Organotitanium Fluorides as Matrices for Trapping Molecular ZnF_2 and MeZnF**

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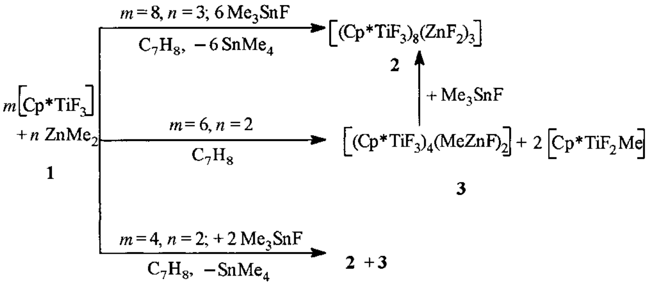
Dedicated to Professor Marianne Baudler

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, MgF_2, CaF_2, and Li_2O, 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 solvents, and in which the cations have the characteristics of a soft acid. Herein we report on the first aggregates containing ZnF_2 and MeZnF soluble in organic solvents.

Although ZnF_2 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*TiF_3] (**1**) (Cp* = C_5Me_5)[8] to form [(Cp*TiF_3)$_8$(ZnF_2)$_3$] (**2**) in moderate yield. The reaction of **1**, Me_3SnF, and $ZnMe_2$ in a molar ratio of 8:3:6 in toluene followed by removal of $SnMe_4$ and the solvent and recrystallization from toluene afforded red crystals of **2** at 0 °C. If **1** was allowed to react with $ZnMe_2$ in a molar ratio of 3:1 in toluene, a red solution was formed immediately, and orange crystals of composition [(Cp*TiF_3)$_4$(MeZnF)$_2$] (**3**) could be isolated. However, the reaction of **1**, $ZnMe_2$, and Me_3SnF 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 $ZnMe_2$ to form **3** and the by-product [Cp*TiF_2Me]. Subsequently, the remaining methyl groups at Zn in **3** can be easily exchanged by Me_3SnF 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*TiF_3)]$^+$ was observed (*m*/*z* 240) by mass spectrometry for **2** and **3**. The ^1H NMR spectra display seven proton signals for **2** ($\delta = 2.07-2.13$ (Cp*)) and two resonances for **3** ($\delta = 1.95$ (Cp*, broad), -0.71 (MeZn)). The ^{19}F NMR spectrum of **2** in C_7D_8 gives seven resonances for the terminal fluorines (Ti$-F_t$) in the range from $\delta = 371.1$ to 305.8 and thirteen signals for the bridging fluorines (Ti-F_b-Ti and Ti-F_b-Zn) in the range from $\delta = 178.1$ to 49.9, while the ^{19}F NMR spectrum of **3** in C_6D_6 exhibits four signals for the fluorine atoms ($\delta = 121.8$ (TiF, broad), 83.8 (Ti(μ-F)Ti), -20 (Ti(μ-F)Zn), -40.0 (Ti(μ_3-F)Zn)). The ^{19}F NMR data indicate that the structures of **2** and **3** in solution are in accordance with those in the solid state.



Scheme 1.

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**[9] crystallize in the triclinic and monoclinic space group $P\bar{1}$ and $P2_1/n$, 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*TiF_3] molecules completely enclose three ZnF_2 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. Moreover 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 ZnF_2.[10] The molecular structure of **3** shows the dimeric

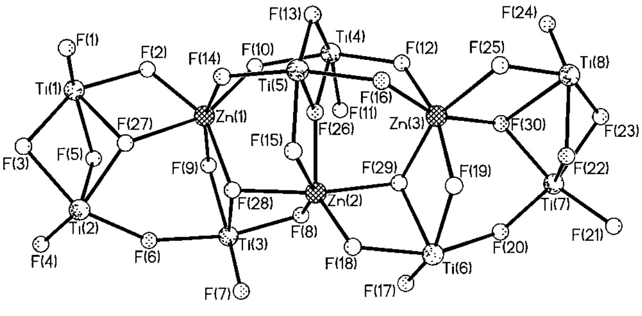


Figure 1. Structure of the inorganic core of **2** in the crystal. For clarity the Cp* groups at Ti are omitted. Selected bond lengths [Å]: Ti$-F_t$ 1.836* (1.823–1.849), Ti$-F_b$ 2.034* (1.912–2.317), Zn$-$F 2.047* (1.924–2.260), Ti(1)$-$F(2) 1.912, Ti(1)$-$F(3) 2.008, Ti(1)$-$F(5) 1.973, Ti(1)$-$F(27) 2.257, Ti(2)$-$F(27) 2.027(2), Ti(3)$-$F(28) 2.139, Ti(4)$-$F(26) 2.120, Ti(5)$-$F(26) 2.132, Ti(6)$-$F(29) 2.152, Ti(7)$-$F(30) 2.030, Ti(8)$-$F(30) 2.317. The values marked with a * are average values.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Witco GmbH.

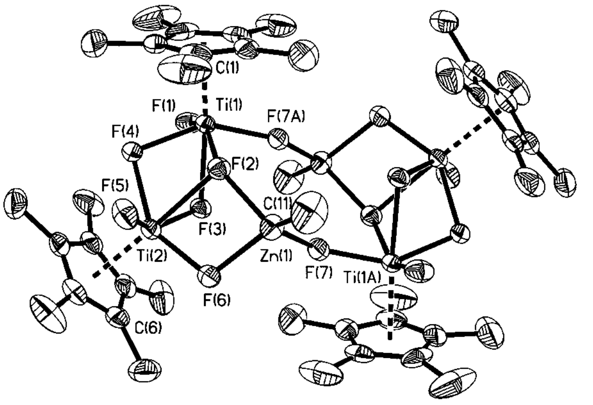

Figure 2. Molecular structure of **3** in the crystal. Selected bond lengths [Å] and angles [°]: Ti(1)−F(1) 1.820, Ti(2)−F(5) 1.823, Ti(1)−F(7A) 1.925, Ti(1)−F(4) 2.008, Ti(1)−F(2) 2.035, Ti(1)−F(3) 2.160, Ti(2)−F(6) 1.934, Ti(2)−F(4) 2.007, Ti(2)−F(3) 1.951, Ti(2)−F(2) 2.302, Zn(1)−F(7) 1.973, Zn(1)−F(6) 2.053, Zn(1)−F(2) 2.035, Zn(1)−C(11) 1.937; F(1)-Ti(1)-F(7A) 93.88, F(1)-Ti(1)-F(4) 92.47, F(4)-Ti(1)-F(7A) 148.24, F(1)-Ti(1)-F(2) 149.28, F(2)-Ti(1)-F(7A) 83.48, F(1)-Ti(1)-F(3) 80.25, F(5)-Ti(2)-F(3) 145.27, F(5)-Ti(2)-F(6) 89.74, F(5)-Ti(2)-F(4) 87.16, F(4)-Ti(2)-F(6) 143.59, F(3)-Ti(2)-F(6) 88.10, F(2)-Zn(1)-F(6) 77.97, F(2)-Zn(1)-F(7) 105.92, F(7)-Zn(1)-F(6) 89.54, Ti(2)-F(6)-Zn(1) 109.96, Ti(1)-F(2)-Zn(1) 143.97, Ti(1)-F(4)-Ti(2) 99.84, Ti(1A)-F(7)-Zn(1) 141.18, C(11)-Zn(1)-F(2) 118.32, C(11)-Zn(1)-F(6) 136.92, C(11)-Zn(1)-F(7) 119.14.

character of the [(Cp*TiF)$_2$(μ-F)$_4$(μ_3-F)(ZnMe)] units that are connected by two Ti(μ-F)Zn bridges. Therefore, compound **3** is a centrosymmetric molecule with a center of inversion in the centroid of the eight-membered Ti$_2$F$_4$Zn$_2$ ring. The distorted tetrahedral environments of the Zn atoms in **3** are very different from those in **2**. The coordination sphere at Zn is formed by three of the bridging fluorines and one terminal methyl group. The titanium atoms in **3**, however, are similarly connected to those found in **2**, they are coordinated to five fluorine atoms and one Cp* ligand to complete a distorted octahedral geometry. The average terminal Ti−F$_t$ bond lengths (1.84 Å for **2** and 1.82 Å for **3**) are shorter than the bridging Ti−F$_b$ distances (2.10 Å for **2** and 2.04 Å for **3**), in which the average μ_3-bridging Ti-(μ_3-F$_b$) distances (2.17 Å for **2** and 2.15 Å for **3**) are slightly longer than the μ-bridging Ti-(μ-F$_b$) ones (2.07 Å for **2** and 2.00 Å for **3**). The average Zn−F$_b$ bond lengths (2.05 Å and 2.02 Å for **2** and **3**, respectively) are comparable to that found in CaZnF$_4$ (Zn−F, 1.93 Å).[11]

In summary, we have demonstrated for the first time that ZnF$_2$ and MeZnF can be trapped as molecular solids. In compound **2** the Zn atoms are surrounded by six fluorine atoms as in the solid-state structure of ZnF$_2$. Moreover, the small molecule MeZnF was isolated and characterized for the first time as an adduct.

Experimental Section

2: ZnMe$_2$ (0.5 mL, 1 mmol, 2.0 M solution in toluene) was added dropwise by syringe to a mixture of **1** (0.65 g, 2.7 mmol) and Me$_3$SnF (0.37 g, 2 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*TiF$_3$], 135 (100) [Cp*]; ^{1}H NMR ([D$_8$]toluene): δ = 2.07, 2.08, 2.09, 2.10, 2.11, 2.12, 2.13 (Cp*); ^{19}F NMR ([D$_8$]toluene): δ = 371.1, 370.1, 353.6, 349.3, 326.5, 313.8, 306.1 (Ti−F$_t$), 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$_b$-Ti, Ti-F$_b$-Zn); elemental analysis for C$_{80}$H$_{120}$F$_{30}$Ti$_8$Zn$_3$: calcd C 43.0, H 5.4, F 25.6; found: C 43.3, H 5.8, F 26.0.

3: ZnMe$_2$ (0.5 mL, 1 mmol, 2.0 M solution in toluene) was addded dropwise by syringe to a solution of **1** (0.72 g, 3 mmol) in toluene (20 mL) at room temperature, and the resulting mixture was stirred for 12 h. The color changed from orange to bright red. After partial removal of the solvent, the solution was kept at −20 °C for several days, and red crystals of compound **3** could be isolated in a 30 % yield (0.18 g) (based on **1**). M.p. 120–122 °C; EI-MS, *m/z* (%): 240 (40) [Cp*TiF$_3$], 135 (100) [Cp*]; ^{1}H NMR ([D$_8$]toluene): δ = 1.98 (s, 60 H, Cp*), −0.71 (s, 6 H, ZnMe); ^{19}F NMR (C$_6$D$_6$): δ = 121.8 (s, 4F, Ti−F$_t$), 83.8 (s, 4F, Ti-F$_b$-Ti), −20 (s, 4F, Ti(μ-F)Zn), −40.0 (s, 2F, Ti(μ_3-F)Zn); elemental analysis for C$_{42}$H$_{66}$F$_{14}$Ti$_4$Zn$_2$: calcd C 43.5, H 5.7, F 23.0; found C 43.7, H 5.6, F 22.8.

Received: June 4, 1999 [Z 13516 IE]
German version: *Angew. Chem.* **1999**, *111*, 3518–3520

Keywords: fluorides · Lewis acids · titanium · zinc

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[9] Crystal structure analyses: a) **2**: C$_{80}$H$_{120}$F$_{30}$Ti$_8$Zn$_3$ · 2C$_7$H$_8$ · 0.5C$_6$H$_6$, M_r = 2230.95 + 2 × 92.14 + 0.5 × 78.11, crystal size: 0.50 × 0.30 × 0.30 mm^3, triclinic, space group $P\bar{1}$, a = 13.260(3), b = 14.217(3), c = 28.568(6) Å, α = 83.39(3), β = 83.31(3), γ = 86.06(3)°, V = 5305.1(2) Å^3, Z = 2, ρ_{calcd} = 1.537 Mg m^{-3}, $F(000)$ = 2514, λ = 0.71073 Å, T = 133 K, $\mu(\mathrm{Mo_{K\alpha}})$ = 1.327 mm^{-1}. The crystal was mounted on a glass fiber in a rapidly cooled perfluoropolyether.[12] 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 Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), performing φ- and ω scans. Total number of reflections measured 52 524, of which 14 965 unique (R_{int} = 0.0441). Data/restraints/parameters: 14 965/4589/1297, data collection range: 2.15 ≤ θ ≤ 23.26°. Final R indices: $R1 = \Sigma|F_o| - |F_o|/\Sigma|F_o| = 0.0379$, $wR2 = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w F_o^4]^{1/2} = 0.0814$ on data with $I > 2\sigma(I)$ and $R1 = 0.0528$, $wR2 = 0.0887$ on all data; goodness of fit $S = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2} = 1.069$; largest difference peak and hole: 0.610 and −0.396 e Å^{-3}. b) **3**: C$_{42}$H$_{66}$F$_{14}$Ti$_4$Zn$_2$ · C$_7$H$_8$, M_r = 1251.42, crystal size: 0.70 × 0.60 × 0.50 mm^3, monoclinic, space group $P2_1/n$, a = 9.7634(10), b = 20.654(3), c = 13.636(2) Å, β = 94.457(11)°, V = 2741.5(7) Å^3, Z = 2, ρ_{calcd} = 1.516 Mg m^{-3}, $F(000)$ = 1284, λ = 0.71073 Å, T = 153 K, $\mu(\mathrm{Mo_{K\alpha}})$ = 1.495 mm^{-1}. The diffraction data of **3** were collected on a Stoe-Siemens-AED2 four-circle-diffractometer at 153(2) K, using Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), performing $2\theta/\omega$ scans. Total number of reflections measured 9538, of which 4776 unique (R_{int} = 0.0316). Data/restraints/parameters: 4768/0/340, data collection range: 3.59 ≤ θ ≤ 24.93°. Final R indices: $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.0314$, $wR2 = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w F_o^4]^{1/2} = 0.0819$ on data with $I > 2\sigma(I)$ and $R1 = 0.0379$, $wR2 = 0.0905$ on all data; goodness of fit $S = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2} = 1.042$; largest difference peak and hole: 0.410 and −0.309 e Å^{-3}. c) The structures were solved by direct methods using the program SHELXS-97[13] and refined against F^2 on all data by full-

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, Cambrige CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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

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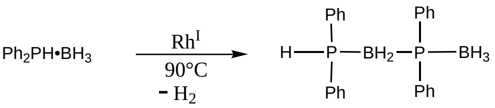
Virtually all currently known and commercially available polymers are based on extended catenated structures containing mainly carbon atoms together with a few other elements such as oxygen and nitrogen. In contrast, the development of extended structures based on atoms of other elements has been much less successful, and their synthesis still represents a substantial challenge.[1, 2] Nevertheless, the relatively few inorganic polymers such as poly(siloxanes) (silicones) $[R_2Si{-}O]_n$, polyphosphazenes $[R_2P{=}N]_n$, polysilanes $[R_2Si]_n$, and more recently poly(silynes), poly(stannanes), sulfur-containing polymers, poly(metallocenes), 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 compounds such as the six-membered ring $[Me_2P{-}BH_2]_3$ show considerable thermal and hydrolytic stability.[6]

Thermally induced dehydrocoupling of phosphane–borane adducts $R_2PH\cdot BH_3$ at elevated temperatures (150–200 °C) has been previously used to prepare cyclic phosphinoborane species (mainly six-membered rings of the type $[R_2P{-}BH_2]_3$).[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 $Ph_2PH\cdot BH_3$ undergoes dehydrocoupling at 180–190 °C to exclusively and quantitatively yield the cyclic trimer $[Ph_2P{-}BH_2]_3$.[11] However, on addition of about 0.3 mol% of a Rh^I catalyst such as $[Rh(1,5\text{-}cod)_2][OTf]$ or $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (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 ^{31}P NMR spectrum of the new compound showed the presence of two different phosphorus environments (δ = −3.3 and −17.7). Additional characterization by ^{11}B and ^{1}H 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.



$$Ph_2PH\cdot BH_3 \xrightarrow[-\,H_2]{Rh^I,\ 90^\circ C} H{-}P(Ph)_2{-}BH_2{-}P(Ph)_2{-}BH_3 \qquad (1)$$

1

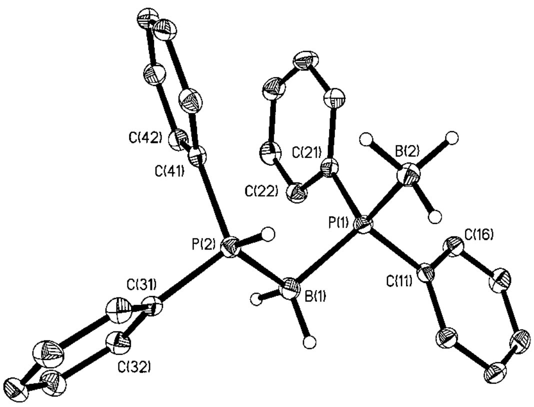


Figure 1. Molecular structure of **1** (thermal ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: P(1)–B(2) 1.932(2), P(1)–B(1) 1.944(2), P(2)–H(1P) 1.349(19), P(2)–B(1) 1.923(2); B(2)-P(1)-B(1) 113.01(11), H(1P)-P(2)-B(1) 112.6(8), P(2)-B(1)-P(1) 109.23(12).

Encouraged by this result and based on our view that the prospective polymer $[Ph_2P{-}BH_2]_n$ might be insoluble and that the anticipated steric congestion at phosphorus in the case

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[**] H.D. thanks the DFG for a Postdoctoral Fellowship. I.M. thanks the Natural Science and Engineering Research Council (NSERC) for an E. W. R. Steacie Fellowship (1997–99) and the University of Toronto for a McLean Fellowship (1997–2003).