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The synthesis and metal coordination chemistry of new 1,1′-*N*-substituted ferrocenediyl ligands derived from 1,1′-diaminoferrocene

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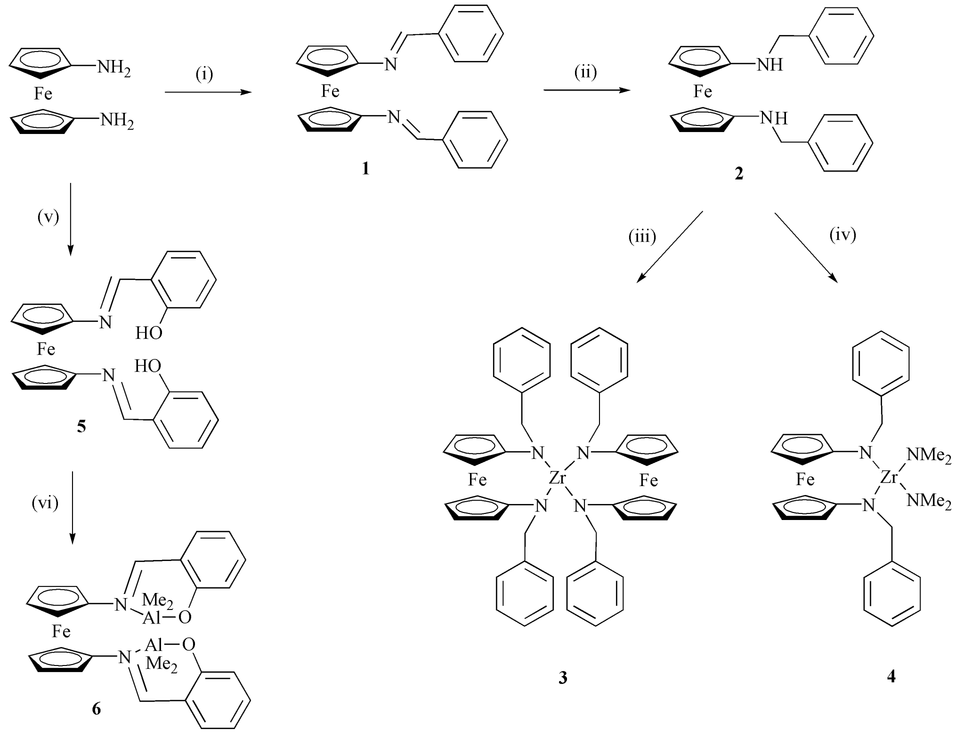
Received 26th February 2001, Accepted 15th March 2001
First published as an Advance Article on the web 29th March 2001

A series of 1,1′-*N*-substituted ferrocenediyl ligands has been synthesised from 1,1′-diaminoferrocene *via* Schiff base condensation reactions and the coordination chemistry probed by reaction with Zr and Al reagents; an unusual dimetallic, bis-chelate Al complex has been structurally characterised.

The substitution of ferrocenes by various donor heteroatoms has led to a series of chelating ligands that have found wide application, *e.g.* incorporation of phosphines for homogeneous catalysis in organic synthesis, chiral phosphines for enantiomeric synthesis and amino alcohols for asymmetric catalysis.[1,2] We have recently reported the potential of transition metal complexes based on ferrocene dithiolato ligands for olefin polymerisation catalysis[3] and have embarked on a study of related *N*-substituted ferrocenediyl species. Although substituted ferrocenylamines are known,[4] the simple chelating ligand 1,1′-diaminoferrocene has been little studied due to difficulties in its synthesis. It was first prepared in 1961 by Knox and Pauson,[5] followed soon after by Nesmeyanov *et al.*,[6] the latter using 1,1′-diazidoferrocene as a precursor. Very recently, Arnold *et al.*[7] have published a more efficient route to its synthesis, again using 1,1′-diazidoferrocene, whilst McGowan *et al.* have formed amino-functionalised ferrocenes from sodium cyclopentadienide salts.[8] We have used a modification of Nesmeyanov's route to access the bis-amine and here describe the synthesis of new sterically-hindered ferrocenediyl ligands (Scheme 1).† We also report a preliminary study into their coordination chemistry.

The air-sensitive orange 1,1′-diaminoferrocene was reacted with excess benzaldehyde to form the bis-imine (**1**) in good yield, as a burgundy-coloured solid. This was then reduced *in situ* using lithium aluminium hydride, and following an aqueous work-up with degassed water, the orange, air-sensitive microcrystalline bis-amine (**2**) was obtained in moderate yield. On reaction of **2** with (tetrabenzyl)zirconium, a yellow, air-sensitive oil was formed, which was triturated with pentane to yield a yellow–brown powder (**3**). Analysis of the product by NMR showed that all of the benzyl ligands had been displaced to give the bis(chelate) product **3**. Conversely, reaction of **2** with tetrakis(dimethylamino)zirconium, produces the mono-chelate complex **4**. The product, a viscous yellow–orange oil, is soluble



Scheme 1 (i) Benzaldehyde, toluene, 3 h; (ii) lithium aluminium hydride, 0 °C, diethyl ether, then reflux, 1 h; (iii) (tetrabenzyl)zirconium, benzene, r.t., 4 h; (iv) tetrakis(dimethylamino)zirconium, benzene, r.t., 2 h; (v) salicylaldehyde, toluene, reflux, 1 h; (vi) trimethylaluminium, toluene, r.t., 6 h.

DOI: 10.1039/b101795k

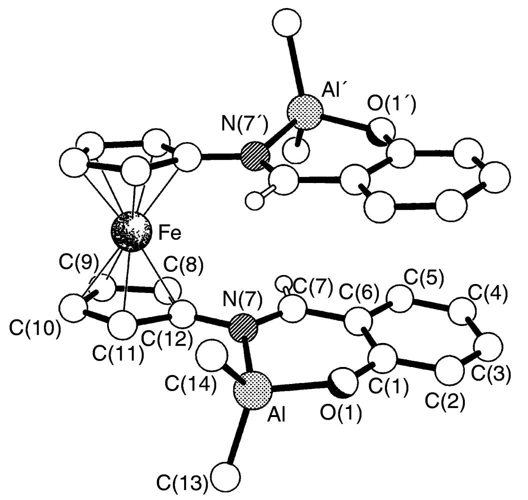


Fig. 1 The molecular structure of **6**. Selected bond lengths (Å) and angles (°); Al–O(1) 1.773(3), Al–C(14) 1.952(4), Al–C(13) 1.953(4), Al–N(7) 1.990(3), C(7)–N(7) 1.299(4), N(7)–C(12) 1.419(4); O(1)–Al–C(14) 108.8(2), O(1)–Al–C(13) 112.2(2), C(14)–Al–C(13) 118.7(2), O(1)–Al–N(7) 94.88(12), C(14)–Al–N(7) 112.9(2), C(13)–Al–N(7) 106.9(2).

in a range of solvents and ^{1}H NMR clearly shows the ferrocenyl protons as two triplets at δ 3.62 and δ 3.86 and the methyl hydrogens of the dimethylamide units at δ 3.09. Both **3** and **4** are light- and moisture-sensitive materials.

The diaminoferrocene can also be condensed with salicylaldehyde to form a range of salicylaldimines. On stirring at room temperature and using excess salicylaldehyde, an efficient, high-yielding reaction occurs. These ligands can potentially bind in a tetradentate fashion, but the reaction with Me_3Al reveals a product containing two bidentate bonding modes, *i.e.* the dinuclear Al complex **6**. Structural examples of bidentate N/O ligand systems featuring 4-coordinate Al complexation are very rare,[9] though 5- and 6-coordinate Al centres with analogous salicyl-type ligands are well known.[10] The structure of **6** was confirmed by a single crystal X-ray analysis which showed the complex to have crystallographic C_2 symmetry about an axis passing through the iron atom and normal to the vector linking the two aluminium centres (Fig. 1). The two salicylaldehyde imine ligands are oriented *syn*, there being only a *ca.* 17° stagger of the two C_5H_4 rings. The two terminal C_6 rings overlay each other and have a centroid···centroid separation of 3.92 Å, indicating a possible weak π–π interaction (their planes are inclined by *ca.* 14°). The six-membered chelate ring has a slightly folded geometry, the aluminium atom lying 0.22 Å out of the plane of the other five atoms (which are coplanar to within 0.03 Å). The aluminium centre has a distinctly distorted tetrahedral geometry with angles ranging between 94.9(1) and 118.7(2)°, the most "acute" angle being associated with the bite of the chelating ligand. The chelate ligand binds to the aluminium in an unsymmetrical fashion with the bond to the oxygen atom being typical of an alkoxide [1.773(3) Å] whilst that to the imino nitrogen atom is, as expected, appreciably longer [1.990(3) Å]; the chelate C=N bond retains its double bond character [1.299(4) Å]. All of these are dimensions very similar to those in related aluminium salicylaldimato complexes.[9] Interestingly, the Al–O and Al–N distances are also similar to those observed in a related structure where the chelate ring is fully saturated.[11] Centrosymmetrically related pairs of complexes pack to form "loose" stacks with the C(1) to C(6) ring of one molecule overlaying the C_5H_4 ring of the next and *vice versa* (the $C_5H_4\cdots C_6H_4$ ring centroid separation is 3.96 Å).

Acknowledgement

This research was supported by the Department of Chemistry, Imperial College, London.

Notes and references

† Synthesis of **1**. Benzaldehyde (5 cm^3) was added to a toluene (50 cm^3) solution of 1,1′-diaminoferrocene (0.25 g, 1.16 mmol). The solution was stirred for 3 h during which the initial yellow colour became deep burgundy. The toluene and excess benzaldehyde were removed *in vacuo* to yield a burgundy solid which was washed with pentane (20 cm^3). Yield (0.34 g, 75%). Elemental analysis (observed/calculated, %) C (73.5/73.6), H (5.1/5.0), N (7.1, 7.0); δ_H (CDCl$_3$) 4.29 (4H, t, C_5H_4), 4.61 (4H, t, C_5H_4), 7.57 (6H, m, C_6H_5), 7.63 (4H, m, C_6H_5), 8.47 (2H, s, N=CH); *m*/*z* 392 (M$^+$).

Synthesis of **2**. A solution of **1** (0.30 g, 0.76 mmol) in diethyl ether (30 cm^3) was slowly added to an ethereal slurry of LiAlH$_4$ (1 g) at 0 °C. The mixture was refluxed for 1 h and '*worked up*' using degassed H$_2$O, to yield an orange coloured solution, which was evaporated to dryness. The crude product was recrystallised from diethyl ether–pentane to give orange crystalline **2** (0.15 g, 50%). Elemental analysis (observed/calculated, %) C (72.7/72.4), H (6.1/6.2), N (7.1, 6.9); δ_H (CDCl$_3$) 2.19 (2H, br s, NH), 3.74 (4H, t, C_5H_4), 3.84 (4H, t, C_5H_4), 3.90 (4H, s, CH$_2$), 7.21 (6H, m, C_6H_5), 7.30 (4H, m, C_6H_5); *m*/*z* 396 (M$^+$).

Synthesis of **3**. A solution of **2** (0.10 g, 0.25 mmol) in benzene (10 cm^3) was slowly added to a solution of (tetrabenzyl)zirconium (0.10 g, 0.26 mmol) also in benzene (10 cm^3) and the mixture stirred for 4 h. The solvent was removed *in vacuo* to leave a yellow oil. Pentane (10 cm^3) was added and the oil was triturated for 48 h to yield a yellow–brown solid. The pentane solution was filtered and the remaining solid washed with pentane (3 × 10 ml) to yield **3** (0.08 g, 36%). δ_H (C$_6$D$_6$) 3.78 (8H, t, C_5H_4), 3.93 (8H, t, C_5H_4), 4.73 (8H, s, CH$_2$), 7.18 (12H, m, C_6H_5), 7.35 (8H, d, C_6H_5-*ortho*); δ_C (C$_6$D$_6$) 63.4 (CH$_2$), 68.1, 69.2 (C_5H_4), 93.7 (*ipso*-C_5H_4), 126.7, 127.9, 128.2, 128.4, 128.7 (C_6H_5), 142.7 (*ipso*-C_6H_5); *m*/*z* 697 (M$^+$ − 2C$_7$H$_7$), 485 (**2** + Zr − 2H), 396 (**2**).

Synthesis of **4**. A solution of **2** (0.15 g, 0.38 mmol) in benzene (10 cm^3) was slowly added to a solution of tetrakis(dimethylamino)zirconium (0.10 g, 0.38 mmol) also in benzene (10 cm^3) and the mixture stirred for 2 h. The solvent was removed *in vacuo* to leave a yellow–orange oil. The product was dissolved in pentane (10 cm^3) and cooled to −30 °C and resulted in precipitation of a yellow solid **4** (0.14 g, 64%). δ_H (C$_6$D$_6$) 3.09 (12H, s, NMe$_2$), 3.62 (4H, t, C_5H_4), 3.86 (4H, t, C_5H_4), 4.59 (4H, s, CH$_2$), 7.09 (2H, m, C_6H_5), 7.18 (4H, m, C_6H_5), 7.31 (4H, m, C_6H_5); δ_C (C$_6$D$_6$) 43.7 (NMe$_2$), 63.8 (CH$_2$), 68.3, 69.4 (C_5H_4), 93.8 (*ipso*-C_5H_4), 126.6, 128.1, 128.3, 128.9, 129.7 (C_6H_5), 143.2 (*ipso*-C_6H_5); *m*/*z* 485 (M$^+$ − 2NMe$_2$).

Synthesis of **5**. Salicylaldehyde (5 mmol) was added to a toluene (50 cm^3) solution of 1,1′-diaminoferrocene (0.21 g, 1 mmol). The solution was refluxed for 1 h and the solvent and excess salicaldehyde were removed *in vacuo* to yield a burgundy, oily solid which was recrystallised from ethanol to yield the product (0.36 g, 85%). Elemental analysis (observed/calculated, %) C (68.1/67.9), H (4.4/4.7), N (6.4/6.6); δ_H (CDCl$_3$) 4.32 (4H, t, C_5H_4), 4.59 (4H, t, C_5H_4), 6.72 (4H, m, C_6H_5), 7.01 (2H, m, C_6H_5), 7.17 (2H, m, C_6H_5), 8.37 (2H, s, N=CH), 13.05 (2H, s, OH); *m*/*z* 424 (M$^+$).

Synthesis of **6**. Trimethylaluminium (0.29 cm^3 as a 2 M solution in toluene, 0.58 mmol, 2.2 equiv.) was added to **5** (0.2 g, 0.26 mmol) in toluene (50 cm^3). The reaction mixture was stirred for 6 h and the solvent removed *in vacuo* to yield a dark burgundy coloured solid, which was washed in pentane (0.19 g, 86%). Elemental analysis (observed/calculated, %) C (62.7/62.5), H (5.6/5.8), N (5.2/5.1); δ_H (C$_6$D$_6$) −0.15 (12H, s, AlCH$_3$), 3.82 (4H, t, C_5H_4), 4.31 (4H, t, C_5H_4), 6.29 (2H, m, C_6H_5), 6.75 (2H, m, C_6H_5), 6.94 (2H, m, C_6H_5), 7.73 (2H, s, N=CH); *m*/*z* 479 (M$^+$ − AlMe$_2$).

Crystal data for **6**: $C_{28}H_{30}N_2O_2Al_2Fe$, $M = 536.4$, monoclinic, $C2/c$ (no. 15), $a = 11.274(2)$, $b = 16.244(3)$, $c = 14.353(2)$ Å, $\beta = 96.47(1)°$, $V = 2611.7(7)$ Å^3, $Z = 4$ (C_2 symmetric), $D_c = 1.364$ g cm^{-3}, μ(Mo-Kα) = 6.73 cm^{-1}, $T = 183$ K, deep red prisms; 2308 independent measured reflections, F^2 refinement, $R_1 = 0.043$, $wR_2 = 0.097$, 1745 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$], 161 parameters. CCDC reference number 159092. See http://www.rsc.org/suppdata/dt/b1/b101795k/ for crystallographic data in CIF or other electronic format.

1 For a detailed literature review see A. Togni and T. Hayashi (Editors), *Ferrocenes: Homogeneous Catalysis – Organic Synthesis – Materials Science*, VCH, Weinheim, Germany, 1995; A. Togni and R. L. Halterman (Editors), *Metallocenes*, Wiley-VCH, Weinheim, Germany, 1998.
2 For a comprehensive overview of ferrocene and other metallocene chemistry see N. J. Long, in *Metallocenes: An Introduction to Sandwich Complexes*, Blackwell Science, Oxford, 1998.
3 V. C. Gibson, N. J. Long, J. Martin, G. A. Solan and J. C. Stichbury, *J. Organomet. Chem.*, 1999, **590**, 115.

4 K.-P. Stahl, G. Boche and W. Massa, *J., Organomet. Chem.*, 1984, **277**, 113; H. Plenio and D. Burth, *Organometallics*, 1996, **15**, 4054; H. Plenio and D. Burth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 800; B. Neumann, U. Siemeling, H.-G. Stammler, U. Vorfeld, J. G. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, F. Fabrizi de Biani and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1997, 4705; M. Herberhold, M. Ellinger and W. Kremnitz, *J. Organomet. Chem.*, 1983, **241**, 227.

5 G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, 1961, 4615.

6 A. N. Nesmeyanov, V. N. Drozd and V. A. Sazonova, *Dokl. Akad. Nauk SSSR*, 1963, **150**, 321.

7 A. Shafir, M. P. Power, G . D. Whitener and J. Arnold, *Organometallics*, 2000, **19**, 3978.

8 S. Bradley, P. C. McGowan, K. A. Oughton, M. Thornton-Pett and M. E. Walsh, *Chem. Commun.*, 1999, 77.

9 P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, G. A. Solan, A. J. P. White, D. J. Williams and S. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, DOI: 10.1039/b100743m.

10 R. Kumar, M. L. Sierra and J. P. Oliver, *Organometallics*, 1994, **13**, 4285.

11 M. P. Hogerheide, M. Wesseling, J. T. B. H. Jastrzebski, J. Boersma, H. Kooijman, A. L. Spek and G. van Koten, *Organometallics*, 1995, **14**, 4483.