

Cyclopentadienylthallium(I) compounds with bulky cyclopentadienyl ligands

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Abstract

Interaction of TlOC_2H_5 with $\text{C}_5\text{Ph}_4\text{H}_2$, $\text{C}_5\text{Ph}_5\text{H}$, $\text{C}_5\text{Ph}_4(^t\text{BuPh})\text{H}$ or $\text{C}_5\text{Bz}_5\text{H}$ gives the new cyclopentadienylthallium(I) compounds $\text{C}_5\text{Ph}_4\text{HTl}$, $\text{C}_5\text{Ph}_5\text{Tl}$, $\text{C}_5\text{Ph}_4(^t\text{BuPh})\text{Tl}$, and $\text{C}_5\text{Bz}_5\text{Tl}$. The compounds have been characterized by IR, NMR and mass spectroscopy.

Introduction

Cyclopentadienylthallium(I) derivatives are very interesting from two points of view: (1) They are mild reagents for the synthesis of cyclopentadienyl transition-metal derivatives, because of the function of thallium as an alkali-metal substitute [1]. This principle was successfully employed in the synthesis of cyclopentadienyl-lanthanoid derivatives using the transmetallation reaction between $\text{C}_5\text{H}_5\text{Tl}$ and lanthanoid metals [2]. Very recently it was shown that synthesis of trifluoromethyl-cyclopentadienide complexes of transition metals seems to be possible only through the thallium salt [3]. (2) The various known thallium cyclopentadienides show a remarkable variation in stability and solubility depending upon the ring substituents. The cyclopentadienylthallium(I) is stable towards oxygen and water but insoluble in common organic solvents [4–6], while the methyl- and pentamethyl-cyclopentadienyl derivatives, $\text{C}_5\text{MeH}_4\text{Tl}$ [7] and $\text{C}_5\text{Me}_5\text{Tl}$ [8] ($\text{Me} = \text{CH}_3$), are soluble in organic solvents but extremely air-sensitive. $\text{C}_5\text{Me}_5\text{Tl}$ is soluble even in pentane. Other alkyl substituted cyclopentadienide derivatives of thallium have similar properties [9]. However, tris(trimethylsilyl)cyclopentadienylthallium, $\text{C}_5(\text{Me}_3\text{Si})_3\text{H}_2\text{Tl}$, is stable in air and fairly soluble in aromatic solvents [10].

The factors influencing the properties of the various thallium cyclopentadienides are not yet fully understood. The contrast between the instability of the pyrophoric derivative $\text{C}_5\text{H}_4\text{MeTl}$ and the stability of $\text{C}_5\text{H}_5\text{Tl}$ in air was explained in terms of the difference in the crystal lattice energy, a consequence of the difference in

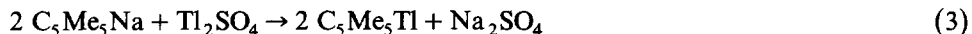
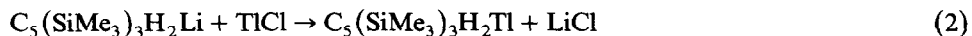
molecular symmetry [11]. However, other authors suggest that mesomeric and inductive effects influence the stability [12]. In the case of $C_5(Me_3Si)_3H_2Tl$, the reduction of molecular interactions by steric effects and the delocalization of negative charge in the cyclopentadienyl ring (thus enhancing covalency of the cyclopentadienyl–thallium bond), seems to be responsible for its physical properties [10]. However, C_5Me_5Tl and C_5H_5Tl have very similar crystal structures despite their different properties. The Tl–Tl distance in C_5Me_5Tl is 1 Å shorter than that in C_5H_5Tl , indicating the greater covalency of the ring–Tl bond in the former [8].

Most thallium cyclopentadienides previously described were synthesized by the original method developed for C_5H_5Tl by Fischer [4] and Meister [5] in which reaction between the hydrocarbon and thallium sulfate or thallium hydroxide in aqueous medium in the presence of alkali leads to precipitation of the thallium cyclopentadienide (eq. 1).



(X = OH, $(SO_4)_{1/2}$; R = H [4,5], Me [7], Et, ^tBu [9], Me_3Si [13])

Novel tris(trimethylsilyl)- [10] and pentamethyl-cyclopentadienylthallium compounds [8,14] were obtained by metathesis between the lithium or sodium cyclopentadienide and thallium(I) chloride or sulfate:



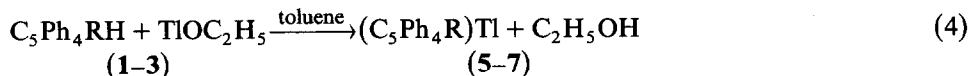
There has recently been an interest in the synthesis and structural investigation of organometallic compounds with sterically demanding cyclopentadienyl ligands such as pentaphenyl-, tetraphenyl- and pentabenzyl-cyclopentadienyl. Examples of such complexes are decaphenylstannocene [15], decabenzylgermanocene, decabenzylstannocene and decabenzylplumbocene [16,17], octaphenylferrocene [18], pentaphenyl-cyclopentadienyl-nickel and -cobalt compounds [19], pentaphenylcyclopentadienyl- and pentabenzylcyclopentadienyl-carbonyl derivatives of cobalt and rhodium [20,21], and pentaphenylstannocene [22]. Sterically demanding ligands enhance the thermal and oxidative stability. Many of the above mentioned complexes are air-stable while the corresponding normal cyclopentadienyl or pentamethylcyclopentadienyl analogues are not. In addition some complexes have electronically interesting molecular structures [15–17].

We decided to prepare new cyclopentadienylthallium derivatives owing to their prospective synthetic potential for further work. For the study we chose the ligands pentaphenylcyclopentadiene, C_5Ph_5H (**1**, Ph = C_6H_5) [23], tetraphenyl(4-*t*-butylphenyl)cyclopentadiene, $C_5Ph_4(^tBuPh)H$ (**2**, ^tBuPh = 4-^t $C_4H_9C_6H_4$) [24c*], tetraphenylcyclopentadiene, $C_5Ph_4H_2$ (**3**) [23], and pentabenzylcyclopentadiene, C_5Bz_5H (**4**, Bz = $CH_2C_6H_5$) [25]. Attempts to prepare thallium(I) complexes of these ligands by the reactions shown in eq. 1 or 2 were not very successful. The desired products were detected by mass spectroscopy, but the yields seemed to be low and purification was not possible. Thus we chose to use the reaction of the acidic cyclopentadienes with thallium(I) ethoxide, $TlOC_2H_5$.

* This and other references marked with an asterisk indicate a note occurring in the list of references.

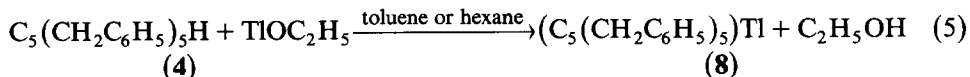
Results and discussion

Thallium(I) ethoxide reacts with pentaphenylcyclopentadiene (**1**), tetraphenyl(4-t-butylphenyl)cyclopentadiene (**2**), and tetraphenylcyclopentadiene (**3**) in toluene with precipitation of the respective thallium salts pentaphenylcyclopentadienylthallium(I) (**5**), tetraphenyl(4-t-butylphenyl)cyclopentadienylthallium(I) (**6**), and tetraphenylcyclopentadienylthallium(I) (**7**) (eq. 4).



(R = C₆H₅ (**1**, **5**), R = C₆H₄-t-C₄H₉-4 (**2**, **6**), R = H (**3**, **7**))

Reaction 4 is quantitative because of the insolubility of the thallium salts formed. The compounds can be conveniently prepared on a 5 to 10 g scale. The reaction is not limited to the synthesis of insoluble products, as shown by the synthesis of soluble pentabenzylcyclopentadienylthallium (**8**) from thallium(I) ethoxide and pentabenzylcyclopentadiene in toluene or hexane:



Compound **8** is stable in air, in contrast to C₅Me₅Tl [10], and it is not sensitive to light. This enhanced stability can be attributed to a shielding effect of the phenyl groups on the reactive centers of the cyclopentadienyl ligand and thallium metal, with a possible intra- or inter-molecular interaction of the phenyl groups with the thallium lone-pair. Such a shielding effect was previously observed, and a lone-pair interaction proposed, for decabenzylcyclopentadienyl compounds of germanium, tin, and lead [16,17]. In contrast to the air-stable pentaphenylcyclopentadienyl- and pentabenzylcyclopentadienyl-thallium derivatives, the tetraphenylcyclopentadienyl compound **7** is unexpectedly air-sensitive.

Infrared spectra

The infrared spectra [26*] of **5**, **6**, **7** and **8** are similar to those of the respective hydrocarbons [27*], with some differences in the region 950 to 500 cm⁻¹. An additional band or number of bands around 400 to 300 cm⁻¹ is observed. The spectrum of **5** is almost identical to those of decaphenylgermanocene, decaphenylstannocene, and decaphenylplumbocene [22], possibly implying a similar metallocene-like structure.

Mass spectra

Mass spectroscopy provides the best method for the identification of these complexes. Complexes **5** to **8** show a clear molecular ion of about 30% intensity (for the C₅R₅²⁰⁵Tl⁺-peak) [28*]. The perphenylated cyclopentadienyl derivatives have ²⁰⁵Tl⁺ as their base peak. For **8** the tropylium-ion, C₇H₇⁺ becomes the base peak owing to the ease of the loss of five benzyl groups. ²⁰⁵Tl⁺ has 47% intensity. Both thallium-containing ions (M⁺ and Tl⁺) exhibit the correct isotopic pattern for thallium (natural abundances: ²⁰³Tl 29.50; ²⁰⁵Tl 70.50).

Another feature in the mass spectra is the ligand fragmentation, tentatively assigned in the experimental section. The pentaphenylcyclopentadienyl and the

tetraphenylcyclopentadienyl ligands undergo a stepwise loss of phenyl and tropylium groups. For the tetraphenyl(4-*t*-butylphenyl)cyclopentadienyl ligand loss of the tertiary-butyl group with or without the connected phenyl group is the first fragmentation step. The benzyl ligand shows a stepwise loss of tropylium and finally phenyl groups. The observed hydrocarbon molecular ion of **1** ($m/e = 446$), **2** ($m/e = 502$) or **3** ($m/e = 370$) in the respective spectra of **5**, **6**, or **7** is not due to hydrocarbon impurities but to a hydrogen-capture of the cyclopentadienyl cation fragment. Complex **8** does not give a normal ligand cation at $m/e = 515$. Hydrogen transfer between two pentabenzylcyclopentadienyl radicals takes place, and ions at $m/e = 516$ ($+H\cdot$) and $m/e = 514$ ($-H\cdot$) are observed, and subsequently undergo fragmentation. This effect was also observed in the spectra of the decabenzyl Group IVa metallocenes [17]. Among Group IVa element derivatives, only decabenzylgermanocene showed a relatively intense ligand-metal fragment, while tin and lead compounds do not exhibit a clear ligand-metal ion. The high intensity of the ligand-thallium fragment (molecular ion) of **8** [30%] is noteworthy.

NMR spectra

Only for **8** could the NMR spectra be recorded, the other thallium complexes being insoluble.

The ^1H NMR spectrum [29*] of **8** shows a doublet for the methylene protons due to thallium-hydrogen coupling ($s = \frac{1}{2}$ for both, ^{203}Tl and ^{205}Tl) and a narrow multiplet for the phenyl protons (no Tl-H interaction). The coupling constant of about 10 Hz shows a slight solvent dependency. Other thallium cyclopentadienides exhibit the following coupling constants $J(\text{TlH})$: $\text{C}_5\text{Me}_5\text{Tl}$: $^3J(\text{Tl}-\text{CH}_3)$ 18.0 Hz [8]; $\text{C}_5(\text{Me}_3\text{Si})_3\text{H}_2\text{Tl}$: $^4J(\text{Tl}-\text{CH}_3)$ 2.8 and 3.0 Hz, respectively, $^2J(\text{Tl}-\text{C}_5\text{H}_2)$ 75.5 Hz [10]; $\text{C}_5\text{MeH}_4\text{Tl}$: $^3J(\text{Tl}-\text{CH}_3)$ 2.0 Hz [13]; $\text{C}_5^t\text{BuH}_4\text{Tl}$: $^4J(\text{Tl}-\text{CH}_3)$ 2.5 Hz, no Tl-C₅H₄ coupling [13].

The ^{13}C NMR spectrum [30*] of **8** shows six signals, indicating free rotation and equilibrium of the benzyl groups in solution. Each signal is split into a doublet by thallium-carbon interaction. Recording of a Dept-3J spectrum [31] permitted assignments to quaternary, tertiary and secondary carbons. From the spectra at two different field strengths, the coupling constants of the overlapping signals of the *ortho*- and *meta*-phenyl carbons were derived but direct assignments of chemical shifts and coupling constant for the *ortho*- and *meta*-phenyl carbon could not be

Table 1

^{13}C NMR data for cyclopentadienyl thallium derivatives (δ in ppm, J in Hz) in C_6D_6

	$\text{C}_5(\text{Me}_3\text{Si})_3\text{H}_2\text{Tl}$ [10]	$\text{C}_5\text{Me}_5\text{Tl}$ [8]	$\text{C}_5\text{Bz}_5\text{Tl}$
$\delta(\text{C}_5)$ ($J(\text{TlC})$)	not clearly observed	114.60 (102.2)	121.73 (88.9)
$\delta(\text{CH}_2)$ ($J(\text{TlC})$)			31.96 (43.7)
$\delta((\text{CH}_3)_5)$ ($J(\text{TlC})$)		10.53 (79.4)	
$\delta(\text{Me}_3\text{Si})$ ($J(\text{TlC})$)	1.50 (20)		
$\delta(\text{Me}_3\text{Si})$ ($J(\text{TlC})$)	2.84 (20)		
$\delta(\text{C}(\text{Ph}, \text{quart.}))$ ($J(\text{TlC})$)			145.87 (9.4)
$\delta(\text{C}(\text{Ph}, \text{meta}))$ ($J(\text{TlC})$)			128.55 (5.8)
$\delta(\text{C}(\text{Ph}, \text{ortho}))$ ($J(\text{TlC})$)			128.99 (43.5)
$\delta(\text{C}(\text{Ph}, \text{para}))$ ($J(\text{TlC})$)			125.76 (3.3)

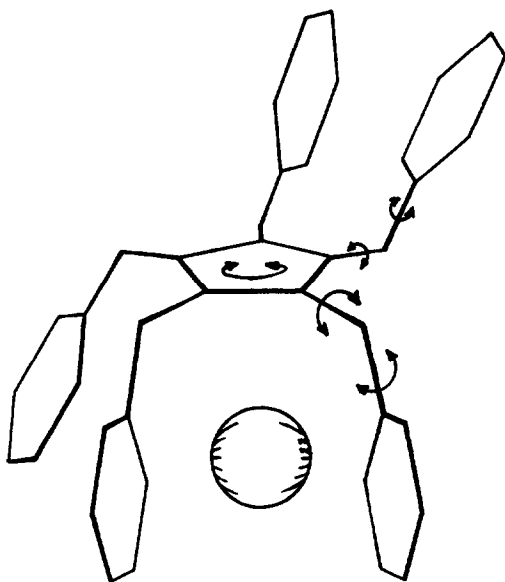


Fig. 1. Drawing of a conformer of **8**; showing the proximity of an *ortho*-phenyl-carbon to thallium and the free rotation or oscillation of the benzyl groups and the cyclopentadienyl ring in solution.

made. Data for comparison are available only for C_5Me_5Tl [8] and $C_5(Me_3Si)_3H_2Tl$ [10] (Table 1).

A decrease of the magnitude of the Tl–C coupling constant should be correlated to an increase in Tl–C distance for comparable carbons, and the large coupling constant for the *ortho*- or *meta*-phenyl carbons of **8** is noteworthy; the values can only be explained by assuming a relative close thallium *ortho*- or *meta*-phenyl carbon contact in solution, as shown in Fig. 1.

Molecular model studies show that the *ortho*-phenyl carbons come closest to the thallium atom, and so have the large coupling constant of 43.5 Hz [32*]. In the solid-state structures of the decabenzyl-Group IVa metallocenes three of the ten benzyl groups are bent towards the metal, and in these three groups the *ortho*-phenyl carbon is always nearest to the metal (except for one benzyl group in the germanium structure where the quaternary-phenyl carbon is closest). The 1H and ^{13}C NMR spectra of decabenzylcyclopentadienyl-germanium, -tin and -lead show the same features [17].

Experimental

All manipulations were carried out under nitrogen. The glassware was flame-dried under vacuum. Solvents were dried over liquid sodium/potassium-alloy, distilled and stored under nitrogen. The melting points and the NMR-spectra [29*,30*] were measured in sealed nitrogen filled capillaries or NMR tubes, respectively. Infrared spectra were recorded as CsI pellets (3 mg sample/300 mg CsI) [26*]. The cyclopentadiene starting materials were prepared by literature procedures or modifications thereof [24]. Thallium(I) ethoxide was purchased from Aldrich Chemical Corp., stored under nitrogen, and used without purification.

Pentaphenylcyclopentadienylthallium (5). Pentaphenylcyclopentadiene (**1**) (3.00 g, 6.72 mmol) was suspended in 50 ml of toluene at 110 °C and a mixture of thallium ethoxide (1.75 g, 7.09 mmol) and 2 ml of toluene was added dropwise during 1 h with rapid stirring. The first drop of TIOEt produced a yellow solution, and a bright yellow precipitate formed. After the addition of thallium ethoxide was complete, stirring was continued for 30 minutes, and the precipitate was then filtered off from hot toluene. The bright-yellow, voluminous precipitate was dried in vacuum over night at room-temperature to give an orange-brown solid, which became yellow upon grinding. Yield: 4.30 g (98%). A small sample was sublimed in vacuo (10^{-5} torr) at 250 °C to give a fine yellow microcrystalline powder and a black sublimate of excess thallium metal. **5** is apparently air-stable (m.p. > 330 °C). Found: C, 64.55; H, 3.95. $C_{35}H_{25}Tl$ calcd.: C, 64.68; H, 3.88%. IR [26]: 3075w, 3052m, 3025m, 1970–1660vw, 1595m to s, 1574vw, 1501s, 1490sh, 1450sh, 1442m, 1320w(br), 1277vw(br), 1180w, 1156w, 1140w, 1072m, 1060sh, 1028m, 1001vw, 970vw(br), 920sh, 908w, 845w, 805m, 776m to s, 737m to s, 708s, 696vs, 673w, 558vw, 548m, 491vw, 422vw, 351m. MS [28]: (70 eV, 230 °C, m/e): 650 (25%) $[C_5Ph_4Tl]^+ = [M]^+$, 446 (39) $[C_5Ph_5H]^+$, $[C_5Ph_5]^+$ with one ^{13}C atom, 445 (33) $[C_5Ph_5]^+$, 367 (26) $[C_5Ph_5 - C_6H_6]^+$, 352 (8) $[C_5Ph_5 - C_7H_9]^+$, 289 (22) $[C_5Ph_5 - 2C_6H_6]^+$, 267 (12) $[C_5Ph_5 - 2C_6H_5 - C_2]^+$, 265 (14) $[C_5Ph_5 - 2C_6H_5 - C_2H_2]^+$, 205 (100) $[Tl]^+$, 167 (19) $[C_{13}H_{11}]^+$, 165 (13) $[C_{13}H_9]^+$, 91 (8) $[C_7H_7]^+$.

*Tetraphenyl(4-*t*-butylphenyl)cyclopentadienylthallium(I) (6)*. Tetraphenyl(4-*t*-butylphenyl)cyclopentadiene (**2**) (3.0 g, 5.97 mmol) was dissolved in 50 ml of toluene at 70 °C and a mixture of thallium ethoxide (1.53 g, 6.13 mmol) and toluene (1 ml) was added dropwise during 15 minutes. A yellow precipitate was formed, and stirring was continued for 2 h. The honey-yellow precipitate was then filtered off, washed with toluene (50 ml), and dried in vacuo overnight at room temperature to give a brown-yellow solid, which became yellow upon grinding. (Yield: 4.15 g, 98%). A small sample was sublimed in vacuo (10^{-5} torr) at 250 °C to give a fine yellow powder together with a sublimate of residual thallium metal. **6** is air-stable for 2 days. Slow decomposition was noted on exposure of the sublimed sample to air for a week (m.p. > 330 °C). Found: C, 66.28; H, 4.81. $C_{39}H_{33}Tl$ calcd.: C, 66.34; H, 4.71%. IR [26*]: 3075w, 3052m, 3025m, 2960m to s, 2900w, 2865w, 1950–1660vw, 1597m to s, 1574w, 1520w, 1500s, 1462vw, 1442m, 1394w, 1363w to m, 1325w, 1312vw, 1269w to m, 1200w, 1179w, 1155w, 1143w to m, 1118w, 1110sh, 1073m, 1059sh, 1025m, 1015sh, 1001vw, 978vw(br), 920sh. 912w to m, 840m to s, 798m, 780m, 775w, 754w, 745m, 735w, 705sh, 696vs, 678w, 590vw, 568m, 540w, 498w, 455w, 368w to m, 347w, 330w. MS [28*]: (70 eV, 205 °C, m/e): 706 (33%) $[C_5Ph_4(C_6H_4C_4H_9)Tl]^+ = [M]^+$, 502 (34) $[C_5Ph_4(C_6H_4C_4H_9)H]^+$ ($[C_5Ph_4(C_6H_4C_4H_9)H]^+$ with one ^{13}C atom), 501 (26) $[C_5Ph_4(C_6H_4C_4H_9)]^+$, 444 (17) $[C_5Ph_4(C_6H_4C_4H_9) - C_4H_9]^+$, 367 (28) $[C_5Ph_4(C_6H_4C_4H_9) - C_4H_9 - C_6H_5]^+$, 352 (4) $[C_5Ph_4(C_6H_4C_4H_9) - C_4H_9 - C_7H_8]^+$, 289 (11) $[C_5Ph_4(C_6H_4C_4H_9) - C_4H_9 - C_6H_5 - C_6H_6]^+$, 267 (6) $[C_5Ph_4(C_6H_4C_4H_9) - C_4H_9 - C_6H_4 - C_6H_5 - C_2]^+$, 265 (7) $[C_5Ph_4(C_6H_4C_4H_9) - C_4H_9 - C_6H_5 - C_6H_6 - C_2H_2]^+$, 205 (100) $[Tl]^+$, 167 (12) $[C_{13}H_{11}]^+$, 165 (6) $[C_{13}H_9]^+$, 91 (7) $[C_7H_7]^+$, 57 (39) $[C_4H_9]^+$.

Tetraphenylcyclopentadienylthallium(I) (7). Tetraphenylcyclopentadiene (**3**) (5.30 g, 14.3 mmol) was dissolved in 50 ml of toluene at 80 °C and a mixture of thallium ethoxide (3.57 g, 14.3 mmol) and 4 ml of toluene was added dropwise during 1 h with rapid stirring. Stirring was continued for 2 h, and the yellow precipitate filtered

off, washed with toluene (20 ml), and dried in vacuo overnight to yield a brown-yellow solid (yellow when ground) (Yield: 7.55 g, 92%). The compound sublimes in vacuo (10^{-5} torr) at 220°C to yield a fine orange-yellow microcrystalline powder and a sublimate of residual thallium metal. **7** is air-sensitive. Decomposition is observed after 10 minutes (m.p. $260\text{--}262^{\circ}\text{C}$, dec.). Found: C, 61.17; H, 3.83. $\text{C}_{29}\text{H}_{21}\text{Tl}$ calcd.: C 60.70; H 3.69%. IR [26]: 3070sh, 3055m, 3025m, 1965–1660vw, 1596m to s, 1573w, 1510s, 1497m to s, 1460vw, 1450sh, 1443m, 1438m, 1390–1250vw, 1193w to m, 1180w, 1155w, 1084w, 1071m, 1061m, 1028m, 1000–965vw, 928w, 905w to m, 845w, 788m to s, 758s, 735m, 694vs, 662w, 630w to m, 615w, 541w, 523w, 508vw, 392w, 310m. MS [28*]: (70 eV, 180°C , m/e): 574 (26) $[\text{C}_5\text{Ph}_4\text{HTl}]^+ = [M]^+$, 370 (10) $[\text{C}_5\text{Ph}_4\text{H}_2]^+$ ($[\text{C}_5\text{Ph}_4\text{H}]^+$ with one ^{13}C atom), 369 (10) $[\text{C}_5\text{Ph}_4\text{H}]^+$, 291 (12) $[\text{C}_5\text{Ph}_4\text{H} - \text{C}_6\text{H}_6]^+$, 289 (7) $[\text{C}_5\text{Ph}_4\text{H} - \text{C}_6\text{H}_6 - \text{H}_2]^+$, 278 (3) $[\text{C}_5\text{Ph}_4\text{H} - \text{C}_7\text{H}_7]^+$, 205 (100) $[\text{Tl}]^+$, 191 (9) $[\text{C}_{15}\text{H}_{11}]^+$, 167 (3) $[\text{C}_{13}\text{H}_{11}]^+$, 165 (3) $[\text{C}_{13}\text{H}_9]^+$, 91 (12) $[\text{C}_7\text{H}_7]^+$.

Pentabenzylcyclopentadienylthallium (8). Pentabenzylcyclopentadiene, **4** (1.40 g, 2.70 mmol) was dissolved in 40 ml of hexane at room-temperature, and a mixture of thallium ethoxide (0.68 g, 2.70 mmol) and hexane (1 ml) was added dropwise during 15 minutes. The solution turned yellow, and only a slight precipitate appeared. Stirring was continued for 10 minutes, the precipitate was allowed to settle, and the clear light yellow solution was decanted. Careful concentration of the solution, ice-cooling or addition of seed-crystals initiated a spontaneous crystal growth at room temperature. After 4 days at room temperature the needle-shaped crystals were collected (yield: 0.95 g, 49%). The mother liquor was carefully concentrated and ice-cooled until further crystallization started. On too rapid cooling or too much concentration of the solution needle-shaped crystals started to appear again, but after 2 days at room temperature they redissolved slowly and large yellow parallelepipeds slowly started to grow in their place. When the needles had been completely transformed into the yellow parallelepipeds, ice-cooling, combined with concentration the mother liquor was resumed (yield: 0.51 g, 26%). Both crystal forms are air-stable. (The presence of unchanged thallium ethoxide may produce a black coating on part of the needles and on the glass surface when vacuum is applied or the needles are first exposed to air.) Recrystallization of the needles from toluene/hexane gave the parallelepipeds. The infrared spectra show small differences between the two crystalline modifications, while other data (^1H , ^{13}C NMR, MS, C/H) are identical [32*]. Complex **8** is fairly soluble in benzene, toluene and tetrahydrofuran, but only slightly soluble in hexane. Both modifications darken at 60°C and soften at 80°C . The needles melt at $133\text{--}136^{\circ}\text{C}$, the parallelepipeds at $137\text{--}140^{\circ}\text{C}$. Found: C, 66.92; H, 5.02. $\text{C}_{40}\text{H}_{35}\text{Tl}$ calcd.: C, 66.72; H, 4.90%. IR [26*]: 3100vw, 3080w, 3055m, 3025m, 3000vw, 2910m, 2840w, 1950–1650vw, 1601m, 1581w, 1530w(br), 1493s, 1451m to s, 1325w(br), 1290w(br), 1181w, 1155w, 1075m, 1029m, 1010–800vw; needles: 733s, 730sh, 696vs, 650vw, 619vw, 591vw, 568w, 478w, 458vw, 310w; parallelepipeds: 752m(sh), 743m(sh), 733s, 719m, 696vs, 663w, 650vw, 633w, 615vw, 591vw, 568w, 480sh, 472w to m, 459w to m, 318w. MS [28*]: (70 eV, 190°C , m/e): 720 (30%) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5\text{Tl}]^+ = [M]^+$, 516 (7) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5\text{H}]^+$, 514 (10) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5 - \text{H}]^+$, 425 (6) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5\text{H} - \text{C}_7\text{H}_7]^+$, 423 (3) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5 - \text{C}_7\text{H}_7 - \text{H}]^+$, 333 (2) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5\text{H} - \text{C}_7\text{H}_7 - \text{C}_7\text{H}_8]^+$, 331 (3) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5 - \text{C}_7\text{H}_7 - \text{C}_7\text{H}_8 - \text{H}]^+$, 255 (8) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5\text{H} - \text{C}_7\text{H}_7 - \text{C}_7\text{H}_8 - \text{C}_6\text{H}_6]^+$, 253 (4) $[\text{C}_5(\text{CH}_2\text{C}_6\text{H}_5)_5$

– C₇H₇ – C₇H₈ – C₆H₆ – H]⁺, 205 (47) [Ti]⁺, 167 (9) [C₁₃H₁₁][†], 165 (4) [C₁₃H₉]⁺, 91 (100) [C₇H₇]⁺. ¹H NMR (C₆D₆ [29*]): δ 3.93 (d, CH₂, ³J(TiH) 10.74 Hz), 7.19 (m, C₆H₅); (C₄D₈O [29*]) δ 3.88 (d, CH₂, ³J(TiH) 9.6 Hz), 7.13 (m, C₆H₅). ¹³C NMR (C₆D₆ [30*]): δ 121.73 (d, C₅, ¹J(TiC) 88.86 Hz), 31.96 (d, CH₂, ²J(TiC) 43.70 Hz), 145.87 (d, quart.-phenyl C, ³J(TiC) 9.27 Hz), 128.99 (d, *o/m*-phenyl C, ^{4/5}J(TiC) 43.53 Hz), 128.55 (d, *o/m*-phenyl C, ^{4/5}J(TiC) 5.78 Hz), 125.76 (d, *p*-phenyl C, ⁶J(TiC) 3.25 Hz); (C₄D₈O [30*]) δ 122.11 (d, C₅, ¹J(TiC) 83.41 Hz), 32.36 (d, CH₂, ²J(TiC) 43.25 Hz), 146.53 (d, quart.-phenyl C, ³J(TiC) 8.10 Hz), 129.47 (d, *o/m*-phenyl C, ^{4/5}J(TiC) 42.44 Hz), 128.91 (d, *o/m*-phenyl C, ^{4/5}J(TiC) 5.80 Hz), 126.09 (d, *p*-phenyl C, ⁶J(TiC) 2.74 Hz).

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- 24 (a) Pentaphenylcyclopentadiene: see [15] and [23].
(b) Tetraphenylcyclopentadiene: see [23].
(c) Tetraphenyl(4-*t*-butylphenyl)cyclopentadiene: this compound was prepared by the procedure described for pentaphenylcyclopentadiene [15,23]. Instead of C₆H₅Br, 4-BrC₆H₄C₄H₉-*t* was converted into the lithium reagent which was treated with tetraphenylcyclopentadienone. The synthesis via the alcohol, C₅Ph₄(C₆H₄C₄H₉)OH, the bromide, C₅Ph₄(C₆H₄C₄H₉)Br, finally gave the hydro-

- carbon (m.p.: 201–204 °C). H. Schumann, C. Janiak, J.J. Zuckerman, unpublished results.
- (d) Pentabenzylcyclopentadiene: see [25]. We found a simpler method: After completion of the reaction, the solvent was distilled off in vacuo and the semi-solid residue washed with water then recrystallized twice from methanol, to give white needle-shaped crystals and a yellow-brownish solid. The white crystals were collected, and the yellow solid recrystallized from methanol to yield another crop of white needles (overall yield 17%, based on C₅H₆, m.p.: 70–72 °C).
- 25 S.S. Hirsch and W.J. Bailey, *J. Org. Chem.*, 43 (1978) 4090.
- 26 Perkin-Elmer infrared spectrometer 580B; vw = very weak, w = weak, m = medium, s = strong, sh = shoulder, br = broad.
- 27 IR in cm⁻¹ [26]: C₅Ph₅H (1): 3100w, 3077m, 3060m, 3022m, 3000w, 2848vw, 1965–1665vw, 1601m, 1584w, 1576w, 1498m to s, 1490sh, 1488s, 1450m, 1443m to s, 1341w, 1331w, 1190vw, 1170w, 1156w, 1125vw, 1071m, 1029m, 1011vw, 1004vw, 931w, 915w, 908m, 837m, 833m, 803w, 785m, 770s, 760m, 738w, 717s, 705s, 692vs, 688sh, 680sh, 566w, 550m, 539m.
 C₅Ph₄(^tBuPh)H (2): 3078m, 3052m, 3025m, 2960m to s, 2900w, 2865w, 1950–1660vw, 1600m, 1575w, 1508w, 1490s, 1460vw, 1452w, 1443m, 1394w, 1364w to m, 1340w, 1330w, 1269w to m, 1201w, 1175w, 1157w, 1130w, 1111w, 1072m, 1029m, 1020sh, 933w, 915w(br), 843m to s, 798w to m, 784m, 767m to s, 760sh, 742m, 720m, 696vs, 693sh, 586w, 571m, 569m, 538w to m.
 C₅Ph₄H₂ (3): 3075m, 3065m, 3050sh, 3030w, 3020w, 2895w, 1950–1670vw, 1604sh, 1596m to s, 1574w, 1495m to s, 1487s, 1440s, 1365m, 1349w, 1215m, 1207w, 1180w, 1153w, 1130vw, 1072m, 1046w, 1029m, 1011vw, 978w, 934w, 918m, 911sh, 902w, 873w, 791m, 767m, 753vs, 740vw, 709w, 700vs, 695vs, 690vs, 680sh, 675sh, 670sh, 653vw, 625w, 615vw, 577vw, 524s, 494m, 485w, 440vw, 360w.
 C₅Bz₅H (4): 3096vw, 3079w, 3055m, 3020m, 2994w, 2920w(br), 2852w(br), 1970–1700vw, 1600m, 1582vw, 1492s, 1450m to s, 1421w, 1400–1100vw to w, 1075m, 1027m, 1000–790vw to w, 755sh, 745sh, 732s, 695vs, 670–500vw to w, 474 m, 454w. The infrared spectra of these hydrocarbons do not seem to have been reported previously.
- 28 Varian MAT 311A Mass-spectrometer, electron-ionization technique; the intensities listed are taken from a spectrum averaged over seven scans.
- 29 Bruker WP 80 SY, 80 MHz, reference TMS.
- 30 Bruker WP 80 SY, 20.15 MHz, reference TMS; Bruker WH 270 SI, 67.89 MHz, reference TMS.
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- 32 *Note added in proof.* X-ray structural analyses of the two crystalline modifications of **8** show that the compound consists of monomeric covalent molecules associated in linear chains (needle modification) or dimeric units (parallelepipeds), the latter exhibiting a weak TI–TI interaction. In both modifications the TI atoms are shielded by the phenyl groups with the *ortho*-phenyl carbons of the directly-bonded pentabenzylcyclopentadienyl ring being nearest (H. Schumann, C. Janiak, J. Pickardt, U. Börner, *Angew. Chem.*, in press).