1936 *Organometallics* 1993, *12*, 1936–1945

Efficient New Synthetic Route to Bidentate, Monomeric Cyclopentadienyl–Amide Complexes of Group 4 Transition Metals: Synthesis and Characterization of the Zirconium and Hafnium Complexes [{η^5:σ-$C_5H_4(CH_2)_3NMe$}$MX_2(NHMe_2)$] (X = Cl, I, M = Zr; X = I, M = Hf) and [{η^5:σ-$C_5H_4(CH_2)_3NMe$}ZrX_2] (X = NMe_2, CH_2Ph, CH_2SiMe_3, BH_4) and Molecular Structure of [{η^5:σ-$C_5H_4(CH_2)_3NMe$}$ZrCl(CH_2Ph)$]$_2$

Andrew K. Hughes, Auke Meetsma, and Jan H. Teuben*

Groningen Centre for Catalysis and Synthesis, Department of Chemistry,
University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

Received November 9, 1992

The synthesis of the amine-substituted cyclopentadiene $C_5H_5CH_2CH_2CH_2N(H)Me$ (**2**, HCpNH) is described. The reaction of **2** with $M(NMe_2)_4$ (M = Zr, Hf) gives the ring-closed species [M(η^5:σ-$C_5H_4CH_2CH_2CH_2NMe$)$(NMe_2)_2$] (M(CpN)$(NMe_2)_2$; M = Zr (**3**), Hf (**4**)) in high yields (60–95%). Aminolysis of **3** and **4** with 2 equiv of $Me_2NH{\cdot}HX$ (X = Cl, I) provides a route to amine adducts of the dihalide complexes [M(CpN)$X_2(NHMe_2)$] (M = Zr, X = Cl (**5**), I (**6**); M = Hf, X = I (**7**)). Aminolysis of **3** with 1 equiv of $Me_2NH{\cdot}HI$ gives the mixed amido–iodide [Zr(CpN)I(NMe_2)] (**8**). The dichloride **5** is an excellent precursor to alkyl complexes; thus, reaction of **5** with $C_6H_5CH_2MgCl$ (2 equiv) gives [Zr(CpN)$(CH_2Ph)_2$] (**9**), that of **5** with Me_3SiCH_2Li gives [Zr(CpN)$(CH_2SiMe_3)_2$] (**10**), and that of **5** with $C_6H_5CH_2MgCl$ (1 equiv) gives the mixed complex [Zr(CpN)$(CH_2Ph)Cl$] (**11**). The ^1H and ^{13}C NMR data for **9** and **10** are discussed in terms of η^2-benzyl (**9**) and *agostic* (**10**) interactions in these formally 14-valence-electron compounds. The reaction of **5** with $LiBH_4$ gives [Zr(CpN)$(\eta^3$-$BH_4)_2$] (**13**). Aminolysis of **3** with cyclopentadiene gives [Zr(CpN)$(\eta$-$C_5H_5)(NMe_2)$] (**14**), while **3** also reacts with phenylacetylene to give the poorly stable bis(acetylide) [Zr(CpN)$(CCPh)_2$] (**15**). Compound **11** has been characterized as a benzene-d_6 solvate by X-ray crystallography: $(C_{32}H_{40}Cl_2N_2Zr_2)_{0.5}$-$(C_6D_6)$, M_r = 437.17, monoclinic, $P2_1/c$, a = 11.649(1) Å, b = 10.360(1) Å, c = 17.802(1) Å, β = 106.750(4)°, V = 2057.3(3) Å^3, Z = 4, D_x = 1.411 g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.710 73 Å, μ = 6.6 cm^{-1}, $F(000)$ = 888, T = 295 K, and R_F = 0.035 for 3691 unique observed reflections with $I \geq 2.5\sigma(I)$ and 260 parameters. The crystal structure consists of dimer molecules of **11**, obeying symmetry $\bar{1}$ and coupled by two bridging Cl atoms, with two different Zr–Cl distances of 2.6288(8) and 2.6797(9) Å, respectively.

Introduction[1]

There is an increasing interest in the use of anionic ligands other than cyclopentadienyl, or its substituted derivatives, as "spectator" ligands in the coordination environment of the early-transition-metal complexes. Some examples of such ligands include benzamidinate,[2] carborane,[3] the so-called "Klaüi-Cp" ligand [Cp-Co{$(EtO)_2PO$}$_3$]$^-$,[4] imide (or nitrene),[5] Schiff bases,[6] porphyrin,[7] hydridotris(pyrazolyl)borate,[8] alkylsiloxamide,[9] diiminophosphinate,[10] and amidodiphosphines.[11] Together with other research groups, one of our interests in this area has been the synthesis of bidentate ligands combining a cyclopentadienyl ligand with a pendant ligand.[12] We have been investigating the coordination chemistry of such ligands with early transition metals and lanthanides.

---

[1] The following abbreviations are used in this article: Cp = η^5-C_5H_5, Cp* = η^5–C_5Me_5, Fv = η^5:η^1–$C_5Me_4CH_2$, CpN = η^5:σ–$C_5H_4CH_2CH_2CH_2$-NMe, THF = tetrahydrofuran.

[2] (a) Wedler, M.; Recknagel, A.; Gilje, J. W.; Nottemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1992**, *426*, 295. (b) Wedler, M.; Nottemeyer, M.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 72. (c) Recknagel, A.; Knosei, F.; Gornitzka, H.; Nottemeyer, M.; Edelmann, F. T.; Behrens, U. *J. Organomet. Chem.* **1991**, *417*, 363. (d) Wedler, M.; Knosel, F.; Edelmann, F. T.; Behrens, U. *Chem. Ber.* **1992**, *125*, 1313. (e) Duchateau, R.; Meetsma, A.; Teuben, J. H.; van Wee, C. T. Manuscript in preparation.

[3] (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Organometallics* **1991**, *10*, 3964.

[4] Klaüi, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *21*, 627.

[5] For some examples see: (a) Jekel-Vroegop, C. T.; Teuben, J. H. *J. Organomet. Chem.* **1985**, *286*, 309. (b) Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 739. (c) Green, M. L. H.; Konidaris, P. C.; Mountford, P.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1992**, 256. (d) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

[6] (a) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 96. (b) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1992**, 367.

[7] (a) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968. (b) Shibata, K.; Aida, T.; Inoue, S. *Tetrahedron Lett.* **1992**, *33*, 1077. (c) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266 and references therein.

[8] Ipaktschi, J.; Sulzbach, W. *J. Organomet. Chem.* **1992**, *426*, 59.

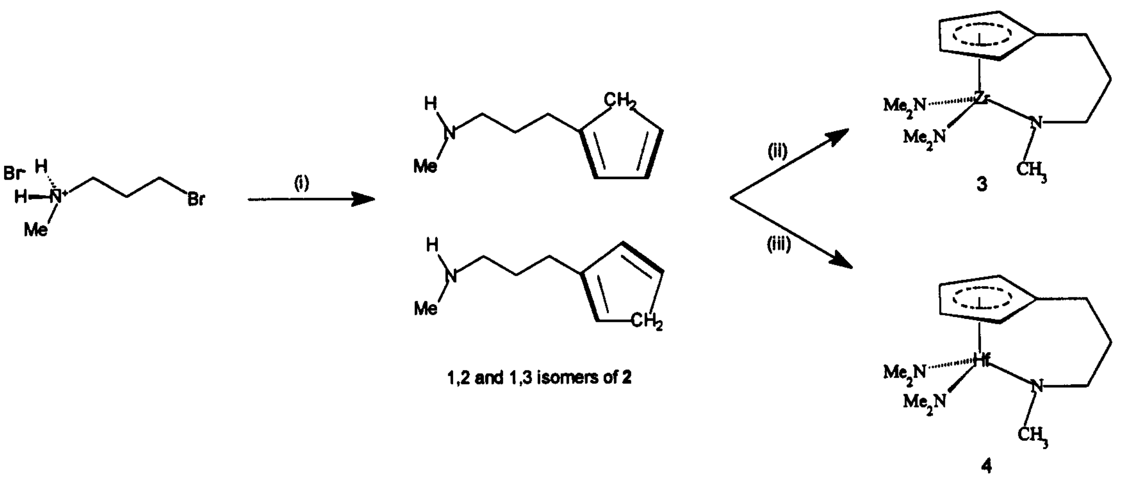
[9] Recknagel, A.; Steiner, A.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *415*, 315.

[10] Recknagel, A.; Steiner, A.; Noltemeyer, M.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *414*, 327.

[11] See: Fryzuk, M. D.; Carter, A.; Rettig, S. *J. Organometallics* **1992**, *11*, 469 and references therein.

0276-7333/93/2312-1936$04.00/0

Scheme I. The Syntheses of $C_5H_5CH_2CH_2CH_2N(H)Me$ (2) and $[M(CpN)(NMe_2)_2]$ (M = Zr (3), and Hf (4))[a]



4

[a] Reagents and conditions: (i) excess NaCp, THF, 20 °C, 20 h, 59%; (ii) $Zr(NMe_2)_4$, toluene, 40 °C, 15 min, 94%; (iii) $Hf(NMe_2)_4$, toluene, 20 °C, 15 h, 58%.

Our interest in such bidentate ligands is 2-fold. First, complexes of the early transition metals are frequently strong Lewis acids and we wish to investigate the effect of coordination of an anionic Lewis base to the metal. Second, we wish to investigate what effect substitution of a cyclopentadienyl ligand in the familiar bis(cyclopentadienyl) complexes with alternative monoanionic ligands has on the electronic character of the metal in such complexes. Both of these influences are expected to have a significant effect on the reactivity of the complexes; in particular, we have been interested in investigating the catalytic activity of such compounds.

Here we describe the results of research into the synthesis of an amine-substituted ligand, $C_5H_5CH_2CH_2CH_2N(H)Me$, and a series of zirconium complexes derived from this ligand. Our work with similar ligands containing a cyclopentadiene and an alkoxide function bridged by either two or three CH_2 units[13] has led us to concentrate on the three-CH_2-unit ligand, as this produces a chain that appears to be more capable of producing a strain-free ring system.

Results and Discussion

Synthesis of $C_5H_5CH_2CH_2CH_2N(H)Me$ and $[M(CpN)(NMe_2)_2]$ (M = Zr, Hf). The addition of an excess of NaCp to $BrCH_2CH_2CH_2N(H)Me{\cdot}HBr$ (1) in THF provides a useful synthetic route to the substituted cyclopentadiene $C_5H_5CH_2CH_2CH_2N(H)Me$ (Scheme I). The spectroscopic and analytical data characterizing 2 and the other new compounds described in this paper are collected in the Experimental Section and will not be further discussed, except where appropriate.

Both ^1H and ^{13}C NMR spectra show that 2 exists as a mixture of two of the three possible isomers (Scheme I), in a ratio very close to 1:1. The ^{13}C spectrum is the more informative and shows two quaternary resonances at δ 149.1 and 146.5 ppm and a total of six olefinic CH resonances between δ 125 and 135 ppm. It has not proved possible to totally assign the C_5H_5 resonances in the ^1H spectrum on account of heavy overlap, although the two sets of each of the NCH_2 and NCH_2CH_2 resonances are clearly resolved.

For the synthesis of group 4 metal complexes from 2 we chose to use the aminolysis reaction of cyclopentadiene and amines with $M(NMe_2)_4$ (M = Ti, Zr, Hf) first described by Lappert.[14] Thus, addition of a toluene solution of $Zr(NMe_2)_4$ to a cold (−30 °C) toluene solution of 2 gave a pale yellow solution, from which crude $[Zr(CpN)(NMe_2)_2]$ (3) was obtained as a yellow oil which could be purified by vacuum distillation, giving a 94% yield of pure 3 as a colorless oil. For subsequent reactivity studies it was found to be useful to prepare a standard solution of 3 in toluene (approximately 0.75 M). The hafnium analogue $[Hf(CpN)(NMe_2)_2]$ (4) was prepared from $Hf(NMe_2)_4$ and 2 using a similar method; again, after a vacuum distillation, a 58% yield of pure 4 was obtained.

The methodology that has been employed for the synthesis of metal complexes from the cyclopentadiene 2 contrasts with the more popular methods using either alkali-metal salts[15] or R_3M (M = Si, Sn) derivatives.[12g,16] In the present case the use of $M(NMe_2)_4$ as a reagent means that fewer synthetic steps are required from the isolation of the cyclopentadiene, and also the organometallic product is readily purified by means of distillation. The drawback to this synthetic route is the need to prepare halides from the resulting amide complexes.

Synthesis of $[M(CpN)X_2(NHMe_2)]$ (M = Zr, X = Cl, I; M = Hf, X = I) and $[Zr(CpN)I(NMe_2)]$. Although the chemistry of early-transition-metal amide ($M{-}NR_2$) complexes has been extensively investigated,[17] compared with halides these compounds do not provide such useful

---

[12] (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P., Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59. (c) Wang, T.-F.; Lee, T.-Y.; Wen, Y.-S.; Liu, L.-K. *J. Organomet. Chem.* **1991**, *403*, 353. (d) Rieger, B. *J. Organomet. Chem.* **1991**, *420*, C17. (e) Wang, T.-F., Lee, T.-Y.; Chou, J.-W.; Ong, C.-W. *J. Organomet. Chem.* **1992**, *423*, 31. (f) Siemeling, U. *J. Organomet. Chem.* **1992**, *429*, C14. (g) Antonelli, D. M.; Green, M. L. H.; Mountford, P. *J. Organomet. Chem.* **1992**, *438*, C4.

[13] Meetsma, A.; Teuben, J. H.; Trouvé, G. Unpublished results.

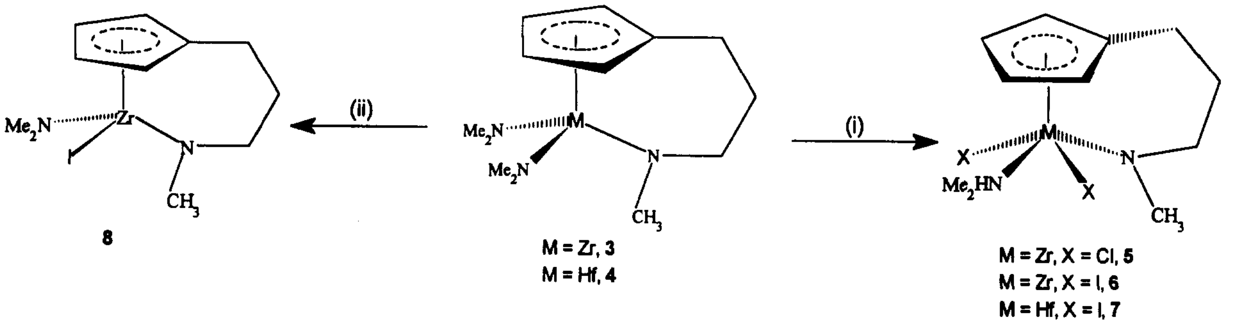
[14] Chandra, G.; Lappert, M. F. *J. Chem. Soc. A* **1968**, 1940.

[15] For reviews see: (a) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-zirconium and -hafnium Compounds*; Ellis Horwood: Chichester, U.K., 1986. (b) *Comprehensive Organometallic Chemistry*; Wilkinson G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 3.

[16] Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426 and references therein.

[17] (a) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C.; *Metal and Metalloid Amides: Synthesis, Structures, and Physical and Chemical Properties*; Ellis Horwood: Chichester, U.K., 1979. (b) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, Chapter 13.4.

Scheme II. Reactions of [M(CpN)(NMe$_2$)$_2$] (M = Zr, Hf) with Me$_2$NH·HX (X = Cl, I)[a]



[a] Reagents and conditions: (i) for 5, 2 equiv of Me$_2$NH·HCl, toluene/THF, −40 to +20 °C, 50%; for 6, 2 equiv of Me$_2$NH·HI, toluene/THF, −80 to +60 °C, 77%, for 7, 2 equiv of Me$_2$NH·HI, toluene/THF, −80 to +60 °C, 10%; (ii) 1 equiv of Me$_2$NH·HI, toluene/THF, −80 to +40 °C, 54%.

starting materials for the synthesis of a wide range of organometallic compounds. Thus, we sought to prepare halide complexes from 3 and 4 (Scheme II).

The stoichiometric addition of acid (HCl or HI), in the form of dimethylamine hydrohalide, to the amide complexes 3 and 4 provides a facile route to the halide derivatives. Thus, adding a toluene solution of 3 to a cold (−40 to −80 °C) suspension of 2 equiv of anhydrous Me$_2$NH·HCl in THF and warming the mixture to room temperature gave [Zr(CpN)Cl$_2$(NHMe$_2$)] (5), in a typical yield of 50% following crystallization from toluene/pentane mixtures. Using exactly the same methods, the following analogues were prepared: [Zr(CpN)Cl$_2$(NDMe$_2$)] (**5**-*d*) from 3 and Me$_2$ND·DCl, [Zr(CpN)I$_2$(NHMe$_2$)] (6) from 3 and Me$_2$H·HI, and [Hf(CpN)I$_2$(NHMe$_2$)] (7) from 4 and Me$_2$NH·HI. In the case of 7 the yield of pure product (10%) was remarkably poor, although moderate yields (35%) were obtained of the crude material prior to recrystallization.

The Lewis acidity of [M(CpN)X$_2$] and the resulting coordination of dimethylamine should be compared with the similar Lewis acidity of CpMCl$_3$ (M = Zr, Hf) and their Lewis-base adducts CpMCl$_3$(THF)$_2$ and CpMCl$_3$(DME) (DME = 1,2-dimethoxyethane).[16]

The ^{1}H NMR spectrum of 6 shows an A$_2$B$_2$ pattern for the protons of the C$_5$H$_4$ ring, a singlet (integral 3H) for the N–CH$_3$ protons of the ligand, and an A$_2$B$_2$C$_2$ pattern for the CH$_2$ protons of the ligand backbone. The most important feature, however, is a doublet for the NMe$_2$ protons of the coordinated amine, together with a broad feature assigned to the N–H. Double-resonance experiments show that these two resonances are coupled (J_{H-H} = 6 Hz). This demonstrates that the N–H proton is on the NMe$_2$ ligand, and not on N–CH$_3$ of the (CpN) ligand. The ^{1}H NMR spectra of 5 and 7 are grossly similar, with the exception that the coupling between the N–H and NMe$_2$ protons appears to be much smaller and is not resolved. The N–H resonance is absent from the ^{1}H NMR spectrum of 5-*d* and is replaced by a corresponding N–D resonance in the ^{2}H NMR of 5-*d*. The IR spectrum of 5 shows a N–H band at 3235 cm^{-1}; there is a corresponding N–D band at 2418 cm^{-1} in the IR spectrum of 5-*d*. The spectroscopic data suggest that the molecular structures of 5, 6, and 7 can be described as four-legged piano stools, with the halide ligands trans disposed (Scheme II). Although no molecular weight determinations have been performed, it is believed that 5–7 are 16-valence-electron monomeric species.

The reaction of 3 with 1 equiv of Me$_2$NH·HI results in aminolysis of only one of the NMe$_2$ ligands and gives a highly crystalline material which is characterized as [Zr(CpN)I(NMe$_2$)] (8). The chloro analogue of 8 has also been prepared; however, it is a low-melting solid which is very soluble in pentane, and it has not proved possible to isolate it in high purity.

As described above, the reactions between [M(CpN)(NMe$_2$)$_2$] (M = Zr, Hf) and either 1 or 2 equiv of acid provide clean routes to [Zr(CpN)I(NMe$_2$)] and [M(CpN)X$_2$(NHMe$_2$)] (M = Zr, X = Cl, I; M = Hf, X = I), respectively; the reaction of [Zr(CpN)(NMe$_2$)$_2$] with 3 equiv of Me$_2$NH·HCl has also been investigated and might be expected to result in cleavage of all three Zr–amide linkages. However, this reaction appears to give more than one product, not one of which has been conclusively characterized.

Salt Metathesis Reactions of [Zr(CpN)Cl$_2$(NHMe$_2$)]. With the aim of preparing zirconium alkyl complexes, the reaction of 5 with a number of alkylating reagents has been investigated (Scheme III). The addition of a slight excess over 2 equiv of C$_6$H$_5$CH$_2$MgCl to a THF solution of 5 gave an immediate reaction with the formation of a yellow solution. The product is poorly soluble in pentane but may be crystallized from toluene, or toluene/pentane mixtures, to give light yellow crystals, which were identified by NMR as the 14-valence-electron dibenzyl complex [Zr(CpN)(CH$_2$C$_6$H$_5$)$_2$] (9).

It is well-documented that electronically unsaturated benzyl complexes of the early transition metals may distort in order to relieve this electronic unsaturation via interaction of the C$_6$H$_5$ π-system (η^2-benzyl) with the metal center;[18] occasionally complexes that might be described as η^3 have been identified by structural determinations.[19] Apart from X-ray crystallographic structural determinations, η^2-benzyl complexes have been characterized in solution by NMR spectroscopy and show the following characteristic features: (a) high-field shifts of the ortho ^{1}H (δ <6.8 ppm) and CH$_2$ ^{13}C (δ <75 ppm) resonances and (b) large $^1J_{C-H}$ coupling constants for the CH$_2$ group (J_{C-H} > 130 Hz).[20] In addition, it has also been noted that in some cases the sp^2 character of the methylene carbon atom in an η^2-benzyl group gives a small geminal coupling constant (4 < J_{H-H} < 7 Hz), while the sp^3-hybridized methylene carbon of an undistorted benzyl ligand gives

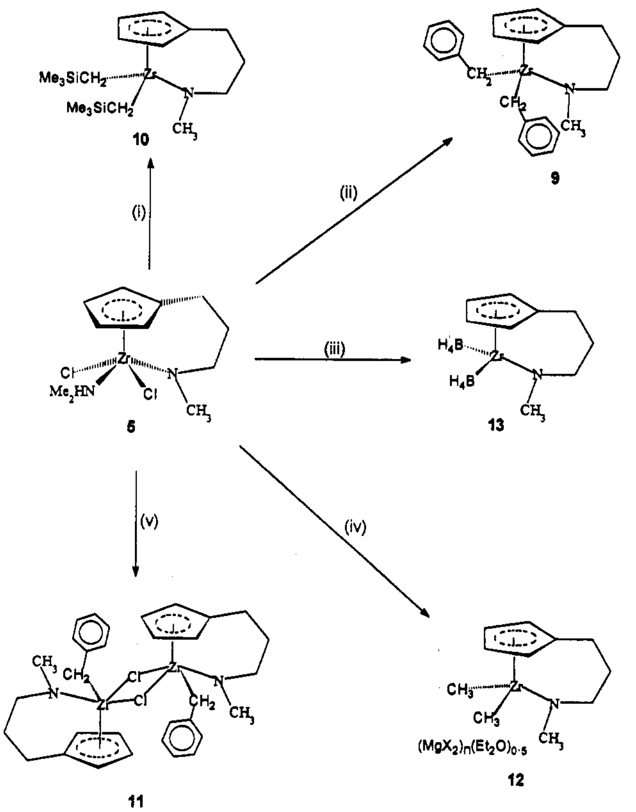
---

[18] For a discussion see: Crowther, D. J.; Jordan, R. F.; Baenziger, N. C.; Verma, A. *Organometallics* **1990**, *9*, 2574.

[19] For a discussion see: Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 2857.

[20] Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

Scheme III. Salt Metathesis Reactions Using 5[a]



[a] Reagents and conditions: (i) 2 equiv of $LiCH_2SiMe_3$, Et_2O, 2 h; (ii) 2 equiv of $C_6H_5CH_2MgCl$, THF, 3 h, 61%; (iii) excess $LiBH_4$, Et_2O, 1.5 h, 90%; (iv) excess MeMgI, Et_2O, 30 min, <5%; (v) 1 equiv of $C_6H_5CH_2MgCl$, THF, 15 min, 55%.

a larger geminal coupling constant ($8 < J_{H-H} < 12$ Hz);[21,22] some data relevant to Zr include the pair of compounds $[(EBTHI)Zr(CH_2Ph)_2]$ (J_{H-H} = 11.2 Hz) and $[(EBTHI)Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)]^+$ (J_{H-H} = 7.1 Hz) (EBTHI = *rac*-ethylenebis(tetrahydroindenyl)).[23]

In the case of the ^{1}H NMR spectrum of **9**, the ortho resonance of the C_6H_5 ring appears as a high-field doublet (δ 6.58 ppm); the multiplicities of the C_5H_4 and $CH_2CH_2CH_2$-backbone resonances indicate that the molecule has C_s symmetry with the mirror plane through the Cp ring centroid and Zr and N atoms (and formally the $CH_2CH_2CH_2$ backbone). An AB pattern (δ_A 1.62, δ_B 1.26 ppm, J_{AB} = 4.7 Hz) is assigned to the two equivalent diastereotopic CH_2Ph groups. In the ^{13}C NMR spectrum, the Zr–CH_2 resonance appears at δ 55.5 ppm (J_{C-H} = 134 Hz). These NMR data suggest that there is some η^2-benzyl interaction present, although the C_s symmetry must be a consequence of either (1) both benzyl groups being distorted or (2) only one ligand being distorted and the η^2-benzyl and η^1-benzyl ligands undergoing rapid exchange. If such exchange processes are involved, it has not proved possible to freeze them out in this case, and the ^{1}H NMR spectrum at low temperature (−80 °C, 300 MHz, toluene-d_8) still shows C_s symmetry. On electron-counting grounds, assuming that an η^2-benzyl group acts as a three-electron ligand, it seems most likely that in **9** only one benzyl ligand is distorted, giving $[Zr(CpN)(\eta^2\text{-benzyl})(\eta^1\text{-benzyl})]$, since this gives a 16-valence-electron Zr center, while a structure with two distorted benzyl ligands gives an 18-valence-electron Zr center.

The reaction of **5** with 2 equiv of $LiCH_2SiMe_3$ gives the dialkyl complex $[Zr(CpN)(CH_2SiMe_3)_2]$ (**10**), although this complex can only be isolated as an oil, which refuses to crystallize. The ^{1}H and ^{13}C NMR spectra of **10** provide little conclusive evidence for or against *agostic*[24] interactions in this formally 14-valence-electron complex; the only relevant evidence is the geminal coupling constant of the Zr–CH_2–$SiMe_3$ group (J_{H-H} = 2.1 Hz). Unfortunately, although a number of Zr–CH_2SiMe_3 complexes are known, there are relatively few examples where the CH_2 group is diastereotopic; one example is $[ZrCp^*Fv(CH_2SiMe_3)]$ (J_{H-H} = 10.6 Hz).[25–27] By analogy with the interpretation afforded to small geminal coupling constants for benzyl complexes (vide supra), the data for **10** might be interpreted as evidence for sp^2 character in the methylene carbon; this in turn might suggest a Zr–C–Si or Zr–C–H angle significantly reduced from tetrahedral. In contrast to the unusual methylene J_{H-H} coupling constant in **10**, the $^1J_{C-H}$ coupling constant for the methylene carbon ($^1J_{C-H}$ = 104 Hz) is quite unremarkable when compared with other complexes containing the Zr–CH_2SiMe_3 function.[28] Unfortunately, the oily nature of **10** prevents us from further investigating the geometry of this complex by X-ray crystallography.

The reaction of **5** with only 1 equiv of $C_6H_5CH_2MgCl$ gave the benzyl chloride complex $[\{Zr(CpN)(CH_2C_6H_5)(\mu\text{-}Cl)\}_2]$ (**11**). Compound **11** is very poorly soluble in pentane, slightly more soluble in toluene, and very soluble in polar solvents such as pyridine and THF; the compound was crystallized as pale yellow microcrystals from a dilute toluene/pentane mixture. The molecular structure of **11** has been determined by X-ray crystallography and will be discussed in detail below. The ^{1}H NMR spectrum in pyridine-d_5 is consistent with C_i symmetry (as a monomer); thus, there are four resonances assigned to the C_5H_4 fragment and an ABCDEF pattern for the $CH_2CH_2CH_2$ backbone. The ortho resonance of the C_6H_5 fragment is at δ 7.04 ppm, and an AB pattern (at δ 2.62 and 2.47 ppm, J_{H-H} = 9.6 Hz) is assigned to Zr–CH_2Ph. In the ^{13}C NMR spectrum, Zr–CH_2 appears at δ 54.9 ppm and the C_6H_5 ipso resonance is at δ 155.4 ppm. These data are consistent with an undistorted η^1-benzyl ligand. The dimeric structure (vide infra) gives a formal 16-valence-electron count to each Zr center; it is unclear if the dimeric structure is maintained in pyridine solution or if a pyridine solvate (still 16 electrons) is formed.

The ^{1}H NMR spectrum of **11** in benzene-d_6 is more complicated than that in pyridine-d_5. The dimer is

---

(21) (a) See reference 19. (b) For a discussion of geminal coupling constants in M–CH_2D groups see: Green, M. L. H.; Hughes, A. K.; Popham, N. A.; Stephens, A.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.*, in press.

(22) It should be noted that the metal complex must have a low symmetry (e.g., C_i, C_s, or C_2) in order to make the methylene group diastereotopic; thus, the CH_2 protons in $Cp_2Zr(CH_2R)_2$ (Cp = any η-C_5R_5) give rise to a singlet and those in $CpCp'Zr(CH_2R)_2$ ($Cp \neq Cp'$) give rise to an AB system, i.e., two doublets.

(23) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

(24) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(25) Pattiasina, J. W. Ph.D. Thesis, University of Groningen, 1988. By comparison for $[Cp^*FvZr(CH_2CMe_3)]$ J_{H-H} = 11.6 Hz and for $[Cp^*FvZr(CH_2C_6H_5)]$ J_{H-H} = 12.6 Hz.

(26) See also the values for $[Ti(\eta^5{:}\sigma\text{-}C_5Me_4CH_2CH_2CH_2O)(CH_2R)_2]$ (R = $SiMe_3$, J_{H-H} = 12 Hz; R = CMe_3, J_{H-H} = 12 Hz): Teuben, J. H.; Zondervan, C. Unpublished results.

(27) For examples of geminal coupling constants in some M–CH_2SiMe_3 (M = Mo, W) complexes, see ref 19.

(28) (a) $[Cp^*_2Zr(CH_2SiMe_3)(THF)]^+(BPh_4)^-$, J_{C-H} = 100.1 Hz: Amorose, D. M.; Lee, R. A.; Petersen, J. L. *Organometallics* **1991**, *10*, 2191. (b) $[Cp^*(\eta^8\text{-}C_8H_8)Zr(CH_2SiMe_3)]$, J_{C-H} = 108 Hz: Sinnema, P.-J.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 184.

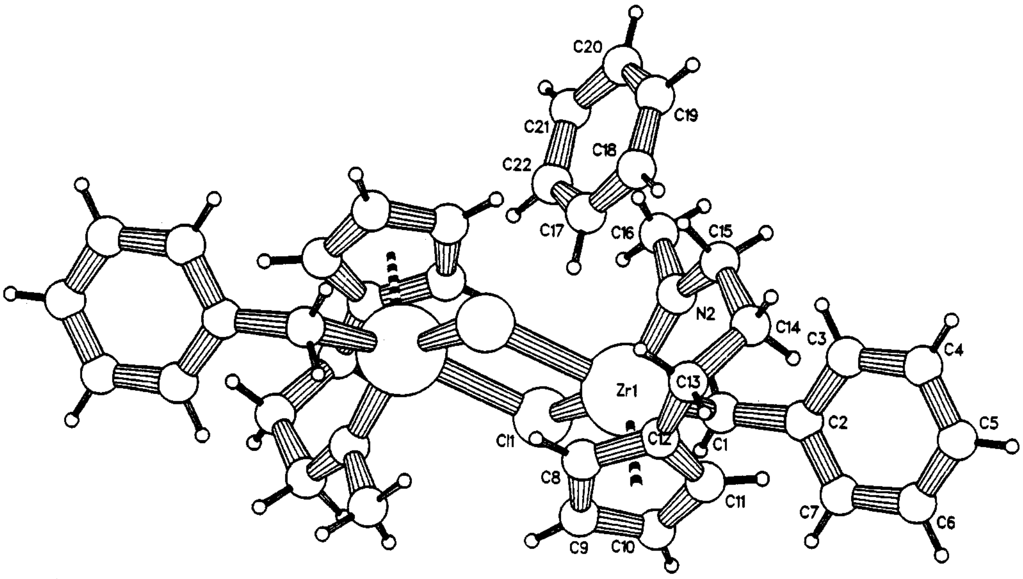
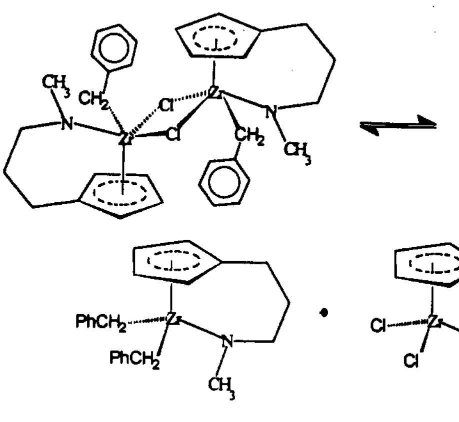


Figure 1. PLUTO plot of 11 showing the puckering of the $CH_2CH_2CH_2$ chain and the adopted labeling scheme for non-hydrogen atoms.

considerably less soluble, and the spectrum shows a number of additional peaks between δ 5 and 7 ppm. In particular, the ortho resonance of the dibenzyl complex 9 is characteristic, and the C_5H_4 resonances of 9 are also identifiable, as are another set of C_5H_4 resonances. Compound 9 and the additional compound each amount to about 5–10% of the total NMR signal. One possible explanation for this behavior is an equilibrium between 11, 9, and "[Zr(CpN)Cl_2]" (eq 1). The unsolvated dichloride has not been independently prepared; therefore, it is not possible to compare chemical shift data.[29]



(1)

Attempts to prepare the dimethyl complex [Zr(CpN)-$(CH_3)_2$] (12) were not successful. Pure 12 could not be obtained reproducibly; instead, there was evidence of incomplete substitution and incorporation of magnesium halide.

The reaction of 5 with an excess of $LiBH_4$ in diethyl ether gave the bis(borohydride) [Zr(CpN)$(BH_4)_2$] (13), which was crystallized from pentane in the form of a white powder. The ^1H NMR spectrum of 13 shows resonances that are assigned to the (CpN) ligand, and also a broad 1:1:1:1 quartet (δ 1.08 ppm, J_{H-B} = 86 Hz), which is integrated to eight protons and is assigned to eight equivalent protons of two BH_4 ligands. The ^{11}B NMR spectrum shows a binomial pentet at δ −18.8 ppm, the equivalent coupling of each boron to four protons being confirmed. These data indicate fast exchange of B–H terminal and Zr–H–B bridging protons, as is also observed for $Cp_2Zr(BH_4)_2$, $CpZr(BH_4)_3$,[30] and $Cp^*Zr(BH_4)_3$.[31] The low-temperature ^1H NMR spectrum of 13 (−80 °C, 300 MHz, toluene-d_8) does not show any "freezing out" of the bridge–terminal exchange. The pattern of the B–H–M bridge and B–H terminal vibrations in the IR spectrum of borohydrides is characteristic of the hapticity (η^2 or η^3) of the M–BH_4 interaction.[32] The solution IR spectrum of 13 shows a strong peak at 2131 cm^{-1} with a shoulder at 2167 cm^{-1} (a "doublet") and a single sharp peak at 2502 cm^{-1}. These data suggest a η^3-BH_4 structure, which might be reasonable given the steric unsaturation of the molecule.

Solid-State Structure of [{Zr(CpN)($CH_2C_6H_5$)(μ-Cl)}$_2$]. Crystals of 11 were obtained from an NMR tube containing a mixture of 9 and 11 in benzene-d_6. The molecular structure of 11 appears in Figure 1; fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table I, while selected bond lengths and angles are given in Table II.

The crystal structure of 11 consists of discrete dimer molecules of [{Zr(CpN)($CH_2C_6H_5$)(μ-Cl)}$_2$], which are located at sites with $\bar{1}$ symmetry, and benzene-d_6 molecules separated by normal van der Waals distances. The coordination geometry around each Zr atom is essentially a four-legged piano stool. The dimer is bridged by two Cl atoms, with two different Zr–Cl distances of 2.6288(8) and 2.6797(9) Å; the longer Zr–Cl distance is trans to the benzyl ligand, and the nonbonding Zr–Zr distance is 4.2615(6) Å. There are relatively few examples of such $Zr_2(\mu\text{-}Cl)_2$ bridges containing zirconium in oxidation state IV with no direct Zr–Zr bond, but examples are found in [Cp*Zr(CH_2CH_2-

---

[29] As support for this proposal, when an NMR tube containing equimolar quantities of 9 and 5 in benzene-d_6 was heated to 50 °C for 20 h, complete conversion occured to a mixture of at least three organozirconium compounds. Approximately 30% of the integrated ^1H NMR spectrum can be assigned to 11 (^1H and ^{13}C NMR); the remainder of the NMR spectrum remains unassigned. It is clear that ligand exchange occurs between 9 and 5, although the presence of Me_2NH appears to complicate the reaction.

[30] (a) Császár, A. G.; Hedberg, L.; Hedberg, K.; Burns, R. C.; Wen, A. T.; McGlinchey, M. J. *Inorg. Chem.* **1991**, *30*, 1371. (b) Smith, B. E.; James, B. D.; Dilts, J. A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1973.

[31] Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

[32] Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

Table I. Selected Bond Distances and Angles for $[\{(CpN)Zr(CH_2C_6H_5)(\mu\text{-}Cl)\}_2]$[a]

	Bond Distances (Å)		
Zr(1)–Cl(1)	2.6288(8)	Zr(1)–Cl(1a)	2.6797(9)
Zr(1)–N(2)	1.988(2)	Zr(1)–C(1)	2.323(3)
N(2)–C(16)	1.459(5)	N(2)–C(15)	1.462(4)
C(14)–C(15)	1.512(6)	C(13)–C(14)	1.513(7)
C(12)–C(13)	1.480(5)		
	Bond Angles (deg)		
Cl(1a)–Zr(1)–Cl(1)	73.21(2)	Cl(1)–Zr(1)–N(2)	133.47(7)
Cl(1a)–Zr(1)–N(2)	89.64(7)	Zr(1)–Cl(1)–Zr(1a)	106.79(3)
Zr(1)–N(2)–C(15)	144.8(2)	Zr(1)–N(2)–C(16)	103.0(2)
C(15)–N(2)–C(16)	112.2(3)	Zr(1)–C(1)–C(2)	119.5(2)

[a] The label a indicates the symmetry operation $-x, -y, -z$.

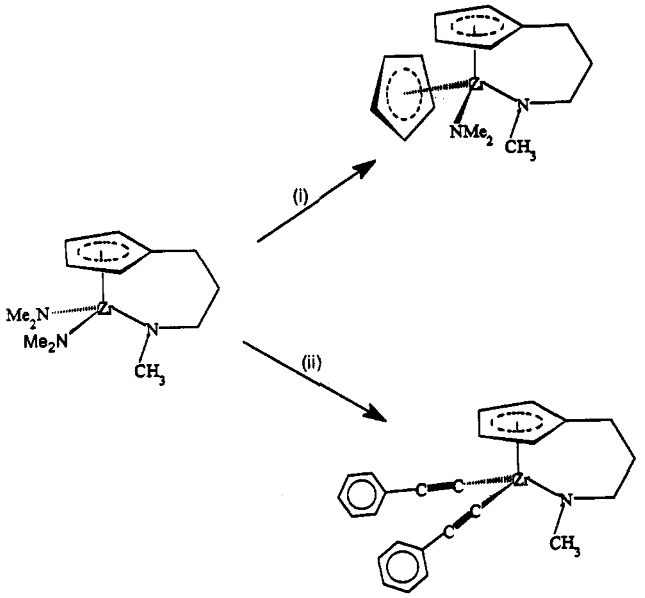
Table II. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters for Non-Hydrogen Atoms in 11

	x	y	z	U_{eq},[a] Å^2
		Residue 1		
Zr(1)	0.11577(2)	0.13975(3)	–0.02766(1)	0.0396(1)
Cl(1)	–0.10615(6)	0.05436(8)	–0.06983(4)	0.0556(2)
N(2)	0.2116(2)	0.2425(2)	0.06313(14)	0.0511(8)
C(1)	0.0117(3)	0.3172(3)	–0.0933(2)	0.0566(10)
C(2)	0.0788(2)	0.4283(3)	–0.11092(18)	0.0498(9)
C(3)	0.1435(3)	0.5114(3)	–0.0531(2)	0.0606(11)
C(4)	0.2074(4)	0.6121(3)	–0.0699(2)	0.0775(16)
C(5)	0.2113(4)	0.6335(4)	–0.1458(3)	0.0809(16)
C(6)	0.1499(3)	0.5542(4)	–0.2034(2)	0.0748(16)
C(7)	0.0832(3)	0.4524(3)	–0.18718(19)	0.0640(11)
C(8)	0.2680(3)	–0.0100(3)	–0.0508(2)	0.0571(11)
C(9)	0.1701(3)	–0.0125(3)	–0.1193(2)	0.0619(11)
C(10)	0.1625(3)	0.1091(4)	–0.15360(18)	0.0609(13)
C(11)	0.2539(2)	0.1868(3)	–0.10731(18)	0.053(1)
C(12)	0.3211(2)	0.1135(3)	–0.04280(19)	0.0524(10)
C(13)	0.4277(3)	0.1570(4)	0.0198(3)	0.0747(15)
C(14)	0.4146(3)	0.2900(5)	0.0514(3)	0.0835(15)
C(15)	0.3306(3)	0.2944(4)	0.1022(2)	0.0742(12)
C(16)	0.1265(4)	0.2668(4)	0.1077(2)	0.0719(16)
		Residue 2		
C(17)	0.5859(5)	0.0218(6)	0.2303(2)	0.101(2)
C(18)	0.6719(4)	0.1007(5)	0.2723(3)	0.098(2)
C(19)	0.6525(4)	0.1726(5)	0.3301(4)	0.107(2)
C(20)	0.5467(5)	0.1639(5)	0.3476(3)	0.106(2)
C(21)	0.4607(4)	0.0825(5)	0.3059(3)	0.0968(19)
C(22)	0.4810(4)	0.0113(5)	0.2472(3)	0.1014(19)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

$SiMe_3)Cl(\mu\text{-}Cl)]_2$[33] (where Zr–Cl = 2.692(2) and 2.579(2) Å, Zr–Cl–Zr = 106.2(1)°, and Cl–Zr–Cl = 73.8(1)°) and $[ZrCl(\mu\text{-}Cl)\{N(SiHMe_2)_2\}_2]_2$[34] (Zr–Cl = 2.599(1) and 2.628(1) Å and Cl–Zr–Cl = 75.07(2)°) and in the benzamidinato complex $[C_6H_5C(NSiMe_3)_2ZrCl_2(\mu\text{-}Cl)]_2$[35] (Zr–Cl = 2.537(1) and 2.649(1) Å, Zr–Cl–Zr = 102.9(1)°, and Cl–Zr–Cl = 77.1(1)°). The Zr–N bond distance is slightly shorter than the Zr–NMe$_2$ distances in $(Me_2N)_2Zr(\mu\text{-}N^tBu)_2Zr(NMe_2)_2$[36] (where Zr–N = 2.057(1) and 2.062(1) Å) and in the parent complex $[(Me_2N)_3Zr(\mu\text{-}NMe_2)_2Zr(NMe_2)_3]$[37] (where terminal Zr–N ranges between 2.045(3) and 2.108(3) Å); the Zr–N bond distance in 11 suggests that N–Zr π-donation is important here. Furthermore, the sum of the angles around nitrogen is 360°, implying a planar sp^2-hybridized nitrogen, and so the amide group can be viewed as a three-electron ligand to the Zr. The Zr–N–CH$_2$ angle (144.8(2)°) is large, while the other angles around nitrogen are in consequence less than 120°; this suggests a slight opening out of the Zr–N–CH$_2$ angle to accommodate the linkage between the C$_5$H$_4$ and amido functions. The Zr–C$_5$H$_5$ bond lengths are unremarkable, and the CH$_2$CH$_2$CH$_2$ linkage can be seen to be only slightly puckered, suggesting that this is an unstrained linkage and that three CH$_2$ units are sufficient to link the C$_5$H$_5$ and Zr–NR$_2$ functions in a strain-free fashion. The Zr–CH$_2$–C$_6$H$_5$ angle is close to 120°, and thus the phenyl ring is bent away from the metal center, implying an undistorted structure; the Zr–CH$_2$ bond length is also unremarkable for a "normal" Zr(η^1-CH$_2$Ph) group (see Cp$_2$ZrBr(CH$_2$Ph):[38] Zr–C = 2.29(1) Å, Zr–C–C = 120(1)°).

Scheme IV. Aminolysis Reaction of $[Zr(CpN)(NMe_2)_2]$[a]



[a] Reagents and conditions: (i) 2 equiv of C$_5$H$_6$, toluene, 60 °C, 10 min, 46%; (ii) 2 equiv of C$_6$H$_5$CCH, benzene-d_6, 15 h, quantitative.

Reactions of [Zr(CpN)(NMe$_2$)$_2$] with Acidic Hydrocarbons. Although the reaction of metal–halide complexes with alkylating reagents is the most widely used method for the synthesis of metal–carbon bonds, there are other means of preparing metal derivatives. As demonstrated by the reaction of 2 with M(NMe$_2$)$_4$ (M = Zr, Hf), one of these methods is the aminolysis reaction of a metal amide and a suitably acidic hydrocarbon (pK_a < ca. 35); the reaction of 3 and 4 with Me$_2$NH·HX is a more extreme example of such a reaction. Some reactions using 3 and weak acids have also been investigated (Scheme IV). Addition of an excess of cyclopentadiene to a toluene solution of 3 immediately gives a bright yellow solution. The product is very soluble in pentane and fails to crystallize; a more satisfactory workup involves vacuum sublimation, which gives a bright yellow, low-melting solid identified as [Zr(CpN)(η-C$_5$H$_5$)(NMe$_2$)] (14). The ^{1}H NMR spectrum of 14 shows a singlet for the C$_5$H$_5$ ligand and two multiplet resonances for the C$_5$H$_4$ ring, although the lack of any symmetry elements would cause us to predict four resonances; indeed, the ^{13}C NMR spectrum shows the expected number of resonances and this suggests

---

(33) Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284.

(34) Hermann, W. A.; Huber, N. W.; Behm, J. *Chem. Ber.* **1992**, *125*, 1405.

(35) Fenske, D.; Hartmann, E.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43B*, 1611.

(36) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

(37) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C. *Polyhedron* **1988**, *7*, 2515.

(38) Randall, C. R.; Silver, M. E.; Ibers, J. A. *Inorg. Chim. Acta* **1987**, *128*, 39.

an accidental isochrony in the ^{1}H NMR spectrum. The ^{1}H NMR resonances of the $CH_2CH_2CH_2$ backbone show an ABCDEF spin system, consistent with the proposed molecular symmetry; this portion of the NMR spectrum was assigned with the assistance of a COSY spectrum. In contrast with this clean reaction with cyclopentadiene, **5** is unreactive toward fluorene (benzene-d_6, 2 days, 100 °C).

The reaction of **3** with phenylacetylene (C_6H_5CCH) proceeds rapidly at room temperature to give an almost colorless solution but, despite repeated attempts, it has not proved possible to isolate a product on a synthetic scale; the isolated material is always dark red and the NMR spectra are broad. The reaction of **3** with 2 equiv of PhCCH in benzene-d_6 in an NMR tube proceeds to completion in less than 15 h at 20 °C and gives ^{1}H and ^{13}C NMR spectra consistent with [Zr(CpN)(CCPh)$_2$] (**15**); however, the liberated Me_2NH appears to be a noninnocent product and the ^{1}H NMR shifts of Me_2NH (δ(CH_3) 2.29, δ(NH) 1.38 ppm) are not at the same chemical shifts as free Me_2NH (δ(CH_3) 2.18, δ(NH) 0.49 ppm). It is possible that the amine may be weakly coordinated and this might account for the difficulties in isolating a product in an open system (Schlenk). In the ^{13}C NMR spectrum the Zr*C*CPh and ZrC*C*Ph chemical shifts are very close to those reported for $Cp_2Zr(CCPh)_2$.[39] In contrast to many of the other compounds described here, **15** is only poorly thermally stable, and heating the NMR sample to 50 °C produced extensive decomposition (>90% after 3 h).

Conclusions

The work that has been described in this report represents an extensive study of the chemistry of the Zr(CpN) system. The results indicate that the Zr–N linkage provides an inert three-electron ligand which, together with the Cp function, provides a good coordination environment to the metal. The thermal stability of [Zr(CpN)R$_2$] alkyl complexes is moderate and reflects the fact that the Zr center in these complexes is sterically unsaturated. The apparent distortions observed in the dialkyl complexes (**9** and **10**) are consistent with an electronically and sterically unsaturated metal center in this system; this provides the potential for some exciting reactivity. It is concluded that the η^5:σ-$C_5H_4CH_2CH_2CH_2$-NMe ligand provides a great deal of potential for further studies.

Experimental Section

General Considerations. Except where otherwise indicated, all manipulations were performed under nitrogen using glovebox and Schlenk techniques. Solvents were dried by distillation over appropriate drying agents. NMR spectra were recorded on a Varian Gemini 200 (^{1}H at 200 MHz, ^{13}C at 50.3 MHz) or Varian VXR-300 (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, ^{2}H at 46 MHz); the ^{11}B and ^{1}H{^{11}B} NMR spectra were recorded on a Bruker AC-200. ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances relative to tetramethylsilane (δ 0 ppm); ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}Et_2O$. In the case of ^{13}C NMR spectra, assignments were confirmed by APT spectra, and proton-coupled spectra were recorded where appropriate; only selected coupling constants are quoted. For solid products elemental analysis was performed by the analytical department of this laboratory; quoted data are the average of at least two independent determinations. For liquids electron-impact mass spectra were recorded on an AEI MS 902 spectrometer operating at 70 eV; parent ion peak positions are reported for ions containing the most abundant nuclei (^{1}H, ^{12}C, ^{14}N, ^{90}Zr (51.46%) and ^{180}Hf (35.24%)). IR spectra were recorded on a Mattson Galaxy FT-IR spectrometer as KBr pellets (solids) or between KBr plates (neat liquids, solutions); only selected IR data are reported.

The syntheses of $M(NMe_2)_4$ (M = Zr,[40] Hf[14]) have been described elsewhere; $BrCH_2CH_2CH_2N(H)Me{\cdot}HBr$ (**1**) was prepared[41] by the reaction of HBr with $HOCH_2CH_2CH_2N(H)Me$.[42] The amine salts $Me_2NH{\cdot}HX$ (X = Cl, I) were prepared by the addition of aqueous acid to a 40% aqueous solution of Me_2NH, followed by removal of water under reduced pressure and drying in vacuo; $Me_2NH{\cdot}HCl$ was further dried by crystallization from CH_2Cl_2/diethyl ether. $Me_2ND{\cdot}DCl$ was prepared by dissolving $Me_2NH{\cdot}HCl$ (500 mg) in D_2O (3 mL) and removing the water under reduced pressure; the solid was dried by washing with THF.

Synthesis of $C_5H_5CH_2CH_2CH_2NHCH_3$ (2). In air, a 3-L three-necked flask with condenser, dropping funnel, and overhead stirrer was charged with 55 g (0.237 mol) of $BrCH_2CH_2CH_2N(H)Me{\cdot}HBr$ (**1**) and THF (over Na wire, 500 mL); the resulting suspension was then degassed and cooled to 0 °C under an N_2 atmosphere. A solution of NaCp (from ca. 85 mL of CpH (0.85 mol) and 20 g of Na in 500 mL of THF) was added dropwise over 10 min. The resulting white suspension was stirred at room temperature overnight. The reaction mixture was then treated with water (400 mL) and the THF layer collected. The water layer was extracted with diethyl ether (2 × 250 mL), and the combined organic extracts were washed with water (100 mL) before being dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure to give a pale brown oil. This oil was distilled into a receiver cooled to 0 °C (bp 35 °C at 0.1 mmHg); yield 30.55 g of a colorless oil, shown to be a 5:1 mixture of **2** and dicyclopentadiene (^{1}H NMR, $CDCl_3$). The oil was taken up in light petroleum ether (bp 40–60 °C, 250 mL) and extracted with three portions of dilute HCl (total 400 mL of ca. 0.625 M, 0.25 mol), the extracts being added directly to a mixture of NaOH (14 g, 0.35 mol), water (200 mL), and diethyl ether (300 mL); the final aqueous extract was acidic (pH 1). The diethyl ether solution of the free amine was separated from the basic solution (pH 14), and this was further extracted with diethyl ether (200 mL, then 150 mL) and light petroleum ether (bp 40–60 °C, 200 mL). The combined organic extracts were dried (Na_2SO_4) and filtered and the solvent removed under reduced pressure to give a pale brown oil. Vacuum distillation (bp 35 °C at 0.1 mmHg) gave 19.04 g (0.139 mmol, 59%) of **2** as a ca. 1:1 mixture of the 1,2- and 1,3-isomers. The product is best stored at −20 °C under nitrogen; samples stored under air slowly become yellow (2 months). MS: *m/e* 137 [P$^+$]. IR (neat, KBr, cm^{-1}): 3292 (s, N–H). ^{1}H NMR ($CDCl_3$): δ 6.43 (overlapped m, 3H, 2 × CH of C_5H_5 ring isomer 1, 1 × CH isomer 2), 6.25 (m, 1H, CH of C_5H_5 ring isomer 2), 6.16 (hept, 1H, J_{H-H} = 1.3 Hz, CH of C_5H_5 ring isomer 2), 6.02 (hept, 1H, J_{H-H} = 1.6 Hz, CH of C_5H_5 ring isomer 1), 2.95 (sext, 2H, J_{H-H} = 1.4 Hz, CH_2 of C_5H_5 ring isomer 1), 2.88 (quart, 2H, J_{H-H} = 1.45 Hz, CH_2 of C_5H_5 ring isomer 2), 2.60 (t, 2H, J_{H-H} = 7 Hz, NCH_2), 2.59 (t, 2H, J_{H-H} = 7 Hz, NCH_2), 2.43 (s, 6H, 2 × NMe), 2.43 (m, 4H, 2 × C_5H_5–CH_2), 1.75 (pent, 2H, J_{H-H} = 7.5 Hz, CH_2–C–N), 1.74 (pent, 2H, J_{H-H} = 7.5 Hz, CH_2–C–N), 1.26 (br s, 2H, 2 × NH). ^{13}C NMR ($CDCl_3$): δ 149.1 (C_5H_5 ipso), 146.5 (C_5H_5 ipso), 134.6 (CH of C_5H_5), 133.7 (CH of C_5H_5), 132.3 (CH of C_5H_5), 130.5 (CH of C_5H_5), 126.4 (CH of C_5H_5), 125.9 (CH of C_5H_5), 51.65 (NCH_2), 51.6 (NCH_2), 43.2 ($C_5H_5CH_2$), 41.2 ($C_5H_5CH_2$), 36.5 (2 × NMe), 29.8 (CH_2), 29.0 (CH_2), 28.2 (CH_2), 27.5 (CH_2).

Synthesis of [Zr(η^5:σ-$C_5H_4CH_2CH_2CH_2NMe$)(NMe_2)$_2$] (3). A solution of $Zr(NMe_2)_4$ (15.64 g, 58.4 mmol) in toluene (25 mL)

---

(39) Sebald, A.; Fritz, P.; Wrack neyer, B. *Spectrochim. Acta, Part A* **1985**, *41A*, 1405.

(40) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.

(41) Cortese, F. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. 2, p 91.

(42) Koepke, S. R.; Kupper, R.; Michejda, C. J. *J. Org. Chem.* **1979**, *44*, 2718.

was cooled to −20 °C, and a solution of **2** (8.02 g, 58.4 mmol) in toluene (10 mL) was added dropwise over 20 min. The resulting solution was warmed to room temperature and then stirred at 40 °C for 15 min. The volatiles were removed under reduced pressure to give a yellow oil, which was extracted with pentane (10 mL), and the extract was transferred to a small distillation apparatus. The pentane was removed under reduced pressure and the residue distilled, giving **3** as a colorless oil: bp 80–90 °C/0.05 mmHg; yield 17.38 g, 94%. This material was made into a standard solution in toluene (ca. 70 mL) for subsequent reactions. MS: *m/e* 313 [P, 32%, correct isotope pattern for Zr], 268 [P − $HNMe_2$, 33%] (100% = [NMe_2]). ^1H NMR (C_6D_6): δ 5.95 (t, 2H, J_{H-H} = 2.5 Hz, C_5H_4), 5.76 (t, 2H, J_{H-H} = 2.5 Hz, C_5H_4), 3.21 (s, 3H, NMe), 2.91 (s, 12H, 2 × NMe_2), 2.76 (m, 2H, N–CH_2), 2.50 (m, 2H, $C_5H_4CH_2$), 1.79 (quint, 2H, CH_2–C–N). ^{13}C NMR (C_6D_6): δ 126.8 (C_5H_4 ipso), 109.5 (CH of C_5H_4), 108.7 (CH of C_5H_4), 58.4 (NCH_2), 44.8 (2 × NMe_2), 41.9 (NMe), 33.4 ($C_5H_4CH_2$), 28.4 (CH_2–C–N).

Synthesis of $[Hf(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)(NMe_2)_2]$ (4). A solution of $Hf(NMe_2)_4$ (3.3 g, 9.3 mmol) in toluene (15 mL) was cooled to 0 °C and treated dropwise with a solution of crude **2** (2.27 g, 70% purity) in toluene (10 mL). After the mixture was stirred at room temperature for 15 h, the volatiles were removed under reduced pressure to give a yellow/orange oil. This was extracted into pentane (10 mL) and transferred to a small distillation apparatus. Vacuum distillation (bp 100 °C, 0.3–0.5 mmHg) gave **4** as a pale yellow oil, yield 2.16 g (58% based on $Hf(NMe_2)_4$). This material was made into a 0.33 M solution in toluene for further reactions. MS: *m/e* 403 [P, 100%, correct isotope pattern for Hf]. ^1H NMR (C_6D_6): δ 5.91 (t, 2H, J_{H-H} = 2.75 Hz, C_5H_4), 5.74 (t, 2H, J_{H-H} = 2.75 Hz, C_5H_4), 3.175 (s, 3H, NMe), 2.955 (s, 12H, 2 × NMe_2), 2.92 (dd, 2H, N–CH_2), 2.48 (m, 2H, $C_5H_4CH_2$), 1.76 (quint, 2H, CH_2–C–N). ^{13}C NMR (C_6D_6): δ 126.6 (C_5H_4 ipso), 109.4 (CH of C_5H_4), 108.4 (CH of C_5H_4), 58.8 (NCH_2), 44.7 (2 × NMe_2), 42.2 (NMe), 34.3 ($C_4H_4CH_2$), 28.5 (CH_2–C–N).

Synthesis of $[Zr(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)Cl_2(NHMe_2)]$ (5). Anhydrous $Me_2NH{\cdot}HCl$ (2.4 g, 29.4 mmol) in THF (40 mL) was cooled to −40 °C and a toluene solution of **3** (18.3 mL of a 0.8 M solution, 14.6 mmol) was added quickly. The suspension was stirred rapidly as it warmed to room temperature, giving a homogeneous yellow solution. After 30 min the volatiles were removed under reduced pressure to give an off-white solid. This was extracted with toluene (70 mL, then 25 mL), and the filtered toluene extracts were treated with pentane (50 mL) until a cloudiness appeared. The solution was filtered and cooled to −20 °C and then −80 °C, giving crystals of **5**: yield 2.4 g (50%). An analytically pure sample was obtained by a further crystallization from toluene/pentane. Anal. Calcd for $C_{11}H_{20}Cl_2N_2Zr$: C, 38.58; H, 5.89; Cl, 20.71. Found: C, 38.78; H, 5.89; Cl, 20.67. IR (KBr pellet, cm^{-1}): 3235 (s, N–H). ^1H NMR (C_6D_6): δ 6.05 (t, 2H, J_{H-H} = 2 Hz, C_5H_4), 5.77 (t, 2H, J_{H-H} = 2 Hz, C_5H_4), 2.94 (s, 3H, NMe), 2.69 (app t, 2H, J_{app} = 5.1 Hz, N–CH_2), 2.38 (m, 2H, $C_5H_4CH_2$), 2.14 (s, 6H, NMe_2), 2.10 (br s, 1H, N–H), 1.72 (m, 2H, CH_2–C–N). ^{13}C NMR (C_6D_6): δ (C_5H_4 ipso missing) 113.1 (CH of C_5H_4), 112.0 (CH of C_5H_4), 55.8 (NCH_2), 39.6 (NMe_2), 38.4 (NMe), 28.9 ($C_5H_4CH_2$), 26.1 (CH_2–C–N).

Synthesis of $[Zr(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)Cl_2(NDMe_2)]$ (5-*d*). This was prepared in the same way as **5** from anhydrous $Me_2ND{\cdot}DCl$ (0.1 g, 1.2 mmol) in THF (10 mL) at −30 °C and a toluene solution of **3** (0.83 mL of 0.73 M solution, 0.6 mmol): yield 0.15 g (72%). IR (KBr pellet, cm^{-1}): 2418 (s, N–D). ^1H NMR (C_6D_6): δ 6.05 (t, 2H, J_{H-H} = 2 Hz, C_5H_4), 5.77 (t, 2H, J_{H-H} = 2 Hz, C_5H_4), 2.95 (s, 3H, NMe), 2.69 (m, 2H, NCH_2), 2.39 (m, 2H, $C_5H_4CH_2$), 2.13 (s, 6H, NMe_2), 1.72 (m, 2H, CH_2–C–N). ^2H NMR (C_6H_6): δ 2.27 (br s, N–D).

Synthesis of $[Zr(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)I_2(NHMe_2)]$ (6). A suspension of anhydrous $Me_2NH{\cdot}HI$ (0.5 g, 2.9 mmol) in THF (20 mL) was cooled to −80 °C and treated with a toluene solution of **3** (2 mL of 0.78 M solution, 1.56 mmol). The suspension was stirred vigorously as it was warmed to room temperature (1 h) and was then briefly warmed to 60 °C. The volatiles were removed under reduced pressure to give a pale yellow solid, and the residue was extracted with toluene (20 mL) to give a yellow solution. This solution was treated with pentane until a slight cloudiness appeared (ca. 35 mL), and the solution was then filtered. Cooling to −80 °C gave very pale yellow crystals of **6** (yield 0.28 g, 34%); a second crop of less pure **6** was obtained from the liquors by adding more pentane and subsequent cooling: yield 0.35 g (43%). Anal. Calcd for $C_{11}H_{20}N_2I_2Zr$: C, 25.15; H, 3.83; I, 48.31. Found: C, 25.56; H, 3.85; I, 50.11. IR (Nujol/KBr, cm^{-1}): 3190 (s, N–H). ^1H NMR (C_6D_6): δ 6.20 (t, 2H, J_{H-H} = 2.6 Hz, C_5H_4), 5.86 (t, 2H, J_{H-H} = 2.6 Hz, C_5H_4), 2.87 (s, 3H, NMe), 2.65 (br s, N–H), 2.28 (app t, 2H, J_{app} = 5.8 Hz, NCH_2), 2.17 (m, 2H, $C_5H_4CH_2$), 2.13 (d, 6H, J_{H-H} = 6 Hz, NMe_2), 1.54 (m, 2H, CH_2–C–N). ^{13}C NMR (C_6D_6): δ (C_5H_4 ipso missing) 112.9 (CH of C_5H_4), 111.7 (CH of C_5H_4), 56.7 (NCH_2), 40.5 (NMe_2), 38.8 (NMe), 28.0 ($C_5H_4CH_2$), 25.8 (CH_2–C–N).

Synthesis of $[Hf(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)I_2(NHMe_2)]$ (7). A suspension of anhydrous $Me_2NH{\cdot}HI$ (0.8 g, 4.62 mmol) in THF (10 mL) was cooled to −80 °C and treated with a toluene solution of **4** (6.95 mL of 0.333 M solution, 2.31 mmol). The suspension was stirred vigorously as it was warmed to room temperature (1.5 h) and was then warmed to 60 °C for 15 min. The volatiles were removed under reduced pressure to give a bright yellow solid, and the residue was extracted twice with warm (60 °C) toluene (20 mL, then 10 mL) to give a yellow solution. The combined extracts were treated with pentane (ca. 4 mL) until a slight cloudiness appeared. Cooling to −80 °C while allowing a further 40 mL of pentane to condense in the solution over 10 days gave yellow crystals of impure **7**: yield 0.54 g (38%). This was recrystallized from a toluene (13 mL) pentane (10 mL) mixture at −20 °C over 15 days to give pure **7**: yield 0.14 g (10%). Anal. Calcd for $C_{11}H_{20}N_2HfI_2$: C, 21.57; H, 3.29. Found: C, 21.47; H, 3.62. IR (KBr pellet, cm^{-1}): 3192 (s, N–H). ^1H NMR (C_6D_6): δ 6.18 (t, 2H, J_{H-H} = 2.6 Hz, C_5H_4), 5.75 (t, 2H, J_{H-H} = 2.6 Hz, C_5H_4), 2.73 (s, 3H, NMe), 2.73 (app t, 2H, NCH_2), 2.63 (br s, 1H, NH), 2.24 (m, 2H, $C_5H_4CH_2$), 2.17 (s, 6H, NMe_2), 1.60 (m, 2H, CH_2–C–N). ^{13}C NMR (C_6D_6): δ 123.5 (C_5H_4 ipso), 112.5 (CH of C_5H_4), 110.3 (CH of C_5H_4), 56.6 (NCH_2), 40.7 (NMe_2), 38.6 (NMe), 28.6 ($C_5H_4CH_2$), 26.2 (CH_2–C–N).

Synthesis of $[Zr(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)I(NMe_2)]$ (8). A THF (20 mL) suspension of $Me_2NH{\cdot}HI$ (1.22 g, 7.05 mmol) was cooled to −80 °C and treated with a toluene solution of **3** (8.75 mL of 0.8 M solution, 7 mmol). The mixture was stirred rapidly as it was warmed to room temperature (1 h) and was then heated to 40 °C for 30 min, giving a bright yellow solution. The volatiles were removed under reduced pressure, and the oily residue was stripped with pentane (5 mL) and dried. Extraction of the yellow powder with a mixture of pentane (20 mL) and toluene (8 mL) gave a yellow solution, which was filtered and cooled to −20 °C, giving pale yellow needles of **8**: yield 1.5 g (54%). Anal. Calcd for $C_{11}H_{19}N_2IZr$: C, 33.25; H, 4.82; I, 31.93. Found: C, 33.01; H, 4.79; I, 33.03. ^1H NMR (C_6D_6): δ 6.51 (q, 1H, J_{H-H} = 2.8 Hz, C_5H_4), 5.88 (q, 1H, J_{H-H} = 2.6 Hz, C_5H_4), 5.60 (t, 2H, J_{H-H} = 2.6 Hz, C_5H_4), 3.18 (s, 3H, NMe), 2.61 (s, 6H, NMe_2), 2.40 (m, 3H, NCH_2 and one $C_5H_4CH_2$), 2.18 (m, 1H, one $C_5H_4CH_2$), 1.64 (m, 2H, CH_2–C–N). ^{13}C NMR (C_6D_6): δ 126.5 (C_5H_4 ipso), 112.2 (CH of C_5H_4), 112.1 (CH of C_5H_4), 108.6 (CH of C_5H_4), 107.1 (CH of C_5H_4), 57.0 (NCH_2), 42.8 (NMe_2), 36.2 (NMe), 30.5 ($C_5H_4CH_2$), 26.6 (CH_2–C–N).

Synthesis of $[Zr(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)(CH_2C_6H_5)_2]$ (9). A THF (20-mL) suspension of **5** (0.62 g, 2.2 mmol) was cooled to 0 °C and treated with $C_6H_5CH_2MgCl$ (5.2 mL, 1.18 M in THF). The resulting yellow solution was stirred at room temperature for 3 h, and then the volatiles were removed under reduced pressure. The pale residue was treated with pentane (10 mL) and the volatiles again removed under reduced pressure. The dry residue was extracted with toluene (30 mL) and filtered. The volume of the filtrate was reduced until crystals just began to form (ca. 20 mL), and the solution was then cooled to −20 °C, giving light yellow crystals of **9**: yield 0.55 g (61%). An analytically pure sample was obtained by a further crystallization from 1:1 toluene/pentane at −20 °C. Although the structural determination shows that **11** cocrystallizes with benzene-d_6, there is no evidence from the NMR or analytical data that toluene also cocrystallizes with **11**. Anal. Calcd for $C_{23}H_{27}NZr$: C, 67.60; H, 6.66; Zr, 22.32. Found: C, 67.74; H, 6.70; Zr, 22.30. ^1H NMR (C_6D_6): δ 7.11 (t, 4H, C_6H_5 meta), 6.93 (t, 2H, C_6H_5 para), 6.58 (d, 4H, C_6H_5 ortho), 5.58 (t, 2H, J_{H-H} = 2.8 Hz, C_5H_4), 5.39 (t, 2H, J_{H-H} = 2.8 Hz, C_5H_4), 2.66 (s, 3H, NMe), 2.48 (app t, 2H, J_{app} = 5.8 Hz, N–CH_2), 2.19 (m, 2H, $C_5H_4CH_2$), 1.62 (d, 2H, J_{H-H} = 4.7 Hz, Zr–CH*H*), 1.54 (m, 2H, CH_2–C–N), 1.26 (d, 2H, J_{H-H} = 4.7 Hz, Zr–*C*HH). ^{13}C NMR (C_6D_6): δ 145.4 (C_6H_5 ipso), 129.6 (C_6H_5 meta), 126.4 (C_6H_5 para), 121.8 (C_6H_5 ortho), (C_5H_4 ipso missing), 110.5 (CH of C_5H_4), 110.1 (CH of C_5H_4), 55.5 (Zr–CH_2, J_{C-H} = 134 Hz), 50.2 (NCH_2), 34.3 (NMe), 29.8 ($C_5H_4CH_2$), 26.6 (CH_2–C–N).

Synthesis of [Zr(η^5:σ-$C_5H_4CH_2CH_2CH_2NMe$)(CH_2SiMe_3)$_2$] (10). A mixture of **5** (0.29 g, 1 mmol) and $LiCH_2SiMe_3$ (0.20 g, 2.1 mmol) was cooled to −196 °C and diethyl ether (20 mL) vacuum-transferred onto the solids. This mixture was warmed to room temperature and stirred for 2 h. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (2 × 20 mL) and the extract filtered. The volatiles were removed under reduced pressure to give **10** as a pale brown oil, which failed to crystallize. ^1H NMR (C_6D_6): δ 6.23 (t, 2H, J_{H-H} = 2.7 Hz, C_5H_4), 5.68 (t, 2H, J_{H-H} = 2.7 Hz, C_5H_4), 3.24 (s, 3H, NMe), 2.54 (app t, 2H, J_{app} = 5.6 Hz, NCH_2), 2.25 (m, 2H, $C_5H_4CH_2$), 1.62 (m, 2H, CH_2–C–N), 0.21 (d, 2H, J_{H-H} = 2.1 Hz, Zr–*C*HH–$SiMe_3$), 0.06 (s, 18H, 2 × $SiMe_3$), 0.00 (d, 2H, J_{H-H} = 2.1 Hz, Zr–CH*H*–$SiMe_3$). ^{13}C NMR (C_6D_6): δ 121.7 (C_5H_4 ipso), 110.6 (CH of C_5H_4), 109.0 (CH of C_5H_4), 55.9 (NCH_2), 46.4 (Zr–CH_2–Si, J_{C-H} = 104 Hz), 36.6 (NMe), 30.9 ($C_5H_4CH_2$), 26.7 (CH_2–C–N), 3.3 ($SiMe_3$).

Synthesis of [{Zr(η^5:σ-$C_5H_4CH_2CH_2CH_2NMe$)($CH_2C_6H_5$)(μ-Cl)}$_2$] (11). A THF solution of **5** (0.54 g, 1.64 mmol) was cooled to 0 °C and treated dropwise with a solution of $C_6H_5CH_2MgCl$ (1.4 mL of 1.18 M, 1.65 mmol), giving an immediate bright yellow coloration. After the mixture was stirred for 15 min at room temperature, the volatiles were removed under reduced pressure to give a yellow foam. Pentane (5 mL) was added and then removed under reduced pressure. The residue was treated with pentane (25 mL) followed by toluene (20 mL), and the resulting solution was filtered and cooled to −20 °C and then −80 °C, giving a yellow microcrystalline powder of **11**: yield 0.32 g (55%). Anal. Calcd for $C_{16}H_{20}ClNZr$: C, 54.44; H, 5.71; Cl, 10.04. Found: C, 54.30; H, 5.74; Cl, 10.18. ^1H NMR (pyridine-d_5): δ 7.25 (t, 2H, J_{H-H} = 7.7 Hz, C_6H_5 meta), 7.04 (d, 2H, J_{H-H} = 7.7 Hz, C_6H_5 ortho), 6.86 (t, 1H, J_{H-H} = 7.7 Hz, C_6H_5 para), 6.44 (q, 1H, J_{H-H} = 2.85 Hz, C_5H_4), 6.00 (q, 1H, J_{H-H} = 2.85 Hz, C_5H_4), 5.60 (q, 1H, J_{H-H} = 2.85 Hz, C_5H_4), 5.30 (q, 1H, J_{H-H} = 2.85 Hz, C_5H_4), 2.93 (s, 3H, NMe), 2.84 (app t, 2H, J_{app} = 5.8 Hz, NCH_2), 2.62 (d, 1H, J_{H-H} = 9.6 Hz, Zr–CH*H*), 2.47 (d, 1H, J_{H-H} = 9.6 Hz, Zr–*C*HH), 2.31 (m, 2H, $C_5H_4CH_2$), 1.82 (m, 1H, one CH_2–C–N), 1.70 (m, 1H, one CH_2–C–N). ^{13}C NMR (pyridine-d_5): δ 155.4 (C_6H_5 ipso), 127.9 (C_6H_5 ortho), 125.6 (C_6H_5 meta), 125.0 (C_5H_4 ipso), 119.5 (C_6H_5 para), 114.1 (CH of C_5H_4), 113.3 (CH of C_5H_4), 112.3 (CH of C_5H_4), 110.2 (CH of C_5H_4), 57.5 (NCH_2), 54.9 (Zr–CH_2Ph, J_{C-H} = 140 Hz), 35.8 (NMe), 29.1 ($C_5H_4CH_2$), 26.1 (CH_2–C–N).

Synthesis of [Zr(η^5:σ-$C_5H_4CH_2CH_2CH_2NMe$)(CH_3)$_2${Et_2O}$_{0.5}$] (12). This synthesis only worked on one occasion; at no time was the reaction mixture warmed above 20 °C. A suspension of **5** (0.22 g, 0.67 mmol) in diethyl ether (20 mL) was cooled to 0 °C and treated with MeMgI (3 mL of ca. 1.0 M in diethyl ether). After the mixture was stirred at room temperature for 30 min, the volatiles were removed under reduced pressure to give an oily brown residue. This was extracted with pentane (3 × 20 mL), and the volatiles were removed from the combined extracts, giving **12** as a pale brown solid: yield ca. 0.03 g (<5%). ^1H NMR (C_6D_6): δ 6.19 (t, 2H, J_{H-H} = 2.5 Hz, C_5H_4), 5.55 (t, 2H, J_{H-H} = 2.5 Hz, C_5H_4), 3.35 (q, 2H, O–CH_2), 3.33 (s, 3H, NMe), 2.52 (app t, 2H, $C_5H_4CH_2$), 2.20 (m, 2H, NCH_2), 1.55 (m, 2H, CH_2–C–N), 0.81 (t, 3H, J_{H-H} = 7 Hz, O–C–CH_3), −0.01 (br s, 6H, Zr–Me). ^{13}C NMR (C_6D_6): δ (C_5H_4 ipso and Zr–Me are missing) 110.3 (CH of C_5H_4), 109.8 (CH of C_5H_4), 66.4 (OCH_2CH_3), 55.2 ($C_5H_4CH_2$), 34.7 (NMe), 30.9 (N-CH_2), 26.7 (CH_2–C–N), 14.1 (OCH_2CH_3).

Synthesis of [Zr(η^5:σ-$C_5H_4CH_2CH_2CH_2NMe$)(BH_4)$_2$] (13). A mixture of **5** (0.42 g, 1.28 mmol) and $LiBH_4$ (0.3 g, 13.6 mmol) was cooled to −196 °C and diethyl ether (20 mL) condensed onto the solids. The mixture was warmed to room temperature and stirred for 1.5 h. The solvents were removed under reduced pressure to give a white residue, which was stripped with pentane (5 mL) and dried under reduced pressure. The residue was then extracted three times with pentane (80 mL) and the combined extracts were reduced to 40 mL. Cooling to −20 °C and then −80 °C overnight gave **13** as a microcrystalline white solid: yield 0.3 g (90%). Anal. Calcd for $C_9H_{21}B_2NZr$: C, 42.21; H, 8.26; Zr, 35.62. Found: C, 42.19; H, 8.30; Zr, 35.33. IR (toluene solution, KBr, B–H data only; cm^{-1}): 2131 (s), 2167 (sh), 2502 (s). ^1H NMR (C_6D_6): δ 5.83 (t, 2H, J_{H-H} = 2.8 Hz, C_5H_4), 5.51 (t, 2H, J_{H-H} = 2.8 Hz, C_5H_4), 3.18 (s, 3H, NMe), 2.43 (m, 2H, NCH_2), 2.03 (m, 2H, $C_5H_4CH_2$), 1.46 (m, 2H, CH_2–C–N), 1.08 (q, 8H, J_{H-B} = 86 Hz, 2 × BH_4). ^{13}C NMR (C_6D_6): δ (C_5H_4 ipso missing) 110.9 (CH of C_5H_4), 109.5 (CH of C_5H_4), 58.5 (NCH_2), 45.4 (NMe), 30.1 ($C_5H_4CH_2$), 26.1 (CH_2–C–N). ^{11}B NMR (C_6D_6): δ −18.8 (pent, J_{B-H} = 86 Hz).

Synthesis of [Zr(η^5:σ-$C_5H_4CH_2CH_2CH_2NMe$)(C_5H_5)(NMe_2)] (14). A dilute toluene (10 mL) solution of **3** (2 mL of 0.73 M, 1.46 mmol) was treated with an excess of cyclopentadiene (ca. 0.5 mL), giving a bright yellow solution. This was stirred for 15 min and then heated to 60 °C for 10 min. The volatiles were removed under reduced pressure, and the residue was sublimed at ca. 100 °C/0.005 mmHg to a water-cooled probe. The yellow sublimate was isolated in the glovebox: yield 0.23 g (46%). EI MS: *m/e* 334 [P, 50%, correct isotope pattern for Zr], 289 [P − $HNMe_2$, 100%]. ^1H NMR (C_6D_6): δ 5.92 (m, 2H, C_5H_4), 5.88 (s, 5H, C_5H_5), 5.32 (m, 2H, C_5H_4), 2.90 (m, 1H, N–*C*HH), 2.80 (s, 9H, NMe_2 and NMe), 2.62 (m, 1 H, N–CH*H*), 2.43 (m, 2H, $C_5H_4CH_2$), 1.87 (m, 1H, *C*HH–C–N), 1.27 (m, 1H, CH*H*–C–N). ^{13}C NMR (C_6D_6): δ (C_5H_4 ipso missing) 111.9 (CH of C_5H_4), 111.0 (CH of C_5H_4), 109.6 (C_5H_5), 107.9 (CH of C_5H_4), 103.2 (CH of C_5H_4), 59.2 (NCH_2), 49.3 (NMe_2), 47.1 (NMe), 34.2 ($C_5H_4CH_2$), 28.3 (CH_2–C–N).

NMR-Tube Reaction of 3 with Phenylacetylene. The volatiles were removed under reduced pressure from a toluene solution of **3** (0.2 mL of 0.73 M solution, 0.146 mmol) and the residue was dissolved in benzene-d_6 (ca. 0.4 mL) and placed in a 5-mm NMR tube. Phenylacetylene (32 μL, 0.292 mmol) was added and the tube sealed. After 15 min at 20 °C a faint red coloration appeared which increased with time. After 15 h a ^1H NMR spectrum showed quantitative conversion to "(CpN)Zr(CCPh)$_2$" (**15**). ^1H NMR (C_6D_6): δ 7.53 (m, 4H, C_6H_5 ortho), 7.05 (m, 6H, C_6H_5 meta and para), 6.40 (t, 2H, J_{H-H} = 2.6 Hz, C_5H_4), 5.87 (t, 2H, J_{H-H} = 2.6 Hz, C_5H_4), 3.18 (s, 3H, NMe), 2.84 (m, 2H, N–CH_2), 2.46 (m, 2H, $C_5H_4CH_2$), 2.29 (d, 12H, J_{H-H} = 5.5 Hz, $HNMe_2$), 1.79 (m, 2H, CH_2–C–N), 1.38 (br s, 2H, *H*NMe_2). ^{13}C NMR (C_6D_6): δ 140.0 (ZrCCPh), 132.3 (ZrCCPh), 131.7 (C_6H_5 ortho), 128.4 (C_6H_5 meta), 127.3 (C_6H_5 ipso), 126.3 (C_6H_5 para), 122.7 (C_5H_4 ipso), 110.6 (CH of C_5H_4), 108.8 (CH of C_5H_4), 56.3 (NCH_2), 39.4 ($NHMe_2$), 37.6 (NMe), 29.1 ($C_5H_4CH_2$), 26.6 (CH_2–C–N).

X-ray Diffraction: Crystal and Molecular Structure of 11. Yellow block-shaped crystals were obtained from benzene-d_6 in an NMR tube. A suitable crystal was selected and mounted inside a Lindemann glass capillary on a goniometer head and transferred to the goniostat of an Enraf-Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Unit cell parameters and orientation matrix were determined from a least-squares treatment of the SET4[43] setting angles of 22 reflections with 16.54° < θ < 18.57°. The unit cell was identified as monoclinic space group $P2_1/c$. Reduced cell calculations did not indicate any higher metric symmetry,[44] and examination of the final atomic coordinates of the structure did not indicate any

---

[43] de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr., Sect. A* **1984**, *40*, C410.

[44] Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

higher metric lattice symmetry elements.[45] Three standard reflections were measured every 3 h of X-ray exposure time as check reflections for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. A 360° ψ-scan for a reflection close to axial $(0\bar{4}0)$ showed a variation in intensity of less than 4% about the mean value. Intensity data were corrected for Lorentz and polarization effects and the scale variation, but not for absorption. Standard deviations of $\sigma(I)$ in the intensities were increased according to an analysis of the excess variance of the reference reflection; variance was calculated on counting statistics and the term P^2I^2, where P (=0.0198) is the instability constant[46] as derived from the excess variance in the reference reflections. Equivalent reflections were averaged, resulting in 3691 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability.

The structure was solved by Patterson methods, and extension of the model was accomplished by direct methods applied to the difference structure factors using the program DIRDIF.[47] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ),[48] minimizing the function $Q = \sum_h[w(|F_o| - k|F_c|)^2]$. A subsequent difference Fourier synthesis gave most of the hydrogen atom positions; some of the sp^2-bonded hydrogen atoms were missing, but they were placed at idealized positions. For the hydrogen atoms the coordinates and one common isotropic thermal parameter were refined, but the sp^2-bonded hydrogen (deuterium) atoms could not be refined well, and so they were ultimately included at their idealized positions (d(C–H) = 0.98 Å), riding upon their respective carbon atoms. Weights were introduced in the final refinement cycles. The crystal exhibited some secondary extinction, for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter.[49] Final refinement on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for all the non-hydrogen atoms and one common isotropic thermal parameter for the hydrogen and deuterium atoms converged at $R_F = 0.035$ ($R_w = 0.040$). A final difference Fourier map did not show any residual peaks outside the range ±0.59 e/Å^3. The fractional atomic coordinates and equivalent isotropic thermal parameters are given in Table II, and selected molecular geometry data are given in Table I. Tables of hydrogen atom positions and thermal displacement parameters comprehensive lists of bond distances and angles are given as supplementary material. Crystal data and experimental details of the structure determination are compiled in Table III. Scattering factors were taken from Cromer and Mann.[50] Anomalous dispersion factors taken from Cromer and Liberman[51] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31 computer at the University of Groningen with the program packages XTAL[52] and PLATON[53] (calculation of geometric data) and a locally modified version of the program PLUTO[54] (preparation of illustrations).

Table III. Details on the Structural Determination of 11

chem formula	$(C_{32}H_{40}Cl_2N_2Zr_2)_{0.5}(C_6D_6)$
fw	437.17
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.649(1)
b, Å	10.360(1)
c, Å	17.802(1)
β, deg	106.750(4)
V, Å^3	2057.3(3)
Z	4
D_{calc}, g cm^{-3}	1.411
$F(000)$, electrons	888
μ(Mo K$\bar{\alpha}$), cm^{-1}	6.6
approx cryst dimens, mm	0.20 × 0.42 × 0.52
radiation, Å	Mo K$\bar{\alpha}$, 0.710 73
monochromator	graphite
temp, K	295
θ range (min, max), deg	1.20, 27.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.80 + 0.34 \tan\theta$
data set	h, −14 to +14; k, −1 to +13; l, 0 to +22
cryst-to-receiving aperture dist, mm	173
horiz, vert aperture, mm	$3.2 + \tan\theta$, 4.0
ref rflns (rms dev, %)	$0\bar{2}4$ (0.9), $2\bar{2}\bar{2}$ (1.0), $\bar{2}\bar{2}\bar{1}$ (1.1)
instability constant, P	0.0198
drift cor	1.000–1.039
X-ray exposure time, h	91.9
total no. of data	5418
no. of unique data	4488
no. of obs data ($I \geq 2.5\sigma(I)$)	3691
$R1$ ($=\sum(I - \bar{I})/\sum I$)	0.010
R2 ($=\sum\sigma/\sum I$)	0.023
no. of equiv rflns	1180
no. of rflns	3691
no. of refined params	260
isotropic secondary extinction coeff, g	$[3.8(1)] \times 10^{-4}$
final agreement factors	
$R_F = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0.035
$R_w = [\sum(w(\lvert F_o\rvert - \lvert F_c\rvert)^2)/\sum w\lvert F_o\rvert^2]^{1/2}$	0.040
weighting scheme	$1/\sigma^2(F)$
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m - n)]^{1/2}$ [a]	2.857
residual electron density in final diff Fourier map, e/Å^3	−0.40, 0.59
max shift/σ, final cycle	0.382
av shift/σ, final cycle	0.018

[a] m = number of observations; n = number of variables.

Acknowledgment. We wish to thank the EC for funding of this research (Contract No. SCI* 0137-C AM). We thank Dr. P. D. Grebenik and Miss H. J. Bullick (Oxford Polytechnic, Oxford, U.K.) for assistance with ^{11}B NMR spectra, and we thank Mr. N. A. Popham (University of Oxford, Oxford, U.K.) for assistance with mass spectra.

Supplementary Material Available: An ORTEP[55] drawing of 11 and tables of crystal data, thermal parameters, atomic coordinates, and all bond lengths, bond angles and torsion angles (11 pages). Ordering information is given on any current masthead page.

OM920708P

---

(45) (a) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264. (b) Le Page, Y. *J. Appl. Crystallogr.* **1988**, *21*, 983.

(46) McLandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr., Sect. A.* **1975**, *31*, 245.

(47) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garciá-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report; Crystallography Laboratory University of Nijmegen, Nijmegen The Netherlands, 1992.

(48) Olthof-Hazekamp, R. "*CRYLSQ*", *XTAL* 3.0 *Reference Manual*; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1992.

(49) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

(50) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(51) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(52) *XTAL* 3.0 *Reference Manual*; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1990.

(53) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

(54) Meetsma, A. *Extended Version of the Program PLUTO*; University of Groningen, Groningen, The Netherlands, unpublished. Motherwell, W. D. S.; Clegg, W. *PLUTO: Program for Plotting Molecular and Crystal Structures*; University of Cambridge, Cambridge, England, unpublished.

(55) Johnson, C. K. ORTEP; Report ORNL-3794; Oak Ridge National Laboratory; Oak Ridge, TN, 1965.