Dithallium complex of 7,9-dicarbollyl dianion

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The preparation of a novel dithallium complex of 7,9-dicarbollyl dianion is described. The reaction of EtOTl with $Cs[7,9\text{-}(PhNHC(O))_2\text{-}7,9\text{-}C_2B_9H_9]$ gives a complex containing three Tl atoms per one substrate molecule.

Key words: thallium, dicarbollyl, complex, synthesis.

Dithallium salts of the 7,8-dicarbollyl dianion obtained in 1972[1] are convenient starting materials for the synthesis of various metallacarboranes[2] in which the metal atom is η^5- or η^1-bonded with the dicarbollyl ligand.[3]

It is known that 7,8-dicarbollyl dianion salts have decreased stability. For example, the dipotassium salt has not been obtained in the solid state, and the dilithium salt reported recently[4] is stable only for one month when kept in the cold under argon. Unlike these salts and the highly hygroscopic acid, $C_2B_9H_{13}$, dithallium salts of the 7,8-dicarbollyl dianion are solid compounds stable in the air and in weakly-alkaline media.

Complexes of this type are generally obtained either by the reaction of $K_2[7,8\text{-}C_2B_9H_{11}]$ with AcOTl[1] in water or by the reaction of the $7,8\text{-}C_2B_9H_{13}$ acid with thallium ethoxide.[5]

On the other hand, dithallium complexes of the 7,9-dicarbollyl dianion, the degradation product of *m*-carborane(12), have not been known until now. The existence of disodium and dipotassium salts of 7,9-dicarbollyl dianions in a solution has been proven by the synthesis of metallacarboranes from them,[6] but the corresponding acid, $7,9\text{-}C_2B_9H_{13}$, has not been isolated in an individual state.

The present work deals with the preparation of the dithallium complex of the $7,9\text{-}C_2B_9H_{11}$ dianion.

Results and Discussion

We attempted to obtain the desired complex under the conditions for the synthesis of $Tl_2[7,8\text{-}C_2B_9H_{11}]$ (**1**) reported in Ref. 1, *i.e.*, by treatment of $Me_3NH[7,9\text{-}C_2B_9H_{12}]$ with aqueous KOH and then with TlOAc at ~20 °C. However, although the reaction gave a yellow product, its rapid decomposition under these conditions prevented its isolation. Nevertheless, we were able to isolate the target product by decreasing the temperature of the process to 5 °C.

$$Me_3NH[7,9\text{-}C_2B_9H_{12}] \xrightarrow[2.Tl_2SO_4]{1.2KOH,\ H_2O} \underset{\mathbf{2}}{Tl_2[7,9\text{-}C_2B_9H_{11}]}$$

Complex **2** is a yellow compound stable in the air but quickly decomposed in organic solvents. It is known that a typical feature of complex **1** is the ability to react with $CoCl_2$ or $FeCl_2$ giving cobalta- or ferracarboranes, respectively.[1]

Unlike complex **1**, compound **2** does not give metallacarboranes under these reaction conditions. Another characteristic feature of compound **1** is the formation of $Tl[7,8\text{-}C_2B_9H_{12}]$ when **1** is dissolved in AcOH.[1] Dissolution of complex **2** in AcOH does not afford the respective salt. The ^{11}B NMR spectrum of the reaction mixture contains an intense unresolved signal at 18 ppm (a boric acid derivative) and a set of doublet signals with the following chemical shifts, δ ($J_{^{11}B-^{1}H}$): −4.4 (J = 135 Hz, B-2,5); −5.7 (J = 128 Hz, B-8); −21.4 (J = 128 Hz, B-3,4); 22.6 (J = 124 Hz, 60 dd, B-10,11); 34.3 (J = 118 Hz, B-6); 35.1 (J = 102 Hz, B-1). This set of signals is related to the $[7,9\text{-}C_2B_9H_{12}]^-$ anion which is present in 4 : 1 ratio with respect to the product of deep degradation. It has been shown previously[7] that the reaction of complex **1** with PPNCl (PPN is bis(triphenylphosphoranylidene)ammonium) results in the removal of the "external" Tl^+ cation, whereas the second thallium atom is a bridging atom between the B-9, B-10, and B-11 atoms of the open face. The reaction of complex **2** with PPNCl resulted in the salt $PPN[7,9\text{-}C_2B_9H_{12}]$.

In order to additionally stabilize the thallium atom above the open face of the $7,9\text{-}C_2B_9H_{11}$ dianion, we studied the reaction of $Cs[7,9\text{-}(PhNHC(O))_2\text{-}7,9\text{-}C_2B_9H_{10}]$ (**3**) with thallium ethoxide. This reaction resulted in an insoluble product. The $CsTl_3[7,9\text{-}(PhNC(O))_2\text{-}7,9\text{-}C_2B_9H_9]$ formula (**4**) was ascribed to this product on the basis of the elemental analysis and X-ray fluorescence data. Evidently, the

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increased thallium content in complex **4** is due to thallation of the NH moiety of the original complex **3**. In fact, the IR spectrum of compound **4** in KBr does not contain the narrow absorption band at 3400 cm^{-1} (νNH) of the original salt **3** (the vibrational spectra of compound **3** obtained from carborane 1,7-$(PhNHC(O))_2$-1,7-$C_2B_{10}H_{10}$ (**5**) have been studied in detail in Ref. 8). Probably, the acidity of the NH fragment is sufficient for the reaction with thallium ethoxide, which readily reacts with C—H, S—H, and some NH acids to give the respective thallium salts. The reaction of compound **5** with EtOTl in ethanol also results in an insoluble product (**6**), whose IR spectrum contains no narrow band at 3400 cm^{-1}. The elemental composition of the product corresponds to a dithallium complex. Unlike the reaction of compound **3**, that of dithallium salt $K_2[7,9\text{-}(CH_2OH)_2\text{-}7,9\text{-}C_2B_9H_9]$ with Tl_2SO_4 does not give thallium complexes, but results in products of the deep degradation of the carborane frame and metallic thallium. A similar result was obtained in the reaction of $Me_3NH[7,9\text{-}(CH_2OH)_2\text{-}7,9\text{-}C_2B_9H_{10}]$ with thallium ethoxide.

Experimental

Dithallium[7,9-dicarbollyl] (2). $Me_3NH[7,9\text{-}C_2B_9H_{12}]$ (1.92 g, 10 mmol) was added to a solution of KOH (0.8 g) in water (50 mL), and the mixture was stirred at -20°C under argon until dissolution of the solids. Then the reaction mixture was cooled to 5°C, and Tl_2SO_4 (3 g) in water (100 mL) was added dropwise. The resulting yellow precipitate was quickly filtered off with cooling, washed with cold water (2×50 mL), and dried *in vacuo* with P_2O_5 to give 1.4 g (26%) of complex **2**, t.dec. > 246°C. Found (%): C, 4.7; H, 2.4; B, 18.8; Tl, 75.5; $C_2H_{11}B_9Tl_2$. Calculated (%): C, 4.4; H, 2.0; B, 18.0; Tl, 75.7. IR (vaseline oil), ν/cm^{-1}: 2550 s.br. (B—H); 3115 avg (C—H).

Reaction of compound 3 with EtOTl. EtOTl (0.2 g, 0.8 mmol) was added to a solution of compound **3** (0.2 g, 0.4 mmol) in an ether/THF mixture. The precipitate that formed was filtered off, washed with THF, ethanol, and ether, and dried to give 0.13 g (30% with respect to the original complex **3**) of complex **4**. Found (%): C, 15.8; H, 2.0; B, 8.5; Tl, 53.2; $C_{16}H_{19}B_9N_2O_2CsTl_3$. Calculated (%): C, 17.2; H, 1.7; B, 8.7; Tl, 54.9. IR (KBr), ν/cm^{-1}, > 2000 cm^{-1}): 2550 s.br.

Reaction of carborane 5 with EtOTl. EtOTl (0.25 g, 1.0 mmol) was added under argon to a solution of compound **5** (0.2 g, 0.5 mmol) in abs. ether (30 mL). The precipitate was washed with ether and ethanol and then dried with P_2O_5 (product **6** turns yellow in the air) to give 0.1 g (25%) of **6**, t.dec. > 190°C. Found (%): C, 22.7; H, 2.6; B, 12.3; Tl, 53.1; $C_{16}H_{20}B_{10}N_2O_2Tl_2$. Calculated (%): C, 24.3; H, 2.5; B, 13.7; Tl, 51.7. IR (KBr, ν/cm^{-1}, > 2000 cm^{-1}): 2600 s.br.

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