CHEMCOMM
Communication
www.rsc.org/chemcomm

Tuning metal coordination number by ancillary ligand steric effects: synthesis of a three-coordinate iron(II) complex

Jeremy M. Smith, Rene J. Lachicotte and Patrick L. Holland*

Department of Chemistry, University of Rochester, Rochester NY 14627, USA.
E-mail: holland@chem.rochester.edu

Received (in Cambridge, UK) 24th April 2001, Accepted 9th July 2001
First published as an Advance Article on the web 31st July 2001

The coordination number of the metal in iron(II) β-diketiminate complexes can be tuned through the size of the alkyl substituents on the ligand backbone.

Low coordinate transition metal complexes are of much interest for their ability to achieve unusual and difficult transformations.[1] Biological interest stems from the low coordinate iron centres found in the iron–molybdenum cofactor of nitrogenase.[2] The high reactivity of coordinatively unsaturated sites on iron surfaces may also be imitated by these complexes.[3]

The chelating β-diketiminate ligands (Fig. 1) have experienced a renaissance in interest recently, in part for their ability to stabilise low-coordinate metal complexes.[4] Here we show how a simple modification of these ligands at a position away from the immediate site of coordination results in dramatic changes to the geometry of the metal atom.

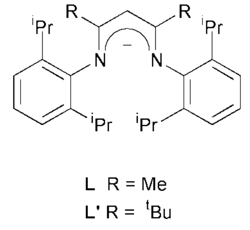

Fig. 1 β-Diketiminate ligands used in this study.

Reaction of equimolar amounts of the lithium salt of 2,4-bis(2,6-diisopropylphenylimido)pentane[5] (LiL) and $FeCl_2(THF)_{1.5}$[6] in THF results in the formation of a yellow solution, from which a yellow air-sensitive solid **1a** can be isolated by crystallisation from THF.† The molecular structure of crystals grown from pentane solution was determined by X-ray diffraction, revealing the product to be the 'ate' complex, $LFe(\mu\text{-}Cl)_2Li(THF)_2$ **1a**.‡ The complex crystallises with two molecules in the asymmetric unit (Fig. 2, only one molecule shown). The iron atom is four-coordinate, and distorted from ideal tetrahedral geometry. Thus, for example, the N(11)–Fe(1)–N(21) bond angle is relatively acute at 93.21(14)°, while the N(11)–Fe(1)–Cl(11) bond angle is relatively obtuse at 114.00(10)°. The bond lengths to iron do not significantly differ from typical values.[7] Interestingly, a second crystal form **1b**‡§ can be grown from THF at −35 °C; it crystallises with 3 molecules in the asymmetric unit. The gross structural features of all the unique molecules in both polymorphs are similar. The analogous diethyl ether solvated complex, $LFe(\mu\text{-}Cl)_2Li(Et_2O)_2$ **1c** can be obtained by crystallisation from diethyl ether at −35 °C.

The solid state magnetic moment is 5.4 μ_B, consistent with tetrahedral high spin iron(II).[8] More complicated behaviour is observed in solution. An unexpectedly large number of signals are observed in the ^1H NMR spectrum of **1a** in C_6D_6, although the correct number of resonances are observed in THF-d_8 solution. The solution magnetic moment[9] in either solvent is 4.4 μ_B. No changes in the spectrum or magnetic moment are observed in either solvent on addition of excess LiCl. Complexes **1a** and **1b** give identical ^1H NMR spectra in C_6D_6.

To determine the effect of the source of the β-diketiminate ligand on the coordination environment at iron, we used the magnesium complex LMg(Cl)(THF),¶ prepared from L and MeMgCl in THF. Reaction of this complex with $FeCl_2(THF)_{1.5}$ in THF solution results in the yellow complex $Mg(THF)_4[LFeCl(\mu\text{-}Cl)]_2$ **2** (Fig. 3).‖ The complex, which is insoluble in less polar solvents, can be isolated in moderate yield by multiple crystallisations from THF at −35 °C. An X-ray diffraction study‡ revealed the product to have an unusual structure, with the two iron centres bridged by a magnesium atom lying on a crystallographic inversion centre. Once again the iron is approximately tetrahedral, with bond lengths and angles similar to those in **1**.

Use of a slightly modified ligand resulted in a completely different product. Thus, refluxing a mixture of toluene, $FeCl_2(THF)_{1.5}$, and one molar equivalent of LiL′,[10] in which the ligand backbone methyls have been replaced by *tert*-butyl groups, results in the formation of a red solution from which a

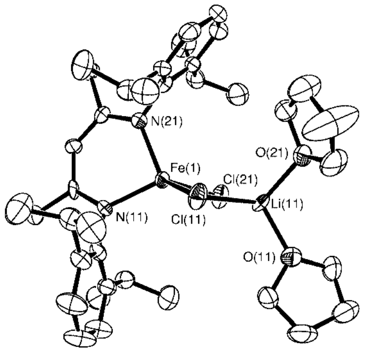

Fig. 2 Molecular structure of $LFe(\mu\text{-}Cl)_2Li(THF)_2$ **1a**. Hydrogen atoms not shown, thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Fe(1)–N(11) 2.006(3); Fe(1)–N(21) 2.021(4), Fe(1)–Cl(11) 2.324(1) Fe(1)–Cl(21) 2.338(1), Cl(11)–Li(11) 2.357(11), Cl(21)–Li(11) 2.363(8); N(11)–Fe(1)–N(21) 93.21(14), N(11)–Fe(1)–Cl(11) 114.00(10).

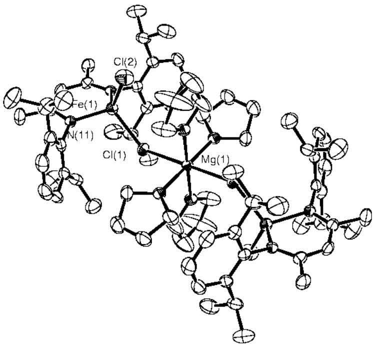

Fig. 3 Molecular structure of $[LFe(\mu\text{-}Cl)_2]Mg(THF)_4$ **2**. Hydrogen atoms not shown, thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Fe(1)–N(11) 2.011(3), Fe(1)–N(21) 2.014(3), Fe(1)–Cl(1) 2.377(1), Fe(1)–Cl(2) 2.267(1), Cl(1)–Mg(1) 2.5201(9); N(11)–Fe(1)–N(21) 92.15(12), N(11)–Fe(1)–Cl(1) 110.25(9).

DOI: 10.1039/b103635c

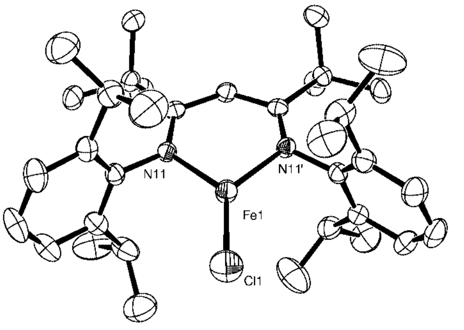

Fig. 4 Molecular structure of L′FeCl **3**. Hydrogen atoms not shown, thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Fe(1)–N(11) 1.948(2), Fe(1)–Cl(1) 2.172(1); N(11)–Fe(1)–N(11)′ 96.35(11), N(11)–Fe(1)–Cl(1) 131.83(5).

highly air-sensitive red solid **3** can be isolated.** The molecular structure of the product L′FeCl **3** was determined by X-ray crystallography (Fig. 4).‡ The iron and chlorine atoms are on a crystallographic mirror plane. The iron atom lies in a planar ring formed with the ligand; the bond angles around the metal reveal a planar geometry (sum of angles = 360°). The N(11)–Fe(1)–N(11)′ bond angle is compressed to 96.35(11)°, while the N(11)–Fe(1)–Cl(1) angle opens up to 131.83(5)°. As expected, the lower coordination number of the iron atom in **3** causes the bond lengths to the metal to decrease as compared to **1** and **2**. Both the solution ($\mu_{\text{eff}} = 5.5\ \mu_B$) and solid state ($\mu_{\text{eff}} = 5.9\ \mu_B$) magnetic moments confirm the high-spin iron(II) oxidation state. The ^{1}H NMR spectrum is relatively simple, consisting of seven paramagnetically shifted resonances.

While the effect of the ligand backbone groups on the coordination number of iron may not be immediately obvious, it can be understood by examining the C–N–C bond angles in the three complexes. In **1** they are in the range 118.6–120.3°, while in **3** they are 128.4(2)°. Thus, the *tert*-butyl groups on the ligand backbone in L′ force the aryl rings to close in on the metal, limiting the space available at the iron centre for more ligands.

In most three-coordinate complexes of Fe(II),[1,11] functionalisation, if it is achieved, is usually at the expense of the low coordination number. In contrast, complex **3** presents many viable pathways for further functionalisation by reactions with the chloride ligand while maintaining the low coordination number.

The University of Rochester is gratefully acknowledged for funding of this work. We would like to thank Kevin Mooney (University at Buffalo) for recording the SQUID data.

Notes and references

† **1a**: Yield 90% based on $FeCl_2(THF)_{1.5}$, mp 310 °C (decomp.) (Anal. Found: C, 63.88; H, 8.37; N, 4.11. $C_{37}H_{57}Cl_2FeLiN_2O_2$ requires C, 63.89; H, 8.25; N, 4.02%), δ_H(400 MHz, C_6D_6, 23 °C) 17.08, 15.33, 9.19, 6.42, 5.15, 2.67, 1.99, 1.14, 0.93, 0.31, −12.89, −13.14, −16.93, −24.25, −35.43, −40.44, −44.60, −65.39; δ_H(THF-d$_8$, 23 °C) 15.28, 6.98, −16.77, −43.60, −64.68.

‡ *Crystal data* For **1a**: $C_{37}H_{57}Cl_2FeLiN_2O_2$, M = 695.54, orthorhombic, space group $Pna2_1$, a = 23.1015(12), b = 9.9748(5), c = 35.9530(18), U = 7786.4(7) Å^3, T = 193(2) K, Z = 8, μ(Mo-Kα) = 0.556 mm^{-1}, 32164 reflections measured, 10201 unique (R_{int} = 0.0307), R_1 = 0.0478, wR_2 = 0.0967 [$I > 2\sigma(I)$].

For **1b**: orthorhombic, space group $P2_12_12_1$, a = 16.7761(8), b = 19.0238(9), c = 36.8905(19), U = 11773.4(10) Å^3, T = 193(2) K, Z = 12, μ(Mo-Kα) = 0.556 mm^{-1}, 53706 reflections measured, 16937 unique (R_{int} = 0.0520), R_1 = 0.0447, wR_2 = 0.0822 [$I > 2\sigma(I)$]. The ratio of the two enantiomorphic components was refined to a value of 0.461(13).

For **2**: $C_{42}H_{70}Cl_2FeMg_{0.5}N_3$, M = 1545.71, monoclinic, space group $P2_1/c$, a = 12.6469(8), b = 13.0103(8), c = 26.414(2), β = 102.853(1), U = 4237.3(5) Å^3, T = 193(2) K, Z = 2, μ(Mo-Kα) = 0.526 mm^{-1}, 18679 reflections measured, 6069 unique (R_{int} = 0.0551), R_1 = 0.0546, wR_2 = 0.1361 [$I > 2\sigma(I)$].

For **3**: $C_{35}H_{53}ClFeN_2$, M = 593.09, monoclinic, space group $C2/c$, a = 16.9014(11), b = 9.3514(6), c = 22.7756(15), β = 107.237(1), U = 3428.0(4) Å^3, T = 193(2) K, Z = 4, μ(Mo-Kα) = 0.540 mm^{-1}, 7361 reflections measured, 2463 unique (R_{int} = 0.0256), R_1 = 0.0398, wR_2 = 0.0704 [$I > 2\sigma(I)$].

CCDC reference numbers 167176–167180. See http://www.rsc.org/suppdata/cc/b1/b103635c/ for crystallographic data in CIF or other electronic format.

§ **1b**: $\mu_{\text{eff}} = 4.4\ \mu_B$ (Evans), $\mu_{\text{eff}} = 5.4\ \mu_B$ (SQUID, 5000 G, 50–300 K).

¶ LMgCl(THF): Yield 75%, δ_H(400 MHz, C_6D_6, 23 °C) 7.2–7.3 (br s, 6H, Ar-H), 4.95 (s, 1H, CH), 3.63 (br s, 4H, CH_2), 3.94 (br s, 4H, CH(CH_3)$_2$), 1.78 (s, 6H, CH_3), 1.48 (br s, 4H, CH_2), 1.39 (br s, 24H, CH(CH_3)$_2$).

‖ **2**: Yield 60% based on $FeCl_2(THF)_{1.5}$, mp 302–304 °C, δ_H(400 MHz, THF-d$_8$, 23 °C) 13.58, 12.95, 5.68, −0.97, −1.25, −1.74, −2.63, −20.76, −28.13, −41.02, −47.98, −69.77; $\mu_{\text{eff}} = 4.2\ \mu_B$.

** **3**: Yield 88% based on $FeCl_2(THF)_{1.5}$, mp 270–272 °C (Anal. Found: C, 70.26; H, 8.86; N, 4.77. $C_{35}H_{53}ClFeN_2$ requires C, 70.69; H, 8.42; N, 4.61%); δ_H(400 MHz, C_6D_6, 23 °C) 48.78, 2.35, 1.21, 0.40, −25.84, −105.33, −115.05; $\mu_{\text{eff}} = 5.5\ \mu_B$ (Evans), $\mu_{\text{eff}} = 5.9\ \mu_B$ (SQUID, 5000 G, 50–300 K).

1 C. C. Cummins, *Prog. Inorg. Chem.*, 1998, **47**, 685; S. Alvarez, *Coord. Chem. Rev.*, 1999, **193**–**195**, 13.

2 J. Kim and D. C. Rees, *Nature*, 1992, **360**, 553; J. B. Howard and D. C. Rees, *Chem. Rev.*, 1996, **96**, 2965; D. C. Rees and J. B. Howard, *Curr. Opin. Chem. Biol.*, 2000, **4**, 559.

3 *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger and J. Weitkamp, Wiley-VCH, Weinheim, 1997, vol. 4.

4 P. H. M. Budzelaar, R. de Gelder and A. W. Gal, *Organometallics*, 1998, **17**, 4121; M. Cheng, E. B. Lobkovsky and G W. Coates, *J. Am. Chem. Soc.*, 1998, **120**, 11018; P. L. Holland and W. B. Tolman, *J. Am. Chem. Soc.*, 1999, **121**, 7270; C. E. Radzewich, I. A. Guzei and R. F. Jordan, *J. Am. Chem. Soc.*, 1999, **121**, 8673; M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583; C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem., Int. Ed.*, 2000, **39**, 4274; V. C. Gibson, J. A. Segal, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2000, **122**, 7120; N. J. Hardman, B. E. Eichler and P. P. Power, *Chem. Commun.*, 2000, 1991; P. J. Bailey, R. A. Coxall, C. M. Dick, S. Fabre and S. Parsons, *Organometallics*, 2001, **20**, 798; A. Akkari, J. J. Byrne, I. Saur, G. Rima, H. Gornitzka and J. Barrau, *J. Organomet. Chem.*, 2001, **622**, 190; N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink and P. P. Power, *Angew. Chem., Int. Ed.*, 2001, **40**, 2172.

5 J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese and S. D. Arthur, *Organometallics*, 1997, **16**, 1514.

6 R. J. Kern, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1105.

7 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

8 C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc. A*, 1968, 1074.

9 M. V. Baker, L. D. Field and T. W. Hambley, *Inorg. Chem.*, 1988, **27**, 2872.

10 P. H. M. Budzelaar, A. B. van Oort and A. G. Orpen, *Eur. J. Inorg. Chem.*, 1998, 1485.

11 W. Seidel and K.-J. Lattermann, *Z. Anorg. Allg. Chem.*, 1982, **488**, 69; D. M. Roddick, T. D. Tilley, A. L. Rheingold and S. J. Geib, *J. Am. Chem. Soc.*, 1987, **109**, 945; P. P. Power and S. C. Shoner, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 330; F. M. MacDonnell, K. Ruhlandt-Senge, J. J. Ellison, R. H. Holm and P. P. Power, *Inorg. Chem.*, 1995, **24**, 1815; S. L. Stokes, W. M. Davis, A. L. Odom and C. C. Cummins, *Organometallics*, 1996, **15**, 4521; M. A. Putzer, B. Neumüller, K. Dehnicke and J. Magull, *Chem. Ber.*, 1996, **129**, 715; U. Siemeling, U. Vorfeld, B. Neumann and H.-G. Stammler, *Inorg. Chem.*, 2000, **39**, 5159.