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Synthesis and characterisation of the first carbene–thallium complexes: molecular structure of [$TlCl_3\{CN(Mes)C_2H_2N(Mes)\}$], Mes = $C_6H_2Me_3$-2,4,6†

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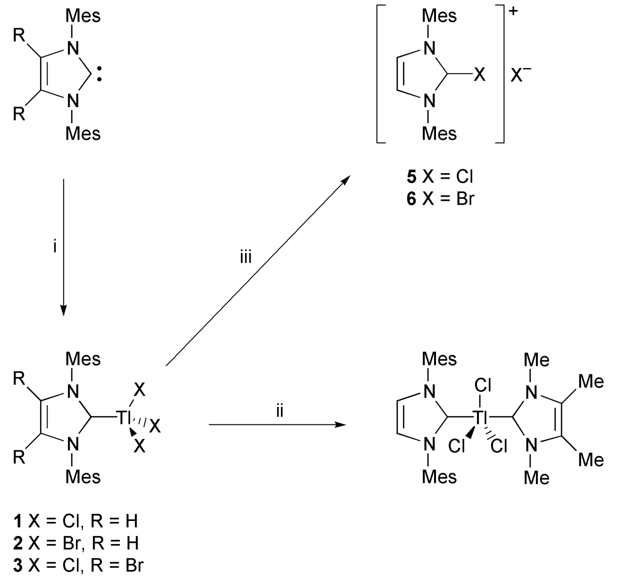
The reaction of the stable carbenes, :CN(Mes)C_2R_2N(Mes), R = H (IMes) or Br (IMesBr), with TlX_3, X = Cl or Br, Mes = mesityl, yields the complexes, [TlX_3\{CN(Mes)-C_2R_2N(Mes)\}], one of which, [$TlCl_3$(IMes)], has been crystallographically characterised and its thermal decomposition studied; further reaction of [$TlCl_3$(IMes)] with one equivalent of :CN(Me)C_2Me_2N(Me) affords the mixed bis-carbene complex [$TlCl_3$(IMes)\{CN(Me)C_2Me_2N(Me)\}] which has been characterised spectroscopically.

The preference of thallium to exist in the +1 oxidation state and consequently the strongly oxidising nature of Tl(III) has led to a paucity of reports on TlX_3 complexes relative to their lighter Group 13 analogues. This is borne out by the fact that all attempts to prepare tertiary phosphine or dialkylsulfide adducts of TlX_3 fragments have resulted in oxidation of either the P- or S-donor centre.[1] Despite this, a handful of both O- and N-donor TlX_3 complexes are known and are relatively stable.[2] We have recently been exploring the use of "Arduengo" carbenes as Lewis bases in the formation of indium trihalide and trihydride complexes.[3] Our efforts in this area have shown these highly nucleophilic ligands to have excellent stabilising properties which are perhaps best displayed in [InH_3(IMes)], a compound that does not decompose in the solid state until 118 °C.[3a] It seemed possible that such ligands might also be useful in stabilising thallium(III) complexes though, intuitively, it might be thought that the carbene centre would be readily oxidised by the metal centres in such species. We have shown that this is not the case as we have prepared a number of stable carbene–thallium(III) complexes which are discussed herein.

Treatment of tetrahydrofuran solutions of TlX_3 with one equivalent of IMes or IMesBr[4] at −30 °C led to moderate yields of [TlX_3\{CN(Mes)C_2R_2N(Mes)\}], **1**–**3**, after crystallisation from either THF or dichloromethane (Scheme 1). All three complexes possess high thermal stability (decomposition temperatures: **1** 208, **2** 182 and **3** 178 °C) but are extremely moisture sensitive in solution and in the solid state. Their ^{1}H and ^{13}C NMR spectra[5]‡ display the expected resonances with the exception of those for the carbene centres. These should occur at *ca.* δ 170 (*cf.* [AlH_3(IMes)], δ 175.3)[6] but were not observed due to the limited solubility of **1**–**3** in CD_2Cl_2 and coupling of the carbenic carbons to the spin-active thallium centre (^{203}Tl, 29%, $I = ½$; ^{205}Tl, 71%, $I = ½$). It is noteworthy that the carbons in the 4- and 5-positions of the heteroycles in **1**–**3** are coupled to the thallium centre with typical three bond thallium–carbon couplings of *ca.* 220 Hz (*e.g.* **1**, $^3J_{TlC}$ 221 Hz). In addition, the protons at the 4,5-positions are also coupled to the co-ordinated metal centres, *e.g.* **1**, $^4J_{TlH}$ 89 Hz. Again, the degree of thallium coupling seen is normal,[7] though resolution of coupling to the different thallium isotopes could not be achieved, even at −70 °C.



Scheme 1 Reagents and conditions: (i) TlX_3, −30 °C; (ii) X = Cl, R = H, :CN(Me)C_2Me_2N(Me), −30 °C; (iii) X = Cl or Br, R = H, mesitylene, reflux, 48 h, −TlX.

The molecular structure§ of complex **1** is depicted in Fig. 1. It exists as a monomer in the solid state without any intermolecular contacts. The thallium centre sits in a distorted tetrahedral environment (av. C(1)–Tl–Cl 112.9°, av. Cl–Tl–Cl 105.8°) with the three Tl–Cl lengths being almost equivalent (av. 2.419 Å). In addition the Tl–C distance is in the normal region and close to the mean length (2.154 Å) for such interactions.[8] Finally, the geometry of the heterocycle is similar to that seen in [$InCl_3$(IMes)][3a] and suggests a degree of delocalisation within the ring.

Our earlier preparations of bis(carbene) adducts of $InCl_3$ and $InBr_3$[3d] and the existence of other 2 : 1 and 3 : 1 donor complexes of TlX_3[1,2] led us to attempt the synthesis of [$TlCl_3$-$(IMes)_2$] *via* the treatment of **1** with one equivalent of IMes in tetrahydrofuran. Unfortunately, this reaction did not proceed, presumably because the proposed complex is not sterically viable. In contrast, addition of the sterically less demanding carbene, :CN(Me)C_2Me_2N(Me), to **1** did give a moderate yield of [$TlCl_3$(IMes)\{CN(Me)C_2Me_2N(Me)\}], **4**, after crystallisation from THF (Scheme 1). Solution state NMR studies on **4** indicate the presence of couplings between the carbons in the 4- and 5-positions of both heterocyclic ligands and the thallium centre [$^3J_{TlC}$ 187 Hz (IMes) and 183 Hz (:$CN_2C_2Me_4$)]. These values are significantly less than the related coupling in **1** which is perhaps not surprising given the perceived weaker interaction of both carbene ligands with the more electronically saturated

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† Electronic supplementary information (ESI) available: synthetic details and spectroscopic data for **2** and **3**. See http://www.rsc.org/suppdata/dt/b1/b105322c/

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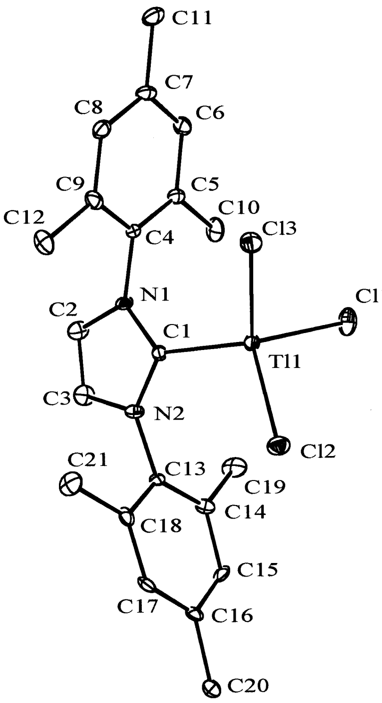

Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles(°): Tl(1)–C(1) 2.179(9), Tl(1)–Cl(3) 2.416(2), Tl(1)–Cl(2) 2.417(2), Tl(1)–Cl(1) 2.423(3), N(1)–C(1) 1.347(11), N(1)–C(2) 1.359(13), N(2)–C(1) 1.345(10), N(2)–C(3) 1.400(10), C(2)–C(3) 1.315(13); C(1)–Tl(1)–Cl(3) 113.8(2), C(1)–Tl(1)–Cl(2) 113.4(2), C(1)–Tl(1)–Cl(1) 110.8(2), Cl(3)–Tl(1)–Cl(2) 105.87(9), Cl(3)–Tl(1)–Cl(1) 104.53(9), Cl(2)–Tl(1)–Cl(1) 107.77(10), N(2)–C(1)–N(1) 107.2(8), N(2)–C(1)–Tl(1) 125.5(6), N(1)–C(1)–Tl(1) 126.7(5), C(3)–C(2)–N(1) 108.8(8), C(2)–C(3)–N(2) 107.1(8).

metal centre in **4**. Unfortunately, X-ray quality crystals of **4** could not be grown so the geometry about its metal centre cannot be certain. However, it is assumed that the chloride ligands take up the equatorial positions of a trigonal bipyramid, as is normally the case for bis-Lewis base adducts of Group 13 trihalides.[1] Despite this, other geometries cannot be ruled out and have been observed in closely related carbene–indium complexes, *e.g.* $[InCl_3\{CN(Pr^i)C_2Me_2N(Pr^i)\}_2]$.[3d]

The thermal stabilities of **1**–**4** are remarkable considering they contain carbene centres coordinated to a potentially oxidising metal centre. Therefore, it was of interest to investigate how these complexes thermally decompose under controlled conditions. To this end, mesitylene solutions of **1** and **2** were heated at reflux (163 °C) for 48 h which led to the quantitative formation of [Cl(IMes)][Cl], **5**, and [Br(IMes)][Br], **6**, with a concomitant precipitation of the respective Tl(I) halide (Scheme 1). Compounds **5** and **6** have been observed previously from the treatment of IMes with C_2Cl_6 and Br_2 respectively,[4] and hence could indicate dihalogen evolution from **1** and **2** prior to the formation of **5** and **6**.

The syntheses of **1**–**4**, the first co-ordination complexes between a carbene and a thallium centre, have prompted us to begin a detailed investigation of carbene–TlX_3 complexes. At present this includes their potential reduction to thallium hydride complexes, which are unknown, and their controlled reduction to carbene stabilised sub-valent thallium halide clusters. The results of these studies will form the basis of forthcoming publications.

Acknowledgements

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Notes and references

‡ Synthesis and spectroscopic data for **1**: A THF solution (20 cm^3) of IMes (0.41 g, 1.35 mmol) was added to a cooled (−30 °C) solution of $TlCl_3$ (0.42 g, 1.35 mmol) in THF (30 cm^3) over 20 minutes. The resulting suspension was stirred overnight and warmed to room temperature. Volatiles were removed *in vacuo* and the residue recrystallised from the minimum volume of THF to yield the product as colourless prisms after placement at −10 °C. (Yield 0.68 g, 83%); mp 208 °C (decomp.). ^{1}H NMR (300 MHz, CD_2Cl_2, 300 K): δ 2.11 (s, 12H, *o*-CH_3), 2.36 (s, 6H, *p*-CH_3), 7.10 (s, 4H, *m*-H), 7.53 (d, 2H, $^4J_{TlH}$ 89 Hz, C_2H_2); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 18.1 (s, *o*-CH_3), 21.8 (s, *p*-CH_3), 126.8 (d, $^3J_{TlC}$ 221 Hz, C_2H_2), 130.6 (s, *m*-C), 135.8 (s, *o*-C), 135.9 (s, *p*-C), 142.5 (s, *ipso*-C); APCI-MS: *m*/*z* (%) 305 ($\{M - TlCl_3\}H^+$, 32), 339 ($\{M - TlCl_2\}^+$, 84), 580 ($\{M - Cl\}^+$, 100); IR (Nujol) ν/cm^{-1}: 606s, 851m(sh), 1022s(br), 1094s(br), 1280s(sh), 1617w, 1661w(sh), 1684w(sh). Found: C, 40.73; H, 3.87; N, 4.46%. $C_{21}H_{24}N_2TlCl_3$ requires: C, 41.00; H, 3.93; N, 4.55%.

For **4**: A THF solution (20 cm^3) of $CN(Me)C_2Me_2N(Me)$ (0.25 g, 2.02 mmol) was added to a cooled (−30 °C) solution of **1** (1.24 g, 2.02 mmol) in THF (70 cm^3) over 20 minutes. The resulting suspension was stirred overnight and warmed to room temperature. Volatiles were removed *in vacuo* and the residue was recrystallised from THF to yield the product as a microcrystalline powder after placement at 0 °C. (Yield 0.87 g, 60%); mp 104 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.35 (s, 6H, C_2Me_2), 2.08 (s, 12H, *o*-CH_3), 2.14 (s, 6H, *p*-CH_3), 3.23 (s, 6H, NMe), 7.03 (s, 4H, *m*-H), 7.44 (d, 2H, $^4J_{TlH}$ 74 Hz, C_2H_2); ^{13}C NMR (100.6 MHz, CD_2Cl_2, 300 K): δ 8.7 (s, $C(CH_3)$), 16.7 (s, *o*-CH_3), 20.2 (s, *p*-CH_3), 34.1 (s, N(Me)), 123.2 (d, $^3J_{TlC}$ 187 Hz, C_2H_2), 124.9 (d, $^3J_{TlC}$ 183 Hz, C_2(Me)), 129.0 (s, *m*-C), 130.0 (s, *p*-C), 133.6 (s, *o*-C), 140.7 (s, *ipso*-C); APCI-MS: *m*/*z* (%) 125 ($HCN_2C_2Me_2^+$, 9), 305 ($IMesH^+$, 100), 616 ($\{M - [CN(Me)C_2Me_2N(Me)]\}H^+$, 23), 620 ($\{M - Mes\}^+$, 13), 740 ($MH^+$, 10); IR (Nujol) ν/cm^{-1}: 804w, 856m, 1030m, 1061s, 1235s, 1260m, 1460s br, 1537m, 1604w, 1624m.

§ Crystal data for **1**: $C_{21}H_{24}Cl_3N_2Tl$, $M = 615.14$, orthorhombic, space group $Pca2_1$, $a = 16.475(3)$, $b = 16.546(3)$, $c = 17.215(3)$ Å; $V = 4692.7(15)$ Å^3, $Z = 8$, $D_c = 1.741$ g cm^{-3}, $F(000) = 2368$, μ(Mo-Kα) = 72.33 cm^{-1}, $T = 150(2)$ K, 4380 unique reflections, $R = 0.0224$ ($I > 2\sigma I$), $wR = 0.0505$ (all data). CCDC reference number 167523. See http://www.rsc.org/suppdata/dt/b1/b105322c/ for crystallographic data in CIF or other electronic format.

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5 Full synthetic and spectroscopic details for **2** and **3** have been deposited as ESI.

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