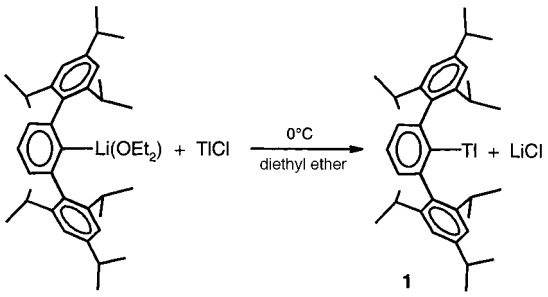
Synthesis and Solid-State Structure of 2,6-Trip$_2$C$_6$H$_3$Tl (Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$): A Monomeric Arylthallium(I) Compound with a Singly Coordinated Thallium Atom**

Mark Niemeyer* and Philip P. Power

For thallium, the heaviest element of Group 13, the univalent state is the most stable oxidation state, at least in aqueous solution. This, however, no longer applies to organothallium(I) compounds with σ-bonded substituents, which have attracted much less attention.[1] Structurally characterized moieties with a Tl^{I}–C bond were limited for a long time to compounds with cyclopentadienyl ligands.[2] Only very recently Uhl et al. described the synthesis of Tl[C(SiMe$_3$)$_3$].[3] This alkylthallium(I) compound is tetrameric in the solid state. Thallium(I) derivatives with thallium bonded to higher homologues of Group 14 have not been obtained so far. Efforts to synthesize corresponding compounds with a Tl–Si bond surprisingly resulted in the formation of the thallium(II) derivatives Tl$_2$[Si(SiMe$_3$)$_3$]$_4$[4a] and Tl$_2$(Si*t*Bu$_3$)$_4$.[4b]

Fully characterized thallium(I) aryl compounds were not previously known. We are interested in their properties, because they could serve as mild reagents for the synthesis of otherwise inaccessible aryl derivatives of main group and rare earth elements. Suitable substituents for this purpose are the terphenyl ligands 2,6-Mes$_2$C$_6$H$_3$ and 2,6-Trip$_2$C$_6$H$_3$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$, Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$). These sterically congested ligands have been used successfully in the last few years for the stabilization of low coordination numbers,[5] compounds free of Lewis donors,[6] and new multiple-bond systems.[7]

Thallium(I) chloride was allowed to react at 0°C with 2,6-Trip$_2$C$_6$H$_3$Li · Et$_2$O[5c] in diethyl ether (Scheme 1). After several minutes the suspension becomes red-orange. The workup procedure affords the thallium(I) aryl product (**1**) as bright orange, extremely air-sensitive crystals in 58% yield. A second compound, 2,6-Mes$_2$C$_6$H$_3$Tl (**2**) can be prepared in a similar manner as shown in Scheme 1. The isolated deep-red solid is thermally very labile and could not be fully characterized. Freshly synthesized **1** is stable in the mother liquid at −40°C for long periods whereas the isolated solid cannot be stored indefinitely, but slowly decomposes even at low temperatures. This decay is accelerated autocatalytically once thallium metal is formed. In solution **1** is thermally fairly stable, but very light sensitive. A solution of **1** in benzene in an NMR tube exposed to bright sunlight forms a thallium mirror after only a few seconds. The characteristic absorption in the UV/Vis spectrum of **1** at 487 nm is the band with the strongest shift to longer wavelengths. No ^{203}Tl or ^{205}Tl couplings are observed in the ^{1}H and ^{13}C NMR spectra even at low temperatures (203 K), which could point to a dynamic exchange in solution.



Scheme 1. Synthesis of **1**.

The X-ray structure analysis[8] reveals the solid-state structure of **1** to consist of monomeric 2,6-Trip$_2$C$_6$H$_3$Tl units with a singly coordinated thallium atom (Figure 1). The

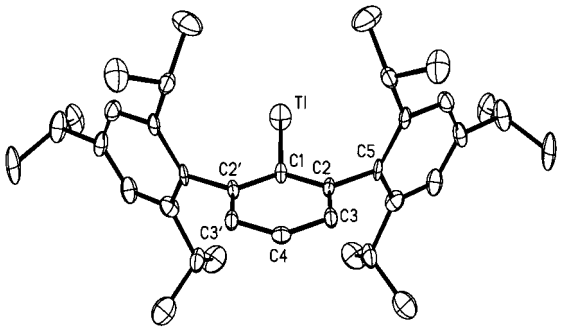


Figure 1. Molecular structure of **1** in the crystal; hydrogen atoms have been omitted for clarity. Selected bond distances [pm] und angles [°]: Tl–C1 234(1), C1–C2 139(1), C2–C3 138(1), C3–C4 138(1), Tl-C1-C2 120.2(6), C2-C1-C2′ 119(1).

shortest intermolecular Tl–Tl and Tl–C distances are 681 and 419 pm. The Tl–C1 bond (234(1) pm) is marginally shorter than the corresponding value for Tl$_4$[C(SiMe$_3$)$_3$]$_4$ (average 237 pm)[3]. As expected, shorter distances of 209 to 221 pm[11] are observed in arylthallium(III) derivatives. The dihedral angle between the phenyl substituents of the Trip groups and the central phenyl ring is 81°. This deviation from orthogonality leads to a displacement of the Tl atom from the C(1)–C(6) plane by 28 pm. Additional contacts of the thallium to C2 (327(1) pm) and C5 (335(1) pm) are observed, but these are geometrically determined. The long-known neutral arenethallium(I) complexes[12] with η^6-coordination show Tl–C contacts between 313 and 352 pm and distances between the Tl atom and the center of the arene ring of 294–311 pm. The corresponding value of 392 pm in **1** indicates no significant interaction with the Trip substituents.

Monomeric Tl^{I} compounds are relatively rare in the solid state. The known examples are mainly limited to thallium(I) trispyrazolylborates, which have a three-coordinate metal center.[1] The recently published gas phase structure of Ga[C(SiMe$_3$)$_3$][13] is a rare example of a monomeric singly coordinated metallorganic compound of a Group 13 element.

[*] Dr. M. Niemeyer
Institut für Anorganische Chemie der Universität
Pfaffenwaldring 55, D-70569 Stuttgart (Germany)
Fax: (+49) 711-685-4241
E-mail: niemeyer@iac.uni-stuttgart.de
Prof. P. P. Power
Department of Chemistry, University of California,
Davis CA 95616 (USA)

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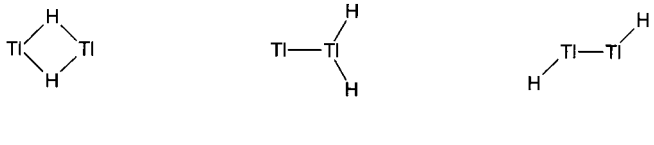
To the best of our knowledge, there are only two published examples of a metal with a coordination number of 1 in the solid state.[14] The composition of the species 2,4,6-$Ph_3C_6H_2M$ (M = Cu, Ag), however, is doubtful as subsequent investigations have revealed.[15] Therefore, the arylthallium(I) compound **1** may be the first example, or at least a good approximation, of a singly coordinated metal atom in the solid state.

Why does **1** show no tendency to oligomerize? According to semiempirical[16a] and ab initio[16b, c] calculations on the model system H_2Tl_2 the potential energy surface contains at least three minima. The most stable valence isomer (Scheme 2) is the dibridged isomer **I**, followed by the



I **II** **III**

Scheme 2. Possible valence isomers for the system Tl_2H_2.

structural type **II** and the *trans*-bent form **III**. Substitution of the hydrogen atoms by 2,6-$Trip_2C_6H_3$ groups leads to severe overcrowding. Therefore valence isomer **II** should not be stable for steric reasons. This is also likely for the bridged form **I**, which has been observed in the less crowded dimers 2,4,6-$(CF_3)_3C_6H_2OTl$[17a] and $TlN(SiMe_3)_2$[17b]. Corresponding dimeric metal(I) compounds ($\{2,6\text{-}Mes_2C_6H_3M\}_2$, M = Li,[6a] Na[6c]) have been synthesized before with the smaller 2,6-$Mes_2C_6H_3$ ligand. It is possible that this structural type is realized in the complex 2,6-$Mes_2C_6H_3Tl$ (**2**, deep-red color!).

For the *trans*-bent form **III** with a H-Tl-Tl angle of 115°, the dissociation energy was calculated to be 14 kJ mol^{-1} taking relativistic pseudopotentials into account.[16b] This structural type was observed for pentabenzylcyclopentadienylthallium(I).[2c] The same compound also crystallizes in a polymorphic form[1e] with a Cp–Tl···Cp arrangement, indicating relatively weak Tl^I–Tl^I interactions. A comparison with the recently published dianion $[2,6\text{-}Trip_2C_6H_3Ga_2]^{2-}$[7c] shows that **1** could assume a *trans*-bent form similiar to **III** for steric reasons. However, relatively small energies, which can be attributed to packing effects and Pauli repulsion forces, seem to be sufficient to stabilize the unusual monomeric structure of **1**.

Experimental Section

Thallium chloride (1.02 g, 4.25 mmol) was added to a solution of 2,6-$Trip_2C_6H_3Li \cdot Et_2O$[5c] (2.39 g, 4.25 mmol) in 25 mL diethyl ether, and the suspension was stirred with exclusion of light for 5 h at 0°C. The precipitated lithium chloride und thallium were rapidly separated over a glass filter frit. Cooling of the filtrate to −40°C afforded orange needles of **1.** Yield 1.69 g (58%). M.p. (under argon) 242°C, crystals change color from orange through red to black from 90°C upwards. A cryoscopic molecular mass determination could not be obtained due to the poor solubility of **1** in benzene. ^{1}H NMR (C_6D_6): $\delta = 1.19$ (d, $^3J(H,H) = 6.9$ Hz, 12H; *o*/*p*-$CH(CH_3)_2$), 1.26 (d, $^3J(H,H) = 6.9$ Hz, 12H; *o*/*p*-$CH(CH_3)_2$), 1.27 (d, $^3J(H,H) = 6.9$ Hz, 12H; *o*/*p*-$CH(CH_3)_2$), 2.86 (sept., $^3J(H,H) = 6.9$ Hz, 2H; *p*-$CH(CH_3)_2$), 3.24 (sept., $^3J(H,H) = 6.9$ Hz, 4H; *o*-$CH(CH_3)_2$), 7.27 (s, 4H; *m*-Trip), 7.31 (t, $^3J(H,H) = 7.4$ Hz, 1H; *p*-C_6H_3), 7.98 (d, $^3J(H,H) = 7.4$ Hz, 2H; *m*-C_6H_3); ^{13}C NMR ([D$_8$]THF): $\delta = 24.6$ (*o*/*p*-$CH(CH_3)_2$), 25.3 (*o*/*p*-$CH(CH_3)_2$), 30.8 (*o*-$CH(CH_3)_2$), 35.4 (*p*-$CH(CH_3)_2$), 121.1 (*m*-Trip), 125.0 (*p*-C_6H_3), 136.5 (br., *m*-C_6H_3), 138.7 (*i*-Trip), 146.0 (br, *o*-C_6H_3), 148.0 (*o*-Trip), 148.3 (*p*-Trip), signal for *i*-C_6H_3 not observed; UV/Vis (toluene): λ_{max} (ε) = 400 (520), 487 nm (250); MS (70 eV): *m*/*z* (%): 686.4 (36) [M^+ with ^{205}Tl], 685.4 (45) [$M^+ - H$ with ^{205}Tl], 482.4 (100) [$C_{36}H_{50}^+$], 205.0 (60) [^{205}Tl]; C,H analysis ($C_{36}H_{49}Tl$): calcd C 63.02, H 7.20; found C 61.35, H 7.34.

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[8] Crystal data for **1**: orange needle (0.70 × 0.10 × 0.07 mm) from diethyl ether, $C_{36}H_{49}Tl$, $M_r = 686.12$, orthorhombic, space group P*nma*, $a = 7.916(5)$, $b = 25.671(8)$, $c = 16.196(6)$ Å, $V = 3291(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.385$ g cm^{-1}, $\mu(Mo_{K\alpha}) = 4.927$ mm^{-1}, diffractometer Syntex P2$_1$, rapidly cooled crystal in Paratone N,[9] T = 173 K, Wyckoff scans, measurement range $3 \le 2\Theta \le 50°$, 3711 observed and 2962 unique reflections, programs SHELXTL 5.03 and SHELXL-97, refinement with all data against F^2, non-hydrogen atoms anisotropic, hydrogen atoms on calculated positions, 198 parameters, absorption correction by Ψ-scans, $R1 = 0.066$ for 1792 reflections with $I > 2\sigma(I)$, $wR2 = 0.158$ (all data), largest residual electron density: 1.07 near the thallium atom. Due to the fact that compounds with the 2,6-$Trip_2C_6H_3$ ligand may form mixed crystals,[10] and because the isotropic temperature factor of the thallium atom has a relatively large value of 0.054 Å^2, the data set was examined for possible contamination with 2,6-$Trip_2C_6H_4$. A site occupation factor of 94% for the thallium atom leads to a minor improvement of the *R* values ($wR2 = 0.157$, $R1 = 0.065$); the isotropic temperature factor of the thallium, however, is not significantly changed. A further possible contaminant, 2,6-$Trip_2C_6H_3I$, was excluded by NMR spectroscopy and mass spectrometry. In our opinion the enlarged motion parameter can be explained solely by the low coordination number of the thallium atom.

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Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100750. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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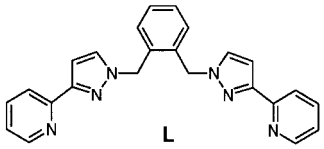
Anion-Templated Assembly of a Supramolecular Cage Complex**

James S. Fleming, Karen L. V. Mann, Charles-Antoine Carraz, Elefteria Psillakis, John C. Jeffery, Jon A. McCleverty,* and Michael D. Ward*

A current goal in supramolecular coordination chemistry is to understand how the self-assembly process between labile metal ions and flexible multidentate ligands is controlled.[1–11] In some cases the course of self-assembly may be controlled by using relatively rigid ligands, in which the symmetry of the arrangement of binding sites dictates only one possible outcome for the self-assembly process with a metal ion of a given stereoelectronic preference; this approach is exemplified by numerous "molecular grids",[2] and by some tetrahedral complexes prepared by Saalfrank et al.[3] and Raymond et al.[4] In other cases two or more different structures can arise from a single metal/ligand combination in which all components have the same stoichiometry (a "virtual combinatorial library" according to Lehn).[5–7] The nature of the product in such cases is thus often impossible to predict and can depend on subtle factors such as interligand stacking interactions[8] and the participation of noncovalently bonded anions[7, 9, 11] or cations[3, 10] in the resultant assembly.

We describe here complexes of the new ligand L, which contains two bidentate pyrazolyl–pyridine binding sites separated by an *o*-xylyl spacer. The complexes are $[Co_4L_6][BF_4]_8$ (**1**) and $[Ni_2L_3][BF_4]_4$ (**2**), which have the same



L

metal-to-ligand stoichiometry but surprisingly different structures given the very similar properties of the metal ions (size, charge, and preference for octahedral coordination).

The ligand L was simply prepared from reaction of 3-(2-pyridyl)pyrazole with 1,2-bis(bromomethyl)benzene.[12] Given that it has four donor atoms an M_2L_3 stoichiometry seemed likely to occur with Co^{II} and Ni^{II}. A material analyzing as $[Co_2L_3][BF_4]_4$ was easily prepared,[13] but the FAB mass spectrum (Figure 1) clearly indicated formation of a Co_4L_6 species, associated with varying numbers of $[BF_4]^-$ anions. The

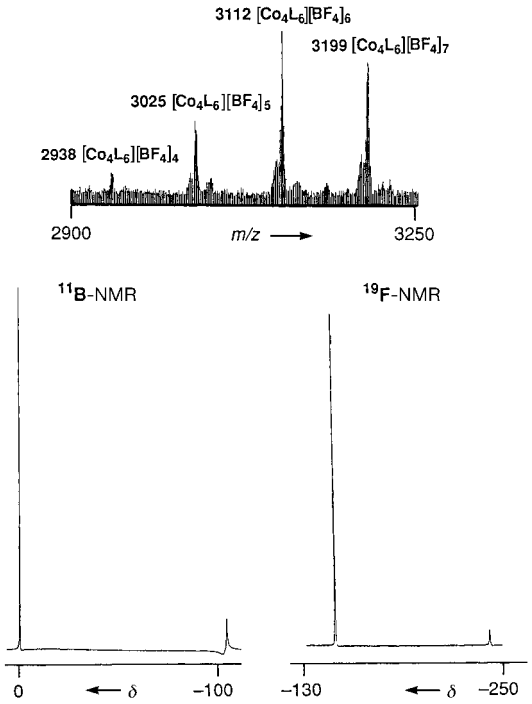


Figure 1. Top: part of the FAB mass spectrum (3-nitrobenzyl alcohol matrix) of **1**. Bottom: ^{11}B and ^{19}F NMR spectra of **1** (MeCN, room temperature): ^{11}B shifts vs. $BF_3(Et_2O)$, ^{19}F shifts vs. $CFCl_3$.

[*] Prof. J. A. McCleverty, Dr. M. D. Ward, Dr. J. S. Fleming, K. L. V. Mann, C.-A. Carraz, Dr. E. Psillakis, Dr. J. C. Jeffery
School of Chemistry, University of Bristol
Cantock's Close, Bristol BS8 1TS (UK)
Fax: (+44) 117-929-0509
E-mail: mike.ward@bristol.ac.uk

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