

Synthesis and characterisation of two monomeric crystalline thallium(I) β -diketiminates†

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Treatment of the appropriate sodium β -diketimate NaL or NaL' with an equivalent portion of TlCl in thf under mild conditions furnishes in good yield the first structurally characterised thallium β -diketiminates: the monomeric, orange, crystalline Tl(I) complexes TIL and TIL' [L = {N(SiMe₃)C(Ph)}₂CH, L' = {N(C₆H₃Prⁱ_{2-2,6})C(H)}₂CPh].

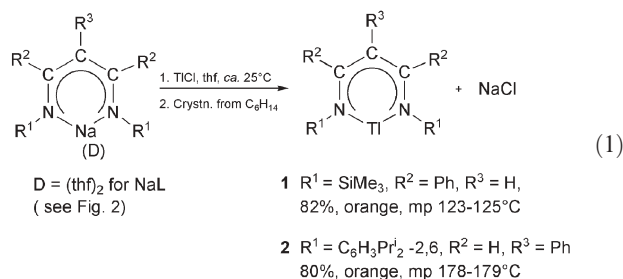
Although the +1 oxidation state is common for inorganic thallium compounds, low molecular aggregated organic univalent Tl compounds are rare.^{1,2} Crystalline monomers include the singly coordinated organothallium compound Tl[C₆H₃(C₆H₂Prⁱ_{3-2',4',6'})_{2-2,6}],³ and a series of triply *N*-coordinated Tl tris(pyrazolyl)borates, the first of which was Tl[$\overline{\text{N}(\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{C}(\text{H})\text{N})}_3\text{BH}$] [av. *l*(Tl–N) 2.585 Å],⁴ one

modification of Tl[$\eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5$],⁵ and [Mg(pmdeta)]Tl($\eta^5\text{-C}_5\text{H}_5$)]₂.⁶ Even with bulky ligands, aggregation is a feature, involving formation of (i) Tl–Tl bonds [the first example was Tl₂{Si(SiMe₃)₃}₂, with *l*(Tl–Tl) 2.9142(5) Å];⁷ (ii) close Tl...Tl contacts, as in [Tl{(NBu^t)₂SiMe₂}₃]₂, *l*(Tl...Tl) 3.16 ± 0.03 Å;⁸ (iii) π -arene...Tl interactions, as in [Tl{N(SiMe₃)(C₆H₃Prⁱ_{2-2,6})}₄, Cent(η -arene)...Tl 3.11 Å],⁹ or (iv) ligand-bridged dimers, as in crystalline [Tl{ μ -N(SiMe₃)₂}₂],^{10a} which dissociates into the monomer in the vapour.^{10b}

Metal β -diketiminates are increasingly useful spectator ligands.¹¹ Notable illustrations are provided by the isolation of the first monomeric Al(I) and Ga(I) complexes ML'' [M = Al,^{12a} Ga;^{12b} L'' = {N(C₆H₃Prⁱ_{2-2,6})C(Me)}₂CH]; although InL'' proved elusive, it has also recently been obtained in modest yield, but was photolabile and slowly decomposed in the dark in an aromatic solvent.^{12c}

We now report the first structurally characterised crystalline Tl β -diketiminates, the monomeric TIL and TIL' [L = {N(SiMe₃)C(Ph)}₂CH, L' = {N(C₆H₃Prⁱ_{2-2,6})C(H)}₂CPh]. The only other Tl β -diketimate in the literature is TIL''', employed as a precursor to [CuL'''($\eta^2\text{-CH}_2\text{=CHR}$)] [L''' = {N(C₆H₃Me_{2-2,6})C(Me)}₂CH, R = H or Ph].¹³

Treatment of thallium(I) chloride with NaL† or NaL'† in thf and crystallisation from hexane yielded the crystalline complex TIL (1) or TIL' (2) in high yield, eqn. (1).‡



The orange, sharp melting, crystalline β -diketiminates **1** and **2** gave satisfactory microanalyses,‡ and multinuclear NMR§ and mass‡ spectra as well as single crystal X-ray data¶.

A feature of the ¹³C{¹H} NMR spectra of **1** and **2** and the ¹H NMR spectrum of **2** was the presence of doublets due to coupling to the ²⁰³Tl (29%) and ²⁰⁵Tl (71%) spin-½ isotopes.§ These splittings were large but unexceptional for Tl compounds.¹⁴ For example, the ¹H NMR spectrum of **2** in toluene-d⁸ or C₆D₆ showed ³J(¹H–^{203,205}Tl) = 127.3 Hz. The individual peaks of the doublets were broad due to efficient CSA (Chemical Shift Anisotropy) relaxation of the Tl isotopes, as confirmed by the observation that the broadening increased when changing from a 300 MHz to a 500 MHz spectrometer and that upon cooling the doublets coalesced to broad singlets at 213 K as Tl relaxation became yet more efficient. Coupling of ¹H or ²⁹Si signals was not observed in the ¹H or ²⁹Si{¹H} (INEPT) NMR spectra of **1** even at 328 K using the lower field spectrometer; the signals were sufficiently broad that coupling of < ca. 20 Hz would not have been noted. {For TIL''', coupling was observed in the ¹³C{¹H} NMR spectrum [⁴J(¹³C–Tl) 9.4, ³J(¹³C–Tl) 44.7 (endocyclic) and 43.4 (CH₃) Hz], but not the ¹H NMR spectrum¹³}. The CH₃ ¹H NMR signals of **2** appeared as doublets at 293 K, attributed to restricted rotation about the N–C_{ipso} and/or C–C (e.g., C15–C19) bonds.

Crystalline **1** (Fig. 1) is a discrete monomer.¶ The TlN1C1C2C3N2 ring has the boat conformation. The Tl, C2, Si1, Si2, C4 and C10 atoms are –1.23, –0.15, +0.69, +0.62, +0.14 and +0.18 Å out of the N1C1C3N2 plane. The angle between the latter plane and the C1C2C3, TlN1N2, and the C4 or C10 phenyl plane is 14.5, 40.4, and 50 or 46°, respectively. The bond lengths and angles are similar to those of [NaL(thf)₂] (see suppl. data), shown schematically in Fig. 2. There is an $\eta^3\text{-Ph}\cdots\text{Tl}''$ close contact (3.634, 3.304 and 3.508 Å for C10, C15 and C14, respectively; Tl...Tl(2 – x, 1 – y, 1 – z) 6.464 Å) and no significant Tl...CH₃ contacts, while the Tl...Tl(1 – x, 1 – y, 1 – z) distance of 4.21 Å is well outside any possible bonding interaction.

† Electronic supplementary information (ESI) available: (i) synthesis of NaL(thf)₂ and NaL'; (ii) X-ray data for **1**, **2** and NaL(thf)₂. See <http://www.rsc.org/suppdata/cc/b4/b413666g/>

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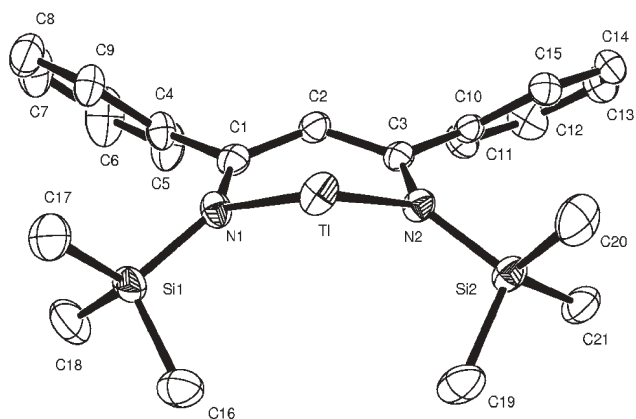


Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): TI–N1 2.456(3), TI–N2 2.449(3), N1–C1 1.330(5), N2–C3 1.314(5), C1–C2 1.408(6), C2–C3 1.416(5), C1–C4 1.513(5), C3–C10 1.502(5), N1–Si1 1.736(3), N2–Si2 1.744(3) Å; N1–TI–N2 78.0(1), TI–N1–C1 116.5(2), TI–N2–C3 117.0(3), N1–C1–C2 126.6(4), N2–C3–C2 126.3(4), C1–C2–C3 128.5(3)°.

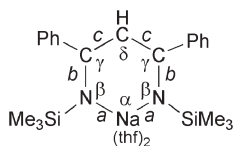


Fig. 2 Molecular structure of crystalline [NaL(thf)₂] with selected bond lengths (Å) and angles (°): *a* 2.358(6), *b* 1.341(8), *c* 1.402(7) Å; α 87.6(3), β 121.4(4), γ 127.5(6), δ 134.3(8)°.

Crystalline **2** (Fig. 3) is a monomer, but has a nearer neighbouring molecule than **1**, the TI···TI' distance being 3.76 Å.¶ The TI, C4, C10 and C22 atoms are –0.48, –0.10, +0.22 and +0.12 Å out of the NIC1C2C3N2 plane. The angle between the latter plane and the C10, C22 and C4 phenyl planes

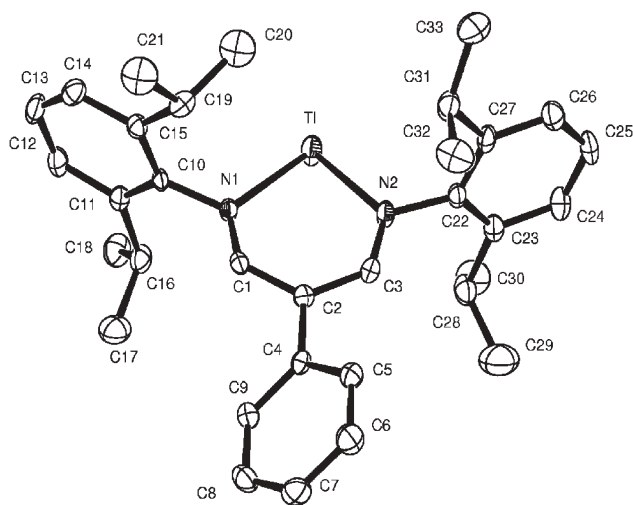


Fig. 3 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): TI–N1 2.471(3), TI–N2 2.423(3), N1–C1 1.311(4), N2–C3 1.309(5), C1–C2 1.413(5), C2–C3 1.411(5), C2–C4 1.487(5), N1–C10 1.430(4), N2–C22 1.439(4) Å; N1–TI–N2 76.20(9), TI–N1–C1 128.6(2), TI–N2–C3 128.6(2), N1–C1–C2 128.4(3), N2–C3–C2 128.8(3), C1–C2–C3 125.0(3)°.

are 89°, 84° and 36°, respectively. The endocyclic bond lengths are closely similar to those in **1**. The most marked differences in endocyclic bond angles are those centred at the nitrogen atoms, which are more than 10° wider in **2** than in **1**, while the angle at C2 is 3.5° narrower and at C1 or C3 *ca.* 2° wider than in **1**. The TI···C20 distance is 3.88 Å, which may imply a weak TI···HC agostic interaction. The bonding in the β -diketiminato ligand of both **1** and **2** shows significant π -delocalisation.

In summary, we have prepared the first structurally characterised β -diketiminates of thallium: the monomeric, crystalline complexes TI{[N(R¹)C(R²)₂CR³]} (**1**: R¹ = SiMe₃, R² = Ph, R³ = H; and **2**: R¹ = C₆H₃Pr¹₂-2,6, R² = H, R³ = Ph); they are potentially useful as convenient precursors for a wider range of compounds (*cf.* ref. 13). Compounds **1** and **2** are also noteworthy in being extremely rare examples of monomeric organic thallium(I) compounds, and having the low metal coordination number of two.

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Notes and references

‡ *Synthesis*: A solution of NaL (see ESI) (0.68 g, 1.75 mmol) in thf (15 ml) was added to a suspension of TiCl₄ (0.42 g, 1.75 mmol) in thf (5 ml) at ambient temperature. The mixture was stirred for *ca.* 12 h, then filtered. The filtrate was concentrated and the residue was crystallised from hexane at –27 °C, yielding orange crystals of **1** (0.82 g, 82%) (Found: C, 44.4; H, 5.08; N, 4.89. C₂₁H₂₉N₂Si₂Tl requires C, 44.2; H, 5.13; N, 4.91%), mp 123–125 °C; EI-MS: *m/z* (%) 571 (MH⁺, 25), 365 [(M – Ti)⁺, 100]. The orange, crystalline **2** (80%) (Found: C, 59.3; H, 6.25; N, 4.06. C₃₃H₄₁N₂Tl requires C, 59.2; H, 6.17; N, 4.18%), mp 178–179 °C, [EI-MS: *m/z* (%) 670 (M⁺, 59)], was obtained similarly from NaL' (see ESI) and TiCl₄.

§ *NMR Spectral data* (293 K, C₆D₆, Bruker DPX 300) **1**: ¹H: δ 7.38–7.41 (m, 4 H, Ph), 7.03–7.11 (m, 6 H, Ph), 5.25 (s, 1 H, CH), 0.04 (s, 18 H, SiMe₃); ¹³C{¹H}: δ 170.9 (d, ²J_{CTI} 48.4 Hz, C1, C3), 149.1 (d, ³J_{CTI} 46.8 Hz, C4, C10), 127.6–127.9 (3 singlets, Ph), 111.5 (d, ³J_{CTI} 103.3 Hz, C2), 3.48 (d, ³J_{CTI} 138.9 Hz, SiMe₃); ²⁹Si{¹H}: δ 0.9. **2**: ¹H: δ 8.47 (d, ³J_{HTI} 127.3 Hz, 2 H, NCH), 6.8–7.4 (m, 11 H, aromatic H), 3.29 (brs, 4 H, CHMe₂), 1.14 [d, ⁶J_{HTI} 6.9 Hz, 12 H, CH(CH₃)₂], 1.07 [d, ⁶J_{HTI} 6.9 Hz, 12 H, CH(CH₃)₂]; ¹³C{¹H}: δ 157.6 (C1, C3), 149.3 (br, C10), 143.8 (C4), 141.9 (C11, C15), [128.7, 126.5, 125.2 (C5, C6, C13)], 124.1 (C7), 123.7 (C12, C14), 28.3 (d, ⁴J_{CTI} 50 Hz, C16), 24.8 (CH₃), 24.6 (d, ⁵J_{CTI} 66 Hz, CH₃) (no signal for C2 observed). The numbering of the carbon atoms corresponds to Figs. 1 (1) or 3 (2).

¶ CCDC numbers: **1**: 249920; **2**: 249921; [NaL(thf)₂]: 249922. See <http://www.rsc.org/suppdata/cc/b4/b413666g/> for crystallographic data in .cif or other electronic format. **1**: C₂₁H₂₉N₂Si₂Tl, *M* = 570.01, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 9.9885(2), *b* = 19.6876(3), *c* = 12.2915(3) Å, β = 107.184(1)°, *U* = 2309.2(1) Å³, *Z* = 4, μ (Mo-K α , λ = 0.71073 Å) = 7.11 mm^{–1}, *T* = 173(2) K, *R*₁ = 0.025 for 3658 (*I* > 2 σ (*I*)) data, *wR*₂ = 0.067 (all data). **2**: C₃₃H₄₁N₂Tl, *M* = 670.05, triclinic, space group *P* $\bar{1}$ (No. 2), *a* = 9.3632(2), *b* = 12.0547(3), *c* = 13.6277(3) Å, α = 72.045(1), β = 84.102(1), γ = 88.813(1)°, *U* = 1455.41(6) Å³, *Z* = 2, μ (Mo-K α) = 5.57 mm^{–1}, *T* = 173(2) K, *R*₁ = 0.026 for 4919 (*I* > 2 σ (*I*)) data, *wR*₂ = 0.056 (all data).

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