Organotitanium Fluorides as Matrices for Trapping Molecular ZnF₂ and MeZnF₂

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Dedicated to Professor Marianne Baudler

The understanding of forming single crystals from solution is still in its infancy. Moreover it is very often precisely this step which is rate-determining for the progress of the research work. Therefore we became interested in studying the behavior of “molecular solids”. A leading strategy in our investigations is the HSAB (hard soft acid base) concept of Pearson.[1] In recent years organometallic fluorides from metals of Group 4 have been extensively employed to act as complexing agents for inorganic compounds such as LiF, NaF, MgF₂, CaF₂, and Li₂O, which are insoluble in organic solvents. This gives rise to solids that are soluble in organic solvents. In these solids not only hard cations of Group 4, but also those of the alkali and alkaline earth metals are connected to the hard base fluoride.[2–7] Hitherto it was not known whether organometallic fluorides for Group 4 metals could also complex the transition metal fluorides that are insoluble in organic solids, and in which the cations have the characteristics of a soft acid. Herein we report on the first aggregates containing ZnF₂ and Me₃SnF soluble in organic solvents.

Although ZnF₂ does not react directly with organotitanium fluorides due to its high lattice energy and insolubility in organic solvents, zinc difluoride, prepared in situ from dimethylzinc and trimethyltin fluoride, has now been successfully trapped by [Cp*TiF₂Me] (1) (Cp* = C₅Me₅)[8] to form [(Cp*TiF₃)(ZnMe₂)] (2) in moderate yield. The reaction of 1, Me₃SnF, and ZnMe₂ in a molar ratio of 8 : 3 : 6 in toluene followed by removal of SnMe₄ and the solvent and recrystallization from toluene afforded red crystals of 2 at 0 °C. If 1 was allowed to react with ZnMe₂ in a molar ratio of 3 : 1 in toluene, a red solution was formed immediately, and orange crystals of composition [(Cp*TiF₃)(MeZnF₃)] (3) could be isolated. However, the reaction of 1, ZnMe₂, and Me₃SnF in a molar ratio of 4 : 2 : 2 in toluene only resulted in a mixture of 2 and 3. Evidently, 3 is the intermediate for the formation of 2. In the first step one fluorine atom of 1 is rapidly exchanged by one methyl group of ZnMe₂ to form 3 and the by-product [Cp*TiF₃Me]. Subsequently, the remaining methyl groups at Zn in 3 can be easily exchanged by Me₃SnF to afford 2 (Scheme 1).

Compounds 2 and 3 are soluble in toluene and chloroform, however only slightly soluble in benzene and n-hexane. The melting points of 2 (155 °C) and 3 (121 °C) were found to be lower than that of the starting material 1 (189 °C). In the gas phase only the ion [(Cp*TiF₃)]⁺ was observed (m/z 240) by mass spectrometry for 2 and 3. The ¹H NMR spectra display seven proton signals for 2 (δ = 2.07 – 2.13 (Cp*)), and two resonances for 3 (δ = 1.95 (Cp*), broad), –0.71 (MeZn)). The ¹⁹F NMR spectrum of 2 in C₆D₆ gives seven resonances for the terminal fluorines (Ti–F) in the range from δ = 371.1 to 305.8 and thirteen signals for the bridging fluorines (Ti–F–Ti and Ti–F–Zn) in the range from δ = 178.1 to 49.9, while the ¹⁹F NMR spectrum of 3 in C₆D₆ exhibits four signals for the atomic fluorines (δ = 121.8 (TiF, broad), 83.8 (Ti(μ-F)Ti), –20 (Ti(μ-F)Zn), –40.0 (Ti(μ-F,Zn)). The ¹⁹F NMR data indicate that the structures of 2 and 3 in solution are in accordance with those in the solid state.

The structures of 2 and 3 have been determined by X-ray single-crystal analysis; the central inorganic core of 2 and the molecular structure of 3 are shown in Figure 1 and Figure 2, respectively. Compounds 2 and 3[8] crystallize in the triclinic and monoclinic space group P1 and P2₁/n, respectively. There is a pseudo-mirror plane in 2 that passes through the atoms Ti(4), Ti(5), F(11), F(13), F(26), F(15), and Zn(2) (mean deviation 0.0179 Å), excluding the seven terminal fluorine atoms (F(1), F(4), F(7), F(17), F(21), F(24)), and containing the thirteen bridging fluorines. The whole molecule of 2 is in an asymmetric arrangement. The eight [Cp*TiF₃] molecules completely enclose three ZnF₂, molecules in such a way that each titanium atom is coordinated to five fluorine atoms and one Cp* group to complete a distorted octahedral geometry. With the exception of Ti(5) each titanium atom has a terminal fluorine atom. Therefore each zinc atom of 2 is coordinated to six fluorine atoms forming a distorted octahedral geometry. This geometry compares well with the rutile structure of ZnF₂.[10] The molecular structure of 3 shows the dimeric...
Experimental Section

2: ZnMe₂ (0.5 mL, 1 mmol, 2.0 mol solution in toluene) was added dropwise by syringe to a mixture of 1 (0.65 g, 2.7 mmol) and Me₂SnF (0.37 g, 2.0 mmol) suspended in toluene (40 mL) at room temperature. The bright red solution was stirred overnight until all the solid disappeared. All volatiles were removed under vacuum and the residue was recrystallized in toluene (15 mL) at room temperature to give red crystals of compound 2, which were isolated at 0°C in 40% yield (0.30 g) (based on 1). M.p. 154 - 156 °C; EI-MS: m/z (%): 240 (30 [Cp*TiF₄]), 135 (100 [Cp⁺]); 1H NMR (D₈-toluene): δ = 2.07, 2.08, 2.09, 2.10, 2.11, 2.12, 2.13 (C₆H₅); 13F NMR ([D₈-toluene): δ = 371.1, 370.1, 353.6, 349.3, 326.5, 313.8, 306.1 (Ti-F), 188.7, 169.2, 149.2, 143.8, 140.1, 138.3, 131.2, 120.6, 115.8, 108.4, 103.7, 73.4, 49.9 (Ti-F), 1.042; largest difference peak and hole: 0.396 eÅ⁻³. The structure was solved by direct methods using the program SHELXS-97 and refined against F² on all data by full-

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[9] Crystal structure analyses: a) 2: C₇H₁₁F₂Zn₂, 2C₇H₆, 0.5C₇H₆, M₁ = 2230.95 + 2 x 92.14 + 0.5 x 78.11, crystal size: 0.50 x 0.30 x 0.30 mm³, triclinic space group P1, a = 13.260(5), b = 14.217(3), c = 28.568(6) Å, α = 83.39(3), β = 83.31(3), γ = 86.06(3). V = 5301.2(12) Å³. Z = 2. ρcalc = 1.537 Mg m⁻³. F(000) = 2514, λ = 0.71073 Å, T = 133 K, μ(MoKα) = 1.327 mm⁻¹. The crystal was mounted on a glass fiber in a rapidly cooled perfuoropolyether[6] Diffraction data of 2 were collected on a Stoe-Siemens-Huber four-circle-diffractometer coupled to a Siemens CCD area-detector at 133(2) K, with graphite-monochromated MoKα radiation (λ = 0.71073 Å), performing ϕ- and ω scans. Total number of reflections measured 52524, of which 14965 unique (Rint = 0.0441). Data/restraints/parameters: 14965/4589/1297, data collection range: 2.15 ≤ θ ≤ 23.26°. Final R indices: R₁ = 0.0379, wR₂ = 0.0814 on data with F > 2σ(F) and R1 = 0.0528, wR2 = 0.0887 on all data; goodness of fit S = [Σw(Fobs-Fcalc)²]/[Σw(Fobs)²] = 1.069; largest difference peak and hole: 0.396 eÅ⁻³. b) 3: C₇H₁₁F₂Zn₂, ZnH₂, M₁ = 1251.42, crystal size: 0.70 x 0.60 x 0.50 mm³, monoclinic space group P2₁/n, a = 9.7634(10) Å, b = 20.654(3), c = 19.457(11), V = 2741.5(7) Å³, Z = 2. ρcalc = 1.516 Mg m⁻³. F(000) = 1204, λ = 0.71073 Å, T = 133 K, μ(MoKα) = 1.495 mm⁻¹. The diffraction data of 3 were collected on a Stoe-Siemens-AED2 four-circle-diffractometer at 153(2) K, using MoKα radiation (λ = 0.71073 Å), performing 2θ scans. Total number of reflections measured 95938, of which 47776 unique (Rint = 0.0316). Data/restraints/parameters: 47680/940, data collection range: 3.59 ≤ θ ≤ 24.93°. Final R indices: R₁ = 0.0314, wR₂ = 0.0819 on data with F > 2σ(F) and R₁ = 0.0379, wR₂ = 0.0905 on all data; goodness of fit S = [Σw(Fobs-Fcalc)²]/[Σw(Fobs)²] = 1.042; largest difference peak and hole: 0.410 and -0.309 eÅ⁻³. c) The structures were solved by direct methods using the program SHELXS-97 and refined against F² on all data by full-

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matrix least squares with SHELXL-97.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 125050 and CCDC 125051. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).


Rhodium-Catalyzed Formation of Phosphorus–Boron Bonds: Synthesis of the First High Molecular Weight Poly(phosphinoborane)**

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Virtually all currently known and commercially available polymers are based on extended catenated structures containing mainly carbon atoms together with a few other elements such as oxygen and nitrogen. In contrast, the development of extended structures based on atoms of other elements has been much less successful, and their synthesis still represents a substantial challenge.[1, 2] Nevertheless, the relatively few inorganic polymers such as poly(siloxanes) (silicones) [R2Si–O–], polyphosphazenes [R2P=N]n, polysilanes [R2Si], and more recently poly(silylenes), poly(stannanes), sulfur-containing polymers, poly(metalloccenes), and other metallopolymers illustrate the potential for accessing materials with fascinating and unexpected properties as well as significant applications.[1–5] As part of a continuing program to develop novel extended chain structures based on main group elements we have explored compounds with skeletons comprising four-coordinate phosphorus and boron atoms. We were encouraged by previous reports that known cyclic phosphinoborane adducts R2PH·BH3 at elevated temperatures (150–200°C) have been previously used to prepare cyclic phosphinoborane species (mainly six-membered rings of the type [R2P·BH3]).[6] In addition, in a few cases low yields of “polymeric” materials have been claimed, but none have been convincingly structurally characterized (by present day standards) and, where reported, the molecular weights were very low.[7, 8] We have reinvestigated this “dehydrocoupling chemistry” (coupling with elimination of hydrogen) with the idea that if lower temperatures could be used and more efficient coupling reactions identified, then linear, high polymeric structures might indeed result.[9, 10]

The phosphane–borane adduct Ph2PH·BH3 undergoes dehydrocoupling at 180–190°C to exclusively and quantitatively yield the cyclical trimer [Ph3P–BH3].[11] However, on addition of about 0.3 mol % of a RhI catalyst such as [Rh(1,5-cod)2][OTf] or [[Rh(µ-Cl)(1,5-cod)]2] (1,5-cod = cycloocta-1,5-diene) dehydrocoupling of the neat adduct is observed at 90°C over 14 h to form a white, crystalline, air-stable product [Eq. (1)]. A 31P NMR spectrum of the new compound showed the presence of two different phosphorus environments (δ = −3.3 and −17.7). Additional characterization by 11B and 1H NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (Figure 1) identified the product as the novel linear dimer 1[12, 13]. Notably, the P–B bonds in 1 (1.92–1.94 Å) are long compared to carbon–carbon bonds (ca. 1.54 Å) and have lengths typical of single bonds between four-coordinate phosphorus and boron centers.

Encouraged by this result and based on our view that the prospective polymer [Ph3P–BH3] might be insoluble and that the anticipated steric congestion at phosphorus in the case

Figure 1. Molecular structure of 1 (thermal ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: P(1)–B(2) 1.932(2), P(1)–B(1) 1.944(2), P(2)–H(1P) 1.349(19), P(2)–B(1) 1.923(2), B(2)–P(1)–B(1) 113.01(11), H(1P)–P(2)–B(1) 112.6(8), P(2)–B(1)–P(1) 109.23(12).

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