A Monomeric, Donor-free Lithium Complex with a New Overcrowded *β*-Diketiminato Ligand

Nobuhiro Takeda, Hirofumi Hamaki, and Norihiro Tokitoh*
Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011

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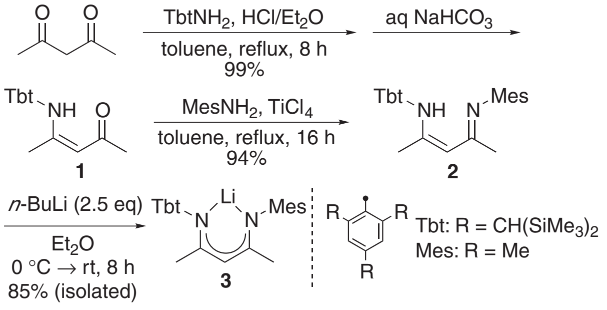
A monomeric, donor-free complex of lithium with a new overcrowded *β*-diketiminato ligand, [Li{TbtNC(Me)CHC(Me)-NMes}] (Tbt = 2,4,6-[CH(SiMe$_3$)$_2$]$_3$C$_6$H$_2$, Mes = mesityl), was synthesized and isolated as colorless crystals. Its unique structure was revealed by X-ray structural analysis to be compared with those of donor-coordinated lithium *β*-diketiminates.

Recently, much attention has been paid to the chemistry of *β*-diketiminato ligands.[1] In particular, *β*-diketiminato ligands having bulky substituents on the nitrogen atoms have been successfully applied to the synthesis of various types of complexes of main group elements and transition metals.[2] Lithium *β*-diketiminates have been most widely used as ligand sources for the preparation of *β*-diketiminato complexes, and their properties have been studied extensively. However, there is no example for X-ray structural analysis of monomeric, donor-free lithium *β*-diketiminates, since they have a tendency to dimerize or oligomelize. Even [Li{[DipNC(Me)]$_2$CH}] bearing bulky Dip (2,6-diisopropylphenyl) groups reportedly exists as a dimer or a dodecamer in the crystalline states.[3] On the other hand, we have succeeded in the synthesis and isolation of a variety of reactive species containing a low-coordinated heavier main group element by taking advantage of 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, which efficiently protects them from the dimerization and oligomerization.[4] In this paper, we present the synthesis of a monomeric, donor-free lithium complex with a new *β*-diketiminato ligand bearing a Tbt group and also the elucidation of its ability at the complexation with solvents.

Refluxing of a toluene solution of TbtNH$_2$, acetylacetone (10 equiv.), and HCl/Et$_2$O (0.5 equiv.) resulted in the almost quantitative formation of enaminoketone **1** via monocondensation reaction (Scheme 1). Further condensation with MesNH$_2$ in the presence of TiCl$_4$ (0.7 equiv.) gave an unsymmetrically substituted enaminoimine **2** in 94% yield. An ether solution of **2** was treated with 2.5 molar amounts of *n*-butyllithium at 0 °C, and then the reaction mixture was stirred at room temperature for 8 h. The subsequent exchange of the solvents to dry hexane resulted in the formation of colorless, moisture-sensitive precipitates of lithium *β*-diketiminate **3**. Since **3** was insoluble in hexane, simple filtration of the mixture yielded **3** as a pure material in 85% yield.[5]



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

The X-ray structural analysis of **3** 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 **3** (Figure 1).[6] To the best of our knowledge, this is the first structural analysis of monomeric, donor-free lithium *β*-diketiminate. It should be noted that [Li{[DipNC(Me)]$_2$CH}],[3] [Li{(Me$_3$Si)NC(R^1)CHC(R^2)N-(SiMe$_3$)}] (R^1 = R^2 = Ph;[7] R^1 = Ph, R^2 = *t*-Bu;[8] 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$_3$)[10] 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 **3**. It should be additional interest for the newly obtained complex **3** that **3** 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.[11] The C$_3$N$_2$Li ring of **3** 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. In addition, the N–C and C–C bond lengths are intermediate values between the typical single [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.[12] These features observed in the C$_3$N$_2$Li ring of **3** clearly indicate that the *π*-bondings in the C$_3$N$_2$Li ring are delocalized as well as those of some donor-coordinated lithium *β*-diketiminates, e.g. [Li{(2-NC$_5$H$_4$)$_2$CH}(thf)$_2$],[13] [Li{[DipNC-(*t*-Bu)]$_2$CH}(thf)],[14] [Li{[DipNC(Me)]$_2$CH}(solv)] (solv = thf or OEt$_2$),[3] and [Li{[Et$_2$N(CH$_2$)$_2$NC(Me)]$_2$CH}],[15] and the dimer and dodecamer of [Li{[DipNC(Me)]$_2$CH}].[3] The Li–N distances are close to those of lithium *β*-diketiminates having weak Li–O or Li···CH interactions such as [Li{[DipNC(*t*-Bu)]$_2$CH}(thf)] [1.927(6) Å],[14] [Li{[DipNC(Me)]$_2$CH}(Et$_2$O)] [1.917(4), 1.912(4) Å],[3] and [Li{[DipNC(Me)]$_2$CH}]$_n$ [$n = 2$ or 12: 1.892(7)–1.919(7) Å],[3] and shorter than those of strong donor-coordinated lithium *β*-diketiminates, e.g. [Li{[(Me$_3$Si)NC(Ph)]$_2$-CH}(thf)$_2$] [av 2.02(2) Å],[8] [Li{[DipNC(Me)]$_2$CH}(thf)]

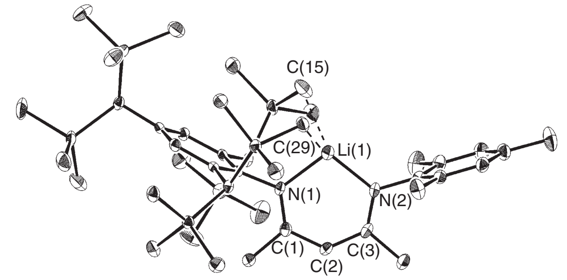


Figure 1. ORTEP drawing of **3** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Li(1)–N(1) 1.917(6), Li(1)–N(2) 1.915(6), N(1)–C(1) 1.322(4), N(2)–C(3) 1.328(4), C(1)–C(2) 1.425(4), C(2)–C(3) 1.418(4), Li(1)···C(15) 2.835(6), Li(1)···C(29) 2.670(5), N(2)–Li(1)–N(1) 103.8(3), Li(1)–N(1)–C(1) 119.0(2), Li(1)–N(2)–C(3) 117.9(3), N(1)–C(1)–C(2) 123.7(3), C(1)–C(2)–C(3) 130.1(3), N(2)–C(3)–C(2) 125.1(3).

[1.958(5) Å],[3] and [Li{[Et$_2$N(CH$_2$)$_2$NC(Me)]$_2$CH}] [1.968(3), 1.974(3) Å].[15]

Interestingly, the solvent-free complex **3** was obtained, when the lithiation reaction of **2** was performed in Et$_2$O. Furthermore, the addition of Et$_2$O to a C$_6$D$_6$ solution of **3** showed very little change in the ^{1}H and ^{7}Li NMR spectra, and the evaporation of an ether solution of **3** gave only solvent-free **3**. By contrast, the addition of THF instead of Et$_2$O lead to the different results, which are most likely attributable to the greater ability of THF as a donor in comparison to Et$_2$O.[3] When 1.3 molar amount of THF was added to the C$_6$D$_6$ solution of **3**, the ^{7}Li NMR signal for the mixture was shifted to up-field region (1.89 ppm) compared with that of **3** (2.33 ppm). In the ^{1}H NMR spectrum of the mixture, the signals assigned to the THF part were observed at lower field than those of free THF. The addition of 9.6 molar amounts of THF to the solution of **3** in C$_6$D$_6$ resulted in the appearance of the ^{7}Li signal at much higher field (1.69 ppm) along with the ^{1}H NMR resonances for the THF moiety being close to those of free THF. These results suggest the rapid equilibrium between the free complex **3** plus THF and the THF adduct [Li{TbtNC(Me)CHC(Me)NMes}(thf)] (**4**) at room temperature within the time scale of NMR spectroscopy. That is, the addition of a large amount of THF may lead to the increase in the ratio of **4** compared to **3** together with the augmentation in the ratio of free THF relative to the coordinated THF in **4**. When the C$_6$D$_6$ solution containing **3** and THF was fully evaporated, the lithium β-diketiminate coordinated by one THF molecule **4** was isolated as colorless solids.[16] Although a single crystal of **4** suitable for X-ray structural analysis has not been obtained yet, we have succeeded in the crystallographic analysis of the analogously prepared lithium complex having Tbt and Ph groups on the N-terminals, [Li{TbtNC(Me)CHC(Me)NPh}(thf)] (**5**).[6]

Figure 2 shows that **5** has a planar C$_3$N$_2$Li ring, in which the two sets of C–C and N–C distances are very similar to each other, indicating the delocalization of the π-bondings, as well as that of **3**. The LiN$_2$O moiety has nonplanar structure (the sum of angles around Li(1): 353.8°), and the coordinated O(1) atom leans to the side of phenyl group as judged by the remarkably larger N(1)–Li(1)–O(1) bond angle than the N(2)–Li(1)–O(1) bond angle. By contrast, the reported lithium β-diketiminates coordinated with one THF molecule, [Li{[DipNC(R)]$_2$CH}(thf)] (R = Me,[3] t-Bu[14]), have a trigonal planar geometry around the lithium atom with a narrower N–Li–N bond angle. This largely distorted T-shaped structure at the lithium atom of **5** is probably due to the severe repulsion between the extremely bulky Tbt group and the coordinated THF molecule. In addition, the small deviation of the O(1) atom from the C$_3$N$_2$Li ring plane in the opposite direction toward the C(18) atom may be explained in terms of the intramolecular Li···CH$_3$ interaction between the Li(1) atom and the C(18)H$_3$ moiety. The bond distance of O(1)–Li(1) for **5** is much longer than those of [Li{[DipNC(R)]$_2$CH}(thf)] (R = Me: 1.790(7) Å,[3] t-Bu: 1.910(6) Å[14]), strongly suggesting the weaker coordination of THF to the lithium in **5**. In addition, the N(2)–Li(1) bond length of **5** is close to those of **3**, while the N(1)–Li(1) bond length being longer. This result indicates that the coordination of THF to the lithium atom of **5** mainly affects the distance of the N(1)–Li(1) bond situated at the pseudo-*trans*-position of the O(1)–Li(1) bond, rather than that of the N(2)–Li(1) bond at the pseudo-*cis*-position.

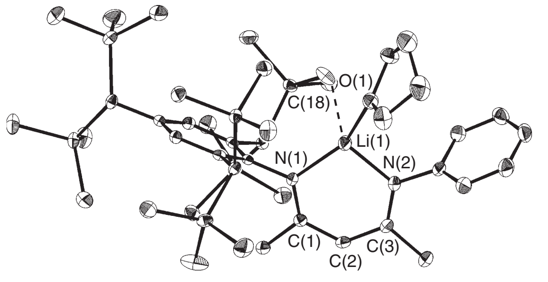


Figure 2. ORTEP drawing of **5** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Li(1)–N(1) 1.976(4), Li(1)–N(2) 1.923(4), Li(1)–O(1) 1.965(4), N(1)–C(1) 1.330(3), N(2)–C(3) 1.326(3), C(1)–C(2) 1.413(3), C(2)–C(3) 1.404(3), Li(1)···C(18) 2.809(4); N(1)–Li(1)–N(2) 100.9(2), N(1)–Li(1)–O(1) 148.5(2), N(2)–Li(1)–O(1) 104.4(2), Li(1)–N(1)–C(1) 118.1(2), Li(1)–N(2)–C(3) 121.1(2), N(1)–C(1)–C(2) 125.2(2), C(1)–C(2)–C(3) 130.6(2), N(2)–C(3)–C(2) 123.2(2).

The unique coordination of THF in **5** implies that transition metal and main group element complexes having this β-diketiminato ligand would show unique properties. Further investigation on the β-diketiminato lithium complex **3** and the application of this ligand to the syntheses of other metal complexes are currently in progress.

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5 Spectral data of **3**: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.06 (s, 18H), 0.18 (s, 18H), 0.22 (s, 18H), 1.43 (s, 1H), 1.76 (s, 3H), 1.90 (s, 3H), 2.20 (s, 2H), 2.23 (s, 3H), 2.27 (s, 6H), 4.91 (s, 1H), 6.58 (br s, 2H), 6.92 (s, 2H); ^{7}Li NMR (116 MHz, C$_6$D$_6$) δ 2.33.

6 Crystal data of **3**: C$_{41}$H$_{77}$LiN$_2$Si$_6$; $M_\mathrm{r} = 773.53$, triclinic, $P\bar{1}$ (no. 2), $a = 9.4485(11)$, $b = 13.2943(11)$ Å, $c = 20.5252(18)$ Å, $\alpha = 99.097(7)$, $\beta = 91.883(8)$, $\gamma = 97.439(8)^\circ$, $V = 2520.6(4)$ Å^3, $Z = 2$, $T = 103(2)$ K, $D_\mathrm{calcd} = 1.019\,\mathrm{g\,cm^{-1}}$, independent reflections 8165 ($R_\mathrm{int} = 0.0362$), R_1 [$I > 2\sigma I$] $= 0.0566$, wR_2 (all data) $= 0.1239$. CCDC-221891. Crystal data of **5**: C$_{42}$H$_{79}$LiN$_2$OSi$_6$; $M_\mathrm{r} = 803.55$, monoclinic, $P2_1/c$ (no. 14), $a = 13.041(2)$, $b = 21.711(4)$ Å, $c = 18.047(3)$ Å, $\beta = 98.7507(19)^\circ$, $V = 5050.2(15)$ Å^3, $Z = 4$, $T = 93(2)$ K, $D_\mathrm{calcd} = 1.057\,\mathrm{g\,cm^{-1}}$, independent reflections 8797 ($R_\mathrm{int} = 0.0243$), R_1 [$I > 2\sigma I$] $= 0.0457$, wR_2 (all data) $= 0.1169$. CCDC-221892.

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16 Spectral data of **4**: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.14 (s, 18H), 0.20 (s, 18H), 0.25 (s, 18H), 1.19 (m, 4H), 1.44 (s, 1H), 1.74 (s, 3H), 1.91 (s, 3H), 2.23 (s, 5H), 2.24 (s, 6H), 3.31 (m, 4 H), 4.91 (s, 1 H), 6.59 (br s, 2 H), 6.87 (s, 2 H); ^{7}Li NMR (116 MHz, C$_6$D$_6$) δ 2.01.

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