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Monomeric Thallium(I) Complexes of Fluorinated Triazapentadienyl Ligands**

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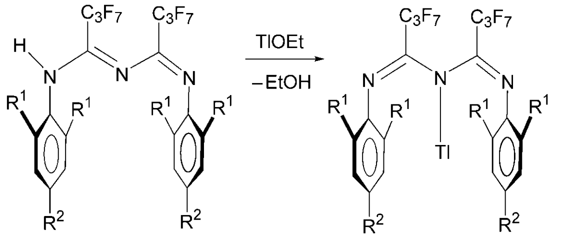
Thallium(I) derivatives of monoanionic, nitrogen-based ligands show interesting structures and properties.[1–3] For example, $[\{Tl[(Me_3Si)_2N]\}_2]$ has a dimeric structure with a four-membered $\{[TlN]_2\}$ motif,[4] and these dimer units further aggregate to form Tl⋯Tl-linked extended chains. The related Tl^I amido derivative $[\{Tl[(dipp)(Me_3Si)N]\}_4]$ (dipp = 2,6-iPr$_2$C$_6$H$_3$) is also known,[5] but it is a tetramer in the solid state with weak Tl⋯arene interactions (mean Tl⋯Ct distance 3.11 Å; Ct = arene ring centroid) and long Tl⋯Tl contacts (average 4.06 Å). The pentaazapentadienylthallium(I) complex $[\{Tl\{[N(tol)N]_2\}\}_2]$ (tol = tolyl) has intermolecular Tl⋯Tl, Tl⋯N, and Tl⋯arene interactions,[6] and the tris(pyrazolyl)borate complex $[\{Tl\{HB[3\text{-(cyclopropyl)}Pz]_3\}\}_4]$ (Pz = pyrazole) is a tetramer with a perfect tetrahedral Tl_4 core.[7] A rare, monomeric Tl^I species $[Tl\{HC[(Ph)C(Me_3Si)N]_2\}]$ involving a diazapentadienyl ligand was also reported recently.[8] In general, neutral thallium(I) compounds tend to aggregate into interesting structures with intermolecular Tl⋯Tl and/or Tl⋯donor-atom interactions.[1–3] Mononuclear complexes of Tl^I are relatively uncommon in the solid state, with most known examples, such as $[Tl\{MeB[3\text{-}(t\text{Bu})Pz]_3\}]$, being confined to sterically demanding poly(pyrazolyl)borate ligands.[1,3] It is also noteworthy that, in contrast to poly(pyrazolyl)borate complexes of Tl^I, thallium adducts of other monoanionic, nitrogen-based ligands are relatively less explored.[1–3]

We have recently investigated the chemistry of triazapentadienyl ligands[9,10] as these ligands show an interesting ability to vary their mode of coordination to fit the needs of the metal fragment.[9–12] Thallium(I) derivatives of triazapentadienyl ligands are of particular interest because they could serve as good ligand-transfer agents (like the commonly used thallium adducts of poly(pyrazolyl)borates and diazapentadienyl systems).[1,3,13–16] We discovered that it is possible to isolate mononuclear thallium(I) complexes containing fluorinated triazapentadienyl ligands. Specifically, $[Tl\{N[C(C_3F_7)N(Mes)]_2\}]$ (**1a**) and $[Tl\{N[C(C_3F_7)N(dipp)]_2\}]$ (**1b**; Mes = 2,4,6-$Me_3C_6H_2$) could be obtained in high yield by treating the parent ligands $HN[C(C_3F_7)N(Mes)]_2$ and $HN[C(C_3F_7)N(dipp)]_2$ with one equivalent of TlOEt in hexane (Scheme 1).[17] These thallium(I) complexes are colorless, crystalline solids that decompose slowly if exposed to air and light for prolonged periods. The ^{1}H and ^{19}F NMR spectra of **1a** and **1b** in $CDCl_3$ at room temperature are much simpler than the corresponding spectra of the related free ligands. For example, the ^{1}H NMR resonances of the iPr protons of **1b** appear as four doublets (two of which are overlapping) and two septets, whereas in $HN[C(C_3F_7)N(dipp)]_2$ [10] these protons give rise to nine separate doublets and four separate septets. This is similar to changes observed during the formation of the silver adducts $[AgL\{N[C(C_3F_7)N(dipp)]_2\}]$ (L = MeCN, tBuNC) from the free ligand.[10,17]



1a: R^1 = Me, R^2 = Me
1b: R^1 = iPr, R^2 = H

Scheme 1. Synthesis of triazapentadienylthallium(I) complexes **1a** and **1b**.

The X-ray structures of **1a** and **1b** (Figure 1) reveal that the thallium ion coordinates to the triazapentadienyl ligand at the central nitrogen atom in both these systems.[18] The ligand backbones adopt a W-shaped configuration (an all-*trans* or zigzag arrangement of the N_3C_2 core) with the two aryl (Mes or dipp groups) moieties flanking the thallium atom. They show a short-long-long-short C−N bond distance pattern consistent with the resonance form illustrated in Scheme 1. The mesityl compound **1a** crystallizes in the $P2/n$ space group with two molecular halves in the asymmetric unit, and is located on a crystallographic twofold rotation axis containing the Tl−N bond. It is monomeric, and has no close Tl⋯Tl contacts. The dipp analog **1b** crystallizes in the $P2_12_12_1$ space group with three molecules in the asymmetric unit. These molecules also do not show intermolecular Tl⋯Tl contacts: the closest contact involving the Tl^I ion and a neighboring molecule is of the Tl⋯F−CF type (3.21 Å), which is at the long end of weak thallium–fluorine interactions[19] and is probably a result of crystal packing. Furthermore, this interaction does not affect the C−F bond distance.

The Tl−N bond distances of **1a** are 2.608(3) and 2.675(4) Å. In **1b**, two molecules have similar Tl−N distances

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

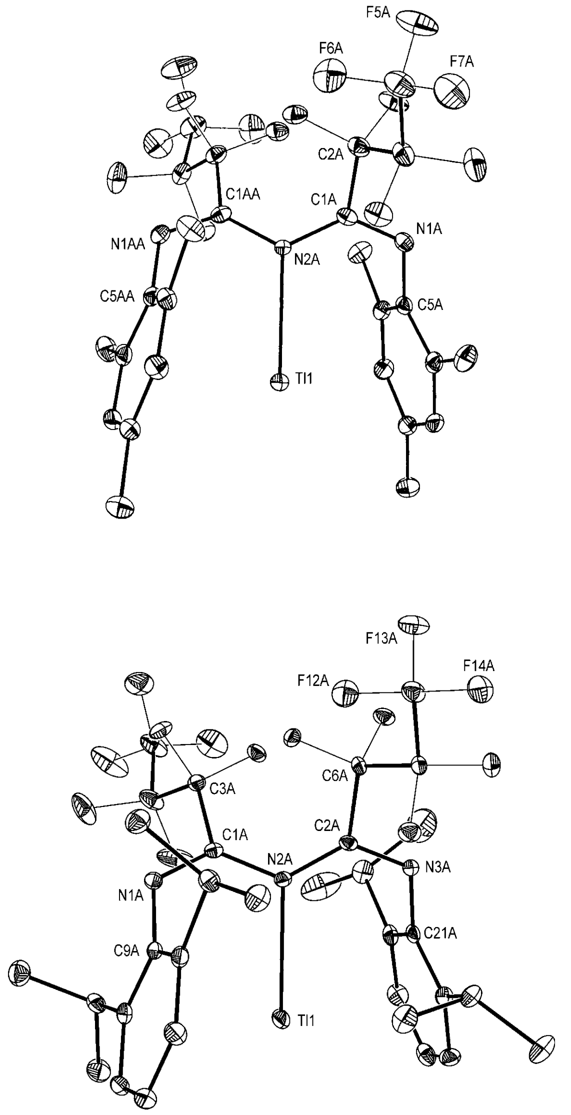

Figure 1. Molecular structures of [Tl{N[C(C_3F_7)N(Mes)]$_2$}] (**1a**, above) and [Tl{N[C(C_3F_7)N(dipp)]$_2$}] (**1b**, below). Only one molecule in the asymmetric unit is shown; hydrogen atoms have been omitted for clarity.

(2.672(2) and 2.666(2) Å) while the third molecule has a slightly longer Tl–N (2.732(2) Å) bond. These distances exceed the sum (2.30 Å) of the covalent radii of Tl (1.55 Å)[20] and N (0.75 Å). The Tl–N bonds in these adducts could therefore be considered as somewhat ionic. For comparison, the Tl–N bond distance in [{Tl[(dipp)-(Me_3Si)N]}$_4$] is 2.307(6) Å.[5] Further analysis of Tl–N distances for neutral complexes in the Cambridge Structural Database (CSD; the N center is restricted to three-coordination) yields a mean distance of 2.42 ± 0.20 Å (345 complexes),[21] thus the observed Tl–N distances in **1a** and **1b** are toward the long end of the range of reported Tl–N bonds, and most similar to Tl–N distances seen in tris(pyrazolyl)borate complexes of Tl^I. Indeed, restricting the search to bis- and tris(pyrazolyl)borate complexes yields a mean Tl–N distance of 2.63 ± 0.20 Å ($n = 107$).

The thallium(I) adducts **1a** and **1b** feature an intriguing structure. In addition to the Tl–N bond, as illustrated in Figure 1, each thallium center is flanked by two aryl moieties. Although the Tl–C distances are significantly longer than the typical Tl–C single bonds (e.g., 2.34(1) Å found in [(2,6-trip$_2C_6H_3$)Tl]; trip = 2,4,6-iPr$_3C_6H_2$),[22] some separations are within the sum of the van der Waals radii of Tl and C (3.66 Å).[23] For example, the Tl–Ct distances (Ct = arene ring centroid) in the two molecules of **1a** and the three molecules of **1b** are 3.00, 3.00; 3.10, 3.10 (with shortest Tl–C separations of 3.02, 3.02; 3.04, 3.04) Å and 2.85, 3.44; 2.85, 3.56; 2.95, 3.08 (with closest Tl–C separations of 3.09, 2.94; 3.10, 2.92; 3.09, 3.08) Å, respectively. Furthermore, the Tl–carbon distances of structurally characterized Tl–arene π complexes are 3.29 ± 0.08 Å (72 complexes),[21] which corresponds to a mean Tl–Ct distance of around 3.00 Å, which is close to the shorter of the Tl–Ct values in the present crystal structures. On the other hand, the Tl···arene contacts in the complexes reported here do not seem to substantially modify the ligand parameters. For example, the C–N distance and C–N–C and N–C–N angles of the W-shaped ligand backbone are very similar in **1a** and **1b**, in the related anion [N{C(C_3F_7)NPh}$_2$]$^-$,[24] and in the κ^1N(central)-bonded metal adducts [LM{N[C(C_3F_7)N-(dipp)]$_2$}] (LM = MeCNAg, tBuNCAg, MeHg).[10,12,17]

To clarify whether Tl···arene contacts are "enforced" by the W-shape ligand conformation that places the aryl groups in a quasi-perpendicular arrangement (see Figure 1) or energetically driven, we undertook a computational study. A density functional (B3LYP/CEP-31G(d)) geometry optimization of D_6 [Tl(η^6-benzene)$_2$]$^+$ yields a Tl–Ct distance of 2.92 Å,[15] in good agreement with the average values obtained from the CSD and the shorter distances measured here for **1a** and **1b**, thus indicating the potential for stabilization of the Tl by π-arene interactions. B3LYP/CEP-31G(d) calculation of the gas-phase dissociation energy of D_6 [Tl(η^6-benzene)$_2$]$^+$ to Tl$^+$ and two benzene molecules shows the reaction to be exothermic by 42 kcal mol^{-1}, thus indicating an average Tl–π-arene interaction energy of 21 kcal mol^{-1}. Not surprisingly, neutral models such as [Tl{N[C(R')NR]$_2$}] yield weaker, Tl–π-arene interaction energies of 11 (R' = H, R = Ph) and 12 kcal mol^{-1} (R' = F, R = Ph). These energies were estimated by taking the difference in the homolytic Tl–ligand bond energies for [Tl{N[C(R')NPh]$_2$}] and [Tl{N[C(R')NH]$_2$}], in which R' = H or F.

Hybrid quantum/molecular mechanical calculations (see Figure 2 and the Supporting Information) on a full experimental model (geometries optimized starting from the three different molecules in the asymmetric unit of **1b**) yield commensurate Tl–π-arene interaction energies of 13 kcal mol^{-1}. The [Tl(2,6-trip$_2C_6H_3$)] complex reported by Niemeyer and Power, which to the best of our knowledge represents the most bona fide example of Tl^I monocoordination,[22] has arene interaction energies of around 3 kcal mol^{-1} between Tl and each aryl substituent. The Tl···arene interaction energies in the triazapentadienyl complexes can be compared to the Tl–N bond energies calculated from triazapentadienyl models without arene substituents—63 (R' = R = H) and 64 kcal mol^{-1} (R' = H, R = F)—at the same B3LYP/CEP-31G(d) level of theory. Therefore, computational estimates

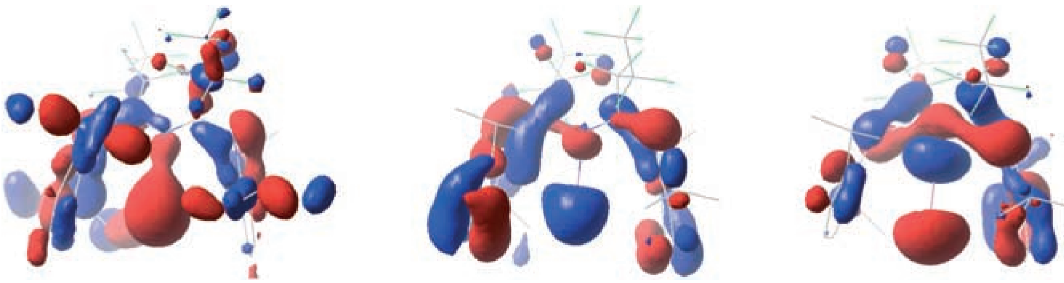

Figure 2. Orbitals derived from QM/MM (UFF force field for C_3F_7 and *i*Pr substituents; B3LYP/CEP-31G(d) for remainder of complex **1b**) geometry optimization that displays delocalization between the arene π-ring and the Tl 6s orbital.

imply an essentially monocoordinate Tl^{I} center in **1a** and **1b** whose stability is supplemented by Tl···arene interactions. A plot of the Kohn–Sham orbitals of **1b** shows three orbitals that display significant interactions; these correspond to the in-phase and out-of-phase combinations of the lowest energy arene π orbital and the Tl 6s orbital (Figure 2). Furthermore, the analogous orbitals (see the Supporting Information) for $[Tl(\eta^6\text{-benzene})_2]^+$ show greater Tl–π-arene delocalization for this cationic system, thus supporting the contention of weaker, albeit significant, Tl–π-arene interactions for the present neutral triazapentadienyl complexes.

The coordination properties of $[N\{C(C_3F_7)NR\}_2]^-$ also merit some comment as it binds to metal ions in several different fashions (e.g., κ^1N(central), κ^1N(terminal), or κ^2N-(terminal) with W- or U-shaped ligand conformers).[9–12] The two lowest energy conformations found for the full ligand models at the PM3 level of theory are U-shaped and W-shaped,[17] with the U-shaped conformer being only 0.1 kcal mol^{-1} lower in energy than the W-shaped conformer. Hence, these conformations are essentially degenerate. One may infer that the backbone conformation adopted upon ligation by a metal fragment will be primarily determined by the steric and electronic characteristics of the metal. The electronic properties for the two lowest energy conformations of $[N\{C(C_3F_7)NR\}_2]^-$ were thus calculated. A plot of the highest-unoccupied molecular orbital (HOMO) for $[N\{C(C_3F_7)NR\}_2]^-$ shows it to be the expected nonbonding π orbital of a conjugated five-atom entity. The HOMO for the W conformer is shown in Figure 3 (the HOMO of the U conformer is the same). Evidently, the HOMO is more or less evenly distributed among the three N atoms of the anionic ligand, which implies that in an orbitally controlled or covalent regime there will be little bias for ligation of the metal at either the terminal or central nitrogen atoms. Thus, it is plausible to infer that discrimination among different coordination modes will be made on the basis of charge considerations, the chelate effect, and/or steric effects. To probe the first of these inferences, the Mulliken charges of the U and W conformations were calculated. They are interesting in that they point to the central nitrogen atom of the N_3C_2 core being more nucleophilic/basic than the terminal nitrogen atoms. The calculated Mulliken charges are −0.2 for the terminal nitrogens and −0.4 for the central nitrogen. Hence, electrophiles/acids are expected to coordinate to the central nitrogen, as seen in the thallium(I) adducts described herein.

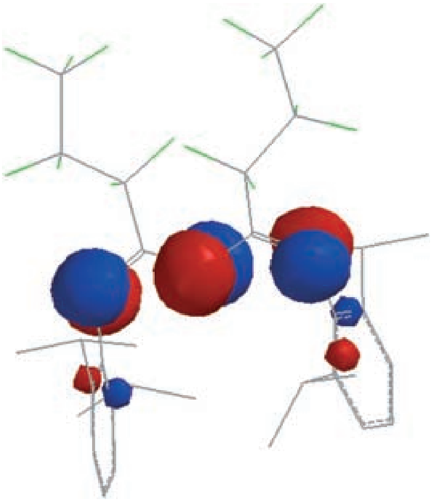

Figure 3. Highest energy molecular orbital (PM3 calculation) of $[N\{C(C_3F_7)N(dipp)\}_2]^-$.

Overall, we report here the isolation of the first monomeric, Tl–N-bonded complexes of triazapentadienyl ligands. Compounds **1a** and **1b** also feature weak Tl···arene contacts. The computational investigation has revealed that these interactions are energetically important, although secondary to Tl–N bond interactions. The thallium(I) ion coordinates to the more nucleophilic nitrogen site of the ligand anion. The triazapentadienyl ligands used in this study may be compared to the diazapentadienyl and pentaazapentadienyl systems. Few thallium(I) adducts of the latter two ligand types are known,[1] and only $[Tl\{PhC[C(H)N(dipp)]_2\}]$,[8] $[Tl\{HC[C(Ph)N(Me_3Si)]_2\}]$,[8] and $[\{Tl\{N[N(tol)N]_2\}\}_2]$[6] have been structurally characterized. Thus, the title compounds represent a rare addition to thallium derivatives of the azapentadienyl ligand family.[25]

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[1] H. V. R. Dias, *Comprehensive Coordination Chemistry II*, *Vol. 3* **2004**, pp. 383–463.

[2] L. H. Gade, *Dalton Trans.* **2003**, 267–278.

[3] C. Janiak, *Coord. Chem. Rev.* **1997**, *163*, 107–215.

[4] K. W. Klinkhammer, S. Henkel, *J. Organomet. Chem.* **1994**, *480*, 167–171.

[5] S. D. Waezsada, T. Belgardt, M. Noltemeyer, H. W. Roesky, *Angew. Chem.* **1994**, *106*, 1413–1414; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1351–1352.

[6] J. Beck, J. Strähle, *Z. Naturforsch. B* **1986**, *41*, 1381–1386.

[7] A. L. Rheingold, L. M. Liable-Sands, S. Trofimenko, *Chem. Commun.* **1997**, 1691–1692.

[8] Y. Cheng, P. B. Hitchcock, M. F. Lappert, M. Zhou, *Chem. Commun.* **2005**, 752–754.

[9] H. V. R. Dias, S. Singh, *Inorg. Chem.* **2004**, *43*, 5786–5788.

[10] H. V. R. Dias, S. Singh, *Inorg. Chem.* **2004**, *43*, 7396–7402.

[11] A. R. Siedle, R. J. Webb, F. E. Behr, R. A. Newmark, D. A. Weil, K. Erickson, R. Naujok, M. Brostrom, M. Mueller, S.-H. Chou, V. G. Young, Jr., *Inorg. Chem.* **2003**, *42*, 932–934.

[12] A. R. Siedle, R. J. Webb, M. Brostrom, R. A. Newmark, F. E. Behr, V. G. Young, Jr., *Organometallics* **2004**, *23*, 2281–2286.

[13] L. D. Amisial, X. Dai, R. A. Kinney, A. Krishnaswamy, T. H. Warren, *Inorg. Chem.* **2004**, *43*, 6537–6539.

[14] X. Dai, P. Kapoor, T. H. Warren, *J. Am. Chem. Soc.* **2004**, *126*, 4798–4799.

[15] P. L. Holland, T. R. Cundari, L. L. Perez, N. A. Eckert, R. J. Lachicotte, *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424.

[16] X. Dai, T. H. Warren, *Chem. Commun.* **2001**, 1998–1999.

[17] See Supporting Information for more details.

[18] X-ray quality crystals of **1a** and **1b** were obtained from hexane solutions at −5 °C. X-ray data for **1a**: $C_{26}H_{22}F_{14}N_3Tl$, monoclinic, space group $P2/n$; $a = 18.1041(7)$, $b = 8.8224(4)$, $c = 18.8037(8)$ Å, $\beta = 105.5130(10)°$, $V = 2900.5(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.939$ Mg m^{-3}. Hydrogen atoms were placed in idealized positions and included as riding atoms. All non-hydrogen atoms were refined anisotropically. $R1$, $wR2$ $(I > 2\sigma(I)) = 0.0278$, $wR2 = 0.0653$. X-ray data for **1b**: $C_{32}H_{34}F_{14}N_3Tl$, orthorhombic, space group $P2_12_12_1$, $a = 17.1432(6)$, $b = 19.4275(7)$, $c = 30.7929(11)$ Å, $V = 10255.6(6)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.809$ Mg m^{-3}. Hydrogen atoms were placed in idealized positions and included as riding atoms. All non-hydrogen atoms were refined anisotropically, $R1$, $wR2$ $(I > 2\sigma(I)) = 0.0217$, 0.0489. CCDC-262530 (**1a**) and -262531 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] H. Plenio, *Chem. Rev.* **1997**, *97*, 3363–3384.

[20] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.

[21] *Cambridge Structural Database*, London, UK, **2004**.

[22] M. Niemeyer, P. P. Power, *Angew. Chem.* **1998**, *110*, 1291–1294; *Angew. Chem. Int. Ed.* **1998**, *37*, 1277–1279.

[23] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

[24] A. R. Siedle, R. J. Webb, M. Brostrom, S.-H. Chou, D. A. Weil, R. A. Newmark, F. E. Behr, V. G. Young, Jr., *Inorg. Chem.* **2003**, *42*, 2596–2601.

[25] Details of the synthesis, characterization, and computational study are given in the Supporting Information.