Quinolylcyclopentadienylthallium: A Donor-Stabilized Thallium(I) Compound

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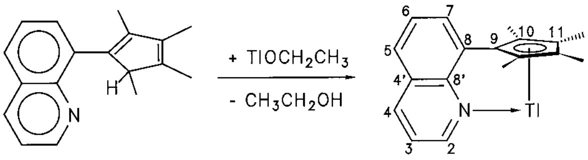
The synthesis and properties of 1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadienyl-thallium(I) (**1**) are described. The functionalised cyclopentadienyl ligand coordinates to the thallium through the five-membered ring and the nitrogen atom. Whereas the NMR investigation indicates a monomeric structure in solution, the crystal structure analysis shows the tendency to form an infinite zigzag polymeric chain in the solid state.

Introduction

Besides Cp thallium(I) compounds, most organothallium derivatives are Tl^{III} species.[1,2] Recently the synthesis of the first monomeric arylthallium(I) compound[2] has been reported. $CpTl^{I}$ compounds are mild reagents for the synthesis of cyclopentadienyl derivatives of main group elements, transition metals and lanthanoid metals.[3] Several solid-state structures of substituted CpTl compounds have been reported. For example C_5H_5Tl,[4] C_5Me_5Tl[5] and $(Me_3Si)C_5H_4Tl$[6] form infinite zigzag chain polymers. In contrast $(Me_3Si)_2C_5H_3Tl$[6] forms hexameric units. Our previous investigations on the complex chemistry of nitrogen-donor functionalised cyclopentadienyl ligands showed that rigid, bifunctional ligands prefer a chelating coordination with formation of half-sandwich compounds.[7] However for ligands in which a nitrogen-donor is connected with an alkyl chain to the cyclopentadienyl ring[8] many conformations are possible. Here we use a cyclopentadienyl system with a quinoline moiety directly attached. In this hemilabile chelate ligand, the two different functionalities are linked by a rigid C_2 spacer, which is itself embedded in the planar heterocycle. Only rotation about one bond is possible. In addition the nitrogen lone pair points towards the space below the plane of the Cp ring. As donor-stabilised thallium(I) compounds are very rare,[9,10] we tried to achieve an interaction between the thallium atom and the nitrogen donor with the help of the rigid 1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadienylligand (Cp^Q). Moreover the resulting Cp^Q-Tl should serve as a source of the Cp^Q ligand.

Results and Discussion

The reaction of 1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadiene with thallium(I) ethoxide in ethanol yields [1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadienyl]thallium(I) (**1**) (Cp^Q-Tl) as an orange precipitate in nearly quantitative yield (Scheme 1).



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Scheme 1. Formation and numbering of **1**

Compound **1** is soluble in aromatic or polar aprotic solvents. Orange crystals are formed from toluene/pentane. They are air-stable for a few minutes and decompose at 142 °C. Compound **1** is less air- and light-sensitive than C_5Me_5Tl[5] or dimethylaminoethyl-Cp-thallium compounds, and the decomposition temperature is higher.[9] These properties indicate that the thallium atom is protected by an interaction with the quinolyl nitrogen. This assumption is supported by the ^1H and ^{13}C NMR spectra.

The ^1H NMR spectrum shows doublets due to coupling with thallium. Natural thallium consists of two isotopes ^{203}Tl ($S = 1/2$, 29.53%) and ^{205}Tl ($S = 1/2$, 70.47%). As the gyromagnetic ratios of the two isotopes differ only slightly ($\gamma(^{205}Tl)/\gamma(^{203}Tl) = 1.01$), the coupling constants $J(X,Tl^{205})$ and $J(X,Tl^{203})$ are nearly identical. The four methyl groups at the cyclopentadienyl ring form two doublets at $\delta = 2.27$ and $\delta = 2.38$ with a coupling constant $^3J(Tl,H) = 15.5$ Hz and 13.3 Hz, respectively. The $^3J(Tl,H)$ coupling constant for C_5Me_5Tl has been reported to be 18 Hz.[11] Only two methyl resonances are observed, because the molecule adopts C_S symmetry on the NMR time scale. Further structural information can be obtained by the analysis of the proton−thallium coupling constants in the quinoline substituent. The exact assignment of the proton resonances has been confirmed by double resonance techniques and by a H,H-COSY NMR spectrum. If the nitrogen atom is not coordinated to the thallium centre it must lie on the opposite side of the Cp ring. For this arrangement we would expect to observe a through-space ^1H,Tl coupling of the hydrogen atom H^7 [13] and no coupling to the protons H^2, H^3 and H^4. However, the opposite is true. All protons in the heterocyclic part of the quinoline couple with the thallium atom and no Tl,H coupling is observed in the homo-

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cyclic part. The coupling constant for the H^2 atom is 17.1 Hz, and for H^3 and H^4 it is 8.2 Hz. The Tl,H coupling behaviour clearly indicates that the nitrogen atom is bound to the thallium atom in solution. In addition, the absence of coupling to a second thallium atom shows that the complex is monomeric in solution.

These interpretations are supported by the ^{13}C NMR spectra. Except for three carbon atoms from the homocyclic part of the quinoline, all resonances are split into doublets because of coupling to a single thallium atom. The largest coupling constants are observed for the quaternary carbon atoms of the Cp ring with values of 124 Hz and 127 Hz. The four methyl groups show two doublets [J(Tl,H) = 69 Hz and 59 Hz].

The EI-MS spectrum of **1** gives the molecular ion at m/z = 453 with an intensity of 27% and a characteristic isotope distribution. The base peak at m/z = 248 originates from the free ligand. The C,H analysis confirms that no solvent molecules are coordinated to **1** in the solid state.

The constitution of **1** in solution, a monomeric molecule with C_s symmetry and nitrogen coordination to the metal atom, is deduced from the NMR spectra. In addition, we investigated the solid-state structure of **1** by X-ray diffraction (Figure 1).

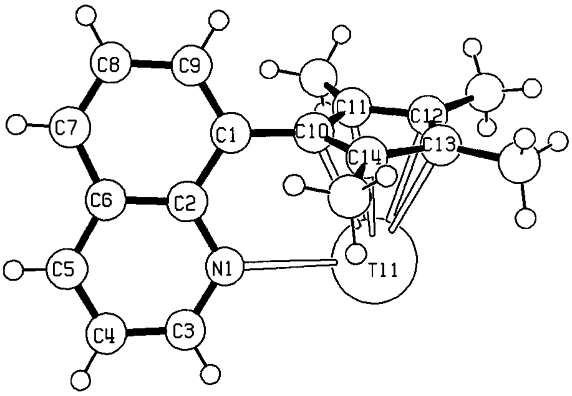

Figure 1. Solid state structure of **1**; selected bond lengths (Å) and angles (°):Tl1−N1 2.977(11), Tl1−C10 2.884(11), Tl1−C11 2.872(11), Tl1−C12 2.869(10), Tl1−C13 2.917(10), Tl1−C14 2.932(11), Tl1−C10′ 3.187(11), Tl1−C11′ 3.081(11), Tl1−C12′ 3.070(10), Tl1−C13′ 3.145(11), Tl1−C14′ 3.229(11), quinoline−Cp 110.2(8); C3−N1−Tl1 120.1(9), C2−N1−Tl1 120.2(8), C2−N1−C3 117.8(12)

In **1** the thallium atom is coordinated to the substituted Cp ring and the nitrogen atom. The distance between the metal and the centre of the Cp ring is 2.63 Å. A longer contact of 2.90 Å is observed to a neighbouring Cp ligand. Although this distance is quite long, **1** can be described as a zigzag chain polymer (Figure 2), an arrangement which is known for several CpTl compounds.[4−6,12] The Tl−Tl−Tl angle is 137.1°, a value similar to that in C_5H_5Tl (137°)[4] but smaller than in C_5Me_5Tl (145°).[5] However, in most reported structures of substituted CpTl complexes, the metal atom lies nearly equidistant between two Cp rings {e.g. C_5H_5Tl: d(Tl−Cp) = 2.75 Å,[4] C_5Me_5Tl: d(Tl−Cp) = 2.71 Å[5]}. In **1** the coordination of the nitrogen donor to the metal centre prevents a second Cp ring from binding strongly to the thallium atom. The Tl−N distance (2.97 Å) is quite long compared to reported Tl^I−N distances (2.52−2.95 Å).[14−18] Nevertheless there is a bonding interaction with formation of a chelating structure. This interpretation is supported by the sum of bonding angles around the nitrogen atom (C2−N−Tl, Tl−N−C3, C3−N−C2) which is 358.1°. Therefore the nitrogen atom lies in the plane of C2, C3 and Tl, so that the lone-pair of the nitrogen points directly at the thallium centre.

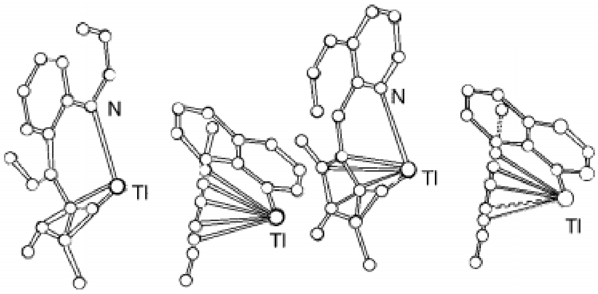

Figure 2. Solid state structure of **1** showing the arrangement as an infinite zigzag chain polymer; selected distances (Å) and angles (°): Tl−Cp 2.63 and 2.90, Tl−Tl 5.52(3); Tl−Tl−Tl 137.1(8)

Experimental Section

All reactions were carried out under nitrogen or argon atmosphere. 1-(8-quinolyl)-2,3,4,5,-tetramethylcyclopentadiene was prepared according to the reported procedure.[7]

1-(8-Quinolyl)-2,3,4,5-tetramethylcyclopentadienyl-thallium(I) (1): 1-(8-Quinolyl)-2,3,4,5-tetramethylcyclopentadiene (4.0 g, 16.0 mmol) was dissolved in 150 mL ethanol. At room temp. thallium ethoxide (4.0 g, 16.0 mmol) was added slowly to the pale yellow solution. Immediately the colour changed to deep orange. After 12 h magnetic stirring with the exclusion of light a bright orange precipitate was formed, which was then separated by filtration and washed with small portions of ethanol. After drying in vacuum, 7.0 g (96.8%) of **1** was obtained.

^1H NMR (C_6D_6): δ = 2.26 [d, ^3J(Tl,H) = 15.5 Hz, 6 H, 2 CH_3]; 2.38 [d, ^3J(Tl,H) = 13.3 Hz, 6 H, 2 CH_3], 6.78 [ddd, ^3J(H3,H4) = 4.0 Hz, ^3J(H3,H2) = 4.0 Hz, ^4J(Tl,H3) = 8.2 Hz, 1 H, H3], 7.31 [d, ^3J(H5,H6) = ^3J(H7,H6) = 4.0 Hz, 2 H, H5 and H7], 7.61 [ddd, ^3J(H4,H3) = 3.5 Hz, ^4J(H4,H2) = 1.9 Hz, ^5J(Tl,H4) = 8.2 Hz, 1 H, H4], 7.72 [t, ^3J(H6,H5) = ^3J(H6,H7) = 4 Hz, 1 H, H6], 8.21 [ddd, ^3J(H2,H3) = 4.2 Hz, ^4J(H2,H4) = 1.8 Hz, ^3J(Tl,H2) = 17.1 Hz, 1 H, H2]. − ^{13}C NMR: (C_6D_6) δ = 11.2 [d, J(Tl,C) = 59.2 Hz, CH_3], 11.7 [d, J(Tl,C) = 69.4 Hz, CH_3], 114.6 [d, J(Tl,C) = 145.2 Hz, C9], 115.1 [d, J(Tl,C) = 126.7 Hz, C10, C11], 117.3 [d, J(Tl,C) = 8.3 Hz, C8′], 120.4 [d, J(Tl,C) = 15.7 Hz, C3], 124.8 and 126.9 (s, C5, C7), 129.7 (s, C4′), 133.2 [d, J(Tl,C) = 29.6 Hz, C6], 136.9 [d, J(Tl,C) = 9.3 Hz, C4], 139.0 [d, J(Tl,C) = 26.8 Hz, C8], 147.2 [d, J(Tl,C) = 27.8 Hz, C2]. The assignment of all quinolyl atoms was confirmed from the H/H-COSY and C/H-COSY spectra. − EI-MS: m/z (%) = 453 (28) [M^+], 248 (100) [M^+ − Tl], 205 (38) [^{205}Tl], 203 (16) [^{203}Tl]. − $C_{18}H_{18}NTl$ (452.731): calcd. C 47.67, H 4.00, N 3.09; found C 47.53, H 4.21, N 2.98.

Crystal Structure Determination of 1: Crystal data: $C_{18}H_{18}NTl$, M = 452.7, monoclinic, $P2_1/a$, a = 10.282(7), b = 15.162(11), c = 10.862(8) Å, β = 109.86(5)°, V = 1593(2) Å^3, Z = 4, d = 1.89 g cm^{-3}, μ = 10.1 mm^{-1}. Intensity data were collected at −70 °C with a Siemens-Stoe AED2 diffractometer [Mo-K_α radiation (λ = 0.71073 Å), ω-scans] up to θ = 25° (2805 unique reflections, 1866 observed with $[I > 2\sigma(I)]$. An empirical absorption correction (ψ-scans) was applied. The structure was solved by direct methods (SHELXS86[19]) and refined by full-matrix least-squares techniques (SHELXL93[19]) based on F^2 using all measured reflections and with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions. $R1 = 0.050$, $wR2 = 0.106$, 187 parameters, rest electron density 0.96, -1.24 e·Å^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-142406. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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