

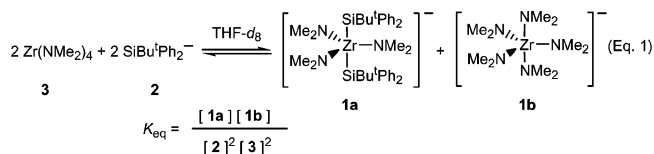
Unusual Equilibria Involving Group 4 Amides, Silyl Complexes, and Silyl Anions via Ligand Exchange Reactions

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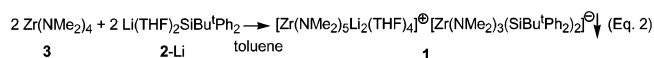
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Nucleophilic substitution reactions have been one of the primary methods to prepare transition-metal silyl complexes.¹ In many such reactions, replacement of halide (X^-) ligands by silyl anions with the precipitation of MX ($M^+ =$ alkali metal) is used to yield metal-silyl bonds, and the reactions are usually *not* reversible.¹ Cleavage of metal-silyl bonds by the attack of nucleophiles has been reported in, e.g., the reactions of $(OC)_4Co-SiPh_3$ with $LiAlH_4$, $MeLi$, and $RMgBr$, affording $HSiPh_3$, “ $LiSiPh_3$ ”, and “ $BrMg-SiPh_3$ ”, respectively.² “ $LiSiPh_3$ ” and “ $BrMg-SiPh_3$ ” were believed to be the intermediates, and they react with H_2O to give $HSiPh_3$. Reversible exchanges of ligands^{3,4} in transition-metal complexes are known, and equilibria of some reactions have been studied. There are, however, few reported reversible exchange reactions and equilibria involving silyl ligands in transition-metal complexes.^{1,3,5} In our studies of metal silyl complexes,⁶ we observed substitutions of amide ligands in $M(NMe_2)_4$ ^{7,8} and $M(NMe_2)_3[N(SiMe_3)_2]$ ($M = Zr, Hf$) by silyl anions to give disilyl and silyl complexes, and $M(NMe_2)_5^-$ and $N-(SiMe_3)_2^-$, respectively. These reactions are reversible, and nucleophilic amides attack the $M-SiR_3$ bonds in the reverse reactions, leading to ligand exchange equilibria such as that in eq 1. Such substitutions of amide ligands by silyl anions and the exchange equilibria, to our knowledge, have not been reported. These exchange reactions and our thermodynamic studies of the equilibria are reported here.



$Zr(NMe_2)_4$ (**3**) reacts with $Li(THF)_2SiBu^tPh_2$ (**2-Li**)⁹ in *toluene*, affording an ionic compound $[Zr(NMe_2)_5Li_2(THF)_4]^+ [Zr(NMe_2)_3-(SiBu^tPh_2)_2]^-$ (**1**) as a solid precipitate (eq 2).¹⁰ In this reaction, substitution of an amide ligand in **3** by silyl anion **2** leads to the formation of disilyl anion **1a**. The amide anion that is replaced apparently reacts with **3** to give the pentaamide cation $Zr(NMe_2)_5Li_2(THF)_4^+$ (**1b-Li**⁺, Figure 1). Chisholm and co-workers have reported the formation of hexaamide $Zr(NMe_2)_6Li_2(THF)_2$ (**4-Li**) from the addition of $LiNMe_2$ to **3**.^{8a} The substitution of an amide ligand by a silyl ligand in this reaction was unexpected. Substitution of amide ligands by alkoxide ligands has been reported.¹¹ To our knowledge, this is the first known case of a replacement of an amide ligand by a silyl anion.¹ Similar to the structure of $[Zr(NMe_2)_4]_2$,^{8a} **1b-Li**⁺ exhibits a distorted trigonal bipyramidal configuration about $Zr(2)$ atom with N(4) and N(4A) atoms in the axial positions.¹⁰



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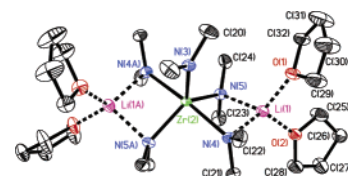


Figure 1. A molecular drawing of **1b-Li**⁺ shown with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): $Zr(2)-N(4)$ 2.243(2), $N(4)-Zr(2)-N(4A)$ 172.54(11).¹⁰ The structure of the anion (**1a**)¹⁰ is similar to that reported earlier.^{6c}

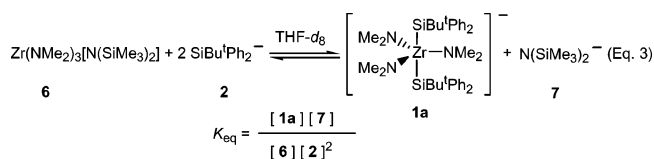
When crystals of **1** were dissolved in $THF-d_8$, the reverse reaction in eq 1 was observed in ¹H and ¹³C NMR spectra of the solution, yielding **3** and $SiBu^tPh_2^-$ (**2**).¹² In fact, $Zr(NMe_2)_3(SiBu^tPh_2)_2^-$ (**1a**), $Zr(NMe_2)_5^-$ (**1b**), **3**, and **2** in the solution of **1** were found to be in an unusual equilibrium in eq 1. This equilibrium was also observed when **2** and **3** were mixed in $THF-d_8$.¹⁰ In ¹H EXSY spectrum¹⁰ of a mixture of **2** and **3** at 32 °C, strong cross-peaks were observed among three $-NMe_2$ peaks and between two $-SiBu^tPh_2$ peaks, indicating an exchange process for the complexes in eq 1. NMR studies of **4-Li**₂ by Chisholm and co-workers suggest that $LiNMe_2$ dissociates from **4-Li**₂.^{8a} Dissociation of $Zr(NMe_2)_3(SiBu^tPh_2)_2^-$ (**1a**) to give **2** and $Zr(NMe_2)_3(SiBu^tPh_2)$ ¹³ is also known.^{6c} Such dissociations may be present in the reactions in eq 1. NMe_2^- dissociated from $Zr(NMe_2)_5^-$ (**1b**) subsequently attacks the $Zr-Si$ bonds in **1a** or in $Zr(NMe_2)_3(SiBu^tPh_2)$ to give $Zr(NMe_2)_4$ (**3**).

Variable-temperature ¹H NMR spectroscopy between 243 and 308 K was used to study this equilibrium. The equilibrium constants K_{eq} range from 242(18) at 243 K to 6.8(0.5) at 308 K,¹⁰ indicating that the forward reaction to give disilyl **1a** and pentaamide **1b** is favored, and that decreasing the temperature shifts the equilibrium toward them. A plot of $\ln K_{eq}$ vs $1/T$ by the van't Hoff equation¹⁴ (Figure 2a) gives the thermodynamic parameters of the equilibrium: $\Delta H^\circ = -8.3(0.2)$ kcal/mol, $\Delta S^\circ = -23.3(0.9)$ eu, and $\Delta G^\circ_{298K} = -1.4(0.5)$ kcal/mol at 298 K.¹⁰ The forward reaction is exothermic, and the entropy change $\Delta S^\circ = -23.3(0.9)$ eu reflects the fact that, in the forward reaction, 2 equiv of **3** and **2** each yield 1 equiv of **1a** and **1b**. The enthalpy change outweighs the entropy change in the forward reaction to give $\Delta G^\circ_{298K} = -1.4(0.5)$ kcal/mol in favor of **1a** and **1b**.

Freezing point depression studies of **1** in benzene suggest that dissolving 1 equiv of $[Zr(NMe_2)_5Li_2(THF)_4]^+ [Zr(NMe_2)_3-(SiBu^tPh_2)_2]^-$ (**1**) in benzene generates ca. 3 equiv of neutral and/or ionic species.^{10,15} This is consistent with the fact that, in solution, **1** is involved in an equilibrium that gives several additional species including **1a**, **1b**, **3**, $Li(THF)_n^+$, **2**, and **4**. The reaction between $Hf(NMe_2)_4$ (**5**) and **2-Li** gives an equilibrium similar to that in eq 1. Overlaps of the ¹H NMR resonances of the $-NMe_2$ ligands in both $THF-d_8$ and *toluene-d*₈ over a large temperature range prevent quantitative studies of the equilibrium.

$Zr(NMe_2)_3[N(SiMe_3)_2]$ (**6**) was prepared from the reaction of $Zr(NMe_2)_3Cl$ with $LiN(SiMe_3)_2$ (**7-Li**).¹⁰ When $LiSiBu^tPh_2$ (**2-Li**) was

added to $\text{Zr}(\text{NMe}_2)_3[\text{N}(\text{SiMe}_3)_2]$ (**6**) in $\text{THF-}d_8$, the equilibrium in eq 3 was observed. In the forward reaction in this equilibrium, the silyl anion **2** selectively replaces the $-\text{N}(\text{SiMe}_3)_2$ ligand in **6**, affording exclusively $\text{Zr}(\text{NMe}_2)_3(\text{SiBu}^t\text{Ph}_2)_2^-$ (**1a**) and $\text{N}(\text{SiMe}_3)_2^-$ (**7**). No substitution of the $-\text{NMe}_2$ ligand in $\text{Zr}(\text{NMe}_2)_3[\text{N}(\text{SiMe}_3)_2]$ (**6**) was observed. In the reverse reaction, amide anion $\text{N}(\text{SiMe}_3)_2^-$ replaces the silyl ligands in **1a** or $\text{Zr}(\text{NMe}_2)_3(\text{SiBu}^t\text{Ph}_2)_2^-$, leading to the equilibrium in eq 3. It is interesting to note that, in the reverse reaction in eq 3, the amide anion $\text{N}(\text{SiMe}_3)_2^-$ (**7**) in $\text{LiN}(\text{SiMe}_3)_2$ did not replace the $-\text{NMe}_2$ ligand in $\text{Zr}(\text{NMe}_2)_3(\text{SiBu}^t\text{Ph}_2)_2^-$ (**1a**). It is not clear why the substitutions in the forward and reverse reactions are selective. In ^1H EXSY spectrum¹⁰ of a mixture of **2** and **6** at 32 °C, cross-peaks were observed between $-\text{NMe}_2$, $-\text{SiBu}^t\text{-Ph}_2$, and $-\text{N}(\text{SiMe}_3)_2$ peaks, respectively, indicating an exchange process for the complexes in eq 3. Thermodynamic studies of this equilibrium by ^1H NMR spectroscopy (223–303 K) were conducted. The equilibrium constants K_{eq} ¹⁰ range from 10.0(0.2) at 223 K to 3.77(0.09) at 303 K. As in eq 1, the forward reaction in eq 3, the selective substitution of the amide $-\text{N}(\text{SiMe}_3)_2$ ligand in **6** by the silyl anion $\text{SiBu}^t\text{Ph}_2^-$, is slightly favored, and lowering the temperature shifts the equilibrium in eq 3 to the right. The plot of $\ln K_{\text{eq}}$ vs $1/T$ (Figure 2b) gives the following thermodynamic parameters for this equilibrium: $\Delta H^\circ = -1.61(0.12)$ kcal/mol, $\Delta S^\circ = -2.6(0.5)$ eu, and $\Delta G^\circ_{298\text{K}} = -0.8(0.3)$ kcal/mol. The forward reaction is exothermic, and the enthalpy change outweighs the entropy change, making the substitution of $-\text{N}(\text{SiMe}_3)_2$ ligand in **6** by $\text{SiBu}^t\text{Ph}_2^-$ anion to give **7** and **1a** slightly favored.



Equilibria were also observed in the reactions of $\text{M}(\text{NMe}_2)_4$ ($\text{M} = \text{Zr}$, **3**; Hf , **5**) and $\text{M}(\text{NMe}_2)_3[\text{N}(\text{SiMe}_3)_2]$ ($\text{M} = \text{Zr}$, **6**; Hf , **8**) with $\text{Li}(\text{THF})_2\text{Si}(\text{SiMe}_3)_3$ (**9-Li**),¹⁶ yielding the monosilyl complexes $\text{M}(\text{NMe}_2)_3[\text{Si}(\text{SiMe}_3)_3]$ ($\text{M} = \text{Zr}$, **10**; Hf , **11**).¹² The bulkiness of

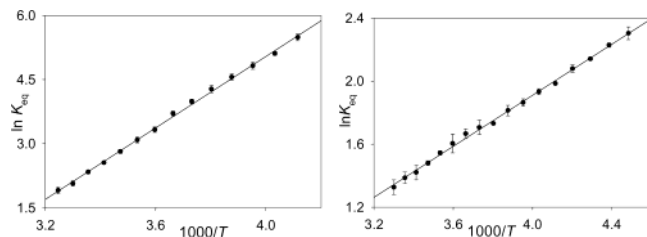
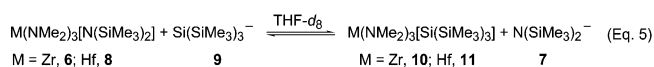
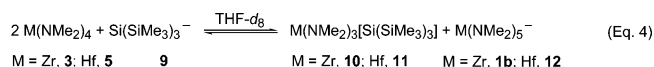


Figure 2. $\ln K_{\text{eq}}$ vs $1/T$ plots of the equilibria: (a) eq 1 and (b) eq 3.

the $-\text{Si}(\text{SiMe}_3)_3$ ligand perhaps prevents the formation of disilyl complexes. In contrast to eq 1, the reverse reactions in eq 4 yielding amides $\text{M}(\text{NMe}_2)_4$ and silyl anion $\text{Si}(\text{SiMe}_3)_3^-$ (**9**) dominate the equilibria. For example, in $\text{THF-}d_8$, $K_{\text{eq}} = 0.0045(0.0009)$ and $\Delta G^\circ_{298\text{K}} = 3.20(0.13)$ kcal/mol for the equilibrium involving **3** in eq 4, and $K_{\text{eq}} = 0.0111(0.0009)$ and $\Delta G^\circ_{298\text{K}} = 2.66(0.06)$ kcal/mol for the equilibrium in eq 5 involving **6**. These data indicate that the formation of silyl complexes $\text{M}(\text{NMe}_2)_3[\text{Si}(\text{SiMe}_3)_3]$ by eqs 4 and 5 is not thermodynamically favored.



Cooling the equilibrium mixtures in eqs 4 and 5 to -36 °C, however, gives crystals of $\text{M}(\text{NMe}_2)_3[\text{Si}(\text{SiMe}_3)_3]$ ($\text{M} = \text{Zr}$, **10**; Hf , **11**), thus shifting the equilibria to the right side.

Studies are underway to probe the scope and kinetics of such reversible amide-silyl substitutions.

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Supporting Information Available: Details of the experiments and calculations of ΔH° and ΔS° , a list of K_{eq} , EXSY spectra, and crystallographic data for **1** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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