Synthesis and Structural Characterization of a Novel Polyheterocyclopentadienyl Thallium(I) Complex

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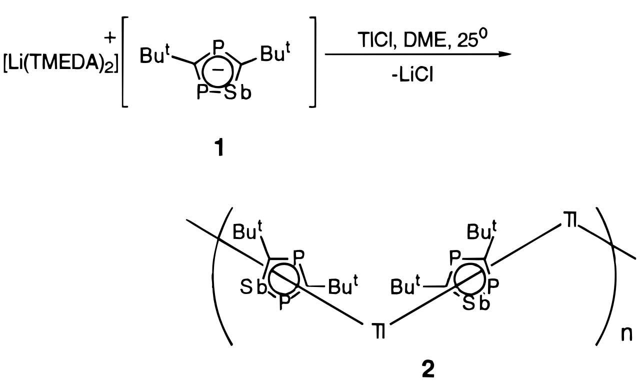
*Summary: The reaction of [Li(TMEDA)$_2$][1,4,2-P$_2$SbC$_2$-Bu$^t{}_2$] (**1**) with TlCl affords the compound [{Tl(μ-η^5:η^5-1,4,2-P$_2$SbC$_2$Bu$^t{}_2$)}$_\infty$] (**2**). Its X-ray crystal structure reveals a double-stranded zigzag polymeric chain structure with intermolecular thallium−phosphorus interactions.*

Introduction

In recent years there has been considerable interest in the chemistry of cyclopentadienyl thallium(I) compounds, as they have been shown to have significant value in synthetic chemistry.[1] The structural information that is available on such systems shows they are generally either polymeric, consisting of zigzag chains of alternating thallium and cyclopentadienyl units (e.g. [{Tl(μ-η^5:η^5-C$_5$Me$_5$)}$_\infty$]),[2] or oligomeric (e.g. [{Tl[μ-η^5:η^5-C$_5$H$_3$(SiMe$_3$)$_2$-1,3]}$_6$])[3] in the solid state. In contrast, electron diffraction studies on cyclopentadienyl thallium(I) compounds, e.g. [Tl(C$_5$H$_5$)], have demonstrated that in the gas phase these compounds exist as monomeric half-sandwich complexes.[4] Despite the attention that has been paid to cyclopentadienyl thallium(I) complexes, η^5-heterocyclopentadienyl thallium(I) systems are extremely rare. To the best of our knowledge, the only structurally characterized example of such a compound is the monomeric heterobimetallic complex [Tl{μ-η^5:η^5-$\overline{\text{B(Me)C(H)B(Me)C(Me)C}}$(Me)}Co($\eta^5$-C$_5H_5$)].[5] In response to this lack of information, we decided to investigate the reaction between TlCl and the diphosphastibolyl ring anion [1,4,2-P$_2$SbC$_2$Bu$^t{}_2$]$^-$ (**1**), which has yielded the first main-group complex of **1**, viz. [{Tl(μ-η^5:η^5-1,4,2-P$_2$SbC$_2$Bu$^t{}_2$)}$_\infty$] (**2**). We have previously described the synthesis of **1** and its use in the formation of a variety of transition-metal complexes in which it can act as an η^1, η^5, or mixed η^1/η^5 ligand.[6a−c] Its use as a precursor in the formation of organometallic cage compounds has also been addressed.[6d] Herein, we report the full synthetic details and the X-ray crystal structure of **2**.

Scheme 1



Results and Discussion

Treatment of a DME (1,2-dimethoxyethane) suspension of TlCl with **1** leads to the formation of **2** in good yield (69%) (Scheme 1). Compound **2** is a heat- and air-stable red powder that has limited solubility in common solvents but can be recrystallized from DME. The structure of **2** was elucidated from a combination of mass spectrometry, multinuclear NMR spectroscopy, and single-crystal X-ray diffraction. The ^{31}P{^{1}H} NMR spectrum of **2** displays two doublets at 333 and 274 ppm with typical two-bond P−P couplings of 51.2 Hz. The chemical shifts are very similar to those in the parent Li complex **1** (308.5 and 277.9 ppm),[6a] which perhaps indicates a degree of ionic character in the bonding in

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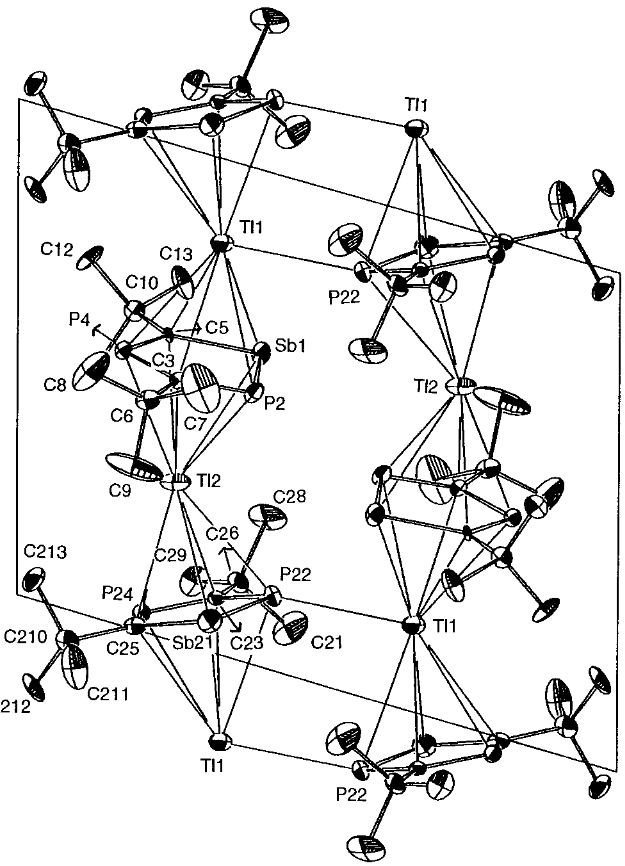

Figure 1. Unit cell diagram of $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}1,4,2\text{-}P_2SbC_2\text{-}Bu^t{}_2)\}_\infty]$ (**2**).

2 in solution. The EI/CI mass spectrum of **2** shows a cluster at *m*/*z* 527 and nothing higher, suggesting that in the gas phase **2** exists predominantly as a monomeric species.

In the solid state **2** exists as a double-stranded zigzag polymer in which there are two crystallographically independent monomers per asymmetric unit (Figure 1). An examination of the thallium-ring bond lengths (Table 1) points to a situation in which the ring is approximately η^5-ligated to the thallium. Between any thallium and a given ring, the thallium−carbon distances and the thallium−phosphorus distances are not significantly different within 3 standard deviations. For example: Tl(2)−C(5) = 3.28(3) Å, Tl(2)−C(3) = 3.15(3) Å; Tl(2)−P(2) = 3.246(9) Å, Tl(2)−P(4) = 3.301(8) Å. The bond lengths within the diphosphastibolyl rings suggest full delocalization, as the antimony−carbon distances 2.03(3) Å (Sb(21)−C(25)) and 2.05(2) Å (Sb(1)−C(5)) compare well with those in other delocalized systems, e.g. 2.050(5) Å in stibabenzene.[7] Similarly, the phosphorus−carbon bond lengths of 1.75(3) Å (C(25)−P(24)), 1.68(2) Å (C(23)−P(24)), 1.79(3) Å (C(23)−P(22)), 1.77(3) Å (C(3)−P(4)), 1.71(3) Å (C(3)−P(2)), and 1.74(2) Å (C(5)−P(4)) are all similar to that of 1.75 Å reported by Becker et al. for the related delocalized triphospholyl anion $[1,2,4\text{-}P_3C_2Bu^t{}_2]^-$.[8] The centroid−thallium−centroid connections are displaced from linearity, being characterized by angles of 158.8(2)° (Cent(a)−Tl(2)−Cent(b), where Cent(a) represents the centroid of the Sb(21)−C(25) ring and Cent(b) represents the centroid of the Sb(1)−C(5) ring) and 154.7(4)° (Cent(b)−Tl(1)−Cent(a)). These angles are not dissimilar from those seen in existing systems, e.g. 148.2(1) and 142.8(1)° in $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)\}_\infty]$[2] and 149° in $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{-}SiMe_3)\}_\infty]$.[3] The thallium−centroid−thallium connections are approximately linear, 176.4(4)° for Tl(2)−Cent(a)−Tl(1) and 175.0(6)° for Tl(1)−Cent(b)−Tl(2), comparing well with 178° in $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4SiMe_3)\}_\infty]$.[3] There are four distinct thallium−ring centroid distances of 2.835(8) Å (Tl(2)−Cent(b)), 2.890(9) Å (Tl(2)−Cent(a)), 2.908(8) Å (Tl(1)−Cent(b)), and 2.935(9) Å (Tl(1)−Cent(a)) (cf. 2.71 and 2.84 Å in $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{-}SiMe_3)\}_\infty]$[3] and 2.91 and 2.99 Å in $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)\}_\infty]$).[2] In addition to these features, an interaction between the thallium center Tl(1) and the least hindered phosphorus center of the neighboring strand, P(22), is seen. This distance of 3.386(9) Å is well within the sum of the van der Waals radii of the two elements ($\sum r(Tl), r(P) = 3.9$ Å).[9] A similar interstrand interaction of 3.583 Å between the ring phosphine substituent and the opposing thallium center has been seen in the related complex $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4PPh_2)\}_\infty]$.[10]

Conclusion

In summary, we have discussed the synthesis and structural characterization of a novel polyheterocyclopentadienyl thallium(I) complex. The X-ray crystal structure of the compound shows it to exist as a zigzag polymer with interstrand interactions. Work continues in our laboratory on examining the utility of **2** as a transfer reagent in organometallic synthesis.

Experimental Section

General Procedures. All procedures were conducted using conventional Schlenk techniques under an atmosphere of argon in flame-dried glassware. The solvents DME and toluene were refluxed over Na/K alloy for at least 10 h before being distilled under a nitrogen atmosphere and freeze−thaw-degassed before use. NMR spectra were recorded in C_6D_6 on a Bruker WM-250 or AC-400 instrument. Mass spectra were recorded on a VG 12-253 quad/70 eV (EI/CI). Melting points were recorded in sealed capillaries under argon. Thallium(I) chloride was used as received (Avocado Chemicals). $[Li(TMEDA)_2][1,4,2\text{-}P_2SbC_2Bu^t{}_2]$ was prepared by the literature procedure.[6a] A reproducible microanalysis of **2** could not be obtained due to persistent contamination with small amounts of the related triphospholyl complex $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}1,2,4\text{-}P_3\text{-}Bu^t{}_2C_2)\}_\infty]$ (**3**; ca. 2%), which arises from the unavoidable contamination of **1** with $[Li(TMEDA)_2][1,2,4\text{-}P_3Bu^t{}_2C_2]$. Compounds **2** and **3** could not be completely separated despite repeated fractional crystallizations.

Synthesis of 2. TlCl (0.529 g, 2.20 mmol) and **1** (916 mg, 1.63 mmol) were stirred together in DME (20 mL) for 3 days in the absence of light. After this time volatiles were removed in vacuo and the residue was extracted with toluene and filtered. Evaporation of the toluene afforded **2** as a red powder; yield 1.13 mmol, 69%. Crystals suitable for X-ray analysis were grown from a concentrated DME solution held at −30 °C. Mp: 160 °C dec. $^{31}P\{^1H\}$ NMR (101.4 MHz, C_6D_6, 85% H_3PO_4 ext.): 274 (d, $^2J_{PP} = 51.2$ Hz), 333 (d, $^2J_{PP} = 51.2$ Hz).

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Table 1. Selected Bond Distances (Å) and Angles (deg) in Compound 2

Distances

Tl(1)−Sb(1)	3.503(3)	Tl(1)−P(2)	3.366(9)	Tl(1)−C(3)	3.16(2)
Tl(1)−P(4)	3.327(7)	Tl(1)−C(5)	3.33(3)	Tl(1)−Sb(21)	3.531(3)
Tl(1)−C(25)	3.33(2)	Tl(1)−P(24)	3.325(8)	Tl(1)−C(23)	3.216(3)
Tl(1)−P(22)	3.389(8)	Tl(2)−Sb(1)	3.412(2)	Tl(2)−P(2)	3.246(9)
Tl(2)−C(3)	3.15(3)	Tl(2)−P(4)	3.301(8)	Tl(2)−C(5)	3.28(3)
Tl(2)−Sb(21)	3.471(3)	Tl(2)−C(25)	3.282(3)	Tl(2)−P(24)	3.320(8)
Tl(2)−C(23)	3.209(3)	Tl(2)−P(22)	3.320(9)	P(4)−C(5)	1.74(2)
C(5)−Sb(1)	2.05(2)	Sb(1)−P(2)	2.428(8)	P(2)−C(3)	1.71(3)
C(3)−P(4)	1.77(3)	P(24)−C(23)	1.68(2)	C(23)−P(22)	1.79(3)
P(22)−Sb(21)	2.393(8)	Sb(21)−C(25)	2.03(3)	C(25)−P(24)	1.75(3)
Tl(2)−Cent(a)[a]	2.890(9)	Tl(2)−Cent(b)[a]	2.835(8)	Tl(1)−Cent(a)	2.935(9)
Tl(1)−Cent(b)	2.908(8)				

Angles

C(3)−P(4)−C(5)	102(1)	Sb(21)−C(25)−P(24)	121(1)
P(4)−C(5)−Sb(1)	121(1)	C(25)−P(24)−C(23)	104(1)
C(5)−Sb(1)−P(2)	90.8(7)	P(24)−C(23)−P(22)	125(1)
Sb(1)−P(2)−C(3)	99(1)	C(23)−P(22)−Sb(21)	99.7(7)
P(2)−C(3)−P(2)	127(2)	P(22)−Sb(21)−C(25)	90.1(7)
Cent(a)−Tl(2)−Cent(b)	158.8(2)	Cent(b)−Tl(1)−Cent(a)	154.7(4)
Tl(1)−Cent(b)−Tl(2)	175.0(3)	Tl(2)−Cent(a)−Tl(1)	176.4(3)

[a] Cent(a) and Cent(b) are defined in the text.

Table 2. Crystallographic Data for 2

formula	$C_{10}H_{18}P_2SbTl$
fw	526.32
a, Å	10.438(1)
b, Å	11.322(2)
c, Å	14.079(2)
α, deg	101.36(1)
β, deg	104.60(1)
γ, deg	105.11(1)
radiation	Mo Kα (λ = 0.710 73)
collection temp, K	296
space group	$P\bar{1}$
D, g cm^{-3}	2.343
Z	4
μ, cm^{-1}	127.8
diffractometer	CAD4
2θ range, deg	2−50
no. of rflns collected	5255
no. of obsd rflns	3370
no. of params varied	254
R	0.068
R_w	0.069

^{1}H NMR (250 MHz, C_6D_6, $SiMe_4$): δ 1.54 (s, 9, Bu^t), 1.68 (s, 9, Bu^t). ^{13}C NMR (100.6 MHz, C_6D_6): δ 37.3 (multiplicity not resolved, C(CH$_3$)$_3$), 38.8 (dd, $^3J_{PC}$ = 4.1 and 12.2 Hz, C(CH$_3$)$_3$), 44.8 (d, $^2J_{PC}$ = 20.3 Hz, C(CH$_3$)$_3$), 45.5 (dd, $^2J_{PC}$ = 20.5 Hz and 16.3 Hz, C(CH$_3$)$_3$), 224 (dd, $^1J_{PC}$ = 75.3 Hz and 97.7 Hz, PCP), 242 (d, $^1J_{PC}$ = 71.2 Hz, PCSb). MS (EI/CI): m/z (relative intensity) 527 (58) [M + H]$^+$, 203 (100) [Tl]$^+$, 58 (5) [Bu^t + H]$^+$.

X-ray Structure Determination of 2. X-ray-quality crystals were obtained from a concentrated DME solution held at −30 °C. A unique room-temperature diffractometer data set ($T \approx 295$ K; monochromatic Mo Kα radiation, $\lambda = 0.710\,73$ Å) was acquired on a capillary-mounted specimen using an Enraf-Nonius CAD4 diffractometer, yielding 5255 independent reflections, with $I > 3\sigma(I)$ being considered "observed" and used in the large-block least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and were not refined. Conventional residuals R and R_w on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed, and computation was by the Xtal3.4 program system, implemented by Hall.[11] Crystal data and details of the data collection and refinement are given in Table 2.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond angles and distances and additional views of the structure of **2** (16 pages). Ordering information is given on any current masthead page.

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