

Aggregation behaviour of thallium(I) β -diketiminates

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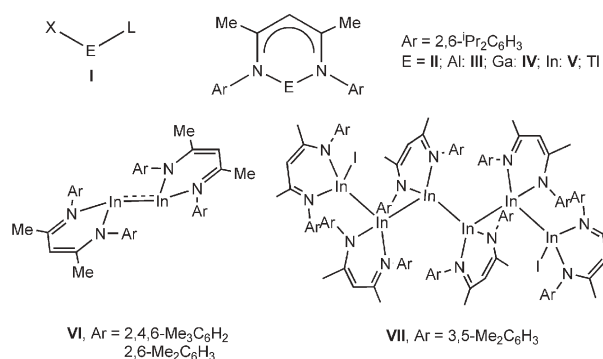
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Modulation of the steric requirements of a number of *N*-aryl β -diketiminato ligands results in the isolation of a variety of Tl(I) compounds with different stabilities and nuclearities.

The chemistry of formally monovalent and charge neutral group 13 species, XLE, **I**, (X = anionic substituent, L = neutral two electron donor, E = group 13 element) with isoelectronic relationships to the much more widely studied group 14 diyls, X₂E' (X = anionic substituent, E' = group 14 element) has advanced enormously since the turn of the century.¹ Central to the development of neutral species of the form, **I**, has been the application of chelating N-donor monoanions. Until very recently,^{2,3} examples were exclusively confined to the widely employed β -diketiminato class of ligand, with either bulky silyl or, more commonly, aryl *N*-substituents.^{4–7} Given the increasing stability of the univalent state as each group is descended (the classical 'inert pair' effect), the discovery of compounds of types **II–V** followed a somewhat unexpected chronology in that the most recently reported contained the heaviest members of the series, indium and thallium.^{6,7} Our own research has concentrated upon the effects of varying steric demands upon the nuclearity of indium β -diketiminato derivatives, **IV**. Unambiguous singlet indium diyls are isolated when Ar = 2,6-ⁱPr₂C₆H₃,⁶ while smaller *ortho*-methyl (2,4,6-Me₃C₆H₂ or 2,6-Me₂C₆H₃) *N*-substituents permit solid-state dimerisation and the formation of compounds, **VI**,⁸ which may be viewed as heavier group 13 'alkene analogues'. Although the maintenance of this interaction in solution is doubtful and the subject of ongoing studies in our group, we have found that further moderation of the steric demands of the *N*-aryl substituents to 3,5-Me₂C₆H₃ results in the isolation of a remarkable linear catenated hexa-indium complex, **VII**, which displays behaviour consistent with a ' σ -delocalized' manifold of molecular orbitals.⁹ We have previously reported that the mononuclear Tl(I) complex, **V**, may be synthesised and handled without apparent difficulty.^{7a} Our own work and recent density functional theory (DFT) calculations have suggested that a satisfactory view of the of the E–E bonding within dimerised 'carbenoid' group 13 species of indium and thallium is as much a question of semantics (*i.e.* when is a double/multiple bond a double/multiple bond?) as the application of conventional bonding theory.^{8,10} As part of a more wide ranging synthetic effort to address these questions, we now report the use of a suite of less sterically demanding β -diketiminato ligands with the aim of synthesising Tl(I) complexes similar to **VI**

and **VII**. Although the resolution of this synthetic challenge has proved problematical, it has highlighted a marked, but somewhat capricious dependence of complex stability upon ligand topology.



Despite numerous attempts, work up of the reaction of Tl(I) and [CH{(Me)CN-2,4,6-Me₃C₆H₂}₂K] (formed *in situ* from K{N(SiMe₃)₂} and the β -iminoamine precursor) provided no identifiable β -diketiminato thallium complexes in pure isolable form. Reaction in THF was accompanied by deposition of elemental thallium. This observation is reminiscent of our previous work in indium chemistry where lower valent complexes have been identified by careful work-up and crystallisation from hydrocarbon solvents. Extraction of the solid dark residue with hexane and filtration produced pale yellow solutions, which proved to be highly unstable toward the production of a metallic thallium mirror on the inner surfaces of the flasks even when stored in the absence of light and at low temperature. Although the intended compound most likely forms under these conditions, we were neither able to crystallise nor identify definitively by spectroscopic means the Tl(I) β -diketiminato. Prolonged storage and repeated filtration of one such solution did, however, result in the isolation of a small number of colourless single crystals. These were identified as the unusual mixed valence [Tl(I)/Tl(III)] Tl₈ cluster, compound **1**, by a single crystal X-ray diffraction analysis.† The structure of **1** is illustrated in Fig. 1 and selected bond lengths and angles are provided in the figure caption. The structure has crystallographically imposed twofold symmetry and may be rationalised as comprising two Tl₄ subunits connected *via* a single oxide (O6) and two hydroxyl (O5, O5') bridging ligands. Each half of the cluster includes a single trivalent and three univalent centres. The formally trivalent and six-coordinate Tl(III) (Tl1') atoms are ligated by the bridging oxide and hydroxyl ligands in a *cis* fashion. The remaining coordination sites about these atoms are provided by the geminal oxygens of two bis-imino acetal ligands formed by apparent oxidation of the β -diketiminato. The formally univalent Tl atoms are all two-coordinate and serve to bridge between the

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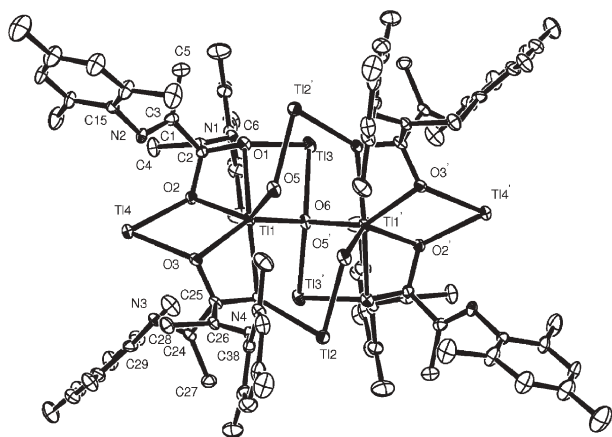


Fig. 1 ORTEP of compound **1** (20% ellipsoids). Selected bond lengths (Å) and angles (°); Tl(1)–O(2) 2.238(6), Tl(1)–O(4) 2.369(6), Tl(1)–O(1) 2.394(6), Tl(2)–O(5') 2.446(6), Tl(2)–O(4) 2.460(6), Tl(3)–O(1) 2.444(6), Tl(3)–O(6) 2.484(3), Tl(4)–O(3) 2.447(7), Tl(4)–O(2) 2.470(6); O(6)–Tl(1)–O(1) 81.73(17), O(5)–Tl(1)–O(1) 88.1(2), O(3)–Tl(1)–O(1) 127.1(2), O(2)–Tl(1)–O(1) 59.2(2), O(4)–Tl(1)–O(1) 166.7(2), O(5')–Tl(2)–O(4) 81.4(2), O(1)–Tl(3)–O(6) 74.65(17), O(3)–Tl(4)–O(2) 70.53(19), where (') in the atom labels indicates that these atoms are at $(3/2 - x, y, 3/2 - z)$.

oxygen atoms about the Tl(III) centres, either 'intra' (Tl4, Tl4') or 'inter' (Tl2, Tl2'/Tl3, Tl3') -molecularly.

Although the process that produces the cluster molecule, **1**, is ill-defined, we were surprised that a similar reaction of Tl(I) and the potassium β -diketiminate $[\text{CH}\{\text{Me}\}\text{CN-2,6-Me}_2\text{C}_6\text{H}_3\}_2\text{K}]$ produced, after work-up, a reasonable (35%) yield of the pale yellow complex **2**.[‡] Warren has previously reported the use of the thallium β -diketiminate $[\text{CH}\{\text{Me}\}_2\text{CN-2,6-Me}_2\text{C}_6\text{H}_3\}_2\text{Tl}]$, synthesised by a different route, as a reagent in the synthesis of copper complexes.¹¹ The isolated crystals of complex **2** displayed notable stability in the solid state and could be stored in ambient light for several days with no apparent darkening or indication of decomposition. Although solutions were somewhat photolabile, promptly collected ¹H NMR spectra of **2** displayed a β -diketiminate environment identical with the data reported for Warren's crystalline (but notably light-sensitive) complex. Our spectra, however, also displayed a second set of resonances in a 1 : 1 ratio with those ascribed to the Tl(I) β -diketiminate, which, from comparison to reference spectra, were identified as resulting from the presence of an equivalent of the (protonated) β -iminoamine precursor. An explanation for these observations became apparent from a further X-ray diffraction experiment performed on single crystals of **2** isolated from hexane solution.[†] The results of this analysis revealed that the compound **2** has crystallographically imposed twofold symmetry and are illustrated in Fig. 2. Selected bond lengths and angles are given in the figure caption. The solid-state structure of **2** is reminiscent of the outcome of the reaction of TlBr and the potassium amidinate $[\{\text{ArNC}(\text{tBu})\text{NAr}\}_2\text{K}]$ (Ar = 2,6-ⁱPr₂C₆H₃) in that it contains a cocrystallised molecule of the protonated ligand precursor.² Both the *N*-mesityl, and the directly analogous In(I) species, $[\text{CH}\{\text{Me}\}\text{CN-2,6-Me}_2\text{C}_6\text{H}_3\}_2\text{In}]$, are isolated as dimeric aggregates in the solid-state, which may be viewed as being formed by the, albeit very weak, interaction of two singlet carbenoid species (*i.e.* heavier group 13 analogues of an alkene). Although there there are no notably shortened contacts

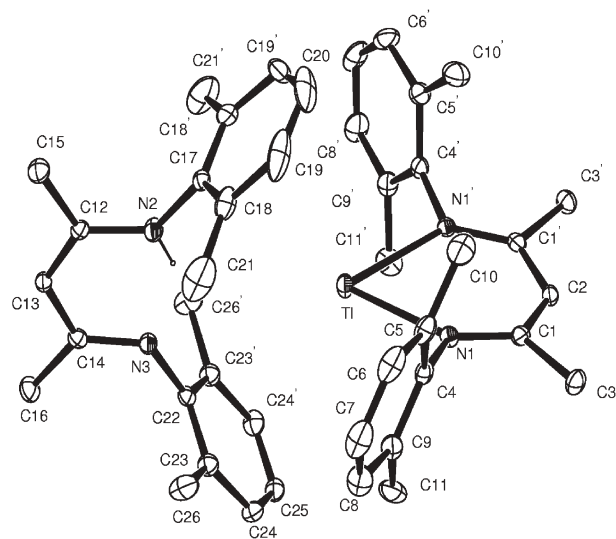


Fig. 2 ORTEP of compound **2** (50% ellipsoids). Selected bond lengths (Å) and angles (°); Tl–N(1) 2.401(2), N(1)–C(1) 1.327(4), N(1)–C(4) 1.417(4), N(2)–C(12) 1.336(5), N(2)–C(17) 1.414(5), N(3)–C(14) 1.300(5), N(3)–C(22) 1.415(5); N(1')–Tl–N(1) 76.84(12), C(1)–N(1)–C(4) 120.8(3), C(1)–N(1)–Tl 130.9(2), C(4)–N(1)–Tl 108.4(2), where (') in the atom labels indicates that these atoms are at $(x, 1/2 - y, z)$.

between the protonated ligand and the thallium centre, the presence of the wholly organic solvate undoubtedly exerts a profound structural influence upon the nuclearity of the isolated thallium species (*vide infra*). We have noted previously that the bond lengths and angles about the N–In–N fragment of monomeric and dimeric In(I) β -diketiminate are little altered by the presence of the In–In contact.⁸ The corresponding bond lengths and angles within the structure of **2** [N(1)–Tl–N(1'), 76.84(12)°; Tl–N(1), 2.401(2) Å] are little affected by the presence of the protonated ligand and lie within the ranges previously established by the unambiguous monomers $[\text{CH}\{\text{Me}\}\text{CN-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3\}_2\text{Tl}]$,^{7a} $[\text{CH}\{\text{Ph}\}_2\text{CN}(\text{SiMe}_3)_2\text{Tl}]$ and $[\text{CPh}\{\text{H}\}\text{CN-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3\}_2\text{Tl}]$.^{7b}

Our work with the similar but less sterically demanding *meta*-xylyl β -diketiminate ligand, $[\text{CH}\{\text{Me}\}_2\text{CN-3,5-Me}_2\text{C}_6\text{H}_3\}]^-$ has not yet yielded a stable univalent In(I) derivative in either monomeric or dimeric form. Rather, the striking, but formally mixed [In(I)/In(II)] valence, species, **VII**, resulted from the reaction of InI and $[\text{CH}\{\text{Me}\}\text{CN-3,5-Me}_2\text{C}_6\text{H}_3\}_2\text{K}]$ under similar reaction and work-up conditions to those described above.⁹ With this result in mind, we performed the analogous reaction of $[\text{CH}\{\text{Me}\}\text{CN-2,4,6-Me}_3\text{C}_6\text{H}_2\}_2\text{K}]$ with an equimolar quantity of Tl(I). This reaction proceeded in a similar manner with concurrent production of a heavy precipitate of elemental thallium and resulted in a light-sensitive pale yellow solution after extraction of the reaction mixture with hexane. Concentration and storage of this solution at –30 °C for one week resulted in the formation of an isolable quantity (*ca.* 10% estimated yield) of bright yellow, but highly light-sensitive, needles, compound **3**. Although a promptly acquired ¹H NMR spectrum of **3** again indicated the presence of a single β -diketiminate environment, it was noted that the sample darkened notably in the intervening time between sample preparation and collection of these spectral data and the isolated crystalline material was subject to unavoidable, but

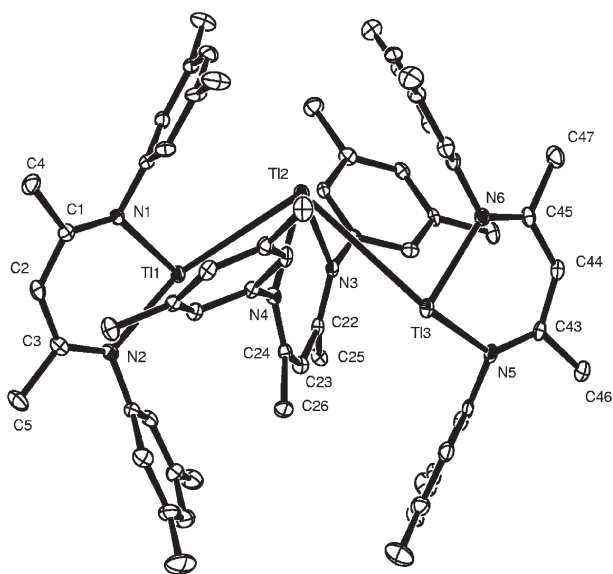


Fig. 3 ORTEP of compound **3** (20% ellipsoids). Selected bond lengths (Å) and angles (°): Tl(1)–N(2) 2.462(6), Tl(1)–N(1) 2.472(6), Tl(1)–Tl(2) 3.5794(4), Tl(2)–N(4) 2.504(6), Tl(2)–N(3) 2.520(6), Tl(2)–Tl(3) 3.7977(4), Tl(3)–N(5) 2.482(6), Tl(3)–N(6) 2.515(6), Tl(3)···Tl(1') 4.1318(4); N(2)–Tl(1)–N(1) 75.94(19), N(2)–Tl(1)–Tl(2) 133.51(14), N(1)–Tl(1)–Tl(2) 86.13(14), N(4)–Tl(2)–N(3) 75.77(18), N(4)–Tl(2)–Tl(1) 59.77(13), N(3)–Tl(2)–Tl(1) 68.80(13), N(4)–Tl(2)–Tl(3) 63.57(13), N(3)–Tl(2)–Tl(3) 56.99(12), Tl(1)–Tl(2)–Tl(3) 107.91(1), N(5)–Tl(3)–N(6) 76.81(19), N(5)–Tl(3)–Tl(2) 128.78(13), N(6)–Tl(3)–Tl(2) 79.23(13).

solution-accelerated, decomposition. This is borne out by the results of a further X-ray diffraction analysis illustrated in Fig. 3,† which revealed that **3** crystallises as a trimer with intermolecular Tl(1)–Tl(2) [3.5794(4) Å] and Tl(2)–Tl(3) [3.7977(4) Å] interactions. Recent DFT studies performed upon the *N*-phenyl analogue of **3** [HC{C(Me)NPh}₂Tl] at the B3LYP level of theory have predicted that dimerisation is endothermic by *ca.* 10 Kcal mol⁻¹ while our own similar calculations upon the crystallographically identified dimeric indium species indicated that negligible energy may be expected to be involved in dissociation to the monomeric singlet ‘carbenoids’.^{8,10} These results and the metrical data provided by the solid-state structure shown in Fig. 3 lead us to conclude that the Tl–Tl interactions within compound **3** are better interpreted as examples of dispersive attractive forces between the closed shell (5d¹⁰6s²–5d¹⁰6s²) Tl(I) centres. While compounds of monovalent gold have provided the most spectacular objects of study in this context,¹² the presence of weak interactions has been accepted as a key factor to explain the supramolecular structures of Tl(I) amide derivatives.¹³ Indeed the Tl–Tl distances within **3** are entirely commensurate with many of the intermetallic contacts observed in compounds such as the tripodal thallium amide [MeSi{SiMe₂N(Tl)^tBu}₃] [3.653(2), 3.673(2) Å] and the polymeric thallium bis(8-quinoliny)amide [3.5336(5) Å].^{14,15}

On this basis any argument that presents the possibility of a thallium(I) ‘alkene analogue’ (*i.e.* providing some element of Tl–Tl multiple bonding comparable to that readily identified in the chemistry of the lighter p-block elements) is most likely specious and raises the possibility that the In–In bonding within **IV** may also be a reflection of similar (*i.e.* 4d¹⁰5s²–4d¹⁰5s²) phenomena.

Any treatment that presupposes or inadvertently imposes either view of the bonding within similar lower valent complexes of the heavier group 13 elements must be treated, therefore, with caution if any possible ‘experimenter effect’ is to be avoided. We are continuing to attempt the synthesis and to study the reactivity of further related compounds in our effort to address these fundamental questions within heavier main group element chemistry.

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Notes and references

† *Crystal data*: 173 K, Nonius Kappa CCD diffractometer, λ(Mo Kα) = 0.71073 Å. **1**: C₉₂H₁₁₄N₈O₁₁Tl₈·2(C₆H₁₄), *M* = 3315.22, monoclinic, *P2₁n* (No. 13), *a* = 12.4127(3), *b* = 15.1224(3), *c* = 29.4433(2) Å, β = 95.743(1)°, *V* = 5499.1(2) Å³, *Z* = 2, μ = 11.73 mm⁻¹, 29498 collected reflections, 9534 independent reflections [*R*(int) = 0.054], *R* indices [*I* > 2σ(*I*)] *R* = 0.045, *wR*2 = 0.083, [all data] *R* = 0.076, *wR*2 = 0.092. **2**: C₄₂H₅₁N₄Tl, *M* = 816.24, orthorhombic, *Pnma* (No. 62), *a* = 22.3307(3), *b* = 16.6863(3), *c* = 10.2310(1) Å, *V* = 3812.24(9) Å³, *Z* = 4, μ = 4.27 mm⁻¹, 61777 collected reflections, 3883 independent reflections [*R*(int) = 0.070], *R* indices [*I* > 2σ(*I*)] *R* = 0.027, *wR*2 = 0.051, [all data] *R* = 0.042, *wR*2 = 0.056. **3**: C₆₃H₇₅N₆Tl₃, *M* = 1529.40, triclinic, *P1* (No. 2), *a* = 10.0548(2), *b* = 12.3991(3), *c* = 24.0307(5) Å, α = 92.243(2), β = 98.399(1), γ = 97.355°, *V* = 2934.29(11) Å³, *Z* = 2, μ = 8.26 mm⁻¹, 39677 collected reflections, 11528 independent reflections [*R*(int) = 0.070], *R* indices [*I* > 2σ(*I*)] *R* = 0.045, *wR*2 = 0.097, [all data] *R* = 0.071, *wR*2 = 0.109. CCDC 609883–609885. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607887g

‡ Selected analytical data; **2**: Elemental analysis: C₄₂H₅₁N₄Tl: calcd C 61.76, H 6.86, N 6.25; found C 59.79, H 7.00, N 8.35% (partially decomposed in transit); ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 1.65 (s, 6H, *CMe*, LH), 1.80 (s, 6H, *CMe*), 2.24 (s, 12H, *o-Me*, LH), 2.26 (s, 12H, *o-Me*), 4.93 (s, 1H, *CH*, LH), 4.95 (s, 1H, *CH*), 7.06–7.21 (m, 12H, *m,p-ArH* and *m,p-ArH*, LH). ¹³C{¹H} (100.7 MHz, C₆D₆) δ = 18.3, 20.0 (*o-Me*), 24.4 (*CMe*), 94.1 (γ-CH), 123.4 (Ar), 124.5 (Ar), 130.7 (Ar), 132.1 (Ar), 144.1 (*i-Ar*), 160.6, 161.6 (CN). **3**: Elemental analysis: sealed sample decomposed in transit. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 2.01 (s, 6H, *CMe*), 2.21 (s, 12H, *m-Me*), 4.96 (s, 1H, *CH*), 6.69 (s, 2H, *p-ArH*), 6.74 (s, 4H, *o-Ar*). ¹³C{¹H} (100.7 MHz, C₆D₆) δ = 20.6 (*CMe*), 21.2 (*m-Me*), 97.6 (γ-CH), 120.5 (Ar), 124.9 (Ar), 138.2 (Ar), 146.2 (*i-Ar*), 158.9 (CN).

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