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Synthesis and properties of alkaline metal complexes with new overcrowded β-diketiminato ligands

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Abstract

Enaminoimines TbtNHC(Me)CHC(Me)NAr (**5**, Tbt = 2,4,6-$[CH(SiMe_3)_2]_3C_6H_2$) bearing a Tbt group were synthesized by the two steps condensation of acetylacetone with bulky amines. Enaminoimines **5** were treated with *n*-BuLi to give the corresponding lithium β-diketiminates, [Li{TbtNHC(Me)CHC(Me)NAr}] (**1**). The X-ray structural analysis of [Li{TbtNC(Me)CHC(Me)NMes}] (**1c**, Mes = mesityl) revealed that it is a monomeric, solvent-free lithium β-diketiminate. The equilibrium between free **1c** plus THF and THF-coordinated (**1c** · thf) was investigated in detail by the determination of the association constant (K_a) in C_6D_6 at 293 K and the Job's plot. The heavier alkali metal complexes, sodium and potassium β-diketiminates (**6c**–**9c**), were prepared by the two routes. THF-coordinated [M{TbtNC(Me)CHC(Me)NMes}(thf)] (**6c**: M = Na. **7c**: M = K) were prepared by the reaction of **5c** (Ar = Mes) with MH (M = Na, K). Solvent-free [M{TbtNC(Me)CHC(Me)NMes}] (**8c**: M = Na. **9c**: M = K) were prepared by the reaction of **1c** with *t*-BuOM (M = Na, K).

Keywords: β-Diketiminato ligand; Alkali metals; ^{7}Li NMR spectra; Association constant; Job's plot; Steric protection

1. Introduction

The β-diketonato ligands, such as acetylacetonate ($acac^-$), 1,3-diphenyl-1,3-propanedionate ($dbzm^-$), etc., are one of the most popular chelating systems in coordination chemistry [1]. In recent years, the isoelectronic β-diketiminato ligands have attracted much attention as spectator ligands, since they strongly coordinate to the metal centers and tune the reactivities on the metal by changing the steric and electronic properties of the substituents of the nitrogen atoms [2]. In particular, crowded β-diketiminato ligands having bulky substituents at the nitrogen atoms, e.g., $[\{(Dip)NC(Me)\}_2CH]^-$ (Dip = 2,6-diisopropylphenyl), have been applied to the synthesis of various complexes of main group elements and transition metals, such as low coordinate complexes, low oxidation state complexes, complexes having activities as catalysts, and model complexes for protein active sites. Most of these complexes were derived from the corresponding alkaline metal β-diketiminates, and their syntheses and properties have been studied extensively [3–12]. In general, the alkaline metals in these complexes are coordinated by bases, such as ethers, amines, or nitriles, due to their extremely high Lewis acidity. Base-free complexes exist as dimers, oligomers, or polymers in the solid states, and there has been no example for X-ray analysis of monomeric, base-free alkaline metal β-diketiminates so far. Even [M{[DipNC(Me)]$_2$CH}] (M = Li [8,11], K [11]) bearing bulky Dip groups reportedly exists as a dimer (M = Li), a dodecamer (M = Li), or a polymer (M = K), in the crystalline states.

On the other hand, we have successfully synthesized a variety of highly reactive species containing heavier main group elements [13–15] and transition metals [16] by taking advantage of 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group (Chart 1) [17]. We have preliminarily reported

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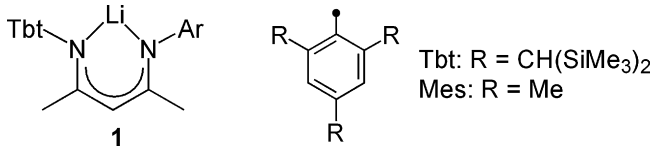


Chart 1.

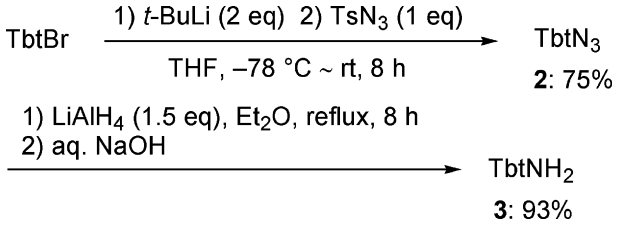
the synthesis of the first monomeric lithium β-diketiminate, [Li{TbtNC(Me)CHC(Me)NHMes}] (**1c**), which has no coordination of heteroatom donors, by use of a new overcrowded β-diketiminato ligand bearing a Tbt group (Chart 1) [18]. Very recently, we have reported the application of **1c** to the synthesis of the corresponding tetravalent group 4 metal β-diketiminates $[M^{IV}Cl_3\{TbtNC(Me)CHC(Me)NHMes\}(thf)_n]$ (M = Ti, Zr, Hf), which show unique reactivities in the reduction with KC_8 [19].

In this paper, we present the details of the synthesis and properties of the lithium β-diketiminate **1** together with the synthesis of sodium and potassium complexes coordinated with the overcrowded β-diketiminato ligand.

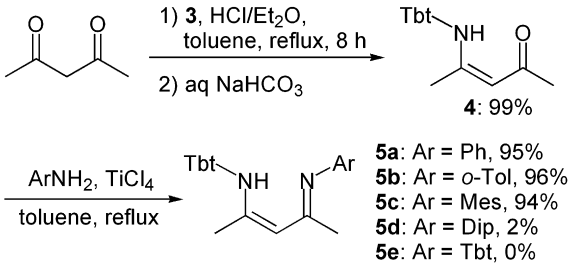
2. Results and discussion

2.1. Synthesis of enaminoimines 5a,b

Enaminoimine **5** bearing a Tbt group was synthesized by successive condensation of acetylacetone with bulky amines as shown in Scheme 2. Tbt-substituted amine **3** was prepared in a good yield by modifying the reported method [20], i.e., the treatment of TbtLi with tosylazide followed by the reduction of the resulting $TbtN_3$ (**2**) with $LiAlH_4$ (Scheme 1) [21]. When Tbt-substituted amine **3** was allowed to react with excess of acetylacetone (10 equiv.) in the presence of HCl/Et_2O (0.5 equiv.) in refluxing toluene, enaminoketone **4** was quantitatively obtained via monocondensation reaction. The exclusive formation of **4** can be explained in terms of the suppression of the nucleophilic attack of **3** to the carbonyl group of **4** due to the steric hindrance of the Tbt group, since the reaction using 0.5 molar amount of acetylacetone under the similar conditions also gave **4** along with the starting material **3**. Further condensation with $PhNH_2$ was investigated by using HCl/Et_2O (0.8 equiv.), $BF_3 \cdot Et_2O$ (0.8 equiv.), and $ZnCl_2$ (0.6 equiv.) as acid catalysts in the presence of molecular sieves 4A to give the expected enaminoimine **5a** in 18%, 41%, and 11% yields, respectively. In contrast to the low yields in



Scheme 1. Synthesis of Tbt-substituted amine **3**.



Scheme 2. Synthesis of enaminoimine **5**.

these conditions, the reaction of **4** with $PhNH_2$ in the presence of $TiCl_4$ (0.6 equiv.) resulted in the almost quantitative formation of **5a**. The synthesis of *o*-tolyl- and Mes-substituted enaminoimine **5b** and **5c** was also achieved by the similar method in almost quantitative yields. However, the condensation reaction with $DipNH_2$ scarcely proceeded under similar conditions, and the reaction with **3** resulted in complete recovery of the starting materials, probably due to the severe steric hindrance.

2.2. Structures of enaminoketone 4 and enaminoimines 5a,c

Enaminoketone **4** and enaminoimines **5a**–**c** were characterized by the ^1H and ^{13}C NMR spectra, high-resolution mass spectra, and elemental analysis, and the molecular structures of these compounds were definitively determined by X-ray structural analysis.

Figs. 1–3 show the ORTEP drawings of **4**, **5a**, and **5c**, respectively. Table 6 shows the crystal data and structure refinements for **4**, **5a**, and **5c**. The N1–C1–C2–C3–N2(O1) moieties of all these compounds are almost planar, and the C–O, C–N (1.285–1.340 Å) and C–C (1.366–1.437 Å) bond lengths (Table 1) are intermediate values between the typical single [C–OH: av. 1.432; C–N: av. 1.469; C–C: av. 1.530 Å] and double [$(C)_2C{=}O$: av. 1.210; C–C=N–C: av. 1.279; $(C)HC_{sp}2 = C_{sp}2(C)_2$: av. 1.326 Å] bond lengths [22]. Although these observations suggest the conjugation

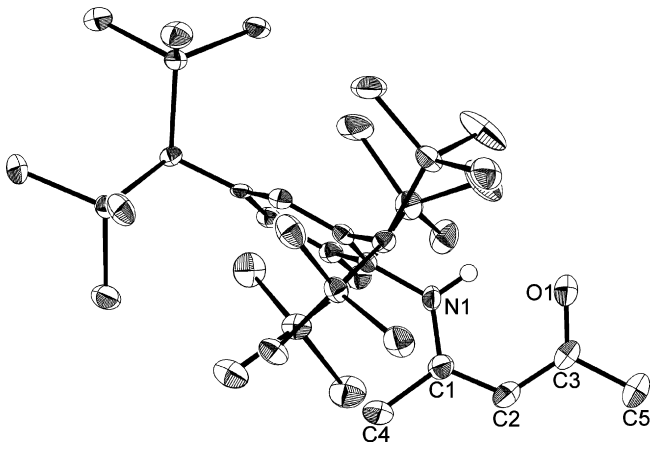


Fig. 1. ORTEP drawing of enaminoketone **4** (50% thermal ellipsoids). Hydrogen atoms, except for NH, are omitted for clarity.

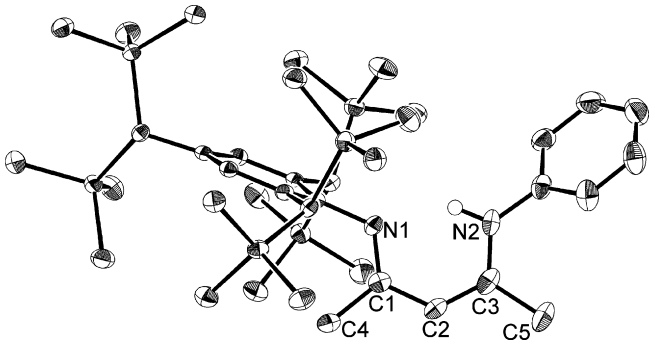


Fig. 2. ORTEP drawing of enaminoimine **5a** (50% thermal ellipsoids). Hydrogen atoms, except for NH, are omitted for clarity.

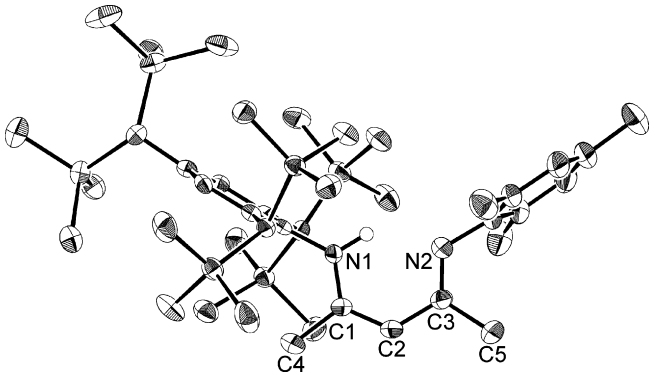


Fig. 3. ORTEP drawing of enaminoimine **5c** (50% thermal ellipsoids). Hydrogen atoms, except for NH, are omitted for clarity.

of the π-bonds in the N1–C1–C2–C3–N2(O1) systems, the C_3NO and C_3N_2 structures clearly show bond alternation (Table 1). Considering these results, the C_3NO and C_3N_2 systems indicate the obvious localization of the double bonds despite the partial delocalization of the π-electrons, as well as the case of other enaminoimines, (Ar)N=C(Me)–CH=C(Me)–NH(Ar) (Ar = Ph [23] or Dip [8]).

Table 1
Selected bond lengths (Å), bond and dihedral angles (°)

Compound	**4**	**5a**	**5c**	**1c**
Bond lengths (Å)				
C1–C2	1.383(5)	1.426(3)	1.372(4)	1.424(4)
C2–C3	1.407(5)	1.366(3)	1.437(4)	1.418(4)
C1–N1	1.342(4)	1.318(3)	1.340(4)	1.323(4)
C3–N2	–	1.354(3)	1.285(4)	1.328(4)
C3–O1	1.259(4)	–	–	–
Bond angles (°)				
C1–C2–C3	123.3(4)	127.4(2)	125.2(3)	130.2(3)
N1–C1–C2	120.9(4)	121.3(2)	122.6(3)	123.6(3)
E–C3–C2 (E = N2 or O1)	122.6(4)	120.2(2)	121.0(3)	125.1(3)
Dihedral angles (°)				
C_3NE plane – Tbt ring	83.40(42)	77.96(26)	86.78(37)	86.76(34)
C_3N_2 plane – Ar ring	–	46.22(36)	88.20(43)	87.86(36)

It should be noted that the pattern of the bond alternation in **5a** is different from that in **5c**, i.e., in **5a**, the N1–C1 bond [1.318(3) Å] tethered with Tbt group is shorter than the N2–C3 bond [1.354(3) Å] tethered with Ph group, while, in **5c**, the (Tbt)N1–C1 bond [1.340(4) Å] is longer than the (Mes)N2–C3 bond [1.285(4) Å]. The bond alternation pattern of **5a** may be explained in terms of the contribution of the resonance structure shown in Chart 2. On the other hand, the structure of **5c** may be little affected by the resonance structure, since the dihedral angles between the C_3N_2 plane and Mes ring are almost orthogonal (Table 1). The longer (Tbt)N1–C1 bond of **5c** is probably due to the relaxation of the steric repulsion between Tbt group and Me(C4) group.

2.3. Synthesis and structure of lithium β-diketiminates *1a,b*

Enaminoimines **5a** and **5c** were treated with 1.5 molar amount of *n*-BuLi in ether at 0 °C, and then the reaction mixture was warmed to room temperature to give a colorless solution. The exchange of the solvents to dry hexane followed by the filtration of the mixture resulted in the isolation of lithium β-diketiminates **1a** and **1c**, which are insoluble in hexane and isolated as colorless, moisture-sensitive crystals in 81% and 85% yields, respectively (Scheme 3).

Lithium β-diketiminates **1a**,**c** were characterized with ^1H, ^{13}C, and ^7Li NMR spectroscopy. The ^1H and ^{13}C NMR spectra showed that no solvent such as ether coordinates to the lithium atoms of **1a**,**c**. These results are in sharp contrast to the case of Li[{(Dip)NC(Me)}$_2$CH](Et$_2$O), which does not lose the coordinated ether even in hydrocarbon solvents such as hexane and C_6D_6 [18]. This difference is probably due to the steric hindrance of the extremely bulky substituent, Tbt group, attached to the nitrogen atom of **1a**,**c**.

The X-ray structural analysis revealed the crystalline-state structure of **1c**, and the ORTEP drawings and the crystal packing diagram of **1c** are shown in Figs. 4 and 5, respectively.

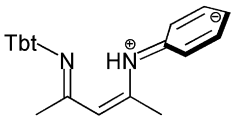
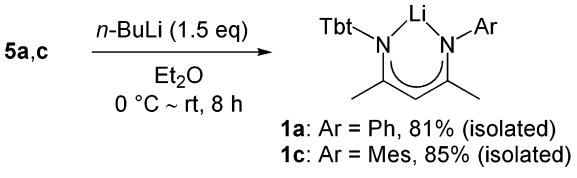


Chart 2.



Scheme 3. Synthesis of lithium β-diketiminate **1**.

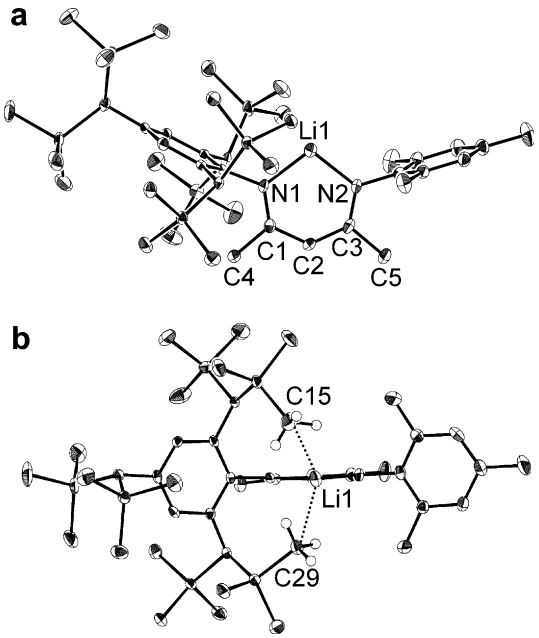


Fig. 4. ORTEP drawing of lithium β-diketiminate **1c** (50% thermal ellipsoids). (a) Top view, (b) side view. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Li(1)–N(1) 1.917(6), Li(1)–N(2) 1.915(6), Li(1)···C(15) 2.835, Li(1)···C(29) 2.670(6), N(2)–Li(1)–N(1) 103.8(3), Li(1)–N(1)–C(1) 119.0(2), C(3)–N(2)–Li(1) 117.9(3).

The X-ray structural analysis of **1c** showed that there is no intermolecular contact between neighboring molecules (the shortest Li···C intermolecular distance: 3.718(6) Å) and no solvent coordinates to the lithium atom of **1c** (Fig. 5). To the best of our knowledge, this is the first example for the structural analysis of monomeric, lithium β-diketiminate free of heteroatom donor. It should be noted that [Li{[DipNC(Me)]$_2$CH}] [8], [Li{(Me$_3$Si)-NC(R^1)CHC(R^2)N(SiMe$_3$)}] (R^1 = R^2 = Ph [3]; R^1 = Ph, R^2 = *t*-Bu [7]; R^1 = R^2 = NMe$_2$ [9]), and [Li{(Me$_3$Si)-NC(R^1)C(R^2)(C$_5$H$_4$N-2)}] (R^1 = *t*-Bu, R^2 = H; R^1 = Ph, R^2 = SiMe$_3$) [6] reportedly exist as dimers or dodecamers in the crystalline states. This difference is most likely due to the steric hindrance of the extremely bulky Tbt group on the nitrogen atom in **1c**.

It should be of additional interest for the newly obtained complex **1c** that it probably has two intramolecular Li···CH$_3$ interactions as judged by the Li···C(15) and Li···C(29) distances. The Li···CH interaction has been reported for some lithium amides, alkyllithiums, and ate complexes (Fig. 4(b)) [18,24]. The C$_3$N$_2$Li ring of **1c** is almost planar and the two sets of Li–N, N–C and C–C distances in the C$_3$N$_2$Li ring are almost equivalent to each other (Table 1). In addition, the N–C and C–C bond lengths are intermediate values between the typical single

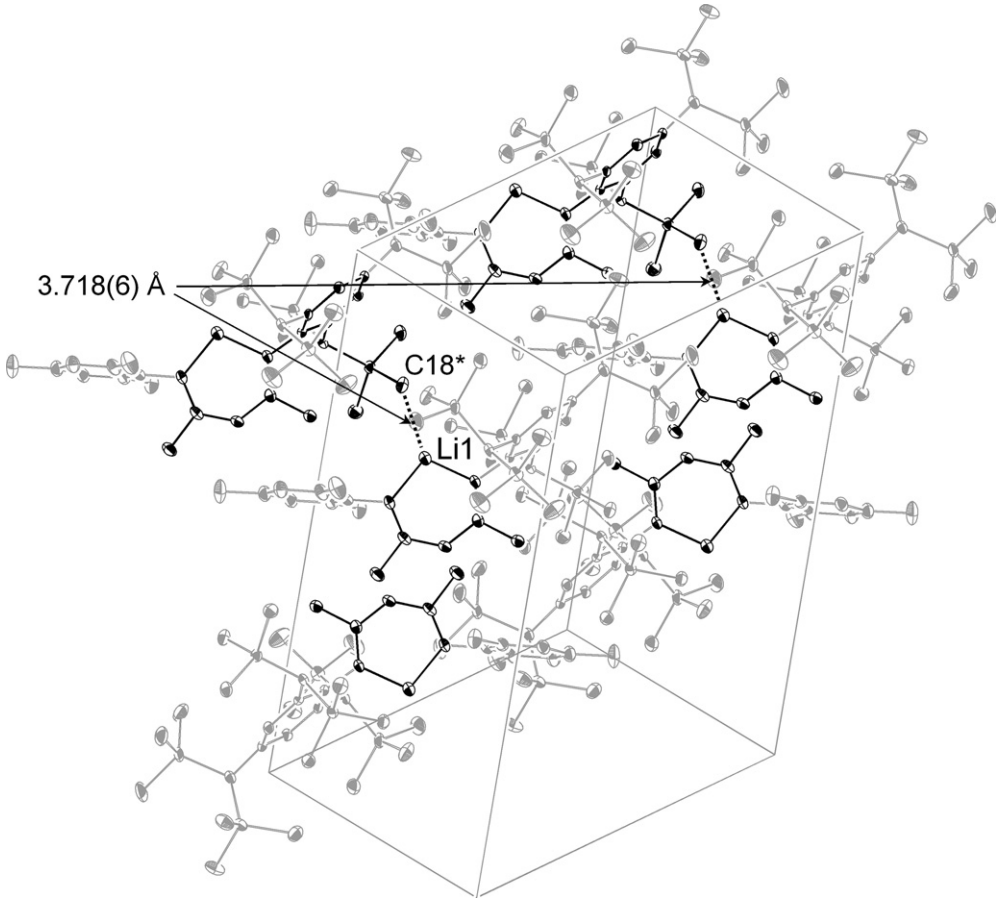


Fig. 5. The crystal packing of lithium β-diketiminate **1c**.

[C–N: av. 1.469; C–C: av. 1.530 Å] and double [C–C=N–C: av. 1.279; (C)HCsp^2 = Csp^2(C)$_2$: av. 1.326 Å] bonds [22].

2.4. Complexation of lithium β-diketiminate *1c* with THF

When various amounts of THF were added to the C_6D_6 solution of **1c**, the ^{7}Li NMR signals shifted to the upper-field with the increase of the amount of THF (Table 2). In addition, the signals assigned to THF in the ^{1}H NMR spectra moved to the lower field by the addition of a larger amount of THF (Table 2). These results suggest the rapid equilibrium at 298 K between free **1c** plus THF and THF-coordinated (**1c** · thf) in the time scale of NMR spectroscopy (Scheme 4). That is, the addition of a large amount of THF leads to the increase of the ratio of (**1c** · thf) compared to **1c** and the ratio of free THF relative to the coordinating THF to **1c**.

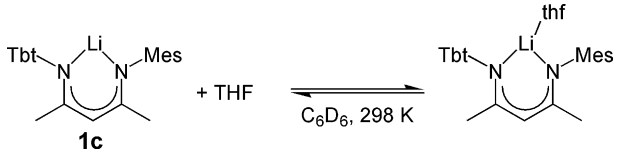
When the C_6D_6 solution containing **1a**–**c** and THF was fully evaporated, the lithium β-diketiminate coordinated by one THF molecule (**1c** · thf) was isolated. We have succeeded in the X-ray structural analysis of the analogously prepared lithium complex having Tbt and Ph groups on the N-terminals, [Li{TbtNC(Me)CHC(Me)NPh}(thf)] (**1a** · thf) [18].

In order to clarify the details of this equilibrium, the determination of the association constant (K_a) between free **1c** and THF in C_6D_6 at 298 K was performed by the measurement of the ^{7}Li NMR spectra. The observed chemical shifts in the ^{7}Li NMR spectra (δ_{obs}) are described by Eq. (1), where α is the mole fraction of (**1c** · thf) and δ_{free} and $\delta_{THF\text{-coordinated}}$ are the ^{7}Li NMR chemical shifts of **1c** and (**1c** · thf), respectively. Eq. (1) can be rearranged to give an expression shown in Eq. (2).

Table 2
The ^{7}Li and ^{1}H NMR measurements of **1c** in C_6D_6/THF

$[THF]_0/[\mathbf{1c}]_0$	^{7}Li NMR δ_{obs} (ppm)	^{1}H NMR (ppm) THF	α[a]	$[THF]_0 - \alpha[\mathbf{1c}]_0$ (M)[a]	$(\alpha^{-1}-1)^{-1}$[a]
0 (pure **1c**)	2.33 (δ_{free})	–	0	0	0
0.533	2.21	1.24, 3.37	0.185	0.0104	0.227
1.02	2.11	1.25, 3.39	0.343	0.0204	0.521
2.31	1.99	1.33, 3.46	0.532	0.0532	1.14
4.33	1.89	1.35, 3.49	0.674	0.110	2.07
6.54	1.84	1.37, 3.51	0.762	0.174	3.21
7.96	1.82	1.38, 3.53	0.792	0.215	3.80
9.86	1.79	1.38, 3.53	0.836	0.271	5.11

Conditions: $[\mathbf{1c}]_0$ = 30.0 mM, C_6D_6 solution, 298 K.
[a] The α values were calculated by using Eq. (2), where the $\delta_{THF\text{-coordinated}}$ value was taken as 1.682 ppm. The chemical shifts of THF in the ^{1}H NMR spectra were 1.40, 3.57 ppm.



Scheme 4. Equilibrium between free **1c** and THF-coordinated (**1c** · thf).

$$\delta_{obs} = (1-\alpha)\delta_{free} + \alpha\delta_{THF\text{-coordinated}} \quad (1)$$

$$\alpha = (\delta_{free} - \delta_{obs})/(\delta_{free} - \delta_{THF\text{-coordinated}}) \quad (2)$$

If the THF molecules coordinates to **1c** with the ratio of 1:1 in the C_6D_6 solution as well as the case of (**1a** · thf) in the crystalline state, K_a is described by Eq. (3), where [(**1c** · thf)], [**1c**], and [THF] are the equilibrium concentrations of THF-coordinated complex, (**1c** · thf), and THF, respectively. Eq. (3) can be rearranged to give Eq. (4) by introducing $[(\mathbf{1c}\cdot thf)] = \alpha[\mathbf{1c}]_0$, $[\mathbf{1c}] = (1-\alpha)[\mathbf{1c}]_0$, and $[THF] = [THF]_0 - \alpha[\mathbf{1c}]_0$, where $[\mathbf{1c}]_0$ and $[THF]_0$ are the total concentrations of **1c** and THF, respectively.

$$K_a = [(\mathbf{1c}\cdot thf)]/[\mathbf{1c}][THF] \quad (3)$$

$$(\alpha^{-1}-1)^{-1} = K_a([THF]_0 - \alpha[\mathbf{1c}]_0) \quad (4)$$

The $(\alpha^{-1}-1)^{-1}$ values were plotted against the $([THF]_0 - \alpha[\mathbf{1c}]_0)$ values, where the α values were calculated by taking the $\delta_{THF\text{-coordinated}}$ value as various values between 1.50 and 1.75 ppm in Eq. (2) (Table 3), since the $\delta_{THF\text{-coordinated}}$ value cannot be directly determined by the measurement [25]. The $\delta_{THF\text{-coordinated}}$ value giving the best correlation coefficient (R^2 = 0.996) is 1.682 ppm, and the linear plots, where the $\delta_{THF\text{-coordinated}}$ value is taken as this value, indicate that the association constant (K_a) is 18 ± 1 M^{-1} (Fig. 6, Tables 2 and 3).

Fig. 7 shows a continuous variation plot (Job's plot) for the complex formation between **1c** and THF [26]. The plots show a maximum at 0.50 of the **1c** fraction, indicating that **1c** form the complex with THF with the ratio of 1:1 in C_6D_6 at 298 K (Table 4).

2.5. Synthesis of sodium and potassium β-diketiminates

We now focus on the heavier alkali metal compounds of the β-diketiminato ligand. Sodium or potassium β-diketiminates are sometimes better precursors for the metal complexes rather than the lithium analogues, because of the ready separation from the heavier alkali metal chlorides

Table 3
The relation between $\delta_{THF\text{-coordinated}}$ and the association constant (K_a)

$\delta_{THF\text{-coordinated}}$ (ppm)	K_a (M)$^{-1}$	R^2
1.50	7.58	0.904
1.60	11.2	0.963
1.61	11.8	0.967
1.62	12.4	0.974
1.63	13.1	0.979
1.64	13.9	0.984
1.65	14.8	0.988
1.66	15.8	0.991
1.67	16.9	0.994
1.68	18.2	0.995
1.682	18.5	0.996
1.69	19.8	0.995
1.70	21.7	0.993
1.71	24.0	0.988
1.72	26.8	0.978
1.75	42.6	0.898

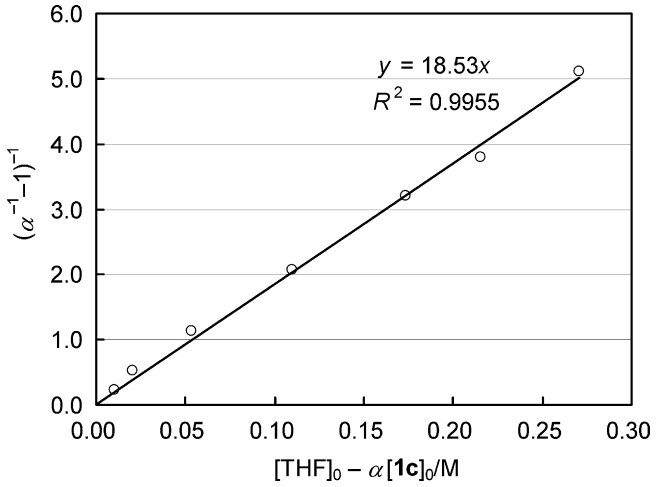


Fig. 6. Plot for determining the association constant for **1c** and (**1c** · thf). The regression line is $y = 18.53x$, ($K_a = 18 \pm 1$, $\delta_{\text{THF-coordinated}} = 1.682$ ppm, $R^2 = 0.996$).

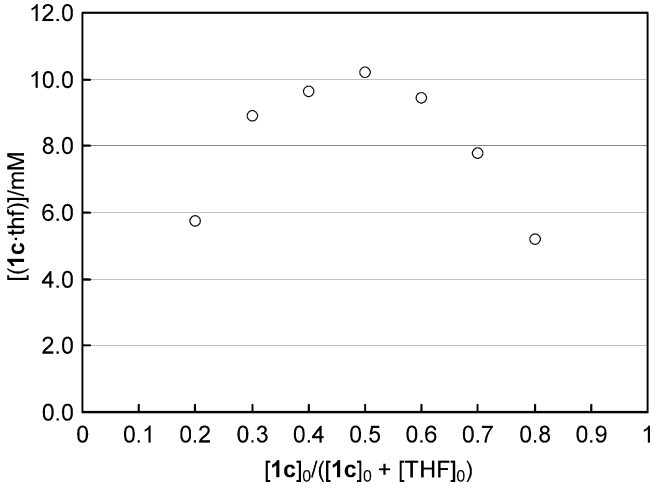


Fig. 7. Job's plot showing the 1:1 stoichiometry of the complex between **1c** and THF in C_6D_6. $[\mathbf{1c}]_0 + [\text{THF}]_0 = 38.8$ mM.

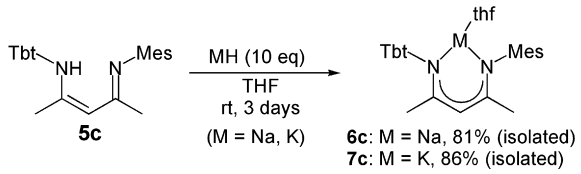
Table 4
The Job's plot between **1c** and THF in C_6D_6

$[\mathbf{1c}]_0/([\text{THF}]_0 + [\mathbf{1c}]_0)$	^{7}Li NMR (ppm)	α	$[\mathbf{1c}]_0$ (mM)	[(**1c** · thf)] (mM)
0.20	2.02	0.478	12.0	5.75
0.30	2.01	0.494	18.0	8.90
0.40	2.07	0.401	24.0	9.64
0.50	2.11	0.340	30.0	10.2
0.60	2.16	0.262	36.0	9.46
0.70	2.21	0.185	42.1	7.79
0.80	2.26	0.108	48.1	5.19

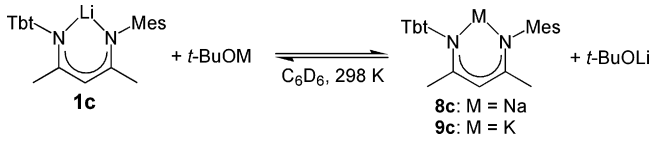
Conditions: $[\mathbf{1c}]_0 + [\text{THF}]_0 = 38.8$ mM (constant), C_6D_6 solution, 298 K.

co-products, as in the synthesis of lanthanide metal β-diketiminates [27].

First, THF-coordinated sodium and potassium β-diketiminates (**6c** and **7c**) were prepared by the reaction of enaminoimine **5c** with the appropriate metal hydrides



Scheme 5. Reaction of enaminoimine **5c** with metal hydrides.



Scheme 6. Reaction of lithium β-diketiminate **1c** with metal *tert*-butoxides.

Table 5
The Reactions of **1c** with *t*-BuOM (M = Na, K)

Entry	Reagent	Equivalent	Yield (%)[a]	
			1c	**8c** or **9c**
1	*t*-BuONa	1.5	38	62 (**8c**)
2	*t*-BuONa	2.0	17	83 (**8c**)
3	*t*-BuONa	10	9	91 (**8c**)
4	*t*-BuOK	1.5	7	93 (**9c**)

[a] Judged by ^{1}H NMR spectrum at 298 K.

MH (M = Na, K) in THF (Scheme 5) [28]. In hydrocarbon (benzene or toluene) or diethyl ether solvents, these reactions did not occur.

Next, we examined the synthesis of the THF-free sodium and potassium β-diketiminates. The lithium β-diketiminate **1c** reacted with sodium or potassium *tert*-butoxide in C_6D_6 at 293 K, giving in high yield the appropriate alkali metal derivative, THF-free complex **8c** or **9c**, respectively (Scheme 6) [11].

In the case of sodium, the reaction of **1c** with 1.5 molar amount of *t*-BuONa gave the corresponding sodium complex **8c** in a moderate yield (62%) together with the starting material **1c** (38%), and the almost quantitative formation of **8c** required the use of 10 molar amounts of *t*-BuONa (Scheme 6, Table 5). Meanwhile, in the case of potassium, the reaction of **1c** with 1.5 molar amount of *t*-BuOK resulted in the almost quantitative formation of **9c**. This difference probably depends on the affinity of the alkali metal with the coordinating nitrogens.

3. Conclusion

Enaminoimines TbtNHC(Me)CHC(Me)NAr (**5**) bearing a Tbt group (Tbt = 2,4,6-$[CH(SiMe_3)_2]_3C_6H_2$) were synthesized by the two-step condensation of acetylacetone with bulky amines. It should be noted that the pattern of the bonds alternation in **5a** (Ar = Ph) is different from that in **5c** [Ar = Mes (mesityl)] as judged by the crystalline state structures.

Enaminoimines **5** were treated with *n*-BuLi, yielding the lithium β-diketiminates [Li{TbtNC(Me)CHC(Me)NAr}] (**1a**: Ar = Ph, **1c**: Ar = Mes). The X-ray structural analysis of [Li{TbtNC(Me)CHC(Me)NMes}] (**1c**) revealed that it is a monomeric, solvent-free lithium β-diketiminate in contrast to the previously reported lithium β-diketiminates, which are oligomeric, solvent-free or monomeric, solvent-coordinated lithium β-diketiminates. The equilibrium between free **1c** plus THF and THF-coordinated (**1c** · thf) is examined from various points of view. The association constant (K_a) for this equilibrium was determined by the ^{7}Li NMR spectra to be $18 \pm 1\ M^{-1}$ in C_6D_6 at 298 K, and the Job's plot indicated a 1:1 stoichiometry of the complex of **1c** with THF.

Enaminoimine **5c** was treated with MH (M = Na, K) in THF to afford the THF-coordinated, sodium and potassium β-diketiminates, [M{TbtNC(Me)CHC(Me)NMes}(thf)] (**6c**: M = Na, **7c**: M = K). In addition, lithium β-diketiminates **1c** was treated with 10 equiv. of *t*-BuONa or 1.5 equiv. of *t*-BuOK to give the THF-free, sodium and potassium β-diketiminates, [M{TbtNC(Me)CHC(Me)NMes}] (**8c**: M = Na, **9c**: M = K), respectively.

4. Experimental

4.1. General experimental details

All solvents used were purified by the reported methods. THF was purified by distillation from sodium diphenylketyl before use. All reactions were carried out under an argon atmosphere, unless otherwise noted. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-300 spectrometer using $CHCl_3$ or C_6D_5H as an internal standard. The ^{7}Li NMR (116 MHz) spectra were measured in C_6D_6 with a JEOL AL-300 spectrometer using LiCl in D_2O (1 mol L^{-1}) as an external standard. The infrared and electronic spectra were recorded on JASCO FT/IR 460 Plus and JASCO V530 UV/Vis spectrometers, respectively. Mass spectral data were obtained on a JEOL JMS-700 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

4.2. Synthesis of $TbtN_3$

To a THF solution (10 mL) of TbtBr (0.632 g, 1.00 mmol) was added *t*-BuLi (2.2 M in pentane, 0.90 mL, 2.0 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 30 min. TsN_3 (0.20 g, 1.0 mmol) was added to the reaction mixture. After stirring at the same temperature for 30 min, the reaction mixture was allowed to warm up to room temperature. The solvent was evaporated under reduced pressure, and hexane was added to the residue. Insoluble inorganic salts were removed by filtration thorough Celite®. The removal of the solvent from the filtrate gave $TbtN_3$. Yield: 0.412 g (69%). M.p. 115.3–117.1 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 18H, Si*Me*$_3$), 0.04 (s, 36H, Si*Me*$_3$), 1.32 (s, 1H, *p*-benzyl), 1.99 (s, 2H, *o*-benzyl), 6.30 (br s, 1H, Tbt *m*-*H*), 6.39 (br s, 1H, Tbt *m*-*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.6 (q, Si*Me*$_3$), 0.7 (q, Si*Me*$_3$), 23.3 (d × 2, *o*-benzyl), 30.0 (d, *p*-benzyl), 122.1 (d, Tbt C_m), 126.9 (d, Tbt C_m), 131.8 (s), 138.7 (s), 141.2 (s), a signal assignable to *ipso*-^{13}C of Tbt group was not observed. HRMS (EI) found *m*/*z* 565.3268 ($[M-N_2]^+$), calcd for $C_{27}H_{59}NSi_6$ ($[M-N_2]^+$) 649.3838. Anal. Calc. for $C_{27}H_{59}N_3Si_6$: C, 54.57; H, 10.01; N, 7.07. Found: C, 54.50; H, 10.04; N, 7.13%.

4.3. Synthesis of $TbtNH_2$

A solution of $TbtN_3$ (2.97 g, 5.0 mmol) in THF (50 mL) was added dropwise to a suspension of $LiAlH_4$ (1.0 g, 26.3 mmol) in THF (20 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 1 day. An aqueous solution of NaOH (15 mL, 0.01 M) was added very slowly, and a vigorous reaction occurred. The mixture was warmed to room temperature, whereupon the grey precipitates turned white. The mixture was filtered and the organic filtrate was dried over Na_2SO_4. Filtration and evaporation of the organic layer resulted in the formation of colorless crystals of $TbtNH_2$. Yield: 2.13 g (75%). The spectral data and elemental analysis of $TbtNH_2$ have been described in Ref. [20].

4.4. Synthesis of TbtNHC(Me)CHC(O)Me (4)

To a mixture of $TbtNH_2$ (886 mg, 1.56 mmol) and acetylacetone (410 μL, 16 mmol) in toluene (10 mL) was added at room temperature an ether solution of hydrogen chloride (1 M solution, 790 μL, 0.79 mmol). The reaction mixture was refluxed for 8 h, and then cooled to ambient temperature. After the addition of a saturated aqueous solution (5 mL) of $NaHCO_3$, the mixture was extracted with hexane (4 mL) 4 times. The combined organic layers were dried with Na_2SO_4, and the solvents were evaporated. The residue was dissolved in a small amount of $CHCl_3$, and CH_3CN was added to the solution to afford colorless precipitates of **4**. Yield: 1.01 g (99%). M.p. 179–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 18H, Si*Me*$_3$), 0.03 (s, 18H, Si*Me*$_3$), 0.04 (s, 18H, Si*Me*$_3$), 1.33 (s, 1H, *p*-benzyl), 1.63 (s, 3H, *Me*C(N)), 1.69 (s, 2H, *o*-benzyl), 2.06 (s, 3H, *Me*C(O)), 5.11 (s, 1H, 3-C*H*), 6.32 (br s, 1H, Tbt *m*-*H*), 6.43 (br s, 1H, Tbt *m*-*H*), 11.57 (s, 1H, N*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.3 (q, Si*Me*$_3$), 0.6 (q, Si*Me*$_3$), 1.4 (q, Si*Me*$_3$), 19.4 (q, *Me*C(NHTbt)), 22.5 (d × 2, *o*-benzyl), 28.9 (q, *Me*C(O)), 30.1 (d, *p*-benzyl), 94.9 (d, 3-*C*H), 122.1 (d, Tbt C_m), 126.8 (d, Tbt C_m), 130.0 (s, Tbt), 142.0 (s, Tbt), 142.1 (s × 2, Tbt C_o), 163.1 (s, *C*(NHTbt)), 195.0 (s, *C*(O)); IR (KBr) 689, 739, 760, 839, 893, 974, 1038, 1248, 1582, 1616, 2955 cm^{-1}; UV–Vis (hexane) 222 (ε 3.1×10^4), 309 nm (ε $1.1 \times 10^4\ M^{-1}\ cm^{-1}$); HRMS (EI) found *m*/*z* 649.3843 (M^+), calcd for $C_{32}H_{67}NOSi_6$ 649.3838. Anal. Calc. for $C_{32}H_{67}NOSi_6$: C, 59.09; H, 10.38; N, 2.15. Found: C, 58.82; H, 10.44; N, 2.32%.

4.5. Synthesis of TbtNHC(Me)CHC(Me)NPh (**5a**)

To a solution of **4** (2.00 g, 3.07 mmol) and $PhNH_2$ (3.0 mL, 31 mmol) in toluene (20 mL) was added $TiCl_4$ (240 μL, 2.2 mmol) at 0 °C. The reaction mixture was refluxed for 16 h, and then cooled to ambient temperature. After the addition of a saturated aqueous solution (20 mL) of $NaHCO_3$, the mixture was extracted with hexane (15 mL) 4 times. The combined organic layers were dried with Na_2SO_4, and then the solvents were evaporated. The residue was dissolved in a small amount of $CHCl_3$, and CH_3CN was added to the solution to afford colorless precipitates of **5a**. Yield: 2.12 g (95%). M.p. 199.4–200.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.07 (s, 18H, Si*Me*$_3$), 0.03 (s, 18H, Si*Me*$_3$), 0.08 (s, 18H, Si*Me*$_3$), 1.30 (s, 1H, Tbt *p*-benzyl), 1.68 (s, 3H, *Me*C(N)), 1.86 (s, 2H, Tbt *o*-benzyl), 1.92 (s, 3H, *Me*C(N)), 4.78 (s, 1H, 3-C*H*), 6.32 (br s, 1H, Tbt *m*-*H*), 6.40 (br s, 1H, Tbt *m*-*H*), 6.79 (d, $J = 7.4$ Hz, 2H, Ph $o-H$), 6.95 (t, $J = 7.4$ Hz, 1H, Ph $p-H$), 7.21 (dd, $J = 7.4$ Hz, $J = 7.4$ Hz, 2H, Ph *m*-*H*), 11.67 (s, 1H, N*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.4 (q, Si*Me*$_3$), 0.7 (q, Si*Me*$_3$), 1.5 (q, Si*Me*$_3$), 20.7 (q, *Me*C(N)), 21.1 (q, *Me*C(N)), 22.2 (d × 2, Tbt *o*-benzyl), 29.8 (d, Tbt *p*-benzyl), 94.7 (d, 3-*C*H), 121.9 (d, Tbt C_m), 122.2 (d, Ph C_p), 122.3 (d, Ph C_o), 126.7 (d, Tbt C_m), 128,3 (d, Ph C_m), 134.1 (s, Tbt), 139.9 (s, Tbt), 140.2 (s × 2, Tbt C_o), 149.2 (s, Ph C_{ipso}), 157.9 (s, *C*(N)), 162.7 (s, *C*(N)); IR (KBr) 687, 737, 760, 837, 893, 926, 974, 1036, 1161, 1188, 1246, 1262, 1377, 1412, 1437, 1485, 1547, 1582, 1620, 2899, 2953 cm^{-1}; UV–Vis (hexane) 223 (ε 5.3×10^4), 330 nm (ε 1.9×10^4 M^{-1} cm^{-1}); HRMS (EI) found *m*/*z* 724.4300 (M^+), calcd for $C_{38}H_{72}N_2Si_6$ 724.4312. Anal. Calc. for $C_{38}H_{72}N_2Si_6$: C, 62.91; H, 10.00; N, 3.86. Found: C, 62.71; H, 10.06; N, 3.95%.

4.6. Synthesis of TbtNHC(Me)CHC(Me)N(*o*-Tol) (**5b**)

TbtNHC(Me)CHC(Me)N(*o*-Tol) (**5b**) was prepared by the procedure similar to that for the synthesis of **5a** from **4** (100 mg, 154 μmol), *o*-$TolNH_2$ (170 μL, 1.54 mmol), and $TiCl_4$ (120 mM toluene solution, 1.28 mL, 154 μmol) in toluene (2 mL). Yield: 109 mg (95%). M.p. 198.2–199.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.07 (s, 18H, Si*Me*$_3$), 0.03 (s, 18H, Si*Me*$_3$), 0.08 (s, 18H, Si*Me*$_3$), 1.31 (s, 1H, Tbt *p*-benzyl), 1.68 (s, 3H, *Me*C(N)), 1.73 (s, 3H, *Me*C(N)), 1.93 (s, 2H, Tbt *o*-benzyl), 2.11 (s, 3H, Tol *o*-*Me*), 4.78 (s, 1H, 3-C*H*), 6.31 (br s, 1H, Tbt *m*-*H*), 6.40 (br s, 1H, Tbt *m*-*H*), 6.65 (dd, $J = 7.4$, 1.0 Hz, 1H, Tol 6-H), 6.90 (ddd, $J = 7.4$, 7.4, 1.0 Hz, 1H, Tol 4-H), 7.06 (dd, $J = 7.4$, 7.4 Hz, 1H, Tol 5-H), 7.12 (d, $J = 7.4$ Hz, 1H, Tol 3-H), 11.29 (s, 1H, N*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.4 (q, Si*Me*$_3$), 0.7 (q, Si*Me*$_3$), 1.5 (q, Si*Me*$_3$), 18.1 (q, Tol *Me*), 20.5 (q, *Me*C(N)), 21.4 (q, *Me*C(N)), 22.3 (d × 2, Tbt *o*-benzyl), 29.9 (d, Tbt *p*-benzyl), 93.9 (d, 3-*C*H), 122.0 (d, Tbt C_m), 122.2 (d, Tol), 122.5 (d, Tol), 126.7 (d, Tbt C_m), 129.3 (s, Tol), 129.9 (d, Tol), 133.2 (s, Tbt), 140.2 (s, Tbt), 140.9 (s × 2, Tbt C_o), 149.3 (s, Tol), 156.6 (s, *C*(N)), 164.4 (s, *C*(N)); HRMS (EI) found *m*/*z* 738.4461 (M^+), calcd for $C_{39}H_{74}N_2Si_6$ 738.4468. Anal. Calc. for $C_{39}H_{74}N_2Si_6$: C, 63.34; H, 10.09; N, 3.79. Found: C, 62.84; H, 10.17; N, 3.87%.

4.7. Synthesis of TbtNHC(Me)CHC(Me)NMes (**5c**)

TbtNHC(Me)CHC(Me)NMes (**5c**) was prepared by the procedure similar to that for the synthesis of **5a** from **4** (3.39 g, 5.21 mmol), $MesNH_2$ (7.3 mL, 52 mmol), and $TiCl_4$ (120 mM toluene solution, 1.0 mL, 120 μmol) in toluene (1 mL). Yield: 3.76 g (94%). M.p. 207.5–209.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.08 (s, 18H, Si*Me*$_3$), 0.04 (s, 18H, Si*Me*$_3$), 0.08 (s, 18H, Si*Me*$_3$), 1.30 (s, 1H, Tbt *p*-benzyl), 1.63 (s, 3H, *Me*C(N)), 1.67 (s, 3H, *Me*C(N)), 1.91 (s, 2H, Tbt *o*-benzyl), 2.07 (s, 6H, Mes *o*-*Me*), 2.24 (s, 3H, Mes *p*-*Me*), 4.76 (s, 1H, 3-C*H*), 6.33 (br s, 1H, Tbt *m*-*H*), 6.38 (br s, 1H, Tbt *m*-*H*), 6.80 (s, 2H, Mes *m*-*H*), 11.08 (s, 1H, N*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.5 (q, Si*Me*$_3$), 0.7 (q, Si*Me*$_3$), 1.6 (q, Si*Me*$_3$), 18.5 (q, Mes *o*-*Me*), 20.8 (q, *Me*C(N)), 21.1 (q, *Me*C(N)), 21.3 (q, Mes *p*-*Me*), 22.2 (d × 2, Tbt *o*-benzyl), 29.7 (d, Tbt *p*-benzyl), 93.5 (d, 3-*C*H), 122.0 (d, Tbt C_m), 126.9 (d, Tbt C_m), 128.3 (d, Mes C_m), 130.1 (s, Mes C_p), 132.2 (s, Mes C_o), 135.2 (s, Tbt), 139.3 (s, Tbt), 139.4 (s × 2, Tbt C_o), 143.6 (s, Mes C_{ipso}), 158.4 (s, *C*(N)), 162.9 (s, *C*(N)); IR (KBr) 687, 719, 760, 839, 893, 974, 1040, 1188, 1248, 1377, 1437, 1480, 1555, 1584, 1622, 2899, 2953 cm^{-1}; UV–Vis (hexane) 222 (ε 7.1×10^4), 316 nm (ε 2.7×10^4 M^{-1} cm^{-1}). HRMS (EI) found *m*/*z* 766.4768 (M^+), calcd for $C_{41}H_{78}N_2Si_6$ 766.4781. Anal. Calc. for $C_{41}H_{78}N_2Si_6$: C, 64.15; H, 10.24; N, 3.65. Found: C, 63.90; H, 10.15; N, 3.64%.

4.8. Synthesis of TbtNHC(Me)CHC(Me)NDip (**5d**)

TbtNHC(Me)CHC(Me)NDip (**5d**) was prepared by the procedure similar to that for the synthesis of **5a** from **4** (130 mg, 200 μmol), $DipNH_2$ (380 μL, 200 μmol), and $TiCl_4$ (430 μL, 3.6 mmol) in toluene (30 mL). The purification was performed using GPLC (eluent: $CHCl_3$) and wet column chromatography (alumina, $CHCl_3$/hexane = 1/5). Yield: 3.2 mg (2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.10 (s, 18H, Si*Me*$_3$), 0.02 (s, 18H, Si*Me*$_3$), 0.07 (s, 18H, Si*Me*$_3$), 1.09 (d, $J = 6.9$ Hz, 6H, Dip *Me*), 1.21 (d, $J = 6.9$ Hz, 6H, Dip *Me*), 1.30 (s, 1H, Tbt *p*-benzyl), 1.67 (s, 3H, *Me*C(N)), 1.81 (s, 3H, *Me*C(N)), 1.91 (s, 2H, Tbt *o*-benzyl), 2.84 (sept, $J = 6.9$ Hz, 1H, Dip C*H*Me$_2$), 3.20 (sept, $J = 6.9$ Hz, 1H, Dip C*H*Me$_2$), 4.80 (s, 1H, 3-C*H*), 6.29 (br s, 1H, Tbt *m*-*H*), 6.39 (br s, 1H, Tbt *m*-*H*), 6.51–7.01 (m, 3H, Dip aromatic *H*), 11.1 (s, 1H, N*H*). MS (EI) found *m*/*z* 808 (M^+), calcd for $C_{44}H_{83}N_2Si_6$ 808.

4.9. Synthesis of [Li{TbtNC(Me)CHC(Me)NPh}] (**1a**)

To an ether solution (40 mL) of **5a** (1.65 g, 2.28 mmol) was added *n*-butyllithium (1.60 M hexane solution, 3.6 mL, 5.7 mmol) at 0 °C. The reaction mixture was grad-

ually warmed to 25 °C, and was stirred at the same temperature for 8 h. After removal of the solvents under reduced pressure, dry hexane was added to the residue in a glovebox. The colorless, moisture-sensitive precipitates were separated by filtration, and were washed with a small amount of hexane to afford pure **1a**. Yield: 1.35 g (81%). M.p. 232.3–233.1 °C (dec). ^{1}H NMR (300 MHz, C_6D_6) δ 0.03 (s, 18H, $SiMe_3$), 0.17 (s, 18H, $SiMe_3$), 0.20 (s, 18H, $SiMe_3$), 1.42 (s, 1H, Tbt *p*-benzyl), 1.91 (s, 3H, *Me*C(N)), 1.99 (s, 3H, *Me*C(N)), 2.12 (s, 2H, Tbt *o*-benzyl), 4.91 (s, 1H, 3-C*H*), 6.57 (br s, 2H, Tbt *m*-*H*), 6.94 (t, $J = 7.6$ Hz, 1H, Ph *p*-*H*), 7.01 (d, $J = 7.6$ Hz, 2H, Ph *o*-*H*), 7.26 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 2H, Ph *m*-*H*); ^{13}C NMR (75 MHz, C_6D_6) δ 0.0 (q, Si*Me*$_3$), 0.9 (q, Si*Me*$_3$), 1.6 (q, Si*Me*$_3$), 21.5 (d, Tbt *o*-benzyl), 22.9 (q, *Me*C(N)), 23.8 (q, *Me*C(N)), 29.7 (d, Tbt *p*-benzyl), 94.5 (d, 3-*C*H), 121.8 (d, Ph), 123.8 (d, Ph), 128.3 (d, Tbt C_m), 129.3 (d, Ph), 135.3 (s), 136.2 (s), 144.9 (s), 154.3 (s), 163.4 (s, *C*(N)), 164.6 (s, *C*(N)); ^{7}Li NMR (116 MHz, C_6D_6) δ 2.31. Anal. Calc. for $C_{38}H_{72}N_2LiSi_6$: C, 62.31; H, 9.91; N, 3.82. Found: C, 62.55; H, 9.99; N, 3.81%.

4.10. Synthesis of [Li{TbtNC(Me)CHC(Me)NMes}] (1c)

[Li{TbtNC(Me)CHC(Me)NMes}] (**1c**) was prepared from **5c** (2.55 g, 3.32 mmol) and *n*-butyllithium (1.60 M hexane solution, 5.2 mL, 8.3 mmol) in Et_2O (40 mL) by the procedure similar to that for the synthesis of **1a**. Yield: 2.18 g (85%). M.p. 255.3–256.1 °C (dec). ^{1}H NMR (300 MHz, C_6D_6) δ 0.06 (s, 18H, Si*Me*$_3$), 0.18 (s, 18H, Si*Me*$_3$), 0.22 (s, 18H, Si*Me*$_3$), 1.43 (s, 1H, Tbt *p*-benzyl), 1.76 (s, 3H, *Me*C(N)), 1.90 (s, 3H, *Me*C(N)), 2.20 (s, 2H, Tbt *o*-benzyl), 2.23 (s, 3H, Mes *p*-*Me*), 2.27 (s, 6H, Mes *o*-*Me*), 4.91 (s, 1H, 3-C*H*), 6.58 (br s, 2H, Tbt *m*-*H*), 6.92 (s, 2H, Mes *m*-*H*); ^{13}C NMR (75 MHz, C_6D_6) δ 0.1 (q, Si*Me*$_3$), 1.0 (q, Si*Me*$_3$), 1.7 (q, Si*Me*$_3$), 18.8 (q, Mes *o*-*Me*), 20.9 (q, Mes *p*-*Me*), 21.5 (d, Tbt *o*-benzyl), 23.0 (q, *Me*C(N)), 23.8 (q, *Me*C(N)), 29.7 (d, Tbt *p*-benzyl), 92.5 (d, 3-*C*H), 128.3 (d, Tbt C_m), 129.3 (d, Mes C_m), 130.1 (s), 131.2 (s), 135.5 (s), 136.1 (s), 145.3 (s), 148.9 (s), 164.3 (s, *C*(N)), 164.6 (s, *C*(N)); ^{7}Li NMR (116 MHz, C_6D_6) δ 2.33. Anal. Calc. for $C_{41}H_{77}N_2LiSi_6$: C, 63.66; H, 10.03; N, 3.62. Found: C, 63.36; H, 10.13; N, 3.77%.

4.11. Determination of the association constant for 1c and (1c · thf)

Solutions of **1c** and THF in C_6D_6 were prepared by mixing a 96.7 mM **1c**/C_6D_6 solution (200 μL, 19.3 μmol of **1c**), a 776 mM THF/C_6D_6 solution and C_6D_6 in a 5∅ NMR tube with the amount shown in Table 7. After the NMR tube was sealed, the ^{7}Li and ^{1}H NMR spectra were measured at 298 K. The amount of THF was evaluated by the integral of the THF peaks in the ^{1}H NMR spectrum.

4.12. Job's plot between 1c and THF

Solutions of **1c** and THF in C_6D_6 were prepared by mixing a 96.7 mM **1c**/C_6D_6 solution, a 776 mM THF/C_6D_6 [sum of the concentrations of **1c** and THF was 38.8 mM (constant)] and C_6D_6 (246 μL) in a 5∅ NMR tube with the ratio shown in Table 8. After the NMR tube was sealed, the ^{7}Li and ^{1}H NMR spectra were measured at 298 K. The amount of THF was evaluated by the integral of the THF peaks in the ^{1}H NMR spectrum.

Table 6
Crystal data and structure refinements for $TbtN_3$, **4**, **5a** and **5c**

Compound	**4**	**5a**	**5c**
Empirical formula	$C_{32}H_{65}NOSi_6 \cdot CHCl_3$	$C_{38}H_{72}N_2Si_6$	$C_{41}H_{78}N_2Si_6$
Formula weight	769.77	725.52	767.59
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a (Å)	9.0850(7)	9.0221(5)	9.2635(6)
b (Å)	10.8042(13)	10.7273(4)	12.9228(5)
c (Å)	23.694(3)	23.6488(9)	22.6743(14)
α (°)	93.432(4)	85.6337(16)	78.0296(16)
β (°)	94.083(3)	86.705(2)	86.5819(19)
γ (°)	99.704(3)	99.334(4)	70.018(5)
V (Å^3)	2280.5(4)	2246.26(17)	2495.3(2)
Z	2	2	2
D_{calc} (Mg m^{-3})	1.121	1.073	1.022
μ (Mo Kα) (mm^{-1})	0.383	0.212	0.194
Crystal size (mm)	$0.30 \times 0.30 \times 0.10$	$0.20 \times 0.20 \times 0.02$	$0.25 \times 0.15 \times 0.10$
Reflections collected	15153	20070	15817
Independent reflections (R_{int})	8133 (0.0510)	8259 (0.0415)	8303 (0.0675)
Parameters	436	439	469
R_1 [$I > 2\sigma(I)$]	0.0554	0.0400	0.0532
wR_2 (all data)	0.1377	0.1050	0.1224
Goodness-of-fit	1.002	1.006	1.006
Largest difference in peak and hole (e Å^{-3})	0.542 and −0.525	0.361 and −0.264	0.299 and −0.300

Table 7
The preparation of **1c**/THF/C_6D_6 solution for determining K_a

$[THF]_0/[\mathbf{1c}]_0$[a]	776 mM THF/C_6D_6 solution (μL)[b]	C_6D_6 (μL)
0.533	13	433
1.02	25	421
2.31	57	389
4.33	108	338
6.54	163	283
7.96	198	248
9.86	245	201

[a] A 96.7 mM **1c**/C_6D_6 solution (3.0 mL), which was prepared by dissolving **1c** (224 mg, 290 μmol) into C_6D_6, was used.
[b] A 776 mM THF/C_6D_6 solution (3.0 mL) was prepared by dissolving THF (189 μL, 2.33 mmol) into C_6D_6.

Table 8
The preparation of **1c**/THF/C_6D_6 solution for Job's plot

Mole fractions of **1c**	96.7 mM **1c**/C_6D_6 solution (μL)[a]	96.7 mM THF/C_6D_6 solution (μL)[b]
0.20	80	320
0.30	120	280
0.40	160	160
0.50	200	200
0.60	240	160
0.70	280	120
0.80	320	80

[a] A 96.7 mM **1c**/C_6D_6 solution (2.0 mL) was prepared by dissolving **1c** (150 mg, 194 μmol) into C_6D_6.
[b] A 96.7 mM THF/C_6D_6 solution (10.0 mL) was prepared by dissolving THF (79 μL, 967 μmol) into C_6D_6.

4.13. Synthesis of [Na{TbtNC(Me)CHC(Me)NMes}(thf)] (6c)

To a THF solution (4 mL) of **4a** (100 mg, 130 μmol) was added NaH (31.3 mg, 1.30 mmol). The reaction mixture was stirred for 3 days. After removal of the solvents under reduced pressure, dry benzene was added to the residue in a glovebox. Insoluble inorganic salts were removed by filtration thorough Celite®. The removal of the solvent from the filtrate gave **6c**. Yield: 90.7 mg (81%). M.p. 221.1–223.3 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6) δ 0.14 (s, 18H, Si*Me*$_3$), 0.21 (s, 18H, Si*Me*$_3$), 0.27 (s, 18H, Si*Me*$_3$), 1.21 (br, 4H, thf β-*H*), 1.45 (s, 1H, Tbt *p*-benzyl), 1.79 (s, 3H, *Me*), 1.95 (s, 3H, *Me*), 2.24 (s, 3H, *Me*), 2.26 (s, 6H, Mes *o*-*Me*), 2.43 (s, 2H, Tbt *o*-benzyl), 3.14 (br, 4H, thf α-*H*), 4.76 (s, 1H, 3-C*H*), 6.59 (br s, 2H, Tbt *m*-*H*), 6.85 (s, 2H, Mes *m*-*H*); ^{13}C NMR (75 MHz, C_6D_6) δ 0.9 (q, Si*Me*$_3$), 1.8 (q, Si*Me*$_3$), 2.0 (q, Si*Me*$_3$), 18.8 (q, Mes *o*-*Me*), 20.7 (q, Mes *p*-*Me*), 21.5 (d, Tbt *o*-benzyl), 22.9 (q, *Me*C(N)), 25.3 (q, *Me*C(N)), 26.3 (t, thf C_β), 29.6 (d, Tbt *p*-benzyl), 66.0 (t, thf C_α), 91.5 (d, 3-*C*H), 128.2 (d, Tbt C_m), 129.1 (d, Mes C_m), 130.3 (s, Mes C_o), 133.5 (s), 135.7 (s, Tbt C_o), 136.2 (s), 147.8 (s), 149.9 (s), 162.2 (s, *C*(N)), 162.8 (s, *C*(N)). Anal. Calc. for $C_{45}H_{85}N_2ONaSi_6$: C, 62.72; H, 9.94; N, 3.25. Found: C, 62.99; H, 10.13; N, 3.55%.

4.14. [K{TbtNC(Me)CHC(Me)NMes}(thf)] (7c)

[K{TbtNC(Me)CHC(Me)NMes}(thf)] (**7c**) was prepared from **5c** (100 mg, 130 μmol) and KH (52.2 mg, 1.30 mmol) in Et_2O (4 mL) by the procedure similar to that for the synthesis of **6c**. Yield: 98.1 mg (86%). M.p. 232.3–233.1 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6) δ 0.12 (s, 18H, Si*Me*$_3$), 0.22 (s, 18H, Si*Me*$_3$), 0.27 (s, 18H, Si*Me*$_3$), 1.40 (br, 4H, thf β-*H*), 1.41 (s, 1H, Tbt *p*-benzyl), 1.42 (s, 3H, *Me*), 1.88 (s, 3H, *Me*), 2.17 (s, 6H, Mes *o*-*Me*), 2.29 (s, 3H, *Me*), 2.30 (s, 2H, Tbt *o*-benzyl), 3.14 (br, 4H, thf α-*H*), 4.60 (br s, 1H, 3-C*H*), 6.55 (br s, 2H, Tbt *m*-*H*), 6.93 (s, 2H, Mes *m*-*H*); ^{13}C NMR (75 MHz, C_6D_6) δ 1.1 (q, Si*Me*$_3$), 1.7 (q, Si*Me*$_3$), 2.0 (q, Si*Me*$_3$), 18.9 (q, Mes *o*-*Me*), 20.9 (q, Mes *p*-*Me*), 21.1 (d, Tbt *o*-benzyl), 23.1 (t, thf C_β), 23.8 (q, *Me*C(N)), 26.4 (q, *Me*C(N)), 29.3 (d, Tbt *p*-benzyl), 65.9 (t, thf C_α), 90.3 (d, 3-*C*H), 128.3 (d, Tbt C_m), 129.0 (d, Mes C_m), 129.7 (s, Mes C_o), 133.6 (s), 135.0 (s, Tbt C_o), 135.5 (s), 148.1 (s), 151.7 (s), 161.8 (s, *C*(N)), 162.1 (s, *C*(N)). Anal. Calc. for $C_{45}H_{85}N_2OKSi_6$: C, 61.57; H, 9.76; N, 3.19. Found: C, 61.47; H, 9.66; N, 3.09%.

4.15. Reactions of 1c with t-BuONa

(1) 1.5 molar amount of sodium *tert*-butoxide. To a mixture of **1c** (39.6 mg, 51.7 μmol) and sodium *tert*-butoxide (7.5 mg, 77.6 μmol) in an NMR tube was added 0.6 mL of C_6D_6. After the NMR tube was sealed, the measurement of the ^{1}H NMR spectrum revealed the formation of a mixture of **1c** and **8c** (**1c**:**8c** = 38:62 as judged by the integral of the 3-CH peaks in the ^{1}H NMR spectrum). (2) 2.0 molar amount of sodium *tert*-butoxide. The experiment was performed by the procedure similar to the case mentioned above using the sample prepared from **1c** (60.0 mg, 77.6 μmol), sodium *tert*-butoxide (14.9 mg, 155 μmol) and C_6D_6 (0.6 mL). The ^{1}H NMR spectrum showed the formation of a mixture of **1c** and **8c** (**1c**:**8c** = 17:83). (3) 10 molar amount of sodium *tert*-butoxide. The experiment was performed by the procedure similar to the case mentioned above using the sample prepared from **1c** (40.0 mg, 51.7 μmol), sodium *tert*-butoxide (49.7 mg, 517 μmol) and C_6D_6 (0.6 mL). The ^{1}H NMR spectrum showed the formation of a mixture of **1c** and **8c** (**1c**:**8c** = 9:91). [Na{TbtNC(Me)CHC(Me)NMes}] (**8c**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.00 (s, 18H, Si*Me*$_3$), 0.22 (s, 18H, Si*Me*$_3$), 0.29 (s, 18H, Si*Me*$_3$), 1.41 (s, 1H, Tbt *p*-benzyl), 1.78 (s, 3H, *Me*C(N)), 1.90 (s, 3H, *Me*C(N)), 2.28 (br s, 11H, Tbt *o*-benzyl + Mes *Me*), 4.73 (s, 1H, 3-C*H*), 6.52 (br s, 2H, Tbt *m*-*H*), 6.97 (s, 2H, Mes *m*-*H*).

4.16. Reactions of 1c with t-BuOK

To a mixture of **1c** (40.2 mg, 51.7 μmol) and potassium *tert*-butoxide (8.7 mg, 77.6 μmol) in an NMR tube was

added 0.6 mL of C_6D_6. After the NMR tube was sealed, the measurement of the ^1H NMR spectrum revealed the formation of a mixture of **1c** and **9c** (**1c**:**9c** = 7:93 as judged by the integral of the 3-CH peaks in the ^1H NMR spectrum). [K{TbtNC(Me)CHC(Me)NMes}] (**9c**): ^1H NMR (300 MHz, C_6D_6) δ 0.09 (s, 18H, Si*Me*$_3$), 0.21 (s, 18H, Si*Me*$_3$), 0.26 (s, 18H, Si*Me*$_3$), 1.45 (s, 1H, Tbt *p*-benzyl), 1.88 (s, 3H, *Me*C(N)), 1.90 (s, 3H, *Me*C(N)), 2.26 (br s, 5H, Tbt *o*-benzyl + Mes *p*-*Me*), 2.30 (s, 6H, Mes *o*-*Me*), 4.62 (br s, 1H, 3-C*H*), 6.53 (br s, 2H, Tbt *m*-*H*), 6.95 (s, 2H, Mes *m*-*H*).

4.17. X-ray crystallography

Single crystals of **1c** were grown by the slow evaporation of the saturated C_6H_6 solution at 25 °C under Ar atmosphere. Single crystals of **4**, **5a** and **5c** were grown by the slow evaporation of the saturated $CHCl_3/CH_3CN$ solution at 25 °C. The preparation of all samples consisted of coating the crystal with silicon grease, mounting it on a glass fiber, and placing it under a cold stream of N_2 on the diffractometer. The intensity data of **1c**, **4**, **5a** and **5c** were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71071$ Å) to $2\theta_{max} = 50°$ at 93 K. The structures of **1c**, **4**, **5a** and **5c** were solved by direct method (SIR-97) [29]. All crystallographic data were refined by full-matrix least-squares procedure on F^2 for all reflections (SHELXL-97) [30]. All the non-hydrogen atoms of **1c**, **4**, **5a** and **5c** were placed using AFIX instruction.

5. Supplementary material

Crystallographic data for the structural analysis of **1c**, **4**, **5a**, and **5b** have been deposited with the Cambridge Crystallographic Data Centre, as CCDC Nos. 221891, 299693, 299694, and 299695, respectively. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (int. code) +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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