

A new entry to *N*-heterocyclic carbene chemistry: synthesis and characterisation of a triscarbene complex of thallium(I)[†]

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The synthesis and characterisation of a thallium(I) triscarbene complex of the chelating, tripodal carbene ligand 1,3,5-[tris(3-*tert*-butylimidazol-2-ylideno)methyl]-2,4,6-trimethylbenzene is reported, in which the thallium ion is coordinated by three *N*-heterocyclic carbene donors in a distorted trigonal planar environment.

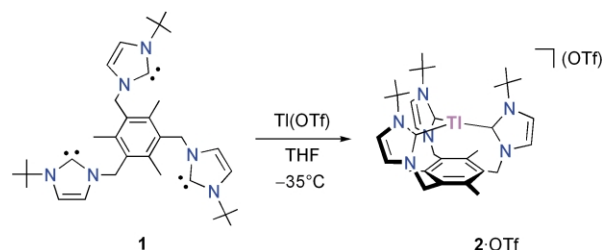
Three-coordinate transition metal complexes with tripodal ligands are known to provide powerful platforms for small molecule activation and functionalisation;¹ however, only a few examples of transition metal complexes using tripodal carbene ligands are reported in the literature.² The considerable potential of *N*-heterocyclic carbenes for application in homogeneous catalysis³ and small molecule activation, has triggered our efforts to develop a new class of metal complexes supported by tripodal *N*-heterocyclic carbene chelators. In this context, we are currently investigating the coordination chemistry of tripodal carbene-based ligands with an arene or a single atom as an anchoring unit. In 1994, the stable tripodal carbene ligand, 1,3,5-[tris(3-*tert*-butylimidazol-2-ylideno)methyl]-2,4,6-trimethylbenzene, **1**, was synthesised by Dias and Jin.⁴ Despite the reported isolation of the free carbene, this potential ligand has not been structurally characterised and there are no examples of metal complexes of this tripodal carbene system. Herein we report the first complex with this tridentate carbene ligand, [(timtmb^{Bu})Tl]⁺ (**2**), together with the crystal structures of free carbene **1** and its protonated precursor derivative [(timtmb^{Bu})Cl](Cl)₂ (**1a**, see ESI[†]).

Free carbene **1** was synthesised *via* deprotonation of the corresponding imidazolium salt with NaH/KO^tBu.⁴ Crystals of **1** suitable for X-ray diffraction analysis were grown from a saturated toluene solution at -35 °C.[‡] The solid-state molecular structure of **1** is depicted in Fig. 1.

The three imidazole rings in **1** are arranged in an asymmetrical fashion with respect to the anchoring mesitylene ring. The electronic and molecular structures of the divalent carbon centres in **1** are similar to structures reported for other simple 1,3-disubstituted imidazole-2-ylidenes.⁵ The average C13–N distance at the carbene centre is 1.37 Å; the average N1–C13–N2 angle in the three imidazole entities is 102.0°. Our X-ray crystallographic results clearly show no evidence for any inter- or intramolecular interactions of the carbene centres of **1** in the solid-state. In contrast, imidazolium salt **1a** (see ESI[†] for crystal structure diagrams of **1a**) crystallises in idealized C₃ symmetry with all imidazolium moieties pointing up, thus providing a cavity for one of the three chloride anions.[‡] The successful application of a wide variety of thallium complexes as ligand transfer reagents⁶ have stimulated our interest in preparing thallium complexes of carbene ligand **1** and its N2-substituted derivatives. Recently, Peters and coworkers have demonstrated a ligand transfer reaction of a Tl(I) complex supported by a tripodal phosphine ligand.⁷ Similarities of *N*-heterocyclic carbenes and organophosphine ligands in terms of their metal coordination chemistry are well known.³ These findings,

together with our observations that the imidazolium precursors of this class of chelators form tripodal cavities and serve as anion hosts,⁸ have encouraged us to prepare a Tl(I) complex with the tridentate *N*-heterocyclic percarbene ligand **1**.

The reaction of one equivalent of **1** with Tl(OTf) in THF at -35 °C led to the formation of the triscarbene thallium(I) complex, **2**, in good yield (54%) as a white powder (Scheme 1).§



Scheme 1 Synthesis of [(timtmb^{Bu})Tl]⁺ (**2**) from free carbene (**1**).

The novel complex **2** is highly temperature sensitive. THF solutions of **2** can be kept at -35 °C for several days without decomposition. Allowing the reaction solutions to gradually warm to r.t., however, leads to black, unidentified decomposition products. This is in contrast to known Tl(III)–carbene complexes that have high thermal stability.⁹ Although the thermal instability and the reduced solubility of **2** at low temperatures impede thorough spectroscopic investigation, **2** was clearly identified in the low temperature ¹H and ¹³C NMR spectra. The ¹H NMR spectrum of free carbene **1** in THF-d₈ at -35 °C exhibits resonances at δ 1.52, 2.47, 5.31, 6.54 and 7.08. When Tl(OTf) was added to a solution of free carbene **1** in THF-d₈ at -35 °C, these signals clearly changed as follows: δ 1.47, 2.34, 5.33, 7.38 and 7.46. The most notable feature in the ¹H NMR spectrum is the downfield shift of the imidazole CH

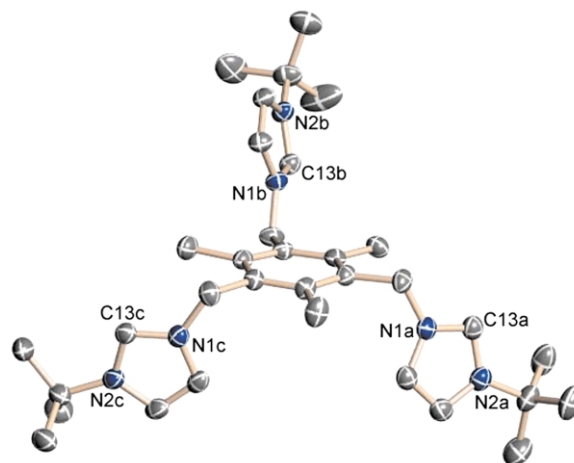


Fig. 1 Solid-state molecular structure of free carbene **1**. Hydrogen atoms are omitted for clarity, thermal ellipsoids at 40% probability. Selected bond lengths (Å) and angles (°): C13a–N1a 1.368(2), C13a–N2a 1.372(2), C13b–N1b 1.370(2), C13b–N2b 1.369(2), C13c–N1c 1.369(2), C13c–N2c 1.363(2); N1a–C13a–N2a 102.04(15), N1b–C13b–N2b 101.97(14), N1c–C13c–N2c 102.25(14).

[†] Electronic supplementary information (ESI) available: structure of [**1a**]₂·5H₂O, orbital interactions in **2**, and computational details. See <http://www.rsc.org/suppdata/cc/b2/b209071f/>

resonances from δ 6.54 and 7.08 of free carbene **1** to δ 7.38 and 7.46 in spectra of samples of complex **2**. However, we were unable to observe potential $^{203/205}\text{Tl}$ - ^1H and/or ^{13}C hyperfine features in our NMR spectra.⁹

The molecular structure of **2** was confirmed by X-ray crystallography. Colourless crystals **2**(OTf) \cdot 2THF suitable for X-ray diffraction analysis were obtained by cooling a saturated THF solution at -35°C overnight.[‡] Fig. 2 shows the solid-state molecular structure of cation **2**.

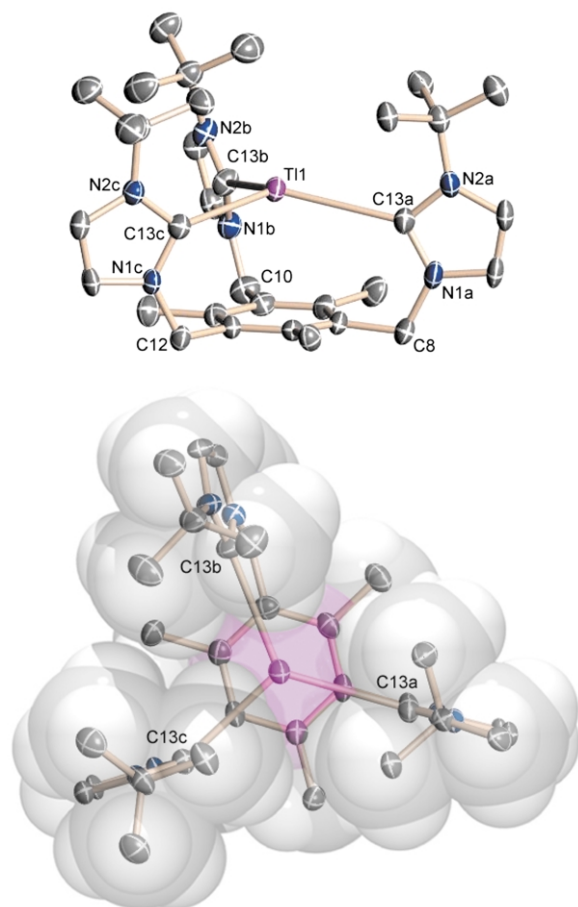


Fig. 2 Two views of the solid-state molecular structure of **2** in crystals of **2**(OTf) \cdot 2THF. Hydrogen atoms and co-crystallised solvent molecules are omitted for clarity, thermal ellipsoids at 40% probability. Selected bond lengths (\AA) and angles ($^\circ$): Tl1–C13a 2.979(4), Tl1–C13b 2.985(5), Tl1–C13c = 2.893(4), C13a–N1a 1.358(6), C13a–N2a 1.368(5), C13b–N1b 1.361(6), C13b–N2b 1.361(6), C13c–N1c 1.360(5), C13c–N2c 1.369(5); C13a–Tl1–C13b 124.05(13), C13a–Tl1–C13c 118.90(12), C13b–Tl1–C13c 109.65(13), N1a–C13a–N2a 102.6(4), N1b–C13b–N2b 102.9(4), N1c–C13c–N2c 102.5(3).

The tripodal carbene ligand **1** coordinates the thallium cation in the expected tridentate conformation. The thallium(i) ion is displaced 0.466 \AA out of a trigonal plane formed by the three carbenic centres and is positioned 2.919 \AA above the arene anchoring unit. Comparison of the ^{13}C resonances of the free carbene ligand with those of the thallium complex imply that there is no significant bonding interaction between the arene fragment and the Tl(i) ion. This observation is further supported by a DFT calculation (ESI[†]) carried out on the cationic thallium complex. Close examination of the frontier orbitals reveals no orbital interaction between the arene moiety and the metal ion. All three imidazole rings are almost perpendicular to the mesitylene entity, however, the solid-state molecular structure suggests that the three carbene centres in **2** are not symmetrically bound to the Tl(i) ion: the Tl1–C13c distance, 2.893(4) \AA , is significantly shorter than the Tl1–C13a and Tl1–C13b distances (2.979(4) and 2.985(5) \AA , respectively). The dihedral angles C(mesitylene)–C(methylene)–N1–C13 are 3.99, 4.91 and 32.86 $^\circ$ for C13a, C13b and C13c, respectively. Despite the

observed differences within the imidazole-2-ylidene units of **2**, the divalent carbon centres are electronically identical (see bond lengths and angles in Fig. 2). A space-filling model helps to rationalize the deviation from an ideal C_3 symmetry. It is obvious that this deviation is due to the large thallium(i) ion and the sterically demanding *tert*-butyl groups bound to N2. It therefore seems reasonable to conclude that the disturbed symmetry observed in the solid-state structure of **2** is due to steric or crystal packing effects rather than electronic origin. Accordingly, we are currently pursuing Tl(i) chemistry of other neutral tripodal carbene ligands conceptually but not sterically related to that described herein.

In summary, we have synthesised and characterised a triscarbene complex of Tl(i). This is the first example of a Tl(i)-carbene complex as well as the only reported complex of this class of percarbene chelator. We are currently investigating the potential of this Tl(i) species as a ligand transfer reagent to low valent transition and actinide metal ions.

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Notes and references

[‡] Crystallographic details for **[1a]** $_2\cdot$ 5H $_2\text{O}$: $\text{C}_{66}\text{H}_{109.43}\text{Cl}_6\text{N}_{12}\text{O}_5$, $M = 1363.78$, colourless plate, $T = 101(2)$ K, monoclinic, space group $P2_1/n$, $a = 19.0580(9)$, $b = 17.9298(8)$, $c = 23.6229(11)$ \AA , $\beta = 113.6460(10)^\circ$, $V = 7394.4(6)$ \AA^3 , $Z = 4$, $R_1 = 0.0653$ [$I > 2\sigma(I)$], GOF = 0.949. CCDC 193368. Crystallographic details for **1**: $\text{C}_{33}\text{H}_{49.25}\text{N}_6$, $M = 530.03$, colourless hexagonal, $T = 100(2)$ K, monoclinic, space group $P2_1/n$, $a = 12.0758(7)$, $b = 11.1310(6)$, $c = 23.7831(14)$ \AA , $\beta = 100.5090(10)^\circ$, $V = 3143.2(3)$ \AA^3 , $Z = 4$, $R_1 = 0.0425$ [$I > 2\sigma(I)$], GOF = 1.037. CCDC 193367. Crystallographic details for **2**(OTf) \cdot 2THF: $\text{C}_{42}\text{H}_{64}\text{F}_3\text{N}_6\text{O}_5\text{STl}$, $M = 1026.42$, colourless needle, $T = 100(2)$ K, monoclinic, space group $P2_1/c$, $a = 12.8495(12)$, $b = 17.1020(16)$, $c = 20.8654(19)$ \AA , $\beta = 97.580(2)^\circ$, $V = 4545.1(7)$ \AA^3 , $Z = 4$, $R_1 = 0.0405$ [$I > 2\sigma(I)$], GOF = 1.005. CCDC 193366. See <http://www.rsc.org/suppdata/cc/b2/b209071f/> for crystallographic data in CIF or other electronic format.

[§] Synthesis and spectroscopic data: for **2**(OTf): a cooled (-35°C) THF solution (5 cm^3) of Tl(OTf) (177 mg, 0.5 mmol) was added to a cooled (-35°C) solution of timtmb^{†Bu} (264 mg, 0.5 mmol) in THF (5 cm^3). The mixture was stored for 12 h at -35°C . The resulting white precipitate was filtered off, washed with cold THF, and dried in vacuum (yield: 237 mg, 54%). Recrystallisation of the crude product from a saturated solution of THF at -35°C yielded needle-shaped crystals of **2**(OTf) \cdot 2THF suitable for X-ray diffraction analysis. ^1H NMR (500 MHz, THF- d_6 , -35°C): δ 1.47 (s, C(CH $_3$) $_3$, 27H), 2.34 (s, Ar–CH $_3$, 9H), 5.33 (s, CH $_2$, 6H), 7.38 (br, NCH, 3H) and 7.46 (br, NCH, 3H). ^{13}C NMR (500 MHz, THF- d_6 , 0°C): δ 16.9 (Ar–CH $_3$), 31.5 (C(CH $_3$) $_3$), 49.6 (Ar–CH $_2$), 57.3 (CMe $_3$), 118.3 (NCC), 121.1 (CCN), 134.8 (Ar–C), 140.2 (Ar–C). For **1**: ^{13}C NMR (500 MHz, THF- d_6 , 0°C): δ 16.9 (Ar–CH $_3$), 31.5 (C(CH $_3$) $_3$), 50.3 (Ar–CH $_2$), 56.2 (CMe $_3$), 116.1 (NCC), 117.5 (CCN), 134.1 (Ar–C), 139.0 (Ar–C), 215.2 (NCN).

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