Coordination Polymers

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Unusual Coordination Behavior of P_n-Ligand Complexes with Tl^+**

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Whereas current approaches in supramolecular chemistry make almost exclusive use of nitrogen-, oxygen-, and/or sulfur-containing organic linkers to connect different metal centers,[1] we have demonstrated that organometallic P_n-ligand complexes are excellent building blocks for supramolecular assemblies. For instance, if copper(I) halides are allowed to react with the P_n-ligand complexes $[Cp^xFe(\eta^5\text{-}P_5)]$ ($Cp^x = Cp^*$ ($C_5(CH_3)_5$; **1a**),[2a] Cp^{Et} ($C_5(CH_3)_4C_2H_5$; **1b**)[2b]), or $[\{CpM(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ ($Cp = C_5H_5$; M = Cr[3a] (**2a**), Mo[3b] (**2b**)), neutral one-dimensional (1D)[4] and two-dimensional (2D)[5] polymers and spherical nanosized fullerene-like molecules[6] are obtained. In contrast, different dimeric and polymeric ionic compounds can be obtained if copper(I) and silver(I) salts of weakly coordinating anions (WCAs) are employed. Thus, we report on a polycationic chain containing Ag^+ ions[7] resulting from the reaction of $Ag[Al\{OC(CF_3)_3\}_4]$[8] and **1a**, and on a series of dicationic complexes incorporating **2b**.[4a,9] The use of the WCA $[Al\{OC(CF_3)_3\}_4]^-$ leads to a high solubility of the resulting products even in weakly coordinating solvents, such as dichloromethane. This greatly facilitated an extensive characterization of the oligomerization equilibria in solution.

The coordination chemistry of main-group metals with arene ligands has developed mainly during the last two decades.[10,11] The first report of a structurally characterized thallium(I)–arene complex, by Schmidbaur et al., dates back to 1985.[12] Only a few additional examples have since been published.[13] Very recently, Bochmann et al. reported on thallium(I)–arene complexes in which no bonding contacts between the $[Tl(arene)_n]^+$ moiety and the WCA used ($[H_2N\{B(C_6F_5)_3\}_2]^-$) exist.[11] The absence of interactions with the counterion facilitates the investigation of the coordination behavior of the free Tl^+ ion. Furthermore, Bochmann et al. prepared compounds containing, for example, one or two ferrocene units coordinated to the Tl^+ ion. However, these complexes have distinct contacts between the thallium center and the WCA used, or to solvent molecules.[11]

Herein we report the first coordination compounds composed of organometallic P_n-ligand complexes and a main-group metal. The thallium complexes have unprecedented P_n-ligand coordination modes and display dynamic behavior in solution and in the solid state.

The reaction of $Tl[Al\{OC(CF_3)_3\}_4]$ (**3**)[14] with $[\{CpMo(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (**2b**) in CH_2Cl_2 at room temperature leads to the formation of the dimeric compound **4**, which is soluble in CH_2Cl_2, THF, Et_2O, and toluene but insoluble in aliphatic hydrocarbons such as *n*-pentane.

$$[Tl_2\{Cp_2Mo_2(CO)_4(\mu,\eta^2:\eta^1\text{-}P_2)\}_4\{Cp_2Mo_2(CO)_4(\mu,\eta^2:\eta^1:\eta^1\text{-}P_2)\}_2][Al\{OC(CF_3)_3\}_4]_2 \quad (\mathbf{4})$$

An X-ray structural analysis of **4**[15] shows that the two thallium cations are asymmetrically bridged by two units of **2b** (Figure 1). A distorted six-membered $\{Tl_2P_4\}$ ring is thus formed, and each Tl^+ is further coordinated to two units of **2b** in a terminal fashion. Thus, a strongly distorted tetrahedral geometry about the thallium centers is observed. The structural features of **4** are in contrast to the recently described Ag^+ complex of **2b** with the same WCA: the core of the silver complex also consists of a six-membered $\{Ag_2P_4\}$ ring, but the coordination sphere of each Ag^I center is completed by one further unit of **2b** attached in a side-on coordination mode.[9] The P–P bond lengths within the P_n-

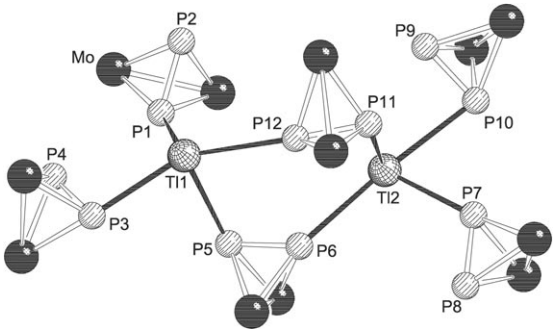

Figure 1. Structure of the dication in **4** (Cp and CO ligands are omitted for clarity).

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ligand complexes of **4** (2.072(15)–2.104(11) Å) are, on average, slightly longer than that in uncoordinated **2** (2.079(2) Å).[3] The Tl–P bond lengths are between 3.044(6) and 3.380(6) Å, and each thallium atom possesses two shorter and two longer bonds. These bonds are fairly long compared to the Tl–P bond lengths in the thallium(I) phosphine adduct $[Tl\{PhB(CH_2PPh_2)_3\}]$ (2.878 Å, 2.953 Å, 2.932 Å).[16] The Tl···Tl distance (5.870(1) Å) is too long to be considered a direct metal–metal interaction. Furthermore, no interactions are found between Tl^+ and the fluorine atoms of the WCA.

In the $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 at room temperature, a singlet at $\delta = -37.3$ ppm is observed, which is shifted downfield relative to uncoordinated **2b** ($\delta = -43.2$ ppm). Even at 153 K in a mixture of CD_2Cl_2 and THF, no splitting of the signal or coupling to the thallium nuclei are observed in the ^{31}P NMR spectrum (both thallium isotopes are NMR active with $I = 1/2$; ^{203}Tl has a natural abundance of 29.5% and ^{205}Tl 70.5%).[17] Only a slight broadening of the singlet occurs. To gain more insight into the dynamic behavior of the system in CH_2Cl_2 solution, electrospray ionization (ESI) MS and vapor-pressure osmometric (VPO) measurements were carried out. Both methods indicate the presence of $[Tl\{Cp_2Mo_2(CO)_4P_2\}][Al\{OC(CF_3)_3\}_4]$. The singlet in the ^{31}P NMR spectrum of **4** and the absence of a signal attributable to uncoordinated **2b** suggest a fast exchange process of ligands **2b** at monocationic Tl^+ species, which renders all phosphorus nuclei chemically equivalent on the NMR spectroscopy timescale, even at low temperature.

Slow diffusion of a toluene solution of **1a** into a solution of **3** in CH_2Cl_2 leads to the formation of crystals of **5** as brown rods. The crystals are stable under an atmosphere of dry argon at ambient temperature. Compound **5** is sparingly soluble in CH_2Cl_2 and insoluble in alkanes. Donor solvents, such as THF, dissolve **5** only with complete dissociation into the starting compounds.

$$[Tl\{Cp^*Fe(\mu,\eta^5:\eta^5:\eta^1\text{-}P_5)\}_3]_n[Al\{OC(CF_3)_3\}_4]_n \qquad (\mathbf{5})$$

The X-ray diffraction analysis of **5**[15] shows a Tl^+ ion that is surrounded by three π-coordinating units of **1a** (Figure 2). This η^5 coordination mode of a pentaphosphaferrocene to a main-group metal is unprecedented; the *cyclo*-P_5 moiety of this complex was only found with η^5 coordination as a middle deck in triple-decker sandwich complexes of transition metals.[18] The distance between the centers of the *cyclo*-P_5 moieties (Ctr) and the π-coordinated thallium ion in **5** is 3.249(1) Å. It is 0.3 Å longer than the Tl–Ctr distances observed in $[Tl_2(FeCp_2)_3]^{2+}$ (**6**), in which only one and two ferrocene complexes, respectively, coordinate to Tl^+ ions (2.9309 and 2.923 Å).[11a] The average P–P bond length within the coordinated units of **1a** is 2.124(2) Å, which is within the range found for the uncoordinated complex (2.116(2)–2.127(2) Å).[7]

Surprisingly, the geometry around each Tl^+ ion is not trigonal planar, but rather trigonal pyramidal, owing to an additional σ bond of one of the phosphorus atoms of each of the P_5 rings to the neighboring Tl^+ ion. Thus, a 1D coordination polymer is formed which contains the *cyclo*-P_5 moieties of **1a** in a hitherto unknown bridging η^5:η^1-coordination mode (Figure 3). The length of the Tl–P σ bond (3.8487(13) Å) is slightly longer than the average distance between the phosphorus atoms and the π-coordinated thallium ion (3.715 Å) but within the sum of the van der Waals radii (3.9 Å). Thus, the geometry around the thallium ions may be considered as a distorted octahedron. In contrast to the silver polymer $[Ag\{Cp^*Fe(\mu,\eta^5:\eta^2:\eta^1\text{-}P_5)\}_2]_n[Al\{OC(CF_3)_3\}_4]_n$,[7] in which the Ag^+ ions are bridged by two units of **1a**, the Tl^+ ions in polymer **5** are triply bridged by units of **1a**. This difference is due to the larger ion radius of Tl^+ (1.64 Å) compared to Ag^+ (1.29 Å). The distance between thallium centers (5.683(1) Å) is too large for a direct Tl···Tl interaction.

Although the thallium–ferrocene complex **6**[11a] displays bonding interactions between the thallium ions and the fluorine atoms of the WCAs, no such contacts can be detected in **5** (d(Tl–F) > 7 Å). In the trigonal crystal system of **5**, the thallium ions form chains along the crystallographic *c* axis, which are surrounded by coordinating moieties of **1a**. These polycationic columns are in turn separated from each other by the counterions. The diameter of the polycationic columns is about 1.5 nm (see the Supporting Information).

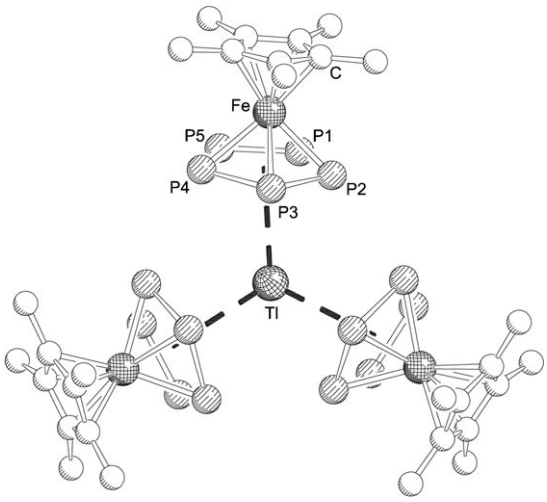

Figure 2. View of the repeat unit of the polycation in **5** along the crystallographic *c* axis (hydrogen atoms are omitted for clarity).

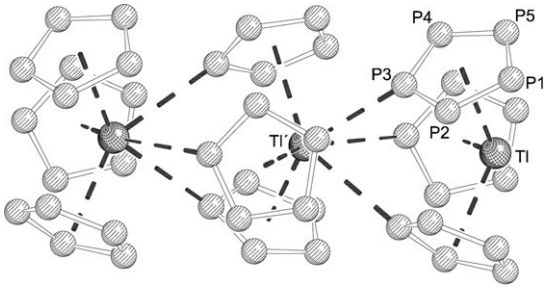

Figure 3. Portion of the polycationic chain in **5** ({Cp*Fe} fragments are omitted for clarity).

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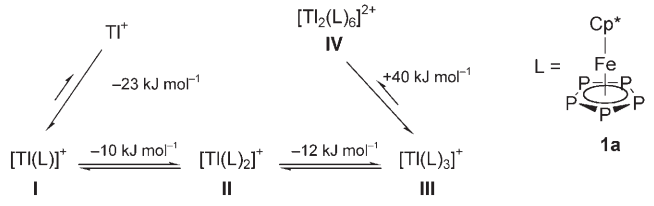
In the $^{31}P\{^1H\}$ NMR spectrum of **5** in CD_2Cl_2 at room temperature, only one singlet at $\delta = 165.1$ ppm is detected, which is shifted downfield relative to uncoordinated **1a** ($\delta =$ 152.2 ppm in CD_2Cl_2 at 300 K). This signal does not show any coupling to the NMR-active thallium nuclei. Even at 193 K, the lowest possible temperature without precipitation of the complex, the signal is only slightly broadened.

Solid-state ^{31}P MAS NMR spectra of **5** were also measured. The spectrum at room temperature displays a triplet at 161.3 ppm with an integration ratio of 1:2:1 ($\omega_{1/2} \approx 124$ Hz). This signal can only be interpreted as arising from the coupling of chemically equivalent phosphorus atoms of rapidly rotating *cyclo*-P_5 units with the two neighboring thallium nuclei. The coupling constant to the σ-coordinated Tl^+ ion is almost the same as that with π coordination to give the pseudotriplet signal with a $^1J_{Tl,P}$ of 305 Hz. Compared to Tl–P coupling constants as found for phosphine adducts of thallium(I), such as 5214 Hz for $[Tl\{PhB(CH_2PPh_2)_3\}]$,[16] this value is very low and relates to the low s character of the weakly bonding interactions to the thallium nuclei. A similar small $^1J_{Tl,P}$ of 500 Hz was found for $[Tl_2\{(\mu,\eta^4{:}\eta^4\text{-}P_4(C_6H_3dipp_2)_2\}]$ (dipp = 2,6-diisopropylphenyl), in which the tetraphosphabutadiene core is capped by two thallium ions.[19] At 190 K the triplet from **5** is only slightly broadened, which indicates that even at that low temperature, fast rotation of the P_5 rings still occurs.

ESI-MS and VPO measurements on **5** in CH_2Cl_2 hint at the presence of $[Tl\{Cp^*FeP_5\}][Al\{OC(CF_3)_3\}_4]$ in solution. To shed more light on the dynamics of **5** in solution, changes in the Gibbs free energy for the reactions shown in Scheme 1 were calculated in CH_2Cl_2 solutions with the density functional theory (DFT) method. The first solvation shell of three CH_2Cl_2 molecules was explicitly included in the calculations, whereas the conductor-like screening model (COSMO)[23] was used to describe the remaining solvent. The species of lowest energy is the monomer **III** with trigonal-planar coordination of the three units of **1a** (see Scheme 1 and the Supporting Information). This species is preferred in solution over thallium ions coordinated by one or two units of **1a** (**I** and **II**, respectively). Dimerization of **III** to form **IV** would be endergonic by $+40$ kJ mol^{-1}. In CH_2Cl_2 solution, the differences in free energy between **III** and **II** and between **III** and **I** are relatively small (12 and 22 kJ mol^{-1}, respectively). Our calculations point to the important role of solvent effects on the dynamics of **5** in solution. Gas-phase calculations give a much stronger interaction energy between Tl^+ and **1a**. For **I** the interaction energy was found to be 172 kJ mol^{-1} (26 kJ mol^{-1} in CH_2Cl_2 solution), which is higher than for the corresponding Tl^+ complexes with ferrocene and C_6Me_6.[11] Similarly, the energy differences between **III** and **II** and between **III** and **I** are higher in the absence of solvent effects (35 and 100 kJ mol^{-1}, respectively) and the dimerization of **III** to form **IV** is endergonic by 126 kJ mol^{-1}. We therefore propose a fast equilibrium between the species **I**, **II**, and **III** in CH_2Cl_2 solutions of **5** that renders all phosphorus atoms chemically equivalent on the NMR spectroscopy timescale and leads to an averaged chemical shift in the ^{31}P NMR spectra.



Scheme 1. Calculated free reaction energies for thallium compounds with different numbers of units of **1a** in CH_2Cl_2 solution at 300 K.

In conclusion, we were able to show that the class of coordination compounds containing P_n-ligand complexes can be extended to the area of main-group metals. A dimer and a 1D coordination polymer were obtained using the thallium(I) salt of the WCA $[Al\{OC(CF_3)_3\}_4]^-$. The P_n-ligand complexes exhibit bridging coordination modes with π- and σ-bonding to the thallium center. In particular, the unprecedented $\eta^5{:}\eta^1$ coordination mode of the pentaphosphaferrocene units in **5** reveals the high potential of this supramolecular approach. ESI-MS and VPO measurements along with DFT calculations support the existence of dynamic motion around the Tl^+ ions with equilibria between distinct monomeric units in CH_2Cl_2 solution. The rapid exchange of the P_n-ligand complexes renders the phosphorus nuclei of all species chemically equivalent on the NMR spctroscopy timescale. Furthermore, in the ^{31}P MAS NMR spectra of **5**, coupling to adjacent thallium atoms by σ- and π-coordination is detected, along with fast rotation of the P_5 rings even at low temperatures. The results demonstrate the excellent suitability of P_n-ligand complexes as linking units for main-group metal cations in supramolecular aggregates.

Experimental Section

All calculations were performed using the TURBOMOLE program package.[24] The BP86 exchange-correlation functional[25] was used along with the triple-zeta plus polarization (TZVP) basis sets on all atoms.[26] To speed up the calculations, the Coulomb part was evaluated by using the MARI-J method[27] along with optimized TZVP auxiliary basis sets on all atoms.[28] Quasirelativistic pseudopotentials were used for thallium.[29] Gibbs free energies at 27 °C were calculated with harmonic approximation using DFT-calculated frequencies.

4: A mixture of **2b** (99 mg, 0.20 mmol), **3** (117 mg, 0.10 mmol), and CH_2Cl_2 (10 mL) was stirred for 3 h at room temperature. The red solution was then filtered through diatomaceous earth, which was subsequently washed with CH_2Cl_2 (3 × 2 mL). The combined filtrate and washings were reduced in volume to about 8 mL and layered with *n*-pentane (8 mL). Orange needles of **4** which were suitable for X-ray crystallography formed at −2 °C within four weeks. The crystals were separated by filtration, washed with *n*-pentane, and dried in vacuum to give 116 mg of **4**. Reducing the volume of the mother liquor to about 3 mL and addition of *n*-pentane (10 mL) led to the isolation of a further crop of **4** (50 mg). Yield: 166 mg (92 %), m.p. 171 °C (decomp.), $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 300 K, referenced to 85 % H_3PO_4): $\delta = -37.3$ ppm (s). For further details including the ^{31}P MAS NMR spectrum of **4**, see the Supporting Information.

5: A solution of **1a** (156 mg, 0.45 mmol) in toluene (10 mL) was layered over a solution of **3** (176 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) using a teflon capillary. Within three days compound **5** formed as brown rods. The crystals were separated by filtration, washed with *n*-pentane, and dried in vacuum to give 42 mg of **5**. A further crop of **5**

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(164 mg) could be obtained by addition of *n*-pentane (10 mL) to the mother liquor and stirring for 1 h. Yield: 206 mg (62%), m.p. >200 °C, ^{31}P MAS NMR (121.49 MHz, 300 K, referenced to NaH_2PO_4): $\delta = 161.3$ ppm (t, $^1J_{P,Tl} = 305$ Hz). For further details, see the Supporting Information.

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[15] The crystal structure analyses were performed on a STOE-IPDS diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved with the programs SIR-97[20] (**4**) and SHELXS-97[21a] (**5**); full-matrix-least-squares refinement on F^2 in SHELXL-97[21b] was performed with anisotropic displacements for heavy atoms in **4** and for all non-H atoms in **5**. As the two counteranions $[Al\{OC(CF_3)_3\}_4]^-$ of **4** were disordered, numerous restraints (SADI) had to be used to order the atoms in appropriate positions,[22] which lead to somewhat elevated wR_2 values. For **5**, a twinning refinement using the merohedral twin law (0 −1 0; −1 0 0; 0 0 −1) was applied. The relative weighting of the two components was refined to 42.1(1) and 57.9(1)%. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **4**: $C_{121}H_{72}Al_2F_{72}Mo_{12}O_{32}P_{12}Tl_2$, $M_r = 5391.41$, crystal dimensions $0.40 \times 0.24 \times 0.20$ mm^3, orthorhombic, space group *Pbca* (No. 61), $a = 35.998(2)$, $b = 20.9594(11)$, $c = 43.1881(19)$ Å, $V = 32585(3)$ Å^3, $Z = 8$, $T = 123(1)$ K, $\rho_{calcd} = 2.169$ g cm^{-3}, $\mu = 3.135$ mm^{-1}, 66420 reflections collected, 15153 unique reflections ($R_{int} = 0.1488$), 1120 parameters, $R_1 = 0.0732$, $wR_2 = 0.1504$. **5**: $C_{46}H_{45}AlF_{36}Fe_3O_4P_{15}Tl$, $M_r = 2209.27$, crystal dimensions $0.30 \times 0.10 \times 0.10$ mm^3, trigonal, space group *P*31*c* (No. 159), $a = 19.401(3)$, $b = 19.401(3)$, $c = 11.367(2)$ Å, $V = 3705.3(10)$ Å^3, $Z = 2$, $T = 100(1)$ K, $\rho_{calcd} = 1.980$ g cm^{-3}, $\mu = 3.211$ mm^{-1}, 26508 reflections collected, 5181 unique reflections ($R_{int} = 0.0304$), 325 parameters, $R_1 = 0.0284$, $wR_2 = 0.0761$. CCDC-658370 (**4**) and CCDC-658371 (**5**) 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.

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