Transition-Metal-Free Boron–Carbon Bond Activation: Insertion of an NNP Fragment into a Boron–Carbon Bond

Markus Kowalewski,^[a] Burkhard Krumm,^[a] Peter Mayer,^[a] Axel Schulz,*^[b,c] and Alexander Villinger^[b]

Dedicated to the memory of Nils Wiberg

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The influence and reactivity of fluorine-containing Lewis acids such as neat BF₃, BF₃·OEt₂, and B(C₆F₅)₃ on Me₃SiCl elimination in (Me₃Si)₂N–N(SiMe₃)–PCl₂ was investigated. The reaction with B(C₆F₅)₃ resulted in the formation of a novel diazadiphosphetidine with a phosphorus(III) atom attached to a pentafluorophenyl group, which can be regarded as a formal NNP fragment insertion into a B–C bond.

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Introduction

The GaCl₃-assisted elimination in silylated dichloro(hydrazino)phosphane,^[1–3] (Me₃Si)₂N–N(SiMe₃)–PCl₂, followed by a formal [3+2] cycloaddition^[4] represents an elegant approach to the formation of triazadiphospholes and tetrazaphospholes, which was introduced only recently (Scheme 1). As this reaction sequence only occurs when GaCl₃ is added into a solution of (Me₃Si)₂N–N(SiMe₃)– PCl₂ (1) in common organic solvents (e.g. CH₂Cl₂, benzene,



Scheme 1. Lewis acid assisted [3+2] cycloaddition with ambivalent dichloro(hydrazino)phosphane (1) to yield a triazadiphosphole $[ER_3 = GaCl_3, B(C_6F_5)_3].$

- [a] LMU München, Department Chemie und Biochemie Butenandt-Str. 5–13, 81377 München, Germany
- [b] Universität Rostock, Institut für Chemie Albert-Einstein-Str. 3a, 18059 Rostock, Germany Fax: +49-381-4986382 E-mail: axel.schul2@uni-rostock.de Universität Rostock.de
- Homepage: www.chemie.uni-rostock.de/ac/schulz[c] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany
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etc.), this new reaction type was named a GaCl₃-assisted [3+2] cycloaddition. The ambivalent (Me₃Si)₂N–N(SiMe₃)–PCl₂ displays both dipolarophile and/or 1,3-dipole characteristics. GaCl₃ is required to release the hidden dipolarophile and/or 1,3-dipole by decreasing the activation barrier to Me₃SiCl elimination. In this context, we studied the influence of fluorine-containing Lewis acids such as neat BF₃, BF₃·OEt₂, and B(C₆F₅)₃ on the Me₃SiCl elimination in



Scheme 2. Proposed mechanism of the $B(C_6F_5)_3$ -assisted 1,2-elimination of Me₃SiCl in 1 followed by an unusual insertion of a NNP fragment into a B–C bond, which finally results in the formation of **3**.



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 $(Me_3Si)_2N-N(SiMe_3)-PCl_2$. Herein, we detail the reactivity of these fluorine-containing Lewis acids towards $(Me_3Si)_2-N-N(SiMe_3)-PCl_2$, which proceeds in the case of $B(C_6F_5)_3$, by the first reported example of an unusual NNP fragment insertion into a boron–carbon bond (Scheme 2).

Results and Discussion

Absolutely no reaction was observed when a large excess of neat BF₃ (b.p. -100 °C, ca. 15 mL) was added to 1 at -110 °C. Also, after further stirring of this reaction mixture for 5 h at -100 °C no Me₃SiCl elimination could be observed; only the starting material was isolated after removal of BF₃. Obviously, thermal activation is needed to trigger Me₃SiCl elimination. Hence, 1 was treated with BF₃ in diethyl ether at ambient temperature. This reaction led to complete decomposition. Compounds [N₂H₃]⁺[BF₄]^{-,[5]} Me₃SiF, and PFCl₂ could be identified amongst the decomposition products.

These failures prompted us to utilize the sterically demanding fluorine-containing Lewis acid $B(C_6F_5)_3$. Again, no reaction was observed when 1 was added to a solution of $B(C_6F_5)_3$ in CH₂Cl₂ at ambient temperature. Only upon heating of this solution in a sealed tube up to 70 °C did slow Me₃SiCl elimination occur, which was completed after 3 d of stirring as shown by ³¹P NMR spectroscopic studies (1: ³¹P NMR: δ = 166.6 ppm disappeared).

Contrary to the reaction of **1** with GaCl₃, the reaction with B(C₆F₅)₃ yielded two products: (1) a highly soluble B(C₆F₅)₃ adduct of the expected trizadiphosphole (**2**) (NMR yield 24%, Scheme 1, multiplets in the ³¹P NMR spectrum at δ = 317.4 and 286.4 ppm; cf. GaCl₃ adduct: 317.2 and 292.1 ppm)^[1] and (2) a new species (NMR yield 42%, ³¹P NMR: δ = 253 ppm). Surprisingly, upon cooling of the above reaction mixture down to 5 °C, a large amount of beautiful orange crystals of the new species was obtained (isolated yield 29%). Single-crystal X-ray studies revealed a surprising 2,4-bis(pentafluorophenyl)-1,3-bis[*N*-trimethylsilyl-*N*-bis(pentafluorophenyl)boranyl]amino[1,3,2,4]diazadiphosphetidine (**3**) as the product (Scheme 2, Figure 1).

Pure dry 3 is stable at temperature up to 400 °C (m.p. 225 °C), is neither heat nor shock sensitive, and decomposes even only slowly in water and on air indicating a good kinetic protection by the bulky C_6F_5 groups. It should be mentioned that 3 is almost insoluble in any common solvent at ambient temperature.

X-ray elucidation of the orange crystals revealed a fourmembered P–N heterocatenated ring (3) with two P–C₆F₅ and two N–R [R = N(SiMe₃)(B(C₆F₅)₂)] centers, and its formation can be described as a dimerization of monomeric R–N–N=P–C₆F₅, which is formed by Me₃SiCl elimination (Figure 1 and Scheme 2) followed by an intriguing transfer of one pentafluorophenyl group (see below). Compound 3 crystallizes in cubes in the triclinic space group $P\bar{1}$ with one unit per cell. The asymmetric unit of 3 consists of only half of the molecule. The entire molecule can be generated by an inversion center sited on the centroid of the P₂N₂ four-



Figure 1. ORTEP drawing of the molecular structure of **3** (conformer **A**) in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: P2–N2 1.664(2), P2–N2' 1.793(2), P2–C13 1.913(3), P2–P2' 2.649(2), Si1–N1 1.818(2), N1–B1 1.400(3), N1–N2 1.442(3); N2–P2–N2' 80.0(1), N2–P2–C13 105.2(2), N2–P2–P2' 41.78(7), B1–N1–N2 117.4(2), B1–N1–Si1 125.4(2), N2–N1–Si1 115.4(1), N1–N2–P2 131.8(2), P2–N2–P2' 100.0(1), N1–B1–C7 122.2(2), C1–B1–C7 114.3(2).

membered ring. Moreover, this molecule is found to be disordered. Two different positions, which displays the existence of two conformers, are found for both P–C₆F₅ moieties with an occupation of 61.5 (A) and 38.5% (B). Both positions correspond to a rotation about the N–N axis with an angle of 109.2° between both rings. In both conformers the P₂N₂ ring is ideally planar [\angle P2–N2–P2'–N2' = 0.0° (A), \angle P1–N2–P1'–N2' = 0.0° (B)].

³¹P MAS NMR studies proved the existence of two conformers in the solid state (Figure S1),^[6] which is indicated by two resonances at $\delta = 264.0$ (isomer **A**, Figures 1 and 2) and 240.7 ppm (isomer **B**, Figure 2). Interestingly, we were able to assign these two resonances on the basis of the excellent agreement between theoretically and experimentally obtained values of the ³¹P NMR chemical shift tensor (see Supporting Information).^[6a]



Figure 2. Illustration of the disorder problem in 3. Conformer A corresponds to the N2–P2–N2'–P2' plane, B to the N2–P1–N2'–P1'. All H, C, and F atoms are omitted for clarity.

Conformer **A** is shown in Figure 1, and it displays a *trans* arrangement of the two C_6F_5 groups attached to the P atoms, which is also found in conformer **B**. As expected for tricoordinated phosphorus(III) species, two rather long and two short P–N distances are found [d(P2-N2) = 1.664(2) Å,

d(P2-N2') = 1.793(2) Å (A); d(P1-N2) = 1.631(2) Å, d(P1-N2') = 1.838(3) Å (B)]. Comparison with the sum of the covalent radii [$d_{cov}(N-P) = 1.8$ Å, $d_{cov}(N=P) = 1.6$ Å] indicates partial π bonding for the shorter P–N distance in both conformers [1.664(2) and 1.631(2) Å]. A large and a small angle are found for the P₂N₂ ring [∠ N2–P2–N2' = 80.0(1)°, ∠ P2–N2–P2' = 100.0(1)° (A); ∠ N2–P1–N2' = 79.5(1)°, ∠ P1–N2–P1' = 100.5(1)° (B)]. Selected structural data of both conformers are summarized in Tables S2 and S3.^[6b]

The complete mechanism for the formation of a triazadiphosphole (2) according to Scheme 1 is still unknown although 1,2-elimination of Me₃SiCl was experimentally proven as the initial step.^[3] When $B(C_6F_5)_3$ is used as the Lewis acid two things are worthy to be discussed: (1) a large thermal activation (3 d at 70 °C) is needed to trigger Me₃. SiCl elimination (cf. GaCl₃ reaction: 1 h at 20 °C) and (2) the formation of a different species, a diazadiphosphetidine (3), as the main product beside 2 is observed (Schemes 1 and 2).

Presumably, after the initial elimination of Me₃SiCl, free borane can attack the second chlorine atom attached to the phosphorus atom of the iminophosphane chloride, which leads to chlorine/ C_6F_5 exchange (Scheme 2). The intermediate ClB(C₆F₅)₂ reacts under Me₃SiCl elimination to give monomeric 3. Reactions of $ClB(C_6F_5)_2$ with Me₃Si-substituted amines are known,^[7] for example, ClB(C₆F₅)₂ treated with HN(SiMe₃)₂ yields HN(SiMe₃)[B(C₆F₅)₂] or HN[B- $(C_6F_5)_2]_2$ depending on the stoichiometry. Moreover, the ClB(C₆F₅)₃⁻ anion is well known.^[8] Finally, dimerization results in the formation of diazadiphosphetidine 3. For kinetic reasons, the formation of **3** is favored when $B(C_6F_5)_3$ is used, whereas only 2 is observed when GaCl₃ is used as the Lewis acid. The overall reaction of 1 with $B(C_6F_5)_3$ can be regarded as the insertion of Me₃Si–NNP (covalent azide analogue containing one phosphorus atom) into one B-C bond, followed by a final dimerization process or a formal [3+2] addition of the borane to Me₃SiNNP, which is generated in situ after elimination of two molecules Me₃SiCl. It should be emphasized that both reactions according to Schemes 1 and 2 can be reproduced.

Transfer reactions involving the C₆F₅ group are well known in transition-metal chemistry,^[9] and they are often responsible for catalyst poisoning.^[10] Such transition-metalinduced C₆F₅ transfer reactions often follow after the formation of intermediates, and they are stabilized by F…M agostic interactions with a cationic transition-metal center (M).^[11] The latter interaction often leads to C–F activation, which may even result in M-F bond formation by C-F bond cleavage. Metal-free C-F bond activation is also known, for example, when secondary phosphanes such as $(Me_3C_6H_2)_2PH$ are treated with $B(C_6F_5)_3$ to yield $(Me_3C_6H_2)_2PH(C_6F_4)BF(C_6F_5)_2$.^[12] Shifts of the C_6F_5 group are known to possess large activation barriers, for example, a large activation barrier for a 1,2-shift of a C_6F_5 group has already been observed by Metzler and Denk in a silylene-borane adduct, which slowly rearranges to a stable silylborane with a half-life of about one month.^[13]

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To estimate the thermodynamics of the formation of 2 and 3 and to obtain insight into the bond-formation process, computations were carried out at the B3LYP/6-31G(d,p) level of theory.^[6d,6e,14] The calculated energy for the formation of triazadiphosphole (2) is an exothermic and an exergonic process for all of the Lewis acids studied [Scheme 1; $\Delta_{298}G^0 = -317.3$, -331.2, -348.6, and $-304.2 \text{ kJ} \text{mol}^{-1}$ for BF₃, BCl₃, BBr₃, and B(C₆F₅)₃, respectively]. The latter value can be compared with the formation of 3 for which a smaller energy release was calculated $(\Delta_{298}G^0 = -258.0 \text{ kJmol}^{-1})$. The formation of the monomeric species [according to 1 + B(C₆F₅)₃ \rightarrow $\frac{1}{2}$ 3 + 2Me₃-SiCl] is associated with an energy gain of $-135.8 \text{ kJmol}^{-1}$, whereas dimerization is slightly endergonic with 13.6 kJ mol⁻¹. It is interesting to note that monomeric **3** is observed with a large intensity in the mass spectrum besides the dimer.

As expected, according to NBO analysis (natural bond orbital)^[6d,6e,15] the NP bonds within the P_2N_2 ring of **3** are purely σ in character and are strongly polarized (N: 77%, P: 23%) with a partial charge of +1.28*e* at the phosphorus atom and -0.95*e* at the nitrogen atom. We calculate a charge of -0.86*e* at the exocyclic nitrogen atom and a positive charge of +0.87*e* and +1.93*e* at the boron and silicon atoms, respectively.

Conclusion

The formation of 3 represents the first example of the insertion of a NNP fragment into a B–C bond. In this context, our results offer a new perspective on the insertion and activation of boron–carbon bonds. Moreover, 3 is the first example of a structurally characterized diazadiphosphetid-ine with phosphorus(III) attached to a perfluoro group.

Experimental Section

3: To a stirred solution of dichloro [N, N', N'-tris(trimethylsilyl)hydrazino]phosphane (1.75 g, 5 mmol) in dichloromethane (10 mL) was slowly added a solution of tris(pentafluorophenyl)borane (2.82 g, 5.5 mmol) in dichloromethane (10 mL) by syringe at ambient temperature. The yellowish solution was heated in a sealed tube under reflux for 3 d at 70 °C, which resulted in an orange suspension. After cooling to room temperature, the solution was concentrated to a total volume of 10 mL and stored at 0 °C overnight to afford an orange, microcrystalline powder. Dichloromethane (10 mL) was added, and the orange residue was filtered (F4) and washed several times by repeated back distillations of the solvent. The product was dried in vacuo to yield 0.94 g (29%) of 3 as an orange solid. M.p. 225 °C. FTIR (KBr): v = 2992 (vw), 2964 (vw), 2908 (vw), 1648 (m), 1519 (s), 1480 (s), 1397 (m), 1366 (m), 1312 (m), 1285 (m), 1259 (m), 1150 (m), 1089 (m), 1043 (w), 1017 (w), 976 (s), 928 (w), 854 (s), 778 (m), 722 (w), 669 (w), 629 (w), 503 (w) cm⁻¹. FTIR (ATR): $\tilde{v} = 2992$ (vw), 2966 (vw), 2912 (vw), 1647 (m), 1516 (s), 1466 (s), 1395 (m), 1365 (m), 1311 (m), 1284 (m), 1257 (m), 1204, w, 1147 (m), 1139 (m), 1084 (m), 1044 (w), 1016 (w), 970 (s), 928 (w), 910 (w), 838 (s), 776 (m), 761 (w), 748 (w), 721 (w), 670 (w), 658, w, 628 (w), 618 (w) cm⁻¹. Raman (200 mW, 25 °C): 2994 (2), 2967 (2), 2911 (6), 2546 (1), 1649 (10), 1520 (2),

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1401 (8), 1363 (7), 1309 (2), 1309 (2), 1288 (2), 1141 (2), 1118 (3), 1094 (2), 1021 (2), 982 (1), 848 (2), 819 (2), 785 (2), 771 (2), 658 (2), 621 (2), 596 (6), 527 (8), 501 (7), 446 (8), 397 (8), 363 (4) cm⁻¹. ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 25 °C): δ = 253 (br.) ppm. ³¹P MAS NMR (25 °C, ω_{rot} = 20 kHz): δ = 240.7 (s), 264.0 (s) ppm. MS (EI, 70 eV, >5%): *m*/*z* (%) = 168 (26.2) [C₆F₅], 277 (26.8), 345 (19.5) [B(C₆F₅)₂], 365 (28.0), 629 (58.4) [½ 3Me], 644 (100) [½ 3], 1288 (30.6) [**3**]. C₄₂H₁₈N₄B₂F₃₀P₂Si₂ (1288.3): calcd. C 39.16, H 1.41, N 4.35; found C 40.62, H 1.00, N 4.22.

Crystals suitable for single-crystal X-ray studies were obtained by cooling the reaction solution slowly to 5 °C. An X-ray quality crystal of 3 was selected in silicon oil at ambient temperature and was cooled to 200(2) K during measurement. The data for compound 3 was collected with a Nonius Kappa CCD diffractometer by using graphite-monochromated Mo-K_a radiation ($\lambda = 0.71073$). The structure was solved by direct methods and refined by full-matrix least-squares procedures (SHELXL-97).^[16] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement at calculated positions by using a riding model. The $P(C_6F_5)$ unit was split over two positions and the occupancy of each part (A and B) refined. For the carbon atoms of the split C₆F₅ rings, rigid group refinement was performed. A second Xray study from a different experiment gave the same result (see Supporting Information). CCDC-653980 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Full experimental details and characterization data, X-ray crystallographic refinement data, selected bond lengths and angles, and computational details of **3**.

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