

Intramolecular Coupling of Two Cyclopentadienyl Ring Systems of Zirconium—Unprecedented Formation of a Dihydride and Preparation of the $[(\text{MeC}_5\text{H}_4)_2\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu\text{-NH}_2)_4]$ Cluster in a Two-Phase System[†]

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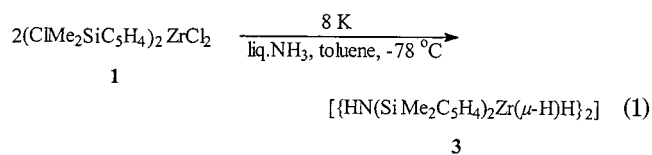
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Summary: Reaction of $(\text{CIme}_2\text{SiC}_5\text{H}_4)_2\text{ZrCl}_2$ (**1**) with K (Na) in liquid ammonia/toluene at -78°C gave the *ansa*-zirconocene dihydride $[\text{HN}(\text{SiMe}_2\text{C}_5\text{H}_4)_2\text{Zr}(\mu\text{-H})\text{H}]_2$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

Organozirconium hydride complexes provide valuable catalysts¹ and reagents for the selective synthesis of various organic derivatives² 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 , $\text{LiAlH}(\text{OCMe}_3)_3$, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2$).⁴ A series of zirconocene dihydride complexes are prepared by hydrogenation of the corresponding dimethyl complexes.⁵ Pez et al.⁶ obtained $[(\text{Cp})_2\text{Zr}(\text{C}_{10}\text{H}_7)(\mu\text{-H})\text{Zr}(\text{Cp})_2]$ from $(\text{Cp})_2\text{ZrCl}_2$ 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 metals⁷ and, in some cases, is accompanied by the formation of amides, imides, and nitrides.⁸ $\text{Al}(\text{NH}_2)_3$ ⁹ and $\text{KV}(\text{NH})_2$ 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 $(\text{CIme}_2\text{SiC}_5\text{H}_4)_2\text{ZrCl}_2$ (**1**) with K (Na) in liquid ammonia/toluene at -78°C , resulting in the formation of the *ansa*-zirconocene dihydride $[\text{HN}(\text{SiMe}_2\text{C}_5\text{H}_4)_2\text{Zr}(\mu\text{-H})\text{H}]_2$ (**3**) (eq 1).^{11a}



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-(BrMe₂Si)THI]₂ZrBr₂ (THI = 4,5,6,7-tetrahydroindenyl)¹² which gave the *ansa*-metallocene *rac*-[μ-O(1-Me₂SiTHI)₂]ZrBr₂) 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

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

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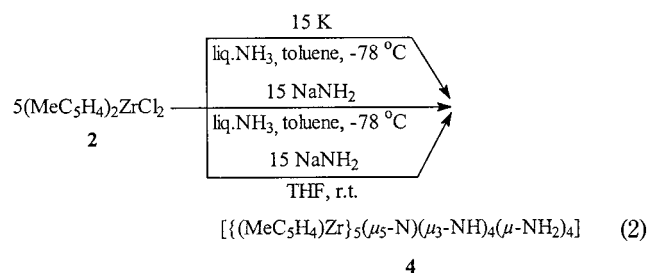
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unit is important for stabilizing and forming the zirconium hydride. Alternatively, treatment of $(\text{MeC}_5\text{H}_4)_2\text{-ZrCl}_2$ (**2**) with K (Na) in liquid ammonia/toluene at -78°C results in the loss of two chloride ligands and one MeC_5H_4 group per Zr and the formation of an unusual pentanuclear zirconium cluster, $[(\text{MeC}_5\text{H}_4)\text{Zr}]_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu\text{-NH}_2)_4$ (**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



reaction is either the sodium or the potassium salt of $(\text{MeC}_5\text{H}_4)\text{M}$ ($\text{M} = \text{Na}, \text{K}$). The loss of MeC_5H_4 during the preparation of **4** is similar to the situation observed for the preparation of $[(\text{CpTi})_6(\mu_3\text{-O})_8]$,^{14a} $[(\text{CpTi})_5(\mu_3\text{-S})_6]$,^{14b} and $[(\text{CpTi})_6(\mu_3\text{-Te})_6(\mu_3\text{-O})_2]$,^{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^*ZrH_2 .¹⁶ The IR spectrum of **4** shows broad absorptions at 3299 and 3371

(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 $^\circ\text{C}$, 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).

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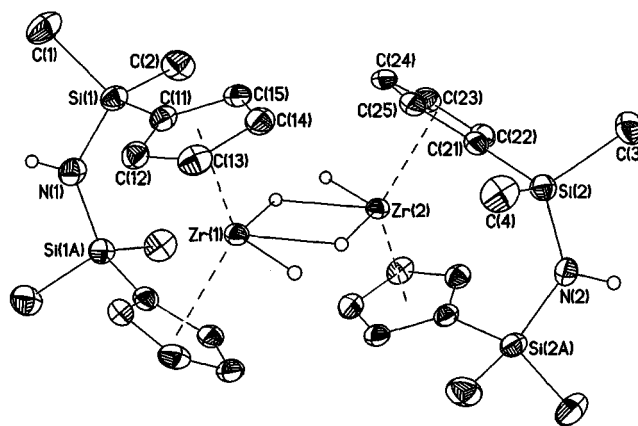


Figure 1. Crystal structure of **3**. H atoms bonded to C are omitted for clarity. Selected bond length (\AA): $\text{Zr}(1)\text{-Zr}(2) = 3.462(1)$.

cm^{-1} , assignable to the NH and NH_2 stretching frequencies, respectively.

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 $\text{Zr}_2(\mu\text{-H})_2$ 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 $\text{HN}(\text{SiMe}_2\text{C}_5\text{H}_4)_2$ group functions as two η^5 ligands (Figure 1). The Zr-

(15) (a) Characterization data for **3** are as follows. Dec pt: $200\text{-}228^\circ\text{C}$. 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) $[\text{M}^+ - \text{H}]$, 348 (100) $[\text{M}^+ - \text{C}_7\text{H}_8 - \text{HN}(\text{SiMe}_2\text{C}_5\text{H}_4)_2 - \text{C}_5\text{H}_4 - 2\text{Me} - 3\text{H}]$. ^1H NMR (500 MHz, $\text{THF}[D_8]$): δ 6.41, 6.03, 5.86, 5.33 (m, 16H, C_5H_4), 3.03 (t, $^2J(\text{H,H}) = 7.5$ Hz, 2H, H_1), 1.33 (s, 2H, NH), 0.28 (s, 12H, SiMeMe), 0.23 (s, 12H, SiMeMe), -3.94 (t, $^2J(\text{H,H}) = 7.5$ Hz, 2H, H_2). ^{13}C NMR (125 MHz, $\text{THF}[D_8]$): 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 $\text{C}_{35}\text{H}_{54}\text{N}_2\text{Si}_4\text{Zr}_2$ (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) $[\text{M}^+]$, 910 (100) $[\text{M}^+ - \text{MeC}_5\text{H}_4]$. ^1H NMR (250 MHz, $\text{THF}[D_8]$): 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, $^2J(\text{H,H}) = 8.3$ Hz, 4H, NHH'), 0.14 (br d, $^2J(\text{H,H}) = 8.3$ Hz, 4H, NHH'). ^{13}C NMR (100 MHz, $\text{THF}[D_8]$): δ 110.50, 109.80, 109.20, 108.18 (C_5H_4), 15.58/15.42 (Me). Anal. Calcd for $\text{C}_{30}\text{H}_{47}\text{N}_5\text{Zr}_5$ (989.87): C, 36.4; H, 4.8; N, 12.7. Found: C, 37.1; H, 5.0; N, 12.3.

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(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 $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), performing φ and ω scans. The structure was solved by direct methods using SHELXS-97²¹ 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}

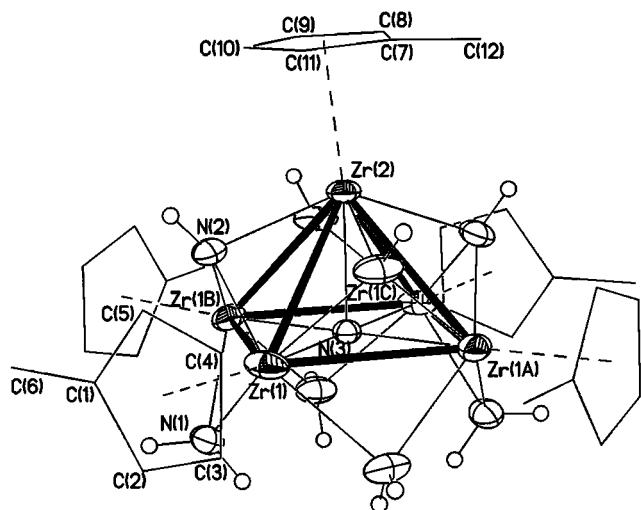


Figure 2. Crystal structure of **4**. H atoms bonded to C are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)–N(2) = 2.195(6), Zr(1)–N(3) = 2.2321(6), Zr(1)–N(1) = 2.278(6), Zr(1)–Zr(2) = 3.143(1), Zr(1)–Zr(1)#2 = 3.1566(8), Zr(2)–N(3) = 2.21(1), Zr(2)–N(2) = 2.253(6); N(2)#1–Zr(1)–N(2) = 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 $[(RC_5H_4)_2Zr(\mu-H)H]_2$ (3.44 Å, R = SiMe₃, CMe₃),^{1c} $[(MeC_5H_4)_2Zr(\mu-H)H]_2$ (3.4599(2) Å),^{4g} and $[(t-BuC_5H_4)_2Zr(\mu-H)H]_2$ (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 NH₂ groups, and in the center of the basal plane of the Zr₅ cluster there is a μ_5 -N atom (Figure 2). The coordination sphere of the Zr atoms is completed by one MeC₅H₄ 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 $[(t-Bu_3CO)Zr]_5(\mu_5-N)(\mu_3-NH)_4(\mu-NH_2)_4$ (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 -NH₂) = 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 (ClMe₂SiC₅H₄)₂-ZrCl₂ and (MeC₅H₄)₂ZrCl₂ 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

Table 1. Crystallographic Data for 2 and 3

	3	4
empirical formula	C ₂₈ H ₄₆ N ₂ Si ₄ Zr ₂ ·C ₇ H ₈	C ₃₀ H ₄₇ N ₉ Zr 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	<i>P</i> 2 ₁ / <i>m</i>	<i>I</i> 4
<i>a</i> (Å)	8.138(2)	13.189(2)
<i>b</i> (Å)	15.444(3)	13.188(2)
<i>c</i> (Å)	15.132(3)	9.522(2)
α (deg)	90	90
β (deg)	98.92(3)	90
γ (deg)	90	90
<i>V</i> (Å ³)	1878.9(6)	1656.1(5)
<i>Z</i>	2	2
ρ_{calcd} (g mm ⁻³)	1.410	1.985
μ (mm ⁻¹)	0.708	1.558
<i>F</i> (000)	828	980
2 θ range (deg)	5.28–52.00	4.36–55.96
no. of data:	47659, 3839	20345, 2012
measd, unique	(<i>R</i> _{int} = 0.0516)	(<i>R</i> _{int} = 0.0252)
<i>R</i> 1, ^a w <i>R</i> 2 ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0397, 0.1022	0.0443, 0.1085
<i>R</i> 1, w <i>R</i> 2 (all data)	0.0455, 0.1049	0.0458, 0.1099
goodness of fit, <i>S</i> ^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 *R*1 = $\sum |F_o| - |F_c| / \sum |F_o|$. ^b w*R*2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$. ^c *S* = $[\sum w(F_o^2 - F_c^2)^2 / \sum (n - p)]^{1/2}$.

two silicon chloride substituted cyclopentadienyl rings. In contrast, the reaction of the (MeC₅H₄)₂ZrCl₂ 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 MeC₅H₄. 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 R₂TiCl₂ resulted in a compound with a rhombohedral Ti₆(μ_3 -NH)₆(μ_3 -N)₂ core structure.²³

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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>.

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