d⁰ Bis(silyl) Complexes Free of Anionic π-Ligands: Syntheses, Structures, and a Novel Exchange between Silyl Ligands and Silyl Anions

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Early-transition-metal silyl chemistry has drawn increasing attention in the past decade.[1] The studies in this area have revealed that d⁰ metal silyl bonds are very reactive, and can undergo insertion reactions[2] and catalyze the dehydropolymerization of organosilanes.[1,3] However, most d⁰ metal silyl complexes contain cyclopentadienyl (Cp) or analogous anionic π-ligands;[1] few Cp-free d⁰ metal silyl complexes have been reported.[2d,4,5] We have recently prepared and characterized a new class of Cp-free d⁰ silyl alkyl, alkylidene, alkylidyne, and amide or related complexes.[4] However, attempts to synthesize Cp-free bis(silyl) complexes "(RCH₂)₂M[Si(SiMe₃)₃]₂" [R = CMe₃, SiMe₃; M = Ti, Zr] and "(Me₃SiO)₂Zr(SiR₃)₂" [SiR₃ = Si(SiMe₃)₃, SiPh₂Buᵗ][4f] have been unsuccessful; reductive elimination of organodisilanes were often observed. Although Cp-free d⁰ metal polyalkyl and peralkyl complexes such as (RCH₂)ₙM (n = 4, M = Ti triad; n = 5, M = Ta; n = 6, M = W) have been known for a long time,[6] no d⁰ silyl analogues (polysilyl and persilyl complexes) have been isolated.[7-9] An early reported tetrasilyl complex Ti-(SiPh₃)₄[7] was found later to be Ti(OSiPh₃)₄.[8] To date only a few

Scheme 1

3 (R₃ = Ph₂Buᵗ) Li(THF)₄⁺ salt, **1**
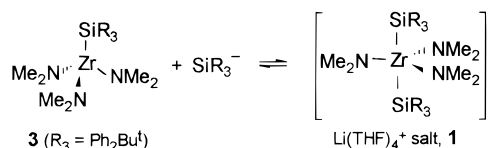
Cp-containing d⁰ bis(silyl) complexes Cp₂M(SiR₃)₂ have been reported.[10] Formation of Cp-free d⁰ metal polysilyl and persilyl complexes remains a considerable synthetic challenge. In this paper, we report the syntheses and characterization of, to our knowledge, the first Cp-free d⁰ bis(silyl) complexes [Li(THF)₄]-[(Me₂N)₃Zr(SiPh₂Buᵗ)₂] (**1**) and (Me₂N)₃Ta[Si(SiMe₃)₃]₂ (**2**) as well as the study of a novel silyl exchange between (Me₂N)₃Zr–SiR₃ and SiR′₃⁻ anions.

The anionic bis(silyl) complex **1** was prepared by the addition of Li(THF)₃SiBuᵗPh₂[11] to (Me₂N)₃Zr(SiPh₂Buᵗ) (**3**)[12] in toluene from which **1** crystallizes at room temperature (Scheme 1).[13] **1** is thermally unstable in solution but may be stored indefinitely as a solid at −20 °C. There is a sharp NMe₂ signal in ¹H and ¹³C{¹H} NMR spectra of **1** at room temperature. However, both ¹H and ¹³C{¹H} NMR peaks of the Buᵗ groups in **1** are broad at room temperature. Upon cooling to 0 °C, the ¹H and ¹³C{¹H} NMR resonances for the Buᵗ groups of SiPh₂Buᵗ ligands in **1** resolve into two separate broad signals which are close to those of (Me₂N)₃Zr(SiPh₂Buᵗ) (**3**) and Li(THF)₃SiPh₂Buᵗ. This indicates that the SiPh₂Buᵗ ligand in **3** is in rapid exchange with Li-(THF)₃SiPh₂Buᵗ in solution at room temperature (Scheme 1). The dynamic NMR of this exchange reaction has been studied; the signals of the two SiPh₂Buᵗ ligands were found to coalesce at 20 °C. The free energy of activation ΔG‡ was estimated to be 14.1-(0.5) kcal/mol for the exchange at the coalescence temperature.[13] Chisholm and co-workers have reported similar equilibria involving M(NMe₂)₄ (M = Zr, Mo), LiNMe₂ and M(NMe₂)₆Li₂(THF)₂ [M(NMe₂)₄ + 2 LiNMe₂ ⇌ M(NMe₂)₆Li₂(THF)₂].[14]

The molecular structure of **1**, determined by X-ray crystallography, shows that **1** consists of a discrete cation and anion pair, and an ORTEP drawing of the bis(silyl) anion is shown in Figure 1.[13] In the bis(silyl) anion, the Zr atom is coordinated by three Me₂N and two SiPh₂Buᵗ ligands to form a trigonal bipyramidal (TBP) geometry with the silyl ligands occupying axial positions and nearly staggered with respect to the amido ligands. This unusual anionic bis(silyl) complex represents a rare example of a pentacoordinated d⁰ Zr(IV) complex. Another reported penta-coordinated homoleptic anionic complex [Li(dme)₃][Zr(SCMe₃)₅] (dme = dimethoxyethane) adopts a distorted TBP structure.[15] In

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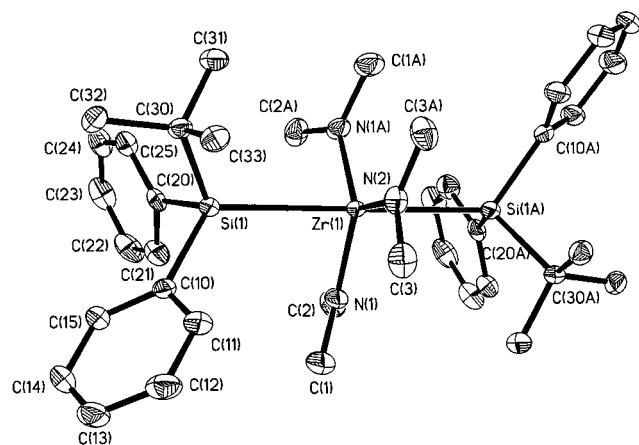
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Figure 1. ORTEP drawing of the bis(silyl) anion in **1** showing 35% probability ellipsoids. Selected bond distances (Å) and angles (deg): Zr-(1)−Si(1) 2.9331(14), Zr(1)−N(1) 2.039(3), Zr(1)−N(2) 2.063(5), Si-(1)−Zr(1)-Si(1A) 177.93(5), N(1)−Zr(1)−N(2) 120.88(12), N(1)−Zr(1)−N(1A) 118.2(2).

comparison, the central MN_6 moieties in hexacoordinated $M(NMe_2)_6Li_2(THF)_2$ (M = Zr, Mo), adducts between $M(NMe_2)_4$ and $LiNMe_2$ in THF, approach an octahedral geometry.[14] The trans angle Si−Zr−Si [177.93(5)°] in **1** is near 180°. The Zr−N bond distances of 2.039(3) and 2.063(5) are close to those found in **3** [2.021(4) Å] and $(Me_2N)_3Zr−Si(SiMe_3)_3$ [**4**, 2.018(7) Å].[12] The Zr−Si bond length of 2.9331(14) Å in **1** represents, to our knowledge, the longest reported Zr−Si bond.[16,17] Other known Zr−Si bond lengths are in the range 2.721(2)−2.860(2) Å.[16,17] This is perhaps mainly the result of the strong trans-influence of silyl groups in **1**. For late-transition-metal complexes, silyl ligands are among the ligands with the strongest trans-influence.[18] Steric factors might play a role in the Zr−Si bond elongation in **1** as well, since the Zr−N bonds in **1** are slightly longer than other known Zr−N bonds.

The NMR evidence of the silyl exchange between $(Me_2N)_3$-$Zr(SiPh_2Bu^t)$ (**3**) and $Li(THF)_3SiBu^tPh_2$ through the pentacoordinated intermediate **1** prompted us to further study this exchange. When $Li(THF)_3SiBu^tPh_2$ was added to a solution of $(Me_2N)_3Zr−$$Si(SiMe_3)_3$ (**4**), **3** and $Li(THF)_3Si(SiMe_3)_3$ were observed in the reaction solution (Scheme 2). K_{eq} at 20 °C was found to be 82.83-(2) in favor of **3** and $Li(THF)_3Si(SiMe_3)_3$. A linear fit of ln K_{eq} vs $1/T$ gave $\Delta H° = −4.6(5)$ kcal/mol and $\Delta S° = −7(2)$ eu between −10(1) and 20(1) °C.[13] It is interesting to note that the preference for **3** is in contrast to the relative stabilities of $(RCH_2)_3$-$Zr−Si(SiMe_3)_3$ and "$(RCH_2)_3Zr−SiBu^tPh_2$"; the former is stable to sublimation at 50 °C, and attempts to prepare the latter have to date been unsuccessful.

Although many mechanistic studies have been performed on ligand-exchange reactions of late-transition-metal complexes,[19]

Scheme 2

$R_3 = Ph_2Bu^t$, $R'_3 = (SiMe_3)_3$; $K_{eq} = 82.83(0.02)$ at 20 °C
$\Delta H° = −4.6(0.5)$ kcal/mol, $\Delta S° = −7(2)$ eu

Scheme 3

(i) $+Li(THF)_3SiR'_3$ (R' = $SiMe_3$), $-LiCl$

there are few such studies involving a d^0 metal center. The silyl exchange as shown in Scheme 2 likely proceeds through an associative ligand substitution mechanism involving a pentaco-ordinated anionic bis(silyl) intermediate **5**. Although **5** was not directly observed, the observation and isolation of its analogue **1** in the silyl exchange shown in Scheme 1 strongly support the associative mechanism in Scheme 2. **1**, to our knowledge, is one of the rare examples of an isolated intermediate in associative (or S_N2) ligand-substitution reactions.

The tantalum bis(silyl) complex $(Me_2N)_3Ta[Si(SiMe_3)_3]_2$ (**2**), a neutral analogue of **1**, was prepared by the reaction shown in Scheme 3.[13,20] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** display only one set of resonances for the silyl and amide ligands between −60 and 27 °C. This suggests that **2** adopts a trigonal bipyramidal structure similar to that of **1** with two $Si(SiMe_3)_3$ ligands in axial positions (Scheme 3). **2** is thermally stable at room temperature under nitrogen, but crystals of **2** were found to decay rapidly under X-ray irradiation, precluding attempts to confirm the structure of **2** by X-ray crystallography. In the preparation of **2** by the reaction shown in Scheme 3, a monosilyl intermediate $(Me_2N)_3Ta[Si-(SiMe_3)_3]Cl$ (**6**) was observed and isolated.[13] The structure of **6**,[13] as determined by X-ray crystallography, shows that the complex adopts a trigonal bipyramidal geometry with an amide and the chloride ligand in axial positions. There are two NMe_2 resonances in a 2:1 ratio in the ^1H NMR spectra of **6** at 23 °C, indicating that the equatorial and axial amide ligands either do not exchange or exchange slowly on NMR time scale.[13]

Supporting Information Available: Details of experiments and calculations of $\Delta H°$ and $\Delta S°$, a table of K_{eq}, ORTEPs of **1** and **6**, and a complete list of the crystallographic data for **1** and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.
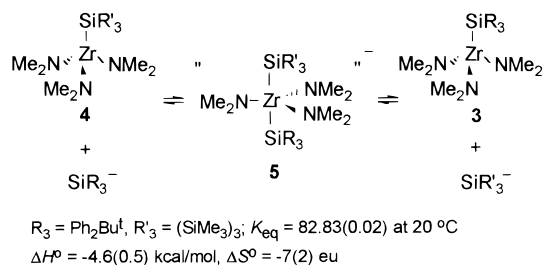
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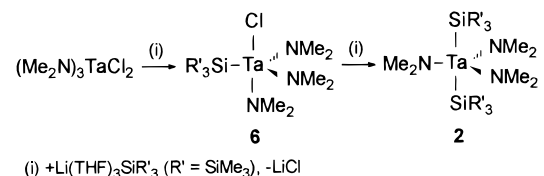(18) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

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