First Examples of a New Family of Redox-Functionalised Chelate Complexes Based on a 1,1′-Ferrocenediyl-Bridged Di(amido) Ligand

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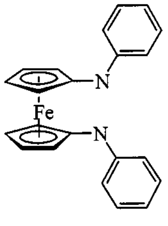
Treatment of $Fe[(C_5H_4)NHPh]_2$ (**1**H_2) with $M(NMe_2)_4$ (**3a**: M = Ti, **3b**: M = Zr) in benzene afforded the chelates (**1**)$Ti(NMe_2)_2$ (**4**) and (**1**)$Zr(NMe_2)_2(HNMe_2)$ (**5**), respectively. Chelate **5** was cleanly oxidised by ferrocenium hexafluorophosphate in acetonitrile. Treatment of **5** with two equivalents of $[Me_2NH_2]Cl$ (**6**) in benzene afforded (**1**)$ZrCl_2(HNMe_2)$ (**7**). The chelates **5** and **7** were characterised by X-ray structure analyses. The new redox-active chelate complexes are precatalysts for the polymerisation of ethylene.

The search for new generation nonmetallocene catalysts for the polymerisation of α-olefins is of continuing interest.[1] Complexes of the Group 4 metals containing chelating di(amido) ligands represent a very promising class of (pre-)catalysts in this context. This has been demonstrated in recent years by the groups of Bochmann,[2] Eisen,[3] Gibson,[4] McConville,[5] Schrock,[6] and others,[7] building on earlier work by Bürger et al.[8] Ziegler and co-workers, using quantum-chemical methods, have rationalised the factors governing the ethylene polymerisation activity of such catalysts.[9]

We decided to utilise the novel 1,1′-ferrocenediyl-bridged ligand system $Fe[(C_5H_4)NPh]_2$ (**1**) in this context. This ligand is related to **2**, recently reported by Kempe and co-workers.[10] They found that, because of the high flexibility of **2**, complexes of the type **2**TiXY (X = Y = NMe_2; X = NMe_2, Y = Cl) are unstable. Not surprisingly, therefore, catalytically active complexes of **2** are unknown. In contrast, **1** would be expected to provide a fairly rigid ligand framework and should furthermore exhibit excellent π-donor qualities (beneficial for olefin insertion),[9] since the amido nitrogen atoms are directly connected to the electron-rich ferrocene moiety.[11]

We note that the electronic properties of our redox-active ligand system can be changed quite dramatically by oxidation. In fact, the development of redox-active ligands which allow the electrochemical control of stoichiometric and catalytic reactivities of transition metal centres is of great current interest.[12]



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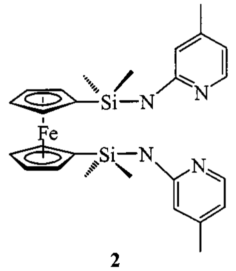

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Metathesis of **1**H_2 [13] with one equivalent of $Ti(NMe_2)_4$ (**3a**) afforded (**1**)$Ti(NMe_2)_2$ (**4**). Analogously, treatment of **1**H_2 with $Zr(NMe_2)_4$ (**3b**) gave (**1**)$Zr(NMe_2)_2(HNMe_2)$ (**5**), and treatment of this with two equivalents of $[Me_2NH_2]Cl$ (**6**) furnished (**1**)$ZrCl_2(HNMe_2)$ (**7**) (Scheme 1). Di(amido)zirconium(IV) complexes may be viewed as relatives of zirconocene derivatives[4] and hence ours are akin to the ferrocenediyl-bridged zirconocene dichloride $\{Fe[(C_5H_4)C_5Me_4]_2\}ZrCl_2$ reported by Brintzinger and co-workers.[14]

Cyclic voltammetric studies have shown that the ligand precursor **1**H_2 undergoes a chemically reversible, one-electron oxidation at $E°' = -0.06$ V (vs. SCE) in dichloromethane solution. Such an easy oxidation matches well the corresponding process exhibited by the related species $Fe[(C_5H_4)NMe_2]_2$ and $Fe[(C_5H_4)NPh_2]_2$.[15,16] Complexation of the metal-ligand fragment causes the ferrocenediyl-centred oxidation of the zirconaferrocenophane (**1**)$Zr(NMe_2)_2(HNMe_2)$ (**5**) to become slightly more difficult, by about 40 mV ($E°' = -0.02$ V), indicating that the $Zr(NMe_2)_2(HNMe_2)$ fragment withdraws electron density from the ferrocene subunit. Chemical oxidation of **5** was cleanly achieved with one equivalent of ferrocenium hexafluorophosphate in acetonitrile.

Single crystal X-ray diffraction studies have been performed for both new zirconium compounds. The zirconium atom in **5** is coordinated by five nitrogen atoms in a distorted trigonal bipyramidal arrangement (Figure 1). The axial positions are occupied by the amino ligand and the

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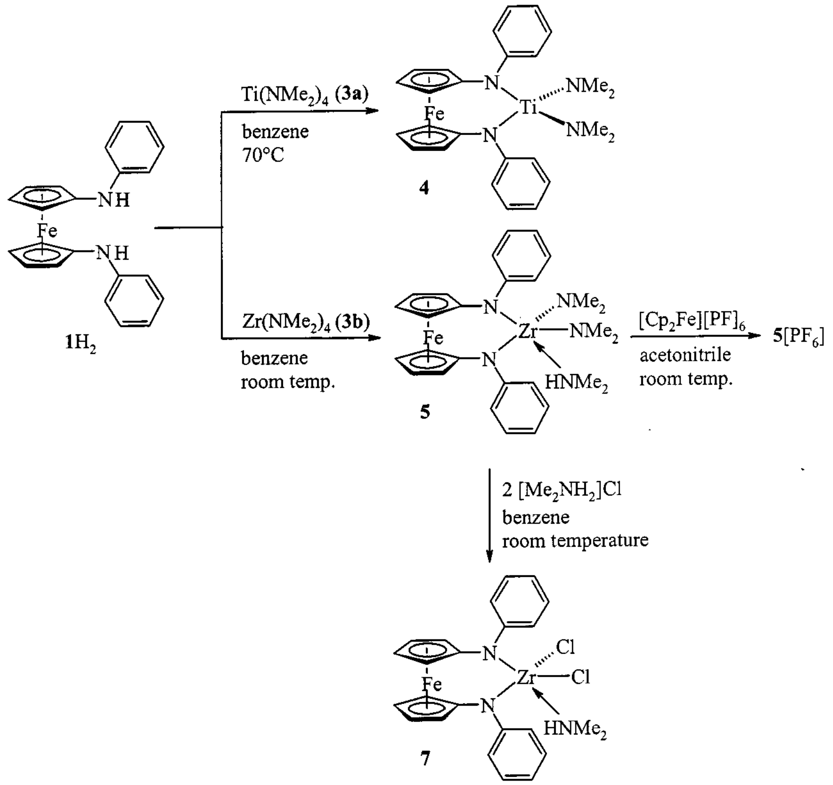

Scheme 1. Synthesis of the chelate complexes **4**, **5**, **5**[PF$_6$], and **7**

amido ligand *trans* to it, their ligating atoms forming an angle of 171.4(3)° with the Zr atom. The N(1)−Zr(1)−N(2) bite angle of the chelating ligand **1** is 132.9(3)°. The amino nitrogen−zirconium distance is 243.8(8) pm — consistent with a Zr−N(sp^3) single bond — while, thanks to their partial double-bond character, the four amido nitrogen−zirconium bonds are much shorter, ranging from 205.7(7) to 215.4(7) pm. These bond lengths are similar to those found for the related compound [Ph$_2$Si(NAr)$_2$]Zr(NMe$_2$)$_2$(HNMe$_2$) (Ar = 2,6-Me$_2$C$_6$H$_3$).[4] The cyclopentadienyl rings of the ferrocene unit are in an eclipsed orientation. The parallel sandwich structure is slightly distorted and opens up towards the zirconium centre with a cyclopentadienyl ring tilt angle of 11.4°. The Fe−Zr distance of 333.9 pm precludes a significant bonding interaction between the two metal atoms.

The core geometry of **7** is also best described as distorted trigonal bipyramidal (Figure 2). Again, the amino ligand is in an axial position, the second axial position being occupied by a chloro ligand [N(3)−Zr(1)−Cl(1) 172.12(10)°]. In related systems containing linked amido-cyclopentadienyl ligands,[17] the amino ligand is positioned between the two chloro ligands. The N(1)−Zr(1)−N(2) bite angle is essentially identical to that in **5**, while the corresponding zirconium−nitrogen bond lengths are slightly shorter, resulting in a smaller cyclopentadienyl tilt angle of 9.4° and a shorter Fe−Zr distance of 331.0 pm. In both compounds, all amido nitrogen atoms are trigonal planar and the phenyl rings lie approximately in the plane defined by the zirconium atom and the amido nitrogen atoms of the chelating ligand **1**.

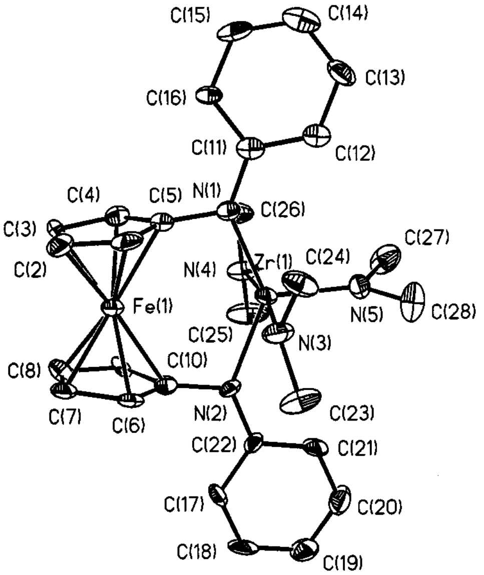

Figure 1. Molecular structure of **5** in the crystal; selected bond lengths (pm) and angles (°): Zr(1)−N(1) 212.8(7), Zr(1)−N(2) 215.3(7), Zr(1)−N(4) 215.4(7), Zr(1)−N(5) 205.7(7), N(1)−C(5) 142.3(11), N(1)−C(11) 139.5(10), N(2)−C(10) 141.3(10), N(2)−C(22) 138.9(9); N(3)−Zr(1)−N(5) 92.5(3), N(4)−Zr(1)−N(5) 96.0(3)

Preliminary investigations have shown that these new compounds are precatalysts for the polymerisation of ethylene.[18] The results of a detailed study, which also addresses the aspect of redox-tuning of catalyst activity, will be reported in due course.

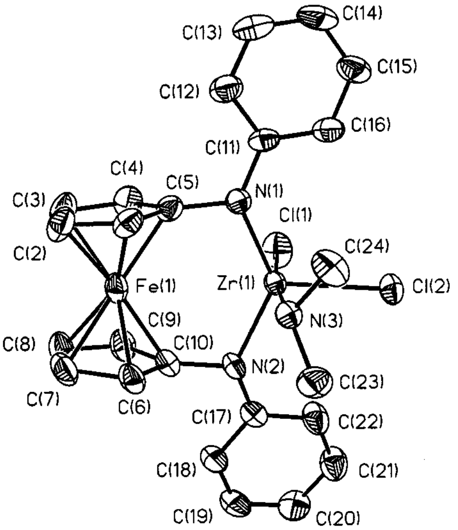

Figure 2. Molecular structure of **7** in the crystal; selected bond lengths (pm) and angles (°): Zr(1)−N(1) 206.0(4), Zr(1)−N(2) 207.6(4), Zr(1)−N(3) 238.3(4), Zr(1)−Cl(1) 245.95(16), Zr(1)−Cl(2) 241.76(14), N(1)−C(5) 141.6(6), N(1)−C(11) 141.4(6), N(2)−C(10) 141.9(6), N(2)−C(17) 139.4(6); N(3)−Zr(1)−Cl(2) 81.56(10), Cl(1)−Zr(1)−Cl(2) 91.02(5)

Experimental Section

General: All manipulations were performed under an inert atmosphere (purified argon or dinitrogen), using standard Schlenk and cannula techniques or a conventional glovebox. Solvents and reagents were dried and purified by standard procedures. − NMR spectra were recorded at 300 K with a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^{1}H; TMS was used as external reference. − The materials and apparatus used for the electrochemical investigations have been described elsewhere.[19] − Elemental analyses were performed by the Microanalytical Laboratory of Universität Bielefeld.

Complex 4: A solution of **1**H_2 (0.87 g, 2.35 mmol) and **3a** (0.53 g, 2.35 mmol) in benzene (1 mL) was kept at 70 °C for 2 h. The volatile components were then removed in vacuo. The residue was extracted with *n*-hexane (20 mL) and the extract filtered. The filtrate was reduced to dryness in vacuo, leaving the product as a brownish yellow solid. Yield 0.90 g (76%). − ^{1}H NMR ($CDCl_3$): $\delta = 3.24$ (s, 12 H, NMe_2), 3.63 (s, 4 H, C_5H_4), 4.54 (s, 4 H, C_5H_4), 6.71 ("t", apparent $J = 6.9$ Hz, 2 H, Ph), 6.78 ("d", apparent $J = 7.9$ Hz, 4 H, Ph), 7.16 ("t", apparent $J = 7.2$ Hz, 4 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 45.1$ (NMe_2), 68.9, 71.0, 87.3 (C_5H_4), 115.4, 118.1, 128.9, 154.5 (Ph). − $C_{26}H_{30}FeN_4Ti$ (502.3): calcd. C 62.17, H 6.02, N 11.15; found C 61.18, H 5.88, N 11.71.

Complex 5: Benzene (7 mL) was added to **1**H_2 (0.87 g, 2.35 mmol) and **3b** (0.60 g, 2.35 mmol), affording a light yellow precipitate. The mixture was stirred for 1 h at room temperature. Crystallisation from a minimal quantity of hot benzene afforded the product as light yellow crystals. Yield 0.99 g (71%). − ^{1}H NMR ($CDCl_3$): $\delta =$ 2.39 (br. s, 6 H, $HN\mathit{Me}_2$), 3.05 (s, 12 H, NMe_2), 3.70 (t, $J = 1.9$ Hz, 4 H, C_5H_4), 4.62 (t, $J = 1.9$ Hz, 4 H, C_5H_4), 6.66 ("t", apparent $J = 7.2$ Hz, 2 H, Ph), 6.74 ("d", apparent $J = 7.8$ Hz, 4 H, Ph), 7.17 ("t", apparent $J = 7.7$ Hz, 4 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 39.1$ ($HNMe_2$), 43.2 (NMe_2), 68.5, 70.5, 89.9 (C_5H_4), 115.3, 117.0, 129.1, 153.9 (Ph). − $C_{28}H_{37}FeN_5Zr$ (590.7): calcd. C 56.93, H 6.31, N 11.86; found C 56.69, H 6.11, N 11.20.

Complex 5[PF$_6$]: A solution of **5** (59 mg, 0.10 mmol) and ferrocenium hexafluorophosphate (33 mg, 0.10 mmol) in acetonitrile (5 mL) was stirred at room temperature for 5 h. The volatile components (solvent and ferrocene) were then removed in vacuo, leaving the product as a brown solid. Yield 73 mg (99%). − $C_{28}H_{37}F_6FeN_5PZr$ (735.6): calcd. C 45.72, H 5.07, N 9.52; found C 45.69, H 5.02, N 8.87.

Complex 7: A solution of **5** (0.28 g, 0.47 mmol) and **6** (77 mg, 0.94 mmol) in benzene (10 mL) was stirred at room temperature for 15 h. The resulting yellow precipitate was then filtered off. Crystallisation from a minimal quantity of chloroform afforded the product as yellow needles. Yield 59 mg (22%). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 39.1$ ($HNMe_2$), 43.2 (NMe_2), 68.9, 71.0, 87.3 (C_5H_4), 115.4, 118.1, 128.9, 154.5 (Ph). − $C_{24}H_{25}Cl_2FeN_3Zr{\cdot}2CHCl_3$ (812.2): calcd. C 38.45, H 3.35, N 5.17; found C 39.04, H 3.23, N 5.20.

Crystal Structure Determinations of 5 and 7:[20] A yellow single crystal of **5** (dimensions 0.5 × 0.5 × 0.25 mm) and **6** (dimensions 0.8 × 0.4 × 0.4 mm), respectively, was used for data collection at 173 K on a Siemens $P2_1$ four-circle diffractometer with graphite-mono-

Table 1. X-ray structure analysis data of **5** and **7**

Chem. formula	$C_{28}H_{37}FeN_5Zr$	$C_{24}H_{25}Cl_2FeN_3Zr{\cdot}2\ CHCl_3$
Mol. wt.	590.70	812.18
Space group	Monoclinic, $P2_1/c$	Orthorhombic, *Pbcn*
a [Å]	12.771(5)	15.029(6)
b [Å]	12.605(5)	17.751(6)
c [Å]	17.149(11)	24.766(10)
β [°]	98.03(4)	
V [Å^3]	2734(2)	6607(4)
Z	4	8
ρ(calcd.) [g/cm^3]	1.435	1.633
μ [mm^{-1}]	0.937	1.424
F(000)	1224	3248
Index ranges	$0 \le h \le 15$, $0 \le k \le 14$, $-20 \le l \le 20$	$0 \le h \le 20$, $0 \le k \le 23$, $0 \le l \le 33$
θ range [°]	1.6−25.0	1.6−28.5
Reflections collected	5046	8388
Independent reflections	4814 [R(int.) = 0.0701]	8388
Data/restraints/parameters	4814/0/322	8388/0/360
Goodness-of-fit on F^2	1.052	1.013
Final $R1$[a] [$I > 2\sigma(I)$]/$wR2$[b]	0.0814/0.1911	0.0609/0.1348
Larg. diff. peak/hole [e/Å^3]	1.041/−0.901	1.041/−1.182

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

chromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods. Programs used were Siemens SHELXTL PLUS[21] and SHELXL-97.[22] Full-matrix, least-squares refinement on F^2 was carried out anisotropically for the non-hydrogen atoms. Hydrogen atoms were included at calculated positions, using a riding model. Further X-ray structure analysis data are given in Table 1.

Acknowledgments

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[1] Review: G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448−468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428−447.

[2] N. A. H. Male, M. Thornton Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* **1997**, 2487−2491.

[3] H. Mack, M. S. Eisen, *J. Organomet. Chem.* **1996**, *525*, 81−87.

[4] V. C. Gibson, B. S. Kimberley, A. J. P. White, D. J. Williams, P. Howard, *Chem. Commun.* **1998**, 313−314.

[5] See, for example: J. D. Scollard, D. H. McConville, N. C. Payne, J. J. Vidal, *Macromolecules* **1996**, *29*, 5241−5243.

[6] See, for example: T. H. Warren, R. R. Schrock, W. M. Davis, *Organometallics* **1998**, *17*, 308−321.

[7] See, for example: [7a] Z. Ziniuk, I. Goldberg, M. Kol, *Inorg. Chem. Commun.* **1999**, *2*, 549−551. − [7b] Y.-M. Jeon, S. J. Park, J. Heo, K. Kim, *Organometallics* **1998**, *17*, 3161−3163. − [7c] F. Jäger, H. W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H.-G. Schmidt, *Chem. Ber./Recl.* **1997**, *130*, 399−403. − [7d] S. Tinkler, R. J. Deeth, D. J. Duncalf, A. McCamley, *Chem. Commun.* **1996**, 2623−2624. − [7e] A. D. Horton, J. de With, A. J. van der Linden, H. van de Weg, *Organometallics* **1996**, *15*, 2672−2674.

[8] See, for example: [8a] H. Bürger, K. Wiegel, *Z. Anorg. Allg. Chem.* **1976**, *419*, 157−162. − [8b] H. Bürger, K. Wiegel, *Z. Anorg. Allg. Chem.* **1976**, *426*, 301−308. − [8c] H. Bürger, K. Wiegel, *J. Organomet. Chem.* **1977**, *124*, 279−292. − [8d] D. J. Brauer, H. Bürger, K. Wiegel, *J. Organomet. Chem.* **1978**, *150*, 215−231. − [8e] H. Bürger, D. Beiersdorf, *Z. Anorg. Allg. Chem.* **1979**, *459*, 111−118. − [8f] H. Bürger, W. Geschwandtner, G. R. Liewald, *J. Organomet. Chem.* **1983**, *259*, 145−156.

[9] [9a] P. Margl, L. Deng, T. Ziegler, *J. Am. Chem. Soc.* **1998**, *120*, 5517−5525. − [9b] P. Margl, L. Deng, T. Ziegler, *Organometallics* **1998**, *17*, 933−946.

[10] A. Spannenberg, P. Arndt, M. Oberthur, R. Kempe, *Z. Anorg. Allg. Chem.* **1997**, *623*, 389−393.

[11] See, for example: H. Plenio, D. Burth, *Organometallics* **1996**, *15*, 4054−4062.

[12] Review: A. M. Allgeier, C. A. Mirkin, *Angew. Chem.* **1998**, *110*, 936−952; *Angew. Chem. Int. Ed.* **1998**, *37*, 894−908.

[13] B. Bildstein, M. Malaun, unpublished results.

[14] P. Scott, U. Rief, J. Diebold, H. H. Brintzinger, *Organometallics* **1993**, *12*, 3094−3101.

[15] K.-P. Stahl, G. Boche, W. Massa, *J. Organomet. Chem.* **1984**, *277*, 113−125.

[16] W. E. Britton, R. Kashyap, M. El-Hashash, M. El-Kady, M. Herberhold, *Organometallics* **1986**, *5*, 1029−1031.

[17] See, for example: [17a] D. W. Carpenetti, L. Kloppenburg, J. T. Kupec, J. L. Petersen, *Organometallics* **1996**, *15*, 1572−1581. − [17b] A. K. Hughes, A. Meetsma, J. H. Teuben, *Organometallics* **1993**, *12*, 1936−1945.

[18] U. Siemeling, O. Kuhnert, M. O. Kristen, G. Hauck, unpublished results.

[19] A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech, H. Keller, *Organometallics* **1994**, *13*, 1224−1234.

[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-149674 (for **5**) and CCDC-149675 (for **7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[21] G. M. Sheldrick, *SHELXTL PLUS*, Siemens Analytical Instruments, Madison, WI, USA, **1990**.

[22] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.

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