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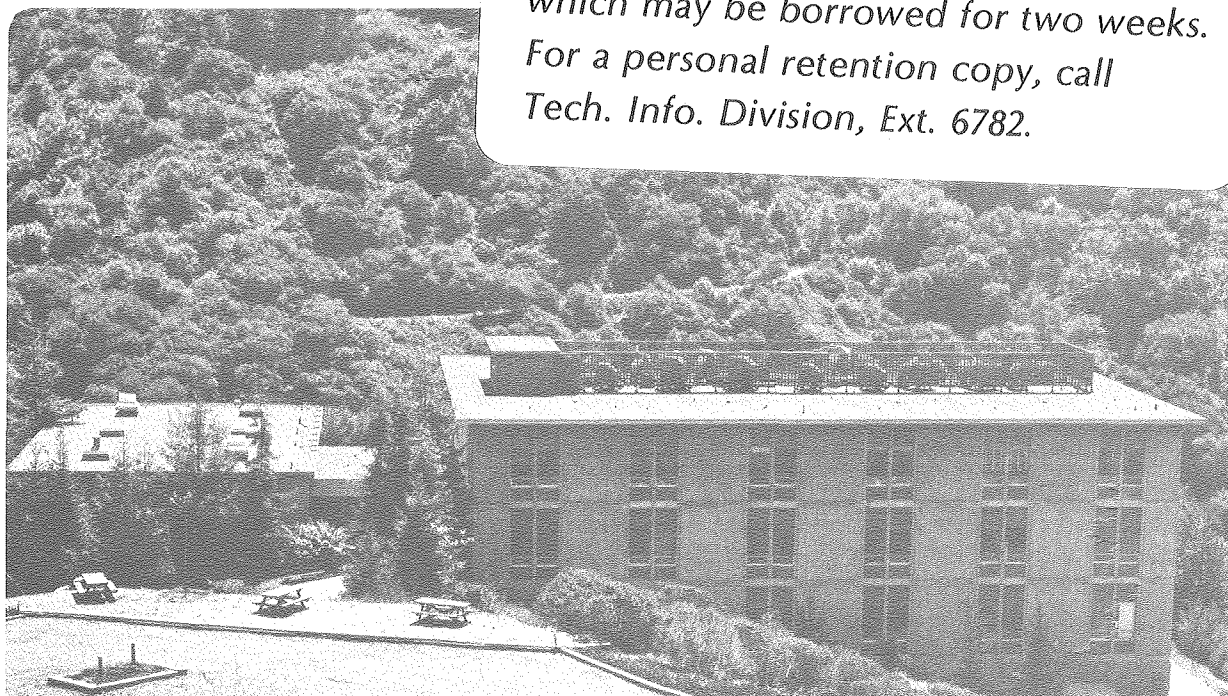
CONCERNING THE REACTION OF METALLOCENE DICHLORIDES
OF TITANIUM (IV) AND ZIRCONIUM(IV) WITH LITHIUM
BIS(TRIMETHYLSILYL)AMIDE

Stephen J. Simpson and Richard A. Andersen

January 1981

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LBL-12195

Concerning the Reaction of Metallocene Dichlorides
of Titanium(IV) and Zirconium(IV)
with Lithium Bis(trimethylsilyl)amide

Stephen J. Simpson and Richard A. Andersen*

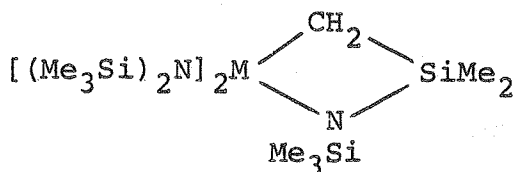
Abstract

Reaction of Cp_2TiCl_2 with one or two molar equivalents of $\text{LiN}(\text{SiMe}_3)_2$ yields the previously described metallocycle, $\text{Cp}_2\text{-TiCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3$. Mass balance shows that for each mole of metallocycle formed, one mole-equivalent of hydrogen chloride is also formed. The related zirconium metallocycle was prepared from $\text{Cp}_2\text{Zr}(\text{H})(\text{Cl})$ and $\text{LiN}(\text{SiMe}_3)_2$. The bis-silylamide of zirconium, $\text{Cp}_2\text{Zr}[\text{N}(\text{SiMe}_3)_2]_2$, was prepared from Cp_2ZrCl_2 and two molar equivalents of $\text{LiN}(\text{SiMe}_3)_2$. The Me_3Si -groups in the latter compound are magnetically non-equivalent at 27°C but coalesce at 84°C on the ^1H NMR time scale.

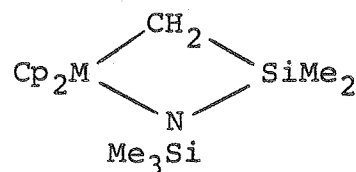
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The four-membered-ring heterocyclic molecules (I) have been prepared recently by γ -elimination of methane from the



I, M = Zr, Hf, Th, U



II, M = Ti, Zr

tris(silylamido)alkyls as shown in eq. 1.¹ A related metallocycle II, M = Ti, was isolated some years ago in the reaction

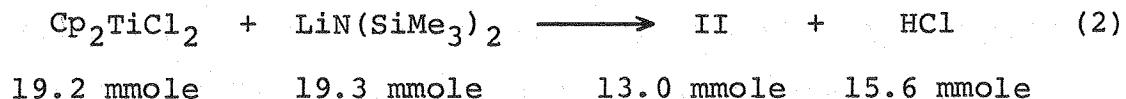


of dicyclopentadienyltitaniumdichloride and two molar equivalents of lithium bis(trimethylsilyl)amide.² It was implicitly suggested that the γ -hydrogen atom of a bis(trimethylsilyl)amido group in hypothetical $\text{Cp}_2\text{Ti}[\text{N}(\text{SiMe}_3)_2]_2$ was eliminated as $(\text{Me}_3\text{Si})_2\text{NH}$, since the latter molecule was detected. Later, an explicit mechanism was proposed which suggested that lithium bis(trimethylsilyl)amide deprotonates a γ -methyl group of the coordinated silylamide ligand in hypothetical $\text{Cp}_2\text{Ti}[\text{N}(\text{SiMe}_3)_2][\text{Cl}]$ yielding $\text{Li}\{\text{Cp}_2\text{Ti}[\text{N}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2)][\text{Cl}]\}$ and $(\text{Me}_3\text{Si})_2\text{NH}$. The former ion-pair then eliminates lithium chloride, yielding II, M = Ti.^{3a} To confuse the matter further, it is said that Me_3SiCl is eliminated.^{3b}

Since we have never observed the coordinated $(\text{Me}_3\text{Si})_2\text{N}$ group to act as an hydrogen-atom acceptor, though this is a well-known reaction in organic chemistry,⁴ we decided to

carefully reexamine this reaction in some detail with respect to its stoichiometry.

Addition of two molar equivalents of lithium bis(trimethylsilyl)amide to dicyclopentadienylnitrogeniumdichloride in either pentane or diethyl ether yielded the metallocycle II, $M = Ti$, after sublimation ($100-110^{\circ}C/10^{-3}$ mm) and ca. one molar equivalent of unreacted lithium bis(trimethylsilyl)amide, isolated by crystallization. The spectroscopic properties of II, $M = Ti$, given in the Experimental Section (including the proton-coupled ^{13}C NMR spectrum) are in agreement with those previously given.² Reaction of dicyclopentadienylnitrogeniumdichloride and one molar equivalent of lithium bis(trimethylsilyl)amide in pentane or diethyl ether also yields metallocycle II, $M = Ti$ and hydrogen chloride. The mass balance for this reaction yields the values shown below (see Experimental Section for details). The 1:1 molar relationship, as shown in eq. 2, is



clearly established. The formation of $(\text{Me}_3\text{Si})_2\text{NH}$, as previously described,² is probably due to reaction of excess lithium bis(trimethylsilyl)amide and hydrogen chloride. The detailed mechanism of this γ -hydrogen chloride elimination, though not the stoichiometry, is obscure.

Reaction of the zirconium analogue, Cp_2ZrCl_2 , with lithium bis(trimethylsilyl)amide takes a different course. Addition of two molar equivalents of lithium bis(trimethylsilyl)amide to

dicyclopentadienylzirconiumdichloride in diethyl ether yields the bis-silylamide, $\text{Cp}_2\text{Zr}[\text{N}(\text{SiMe}_3)_2]_2$. The cyclopentadienyl rings are equivalent in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra but the trimethylsilyl groups are non-equivalent at 27°C. Thus, a symmetry plane is present in the molecule that contains the Cp(centroid)-Ti-Cp(centroid) unit, though the $(\text{Me}_3\text{Si})_2\text{N-Ti-N}(\text{SiMe}_3)_2$ unit cannot contain such a plane at this temperature. Hence, the $(\text{Me}_3\text{Si})_2\text{N}$ groups are oriented neither parallel nor perpendicular to each other but the orientation is somewhere in-between these two extremes, and the Me_3Si -groups are proximal and distal. The in-between orientation of $(\text{Me}_3\text{Si})_2\text{N}$ groups is the situation found in binary silylamide compounds.⁵

A variable temperature ^1H NMR experiment shows that the trimethylsilyl groups coalesce at 84°C. The barrier to rotation, most reasonably ascribed to severe steric congestion about the zirconium atom, is slow on the ^1H NMR time scale at room temperature though fast at temperatures greater than 85°C. Line shape analysis⁶ yields a barrier ($\Delta G_{\text{TC}}^\ddagger$) of 18 kcal mol⁻¹.

The zirconium metallocycle (II, M = Zr) can be prepared by allowing dicyclopentadienylzirconiumhydrido-chloride to react with one molar equivalent of lithium bis(trimethylsilyl)amide at room temperature in diethyl ether. The γ -hydrogen elimination is facile, since we could see no evidence in the ^1H NMR nor infrared spectra of the crude reaction produce for a hydride-containing species. This conclusion is in accord with the metallation processes described earlier.¹

Experimental Section

All reactions were performed under argon. Analyses were done by the microanalytical laboratory of this department. Proton and carbon nuclear magnetic resonance spectra were obtained at 89.56 and 22.50 MHz, respectively, on a JEOL-FX90Q spectrometer. Chemical shifts are reported in δ -units ($\text{Me}_4\text{Si} = 0$), positive values being to high frequency. Room temperature spectra were obtained on benzene- d_6 solutions and variable temperature spectra were measured on toluene- d_8 solutions.

Preparation of $\text{Cp}_2\text{TiCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3$. (a) From two molar equivalents of $\text{LiN}(\text{SiMe}_3)_2$. A suspension of dicyclopentadienyltitaniumdichloride⁷ (1.8 g, 0.0072 mol) and lithium bis(trimethylsilyl)amide [prepared by heating (75°C) a melt of $\text{LiN}(\text{SiMe}_3)_2 \cdot 2 \text{OEt}_2$ in vacuum (10^{-2} mm) until sublimation was evident] (2.4 g, 0.014 mol) in pentane (100 mL) were stirred at room temperature for 24 h. The resulting red solution was filtered and the filtrate was concentrated under reduced pressure to ca. 30 mL and cooled (-20°C). The white blocks were collected, dried under vacuum, and identified as $\text{LiN}(\text{SiMe}_3)_2$ by ^1H NMR and mp 70-72°C (lit.⁸ 71-72°C). Yield was 1.4 g (0.0084 mol) (58%). The pentane was removed under reduced pressure from the filtrate to yield a red, gummy residue which yielded the metallocycle on sublimation (110-120°C/ 10^{-3} mm) in 49% (1.2 g) yield as a red, waxy solid. The ^1H NMR consisted of a singlet at δ 5.86 due to Cp_2Ti , a singlet at δ 3.14 due to $\text{TiCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3$, a singlet at δ 0.11 due to $\text{TiCH}_2\text{Si}(\text{Me})_2\text{N-SiMe}_3$, and a singlet at δ -0.05 due to $\text{TiCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3$ in

an area ratio of 10:2:9:6. The ^{13}C NMR spectrum consisted of a doublet centered at δ 113.7 ($J_{\text{CH}} = 174$ Hz) due to Cp_2Ti , a triplet centered at δ 71.3 ($J_{\text{CH}} = 123$ Hz) due to TiCH_2 , a quartet centered at δ 4.42 ($J_{\text{CH}} = 117$ Hz) due to Me_3SiN , and a quartet centered at δ 2.05 ($J_{\text{CH}} = 118$ Hz) due to Me_2Si .

(b) From two molar equivalents of $\text{LiN}(\text{SiMe}_3)_2 \cdot 2 \text{OEt}_2$. The lithium bis(trimethylsilyl)amide bis(diethyl ether) complex (3.7 g, 0.012 mol) in diethyl ether (100 mL) was added to a suspension of dicyclopentadienyltitaniumdichloride (1.5 g, 0.0058 mol) in diethyl ether (60 mL). The red suspension was stirred at room temperature for 16 h, then filtered. Diethyl ether was evaporated from the filtrate and the residue was exposed to vacuum for 4 h at 50°C . The residue was extracted with pentane (3 x 40 mL) and the extract was concentrated to ca. 30 mL under reduced pressure and cooled (-20°C). The large, colorless blocks were isolated and shown to be $\text{LiN}(\text{SiMe}_3) \cdot 0.5 \text{OEt}_2$ by ^1H NMR (1.1 g, 0.0054 mol). The red mother liquor was taken to dryness and sublimation ($110\text{--}120^\circ\text{C}/10^{-3}$ mm) yielded the metallocycle in 62% (1.2 g) yield.

(c) From one molar equivalent of $\text{LiN}(\text{SiMe}_3)_2 \cdot 2 \text{OEt}_2$. Lithium bis(trimethylsilyl)amide bis(diethyl ether) (2.8 g, 0.0089 mol) in diethyl ether (60 mL) was added to dicyclopentadienyltitaniumdichloride (2.2 g, 0.0088 mol) in diethyl ether (100 mL). The suspension was stirred at room temperature (16 h), filtered, and diethyl ether was removed under reduced pressure. The residue was exposed to vacuum for 5 h (50°C), then extracted with pentane (2 x 50 mL). The combined extracts were concentrated

to ca. 10 mL and cooled (-20°C) to give $\text{LiN}(\text{SiMe}_3)_2 \cdot 0.5 \text{ OEt}_2$ (0.20 g, 0.00098 mol). The mother liquor was evaporated to dryness and sublimation afforded the metallocycle in 71% (2.1 g) yield.

In order to investigate the stoichiometry of the reaction, $\text{LiN}(\text{SiMe}_3)_2 \cdot 2 \text{ OEt}_2$ (6.4 g, 0.020 mol) and Cp_2TiCl_2 (4.8 g, 0.019 mol) were treated as in (c), above. After removal of $\text{LiN}(\text{SiMe}_3)_2 \cdot 0.5 \text{ OEt}_2$ (0.20 g, 0.00098 mol) by crystallization the red, gummy solid obtained by solvent evaporation from the mother liquor was treated as follows. (a) A small portion was examined by ^1H NMR spectroscopy. The spectrum consisted of two broad resonances at ca. δ 6 and δ 0 of approximate $w_{1/2} = 100$ Hz. This is consistent with the presence of some paramagnetic material in a largely diamagnetic sample, as previously described.² (b) The remaining red material was sublimed ($120^{\circ}\text{C}/10^{-3}$ mm) onto a cold-finger, the sublimation apparatus being connected to a trap containing pyridine (10 mL) at -196°C . When the sublimation was complete [the yield of the metallocycle was 4.4 g (68%)] the trap containing the pyridine was isolated from vacuum, warmed to room temperature, and gently agitated for 30 min. The trap was opened and the white solid was collected, washed with diethyl ether (2 x 60 mL) and dried under vacuum. The white solid (1.8 g, 0.0016 mol) was shown to be pyridinehydrochloride by mp, $81-82^{\circ}\text{C}$ (lit.⁹ 81°C).

Bis(Cyclopentadienyl)Bis[bis(trimethylsilyl)amido]-Zirconium(IV). Lithium bis(trimethylsilyl)amide bis diethyl ether (100 mL) was added to dicyclopentadienylzirconiumdichloride⁷

(2.4 g, 0.0082 mol) suspended in diethyl ether (100 mL). The pale yellow suspension was stirred at room temperature for 24 h. Diethyl ether was removed under reduced pressure and the residue was heated (60°C) under vacuum (6 h). Trituration with pentane (2 x 100 mL) followed by filtration yielded a pale yellow solution which was concentrated under reduced pressure to ca. 20 mL. Cooling (-70°C) afforded white blocks which were identified as $\text{LiN}(\text{SiMe}_3)_2 \cdot 0.5 \text{OEt}_2$ (1.3 g) by ^1H NMR spectroscopy. The mother liquor was further concentrated under reduced pressure to ca. 5 mL. Cooling (-70°C) yielded the zirconium amide which was collected and dried under vacuum. The amide was dissolved in cold (0°C) pentane (10 mL). Concentration to ca. 3 mL and cooling (-70°C) afforded the pure compound in 18% yield (0.8 g). Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{N}_2\text{Si}_4\text{Zr}$: C, 48.8; H, 8.50; N, 5.18. Found: C, 48.5; H, 8.77; N, 5.02. The ^1H NMR spectrum consisted of singlets at δ 6.11, δ 0.53, and δ 0.30 due to Cp_2Zr and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}$, in area ratio 10:18:18, respectively. The ^{13}C NMR spectrum consisted of a doublet centered at δ 115.2 ($J_{\text{CH}} = 174$ Hz) due to Cp_2Zr and a pair of quartets centered at δ 7.3 ($J_{\text{CH}} = 117$ Hz) and δ 6.7 ($J_{\text{CH}} = 117$ Hz) due to $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}$.

Preparation of $\text{Cp}_2\text{ZrCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3$. Lithium bis(trimethylsilyl)amide bis diethyl ether (2.3 g, 0.0075 mol) in diethyl ether (100 mL) was added to a suspension of dicyclopentadienylzirconiumhydrido-chloride¹⁰ (1.9 g, 0.0074 mol) in diethyl ether (50 mL). The mixture was stirred at room temperature (24 h) in the dark, and then filtered. The diethyl ether

was evaporated from the filtrate and the yellow powder was extracted with pentane (2 x 50 mL). The extract was filtered and the filtrate was concentrated under reduced pressure to ca. 10 mL and cooled (-70°C). The white blocks were collected and shown to be $\text{LiN}(\text{SiMe}_3)_2 \cdot \text{OEt}_2$ by ^1H NMR spectroscopy (0.70 g). The mother liquor was concentrated to ca. 3 mL and cooled (-70°C) to yield the waxy, pale-yellow metallocycle. The metallocycle sublimed (70-80°C/ 10^{-3} mm) as pale yellow sheets (0.5 g, 18%). Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{NSi}_2\text{Zr}$: C, 49.2; H, 6.92; N, 3.59. Found: C, 48.5; H, 6.88; N, 3.60. The ^1H NMR spectrum consisted of singlets at δ 5.93, δ 1.88, δ 0.27, and δ 0.17 due to Cp_2Zr , ZrCH_2 , $\text{ZrCH}_2\text{Si}(\text{Me})_2$, and $\overline{\text{ZrCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3}$ in area ratio of 10:2:6:9, respectively. The ^{13}C NMR spectrum consisted of a doublet centered at δ 111.6 ($J_{\text{CH}} = 171$ Hz), a triplet centered at δ 42.0 ($J_{\text{CH}} = 128$ Hz), and a pair of quartets centered at δ 3.50 ($J_{\text{CH}} = 119$ Hz) and δ 4.60 ($J_{\text{CH}} = 117$ Hz) due to Cp_2Zr , ZrCH_2 , $\text{ZrCH}_2\text{SiMe}_2$, and $\overline{\text{ZrCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3}$, respectively.

Neither metallocycle reacts with deuterium (20 atm) at room temperature in pentane.

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