Thallium Perfluorotetraphenylborate

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Summary: Thallium perfluorotetraphenylborate, Tl[B(C_6F_5)$_4$], has been prepared by the reaction of thallium ethoxide with [H(OEt_2)$_2$][B(C_6F_5)$_4$]. Its use in the preparation of [(η^3-C_3H_5)Ni($Me_2PC_2H_4PMe_2$)][B(C_6F_5)$_4$] is described.

Introduction

There is an enduring interest in the chemistry of noncoordinating (or weakly coordinating) anions.[1,2] In many cases, classical anions such as ClO_4^-, $SO_3CF_3^-$, BF_4^-, BPh_4^-, and PF_6^- still act as weak nucleophiles and thus bind to strong electrophiles. Anion nucleophilicity can, however, be further reduced when the charge is delocalized by increasing ionic size and introducing an array of electron-withdrawing fluorine substituents. Typical developments, mainly over the last two decades, are B(C_6F_5)$_4^-$, MeB(C_6F_5)$_3^-$, B{3,5-C_6H_3(CF_3)$_2$}$_4^-$ (TFPB, BArF),[1a,b] and the carborane $CB_{11}H_{12}^-$ and its derivatives.[1c]

Of these, B(C_6F_5)$_4^-$, discovered by Massey and Park,[3] and Kobayashi's TFPB[4a] are of particular interest, due to their structural simplicity, high symmetry, and ready availability. In a comparison of the two anions, B(C_6F_5)$_4^-$ is more stable[1c,5a] than B{3,5-C_6H_3(CF_3)$_2$}$_4^-$, but the latter seems to be less nucleophilic,[5b,c] though there is also a contending view.[5a] Introduction of these anions into a compound can typically occur by halide exchange with an alkali-metal salt, e.g., Li[B(C_6F_5)$_4$][3] and Na[TFPB],[4] by protolysis with the corresponding oxonium acids, [H(OEt_2)$_2$][B(C_6F_5)$_4$][6] and [H(OEt_2)$_2$][TFPB],[7] or by halide exchange with the silver or thallium salts, Ag[B(C_6F_5)$_4$],[8] Ag[TFPB],[9] and Tl[TFPB].[10] While the silver salts are substantially less toxic, they sometimes undergo unwanted redox side reactions. Thus, metathesis with a thallium salt is usually more efficient and cleaner to carry out.

Attempting the preparation of [(η^3-C_3H_5)NiL]$^+$ and [(η^3-C_3H_5)PdL]$^+$ complexes with noncoordinating (or weakly coordinating) counterions, we noticed that Tl[B(C_6F_5)$_4$] (**1**), a potentially useful reagent in the context of the above, is apparently not known. Here, we report the synthesis and properties of the compound.

Experimental Section

All manipulations were carried out under argon with Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$ or P_4O_{10}. LiC_6F_5,[3b,11a,c] B(C_6F_5)$_3$,[3,11b,c] Li[B(C_6F_5)$_4$],[3a,b] [H(OEt_2)$_2$][B(C_6F_5)$_4$],[6] and (η^3-C_3H_5)Ni(dmpe)Br[12a] were prepared according to the literature. TlOEt (98%) and C_6F_5I (99%) were obtained from Aldrich and used without further purification. Additional information on the synthesis and properties of some of the compounds is given below. Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. NMR spectra were measured on Bruker AMX-300 and DPX-300 instruments in CD_2Cl_2 as a solvent at 25 °C.

LiC_6F_5. Synthesis was performed as described in ref 11a but using C_6F_5I instead of C_6F_5Br: to a stirred solution of C_6F_5I (29.4 g, 100 mmol) in 250 mL of diethyl ether was added dropwise a 1.6 M solution of Li^{n}Bu in *n*-hexane (62.5 mL, 100 mmol) at −78 °C. After the mixture was stirred for an additional 1 h, the reaction was complete. The product was used without isolation.

Li[B(C_6F_5)$_4$]. Following the protocol of ref 3b, the isolated yield was increased to 83% (instead of a reported 43%) due to the higher yield of the in situ prepared LiC_6F_5. Thus, the solution of LiC_6F_5 (assumed to be 100 mmol) was added in portions to a suspension of B(C_6F_5)$_3$ (46.1 g, 90 mmol) in 250 mL of pentane at −40 °C. The mixture was stirred overnight at ambient temperature. The resulting solid was isolated by filtration, washed with pentane, and dried under vacuum: yield 51.2 g (83%). ESIneg-MS (CH_2Cl_2): *m/e* (%) 679 ([B(C_6F_5)$_4$]$^-$, 100).

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[H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$].[6] ^{13}C NMR (75.5 MHz): δ 148.7 (d, J(CF) = 240 Hz, C$_{ortho}$), 138.7 (d, J(CF) = 245 Hz, C$_{para}$), 136.8 (d, J(CF) = 247 Hz, C$_{meta}$), ~125 (C$_{ipso}$), 70.7 (CH$_2$), 13.7 (CH$_3$). ^{11}B NMR (96.3 MHz): δ −16.7.

Tl[B(C$_6$F$_5$)$_4$] (1). TlOEt (12.5 g, 50 mmol) was added dropwise to a solution of [H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$] (41.4 g, 50 mmol) in 250 mL of diethyl ether at ambient temperature. The resulting light yellow reaction mixture was stirred for 1 h and filtered to remove a small amount of an insoluble impurity (presumably TlCl). Evaporating the solvent under vacuum gave a white microcrystalline residue: yield 37.6 g (85%). ESIpos-MS (CH$_2$Cl$_2$): *m*/*e* (%) 205 ([Tl]$^+$, 100). ESIneg-MS (CH$_2$Cl$_2$): *m*/*e* (%) 679 ([B(C$_6$F$_5$)$_4$]$^-$, 100). ^{13}C NMR (75.5 MHz): δ 148.2 (d, J(CF) = 242 Hz, C$_{ortho}$), 138.3 (d, J(CF) = 246 Hz, C$_{para}$), 136.4 (d, J(CF) = 246 Hz, C$_{meta}$), ~124 (C$_{ipso}$). ^{11}B NMR (96.3 MHz): δ −16.7. ^{19}F NMR (282.4 MHz): δ −132.8 (s, F$_{ortho}$), −163.2 (t, F$_{para}$), −167.0 (“t”, F$_{meta}$). Anal. Calcd for BC$_{24}$F$_{20}$Tl (883.4): C, 32.63; B, 1.22; F, 43.01; Tl, 23.14. Found: C, 32.82; B, 1.23; F, 42.59; Tl, 23.29.

[(η^3-C$_3$H$_5$)Ni(Me$_2$PC$_2$H$_4$PMe$_2$)][B(C$_6$F$_5$)$_4$] (2). A solution of (η^3-C$_3$H$_5$)Ni(dmpe)Br (1.65 g, 5.00 mmol) in 15 mL of CH$_2$Cl$_2$ was stirred with solid **1** (4.42 g, 5.00 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration. After addition of an equal volume of diethyl ether the solution was cooled to −60 °C to give yellow-orange crystals, which were freed from the mother liquor by cannulation, washed with a small volume of cold pentane (−78 °C), and dried under vacuum (20 °C): yield 3.30 g (71%); mp 174 °C. ESIpos-MS (CH$_2$Cl$_2$): *m*/*e* (%) 249 ([(C$_3$H$_5$)Ni(dmpe)]$^+$, 100). ESIneg-MS (CH$_2$Cl$_2$): *m*/*e* (%) 679 ([B(C$_6$F$_5$)$_4$]$^-$, 100). ^{1}H NMR (300 MHz): δ 5.13 (m, 1H, H$_{meso}$), 4.28 (m, 2H, H$_{syn}$), 2.45 (m, 2H, H$_{anti}$), allyl; 1.97 (m, 4H, PCH$_a$H$_b$), 1.64, 1.52 (each d, 6H, Me), dmpe. ^{13}C NMR (75.5 MHz): δ 117.5 (s, 1C), 65.4 (m, 2C), allyl; 27.8 (m, 2C, PCH$_2$), 13.5, 12.7 (each m, 2C, Me), dmpe; 148.2 (d, C$_{ortho}$), 138.3 (d, C$_{para}$), 136.4 (d, C$_{meta}$), ~124 (C$_{ipso}$), borate. ^{31}P NMR (121.5 MHz): δ 36.9. Anal. Calcd for C$_9$H$_{21}$NiP$_2$·BC$_{24}$F$_{20}$ (929.0): C, 42.67; H, 2.28; B, 1.16; F, 40.90; Ni, 6.32; P, 6.67. Found: C, 42.52; H, 2.32; B, 1.13; Ni, 6.14; P, 6.48.

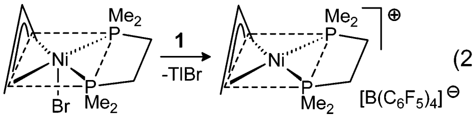
Results and Discussion

LiC$_6$F$_5$ is prepared in quantitative yield from C$_6$F$_5$I and Li^{n}Bu in diethyl ether/*n*-hexane solution at −78 °C. It reacts with B(C$_6$F$_5$)$_3$ to afford Li[B(C$_6$F$_5$)$_4$] (83%), which in diethyl ether is converted with HCl into [H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$], as described by Jutzi et al.[6] Reaction of the oxonium acid with thallium(I) ethoxide by the method of Hughes et al.[10] afforded Tl[B(C$_6$F$_5$)$_4$] (**1**) in 85% yield (eq 1).

$$\mathrm{LiB(C_6F_5)_4} \xrightarrow[-\mathrm{LiCl}]{\mathrm{HCl/Et_2O}} \mathrm{[H(OEt_2)_2][B(C_6F_5)_4]} \xrightarrow[-\mathrm{EtOH}]{\mathrm{TlOEt}} \underset{\mathbf{1}}{\mathrm{Tl[B(C_6F_5)_4]}} \quad (1)$$

Compound **1** crystallizes from cold diethyl ether in large colorless chunks of microcrystalline material. The compound has so far not been amenable to single-crystal X-ray analysis.[13] The product contains small amounts of diethyl ether and ethanol as solvates, which are removed upon heating to 100 °C under vacuum. According to DSC, a phase transition occurs at about 140 °C, but no melting or decomposition is observed up to 200 °C. The compound can be stored indefinitely at ambient temperature. **1** has been characterized by its ESIpos-MS and ESIneg-MS spectra, which gave single peaks for [Tl]$^+$ (*m*/*z* 205) and [B(C$_6$F$_5$)$_4$]$^-$ (*m*/*e* 679). It dissolves well in CH$_2$Cl$_2$, diethyl ether, and THF but not in toluene or hydrocarbons. The solution NMR data agree well with the previously reported data for the B(C$_6$F$_5$)$_4$ anion.[14]

The applicability of **1** as a reagent for the formation of B(C$_6$F$_5$)$_4$ salts is demonstrated by its reaction with (η^3-C$_3$H$_5$)Ni(dmpe)Br (dmpe = Me$_2$PC$_2$H$_4$PMe$_2$) to afford the ionic **2**, which is easily separated from the insoluble TlBr (eq 2). Complex **2** extends a series of likewise ionic complexes [(η^3-C$_3$H$_5$)Ni(dmpe)]X (X = SO$_3$CF$_3$, PF$_6$)[12] to X = B(C$_6$F$_5$)$_4$. For these complexes (in contrast to the halides) the ^{1}H and ^{13}C NMR spectra in CD$_2$Cl$_2$ are sharply resolved at ambient temperature, indicating a rigid structure of the cation on the NMR time scale. We conclude from the spectra that, despite substantial ion pairing, the nucleophilicity of the anions toward the [(η^3-C$_3$H$_5$)Ni(dmpe)]$^+$ cation is marginal.[12]



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(2)

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(13) By the end of 2003 the Cambridge Structural Data File had listed about 100 known structures of B(C$_6$F$_5$)$_4$ salts.

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