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An Iron(II) Complex of a Diamine-Bridged Bis-N-Heterocyclic Carbene

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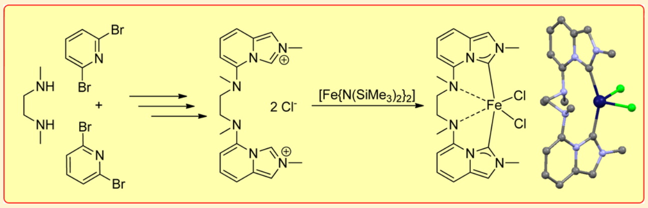
S *Supporting Information*

ABSTRACT: A diamine-bridged bis-N-heterocyclic carbene ligand was synthesized as imidazolium salts with chloride or triflate counteranions. Deprotonation of the chloride salt by an iron bis-amide complex or addition of the free diamine-bis-carbene ligand to $FeCl_2$ led to the formation of an Fe(II) dichloride complex having a diamine-bis-carbene ligand, in which the iron atom is in a highly distorted octahedral geometry with weak Fe-N interactions. This iron complex was found to catalyze the hydrosilylation of acetophenone.



N-heterocyclic carbenes (NHCs) have already become an indispensable class of ligands for transition-metal complexes applied in homogeneous catalysis.[1,2] Their strong σ-donating ability renders them valuable substitutes for phosphine ligands, exhibiting more stable metal−ligand bonding and thus increased complex robustness. In addition to complexes of noble metals, recently Fe-NHC complexes have also gained considerable attention, due to their possible application as cheap, environmentally benign, and powerful catalyst precursors.[3] Well-defined[4,5] and in situ generated[6] Fe-NHC complexes have been applied in homogeneous catalysis, and most of them carry monodentate NHC ligands. NHCs incorporated in a chelating scaffold have advantages in preventing undesirable substitution of the NHC moiety, leading to enhanced complex stability and to possible modulation of reactivity. This concept has been demonstrated for iron complexes having alkyl-bridged bidentate bis(imidazolylidene),[7] tripodal tris(imidazolylidene)borate[8] and -amine,[9] pincer type 2,6-bis(imidazolylidene)pyridine,[10] and tetradentate tetrakis(imidazolylidene)[11] ligands.

Our design of a new chelating NHC ligand was inspired by the cis-α coordination geometry of nonheme iron(II) catalysts with tetradentate nitrogen ligands, which provide two cis-oriented binding sites at the iron center. Representative examples are BPMEN[12a,b] and BQEN[12c,d] (Figure 1), each using two pyridine/quinoline and amine donors; these have been shown to afford iron complexes effective for challenging C−H oxidation reactions.[12e−i] In this study, we envisioned the replacement of the terminal nitrogen donor groups by NHCs, such as **A** in Figure 1, but taking into account the possible side reactions at the aminal moiety of **A**, we chose to incorporate an aromatic ring system in place of the bridging methylene unit of **A**. We also considered a sterically less demanding methyl group as the substituent of the NHC moiety, to reduce the possible steric congestion around the metal center.

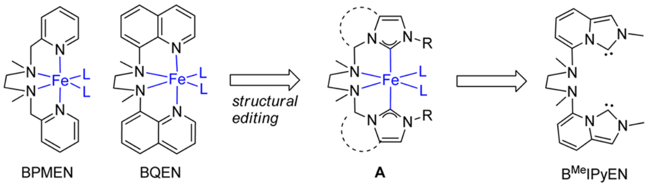


Figure 1. Design of the chelating bis-carbene ligand.

Herein, we report the synthesis and characterization of a new Fe-NHC complex bearing the bis(imidazo[1,5-*a*]pyridine-3-ylidene) ligand $B^{Me}IPyEN$, which features two amine moieties in addition to two NHC groups. Preliminary results on the hydrosilylation of acetophenone catalyzed by the new Fe-NHC complex are also presented.

As shown in Scheme 1, the synthesis of the imidazolium salt starts from the reaction of *N*,*N*′-dimethylethylenediamine (DMEDA) with 2,6-dibromopyridine in the presence of K_2CO_3, where compound **1** was obtained in 92% yield. Subsequent formylation with *n*-butyllithium and dimethylformamide afforded the dialdehyde **2** in 77% yield. For the following step to prepare the imidazolium salts, two routes were engaged: one follows a method reported by Aron et al.,[13] and the dialdehyde **2** was reacted with methylamine hydrochloride and formaldehyde in ethanol at 50 °C to afford the imidazolium chloride **3a** in 75% yield. Alternatively, the imine **4** was formed by the reaction of dialdehyde **2** with methylamine in THF, and **4** was treated with a reagent mixture of silver triflate and chloromethylpivalate to give the imidazolium triflate **3b**, in accordance with the reported procedure.[14] Both routes proved

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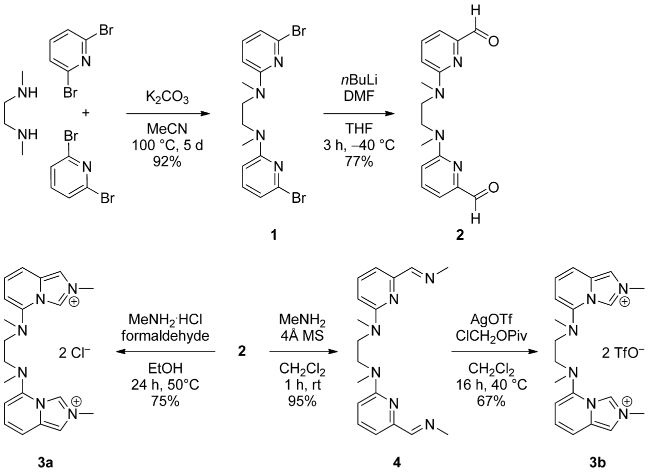
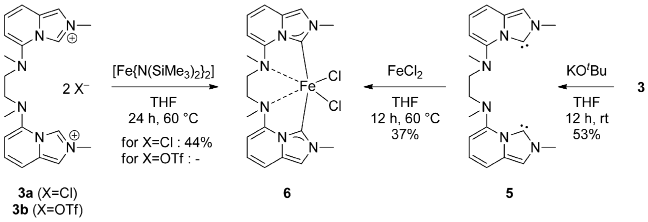
Scheme 1. Synthesis of the Imidazolium Salts



to be suitable for the preparation of the bis(imidazolium)salts. Single crystals were obtained for the triflate salt **3b**, and its structure was determined by an X-ray analysis (Figure S1, Supporting Information).

Scheme 2. Preparation of a Bis-Carbene Iron(II) Chloride Complex from Imidazolium Salts



The iron complex of the new chelating NHC ligand was synthesized via two routes (Scheme 2).[4,7,10] Treatment of the imidazolium chloride **3a** with $Fe\{N(SiMe_3)_2\}_2$[15] in THF at 60 °C afforded the iron(II) dichloride complex **6** as a yellow crystalline powder in 44% yield. Complex **6** was alternatively prepared from the reaction of $FeCl_2$ with free NHC ligand **5**, which was prepared by treatment of **3a** with potassium *tert*-butoxide in THF. Formation of the triflate analogue of **6** was indicated by an ESI-MS analysis of the reaction mixture of **3b** with $Fe\{N(SiMe_3)_2\}_2$; however, we have been unable to isolate it.[16]

Complex **6** is moderately sensitive to air and moisture, both in the solid state and in solution. The magnetic moment of **6** measured by SQUID magnetometry was 5.39−5.65 μ_B at 50−300 K (Figure S2, Supporting Information), which is slightly larger than the spin-only value for the $S = 2$ state (4.90 μ_B). The $S = 2$ state is in accordance with the high-spin electronic configuration of the d^6 iron complex. The ESI-MS spectrum of **6** in acetonitrile displays a major signal at m/z 439.1, which can be attributed to the cationic species $[\mathbf{6} - Cl]^+$ generated by dissociation of a chloride from **6**. Thus, this cationic species probably exists in a minor quantity in equilibrium with **6** in acetonitrile solution. Cyclic voltammetry was measured in acetonitrile and showed a reversible Fe^{II}/Fe^{III} redox couple at −0.37 V versus Ag/Ag^+ (Figure S3, Supporting Information),[17] which is assignable to $[\mathbf{6}]^{0/+}$.

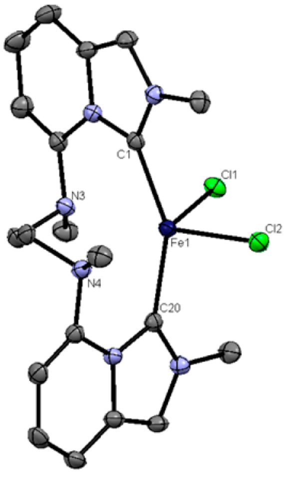


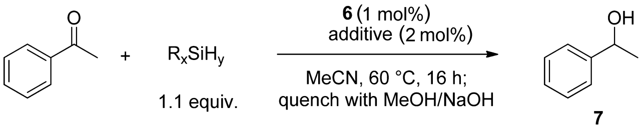
Figure 2. Crystal structure of **6** with 50% probability ellipsoids. Hydrogen atoms and a solvent molecule (MeCN) are omitted for clarity. Selected bond lengths (Å): Fe(1)−C(1), 2.1380(14); Fe(1)−C(20), 2.1172(14); Fe(1)−Cl(1), 2.4386(10); Fe(1)−Cl(2), 2.4130(10); Fe(1)−N(4), 2.5591(19); Fe(1)−N(3), 2.5803(15). Selected bond angles (deg): C(1)−Fe(1)−C(20), 151.66(6); Cl(1)−Fe(1)−C(20), 104.13(5); Cl(2)−Fe(1)−C(1), 101.76(7); Cl(1)−Fe(1)−Cl(2), 98.51(2).

The molecular structure of **6** was determined by X-ray crystallography (Figure 2). The iron atom is in a distorted-octahedral geometry with two NHC ligands, two chlorides, and two weakly interacting nitrogen donors of the ligand backbone. The Fe−C(carbene) distances of 2.1172(14) and 2.1380(14) Å are comparable to those in the high-spin Fe(II) bis-carbene complexes.[7] Due to the rigid framework of the ligand, the C−Fe−C angle of 151.66(6)° is smaller than that expected for an ideal octahedral geometry. Whereas **6** can be also seen as a highly distorted tetrahedral complex, the Fe−N(backbone) distances of 2.5591(14) and 2.5803(15) Å display weak interactions between the iron center, indicating more resemblance to an octahedral geometry. Thus, complex **6** exhibits a unique structure, with a distorted geometry of iron between octahedral and tetrahedral.[18]

With the new iron complex **6** in a unique and rigid coordination geometry, we were interested in the hydrosilylation of acetophenone. Whereas there has been considerable progress in iron-catalyzed hydrosilylation over the last years,[19] only a limited number of Fe-NHC complexes have been employed.[4k,5]

Table 1 summarizes the results of catalytic hydrosilylation of acetophenone using diphenylsilane in slight excess (1.1 equiv). Acetonitrile was used as the solvent to readily dissolve **6** in entries 1 and 3−5. Heating the reaction mixture at 60 °C for 16 h followed by workup afforded the alcohol **7** in 56% yield (entry 1).[20] Analogous reactions in a mixed solvent of MeCN and THF (entry 2) or at higher temperature (entry 3) were not effective in improving the yield. Addition of sodium or silver salts (entries 4 and 5) for removal of chlorides in **6** resulted in lower conversion, possibly due to decreased stability of the cationic complex. Interestingly, when methyllithium was added to generate an Fe-methyl species (entry 6),[21] the catalytic reaction reached full conversion and gave 95% yield of alcohol **7**. Among other silanes tested,[22] only triethoxysilane (entry 7) afforded alcohol **7** in good yield, whereas triethylsilane (entry 8) gave no considerable conversion. To rule out the possibility of a base-catalyzed hydrosilylation,[23] the reaction was performed without addition of iron complex **6**, showing only

Table 1. Hydrosilylation of Acetophenone Catalyzed by 6[a]



entry	additive	silane	reaction conditions	yield, %
1		Ph_2SiH_2	MeCN	56
2		Ph_2SiH_2	MeCN/THF (1/1)	48
3		Ph_2SiH_2	MeCN, 80 °C, 16 h	38
4	NaOAc	Ph_2SiH_2	MeCN	20
5	$AgSbF_6$	Ph_2SiH_2	MeCN	<5
6	MeLi	Ph_2SiH_2	THF, 60 °C, 16 h	95
7	MeLi	$(EtO)_3SiH$	THF, 60 °C, 16 h	78
8	MeLi	Et_3SiH	THF, 60 °C, 16 h	<5
9[b]	MeLi	Ph_2SiH_2	THF, 60 °C, 16 h	5

[a] Reaction conditions unless stated otherwise: acetophenone (0.25 mmol), diphenylsilane (0.28 mmol), complex **6** (1 mol %), acetonitrile (1 mL), 60 °C, 16 h. Quenched with MeOH/NaOH (2 M). Yields determined by crude ^1H NMR using mesitylene (11.4 μL) as internal standard. [b] In the absence of complex **6**.

poor conversion of acetophenone in presence of a catalytic amount of methyllithium (entry 9).

In conclusion, we have developed an efficient route to new bis(imidazolium) salts containing two nitrogen donor atoms in the backbone. An iron(II) complex of a diamine-bridged bis-N-heterocyclic carbene was synthesized from the bis(imidazolium) salt and $Fe\{N(SiMe_3)_2\}_2$ or the free diamine-bis-carbene and $FeCl_2$. The molecular structure of the new iron complex reveals a highly distorted geometry of iron between octahedral and tetrahedral, which is in agreement with a high-spin d^6 configuration. The iron complex was found to serve as a catalyst precursor for the hydrosilylation of acetophenone. The iron complex may be also applied to other reactions such as C−H oxidations, which will be the subjects of further study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving experimental procedures and analytical data for all new compounds, including crystallographic data, cyclic voltammograms and SQUID measurements of compound **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.

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(16) Formation of Fe-NHCs using $Fe\{N(SiMe_3)_2\}_2$ and imidazolium salts containing weakly coordinating counteranions can be problematic; see refs 10a−c.

(17) See the Supporting Information for further details.

(18) While topological isomers of **6** are conceivable, the growing bite angle strain of the DMEDA backbone and steric repulsion of the methyl substituents on the NHCs should restrict interconversion to different topologies. Also, the structurally most related BQEN ligand exhibits only the cis-α topology in both the solid state and solution. See also ref 12c.

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(20) Partial dissociation of a chloride anion from **6** takes place in a polar solvent such as CH_3CN, as suggested by the ESI-MS spectrum. The resultant cationic complex $[\mathbf{6} - Cl]^+$ possibly interacts with the *H*-Si group of silanes, promoting the heterolytic activation of the Si−H bond.

(21) Attempts to isolate the dimethyl complex $(\mathbf{5})FeMe_2$ were unsuccessful. In our previous work, the replacement of chloride by methyl ligands increased the catalytic activity of the Fe-NHC in hydrosilylation; see ref 4k.

(22) Diphenylmethylsilane, phenyldimethylsilane, and phenylsilane were also used, but monitoring of the reactions by GC-MS indicated only poor conversions.

(23) Alkoxide bases are known to catalyze the hydrosilylation: (a) Hosomi, A.; Hayashida, H.; Kohra, S.; Tominaga, Y. *J. Chem. Soc. Chem.Commun.* **1986**, 1411. (b) Corriu, R.; Guérin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *365*, C7. See also ref 5d.