Intramolecular Coupling of Two Cyclopentadienyl Ring Systems of Zirconium−Unprecedented Formation of a Dihydride and Preparation of the $[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$ Cluster in a Two-Phase System†

Guangcai Bai, Peter Müller, Herbert W. Roesky,* and Isabel Usón

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

Received May 30, 2000

Summary: Reaction of $(ClMe_2SiC_5H_4)_2ZrCl_2$ (**1**) *with K (Na) in liquid ammonia/toluene at −78 °C gave the ansa-zirconocene dihydride* $[\{HN(SiMe_2C_5H_4)_2Zr(\mu\text{-}H)H\}_2]$ (**3**). *Alternatively, treatment of* $(MeC_5H_4)_2ZrCl_2$ (**2**) *with K (Na) or* $NaNH_2$ *in liquid ammonia/toluene produced the zirconium cluster* $[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$ (**4**). *The reaction of* **2** *with* $NaNH_2$ *in THF led also to the formation of* **4**.

Organozirconium hydride complexes provide valuable catalysts[1] and reagents for the selective synthesis of various organic derivatives[2] and for CO reduction.[3] In general the hydrides are obtained by treating zirconium precursors with various hydride sources ($LiAlH_4$, $LiBH_4$, $LiBH_3Me$, $LiBHEt_3$, $NaBHEt_3$, H_2SiR_2, $LiAlH(OCMe_3)_3$, $NaAlH_2(OCH_2CH_2OMe)_2$).[4] A series of zirconocene dihydride complexes are prepared by hydrogenation of the corresponding dimethyl complexes.[5] Pez et al.[6] obtained $[(Cp)_2Zr(C_{10}H_7)(\mu\text{-}H)Zr(Cp)_2]$ from $(Cp)_2ZrCl_2$ and potassium naphthalene.

Earlier work has shown that the reduction of transition-metal compounds by means of alkali-metal ammonia solutions results in the formation of the corresponding metals[7] and, in some cases, is accompanied by the formation of amides, imides, and nitrides.[8] $Al(NH_2)_3$[9] and $KV(NH)_2$[10] were prepared by treating AlI_3 and VBr_3, respectively, with alkali-metal ammonia solutions. In general, alkali-metal ammonia solutions have not been used for the preparation of transition-metal hydrides due to the easy formation of H_2.

Herein we report on the treatment of $(ClMe_2SiC_5H_4)_2ZrCl_2$ (**1**) with K (Na) in liquid ammonia/toluene at −78 °C, resulting in the formation of the *ansa*-zirconocene dihydride $[\{HN(SiMe_2C_5H_4)_2Zr(\mu\text{-}H)H\}_2]$ (**3**) (eq 1).[11a]

$$\underset{\mathbf{1}}{2(ClMe_2SiC_5H_4)_2ZrCl_2} \xrightarrow[\text{liq.}NH_3,\ \text{toluene, -78 °C}]{8\ K} \underset{\mathbf{3}}{[\{HN(SiMe_2C_5H_4)_2Zr(\mu\text{-}H)H\}_2]} \quad (1)$$

Since the cleavage reaction of the Si−Cl bond is faster in comparison to that of the Zr−Cl bond in **1** (this step is comparable to the hydrolysis of *rac*-[1-$(BrMe_2Si)$-THI]$_2ZrBr_2$ (THI = 4,5,6,7-tetrahydroindenyl)[12] which gave the *ansa*-metallocene *rac*-[μ-O(1-$Me_2SiTHI)_2$]$ZrBr_2$) and the *ansa*-metallocenes are kinetically more stable compared to the unbridged congeners,[13] therefore, the *ansa*-zirconocene formation should be the first step of the reaction. Moreover, we assume that the Si−NH−Si

* To whom correspondence should be addressed. Fax: +49(0)-551393373. E-mail: hroesky@gwdg.de.

† Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday.

(1) (a) Couturier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291. (b) Choukroun, R.; Basso-Bert, M.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1317. (c) Larsonneur, A.-M.; Choukroun, R. *Organometallics* **1993**, *12*, 3216. (d) Carr, A. G.; Dawson, D. M.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1999**, *18*, 2933. (e) Corker, J.; Lefebvre, F.; Lécuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966.

(2) (a) Maraval, A.; Donnadieu, B.; Igau, A.; Majoral, J.-P. *Organometallics* **1999**, *18*, 3138. (b) Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349. (c) Jones, S. B.; Petersen, J. L. *Organometallics* **1985**, *4*, 966. (d) Negishi, E. −I.; Miller, J. A.; Yoshida, T. *Tetrahedron Lett.* **1984**, *25*, 3407. (e) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521. (f) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (g) Edelbach, B. L.; Rahman, A. K. F.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 3170.

(3) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (c) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (d) Shoer, L. I.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 5831.

(4) (a) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405. (b) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793. (c) Kot, W. K.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1987**, *26*, 1339. (d) Cuenca, T.; Galakhov, M.; Royo, E.; Royo, P. *J. Organomet. Chem.* **1996**, *515*, 33. (e) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501. (f) Liu, X.; Wu, Z.; Peng, Z.; Wu, Y.-D.; Xue, Z. *J. Am. Chem. Soc.* **1999**, *121*, 5350. (g) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889. (h) Choukroun, R.; Dahan, F.; Larsonneur, A.-M.; Samuel, E.; Petersen, J.; Meunier, P.; Sornay, C. *Organometallics* **1991**, *10*, 374.

(5) (a) Chirik, P. J.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1873. (b) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255. (c) Curtis, C. J.; Haltiwanger, R. C. *Organometallics* **1991**, *10*, 3220. (d) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701. (e) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136. (f) Couturier, S.; Gautheron, B. *J. Organomet. Chem.* **1978**, *157*, C61. (g) Weigold, H.; Bell, A. P.; Willing, R. I. *J. Organomet. Chem.* **1974**, *73*, C23.

(6) Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933.

(7) (a) Watt, G. W.; McCarley, R. E.; Dawes, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 5163. (b) Watt, G. W.; Walling, M. T., Jr.; Mayfield, P. I. *J. Am. Chem. Soc.* **1953**, *75*, 6175. (c) Watt, G. W.; Mayfield, P. I. *J. Am. Chem. Soc.* **1953**, *75*, 6178. (d) Watt, G. W.; Hall, J. L.; Choppin, G. R. *J. Phys. Chem.* **1953**, *57*, 567.

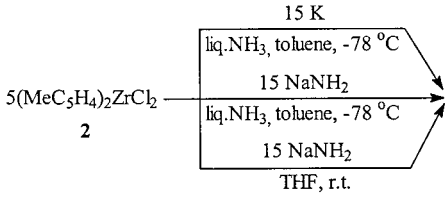
(8) (a) Watt, G. W.; Jenkins, W. A., Jr. *J. Am. Chem. Soc.* **1951**, *73*, 3275. (b) Watt, G. W.; Roper, W. F.; Parker, S. G. *J. Am. Chem. Soc.* **1951**, *73*, 5791.

(9) Taylor, W. L.; Griswold, E.; Kleinberg, J. *J. Am. Chem. Soc.* **1955**, *77*, 294.

(10) Nicholls, D. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1001.

10.1021/om0004500 CCC: $19.00
Publication on Web 10/21/2000

unit is important for stabilizing and forming the zirconium hydride. Alternatively, treatment of $(MeC_5H_4)_2ZrCl_2$ (**2**) with K (Na) in liquid ammonia/toluene at −78 °C results in the loss of two chloride ligands and one MeC_5H_4 group per Zr and the formation of an unusual pentanuclear zirconium cluster, $[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$ (**4**). The reaction of **2** with $NaNH_2$ in liquid ammonia/toluene at −78 °C or alternatively with $NaNH_2$ in THF at room temperature leads also to the formation of **4** (eq 2).[11b] One of the byproducts in this



$$[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4] \quad (2)$$

4

reaction is either the sodium or the potassium salt of $(MeC_5H_4)M$ (M = Na, K). The loss of MeC_5H_4 during the preparation of **4** is similar to the situation observed for the preparation of $[(CpTi)_6(\mu_3\text{-}O)_8]$,[14a] $[(CpTi)_5(\mu_3\text{-}S)_6]$,[14b] and $[(CpTi)_6(\mu_3\text{-}Te)_6(\mu_3\text{-}O)_2]$,[14c] respectively.

Compounds **3** (pale yellow) and **4** (colorless) are crystalline solids.[15] In solution (toluene or THF) no decomposition is observed for **3** and **4** over a period of 1 year. However, the reactivity of **3** toward ammonia is highly reduced in comparison to $Cp^*_2ZrH_2$.[16] The IR spectrum of **4** shows broad absorptions at 3299 and 3371 cm^{-1}, assignable to the NH and NH_2 stretching frequencies, respectively.

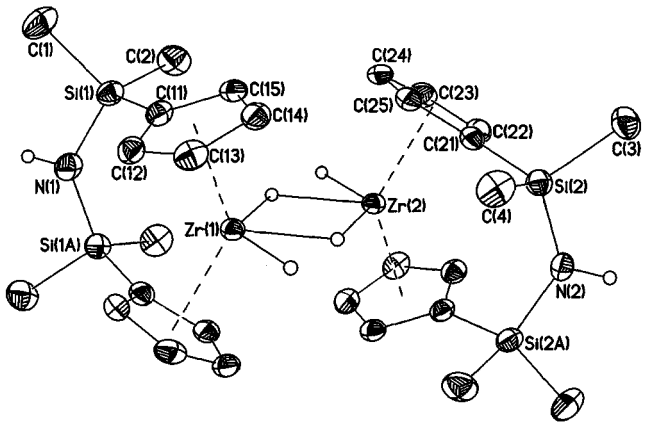


Figure 1. Crystal structure of **3**. H atoms bonded to C are omitted for clarity. Selected bond length (Å): Zr(1)−Zr(2) = 3.462(1).

X-ray Crystal Structures of 3 and 4. The molecular structures of **3** and **4**[17] are shown in Figures 1 and 2. Details of the data collection, structure solution, and refinement are given in Table 1.

The molecular structure of **3** is constrained by a crystallographic mirror passing through the two Zr and two N atoms. The core of **3** consists of a four-membered $Zr_2(\mu\text{-}H)_2$ ring, with each Zr atom bound to a terminal H atom. Residual electron density for each of the four independent hydrides was resolved in an electron-density difference map. The chelating $HN(SiMe_2C_5H_4)_2$ group functions as two η^5 ligands (Figure 1). The Zr−

(11) (a) The synthesis of **3** was carried out as follows. Ammonia (50 mL) was condensed onto a suspension of **1** (1.43 g, 3.00 mmol) and K (0.47 g, 12.02 mmol) in toluene (80 mL) at −78 °C with stirring. The stirring of the mixture was continued for 1 h at this temperature. Then the excess ammonia was allowed to evaporate from the reaction mixture with stirring over 4 h. During this time the mixture was slowly warmed to room temperature. The resulting solution was filtered, and the remaining brown precipitate was extracted with warm toluene (50 °C, 2 × 30 mL). The combined pale yellow solution was concentrated (to 30 mL) and kept at −20 °C for 2 weeks. Pale yellow crystals of **3** (0.12 g) were obtained. After concentration of the filtrate (to 5 mL) and addition of hexane (20 mL), the solution was kept at −20 °C overnight. Slightly impure microcrystalline **3** (0.60 g) was formed. Yield: 0.72 g (60.2%). (b) The synthesis of **4** was carried out as follows. Method A: ammonia (80 mL) was condensed onto a suspension of **2** (2.56 g, 8.0 mmol) and potassium (0.94 g, 24 mmol) in toluene (80 mL) at −78 °C. The mixture was stirred for 1 h at −78 °C. Then the excess ammonia was allowed to evaporate from the reaction mixture with stirring over 4 h. During this period the mixture was warmed slowly to room temperature. The reaction mixture was filtered, and the light yellow solution was kept at room temperature for 4 weeks. Colorless crystals of **4** were obtained in 25% yield (0.40 g). Method B: ammonia (50 mL) was condensed onto a solution of **2** (1.61 g, 5.0 mmol) in toluene (60 mL) at −78 °C. $NaNH_2$ (0.59 g, 15.1 mmol) was added to the resulting mixture. The mixture was stirred for 1 h at −78 °C. Then the excess ammonia was allowed to evaporate from the reaction mixture with stirring over 4 h. During this period the mixture was warmed slowly to room temperature. Colorless crystals of **4** were obtained in 53% yield (0.52 g). Method C: THF (50 mL) was added onto the mixture of **2** (1.61 g, 5.0 mmol) and $NaNH_2$ (0.59 g, 15.1 mmol) at room temperature. The mixture was stirred for 4 h at room temperature. After filtration and concentration to about 20 mL in vacuo, the pale yellow solution was kept at room temperature for 2 weeks. Colorless crystals of **4** were obtained in 28% yield (0.28 g).

(12) Lofthus, O. W.; Slebodnick, C.; Deck, P. A. *Organometallics* **1999**, *18*, 3702.

(13) (a) Labella, L.; Chernega, A.; Green, M. L. H. *J. Organomet. Chem.* **1995**, *485*, C18. (b) Chernega, A.; Cook, J.; Green, M. L. H.; Labella, L.; Simpson, S. J.; Souter, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225.

(14) (a) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829. (b) Bottomley, F.; Egharevba, G. O.; White, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 4353. (c) Gindelberger, D. E. *Acta Crystallogr., Sect. C* **1996**, *52*, 2493.

(15) (a) Characterization data for **3** are as follows. Dec pt: 200−228 °C. IR (Nujol): $\tilde{\nu}$ 1612, 1586, 1316, 1260, 1251, 1186, 1163, 1096, 1046, 929, 904, 828, 804, 789, 731, 693, 650, 611 cm^{-1}. EI-MS: *m/z* (%) 795 (1) [M^+ − H], 348 (100) [$M^+ - C_7H_8 - HN(SiMe_2C_5H_4)_2 - C_5H_4$ − 2Me − 3H)]. ^1H NMR (500 MHz, THF[D_8]): δ 6.41, 6.03, 5.86, 5.33 (m, 16H, C_5H_4), 3.03 (t, ^2J(H,H) = 7.5 Hz, 2H, H_t), 1.33 (s, 2H, NH), 0.28 (s, 12H, SiMeMe′), 0.23 (s, 12H, SiMeMe′), −3.94 (t, ^2J(H,H) = 7.5 Hz, 2H, H_b). ^{13}C NMR (125 MHz, THF[D_8]): δ 113.99 (substituted C, C_5H_4), 108.45, 106.47, 105.80, 105.76 (C_5H_4), 2.37 (SiMeMe′), 2.18 (SiMeMe′). Anal. Calcd for $C_{35}H_{54}N_2Si_4Zr_2$ (797.60): C, 52.7; H, 6.8; N, 3.5. Found: C, 52.5; H, 6.9; N, 3.9. (b) Characterization data for **4** are as follows. Mp: 302 °C. IR (Nujol): $\tilde{\nu}$ 3371, 3299, 1718, 1557, 1039, 1033, 933, 841, 787, 722, 669, 519, 452, 364, 346 cm^{-1}. EI-MS: *m/z* (%) 989 (62) [M^+], 910 (100) [$M^+ - MeC_5H_4$]. ^1H NMR (250 MHz, THF[D_8]): δ 6.56 (br s, 4H, NH), 5.73−5.56 (m, 20H, C_5H_4), 2.13/2.11 (2s, 15H, CH_3), 0.69 (br d, ^2J(H,H) = 8.3 Hz, 4H, NHH′), 0.14 (br d, ^2J(H,H) = 8.3 Hz, 4H, NHH′). ^{13}C NMR (100 MHz, THF[D_8]): δ 110.50, 109.80, 109.20, 108.18 (C_5H_4), 15.58/15.42 (Me). Anal. Calcd for $C_{30}H_{47}N_9Zr_5$ (989.87): C, 36.4; H, 4.8; N, 12.7. Found: C, 37.1; H, 5.0; N, 12.3.

(16) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

(17) (a) X-ray structure determination of **3**: single crystals of **3** were obtained from toluene after some weeks at −20 °C. The crystals of **3** were removed from the flask under argon gas and mounted on a glass fiber in a rapidly cooled perfluoropolyether.[20] Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area detector at 133(2) K with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), performing φ and ω scans. The structure was solved by direct methods using SHELXS-97[21] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[22] All non-hydrogen atoms were refined anisotropically with similarity and rigid bond restraints. All hydrogen atoms bonded to carbon were included in the models at geometrically calculated positions and refined using a riding model. The other hydrogen atoms were located in the difference Fourier synthesis and refined freely and—in the case of N−H bonds—were refined with the help of distance restraints. The isotropic displacement parameters of the hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Details of the data collection, structure solution, and refinement are listed in Table 1. (b) X-ray structure determination of **4**: single crystals of **4** were obtained from toluene at room temperature.[17a]

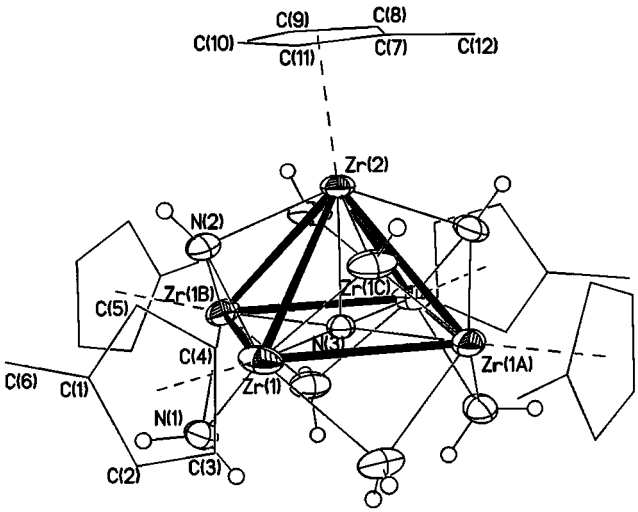


Figure 2. Crystal structure of **4**. H atoms bonded to C are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)−N(2) = 2.195(6), Zr(1)−N(3) = 2.2321(6), Zr(1)−N(1) = 2.278(6), Zr(1)−Zr(2) = 3.143(1), Zr(1)−Zr(1)#2 = 3.1566(8), Zr(2)−N(3) = 2.21(1), Zr(2)−N(2) = 2.253(6); N(2)#1−Zr(1)−N(2) = 86.0(3), N(2)−Zr(1)−N(3) = 69.9(2), N(2)−Zr(1)−N(1) = 82.4(2), N(3)−Zr(1)−N(1) = 74.2(2), N(2)−Zr(1)−N(1)#1 = 143.4(2), N(1)−Zr(1)−N(1)#1 = 87.8(3), Zr(2)−Zr(1)−Zr(1)#2 = 59.86(1), N(2)#1−Zr(2)−N(2)#2 = 138.6(3), N(3)−Zr(2)−N(2) = 69.3(1), N(2)#1−Zr(2)−N(2) = 82.81(9), Zr(1)−N(1)−Zr(1)#2 = 86.8(2), Zr(1)#2−N(2)−Zr(1) = 92.5(2), Zr(1)−N(2)−Zr(2) = 89.9(2), Zr(2)−N(3)−Zr(1) = 90.1(3), Zr(1)−N(3)−Zr(1)#3 = 179.8(5).

Zr distance (3.462(1) Å) is very similar to those found in $[\{(RC_5H_4)_2Zr(\mu\text{-}H)H\}_2]$ (3.44 Å, R = $SiMe_3$, CMe_3),[1c] $[\{(MeC_5H_4)_2Zr(\mu\text{-}H)H\}_2]$ (3.4599(2) Å),[4g] and $[\{(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}H)H\}_2]$ (3.4708(7) Å).[4h]

The crystal structure of **4** is constrained by a crystallographically imposed C_4 axis passing through the Zr(2) and N(3). The core of **4** consists of five Zr atoms forming a square pyramid. The four triangular faces of this pyramid are capped by NH groups, the four edges of the base are bridged by NH_2 groups, and in the center of the basal plane of the Zr_5 cluster there is a μ_5-N atom (Figure 2). The coordination sphere of the Zr atoms is completed by one MeC_5H_4 group per Zr. The average Zr(2)−N(3) (2.210 Å), Zr(1)−N(3) (2.232 Å), Zr(2)−N(2) (2.253 Å), Zr(1)−N(2) (2.186 Å), and Zr(1)−N(1) (2.296 Å) bond lengths are very similar to the respective lengths found in $[\{(t\text{-}Bu_3CO)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$ (Zr_a−(μ_5-N) = 2.35 Å, Zr_b−(μ_5-N) = 2.23 Å, Zr_a−(μ_3-NH) = 2.27 Å, Zr_b−(μ_3-NH) = 2.19 Å, and Zr_b−(μ-NH_2) = 2.31 Å; Zr(2) = Zr_a, Zr(1) = Zr_b).[18]

In summary, we have shown that the reactions of alkali-metal ammonia solutions with $(ClMe_2SiC_5H_4)_2ZrCl_2$ and $(MeC_5H_4)_2ZrCl_2$ in toluene generate very different products. The alkali-metal ammonia solutions can be used to prepare a zirconium dihydride via an intramolecular reaction with simultaneous coupling of two silicon chloride substituted cyclopentadienyl rings. In contrast, the reaction of the $(MeC_5H_4)_2ZrCl_2$ with alkali-metal ammonia solutions in toluene is similar to that with alkali-metal amide and liquid ammonia in toluene or alkali-metal amide in THF, which leads to larger nitrogen zirconium aggregates with elimination of MeC_5H_4. The intermediates might be similar to the zirconium amide and imide formation proposed by Allbutt et al.[19] in the ammonolysis of zirconium(IV) bromide. The formation of cluster **4** in moderate yield using the two-phase system ammonia/toluene allows further reactions with **4**. The ammonolysis of R_2TiCl_2 resulted in a compound with a rhombohedral $Ti_6(\mu_3\text{-}NH)_6(\mu_3\text{-}N)_2$ core structure.[23]

Table 1. Crystallographic Data for 2 and 3

	3	**4**
empirical formula	$C_{28}H_{46}N_2Si_4Zr_2{\cdot}C_7H_8$	$C_{30}H_{47}N_9Zr_5$
fw	705.46 + 92.14	989.87
cryst size (mm)	0.4 × 0.2 × 0.1	0.4 × 0.3 × 0.3
cryst syst	monoclinic	tetragonal
space group	$P2_1/m$	$I4$
a (Å)	8.138(2)	13.189(2)
b (Å)	15.444(3)	13.188(2)
c (Å)	15.132(3)	9.522(2)
α (deg)	90	90
β (deg)	98.92(3)	90
γ (deg)	90	90
V (Å^3)	1878.9(6)	1656.1(5)
Z	2	2
ρ_{calcd} (g mm^{-3})	1.410	1.985
μ (mm^{-1})	0.708	1.558
F(000)	828	980
2θ range (deg)	5.28−52.00	4.36−55.96
no. of data: measd, unique	47659, 3839 (R_{int} = 0.0516)	20345, 2012 (R_{int} = 0.0252)
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0397, 0.1022	0.0443, 0.1085
R1, wR2 (all data)	0.0455, 0.1049	0.0458, 0.1099
goodness of fit, S[c]	1.222	1.035
no. of refined params	526	152
no. of restraints	412	281
largest diff peak/ hole (e Å^{-3})	+1.658/−0.855	+1.417/−1.983

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n - p)]^{1/2}$.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0004500

(18) Banaszak Holl, M. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1992**, *114*, 3854.

(19) Allbutt, M.; Fowles, G. W. A. *J. Inorg. Nucl. Chem.* **1963**, *25*, 67.

(20) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(22) Sheldrick, G. M. SHELX 97; Universität Göttingen, Göttingen, Gerany, 1997.

(23) Bai, G.; Roesky, H. W.; Noltemeyer, M.; Hao, H.; Schmidt, H.-G. *Organometallics* **2000**, *19*, 2823.