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

**Yanxiang Cheng, Peter B. Hitchcock, Michael F. Lappert* and Meisu Zhou**

*Received (in Cambridge, UK) 7th September 2004, Accepted 15th November 2004*
*First published as an Advance Article on the web 15th December 2004*
**DOI: 10.1039/b413666g**

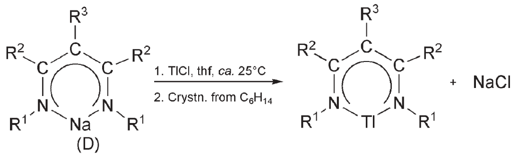
**Treatment of the appropriate sodium β-diketiminate NaL or NaL′ with an equivalent portion of TlCl in thf under mild conditions furnishes in good yield the first structurally characterised thallium β-diketiminates: the monomeric, orange, crystalline Tl(I) complexes TlL and TlL′ [L = $\{N(SiMe_3)C(Ph)\}_2CH$, L′ = $\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh$].**

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 $Tl[C_6H_3(C_6H_2Pr^i_3\text{-}2',4',6')_2\text{-}2,6]$,[3] and a series of triply *N*-coordinated Tl tris(pyrazolyl)borates, the first of which was $\mathrm{Tl}\left[\{\overline{\mathrm{NC(Bu^t)C(H)C(H)N}}\}_3\mathrm{BH}\right]$ [av. *l*(Tl–N) 2.585 Å],[4] one modification of $Tl[\eta^5\text{-}C_5(CH_2Ph)_5]$,[5] and $[Mg(pmdeta)][Tl(\eta^5\text{-}C_5H_5)_2]$.[6] Even with bulky ligands, aggregation is a feature, involving formation of (i) Tl–Tl bonds [the first example was $Tl_2\{Si(SiMe_3)_3\}_2$, with *l*(Tl–Tl) 2.9142(5) Å];[7] (ii) close Tl···Tl contacts, as in $[Tl\{(NBu^t)_2SiMe_2\}_3]_2$, *l*(Tl···Tl) 3.16 ± 0.03 Å;[8] (iii) π-arene···Tl interactions, as in $[Tl\{N(SiMe_3)(C_6H_3Pr^i_2\text{-}2,6)\}]_4$, Cent(η-arene)···Tl 3.11 Å];[9] or (iv) ligand-bridged dimers, as in crystalline $[Tl\{\mu\text{-}N(SiMe_3)_2\}]_2$,[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″ = $\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH$]; 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 TlL and TlL′ [L = $\{N(SiMe_3)C(Ph)\}_2CH$, L′ = $\{N(C_6H_3Pr^i_2\text{–}2,6)C(H)\}_2CPh$]. The only other Tl β-diketiminate in the literature is TlL‴, employed as a precursor to $[CuL'''(\eta^2\text{-}CH_2{=}CHR)]$ [L‴ = $\{N(C_6H_3Me_2\text{-}2,6)C(Me)\}_2CH$, R = H or Ph].[13]

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



(1)

D = $(thf)_2$ for NaL
( see Fig. 2)

**1** $R^1 = SiMe_3$, $R^2 = Ph$, $R^3 = H$,
82%, orange, mp 123-125°C

**2** $R^1 = C_6H_3Pr^i_2$ -2,6, $R^2 = H$, $R^3 = Ph$
80%, orange, mp 178-179°C

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 $^{13}C\{^1H\}$ NMR spectra of **1** and **2** and the $^1H$ NMR spectrum of **2** was the presence of doublets due to coupling to $^{203}Tl$ (29%) and $^{205}Tl$ (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 $C_6D_6$ showed $^3J(^1H\text{–}^{203,205}Tl)$ = 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 $^{29}Si$ signals was not observed in the $^1H$ or $^{29}Si\{^1H\}$ (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 TlL‴, coupling was observed in the $^{13}C\{^1H\}$ NMR spectrum [$^4J(^{13}C\text{–}Tl)$ 9.4, $^3J(^{13}C\text{–}Tl)$ 44.7 (endocyclic) and 43.4 ($CH_3$) Hz], but not the $^1H$ NMR spectrum[13]}. The $CH_3$ $^1H$ NMR signals of **2** appeared as doublets at 293 K, attributed to restricted rotation about the $N\text{–}C_{ipso}$ 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 $\eta^3$-Ph···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···$CH_3$ 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/

*m.f.lappert@sussex.ac.uk

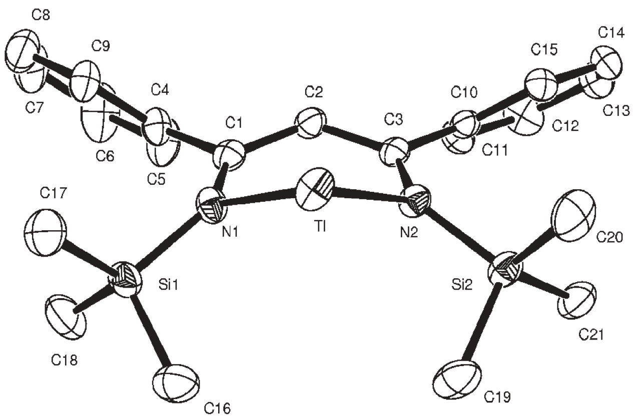


**Fig. 1** Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Tl–N1 2.456(3), Tl–N2 2.449(3), N1–C1 1.330(5), N2–C3 1.314(5), C1–C2 1.408(6), C2–C3 1.416(5), C1–C4 1.513(5), C3–C10 1.502(5), N1–Si1 1.736(3), N2–Si2 1.744(3) Å; N1–Tl–N2 78.0(1), Tl–N1–C1 116.5(2), Tl–N2–C3 117.0(3),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

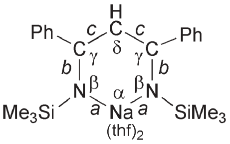


**Fig. 2** Molecular structure of crystalline [NaL(thf)$_2$] with selected bond lengths (Å) and angles (°): *a* 2.358(6), *b* 1.341(8), *c* 1.402(7) Å; α 87.6(3), β 121.4(4), γ 127.5(6), δ 134.3(8)°.

Crystalline **2** (Fig. 3) is a monomer, but has a nearer neighbouring molecule than **1**, the Tl···Tl′ distance being 3.76 Å.¶ The Tl, C4, C10 and C22 atoms are −0.48, −0.10, +0.22 and +0.12 Å out of the N1C1C2C3N2 plane. The angle between the latter plane and the C10, C22 and C4 phenyl planes 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 Tl···C20 distance is 3.88 Å, which may imply a weak Tl···HC agostic interaction. The bonding in the β-diketiminato ligand of both **1** and **2** shows significant π-delocalisation.

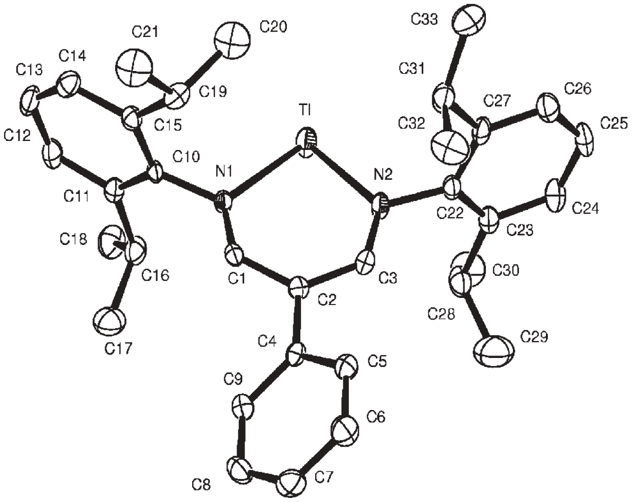


**Fig. 3** Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Tl–N1 2.471(3), Tl–N2 2.423(3), N1–C1 1.311(4), N2–C3 1.309(5), C1–C2 1.413(5), C2–C3 1.411(5), C2–C4 1.487(5), N1–C10 1.430(4), N2–C22 1.439(4) Å; N1–Tl–N2 76.20(9), Tl–N1–C1 128.6(2), Tl–N2–C3 128.6(2), N1–C1–C2 128.4(3),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

In summary, we have prepared the first structurally characterised β-diketiminates of thallium: the monomeric, crystalline complexes Tl[{N(R$^1$)C(R$^2$)}$_2$CR$^3$] (**1**: R$^1$ = SiMe$_3$, R$^2$ = Ph, R$^3$ = H; and **2**: R$^1$ = C$_6$H$_3$Pr$^i_2$-2,6, R$^2$ = H, R$^3$ = 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.

We thank the Royal Society for the award of a Sino-British (Y. C.) and a K. C. Wong (M. Z.) Fellowship, Dr R. Sablong for providing the data for NaL(thf)$_2$ (Fig. 2) and Drs A. G. Avent and A. V. Protchenko for useful discussions.

**Yanxiang Cheng, Peter B. Hitchcock, Michael F. Lappert* and Meisu Zhou**
*Chemistry Department, University of Sussex, Brighton, UK BN1 9QJ.*
*E-mail: m.f.lappert@sussex.ac.uk*

## 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 TlCl (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. $C_{21}H_{29}N_2Si_2Tl$ requires C, 44.2; H, 5.13; N, 4.91%), mp 123–125 °C; EI-MS: *m*/*z* (%) 571 (MH$^+$, 25), 365 [(M − Tl)$^+$, 100]. The orange, crystalline **2** (80%) (Found: C, 59.3; H, 6.25; N, 4.06. $C_{33}H_{41}N_2Tl$ 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 TlCl.

§ *NMR Spectral data* (293 K, $C_6D_6$, Bruker DPX 300) **1**: $^1$H: 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, SiMe$_3$); $^{13}$C{$^1$H}: δ 170.9 (d, $^2J_{\rm CTl}$ 48.4 Hz, C1, C3), 149.1 (d, $^3J_{\rm CTl}$ 46.8 Hz, (C4, C10)], 127.6–127.9 (3 singlets, Ph), 111.5 (d, $^3J_{\rm CTl}$ 103.3 Hz, C2), 3.48 (d, $^3J_{\rm CTl}$ 138.9 Hz, SiMe$_3$); $^{29}$Si{$^1$H}: δ 0.9. **2**: $^1$H: δ 8.47 (d, $^3J_{\rm HTl}$ 127.3 Hz, 2 H, NC*H*), 6.8–7.4 (m, 11 H, aromatic H), 3.29 (brs, 4 H, C*H*Me$_2$), 1.14 [d, $^6J_{\rm HTl}$ 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.07 [d, $^6J_{\rm HTl}$ 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$]; $^{13}$C{$^1$H}: 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, $^4J_{\rm CTl}$ 50 Hz, C16), 24.8 (CH$_3$), 24.6 (d, $^5J_{\rm CTl}$ 66 Hz, CH$_3$) (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**: $C_{21}H_{29}N_2Si_2Tl$, $M$ = 570.01, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 9.9885(2), $b$ = 19.6876(3), $c$ = 12.2915(3) Å, $\beta$ = 107.184(1)°, $U$ = 2309.2(1) Å$^3$, $Z$ = 4, $\mu$(Mo-Kα, $\lambda$ = 0.71073 Å) = 7.11 mm$^{-1}$, $T$ = 173(2) K, $R_1$ = 0.025 for 3658 ($I > 2\sigma(I)$) data, $wR_2$ = 0.067 (all data). **2**: $C_{33}H_{41}N_2Tl$, $M$ = 670.05, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 9.3632(2), $b$ = 12.0547(3), $c$ = 13.6277(3) Å, $\alpha$ = 72.045(1), $\beta$ = 84.102(1), $\gamma$ = 88.813(1)°, $U$ = 1455.41(6) Å$^3$, $Z$ = 2, $\mu$(Mo-Kα) = 5.57 mm$^{-1}$, $T$ = 173(2) K, $R_1$ = 0.026 for 4919 ($I > 2\sigma(I)$) data, $wR_2$ = 0.056 (all data).

1 C. Janiak, *Coord. Chem. Rev.*, 1997, **163**, 107.
2 L. H. Gade, *Dalton Trans.*, 2003, 267.
3 M. Niemeyer and P. P. Power, *Angew. Chem., Int. Ed.*, 1998, **37**, 1277.
4 A. H. Cowley, R. L. Geerts, C. M. Nunn and S. Trofimenko, *J. Organomet. Chem.*, 1989, **365**, 19.

5 H. Schumann, C. Janiak, M. A. Khan and J. J. Zuckerman, *J. Organomet. Chem.*, 1988, **354**, 7.

6 D. R. Armstrong, R. Herbst-Irmer, A. Kuhn, D. Moncrieff, M. A. Paver, C. A. Russell, D. Stalke, A. Steiner and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1774.

7 S. Henkel, K. W. Klinkhammer and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 681.

8 M. Veith, A. Spaniol, J. Pöhlmann, F. Gross and V. Huch, *Chem. Ber.*, 1993, **126**, 2625.

9 (*a*) H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 893; (*b*) S. D. Waeszada, T. Belgardt, M. Noltemeyer and H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1351.

10 (*a*) K. W. Klinkhammer and S. Henkel, *J. Organomet. Chem.*, 1994, **480**, 167; (*b*) A. Haaland, D. J. Shorokhov, H. V. Volden and K. W. Klinkhammer, *Inorg. Chem.*, 1999, **38**, 1118.

11 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.

12 (*a*) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem., Int. Ed.*, 2000, **39**, 4274; (*b*) N. J. Hardman, B. E. Eichler and P. P. Power, *Chem. Commun.*, 2000, 1991; (*c*) M. S. Hill and P. B. Hitchcock, *Chem. Commun.*, 2004, 1818.

13 X. Dai and T. H. Warren, *Chem. Commun.*, 2001, 1998.

14 *Multinuclear NMR*, ed. J. Mason, Plenum, New York, 1st edn, 1987.