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Article

A Kinetic Study of the Silyl Substitution in Tantalum Amide Silyl Complex $(Me_2N)_3Ta[Si(SiMe_3)_3]_2$

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Kinetic studies have been performed for the substitution of the first silyl ligand in $(Me_2N)_3Ta[Si(SiMe_3)_3]_2$ (**1**) by $Li(THF)_3SiBu^tPh_2$ at 233 K (THF = tetrahydrofuran). In the presence of excess $Li(THF)_3SiBu^tPh_2$, these studies reveal that the reaction likely follows a dissociative pathway. THF, a polar solvent, is found to promote the substitution, and the order of the reaction with respect to THF is 1.7(0.3).

Substitution is a fundamental reaction of organometallic complexes,[1] and it has played an important role in the formation of metal complexes.[2−6] The substitution of ligands by silyl anions SiR_3^- is a common synthetic pathway to yield metal silyl complexes. There have been relatively few studies of kinetics and mechanism in the substitution reactions involving silyl ligands.[2−6] We recently found that the silyl ligand in tetracoordinated $(Me_2N)_3Zr{-}Si(SiMe_3)_3$ undergoes a reversible exchange with $SiBu^tPh_2^-$, probably through a pentacoordinated, bis(silyl) intermediate $\{[(Me_2N)_3Zr(SiBu^tPh_2)[(SiMe_3)_3]\}^-$, to reach the equilibrium in eq 1.[6] In an analogous exchange involving $(Me_2N)_3Zr(SiBu^tPh_2)$ and $SiBu^tPh_2^-$ (eq 2), an unusual bis(silyl) intermediate *trans*-$(Me_2N)_3Zr(SiBu^tPh_2)_2^-$ was isolated and structurally characterized.

$$(Me_2N)_3Zr\text{-}Si(SiMe_3)_3 + SiBu^tPh_2^{\ominus} \rightleftharpoons (Me_2N)_3Zr\text{-}SiBu^tPh_2 + Si(SiMe_3)_3^{\ominus} \qquad (1)$$

$$\Delta H^\circ = -4.6(0.5)\ \text{kcal/mol and}\ \Delta S^\circ = -7(2)\ \text{eu}$$

In comparison, the substitution of the silyl ligands in pentacoordinated $(Me_2N)_3Ta[Si(SiMe_3)_3]_2$ (**1**) by $SiBu^tPh_2^-$ at 23 °C (Scheme 1) was found to be irreversible.[6b] The two $-Si(SiMe_3)_3$ ligands in **1** are replaced sequentially by $SiBu^tPh_2^-$ to give $(Me_2N)_3Ta(SiBu^tPh_2)[Si(SiMe_3)_3]$ (**2**) and then $(Me_2N)_3Ta(SiBu^tPh_2)_2$ (**3**) (eqs 3−4).[6b,7] Complex **3** is, however, inert to the exchange with $Si(SiMe_3)_3^-$.

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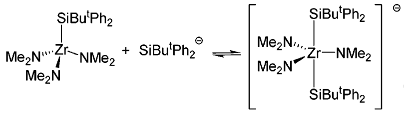
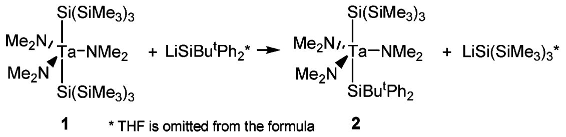

(2)

$\Delta G^{\neq}_{293\ \mathrm{K}} = 14.1(0.5)$ kcal/mol

We were interested in whether the substitution of a silyl ligand in the pentacoordinated **1** by $SiBu^tPh_2^-$ followed the dissociative or associative mechanism. The two, consecutive reactions in eqs 3−4 were both silyl substitutions involving an amide silyl complex **1** or **2**. They were expected to follow similar mechanistic pathways, and we thus decided to investigate the first substitution in eq 3. This reaction was found to follow the dissociative mechanism. Tetrahydrofuran (THF) in mixed THF−toluene-d_8 solvents promoted the substitution. Our studies are reported here.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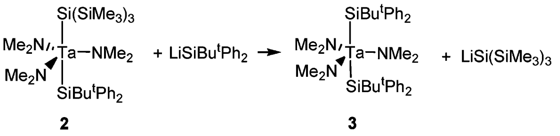
(4)

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere. THF was purified by distillation from K/benzophenone ketyl. Toluene-d_8 was dried over molecular sieves. $(Me_2N)_3TaCl_2$,[8] $Li(THF)_3SiBu^tPh_2$,[9a] and $Li(THF)_3Si(SiMe_3)_3$[9b] were prepared according to the literature procedures. ^{1}H NMR spectra were recorded on a Bruker AMX-400 spectrometer and referenced to toluene-d_8. The NMR spectrometer was precooled to 233(1) K. Values of k_{obs} were obtained from at least two separate experiments for a concentration of THF, and their averages are listed. The order n and its uncertainty were calculated from an unweighted nonlinear least-squares procedure and the error propagation formulas in eq 5, respectively.[10]

$$(\sigma n)^2 = \frac{2(\Delta \ln k)^2}{(\Delta \ln C_{\mathrm{THF}})^4}\left(\frac{\sigma C_{\mathrm{THF}}}{C_{\mathrm{THF}}}\right)^2 + \frac{2}{(\Delta \ln C_{\mathrm{THF}})^2}\left(\frac{\sigma k}{k}\right)^2$$

$$\Delta \ln C_{\mathrm{THF}} = (\ln C_{\mathrm{THF_{max}}} - \ln C_{\mathrm{THF_{min}}}) \qquad (5)$$

1 was prepared in situ at 23 °C in a Young NMR tube from $(Me_2N)_3TaCl_2$ (5.0 mg, 0.013 mmol) and $Li(THF)_3Si(SiMe_3)_3$ (16.4 mg, 0.0349 mmol) in toluene-d_8, using 4,4′-dimethylbiphenyl (4.0 mg) as an internal standard (volume = 1.07 mL). A small piece of filter paper was placed on the top of the NMR tube in a glovebox. $Li(THF)_3SiBu^tPh_2$ (50.0, 60.0, 80.0, 100.0, or 120.0 mg; 0.108, 0.130, 0.173, 0.216, or 0.260 mmol) was then put on the paper and separated from the solution prior to the cooling of the solution. After the solution was cooled at 203 K for 10 min, the NMR tube was flipped over to mix the solution and $Li(THF)_3SiBu^tPh_2$ and then immediately inserted into the NMR spectrometer. Values of $C_1/C_{1(0)}$ and C_{THF} (0.61−0.74 M) were measured through the integration of their ^{1}H NMR resonances ($-NMe_2$ at 3.20 ppm for **1** and $-CH_2-$ at 1.34−1.35 ppm for THF). Values of k_{obs} were derived from the fitting of the data by first-order kinetics (rate = $k_{obs}C_1$; $k_{obs}' = k_{obs}/C_{\mathrm{THF}}^{1.7}$) and are given in Table 1. Similar studies were performed with different C_{THF}. C_{THF} and the rate constants ($k_{obs} = k_1C_{\mathrm{THF}}^n$) are listed in Table 2.

Results and Discussion

Kinetic Studies of the First Silyl Substitution in 1. Unlike **1**, the intermediate $(Me_2N)_3Ta(SiBu^tPh_2)[Si(SiMe_3)_3]$ (**2**) is thermally unstable[6b] and has not been isolated. In addition, the change in the concentration of **2** during the reaction between **1** and $Li(THF)_3SiBu^tPh_2$ at 233 K was below the detection limit in ^{1}H NMR spectra.[11] In addition, the two steps in the consecutive substitutions in eqs 3 and 4 are similar. The current work thus focused on the first substitution (**1** → **2**, eq 3), and studies of the second substitution (**2** → **3**, eq 4) were not conducted.

Two possible reaction pathways in Scheme 1 have been considered for eq 3. The first pathway (Path I), a dissociative process, involves $Si(SiMe_3)_3^-$ dissociation from **1** to give a tetracoordinated intermediate (**A**), followed by the addition of $SiBu^tPh_2^-$. The second pathway (Path II), an associative process, involves the addition of $SiBu^tPh_2^-$ to **1** to give a hexacoordinated intermediate (**B**), followed by $Si(SiMe_3)_3^-$ dissociation. Each substitution in eqs 3−4 consumes 1 equiv of $Li(THF)_3SiBu^tPh_2$. To minimize the effect of eq 4 on eq 3, excess $Li(THF)_3SiBu^tPh_2$ (8- to 20-fold) was used.

If the *dissociative* mechanism in Path I (Scheme 1) is operative, the kinetic law for the **1** → **2** conversion through the steady-state approximation is given in eq 6.[1g]

$$-\frac{\mathrm{d}C_1}{\mathrm{d}t} = \frac{k_1k_2C_{\mathrm{LiSiBu^tPh_2}}C_{\mathrm{THF}}{}^n}{k_{-1}C_{\mathrm{LiSi(SiMe_3)_3}} + k_2C_{\mathrm{LiSiBu^tPh_2}}}C_1 = k_{obs}C_1 \qquad (6a)$$

$$k_{obs} = \frac{k_1k_2C_{\mathrm{LiSiBu^tPh_2}}C_{\mathrm{THF}}{}^n}{k_{-1}C_{\mathrm{LiSi(SiMe_3)_3}} + k_2C_{\mathrm{LiSiBu^tPh_2}}} \qquad (6b)$$

The effect of C_{THF} will be discussed below. Let $k_{obs}' = k_{obs}/$

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(5) (a) Xue, Z.; Li, L.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169. (b) McAlexander, L. H.; Hung, M.; Li, L.; Diminnie, J. B.; Xue, Z.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 5231. (c) Diminnie, J. B.; Hall, H. D.; Xue, Z. *Chem. Commun.* **1996**, 2383. (d) Li, L.; Diminnie, J. B.; Liu, X.; Pollitte, J. L.; Xue, Z. *Organometallics* **1996**, *15*, 3520. (e) Diminnie, J. B.; Xue, Z. *J. Am. Chem. Soc.* **1997**, *119*, 12657. (f) Wu, Z.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 2917. (g) Wu, Z.; McAlexander, L. H.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 4853.

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(7) See the Supporting Information for ^{1}H NMR spectra of the reaction mixture.

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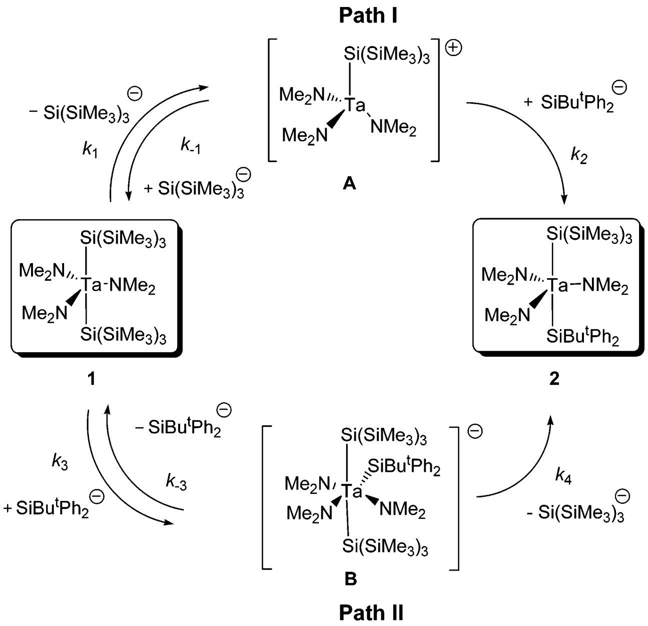
(11) No detectable change in the concentration of **2** was observed by ^{1}H NMR over the course (124 min) of one current kinetic study of the reaction between **1** and 12 equiv of $Li(THF)_3SiBu^tPh_2$ at 233 K.

(12) $C_{\mathrm{LiSi(SiMe_3)_3}}(\mathrm{av}) = (0.0089\ \mathrm{mmol} + 0.0349\ \mathrm{mmol})/(1.07\ \mathrm{mL} \times 2) = 0.0205$ M.

Scheme 1. Possible Mechanic Pathways in the Conversion of **1** to **2**



$C_{THF}{}^n$, and eq 6b is thus

$$k_{obs}' = \frac{k_1 k_2 C_{LiSiBu^tPh_2}}{k_{-1}C_{LiSi(SiMe_3)_3} + k_2 C_{LiSiBu^tPh_2}} \qquad (7a)$$

or

$$\frac{1}{k_{obs}'} = \frac{k_{-1}C_{LiSi(SiMe_3)_3}}{k_1 k_2 C_{LiSiBu^tPh_2}} + \frac{1}{k_1} \qquad (7b)$$

In other words, a plot of $1/k_{obs}'$ vs $C_{LiSi(SiMe_3)_3}/C_{LiSiBu^tPh_2}$ would be linear, yielding values of k_1 and the ratio k_{-1}/k_2 in the dissociative Path I.

If the reaction proceeds by the *associative* pathway in Path II, a steady-state approach gives eq 8a.

$$-dC_1/dt = \frac{k_3 k_4}{k_{-3} + k_4} C_{THF}{}^n C_{LiSiBu^tPh_2} C_1 \qquad (8a)$$

When the forward reaction for **B** is faster than its reverse reaction (i.e., $k_4 \gg k_{-3}$) and $Li(THF)_3SiBu^tPh_2$ is in much excess, k_{obs}'' is a function of $C_{LiSiBu^tPh_2}$ (parts b and c of eq 8)

$$-dC_1/dt = k_3 C_{THF}{}^n C_{LiSiBu^tPh_2} C_1 = k_{obs}'' C_1 \qquad (8b)$$

$$k_{obs}'' = k_3 C_{THF}{}^n C_{LiSiBu^tPh_2} \qquad (8c)$$

The substitution with excess $Li(THF)_3SiBu^tPh_2$ in mixed THF−toluene-d_8 was completed in a few minutes at room temperature. Current kinetic studies were thus performed at 233 K. Even at 233 K, the reaction was found to be fast, and the fine control of both temperature and time of mixing **1** with $Li(THF)_3SiBu^tPh_2$ is important to obtaining accurate kinetic data. In addition, C_{THF} needs to be controlled, as it was found to affect the rate. The kinetics of this silyl substitution was monitored by the disappearance of **1** in ^{1}H NMR spectra.[7] Under these conditions, the disappearance of **1** was found to follow the kinetic law in eq 7. A plot of k_{obs}' vs $C_{LiSi(SiMe_3)_3}(av)/C_{LiSiBu^tPh_2}(av)$ (Figure 1) is linear, as expected for the dissociative Path I.

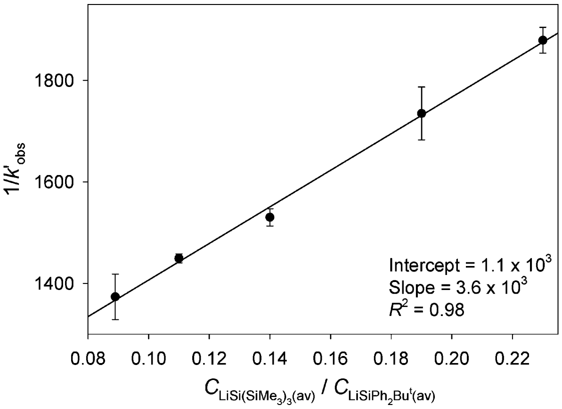


Figure 1. Kinetic plot of the **1** → **2** conversion.

Table 1. Observed Rate Constants for the **1** → **2** Conversion

C_{THF} (M)	$k_{obs} \times 10^4$ (s^{-1})	$k_{obs}' \times 10^4$ (s^{-1})	$C_{LiSiBu^tPh(0)}$ (M)	$C_{LiSi(SiMe_3)_3}(av)/C_{LiSiBu^tPh_2}(av)^{12}$
0.67	2.7	5.4	0.101	0.23
0.68	2.7	5.3	0.101	0.23
0.72	3.3	5.6	0.121	0.19
0.72	3.4	5.9	0.121	0.19
0.72	3.7	6.5	0.162	0.14
0.74	3.9	6.6	0.162	0.14
0.67	3.5	6.9	0.202	0.11
0.70	3.8	6.9	0.202	0.11
0.67	3.6	7.1	0.243	0.089
0.61	3.2	7.5	0.243	0.089

Table 2. Rate Constants k with Different C_{THF} Values[a]

C_{THF} (M)	$[k_{obs} \pm \delta k_{(ran)}] \times 10^4$ (s^{-1})
0.37	1.1 ± 0.1
0.47	1.5 ± 0.1
0.53	1.9 ± 0.1
0.62	2.4 ± 0.1
0.72	3.3 ± 0.1

[a] The total uncertainty of $\delta k/k = 10\%$ was calculated from $\delta k_{(ran)}/k = 9.1\%$ and $\delta k_{(sys)}/k = 5\%$; $C_{1(0)}$ at 0.141 M.

THF Dependence of the 1 → 2 Conversion. Both silyl reagents $Li(THF)_3Si(SiMe_3)_3$ and $Li(THF)_3SiBu^tPh_2$ contain THF. $Li(THF)_3Si(SiMe_3)_3$ was also used to prepare **1** in situ, which was then employed in the kinetic studies. The presence of THF is thus inevitable in the reactions. In studies to establish the order (n) of the reaction with respect to THF, six THF concentrations were used, giving the kinetic plots in Figure 2 and k_{obs} in Table 2. The plot of ln ($k_{obs} \times 10^4$) vs C_{THF} (eq 9) gives a slope (n) of 1.7(0.3) (Figure 3).

$$\ln k_{obs} = n \ln C_{THF} + \ln k_1 \qquad (9)$$

As a polar solvent, THF perhaps helps the dissociation of the anionic $Si(SiMe_3)_3^-$ ligand in **1** to give the cationic intermediate $[Ta(NMe_2)_3Si(SiMe_3)_3]^+$ **A** (Scheme 1). In the transition state leading to the formation of cationic **A** (from neutral **1**), there is a significant degree of charge separation. THF may lower the energy of the transition state and the activation energy of the Ta−Si bond cleavage process to give

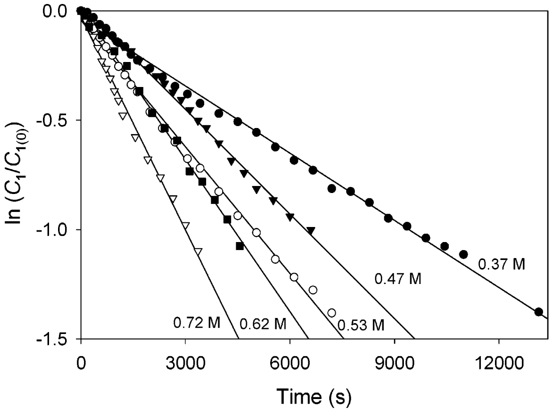


Figure 2. Kinetic plots of the **1** → **2** conversion with different C_{THF} values.

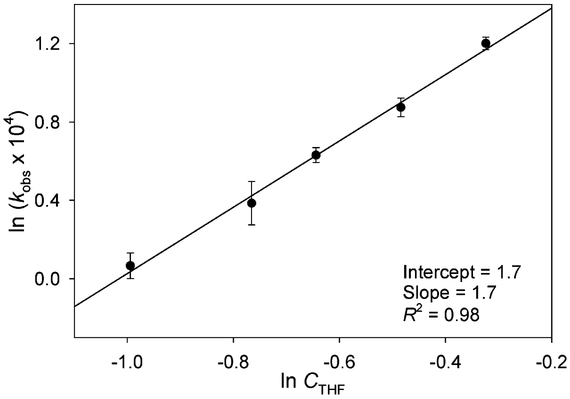
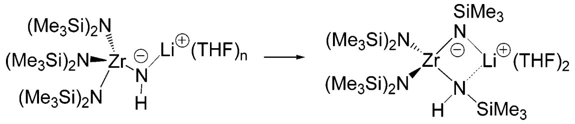


Figure 3. Plots of (k_{obs} × 10^4) vs (ln C_{THF}) with different C_{THF} values.

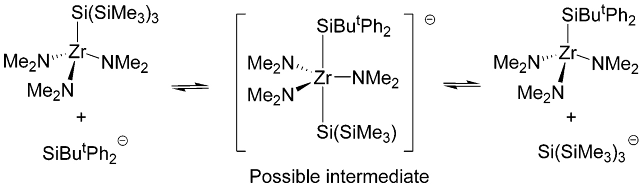
A. A highly solvent-dependent alkylation was reported by DePue and Collum with a seventh order on THF.[13] We have also reported that, in a $-SiMe_3^+$ migration process (Scheme 2), the reaction rate is increased by added THF. The reaction is 3.4(0.6)th order with respect to C_{THF}, and this is attributed to a possible multishell of THF molecules around Li^+ cations at the transition state.[10]

Mechanistic Considerations. As noted earlier, the silyl exchange equilibrium involving *monosilyl* complexes $(Me_2N)_3ZrSi(SiMe_3)_3$ and $(Me_2N)_3ZrSiBu^tPh_2$ in eq 1 is likely an associative process through a pentacoordinated, bis(silyl) intermediate $\{(Me_2N)_3Zr(SiBu^tPh_2)[Si(SiMe_3)_3]\}^-$ (Scheme 3).[6a] $[(Me_2N)_3Zr(SiBu^tPh_2)_2]^-$, an analogue of this intermediate, was directly observed in the exchange involving tetracoordinated $(Me_2N)_3Zr{-}SiBu^tPh_2$ and $SiBu^tPh_2^-$ (eq 2).[6a] In the exchange in Scheme 3, $(Me_2N)_3ZrSiBu^tPh_2$ is thermodynamically favored over $(Me_2N)_3Zr{-}Si(SiMe_3)_3$ with, e.g., $K_{eq} = 193(1)$ at 263(1) K (eq 1). The $-Si(SiMe_3)_3$ ligand is bulkier than the $-SiBu^tPh_2$ ligand, although this alone may not be the deciding factor. The high stability of complexes containing the $-SiBu^tPh_2$ ligand(s) may also explain why $[(Me_2N)_3Zr(SiBu^tPh_2)_2]^-$ was observed (and structurally characterized) but not its bis(silyl) analogues containing either one or two $-Si(SiMe_3)_3$ ligands. The observations that complexes containing the $-SiBu^tPh_2$ silyl ligand are more stable than their $-Si(SiMe_3)_3$ analogues may also explain why the substitution of the $-Si(SiMe_3)_3$ ligands in **1** and **2** by $SiBu^tPh_2^-$ is irreversible (eqs 3−4).

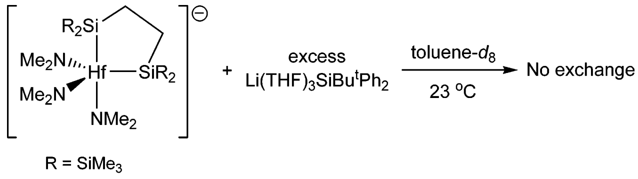
Scheme 2 [10]



Scheme 3. Silyl Exchanges Involving $(Me_2N)_3ZrSi(SiMe_3)_3$ and $(Me_2N)_3ZrSiBu^tPh_2$[6a]



Scheme 4



Given the bulky structure of the pentacoordinated, Zr bis(silyl) complex $[(Me_2N)_3Zr(SiBu^tPh_2)_2]^-$ (eq 2),[6a] it is perhaps not surprising that its Ta bis(silyl) analogue $(Me_2N)_3Ta[Si(SiMe_3)_3]_2$ (**1**) undergoes a dissociative pathway in the substitution by $SiBu^tPh_2^-$ (Scheme 1, Path I). The first step in this dissociative pathway is similar to the dissociation of one silyl group from the Zr intermediates $[(Me_2N)_3Zr(SiBu^tPh_2)(SiR_3)]^-$ ($R_3 = (SiMe_3)_3$, (Bu^tPh_2)) in Scheme 3 and eq 2, except that this step yields the cationic intermediate **A**. **A** reacts with anionic $SiBu^tPh_2^-$ to give **2**.

We reported earlier[6b] that a mixture of chelating silyl complex $K(18\text{-crown-}6)_{3/2}\{(Me_2N)_3Hf[\eta^2\text{-}(Me_3Si)_2Si(CH_2)_2\text{-}Si(SiMe_3)_2]\}$ and excess $Li(THF)_3SiBu^tPh_2$ revealed no exchange at 23 °C in 24 h (Scheme 4). This is perhaps not surprising, as the substitution of the chelating ligand by $SiBu^tPh_2^-$ is thermodynamically unfavorable.

The current studies focus on the substitution reaction between **1** and $Li(THF)_3SiBu^tPh_2$. Although limited in scope, the work reveals that the first substitution likely follows a dissociative pathway. A polar solvent was found to promote the substitution. Given the similarities between the first andthe second substitution, the latter, converting **2** to **3**, perhaps also follows a dissociative pathway.

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Supporting Information Available: ^1H NMR spectra of the reaction mixture. This material is available free of charge via the Internet at http://pubs.acs.org.

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