1,2-*N*,*N*-Dimethylaminomethylferrocenyl as a ligand towards titanium and vanadium

Peter B. Hitchcock,[a] **David L. Hughes,**[b] **G. Jeffery Leigh,***[a] **J. Roger Sanders**[b] **and Jaisa S. de Souza**[c]

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ*
[b] *Nitrogen Fixation Laboratory, John Innes Centre, Norwich Research Park, Colney, Norwich, UK NR4 7UH*
[c] *Departamento de Química, Universidade Federal do Paraná, Centro Politécnico, Jardim das Américas, 81531-970 Curitiba-PR, Brasil*

Organometallic complexes of titanium(IV) and vanadium(III) containing monodentate and bidentate 1,2-*N*,*N*-dimethyl- aminomethylferrocenyl (L^-) are synthesised and unequivocally characterised, some by crystal structure analysis; in addition, in one titanium derivative, L^- generates a novel tridentate ligand by intramolecular C–H activation of a methyl substituent on the tertiary amino group.

The ligand 1,2-*N*,*N*-dimethylaminomethylferrocenyl (L^-) has been used with several transition-metal ions,[1] but structures have been determined only for $[M(C_5H_5)_2L_2]$ (M = Ti, Zr)[2] and $[(ML)_4]$ (M = Ag^{I}, Cu^{I}),[3] in which L^- is monodentate and binding through a ring carbon atom, for $[(\mu\text{-}Cl)_2Li(thf)_2YbL_2]$,[4] in which it is C,N-bidentate, and for $[(\mu\text{-}L)_2LiY(C_5H_5)_2]$[5] in which it is both bidentate and bridging. In addition, the related HL appears to act as a simple N-donor to Cu^{I}.[6]

Clearly L^- is a versatile ligand, but there are no reliable spectral criteria for its mode of binding. On electron-counting grounds bidentate binding would seem possible in all these complexes, but the splitting of the CH_2NMe_2[7,8] resonances in the ^{1}H NMR spectra and various ^{1}H chemical shifts only attest that coordination has occurred. We wished to use L^- as an additional redox centre bound closely to nitrogen-fixing centres on titanium and vanadium, and so we commenced a survey of the binding properties of this particular ligand, and we confirmed not only that the mode of binding is not easily determined spectrally, but also that there is a further mode of reaction which makes the preparative chemistry and spectral evaluation of the mode of complexation even more difficult.

By careful control of reaction conditions, we were able to isolate $[Ti(C_5H_5)_2ClL]$ **1** whereas other workers[2] have reported only the bis-L derivative. The structure of this compound (Fig. 1) reveals that L^- is monodentate, although the compound is formally more electron-deficient than the bis-L analogue. The dimensions of the L^- ligand are not essentially different from those in the bis-L homologue and imply that there is little difference in the tendencies to form bidentate derivatives in either case.

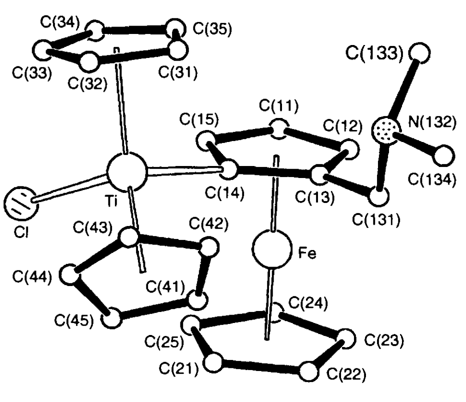

Fig. 1 Representation of the molecular structure of **1**, showing monodentate coordination of L^-. Selected molecular dimensions: Ti–Cl, 2.346(2); Ti–C(14), 2.186(4); mean Ti–C(cyclopentadienyl), 2.38(8) Å; M(3)–Ti–C(14), 102.5; M(4)–Ti–C(14), 108.6; M(3)–Ti–M(4), 130.6; M(4)–Ti–Cl, 107.0° (M denotes centroid of a cyclopentadienyl ring).

The presence of the two C_5H_5 rings in this complex may force the L^- to be monodentate, and we surmised that it would be more likely to exhibit chelating behaviour in mono-C_5H_5 derivatives, as might be formed by reaction with $[Ti(C_5H_5)Cl_3]$. By appropriate choice of reaction conditions we have been able to isolate and characterise all three derivatives $[Ti(C_5H_5)Cl_2L]$ **2**, $[Ti(C_5H_5)ClL_2]$ **3**, and $[Ti(C_5H_5)L_3]$ **4**. Complex **2** (Fig. 2) shows the hoped-for bidentate binding for L^-, though there are no unambiguous spectral data to confirm that this structure is retained in solution. We could not determine structures for complexes **3** and **4**, because no suitable crystals were obtained, but they were characterised by ^{13}C–^{1}H HETCOR NMR (^{13}C-detected), Mössbauer, and mass (EI) spectroscopies. In addition, **4** is unstable at room temperature and above, changing to a further compound **5** for which the structure was determined (Fig. 3).

Elimination of HL and related metallation in **4** occurs cleanly and in high yield to produce **5**, containing L′, $(C_5H_5)Fe(C_5H_3CH_2NMeCH_2)$-*C*,*N*,*C*. This is a novel reaction of ligands of this kind, although a similar species has been observed in *N*-ferrocenylmethyl-*N*-methylaminomethylenetetracarbonylmanganese.[8] The metallation is presumably assisted by relief of steric pressure in **4** as HL is eliminated. The electron count on titanium changes from a formal value between 12 and

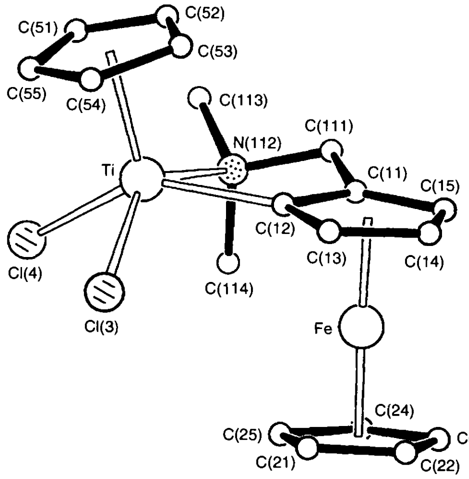

Fig. 2 Representation of the molecular structure of **2**, showing bidentate coordination of L^-. Selected molecular dimensions: Ti–Cl(3), 2.324(2); Ti–Cl(4), 2.317(2); Ti–C(12), 2.107(7); Ti–N(112), 2.446(6); mean Ti–C(cyclopentadienyl), 2.345(3) Å; C(12)–Ti–M(5), 107.1; Cl(3)–Ti–M(5), 111.4; N(112)–Ti–M(5), 110.1; Cl(4)–Ti–M(5), 112.3° (M denotes centroid of a cyclopentadienyl ring).

18 in **4**, depending upon how the three L^- coordinate, to 14 in **5**. Further reactions of the metallated product should yield a wide variety of complexed ferrocenyls substituted in both the ring and in the amine methyl group. The occurrence of similar metallation reactions may be the reason why we have been unable to obtain clean and reproducible yields of a dinitrogen complex from the reaction[9,10] of $[VCl_2(tmeda)_2]$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) and $LiC_6H_4CH_2NMe_2$ under N_2, since this lithium salt should also be prone to metallation.

We have now established[11] that a mixture of $[VCl_2(tmeda)_2]$[9] and LiL[12] can absorb up to one molecule of N_2 per two V atoms, but we have been unable to isolate a clean product, possibly due to competitive metallation. Nevertheless, we have now succeeded in preparing the complex $[VClL_2]$[13] **6** directly from $[VCl_3(thf)_3]$ (Fig. 4). This contains two bidentate L^-, with expected dimensions. In the absence of NMR data, we cannot use this complex to infer spectral criteria of structure, but the complex should react with N_2 upon reduction to vanadium(II), and this we are currently investigating.

We acknowledge financial support to J. S. de S. from CNPq (Brasil) and the British Council, and we thank Dr Shirley Fairhurst for NMR data, Dr David Evans and Ms Elaine Barclay for Mössbauer spectra, and Dr Abdul Sada for mass spectra.

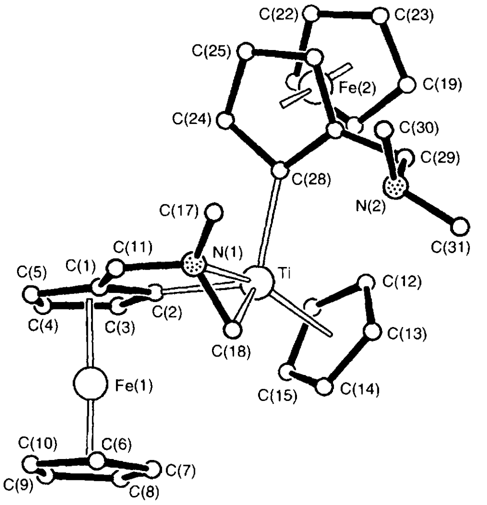

Fig. 3 Representation of the molecular structure of $[Ti(C_5H_5)L(L')]$ **5**, showing monodentate coordination of L^- and metallation involving L'^{2-}. Selected molecular dimensions: Ti–C(18), 2.076(4); Ti–N(1), 2.172(3); Ti–C(2), 2.110(4); Ti–C(28), 2.155(4); Ti–M(3), 2.051(4); N(1)–C(18), 1.436(5) Å; C(2)–Ti–N(1), 80.72(14); C(18)–Ti–N(1), 39.43(13); C(2)–Ti–C(18), 96.1(2); C(2)–Ti–M(3), 112.1(2); C(18)–N(1)–Ti, 66.7(2)° [M(3) denotes centroid of the ring C(12)–C(16)].

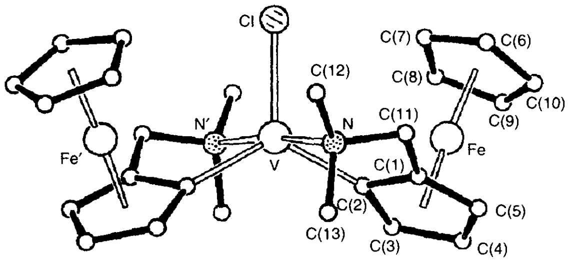

Fig. 4 Representation of the molecular structure of **6**, showing bis(bidentate) coordination of L^-. Selected molecular dimensions: V–N, 2.333(10); V–Cl, 2.293(5); V–C(2), 2.087(13) Å, N–V–N, 173.9; N–V–Cl, 93.1(2); C(2)–V–C(2′), 125.0(7); C(2)–V–N, 96.9(4); C(2)–V–Cl, 117.5(3)°.

Footnote

† *Crystal data*: $[Ti(C_5H_5)_2ClL]$ **1**: $C_{23}H_{26}ClFeNTi$, $M = 455.7$, orthorhombic, space group $P22_12_1$ (equiv. to no. 18), $a = 7.8564(9)$, $b = 14.169(2)$, $c = 18.830(2)$ Å, $U = 2096.0$ Å^3, $Z = 4$, $D_c = 1.44$ g cm^{-3}, $F(000) = 944$, μ(Mo-Kα) = 12.1 cm^{-1}, λ(Mo-Kα) = 0.71069 Å. 2127 Unique intensities measured, 1921 with $I > 2\sigma_I$; structure refined to $R = 0.041$, $R_g = 0.047$ for observed data.

$[Ti(C_5H_5)Cl_2L]$ **2**: $C_{18}H_{21}Cl_2FeNTi$, $M = 426.0$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.821(3)$, $b = 7.6690(6)$, $c = 13.938(2)$ Å, $\beta = 109.272(12)°$, $U = 1798.2$ Å^3, $Z = 4$, $D_c = 1.573$ g cm^{-3}, $F(000) = 872$, μ(Mo-Kα) = 15.4 cm^{-1}, λ(Mo-Kα) = 0.71069 Å. 1674 Unique intensities measured, 1349 with $I > 2\sigma_I$; structure refined to $R = 0.056$; $R_g = 0.084$ for all data.

$[Ti(C_5H_5)L(L')]$ **5**: $C_{31}H_{36}Fe_2N_2Ti$, $M = 596.2$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.598(6)$, $b = 11.697(6)$, $c = 13.008(7)$ Å, $\alpha = 68.86(4)$, $\beta = 73.85(5)$, $\gamma = 79.11(5)°$, $U = 1301(9)$ Å^3. $Z = 2$, $D_c = 1.52$ g cm^{-3}, $F(000) = 620$, μ(Mo-Kα) = 14.2 cm^{-1}, λ(Mo-Kα) = 0.71073 Å. 4576 Unique reflections measured, 3776 with $I > 2\sigma_I$; structure refined to $R = 0.045$ for observed data; $wR2$ for all data = 0.122.

$[VClL_2]$ **6**: $C_{26}H_{32}ClFe_2N_2V$, $M = 570.63$, orthorhombic, space group *Pbcn* (no. 60), $a = 20.761(6)$, $b = 11.846(7)$, $c = 9.63(2)$ Å, $U = 2368$ Å^3, $Z = 4$, $D_c = 1.60$ g cm^{-3}, $F(000) = 1176$, μ(Mo-Kα) = 17.3 cm^{-1}, λ(Mo-Kα) = 0.71073 Å. 1443 Unique reflections measured, 915 with $I < 2\sigma_I$; structure refined to $R = 0.100$ for observed data; $wR2 = 0.276$ for all data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/175.

References

1 Hg: D. W. Slocum and T. R. Engelmann, *J. Organomet. Chem.*, 1970, **24**, 753; Pd: J. C. Gaunt and B. L. Shaw, *J. Organomet. Chem.*, 1975, **102**, 511; V: K. Jacob, W. Kretschmer, K.-H. Thiele, I. Pavlik, A. Lycka and J. Holecek, *Z. Anorg. Allg. Chem.*, 1991, **606**, 133; 1992, **613**, 88; K. H. Thiele and H. Baumann, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1111; Ti: K.-H. Thiele, C. Krüger, R. Boese, G. Schmid, T. Bartik and G. Pályi, *Z. Anorg. Allg. Chem.*, 1990, **590**, 55; V. I. Sokolov, L. L. Troitskaya and O. A. Reutov, *J. Organomet. Chem.*, 1979, **182**, 537; T. Komatsu, M. Nonoyama and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 186; V. I. Sokolov, K. S. Nechaeva and O. A. Reutov, *J. Organomet. Chem.*, 1983, **253**, C59; J. C. Kotz, E. E. Getty and L. Lin, *Organometallics*, 1985, **4**, 610; R. V. Honeychuck, M. O. Okoroafor, L.-H. Shen and C. H. Brubaker Jr., *Organometallics*, 1986, **5**, 482; L. L. Troitskaya and V. I. Sokolov, *J. Organomet. Chem.*, 1987, **328**, 169; C. Krüger, K.-H. Thiele, M. Dargatz and T. Bartik, *J. Organomet. Chem.*, 1989, **362**, 147; K. Jacob, W. Kretschmer, K.-H. Thiele, H. Gornitzka, F. T. Edelmann, I. Pavlik, A. Lycka and J. Holecek, *J. Organomet. Chem.*, 1992, **436**, 231.

2 K.-H. Thiele, C. Krüger, T. Bartik and M. Dargatz, *J. Organomet. Chem.*, 1988, **352**, 115.

3 A. N. Nesmeyanov, Yu. T. Struchkov, N. N. Sedova, V. G. Andrianov, Yu. V. Volgin and V. A. Sazonova, *J. Organomet. Chem.*, 1977, **137**, 217; Ag: A. N. Nesmeyanov, N. N. Sedova, Yu. T. Struchkov, V. G. Andrianov, E. N. Stakheeva and V. A. Sazonova, *J. Organomet. Chem.*, 1978, **153**, 115.

4 H. Gornitzka, A. Steiner, D. Stalke, U. Kilimann, F. T. Edelmann, K. Jacob and K.-H. Thiele, *J. Organomet. Chem.*, 1992, **439**, C6.

5 K. Jacob, M. Schäfer, A. Steiner, G. M. Sheldrick and F. T. Edelmann, *J. Organomet. Chem.*, 1995, **487**, C18.

6 M. A. El-Sayed, A. Ali, G. Davies, S. Larsen and J. Zubieta, *Inorg. Chim. Acta*, 1992, **194**, 139.

7 J. Azizian, R. M. G. Roberts and J. Silver, *J. Organomet. Chem.*, 1986, **303**, 397; J. C. Randall, J. J. McLeskey, P. Smith and M. E. Hobbs, *J. Am. Chem. Soc.*, 1964, **86**, 3229.

8 S. S. Crawford and H. D. Kaesz, *Inorg. Chem.*, 1977, **16**, 3193.

9 J. J. H. Edema, W. Stauthamer, F. van Bolhuis, S. Gambarotta, W. J. J. Smeets and A. L. Spek, *Inorg. Chem.*, 1990, **29**, 1302.

10 J. J. H. Edema, A. Meetsma and S. Gambarotta, *J. Am. Chem. Soc.*, 1989, **111**, 6878.

11 G. J. Leigh and J. R. Sanders, unpublished work.

12 M. D. Rausch, G. A. Moser and C. F. Meade, *J. Organomet. Chem.*, 1973, **51**, 1.

13 K. Jacob and W. Palitzsch, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1489.

Received, 7th May 1996; Com. 6/03131E