Inorg. Chem. **2005**, *44*, 3368–3370

Inorganic Chemistry
Communication

A Monomeric Thallium(I) Amide in the Solid State: Synthesis and Structure of TlN(Me)Ar^{Mes_2} (Ar^{Mes_2} = C_6H_3-2,6-Mes_2)

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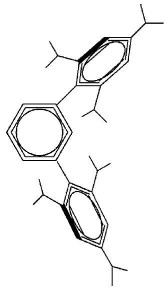
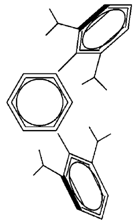
Received January 7, 2005

Reaction of TlCl and [LiN(Me)Ar^{Mes_2}]$_2$ [Ar^{Mes_2} = C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$] in Et_2O generated the thallium amide, TlN(Me)Ar^{Mes_2} (**1**). X-ray data showed that it has a monomeric structure with an average Tl–N distance of 2.364(3) Å. There was also a Tl–arene approach [Tl–centroid = 3.026(2) Å (avg)] to a flanking mesityl ring from the terphenyl substituent. DFT calculations showed that this interaction is weak and supported essentially one coordination for thallium. The electronic spectrum of **1** is hypsochromically shifted in comparison to the monomeric TlAr^{Trip_2} (Trip = C_6H_2-2,4,6-Pr$^i_3$).

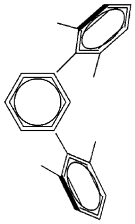
Metal–metal σ and π bonding in neutral, heavier group 13 metal (Al–Tl; i.e., heavier triels) clusters is an area that has received considerable attention over the past decade.[1–9] The M–M bonded clusters, in which the triel metal has a 1+ oxidation state and a [core]s^2 electronic configuration, are of particular interest because of the nature of the bonding and the unusual optical properties[10] that can be produced by M–M interactions, particularly those involving thallium. The use of terphenyl ligands has allowed Tl(I)–Tl(I)[11] interactions to be studied in compounds where thallium is η^1-bound to a ligand.[12] Variation in the ligand size has resulted in the isolation of monomeric[12a] TlAr^{Trip_2} (Trip = C_6H_2-2,4,6-Pr$^i_3$), dimeric[12b] (TlAr^{Dipp_2})$_2$ (Dipp = C_6H_3-2,6-Pr$^i_2$), and trimeric[12b] (TlAr^{Xyl_2})$_3$ (Xyl = C_6H_3-2,6-Me_2) complexes by use of the ligands shown below.



Ar^{Trip_2}



Ar^{Dipp_2}



Ar^{Xyl_2}

The application of other common monodentate ligands such as amides to synthesize unassociated Tl(I) complexes has yielded dimers or higher aggregates in the solid state.[13]

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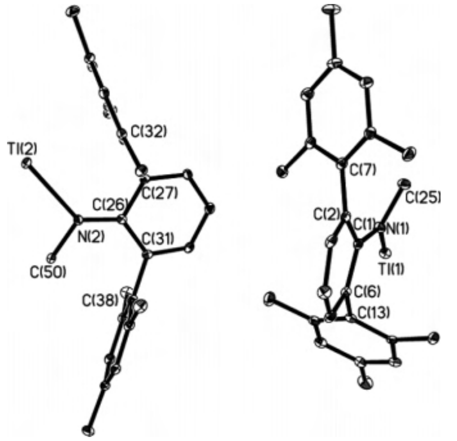

Figure 1. Molecular structure of **1** (two independent molecules) with thermal ellipsoids at 30%. Selected bond distances (Å) and angles (deg): Tl(1)−N(1) = 2.348(3), Tl(2)−N(2) = 2.379(3), Tl(1)−centroid(1) = 2.970(2), Tl(2)−centroid(2) = 3.081(2), N(1)−C(1) = 1.359(4), N(2)−C(26) = 1.359(4), N(1)−C(25) = 1.451(4), N(2)−C(50) = 1.472(4), C(1)−N(1)−C(25) = 119.4(3), C(1)−N(1)−Tl(1) = 132.7(2), C(25)−N(1)−Tl(1) = 107.9(2), C(26)−N(2)−C(50) = 120.9, C(26)−N(2)−Tl(2) 132.4(2), C(50)−N(2)−Tl(2) = 105.5(2), N(1)−C(1)−C(6) = 118.6(3), N(1)−C(1)−C(2) = 125.4(3), C(6)−C(1)−C(2) = 116.0(3), N(2)−C(26)−C(27) = 117.4(3), N(2)−C(26)−C(31) = 127.5(3), C(27)−C(26)− C(31) = 115.1(3). Angle between Tl(1)−N(1)−C(25) plane and central Ph = 20.1(1)°. Angle between Tl(2)−N(2)−C(50) plane and central Ph = 12.9(4)°.

The use of bulky amide ligands has often been studied in parallel with alkyls or aryls, and useful insights have been obtained by comparison of their properties.[14] Therefore, we decided to synthesize a series of monomeric metal derivatives $\mathrm{R_2NM}$ (M = Al−Tl), to compare their structures and properties with those of organosubstituted compounds. We now show that reaction of the lithium amide $[\mathrm{LiN(Me)Ar^{Mes_2}}]_2$[15] with TlCl affords the heaviest member of the series: an unassociated thallium amide.[16] It was synthesized as follows

$$[\mathrm{LiN(Me)Ar^{Mes_2}}]_2 + 2\mathrm{TlCl} \xrightarrow[-20\ ^\circ\mathrm{C\ Et_2O}]{-2\mathrm{LiCl}} 2\mathrm{TlN(Me)Ar^{Mes_2}}$$

Compound **1** was obtained as orange crystals upon storing the reaction mixture at ca. −30 °C for 12 h. It was characterized by UV−vis spectroscopy and X-ray crystallography.[17]

Solutions of **1** are thermally unstable and decompose above −10 °C with the deposition of Tl metal. The UV−vis spectrum of **1** was obtained using the reaction mixture because isolated crystals of **1** could not be redissolved in hydrocarbons (diethyl ether, THF, hexane, toluene, or benzene) without decomposition. However, the instability of **1** did not hinder solid-state characterization.

Crystals of **1** contained two crystallographically independent molecules of **1** and a disordered ether molecule at one-

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(15) $[\mathrm{LiN(Me)Ar^{Mes_2}}]_2$ was synthesized from $\mathrm{HN(Me)Ar^{Mes_2}}$ and BuLi in hexane and obtained as a colorless solid. The synthesis of the secondary amine was by reaction of $\mathrm{H_2NAr^{Mes_2}}$[a] with MeI. (a) Twamley, B.; Hwang, C.-S.; Hardman, N. J.; Power, P. P. *J. Organomet. Chem.* **2000**, *609*, 152

(16) $[\mathrm{LiN(Me)Ar^{Mes_2}}]_2$ (0.349 g, 0.5 mmol) was dissolved in $\mathrm{Et_2O}$ (40 mL), and the mixture was cooled to −20 °C. This solution was added dropwise over 20 min to a foil-wrapped Schlenk flask charged with TlCl (0.119 g, 0.5 mmol) and $\mathrm{Et_2O}$ (20 mL). The resulting orange solution was stirred at −20 °C for 2 h and concentrated to ca. 30 mL under reduced pressure. Overnight storage at ca. −30 °C afforded pale orange X-ray-quality crystals. Yield 0.190 g (35%). Mp dec 45 °C.

(17) Crystal data for **1**: $\mathrm{C_{51.5}H_{60}N_2O_{0.5}Tl_2}$, $M_r = 1123.76$, monoclinic, $P2_1/c$, $Z = 4$, $a = 14.0469(8)$ Å, $b = 23.9451(13)$ Å, $c = 14.2106(8)$ Å, $\alpha = 90°$, $\beta = 110.8800(10)°$, $\gamma = 90°$, $V = 4465.9(4)$ Å^3, $\mu = 7.245$ mm^{-1}, $R(I > 2\sigma I) = 0.0301$, GOF = 1.033.

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(21) Calculations were performed using DFT for the gaseous phase with a hybrid B3LYP functional, including Becke's three-parameter nonlocal exchange potential and the nonlocal Lee−Yang−Parr correlation functional. To reduce computational costs without neglecting relativistic effects, core electrons on the Tl valence shell were represented by the quasirelativistic effective-core potential (ECP). For this purpose, the small-core CRENBL shape-consistent pseudopotential {ECP with a valence basis (3s, 3p, 4d) → [1s, 1p, 1d] and 68 electrons in the core} was used for the Tl atom. H, C, and N atoms were described with a 6-31G* basis set or with 6-31+G** basis sets augmented with a single diffuse function for the calculations of the interaction energies. The interaction energies were corrected for basis set superposition error (BSSE) using the counterpoise method of Boys and Bernardi.[21a] The geometry optimizations of the model thallium complex were performed with the LANL2DZ basis set and subsequently with a combination of the CRENBL basis set for the thallium atom and 6-31G* basis sets for all other atoms.[21b] The DFT calculations were carried out using the Gaussian 03 package,[21c] and the representations of the molecular structures and molecular orbitals were generated with the MOLEKEL program.[21d] The DFT-optimized structure of the model complex in which the terphenyl methyls are replaced by hydrogen atoms remains close to that obtained from the X-ray study with; nevertheless, some differences arose depending on the basis set used for the optimization. For clarity, the central phenyl ring in the model molecule is denoted $\mathrm{Ph_C}$; the flanking ring close to Tl is denoted $\mathrm{Ph_T}$, and that close to the methyl is denoted $\mathrm{Ph_M}$. The LANL2DZ-optimized structure exhibits the following bond distances (Å) and angles (deg): C(Ph)−N = 1.397, N−C(Me) = 1.482, N−Tl = 2.353, Tl−centroid = 3.208, $\mathrm{Ph_C/Ph_M}$ = 51, $\mathrm{Ph_C/Ph_T}$ = 81. In the CRENBL/6-31G*-optimized structure these distances (Å) and angles (deg) are 1.371, 1.454, 2.374, 3.015, 53, and 64, respectively. The interaction of the Tl atom with the closest flanking aryl ring was investigated by calculating the interaction energy for the simplified system in which the distance between a benzene molecule and the thallium atom in a PhNMeTl model was varied over a range of distances from 1.4 to 4.6 Å. The minimum interaction is found at a centroid distance of 3.6−3.8 Å. At this distance, the calculated interaction energy is ca. 0.62 kcal mol^{-1}. At a centroid distance of 3.0 A (corresponding to that found in the crystal structure), this energy is 3.01 kcal mol^{-1}. (a) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553 (b) Kuechle, W.; Dolg, K.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245. (c) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.01; Gaussian, Inc.: Pittsburgh, PA, 2003. (d) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.3*; Swiss Center for Scientific Computing: Manno, Switzerland, 2000−2002.

half occupancy in the asymmetric unit.[17] The structural parameters of **1** are similar, and both molecules are shown in Figure 1. The Tl(1)−Tl(2) separation is 7.008(3) Å; cf. Tl−Tl = 4.06 Å in the tetrameric amide $[TlN(SiMe_3)Dipp]_4$ (**2**).[13c] The coordination at nitrogen is planar with an average Tl−N distance of 2.364(3) Å. This distance is greater than predicted by the sum of the covalent radii Tl (1.55)[18] and N (0.70 Å)[18] and is ca. 0.20 Å longer than the Tl−N distance [2.15(1) Å] in the gas-phase monomer $TlN(SiMe_3)_2$. However, the Tl−N distance in **1** is similar to that determined for weakly associated **2** [2.307(6) Å] and is ca. 0.2 Å shorter than the 2.581(7) Å in the dimer $Tl_2\{\mu\text{-}N(SiMe_3)_2\}_2$.[19] Compound **1** also features an apparent Tl−arene interaction[13a,13c,20] with the flanking mesityl substituent [centroid−Tl = 3.026(2) Å (avg)] and a longer interaction of 3.569(2) Å to the centroid of an aryl ring of a neighboring molecule. The mesityl ring subtends an angle of 81.75(3)° (avg) with respect to the Tl−N−Me coordination plane, and in turn, the dihedral angle between the N coordination plane and the central phenyl is 16.5(4)° (avg). The lengthening of the Tl−N bond is consistent with an increase in the effective coordination number of the metal caused by the thallium−arene interaction (but see below).

The Tl−centroid distance in **1** is ca. 0.3−0.6 Å shorter than the Tl−C distances recently reported in $[YCl_3(Tp^{Ms*})Tl]$, Tp^{Ms*} = [HB(3-mesityl-pyrazolyl)$_2$-(5-mesitylpyrazolyl)]$^-$.[20a] However, the Tl−centroid distance in **1** falls within the ranges spanned by those in $[(Mes)_6Tl_4(GaBr_4)_4]$[20b] (2.94−3.03 Å) and $\{[Mes_2Tl][AlCl_4]\}_2$[20c] and $[Mes_2TlOTeF_5]_2$ (2.94−3.35 Å).[20d] The metal−arene interactions in the aluminum salt are dynamic in solution, with rapid exchange of the arene as indicated by ^1H NMR spectroscopy.[20c] The instability of **1** precluded detailed NMR studies. However, inspection of the structural details of the terphenyl ligand revealed no differences in C−C bond lengths between the two mesityl rings. Moreover, the thallium−arene centroid interactions in **1** are substantially longer than the Tl−C distances in the dimer $[C_5(CH_2Ph)_5Tl]_2$ (2.49 Å).[7]

To gauge the strength of the thallium−arene interactions in **1**, DFT calculations[21] were carried out on the molecular model $TlN(Me)Ar^{Ph_2}$ and the model complex TlN(Me)Ph/benzene (Figure 2), in which the Tl−centroid distance was varied. At the B3LYP/LANL2DZ level, the optimized structure of $TlN(Me)Ar^{Ph_2}$ reproduced the major structural parameters (C_{ipso}−N = 1.397 Å, N−Me = 1.482 Å, N−Tl = 2.353 Å, Tl−centroid = 3.20 Å) of **1** with good accuracy.

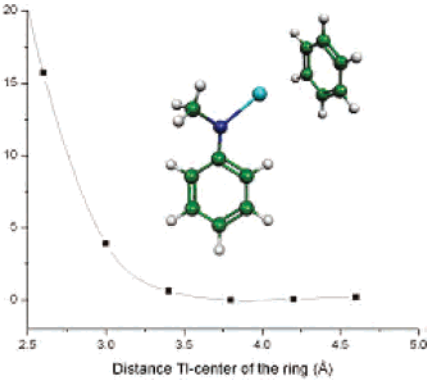

Figure 2. Plot of Tl−arene interaction energy versus Tl−centroid distance.

The TlN(Me)Ph/benzene model gave a minimum of energy at a Tl−centroid distance of ∼3.6−3.8 Å, which corresponds to a BSSE-corrected interaction energy of 0.60 kcal mol^{-1}. The calculated energy at the experimental centroid distance [3.026(2) Å] is 3.0 kcal mol^{-1}. Thus, the DFT calculations further underscore the weak nature of the Tl−arene interactions. Given the large variation in Tl−N bond lengths in Tl(I) amides,[13] it seems likely that weak secondary interactions can have a very large effect on the Tl−N bond length in such compounds.

The electronic spectrum of **1** is dominated by a decreasing absorbance (inflection point ca. 350 nm; 0.01 M solution) that extends into the visible region. This signal is blue-shifted compared to that of $TlAr^{Trip_2}$, which exhibits two absorbances at ca. 366 and 492 nm. The shifted spectrum is probably a result of the increased singlet−triplet energy. Theoretical calculations on the lighter group 13 element complexes MeM and $(H_3Si)_2NM$ (M = B−In) predicted a ca. 20 kcal mol^{-1} greater singlet−triplet energy for the amides.[22] Current work is focused on the synthesis of lighter triel compounds of the general formula $(R_2NM)_n$ (n = 1, 2, 3, ..., etc.) that will allow the effects of nitrogen substitution on M−M interactions to be determined experimentally.

Acknowledgment. We are grateful to the National Science Foundation for financial support. R.J.W. thanks Dr. Jim Fettinger for crystallographic assistance.

Supporting Information Available: X-ray data (CIF) for **1** is available free of charge via the Internet at http://pubs.acs.org.

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