Square planar bis(imino)pyridine iron halide and alkyl complexes†‡

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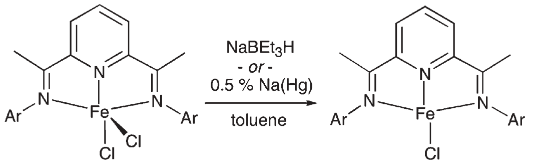
Square planar iron methyl complexes containing bis(imino)-pyridine (PDI) ligands have been prepared by reductive alkylation of the corresponding ferrous dichloride; dialkylation is observed upon treatment with a larger alkyl lithium.

Interest in well-defined iron complexes as precious metal surrogates in catalytic bond-forming reactions relevant to organic synthesis continues to be an area of ongoing development.[1] Reports of catalytic olefin hydrogenation, hydrosilation and isomerization by a transient [$Fe(CO)_3$] fragment, generated either by high temperature thermolysis (> 100 °C)[2] or continued photolysis[3] of $Fe(CO)_5$, inspired the exploration of related [L_3Fe] species that could be accessed under mild conditions. The bis(dinitrogen) complex, (^{iPr}PDI)Fe(N_2)$_2$ (**1-(N_2)$_2$**), prepared by reduction of the corresponding ferrous dichloride or dibromide,[4] readily dissociates one equivalent of dinitrogen in solution and serves as an active catalyst for the aforementioned transformations.[5] Significantly, these reactions operate efficiently at part per million levels of iron without the need for organic solvent. Inspired by the reports of olefin polymerization with (PDI)FeX_2 (X = Cl, Br) when activated by methylalumoxane (MAO),[4] we targeted the preparation of well-defined iron alkyl complexes for catalytic bond-forming reactions involving small molecule organic substrates. Here we describe our initial synthetic efforts toward this goal with the preparation and characterization of four- and five-coordinate iron alkyl and dialkyl derivatives.

During the synthesis of **1-(N_2)$_2$** prepared by Na(Hg) reduction of **1-Cl_2**, an intermediate C_{2v} symmetric product was identified. Subsequent experiments revealed that this species could be cleanly isolated by treatment of **1-Cl_2** with one equivalent of $NaBEt_3H$ or by stirring the alkali metal reduction for shorter reaction times. A combination of ^1H NMR spectroscopy, combustion analysis and solution magnetometry identified the green product as the iron monochloride complex, **1-Cl** (eqn. 1). This synthetic procedure has been extended to include compounds containing the 2,6-diethyl- and 2,4,6-trimethylphenyl substituted bis(imino)pyridine ligands as well as the monobromide complex, **1-Br**, of the 2,6-diisopropyl variant.



(1)

1-Cl_2: Ar = 2,6-$^iPr_2$-C_6H_3
2-Cl_2: Ar = 2,6-Et_2-C_6H_3
3-Cl_2: Ar = 2,4,6-Me_3-C_6H_2

1-Cl: μ_{eff} = 3.7 μB (83 %)
2-Cl: μ_{eff} = 4.0 μB (75 %)
3-Cl: μ_{eff} = 4.0 μB (77 %)

Solution magnetometry (benzene-d_6, 23 °C) on each of the dark green complexes produced magnetic moments consistent with the spin-only value for three unpaired electrons and is consistent with one electron reduction of the ferrous dihalide precursor (eqn. 1). Paramagnetically broadened and isotropically shifted ^1H NMR resonances are observed over a 600 ppm chemical shift range. Hydrogens in the plane of the three nitrogens and hence in conjugation with the iron center[6] exhibit large displacements from their diamagnetic reference values while those on the orthogonal aryl groups have smaller isotropic shifts.

Cooling a concentrated diethyl ether solution of **2-Cl** to −35 °C afforded green crystals suitable for X-ray diffraction. The solid state structure (Fig. 1) reveals coordination of a diethyl ether ligand in the apical position of the molecule. Dissolving the crystals in hydrocarbons such as pentane and toluene induced rapid dissociation of Et_2O and allowed isolation of the square planar complex upon trituration. Spectroscopic characterization of single crystals of **1-Cl** isolated from Et_2O provided no evidence for ether coordination, highlighting the greater steric protection imparted by the larger 2,6-diisopropyl aryl substituents. The metrical parameters (Table 1) for **2-Cl·Et_2O** reveal slight perturbations (0.05–0.1 Å) from the corresponding five-coordinate ferrous dichloride complexes.[4,7] For the monochloride, the C–N bond lengths are slightly elongated and the iron–nitrogen bonds are contracted, consistent with greater reduction of the bis(imino)pyridine ligand by the low-valent iron center.

With well-defined monohalide complexes in hand, salt metathesis reactions with alkyl lithiums were explored. Methylation of each of the bis(imino)pyridine iron monochloride complexes was accomplished by addition of one equivalent of MeLi in diethyl ether (eqn. 2). The monomethyl derivatives, **1-Me**, **2-Me** and **3-Me**, were isolated as green solids in modest to good yields. Using a similar procedure, **2-CH_2SiMe_3** was prepared from **2-Cl**. Attempts to synthesize **1-CH_2SiMe_3** in this manner produced no reaction, again demonstrating the impact of the aryl substituents on the reactivity of the monochloride complexes. Solution magnetometry (benzene-d_6, 23 °C) of each alkyl derivative produced moments consistent with the spin only value for three unpaired electrons, similar to the electronic structure of the monochloride compounds.

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† Electronic supplementary information (ESI) available: experimental details and details of the refinement and crystal structures. See http://www.rsc.org/suppdata/cc/b5/b504063a/
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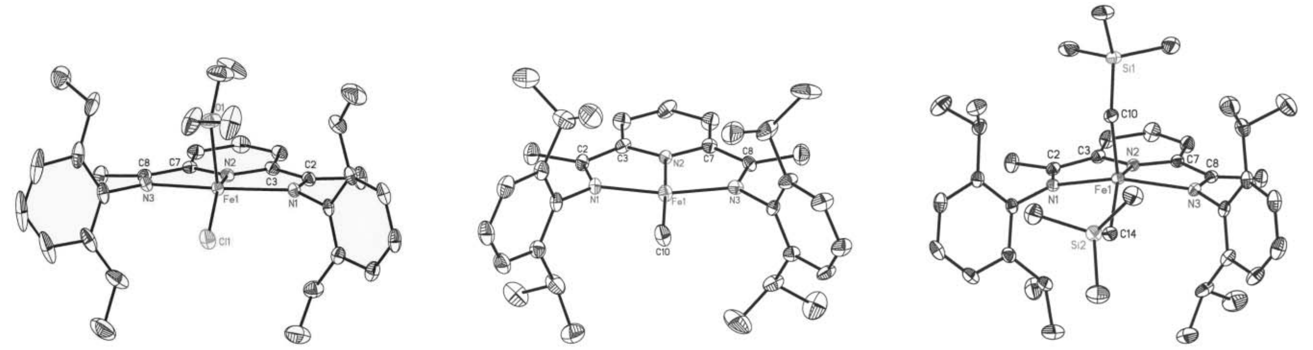
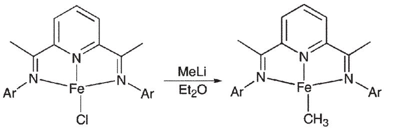


Fig. 1 Solid state structures of **2-Cl·Et$_2$O**, **1-Me** and **1-(CH$_2$SiMe$_3$)$_2$** at 30% probability ellipsoids.

Table 1 Selected bond distances (Å) and angles (°)

	2-Cl·Et$_2$O	**1-Me**	**1-(CH$_2$SiMe$_3$)$_2$**
Fe(1)–N(1)	2.181(2)	1.968(5)	2.2030(19)
Fe(1)–N(2)	2.009(2)	1.893(4)	2.0133(19)
Fe(1)–N(3)	2.209(2)	1.952(5)	2.263(2)
Fe(1)–Cl(1)	2.2668(8)		
Fe(1)–O(1)	2.213(2)		
Fe(1)–C(10)		2.001(6)	2.062(3)
Fe(1)–C(14)			2.054(3)
N(1)–C(2)	1.313(3)	1.337(7)	1.302(3)
N(3)–C(8)	1.301(3)	1.332(7)	1.301(3)
C(2)–C(3)	1.443(4)	1.432(8)	1.448(3)
C(7)–C(8)	1.453(4)	1.442(8)	1.454(3)
N(1)–Fe(1)–N(3)	149.56(8)	159.2(2)	141.07(7)
N(1)–Fe(1)–N(2)	75.22(8)	79.1(2)	74.03(7)
N(2)–Fe(1)–N(3)	74.57(8)	80.1(2)	72.88(7)
N(2)–Fe(1)–Cl(1)	150.96(6)		
N(2)–Fe(1)–O(1)	108.99(8)		
N(2)–Fe(1)–C(10)		176.0(2)	107.93(9)
N(2)–Fe(1)–C(14)			140.02(10)



1-Me: μ_{eff} = 3.5 μB (53 %)
2-Me: μ_{eff} = 4.1 μB (78 %)
3-Me: μ_{eff} = 3.9 μB (27 %)

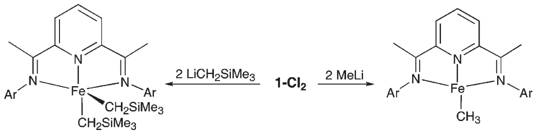
(2)

The benzene-d_6 ^{1}H NMR spectra of these molecules exhibit the number of peaks anticipated for C_{2v} symmetric compounds, with resonances ranging between −170 and 225 ppm. While this chemical shift dispersion is slightly less than that observed with the monochloride complexes, the hydrogens attached to carbons in conjugation with the iron center still display larger isotropic shifts than those on the orthogonal aryl substituents. Resonances for the iron–methyl groups or the methylene hydrogens on the carbon bound to iron in **2-CH$_2$SiMe$_3$** were not located.

The solid state structure of **1-Me** (Fig. 1) was elucidated by X-ray diffraction. A square planar molecular geometry is observed with the bond angles around the iron summing to 360.0(4)°. The iron methyl group lies 0.112 Å below the idealized square plane flanked by the orthogonal aryl substituents. The metrical distortions (Table 1) in the bis(imino)pyridine ligand are more severe than those observed in **2-Cl·Et$_2$O**, with more contracted iron–nitrogen bonds, elongated imine carbon–nitrogen distances and an expanded N(1)–Fe(1)–N(3) bond angle. These observations are consistent with increased iron to ligand backdonation, a consequence of replacing an inductively withdrawing chloride ligand with a strong field alkyl substituent.

Synthesis of a family of four-coordinate bis(imino)pyridine iron alkyl complexes by straightforward salt metathesis reactions prompted investigation into the alkylation chemistry of the corresponding ferrous dichloride complexes. While ferrous monoalkyl[8] and dialkyl[9] complexes are known, those containing bis(imino)pyridine ligands have remained elusive. Interest in these molecules stems from their potential to serve as precursors for single component olefin polymerization catalysts and ability to provide insight into the nature of the propagating species.[7,10] It should be noted that related monomethyl and dimethyl derivatives of a bis(imino)carbazolide iron complex have been reported.[11] Treatment of either of these alkyls or the halide precursors with a variety of activators did not induce ethylene polymerization activity.

Addition of two equivalents of MeLi to a THF or diethyl ether slurry of **1-Cl$_2$** did not furnish the corresponding dimethyl complex. Rather, **1-Me**, the product of reductive alkylation, was isolated in moderate yield (eqn. 3). Following an identical procedure with **2-Cl$_2$** and **3-Cl$_2$** afforded **2-Me** and **3-Me**, respectively, demonstrating the generality of the transformation. Similar results have been reported with an analogous cobalt complex, as treatment of (^{iPr}PDI)CoCl$_2$ resulted in isolation of (^{iPr}PDI)CoMe.[12] For the iron reactions, methane and ethane have been identified by ^{1}H NMR spectroscopy as byproducts of the reductive alkylation procedure.



1-(CH$_2$SiMe$_3$)$_2$, (45 %)
μ_{eff} = 4.8 μB

Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$

1-Me, (74 %)

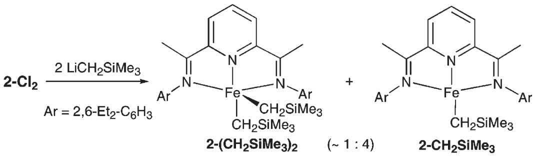
(3)

Alkylation of **1-Cl$_2$** with two equivalents of LiCH$_2$SiMe$_3$ produced a different outcome. In this case, a purple solid identified as the bis(imino)pyridine ferrous *dialkyl*, (^{iPr}PDI)Fe(CH$_2$SiMe$_3$)$_2$ (**1-(CH$_2$SiMe$_3$)$_2$**), was isolated in 45% yield (eqn. 3). The benzene-d_6 ^{1}H NMR spectrum of the compound exhibited the number of resonances expected for a C_{2v} symmetric molecule, with isotropically shifted imine methyl groups centered at −150.8 ppm and a *para* pyridine resonance at 281.9 ppm. The SiMe$_3$ groups are equivalent, appearing as a broad singlet centered at approximately 15 ppm. The methylene protons on the carbons bound to the iron were not located. Solution magnetometry (benzene-d_6, 23 °C) produced a magnetic moment of 4.8 μB, consistent with the spin only value for four unpaired electrons.

The solid state structure of **1-(CH_2SiMe_3)$_2$** was determined by X-ray diffraction (Fig. 1). Unlike **2-Cl·Et_2O** and **1-Me**, the iron atom in **1-(CH_2SiMe_3)$_2$** lies 0.543 Å out of the plane of the three nitrogen atoms of the bis(imino)pyridine ligand. As a result, relatively long Fe(1)–N(1) and Fe(1)–N(2) bond distances of 2.2030(19) and 2.0133(19) Å are observed, indicative of little backdonation from the metal center. Accordingly, contracted N(1)–C(2) and N(3)–C(8) distances of 1.302(3) and 1.301(3) are also noted, in agreement with the metrical parameters reported for the corresponding dichloride complex.[4] The two alkyl substituents are oriented above and below the plane of the bis(imino)pyridine ligand, rendering the geometry of the molecule intermediate between the square planar and trigonal bipyramidal extremes.

In light of the observations with MeLi, isolation of **1-(CH_2SiMe_3)$_2$** by alkylation of **1-Cl_2** seemed puzzling and prompted further experimentation. Addition of one equivalent of $LiCH_2SiMe_3$ to **1-Cl_2** induced reduction, resulting in the clean isolation of **1-Cl** in good yield. Because **1-Cl** does not undergo facile alkylation upon addition of $LiCH_2SiMe_3$ in either THF or diethyl ether, the monochloride is not an intermediate on the pathway to **1-(CH_2SiMe_3)$_2$**. This observation contrasts the chemistry with MeLi, where the monochloride compounds serve as precursors for the observed reductive alkylation products.

To further explore the reactivity difference between the two alkyl lithiums, the alkylation of **2-Cl_2** was investigated in more detail. In this case, the monochloride complex, **2-Cl**, undergoes alkylation with $LiCH_2SiMe_3$ and the product of reductive alkylation, **2-CH_2SiMe_3**, may be accessible. Addition of two equivalents of $LiCH_2SiMe_3$ to a THF solution of **2-Cl_2** furnished both green and purple solids after workup. Attempts to separate the two products by washing or recrystallization have not been successful. However, analysis of the mixture by ^1H NMR spectroscopy revealed formation of a 4 : 1 ratio of **2-CH_2SiMe_3**, the green product of reductive alkylation, and **2-(CH_2SiMe_3)$_2$**, the purple material arising from dialkylation (eqn. 4).



2-(CH_2SiMe_3)$_2$ **2-CH_2SiMe_3** (4)

Based on these initial observations, it appears that the reactivity of the putative (PDI)Fe(R)Cl intermediate dictates the outcome of the alkylation reaction. Additional alkyl lithium can serve to either alkylate or reduce this compound. Smaller, more reducing MeLi affords solely the products of reductive alkylation, whereas the more sterically hindered $LiCH_2SiMe_3$ either reduces or alkylates, depending on the steric environment of the ligand. In the absence of either alkyl lithium, (PDI)Fe(R)Cl undergoes ejection of the alkyl radical to yield the monochloride complex. The origin of these differences remains an active area of investigation in our laboratory.

In summary, a family of square planar bis(imino)pyridine iron monohalide and monomethyl complexes have been prepared and isolated. The electronic structure and catalytic activity of these species, as well as the corresponding ferrous dialkyl, in olefin polymerization and bond-forming reactions relevant to organic synthesis will be the subject of future studies in our laboratory.¶

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Notes and references

¶ Crystal data for **2-Cl·Et_2O**, **1-Me**, and **1-(CH_2SiMe_3)$_2$**. $C_{33}H_{45}ClFeN_3O$, M = 591.02, monoclinic, a = 13.1161(5), b = 19.2048(8), c = 13.5204(6) Å, β = 115.1460(10)°, U = 3082.9(2) Å^3, T = 173(2) K, space group $P2(1)/n$, Z = 4, μ(Mo-Kα) = 0.606 mm^{-1}, 25123 reflections measured, 7615 unique (R_{int} = 0.0483) which were used in all calculations. The final R_1 was 0.0522 (all data). $C_{34}H_{46}FeN_3$, M = 552.59, triclinic, a = 16.0725(12), b = 16.2819(11), c = 17.0074(12) Å, α = 86.074(2), β = 64.426(2), γ = 62.003(2)°, U = 3494.2(4) Å^3, T = 173(2) K, space group P-1, Z = 4, μ(Mo-Kα) = 0.454 mm^{-1}, 17737 reflections measured, 7309 unique (R_{int} = 0.0689) which were used in all calculations. The final R_1 was 0.0674 (all data). $C_{41}H_{65}FeN_3Si_2$, M = 711.99, orthorhombic, a = 15.8771(7), b = 20.0007(7), c = 26.177(1) Å, U = 8312.6(6) Å^3, T = 173(2) K, space group $Pbca$, Z = 8, μ(Mo-Kα) = 0.450 mm^{-1}, 67211 reflections measured, 5980 unique (R_{int} = 0.0446) which were used in all calculations. The final R_1 was 0.0340 (all data). CCDC 267323–267325. See http://www.rsc.org/suppdata/cc/b5/b504063a/ for crystallographic data in CIF or other electronic format.

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