applications in redox catalysis: they have been successfully applied in hydrogenation,^{1,6} hydrogen transfer,^{6m,n,7c} including asymmetric versions, ${}^{6h-j}$ oxidation, reductive amination, and more recently in hydrogen-borrowing reactions.9

From the point of view of ligand design, two main strategies concerning the modification of the framework of the Knölkertype complexes have been followed, in order to improve the catalytic activities or achieve novel reactivity. The first deals with the modification of the substitution pattern of the cyclopentadienone ring. Representative examples are given in Figure 1, showing the modification of the nature of the substituents at the 2- and 5-positions by substituting the TMS groups with various silvlated motifs^{6k,8b} or with a phenyl group.^{8b} The nature of the cycle fused to the cyclopentadienone ring has also been modulated: five- or sixmembered rings including alkyl chains, heteroatoms (O, S_1^{4b} N⁸), and chiral versions.^{6h,l,m} Finally, the carbonyl moiety has also been recently silvlated.¹⁰ The second strategy to modulate the structure of these complexes relies on the substitution of



Figure 1. Principal modifications of Knölker-type complexes.

one of the carbonyl ligands, by a nitrile (acetonitrile^{4d,7c,d} or benzonitrile^{6a}), a pyridine,^{6a} a phosphine,¹¹ or a chiral phosphoramidite.^{6h} Thus, Knölker-type complexes can now be seen as an easily modulated organometallic platform that can be subjected to further modifications due to the growing impact of iron complexes in catalysis.¹² Surprisingly, Knölker-type derivatives bearing an N-heterocyclic carbene (NHC) as a ligand have not been described to date.¹³ Hence, we have explored the synthesis and catalytic activities of Knölker-type complexes bearing various N-heterocyclic carbene ligands.

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RESULTS AND DISCUSSION

Preparation of the Complexes. Previously, two routes have been developed to introduce a phosphine or a nitrile by exchange with a CO ligand, either under thermal conditions in refluxing Bu_2O or acetone in the presence of Me_3NO^{4a-c} or under photochemical conditions using UV irradiation.^{4d} To introduce the N-heterocyclic carbene ligand in the coordination sphere of the iron, we have chosen the photochemical pathway on the basis of our experience in the photochemistry of iron carbonyl complexes.¹⁴ As a model reaction, a solution of **1** and of the free 1,3-dimesitylimidazol-2-ylidene carbene (IMes) (obtained by deprotonation with potassium hexamethyldisilazide (KHMDS) of the corresponding chloride salt, IMes·HCl) was irradiated under UV (350 nm) in toluene for 20 h at room temperature, leading to the expected ligand exchange of one CO for the N-heterocylic carbene (Scheme 1). During the

Scheme 1. General Synthesis of the Complexes



course of the reaction, the solution turned from brown to dark deep yellow. The ¹H NMR of the crude mixture indicated a conversion of 90% of 1 to the expected complex 2 (10% of unreacted 1 was also detected). Interestingly, the complex was purified by column chromatography on silica gel in air, leading to the isolation of 2 as a golden yellow solid in 78% yield. It should also be pointed out that the reaction was performed on a gram scale.

The same procedure was applied to the preparation of complexes bearing various symmetrical unsaturated NHC ligands bearing respectively a methyl (IMe), an isopropyl (IiPr), or a cyclohexyl (ICy) substituent on each of the nitrogen atoms, leading to 3-5 in good yields (Figure 2). It is noteworthy that the coordination of the saturated 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (SIMes) N-heterocylic carbene on 1 took place, as monitored by ¹H NMR, but unfortunately



Figure 2. NHC-substituted Knölker-type complexes (isolated yield indicated under the structure).

this complex was not stable and decomposed during the steps of purification.

To synthesize unsaturated unsymmetrical NHC ligands, we have followed the recent procedure described by Baslé and Maudit¹⁵ to prepare the *N*-mesityl-*N*-cyclohexylimidazolium salt. In a similar fashion, starting from (*R*)-phenylethylamine and mesitylamine, a chiral dissymmetric imidazolium chloride was prepared in moderate yield (28%). Both ligands have also been successfully coordinated to the iron center following the route described above (**6** and 7; 65 and 76% yields, respectively) (Figure 2).

Characterization of the Complexes. All of the complexes have been fully characterized by ¹H and ¹³C{¹H} NMR, IR, X-ray diffraction studies, cyclic voltammetry, HR-MS, and elemental analysis.

NMR and IR Studies. The coordination of the N-heterocyclic carbene has been ascertained by ¹³C{¹H} NMR, where the carbene carbon atoms appear between 181.5 and 187.8 ppm. These chemical shifts are in agreement with those of the carbene carbon of the analogous (NHC)Fe(CO)₄ complexes.¹⁶ In a similar manner, the carbons of the carbonyl groups appear between 216.7 and 219.3 ppm, in accordance with the (NHC)Fe(CO)₄ complexes.¹⁶ These signals are shifted to low field in comparison to the CpFe(CO)₂(NHC)⁺ cationic complexes, which display a chemical shift typically around 209–210 ppm.^{14,17} This is in agreement with the poorer donating ability of the neutral cyclopentadienone ligand in comparison to the anionic cyclopentadienide ligand. In the case of the chiral complex 7, the two resonances appear for the diastereotopic CO ligands at 216.7 and 217.1 ppm.

The ¹H NMR spectra of the complexes at room temperature are straightforward: all of them show the presence of the cyclopentadienone ring and the NHC ligand.

The stretching frequencies of the carbonyl ligands in IR are reported in Table 1. In comparison to the unsubstituted

Table 1. Summary of	Relevant	Spectroscopic	and
Electrochemical Data			

complex	$ u_{\rm CO}~({\rm cm}^{-1})$	$\nu_{\rm CO}^{\rm av} ({\rm cm}^{-1})^a$	$\begin{bmatrix} E_{1/2} (V) \\ [\Delta E_{p} (mV)]^{b} \end{bmatrix}$	$\frac{\text{TEP value}}{(\text{cm}^{-1})^c}$
2	1978, 1913	1945	0.11^{d} [-]	2050.5
3	1975, 1919	1947	0.16 [75]	2054.1
4	1975, 1924	1949	0.12 [78]	2051.5
5	1969, 1907	1938	0.10 [93]	2049.7
6	1980, 1919	1949	0.04 [108]	2050.8
7	1973, 1915	1944	0.14^d [91]	

 ${}^{a}\nu_{\rm CO}{}^{\rm av}$ is the average value of the frequencies of the two CO stretching bands (recorded in the solid state using ATR equipment). b Conditions unless stated otherwise: sample concentration 1 mM, Bu₄NPF₆ (0.2 M) in CH₂Cl₂, $\nu = 100$ mV s⁻¹, potentials reported in V vs [FeCp₂]/ [FeCp₂]⁺. The internal decamethylferrocene standard showed a wave with $\Delta E_{\rm p} = 60-70$ mV. ^cTolman electronic parameters according to refs 15 and 18. d Measured at 800 mV s⁻¹.

Knölker-type complex 1 ($\nu_{\rm CO}$ 2061, 2053, 1987 cm⁻¹, $\nu_{\rm CO}^{\rm av}$ 2033 cm⁻¹),^{8c} or substituted Knölker-type derivatives with a benzonitrile (1971 cm⁻¹),^{6a} a triphenylphosphine (1965 cm⁻¹),^{11a} or an acetonitrile (1953.5 cm⁻¹)^{7c} motif, the $\nu_{\rm CO}^{\rm av}$ values for all of the complexes appear at lower frequencies, which demonstrate the strongly electron donating character of the NHC ligand. In addition, the stretching frequencies were approximated to the reported TEP values for the NHCs.^{15,18}

Electrochemical Studies. In order to understand more specifically the electronic properties of the metal center, we have also performed electrochemical studies of the NHC-Knölker complexes. Cyclic voltammetry measurements have been performed in dichloromethane (0.2 M Bu₄NPF₆). The six complexes showed an oxidation process at potentials between 0.04 and 0.16 V vs [FeCp₂]/[FeCp₂]⁺ (Table 1 and Figures 3



Figure 3. Normalized CV traces of complexes **3**, **5**, and **6** in CH₂Cl₂. Conditions: sample concentration 1 mM, 0.2 M Bu₄NPF₆, $\nu = 100$ mV s⁻¹.



Figure 4. Normalized CV traces of complexes **2** and **7** in CH₂Cl₂. Conditions: sample concentration 1 mM, 0.2 M Bu₄NPF₆, $\nu = 100$ mV s⁻¹.

and 4). This process can be assigned to the Fe(II)/Fe(III) redox couple. It occurs at a low potential due to the donating effect of the carbene ligand (note: that the oxidation process of an analogous complex in which the carbene ligand is replaced by a phosphine ligand is found at 0.52 V; see Figure S1 in the Supporting Information). In the case of complexes 3-6, the monoelectronic wave is reversible (3 and 4) or quasi-reversible (5 and 6) with i_c/i_a ratios of 1. However, for complex 2, the oxidation wave is chemically irreversible at low scan rates $(i_c/i_a = 0.56 \text{ at } 100 \text{ mV s}^{-1})$. This is an indication that the Fe(III) species is not stable in that case. The oxidation potential $E_{1/2}$ could be measured only at higher scan rates, at which the chemical reversibility was obtained. A similar behavior is obtained for the complex 7 $(i_c/i_a = 0.75 \text{ at } 100 \text{ mV s}^{-1})$. For

complexes 2–5, the values of the oxidation potentials correlate well with the TEP values: the iron center is electron richer and therefore easier to oxidize as the ligands are stronger donors (5 > 2 > 4 > 3). For the complexes bearing unsymmetrically substituted carbene ligands (6 and 7), the correlation is less obvious. Quite unexpectedly, complex 6 is more prone to oxidation than the symmetrical conterparts 2 and 5, whereas the $E_{1/2}$ of 7 ranks, as expected, between those of 2 and 3.

X-ray Diffraction Studies. For each of the complexes, suitable single crystals have been obtained by diffusion of pentane in a concentrated solution of the complex in CH₂Cl₂. The X-ray diffraction studies confirmed the molecular structure of the complexes (Figures 5 and 6). In the solid state, the piano-stool geometry of the precursor is maintained with angles around the metal close to 90° (for example, in 2, the angles OC-Fe-CO and OC-Fe-NHC are 86.58(9), 94.73(9), and $98.57(8)^{\circ}$). In the cases of the complexes bearing at least one mesityl substituent on the imidazolidene motif, i.e. 2, 6, and 7, an interesting geometrical feature is the proximity of one CO ligand and the ipso carbon of the mesityl group and the pronounced bent structure of the same carbonyl ligand (Figure 7). Indeed, for the complexes 2, 6, and 7, the angles involving the Fe–C–O atoms are 168.7(2), 170.0(3), and $170.6(5)^{\circ}$, respectively, and the distances $CO-C_{ipso}$ are 2.778(3), 2.852(4), and 2.849(8) Å, respectively. Such features, i.e. a short distance d < 3.1 Å and an angle $\alpha < 175^{\circ}$, has been described as the signature of a latent Cipso-CO interligand interaction by Lugan on the basis of the studies of Fischer-type manganese carbene complexes.¹⁹ This noncovalent interaction can be found in various NHC/carbonvl or NHC/alkvlidene complexes, including Fe-NHC and Ru-NHC complexes, and its role has been identified in the case of the metathesis reaction.¹⁹⁶

Catalytic Applications. With these new complexes in hand, we have explored their potential in catalytic reactions to enlarge the scope of applications of Knölker-type derivatives in the reduction area. On the basis of our research interest in hydrosilylation reactions with iron carbonyl catalysts such as Fe(NHC)(CO)₄, Fe(CO)₃(cod), and Fe(CO)₃(trans-4-phenylbuten-2-one) complexes, which were respectively applied for the hydrosilylation of esters^{16b} and carboxylic acids²⁰ into aldehydes, we have evaluated the activity of the new complexes 2-6 in the dehydration of primary amides into nitrile derivatives.²¹ To the best of our knowledge, only two examples of the latter reaction catalyzed with iron have been reported by Beller^{21b} and us,^{21c} using respectively diethoxymethylsilane and phenylsilane as the dehydrating reagents. In this study, we have selected the inexpensive PMHS (polymethylhydrosiloxane) as the dehydration reagent, complex 2 as the model precatalyst, and benzamide as the model substrate to optimize the conditions of the reaction (Scheme 2 and Table 2).

To our delight, benzamide can be converted to benzonitrile in high yield using 5 mol % of catalyst **2** at 100 °C in the presence of 5 equiv of PMHS in different solvents, such as toluene, CPME (cyclopentyl methyl ether), and 1,4-dioxane (Table 2, entries 1–3). The reaction did not proceed in THF, dimethyl carbonate, or ethanol (see Table S1 in the Supporting Information). It must be pointed out that decreasing the temperature (entry 4), the catalyst loading (entry 5), or the quantity of hydrosilanes (entries 6 and 7) has a deleterious effect on the reaction. We have also checked the effect of UV irradiation to promote the reaction at 35 °C, but the conversion was very low (entry 8).







5



7

Figure 6. ORTEP views of complexes 5-7, with thermal ellipsoids drawn at the 50% probability level.



Figure 7. Noncovalent $CO-C_{ipso}$ interaction in the solid state.

noteworthy that, except for the benzamide, the poor solubility of other primary amides in toluene or CPME was problematic.

Figure 5. ORTEP views of complexes 2-4 with thermal ellipsoids drawn at the 50% probability level. One molecule of CH_2Cl_2 was omitted for clarity for complex **2**. The fused ring of the cyclopentadienone ligand of complex **4** is disordered over two positions, only one of which is depicted.

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We then compared the efficiencies of the different catalysts: at 100 °C in toluene, under the optimized conditions, complexes 2-6 displayed similar activities, as full conversions were obtained in each case (see Table S2 in the Supporting Information).²² Interestingly, under such conditions, Knölker catalyst 1 was completely inactive (entry 9) and Fe(IMes)-(CO)₄ led to a moderate yield of 57% (entry 10), which demonstrates both the importance of the N-heterocyclic carbene and the influence of the cyclopentadienone as the ligand.

Once the optimized conditions were found, the scope of the dehydration of primary amides with PMHS catalyzed by **2** was then explored, and the results are summarized in Table 3. It is

Scheme 2. Dehydration of Benzamide into Benzonitrile Catalyzed by Iron



 Table 2. Optimization of the Parameters of the Iron-Catalyzed Dehydration of Benzamides^a

entry	amt of PMHS (equiv)	solvent	temp (°C)	yield (%) ^b
1	5	toluene	100	97
2	5	1,4-dioxane	100	94
3	5	CPME	100	97
4	5	CPME	80	18
5°	5	CPME	100	51
6	3	CPME	100	87
7	2	CPME	100	35
8 ^d	5	CPME	UV	6
9 ^e	5	toluene	100	2
10 ^f	5	toluene	100	57

^{*a*}Typical conditions: catalyst **2** (5 mol %), benzamide (0.25 mmol), toluene (2 mL), and PMHS (5 equiv) were added in that order under an argon atmosphere, and the solution was heated to 100 °C for 24 h. ^{*b*}Determined by GC using dodecane as the internal standard. ^{*c*} 3 mol % of catalyst **2** was used. ^{*d*} 350 nm, 35 °C. ^{*e*} **1** as the catalyst. ^{*f*}(IMes)Fe(CO)₄ as the catalyst.

Table 3. Scope of Primary Amides to Nitriles^a

Entry	Amide	Cat (mol%)	Time (h)	Conv. ^b (%)	Yield ' (%)
1	NH ₂	5	24	>97	72
2	NH ₂	5	24	>97	84
3	NH ₂	5	48	>97	77
4	NH ₂	8	48	82	72
5	Br NH ₂	8	48	75	53
6	NH ₂	8	48	63	52
7 ^d	NH ₂	8	48	65	61

^{*a*}Reaction conditions: catalyst **2** (5–8 mol %), amide (1 mmol), THF/ 1,4-dioxane (2:2 mL), and PMHS (5 equiv), 100 °C, under an argon atmosphere. ^{*b*}The conversion was determined by ¹H NMR. ^{*c*}Isolated yield. ^{*d*}2% of 3-phenylpropionitrile was detected.

Therefore, the solvent of the reaction was switched to a mixture of THF and dioxane (1/1, v/v). The dehydration proceeded well for amides bearing an electron-donating group (Table 3, entries 1–4), giving full conversions with good isolated yields (72–84%). Benzamides with electron-withdrawing groups (Table 3, entries 5 and 6) such as bromo and chloro were also well tolerated, as no dehalogenation product was detected.

Finally, the conjugated cinnamic amide (Table 3, entry 7) was converted to the cinnamyl nitrile (65% conversion, 61% yield). Interestingly, only 2% of the saturated product 3-phenyl-propionamide, resulting from the reduction of the conjugated C=C bond, was detected.

CONCLUSION

In conclusion, we have synthesized and fully characterized a new family of NHC-substituted iron Knölker-type complexes by UV-promoted substitution of one CO ligand by the corresponding NHC ligand. All of the complexes have been obtained in good yields and fully characterized. Their potential in catalysis has been demonstrated in the case of the dehydration of primary benzamides into benzonitrile derivatives using the inexpensive PMHS as the dehydrating reagent. These results open the way to apply Knölker-type complexes in hydrosilylation reactions.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out with oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon or in an argon-filled glovebox. Toluene, THF, diethyl ether (Et₂O), and CH₂Cl₂ were dried over a Braun MB-SPS-800 solvent purification system and degassed by thaw-freeze cycles. Technical grade pentane and diethyl ether were used for column chromatography. Analytical TLC was performed on Merck $60F_{254}$ silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 μ m, 60 Å). All reagents were obtained from commercial sources, and liquid reagents were dried on molecular sieves and degassed prior to use. ¹H and ¹³C{¹H} NMR spectra were recorded in CDCl₃ or C_6D_6 at ambient temperature unless otherwise stated, on Bruker AVANCE 500, AVANCE 400, and AVANCE 300 spectrometers at 500, 400, and 300 MHz, respectively. $^1\mathrm{H}$ and $^{13}\mathrm{\dot{C}}$ spectra were calibrated using the residual solvent signal as an internal standard ($^1\mbox{H},$ CDCl₃ 7.26 ppm, C₆D₆ 7.16 ppm; ¹³C, CDCl₃ central peak is 77.00 ppm, C₆D₆ central peak is 128.06 ppm). IR spectra were measured with a Shimadzu IR-Affinity 1 instrument with ATR equipment. HR-MS spectra and microanalyses were carried out by the corresponding facilities at the CRMPO, Centre Régional de Mesures Physiques de l'Ouest, University of Rennes 1.

X-ray diffraction data were collected on an APEXII Bruker-AXS diffractometer equipped with a CCD detector, using graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) at T = 150(2) K. The structure was solved by direct methods using the SIR97 program²³ and then refined with full-matrix least-squares methods based on F^2 (SHELXL-97)²⁴ with the aid of the WINGX²⁵ program.

Electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat; the working electrode was a Pt disk, and the SCE electrode was used as the reference electrode. The sample concentration was ~1 mM (CH₂Cl₂, 0.2 M Bu₄NPF₆), and the solution was carefully deoxygenated by argon bubbling. The applied potential was measured with decamethylferrocene as the internal reference and calculated versus ferrocene with $E^{\circ}([FeCp_2]/$ $[FeCp_2]^+) = +0.542$ V vs $[FeCp*_2]/[FeCp*_2]^+$. UV irradiation was performed in a Rayonet RPR-100 apparatus at 350 nm. The imidazolium salts NHC·HX^{15,26} and Knölker's complex 1^{7c}

The imidazolium salts NHC·HX^{15,20} and Knölker's complex 1⁷ were prepared according to the published procedures.

Synthesis of the Complexes. Synthesis of Complex 2: Representative Procedure. To a suspension of 1,3-dimesitylimidazolium chloride (1.20 g, 3.6 mmol, 1.5 equiv) in toluene (10 mL) was added KHMDS (0.5 M in toluene, 7.9 mL, 3.9 mmol, 1.6 equiv) dropwise at room temperature, and the solution was vigorously stirred for 30 min. The resulting white suspension was directly filtered through Celite into a Schlenk tube containing Knölker's precursor 1 (1.00 g, 2.3 mmol, 1 equiv) in toluene (10 mL). Then, the reaction mixture was irradiated under UV (350 nm) at room temperature for 20 h. After completion of the reaction, the initial brown solution turned dark yellow. The solvent was evaporated under vacuum. The resulting residue was purified by column chromatography on silica gel. A yellow fraction of the expected complex was collected (petroleum ether/ethyl acetate 80/20) and concentrated under vacuum to give 2 (1.25 g, 78%) as a golden yellow powder. Single crystals suitable for X-ray diffraction studies were grown by layering a concentrated solution of the complex in CH_2Cl_2 with pentane.

¹H NMR (400 MHz, CDCl₃): δ 6.99 (s, 4 H, CH_{Mes}), 6.85 (s, 2 H, CH_{NHC}), 2.35 (s, 6 H, *p*-CH₃), 2.19–2.17 (m, 4 H, CH₂), 2.15 (s, 12 H, *o*-CH₃), 1.34–1.31 (m, 2 H, CH₂), 0.98–0.95 (m, 2 H, CH₂), 0.05 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 217.4 (2 CO), 187.8 (NCN), 179.5 (C=O), 139.6 (Co), 138.2 (Ci), 136.4 (Cp), 129.4 (Cm), 126.2 (CH_{NHC}), 104.9 (C=CSi), 67.5 (CSi), 24.6 (CH₂), 21.9 (CH₂), 21.0 (*p*-CH₃), 19.1 (*o* –CH₃), 0.5 (SiMe₃). IR (ATR, ν , cm⁻¹): 1978, 1913, 1577. Anal. Calcd for C₃₈H₅₀N₂O₃FeSi₂: C, 65.69; H, 7.25; N, 4.03. Found: C, 65.24; H, 7.18; N, 3.92. HR-MS [ESI]: *m*/z [M + H]⁺ calcd for C₃₈H₅₁N₂O₃⁵⁶FeSi₂ 695.2787, found 695.2782 (0 ppm).

Synthesis of Complex 3. Following the representative procedure using 1,3-dimethylimidazolium hexafluorophosphate (87 mg, 0.35 mmol) and 1 (100 mg, 0.24 mmol), complex 3 was obtained as a yellow powder (75 mg, 64%).

¹H NMR (500 MHz, CDCl₃): δ 6.98 (s, 2 H, CH_{NHC}), 3.91 (s, 6 H, Me_{NHC}), 2.45 (m, 4 H, CH₂), 1.85–1.78 (m, 4 H, CH₂), 0.17 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 217.2 (2 CO), 185.0 (NCN), 176.8 (C=O), 123.6 (CH_{NHC}), 103.7 (C=CSi), 70.9 (CSi), 39.9 (Me_{NHC}), 24.6 (CH₂), 22.6 (CH₂), 0.3 (SiMe₃). IR (ATR, ν , cm⁻¹): 1975, 1919, 1548. Anal. Calcd for C₂₂H₃₄N₂O₃FeSi₂: C, 54.31; H, 7.04; N, 5.76. Found: C, 54.29; H, 7.03; N, 5.58. HR-MS [ESI]: *m*/z [M + H]⁺ calcd for C₂₂H₃₅N₂O₃⁵⁶FeSi₂ 487.1530, found 487.1533 (1 ppm).

Synthesis of Complex 4. Following the representative procedure using 1,3-diisopropylimidazolium hexafluorophosphate (107 mg, 0.35 mmol) and 1 (100 mg, 0.24 mmol), complex 4 was obtained as a yellow powder (110 mg, 84%).

¹H NMR (500 MHz, C_6D_6): δ 6.53 (s, 2 H, CH_{NHC}), 5.13 (sept, ³*J* = 6.4 Hz, 2 H, CH_{1pr}), 2.59–2.54 (m, 2H, CH₂), 2.45–2.37 (m, 2 H, CH₂), 1.83–1.79 (m, 2 H, CH₂), 1.57–1.53 (m, 2 H, CH₂), 1.24 (d, 12 H, ³*J* = 6.4 Hz, CH_{3ipr}), 0.32 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (125 MHz, C_6D_6) δ 219.3 (2 CO), 183.1 (NCN), 177.7 (C=O), 119.0 (CH_{NHC}), 103.4 (C=CSi), 72.6 (CSi), 51.8 (CH_{1pr}), 25.5 (CH₂), 24.7 (CH_{3ipr}), 22.8 (CH₂), 0.5 (SiMe₃). IR (ATR, ν , cm⁻¹): 1975, 1924, 1583. Anal. Calcd for $C_{26}H_{42}N_2O_3FeSi_2$: C, 57.55; H, 7.80; N, 5.16. Found: C, 57.48; H, 7.85; N, 4.96. HR-MS [ESI]: m/z [M + H]⁺ calcd for $C_{26}H_{43}N_2O_3^{56}FeSi_2$ 543.2156 found 543.2158 (0 ppm).

Synthesis of Complex 5. Following the representative procedure using 1,3-dicyclohexylimidazolium tetrafluoroborate (229 mg, 0.72 mmol) and 1 (200 mg, 0.48 mmol), complex 5 was obtained as a yellow powder (210 mg, 70%).

¹H NMR (500 MHz, CDCl₃): δ 7.08 (s, 2 H, CH_{NHC}), 4.81–4.75 (m, 2 H, CH_{Cy}), 2.48–2.35 (m, 4 H, CH₂), 2.06–1.20 (m, 24 H), 0.11 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 217.4 (2 CO), 181.5 (NCN), 178.3 (C=O), 119.6 (CH_{NHC}), 104.1 (C=CSi), 68.5 (CSi), 58.9 (CH_{Cy}), 35.5 (CH₂), 25.3 (CH_{2Cy}), 25.2 (CH_{2Cy}), 24.0 (CH₂), 22.6 (CH_{2Cy}), 0.01 (SiMe₃). IR (ATR, ν , cm⁻¹): 1969, 1907, 1585. Anal. Calcd for C₃₂H₅₀N₂O₃FeSi₂: C, 61.72; H, 8.09; N, 4.50. Found: C, 61.98; H, 8.32; N, 4.45. HR-MS [ESI]: m/z [M + H]⁺ calcd for C₃₂H₅₁N₂O₃⁵⁶FeSi₂ 623.2782, found 623.2781 (0 ppm).

Synthesis of Complex 6. Following the representative procedure using 3-cyclohexyl-1-mesitylimidazolium chloride (220 mg, 0.72 mmol) and 1 (200 mg, 0.48 mmol), complex 6 was obtained as a yellow powder (203 mg, 65%).

¹H NMR (400 MHz, CDCl₃): δ 7.30 (s, 1 H, CH_{NHC}), 6.95 (s, 2 H, CH_{Mes}), 6.86 (s, 1 H, CH_{NHC}), 4.79–4.73 (m, 1 H, CH_{Cy}), 2.33–2.25 (m, 8 H), 1.97 (s, 6H, *o*-CH₃), 1.85–1.56 (m, 9 H), 1.28–1.21 (m, 4 H); 0.14 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 217.6 (2 CO), 186.9 (NCN), 177.5 (C=O), 139.3 (C_{qMes}), 137.9 (C_{qMes}), 136.3 (C_{qMes}), 129.2 (CH_{Mes}), 125.1 (CH_{NHC}), 120.5 (CH_{NHC}), 102.9 (C=CSi), 70.4 (CSi), 58.3 (CH_{Cy}), 35.2 (CH₂), 29.7 (CH₂), 25.4

(CH₂), 24.8 (CH₂), 24.4 (CH₂), 22.3 (CH₂), 21.0 (*p*-CH₃), 18.9 (*o*-CH₃), 0.71 (SiMe₃). IR²⁷ (ATR, ν , cm⁻¹): 1980, 1919, 1575, 1548. IR²⁷ (CH₂Cl₂, ν , cm⁻¹): 1979, 1919, 1570. Anal. Calcd for C₃₅H₅₀N₂O₃FeSi₂: C, 63.61; H, 7.65; N, 4.25. Found: C, 64.09; H, 7.80; N, 3.89. HR-MS [ESI]: m/z [M + H]⁺ calcd for C₃₅H₅₁N₂O₃⁵⁶FeSi₂ 659.2782, found 659.2779 (0 ppm).

Synthesis of Complex 7. Following the representative procedure using 1-mesityl-3-[(R)-1-phenylethyl]imidazolium chloride (235 mg, 0.32 mmol) and 1 (200 mg, 0.48 mmol), complex 7 was obtained as a yellow powder (250 mg, 76%).

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, ³J = 7.8 Hz, 2H), 7.36 (d, ³J = 7.5 Hz, 2H), 7.28 (m, 1H), 6.98 (s, 1H, CH_{Mes}), 6.97 (s, 1H, CH_{Mes}), 6.91 (d, ${}^{3}J$ = 1.8 Hz, 1H, CH_{NHC}), 6.84 (d, ${}^{3}J$ = 1.8 Hz, 1H, CH_{NHC}), 6.06 (q, ³J = 6.5 Hz, 1 H, CH), 2.34 (s, 3H, CH_{3Mes}), 2.40-2.21 (m, 4H, CH₂), 2.08 (s, 3H, CH_{3Mes}), 2.05 (s, 3H, CH_{3Mes}), 1.94 $(d, {}^{3}J = 6.5 Hz, 3H, CH_{3}), 1.70-1.40 (m, 4H, CH_{2}), 0.11 (s, 9H, 3H)$ SiMe₃), 0.06 (s, 9H, SiMe₃). ${}^{13}C{}^{1}H{}$ NMR (125 MHz, CDCl₃) δ 217.1 (CO), 216.7 (CO), 187.4 (NCN), 180.0 (C=O), 142.2 (C_{gAr}), 139.5 (C_{qMes}), 138.2 (C_{qMes}), 136.5 (C_{qMes}), 136.2 (C_{qMes}), 129.3 (CH_{Mes}), 129.2 (CH_{Mes}), 128.3 (m-CH_{Ar}), 127.3 (p-CH_{Ar}), 127.2 (o- CH_{Ar}), 125.0 (CH_{NHC}), 121.8 (CH_{NHC}), 104.6 (C=CSi), 99.7 (C=CSi), 70.6 (CSi), 69.5 (CSi), 57.7 (CH), 25.0 (CH₂), 23.8 (CH₂), 22.2 (CH₂), 22.0 (CH₂), 21.9 (CH₃), 21.0(CH_{3Mes}), 19.1(CH_{3Mes}), 18.4 (CH_{3Mes}) , 0.5 (SiMe₃), 0.4 (SiMe₃). IR²⁷ (ATR, ν , cm⁻¹): 1973, 1915, 1585, 1552. IR²⁷ (CH₂Cl₂, *ν*, cm⁻¹): 1980, 1921, 1574. Anal. Calcd for C37H48N2O3FeSi2: C, 65.28; H, 7.11; N, 4.11. Found: C, 65.39; H, 7.04; N, 4.07. HR-MS [ESI]: m/z [M + Na]⁺ calcd for C37H48N2O3NaSi256Fe 703.2450, found 703.2467 (2 ppm).

Typical Procedure for the Iron-Catalyzed Dehydration of Primary Benzamide to Nitriles. A Schlenk tube containing a stirring bar was loaded with the primary amide (1.0 mmol), followed by the addition of the iron complex (0.05–0.08 mmol), the solvent (dry toluene or 1,4-dioxane/THF, 4 mL), and finally PMHS (5.0 mmol). The mixture was stirred for 24 h at 100 °C. After completion of the reaction, the mixture was cooled to room temperature. The latter was diluted with ethyl acetate (5 mL) and concentrated under reduced pressure (850 mbar, 40 °C). The residue was purified by silica gel column chromatography, giving the corresponding nitrile.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00553. Complete details of the X-ray analyses reported herein have also been deposited at the Cambridge Crystallographic Data Center (CCDC 1414335 (2), 1414336 (3), 1414337 (4), 1414338 (5), 1414339 (6), 1414340 (7)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, by emailing data_request@ccdc.cam.ac.uk ,or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, U.K.; fax + 44 1223 336033.

NMR spectra and characterization data for the complexes and the products of catalysis (PDF) Crystallographic data for 2–7 (CIF)

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Notes

The authors declare no competing financial interest.

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