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Reactions of Topologically Related "nacnacH-CN" and "P-nacnacH-CN" Chelate Ligand Systems with $HB(C_6F_5)_2$

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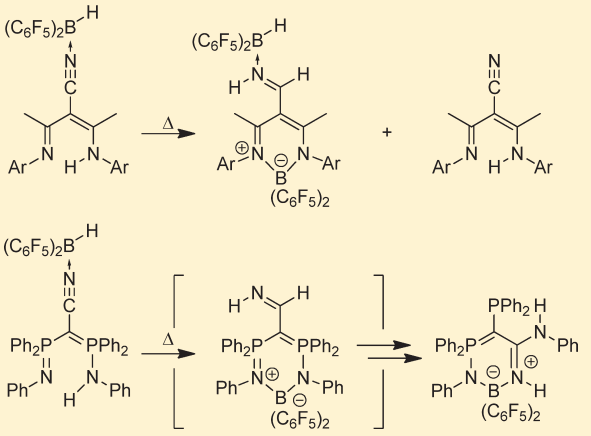
Supporting Information

ABSTRACT: The chelate bis-imine nacnacH-CN (**1**) and its bis-phosphinimine analogue P-nacnacH-CN (**2**) are shown to have similar reactivities with $HB(C_6F_5)_2$. In a 1:1 stoichiometry simple Lewis acid/Lewis base adducts are observed: $HB(C_6F_5)_2$ just adds to the nitrile functionality to yield compounds **3** and **6**, respectively. With two molar equivalents of $HB(C_6F_5)_2$, both systems **1** and **2** react at 70 °C with reduction of the nitrile group to an imine that is in both reactions found to be coordinated to a second equivalent of the $HB(C_6F_5)_2$ Lewis acid. The remaining $B(C_6F_5)_2$ unit becomes part of a six-membered heterocycle, where it is found to be coordinated to the pair of (C-NAr) (**4**) or (P-NPh) (**7**) units. Heating of the nacnacH-CN/$HB(C_6F_5)_2$ adduct **3** results in a disproportionation reaction yielding a mixture of the heterocycle (**4**) and the borane-free starting material **1**. In marked contrast, the thermolysis of the P-nacnacH-CN/$HB(C_6F_5)_2$ adduct (**6**) yields a new product (**8**), generated via an intramolecular $-Ph_2P{=}NPh$ vs $-CH{=}NH$ exchange at the boron center and a formal "Umpolung" of a hydridic to a protic hydrogen atom. The compounds **3**, **4**, **6**, **7**, and **8** were characterized spectroscopically and by X-ray diffraction.



INTRODUCTION

The 2,4-bis(*N*-arylimino)pentane system ("nacnacH") shows a very rich coordination chemistry in the monoanionic state.[1,2] The closely related 3-cyano substituted "nacnacH-CN" derivative **1** has recently been shown to form zirconium complexes [(nacnac-CN)$CpZrCl_2$] that effectively use the cyano group as an anchor to attach a Lewis acid upon Ziegler−Natta catalyst activation.[3,4]

Bis(diphenylphosphinimino)methane ("P-nacnacH") is topologically related to the nacnacH system. It forms closely related metal coordination complexes in the monoanionic state.[5,6] The high acidity of the central P=CH-P unit allows for a facile second deprotonation and consequently for the formation of very interestingly structured metallabicyclic frameworks.[7,8] The installation of a central cyano substituent eliminates the possibility for a secondary deprotonation pathway. Consequently, bis(diphenylphosphinimino)acetonitrile (**2**) ("P-nacnacH-CN")[8] is topologically closely related to nacnacH-CN (**1**). This behavior was illustrated in a series of reactions of **1** and **2** with the strong Lewis acid $HB(C_6F_5)_2$ ["Piers' borane"],[10] which will be described in this account. This study revealed a marked difference in the reactivity of a topological pair of $HB(C_6F_5)_2$ reaction products that eventually revealed a remarkable new reaction mode of the phosphorus-derived system.

RESULTS AND DISCUSSION

Reaction of [nacnacH-CN] (1) with $HB(C_6F_5)_2$. We decided to investigate the nacnacH-CN ligand system **1** as one basis for this study. Its unsymmetrical *N*-aryl substitution pattern represents a close to ideal set for combining sufficient reactivity with steric and electronic product stabilization. The ligand **1** was prepared as recently described by us,[3] namely, by selective condensation of acetyl acetone with 2,6-diisopropylaniline in a 1:1 stoichiometry followed by treatment with aniline. The 3-CN substituent was then subsequently introduced by treatment with *p*-toluolsulfonylcyanide.[11] Ligand system **1** was then reacted with Piers' borane $HB(C_6F_5)_2$. Stirring of the reaction mixture for one hour at room temperature in toluene eventually yielded the adduct **3** [i.e., **1**-$HB(C_6F_5)_2$] as a colorless crystalline solid in 85% isolated yield. Single crystals of **3** suitable for X-ray crystal structure analysis were obtained from toluene/pentane by the diffusion method.

The X-ray crystal structure analysis of compound **3** features a U-shaped nacnacH section of the framework. The internal bonding situation is found to be slightly unsymmetrical. The

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C1−N1 bond (1.315(3) Å) is markedly longer than the opposite C3−N2 linkage (1.282(3) Å), and consequently, the C1−C2 bond (1.415(3) Å) is shorter than the C2−C3 bond (1.458(3) Å). The internal angles and dihedral angles of this subunit are within the expected range for such species (e.g., N1−C1−C2 119.4(2)°, C1−C2−C3 125.2(2)°, N2−C3−C2 118.5(2)°, N1−C1−C2−C3 2.1(4)°). Carbon atom C2 is trigonal planar (sum of the bonding angles at C2 360.0°). The $HB(C_6F_5)_2$ Lewis acid is found to be coordinated to the nitrogen atom (N3) of the cyano substituent[12] that is attached at the central carbon atom (C2) of the nacnacH framework (see Figure 1). The boron atom shows a distorted tetrahedral coordination geometry with typical bond angles of 111.8(2)° (N3−B1−C41), 108.6(2)° (N3−B1−C51), and 111.3(2)° (C41−B1−C51). The C2, C5, N3, B1 unit is close to linear (angles C2−C5−N3 178.7(3)°, C5−N3−B1 175.7(2)°). The C5−N3 bond length (1.146(3) Å) is within the typical C≡N triple bond range. Interestingly, the parent system **1** is found to be nearly unperturbed upon adduct formation with $HB(C_6F_5)_2$ as observed in **3**.

The IR spectrum of the borane adduct **3** shows a sharp C≡N stretching band at $\tilde{\nu}$ = 2268 cm^{-1}, which is shifted by $\tilde{\nu}$ = 76 cm^{-1} to higher wave numbers as compared to its parent ligand system **1**. This is what would be expected from simple addition of a nitrile to a strong Lewis acid: sharing of the nitrogen lone pair with the boron atom effectively reduces the electronic repulsion between nitrogen and carbon to make the C≡N triple bond in **3** slightly stronger.[13]

In the ^{1}H NMR spectrum of **3** we see the N−H resonance at δ 15.03 (in [D_2]-dichloromethane), while a broad B−H signal is observed at δ 4.06. The ^{11}B NMR spectrum features a typical four-coordinate boron resonance (δ −18.0), which is supported by a characteristically small $\Delta\delta(p,m)$ C_6F_5 chemical shift difference[14] in the ^{19}F NMR spectrum [δ −134.8 (*o*), −159.9 (*p*), −165.3 (*m*)]. The system **3** exhibits a pair of characteristic ^{13}C NMR resonances for the C=N−Ar units (δ^{13}C: 170.0, 167.8) and the C2 resonance at δ 75.6.

The adduct **3** was generated *in situ* from **1** plus $HB(C_6F_5)_2$ in a 1:1 molar ratio in toluene and was then heated at 70 °C for three hours. This revealed the formation of a mixture of the new compound **4** with ca. one equivalent of the free starting material **1**.[15]

Treatment of **1** with two molar equivalents of $HB(C_6F_5)_2$ at 70 °C (12 hours) led to complete conversion to **4**, which was isolated from the reaction mixture in 76% yield. Single crystals of **4** were obtained at ambient temperature from toluene/pentane by the diffusion method.

The X-ray crystal structure analysis of compound **4** confirms that the nitrile functionality of the starting material was reduced to an imine under the forcing conditions. We find a −CH=NH functional group (C7−N8 attached to the ligand framework at carbon atom C4). One equivalent of the intact borane $HB(C_6F_5)_2$ first forms a Lewis acid/Lewis base adduct[16] with the nitrogen atom of this newly generated imine (N8−B9 1.568(4) Å, angles C7−N8−B9 125.3(2)°, C4−C7−N8 127.1(2)°, dihedral angle C4−C7−N8−B9 167.7(3)°). It is assumed that the reduction of the nitrile of the imine functionality is facilitated by the second equivalent of $HB(C_6F_5)_2$. Deprived of a hydride, the residual $B(C_6F_5)_2$ unit is trapped nearly symmetrically to both distal nitrogens of the nacnac chelate system (N2−B1 1.582(3) Å, N6−B1 1.593(3) Å, angle N2−B1−N6 101.3(2)°). The resulting six-membered heterocycle adopts a distorted boat-shaped conformation. The boron atom is arranged markedly outside the central N_2C_3 unit (θ C4−C5−N6−B1 19.0(3)°, C4−C3−N2−B1 −19.3(3)°). The central N_2C_3 unit is found

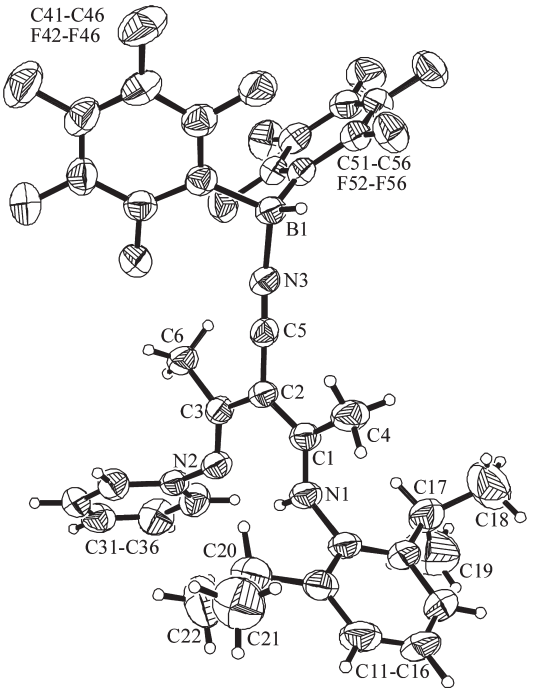
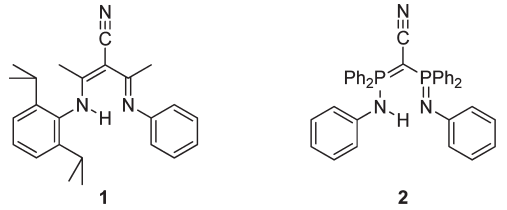
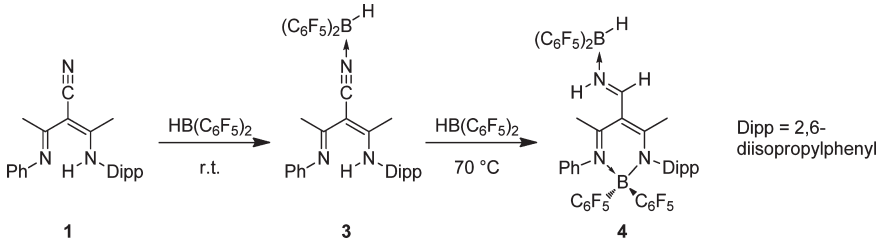


Figure 1. Molecular structure of $HB(C_6F_5)_2$ adduct **3**.

Scheme 1



Scheme 2



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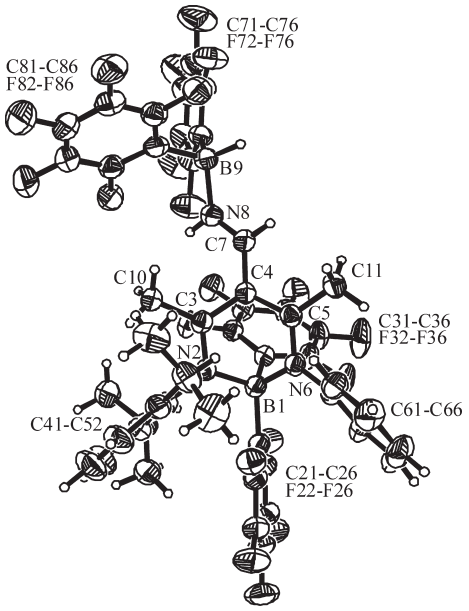
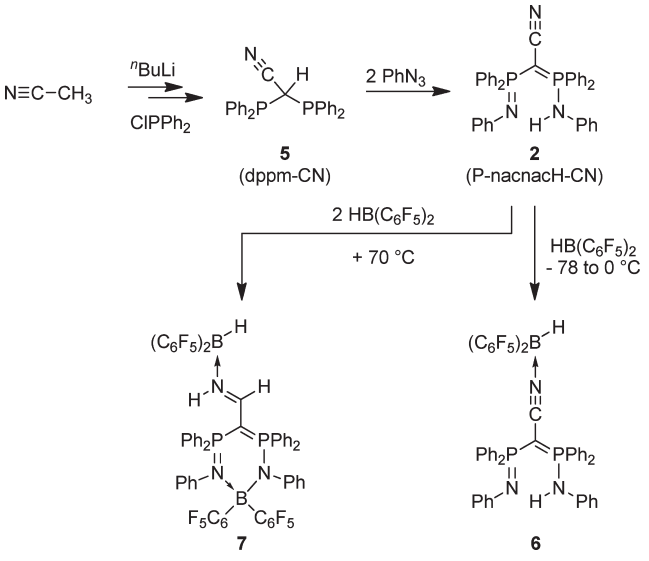


Figure 2. View of the molecular structure of the product **4** (toluene solvate was omitted for clarity).

Scheme 3



to be delocalized (N6−C5 1.334(3) Å, N2−C3 1.324(3) Å, C4−C5 1.430(3) Å, C4−C3 1.434(3) Å).

In the NMR spectrum of **4** the typical signals for the [B]−imine unit [^{1}H: δ 8.64 ═NH; δ 8.50 (N═CH−); ^{13}C: δ 164.2] and a broad [B]−H ^{1}H NMR resonance of this unit at δ 3.74 are observed. The central N_2C_3 moiety features a pair of C═N ^{13}C NMR signals at δ 170.7/167.7 and the central C4 resonance at δ 111.4. At 213 K two nonidentical pairs of C_6F_5 groups at boron were monitored in the ^{19}F NMR spectra. Under these conditions, some o/o' and m/m' pairs are differentiated due to hindered B−C_6F_5 rotation (for further information see the Experimental Section and the Supporting Information).

Reaction of the [P-nacnacH-CN] System 2 with HB(C_6F_5)$_2$. The cyano-substituted bis-phosphinimine system **2** was prepared as previously described by us starting from the cyano-substituted dppm system **5**,[17] which in turn was obtained in a convenient one-pot double phosphorylation of acetonitrile using *n*-butyllithium and $ClPPh_2$. Compound **2** ("P-nacnacH-CN") was then prepared by 2-fold Staudinger reaction of **5** with phenylazide (see Scheme 3).[18]

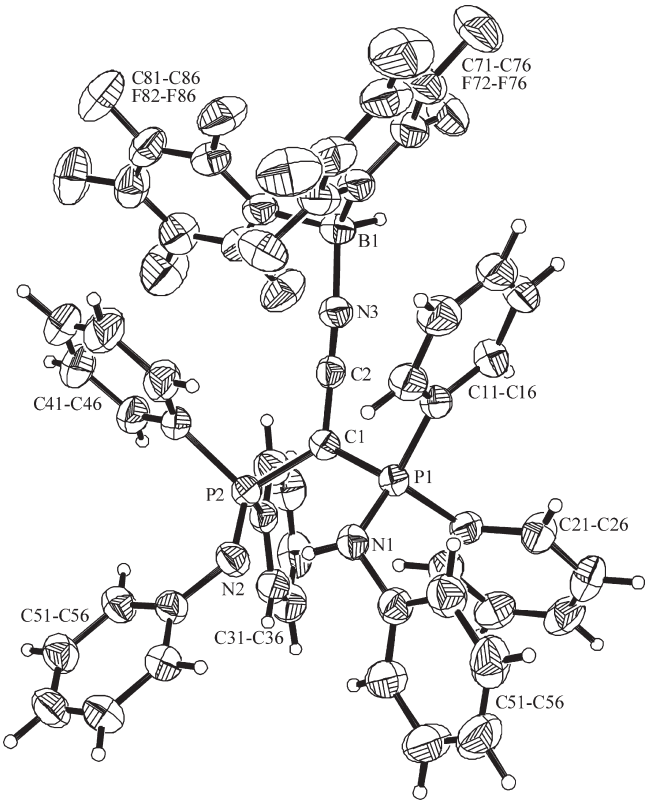


Figure 3. Molecular structure of the [(P-nacnacH-CN)HB(C_6F_5)$_2$] adduct **6**.

Compound **2** was reacted with one molar equivalent of HB(C_6F_5)$_2$ at −78 °C (two hours) and worked up at 0 °C, yielding the adduct **6** in 76% isolated yield. Single crystals of **6** suited for X-ray crystal structure analysis were obtained from a toluene/pentane solution at −35 °C via the gas diffusion method. This analysis shows that the Lewis acid HB(C_6F_5)$_2$ has just added to the external nitrile nitrogen atom. The boron atom has taken up a distorted tetrahedral coordination geometry in the adduct. It features bond angles of 107.1(2)° (N3−B1−C71), 106.4(2)° (N3−B1−C81), and 114.4(2)° (C71−B1−C81). The N3−B1 bond length is found to be at 1.568(3) Å. The C2−N3 triple bond is short (1.151(2) Å), and the C1−B1 moiety is linear (C1−C2 1.379(3) Å, angles C1−C2−N3 179.8(2)°, C2−N3−B1 172.3(2)°). The central carbon atom C1 of the framework is trigonal planar (sum of the bonding angles 359.9°). The central N_2P_2C unit is not delocalized. It exhibits a bond length alternation with a slightly longer N1−P1 (1.637(2) Å) and a shorter N2═P2 linkage (1.584(2) Å). Consequently, the P1−C1 bond (1.746(2) Å) is shorter than the adjacent P2−C1 linkage (1.779(2) Å)

As expected, the adduct **6** shows a ν(C≡N) stretching band ($\tilde{\nu}$ = 2235 cm^{-1}) that is shifted to higher wave numbers as compared to its free precursor **2** ($\tilde{\nu}$ = 2157 cm^{-1}). The adduct **6** features a ^{11}B NMR resonance at δ −18.5 and ^{19}F NMR signals at δ −134.0 (*o*), −160.2 (*p*), and −164.9 (*m*) for the C_6F_5 substituents

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on boron. It shows a triplet structure for the ^{13}C NMR P_2C signal at δ 21.4 ($^1J_{PC}$ = 134.1 Hz) and a single ^{31}P NMR resonance at δ 27.2. In the ^1H NMR spectrum of **6** there are two sets of phenyl groups, one for the N−Ph and one for the P−Ph in an integral ratio of 1:2. The broad B−H resonance is observed at δ 4.05.

The P-nacnacH-CN system **2** was then reacted with two molar equivalents of $HB(C_6F_5)_2$. Similar to the reaction between nacnacH-CN and Piers' borane, this reaction required heating to 70 °C to proceed. After heating the reaction mixture of **2** plus two equivalents of $HB(C_6F_5)_2$ for three hours at this temperature in toluene, **7** was isolated as a pale solid in 84% yield upon workup. Its structure is analogous to **4**, which was isolated from the reaction of **1** with two equivalents of $HB(C_6F_5)_2$ (see above). This was revealed from the typical spectroscopic data (see below), the CHN elemental analysis, and the result of the X-ray crystal structure analysis (single crystals were obtained from toluene).

The crystal structure analysis shows that the nitrile functionality of **7** was reduced by treatment with $HB(C_6F_5)_2$ under the applied reaction conditions. An imine bonded to the central carbon atom C1 of the N_2P_2C framework (C1−C2 1.407(4) Å, C2−N3 1.302(4) Å, angle C1−C2−N3 129.0(3)°) was observed. The newly formed imine functional group is coordinated to an intact $HB(C_6F_5)_2$ Lewis acid moiety (N3−B2 1.573(4) Å, angles N3−B2−C91 109.0(2)°, N3−B2−C101 107.1(2)°, C91−B2−C101 116.4(2)°). The remaining $B(C_6F_5)_2$ unit has lost its hydride (that was used in the reduction of the −CN function to give the imine) and is found to be symmetrically bonded by both N1 and N2 inside the delocalized BN_2P_2C six-membered-ring structure of **7** (B1−N1 1.584(4) Å, B1−N2 1.588(4) Å, P1−N1 1.628(2) Å, P2−N2 1.633(2) Å, P1−C1 1.749(3) Å, P2−C1 1.744(3) Å, angles N1−B1−N2 112.7(2)°, P1−C1−P2 124.4(2)°). The central six-membered heterocycle is slightly boat-shaped (dihedral angles C1−P2−N2−B1 4.3(3)° and P2−N2−B1−N1 −7.0(4)°).

Compound **7** features a pair of ^{11}B NMR signals at δ −0.3 and −14.7, respectively. An AX spin pattern is observed in the ^{31}P NMR spectrum, with resonances at δ 36.9 and 25.4 ($^2J_{PP}$ = 18.0 Hz). At 233 K pairs of *o*, *p*, and *m* ^{19}F NMR signals of the $[N]BH(C_6F_5)_2$ unit and a total of four *o*-C_6F_5 ^{19}F NMR resonances of the central endocyclic $B(C_6F_5)_2$ unit were monitored (for details see Experimental Section and the Supporting Information). The imine ^{13}C NMR resonance of compound **7** occurs at δ 165.0 (δ^1H = 7.33), and the corresponding [B]-NH═ ^1H NMR resonance is found at 6.00 (corresponding broad B−H signal at δ 2.94).

The Unusual Reactivity of Compound 6. The thermolysis of the P-nacnacH-CN/$HB(C_6F_5)_2$ adduct **6** was investigated, in the same way as we had done for the nacnacH-CN/$HB(C_6F_5)_2$ adduct **3** (see above). However, in contrast to the P-nacnacH-CN/$HB(C_6F_5)_2$ and nacnacH-CN/$HB(C_6F_5)_2$ results so far, here we encountered a remarkable difference.

The adduct **6** was heated for 26 h at 80 °C in toluene. Workup of the reaction mixture resulted in a mixture of the unusual product **8** and the starting material **2** in a ratio of 7:1 in a combined 64% yield. Compound **8** was unambiguously characterized from its spectroscopic data and the result of the X-ray crystal structure analysis (single crystals were obtained from the DMSO solution at room temperature).

The X-ray crystal structure analysis revealed that the nitrile functionality of the starting material **6** had been reduced to an imine functionality by $HB(C_6F_5)_2$. However, we have not isolated the single imine product due to extensive rearrangement that takes place during the thermolysis reaction (see Figure 5 and Scheme 4). This resulted in the formation of a six-membered heterocycle that contains a boron atom, two nitrogen atoms, and a phosphorus atom. In contrast to the previously observed

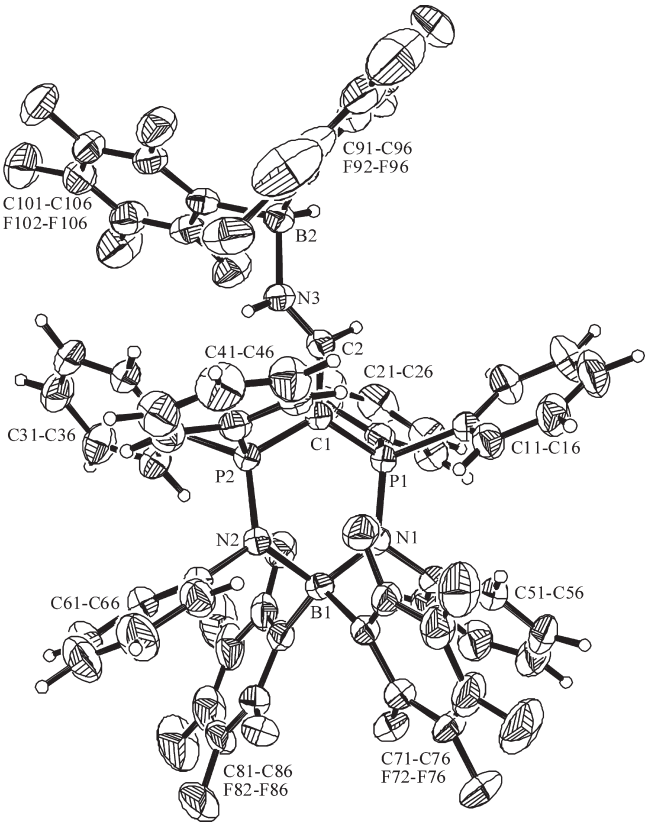


Figure 4. View of the molecular structure of compound **7**.

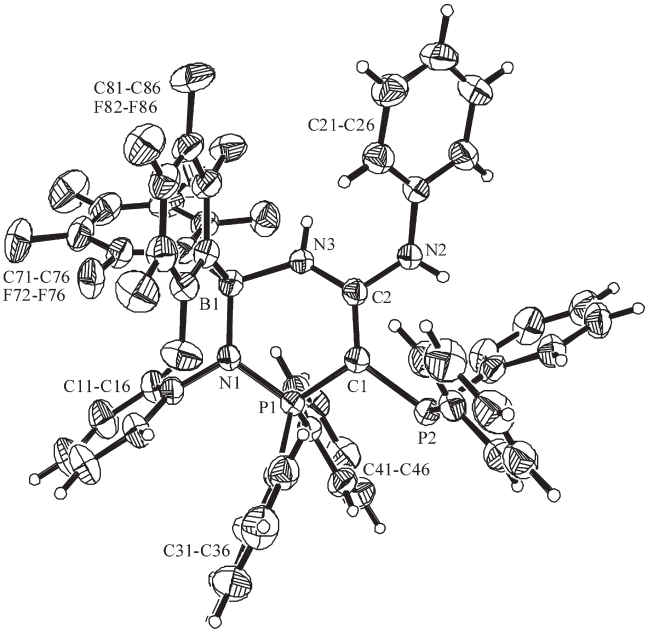
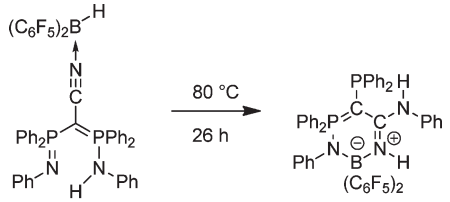


Figure 5. View of the molecular structure of the thermolysis product **8**.

Scheme 4



reaction products, in this series one of the phosphorus atoms is no longer found within the central heterocycle core, but it has been converted to a simple $-PPh_2$ substituent attached at a carbon atom of the central BN_2PC_2 core. The boron center is found to be four-coordinate. It is bonded to a pair of C_6F_5 groups and the nitrogen atoms N1 and N3 (B1−N1 1.570(3) Å, B1−N3 1.550(3) Å, angle N1−B1−N3 108.0(2)°), respectively. The ring parameters continue with the N1−P1 linkage (1.640(2) Å), the short ylidic P1−C1 bond (1.738(2) Å), and the C1−C2 bond (1.405(3) Å). The C2−N3 bond (1.342(2) Å) then closes the ring structure. Carbon atom C2 bears the newly formed N2(H)Ph substituent (C2−N2 1.367(2) Å). This unit should be regarded as a delocalized cationic amidinium substructure.

In solution compound **8** possesses a ^{13}C NMR signal for the "amidinium" carbon atom (C2)[19] at δ 163.0. The adjacent "ylidic" carbon atom C1[20] shows a ^{13}C NMR resonance at δ 42.8 with a pair of substantially different $^1J_{PC}$ coupling constants of 120.5 and 27.9 Hz.[21] Typical of a borate center, three distinct resonances of **8** were observed in the ^{19}F NMR spectrum [δ −132.5 (*o*), −160.0 (*p*), −165.3 (*m*)] with a relatively sharp ^{11}B NMR signal at δ −4.1 ($\nu_{1/2} \approx 50$ Hz). There is a ^{31}P NMR AX spin pattern observed for the pair of phosphorus atoms in **8** (δ 37.6, δ −30.3, $^2J_{PP}$ = 170.1 Hz). The ^1H NMR spectrum reveals a set of broad N−H resonances at δ 6.40 ([B]N−H) and δ 5.87 ([C]N−H), respectively.

The presence of two NH units in compound **8** might give us a clue to formulate how this unusual product might actually have been formed starting from **6**. Comparison of **6** and **8** reveals that in principle the NH functionality has been carried through from **6** all the way to **8**. The truly unusual feature of the **6** → **8** reaction is that the hydridic [B]−H hydrogen in **6** eventually must have been converted to a protic [N]−H hydrogen in **8**.[22] The detailed mechanism of this unexpected reaction is not clear at present. For a possible reaction pathway see the Supporting Information.

CONCLUSIONS

Our study reveals a number of quite remarkable similarities between the conventional nacnacH-CN system **1** and its phosphorus analogue P-nacnacH-CN **2**. Both have similar structures and form analogously composed and structured adducts with the strong Lewis acid $HB(C_6F_5)_2$. In both these systems the $HB(C_6F_5)_2$ Lewis acid binds to the −C≡N functional group through the terminal nitrogen atom in a linear fashion, and the adduct is "protected" from direct reduction by a substantial activation barrier. Nevertheless, the CN groups of both the systems are eventually reduced to the imine stage. Upon treatment with two molar equivalents of $HB(C_6F_5)_2$, the respective heterocycles **4** and **7** are formed, respectively. In each instance, one $HB(C_6F_5)_2$ unit is used as a reduction equivalent, while the second unit simply binds as a Lewis acid to the newly formed imino group. The generation of these conceptually closely related products and the general structural appearance in both series are certainly noteworthy.

The similarity between the nacnacH-CN and P-nacnacH-CN systems abruptly ends in the behavior of the mono-$HB(C_6F_5)_2$ adducts (**3** and **6**, respectively) upon thermolysis. The nacnacH-CN/$HB(C_6F_5)_2$ system typically undergoes ligand disproportionation to enter the typical nacnacH-CN plus two equivalents of $HB(C_6F_5)_2$ chemistry to eventually yield ca. equal amounts of the two-boron-containing heterocycle **4** and the boron-free starting material **1**.

The thermally initiated reaction of the P-nacnacH-CN/$HB(C_6F_5)_2$ adduct **6** is markedly different. It probably commences with −C≡N to −CH═NH reduction, but here the small and reactive imino group takes up an active part in the subsequent rearrangement course (see the Supporting Information). It is an unexpected interesting consequence of this ready rearrangement that it generates a situation that ultimately results in a possibility to achieve a novel "Umpolungsreaction" of the former B−H hydrogen to a protic hydrogen situation potentially via an incipient nitrenium-like reactive intermediate.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an inert gas atmosphere (argon) in Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The following instruments were used for the physical characterization of the compounds. NMR: Varian Inova 500 (^1H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{31}P: 202 MHz, ^{11}B: 160 MHz), Bruker Unity Plus 600 (^1H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{31}P: 243 MHz, ^{11}B: 192 MHz). Most NMR assignments were supported by additional 2D experiments. Melting points: Ta-Instruments differential scanning calorimeter Q20 (heating rate: 10 °C/min). IR: Varian 3100 FT-IR spectrometer (KBr pellet or ATR). Elemental analyses: Elementar Vario El III. X-ray structure analysis: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B. V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122), graphics XP (BrukerAXS, 2000). Graphics show the thermal ellipsoids with 50% probability, *R* values are given for the observed reflections, wR_2 values for all reflections.

Synthesis of 3. Bis(pentafluorophenyl)borane, [$HB(C_6F_5)_2$] (45 mg, 0.130 mmol, 1.04 equiv), in toluene (1 mL) was added to a solution of **1**[3] (45 mg, 0.125 mmol) in toluene (3 mL). The reaction mixture was stirred for one hour, and the volatiles were removed under vacuum, redissolved in pentane, and filtered over Celite. Concentration of the solution by slow evaporation of pentane gave **3** as a colorless crystalline material in 85% yield (75 mg, 0.106 mmol). Single crystals of **3** suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane to toluene at room temperature. Mp (DSC): 127 °C. IR (KBr): $\tilde{\nu}$/cm^{-1} 2430 (ν(BH), s), 2268 (ν(C≡N), s). Anal. Calcd for $C_{36}H_{30}BF_{10}N_3$: C, 61.29; H, 4.29; N, 5.96. Found: C, 61.44; H, 4.48; N, 6.32. ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ 15.03 (s, 1H, NH), 7.37 (m, 2H, *m*-Ph), 7.28 (m, 1H, *p*-Ar), 7.21 (m, 2H, *m*-Ar), 7.20 (m, 1H, *p*-Ph), 6.91 (m, 2H, *o*-Ph), 4.06 (br, 1H, BH), 2.83 (hept, 2H, J = 6.9 Hz, HC^{iPr}), 2.22 (s, 3H, Me^{Ph}), 2.04 (s, 3H, Me^{Ar}), 1.24 (d, 6H, J = 6.9 Hz, Me^{iPr}), 1.11 (d, 6H, J = 6.9 Hz, Me^{iPr}). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): δ 170.0 ($C{=}N^{Ar}$), 167.8 ($C{=}N^{Ph}$), 144.3 (*i*-Ph), 142.7 (*o*-Ar), 136.0 (*i*-Ar), 129.7 (*m*-Ph), 128.2 (*p*-Ar), 126.0 (*p*-Ph), 124.2 (*m*-Ar), 122.9 (*o*-Ph), n.

o. (C≡N), 75.6 (C^{CN}), 29.1 (HC^{iPr}), 24.4 ($Me^{iPr'}$), 22.5 (Me^{iPr}), 19.4 (Me^{Ph}), 19.1 (Me^{Ar}), [C_5F_6 are not listed]. ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ −134.8 (m, 2F, *o*-C_6F_5), −159.9 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), −165.3 (m, 2F, *m*-C_6F_5) [$\Delta\delta(p,m)$ = 5.4]. ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ −18.0 (br $\nu_{1/2} \approx$ 450 Hz)

X-ray crystal structure analysis of **3**: formula $C_{36}H_{30}BF_{10}N_3$, M = 705.44, colorless crystal 0.25 × 0.20 × 0.05 mm, a = 9.1730(5) Å, b = 13.9793(6) Å, c = 14.9065(7) Å, α = 66.006(2)°, β = 85.949(2)°, γ = 87.231(2)°, V = 1741.55(15) Å^3, ρ_{calc} = 1.345 g cm^{-3}, μ = 1.010 mm^{-1}, empirical absorption correction (0.786 ≤ T ≤ 0.951), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 19 628 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 6016 independent (R_{int} = 0.056) and 4539 observed reflections [$I \geq 2\,\sigma(I)$], 460 refined parameters, R = 0.053, wR_2 = 0.144, max. (min.) residual electron density 0.22 (−0.24) e Å^{-3}, hydrogen atom at N1 from difference Fourier calculations, the others calculated and refined as riding atoms.

Synthesis of 4. Bis(pentafluorophenyl)borane (60 mg, 0.17 mmol, 1.0 equiv) in toluene (1 mL) was added to a solution of **1** (61 mg, 0.170 mmol) in toluene (3 mL). The reaction mixture was stirred for one hour, then warmed to 70 °C and kept at this temperature for three hours. [After this time, ^{1}H NMR spectroscopy shows the formation of compound **4** plus free ligand **1**.] Then one additional equivalent of $HB(C_6F_5)_2$ (60 mg, 0.170 mmol) in toluene (1 mL) was added to the reaction mixture and kept at 70 °C for another 12 hours. Volatiles were removed under vacuum, redissolved in pentane, and filtered over Celite. Concentration of the solution by slow evaporation of pentane gave **4** as a crystalline, colorless material in 76% yield (145 mg, 0.127 mmol). Single crystals of **4** suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane to toluene at room temperature. Mp (DSC): 155 °C. IR (KBr): $\tilde{\nu}$/cm^{-1} 3385 (ν(NH), s), 2406 (ν(BH), s), 2369. Anal. Calcd for $C_{48}H_{31}B_2F_{20}N_3 \cdot C_7H_8$: C, 57.77, H, 3.44; N, 3.67. Found: C, 57.33; H, 3.32; N, 4.02. ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): δ 8.64 (dd, 1H, J = 19.1, 6.1 Hz, NH), 8.50 (d, 1H, J = 19.1 Hz, N=CH), 7.33[a], 7.29[b], 7.15[c], 7.12[d], 6.75[e] (each m, each 1H, Ph), 7.21 (m, 1H, *p*-Ar), 7.09 (m, 1H, *m*-Ar), 6.92 (m, 1H, *m*′-Ar), 3.74 (br, 1H, BH), 2.59 (m, 1H, $HC^{iPr(o')}$), 2.57 (s, 3H, Me^{Ar}), 2.47 (s, 3H, Me^{Ph}), 2.14 (quint, 1H, J = 6.5 Hz, $HC^{iPr(o)}$), 1.12 (d, 3H, J = 6.5 Hz, $Me^{iPr(o)}$), 1.06 (d, 3H, J = 6.5 Hz, $Me^{iPr(o')}$), 1.04 (d, 3H, J = 6.5 Hz, $Me^{iPr(o)'}$), 0.58 (d, 3H, J = 6.5 Hz, $Me^{iPr(o')'}$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 213 K): δ 170.7 ($C{=}N^{Ar}$), 167.7 ($C{=}N^{Ph}$), 164.2 (N=CH), 145.4 (*o*′-Ar), 144.6 (*o*-Ar), 141.5 (*i*-Ph), 136.8 (*i*-Ar), 129.3[e], 128.45[d], 128.38[a], 128.1[b], 124.8[c] (Ph), (*p*-Ph), 128.9 (*p*-Ar), 125.1 (*m*-Ar), 124.0 (*m*′-Ar), 111.4 ($C^{C\equiv N}$), 29.4 ($HC^{iPr(o')}$), 28.2 ($HC^{iPr(o)}$), 26.9 (m, $Me^{iPr(o')}$), 24.7 ($Me^{iPr(o)}$), 24.3 (d, J = 11.7 Hz, $Me^{iPr(o)'}$), 22.0 (m, Me^{Ar}), 21.1 ($Me^{iPr(o')'}$), 20.5 (Me^{Ph}) [C_5F_6 not listed]. ^{19}F NMR (470 MHz, CD_2Cl_2, 213 K): δ −120.3 (*o*′), −130.6 (*o*), −154.3 (*p*), −164.5 (*m*), −166.4 (*m*′) (each m, each 1H, $C_6F_5{}^A$) [$\Delta\delta(p,m)$ = 10.2, 12.1], −133.3 (*o*), −137.2 (*o*′), −158.2 (*p*), −164.5 (*m*), −166.3 (*m*′) (each m, each 1H, $C_6F_5{}^B$) [$\Delta\delta(p,m)$ = 6.3, 8.1], −137.2 (2F, *o*), −160.8 (1F, *p*), −165.7 (2F, *m*) (each m, $C_6F_5{}^C$) [$\Delta\delta(p,m)$ = 4.9], −136.8 (2F, *o*), −160.8 (1F, *p*), −165.4 (2F, *m*) (each m, $C_6F_5{}^D$) [$\Delta\delta(p,m)$ = 4.6].

X-ray crystal structure analysis of **4**: formula $C_{48}H_{31}B_2F_{20}N_3 \cdot C_7H_8$, M = 1143.51, colorless crystal 0.10 × 0.07 × 0.05 mm, a = 16.0952(4) Å, b = 10.0282(3) Å, c = 31.9122(9) Å, β = 90.840(1)°, V = 5150.3(2) Å^3, ρ_{calc} = 1.475 g cm^{-3}, μ = 1.206 mm^{-1}, empirical absorption correction (0.889 ≤ T ≤ 0.942), Z = 4, monoclinic, space group $P2/c$ (No. 13), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 71 703 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 8989 independent (R_{int} = 0.084) and 6613 observed reflections [$I \geq 2\sigma(I)$], 734 refined parameters, R = 0.051, wR_2 = 0.140, max. (min.) residual electron density 0.43 (−0.31) e Å^{-3}, hydrogen atoms at N8 and B9 from difference Fourier calculations, the others calculated and refined as riding atoms.

Synthesis of 6. The bis(phosphinimine) **2**[9] (200 mg, 0.338 mmol, 1.0 equiv) was dissolved in dichloromethane (3 mL) and cooled to −78 °C. To this solution was added $HB(C_6F_5)_2$ (117 mg, 0.338 mmol, 1.0 equiv) in dichloromethane (3 mL), and the reaction mixture was stirred for two hours at −78 °C. After removing the solvent *in vacuo* at 0 °C, **6** was yielded as a pale powder (240 mg, 0.256 mmol, 76%). Single crystals of **6** suitable for X-ray crystal structure analysis were obtained through vapor diffusion of pentane into a solution of **6** in toluene at −35 °C. Dec: 149 °C, mp 177 °C. IR (KBr): $\tilde{\nu}$/cm^{-1} 2419 (ν(BH), w), 2235 (ν(C≡N), s). Anal. Calcd for $C_{50}H_{32}BF_{10}N_3P_2$: C, 64.05; H, 3.44; N, 4.48. Found: C, 63.78; H, 3.20; N, 4.44. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 11.15 (br, 1H, NH)[t], 7.60 (m, 8H, *o*-Ph^P), 6.96 (m, 4H, *p*-Ph^P), 6.91 (m, 4H, *m*-Ph^N), 6.88 (m, 8H, *m*-Ph^P), 6.78 (m, 4H, *o*-Ph^N), 6.69 (m, 2H, *p*-Ph^N), 4.05 (br, 1H, B-*H*), [t tentative assignment]. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ 148.1 (dm, $^1J_{FC} \approx$ 235 Hz, *o*-C_6F_5), 145.1 (*i*-Ph^N), 139.6 (dm, $^1J_{FC} \approx$ 247 Hz, *p*-C_6F_5), 137.2 (dm, $^1J_{FC} \approx$ 251 Hz, *m*-C_6F_5), 133.1 (*p*-Ph^P), 132.6 (m, *o*-Ph^P), 129.7 (*m*-Ph^N), 129.1 (m, *m*-Ph^P), 127.4 (AXX′, $^1J_{PC} + {}^3J_{P'C}$ = 99.5 Hz, *i*-Ph^P), 122.3 (t, $^2J_{PC}$ = 10.4 Hz, C≡N)[t], 121.2 (*p*-Ph^N), 121.1 (m, *o*-Ph^N), 118.8 (br, *i*-C_6F_5), 21.4 (t, $^1J_{PC}$ = 134.1 Hz, $[P]_2C$), [t tentative assignment]. ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −134.0 (m, 2F, *o*-C_6F_5), −160.2 (m, 1F, *p*-C_6F_5), −164.9 (m, 2F, *m*-C_6F_5) [$\Delta\delta(p,m)$ = 4.7]. ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K): δ 27.2 ($\nu_{1/2} \approx$ 3 Hz). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ −18.5 ($\nu_{1/2} \approx$ 350 Hz).

X-ray crystal structure analysis of **6**: formula $C_{50}H_{32}BF_{10}N_3P_2$, M = 937.54, colorless crystal 0.40 × 0.30 × 0.30 mm, a = 12.8718(4) Å, b = 13.1734(4) Å, c = 16.1600(6) Å, α = 94.010(1)°, β = 109.163(2)°, γ = 119.124(3)°, V = 2171.72(15) Å^3, ρ_{calc} = 1.434 g cm^{-3}, μ = 1.641 mm^{-1}, empirical absorption correction (0.560 ≤ T ≤ 0.639), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 27 024 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 7617 independent (R_{int} = 0.040) and 7028 observed reflections [$I \geq 2\sigma(I)$], 601 refined parameters, R = 0.043, wR_2 = 0.115, max. (min.) residual electron density 0.41 (−0.28) e Å^{-3}, hydrogen atoms at N1 and B1 from difference Fourier calculations, the others calculated and refined as riding atoms.

Synthesis of 7. The bis(phosphinimine) **2** (250 mg, 0.423 mmol) and $HB(C_6F_5)_2$ (292 mg, 0.854 mmol, 2.02 equiv) were dissolved in toluene (6 mL) and stirred for three hours at 70 °C. After removing the solvent under reduced pressure, the residue was washed with pentane (25 mL) and dried *in vacuo* to yield **7** as a pale powder (458 mg, 0.357 mmol, 84%). Single crystals of **7** suitable for X-ray crystal structure analysis were obtained from a toluene solution of **7** at room temperature. Mp (DSC): 200 °C. IR (KBr): $\tilde{\nu}$/cm^{-1} 4062, 3373 (ν(N−H), s), 2397 (ν(BH), w). Anal. Calcd for $C_{62}H_{33}B_2F_{20}N_3P_2$: C, 58.02; H, 2.59; N, 3.27. Found: C, 58.12; H, 2.35; N, 3.49. ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ 7.90 (m, 2H, *o*-$Ph'^{P(A)}$), 7.81 (m, 2H, *o*-$Ph'^{P(B)}$), 7.80 (m, 1H, *p*-$Ph^{P(B)}$), 7.79 (m, 1H, *p*-$Ph^{P(A)}$), 7.65 (m, 1H, *p*-$Ph'^{P(B)}$), 7.57 (m, 2H, *m*-$Ph^{P(B)}$), 7.55 (m, 2H, *m*-$Ph'^{P(B)}$), 7.50 (m, 1H, *p*-$Ph'^{P(A)}$), 7.44 (m, 2H, *m*-$Ph'^{P(A)}$), 7.43 (m, 2H, *m*-$Ph^{P(A)}$), 7.33 (ddd, $^3J_{PH}$ = 31.6 Hz, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 18.0 Hz, 1H, =CH), 7.30 (m, 2H, *o*-$Ph^{P(B)}$), 7.11 (m, 2H, *o*-$Ph^{P(A)}$), 7.06 (m, 2H, *p*-$Ph^{N(B)}$, *p*-$Ph^{N(A)}$), 7.04 (m, 1H, *m*′-$Ph^{N(A)}$), 6.98 (m, 1H, *m*′-$Ph^{N(B)}$), 6.91 (m, 1H, *o*′-$Ph^{N(A)}$), 6.77 (m, 1H, *o*′-$Ph^{N(B)}$), 6.72 (m, 1H, *m*-$Ph^{N(B)}$), 6.64 (m, 1H, *m*-$Ph^{N(A)}$), 6.00 (dd, $^3J_{HH}$ = 18.0 Hz, $^3J_{HH(B)}$ = 6.1 Hz, 1H, NH), 5.82 (m, 1H, *o*-$Ph^{N(B)}$), 5.55 (m, 1H, *o*-$Ph^{N(A)}$), 2.94 (br, 1H, BH). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 233 K): δ 165.0 (d, $^2J_{PC}$ = 14.4 Hz, =CH), 138.3 (*i*-$Ph^{N(B)}$), 137.5 (*i*-$Ph^{N(A)}$), 134.7 (d, $^2J_{PC}$ = 8.8 Hz, *o*-$Ph^{P(B)}$), 134.2 (d, $^2J_{PC}$ = 10.1 Hz, *o*-$Ph^{P(A)}$), 134.0 (d, $^4J_{PC}$ = 1.5 Hz, *p*-$Ph^{P(A)}$), 133.9 (d, $^4J_{PC}$ = 2.3 Hz, *o*-$Ph^{N(A)}$), 133.73 (d, $^4J_{PC}$ = 1.7 Hz, *p*-$Ph^{P(B)}$), 133.66 (m, *o*′-$Ph^{N(A)}$), 133.66 (m, *o*′-$Ph^{N(B)}$), 133.39 (m, *p*-$Ph'^{P(A)}$), 133.37 (m, *o*-$Ph^{N(B)}$), 133.23 (dd, $^2J_{PC}$ = 11.2 Hz, $^4J_{PC}$ = 3.6 Hz, *o*-$Ph'^{P(A)}$), 133.16 (m, *p*-$Ph'^{P(B)}$), 133.0 (dd, $^2J_{PC}$ = 11.2 Hz, $^4J_{PC}$ = 3.5 Hz, *o*-$Ph'^{P(B)}$), 130.7 (d, $^1J_{PC}$ = 106.6 Hz, *i*-$Ph'^{P(B)}$), 129.3 (d, $^3J_{PC}$ = 12.3 Hz, *m*-$Ph'^{P(B)}$), 129.2 (d, $^3J_{PC}$ = 11.8 Hz, *m*-$Ph'^{P(A)}$), 128.7 (*m*′-$Ph^{N(B)}$), 128.6 (*m*′-$Ph^{N(A)}$), 128.5 (d, $^3J_{PC}$ = 12.4 Hz, *m*-$Ph^{P(A)}$), 128.3 (d, $^3J_{PC}$ =

12.3 Hz, *m*-Ph$^{P(B)}$), 127.9 (*m*-Ph$^{N(B)}$), 127.7 (*m*-Ph$^{N(A)}$), 127.45, 127.41 (*p*-Ph$^{N(B)}$, *p*-Ph$^{N(A)}$), 127.36 (d, $^1J_{PC}$ = 104.8 Hz, *i*-Ph$^{\prime P(A)}$), 123.5 (d, $^1J_{PC}$ = 101.2 Hz, *i*-Ph$^{P(B)}$), 119.9 (d, $^1J_{PC}$ = 100.3 Hz, *i*-Ph$^{P(A)}$), 44.4 (dd, $^1J_{PC}$ = 119.2, 113.2 Hz, [P]$_2$C), [C_5F_6 not listed]. ^{19}F NMR (470 MHz, CD_2Cl_2, 233 K): δ −129.9 (*o*′), −131.6 (*o*), −158.3 (*p*), −164.7 (*m*), −165.5 (*m*′) (each m, each 1F, $C_6F_5^A$) [$\Delta\delta(p,m)$ = 6.4, 7.2], −130.0 (*o*), −131.3 (*o*′), −158.4 (*p*), −165.7 (*m*), −164.7 (*m*′) (each m, each 1F, $C_6F_5^B$) [$\Delta\delta(p,m)$ = 7.3, 6.3], −135.2 (2F, *o*), −160.8 (1F, *p*), −165.3 (2F, *m*) (each m, $C_6F_5^C$) [$\Delta\delta(p,m)$ = 4.5], −136.0 (2F, *o*), −161.1 (1F, *p*), −165.5 (2F, *m*) (each m, $C_6F_5^D$) [$\Delta\delta(p,m)$ = 4.4]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 233 K): δ 36.9 (d, $^2J_{PP}$ = 18.0 Hz, 1P, $\nu_{1/2}$ = 11.6 Hz), 25.4 (d, $^2J_{PP}$ = 18.0 Hz, 1P, $\nu_{1/2}$ = 13.1 Hz). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 233 K): δ −0.3 (N_2B, $\nu_{1/2}$ = 400 Hz), −14.7 (BH, $\nu_{1/2}$ = 500 Hz).

X-ray crystal structure analysis of **7**: formula $C_{62}H_{33}B_2F_{20}N_3P_2 \cdot C_7H_8$, M = 1375.61, colorless crystal 0.30 × 0.20 × 0.15 mm, a = 14.8112(4) Å, b = 22.0942(6) Å, c = 19.1294(5) Å, β = 105.550(2)°, V = 6030.8(3) Å^3, ρ_{calc} = 1.515 g cm^{-3}, μ = 1.628 mm^{-1}, empirical absorption correction (0.641 ≤ T ≤ 0.792), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 50 565 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 10 698 independent (R_{int} = 0.062) and 8675 observed reflections [$I \geq 2\sigma(I)$], 854 refined parameters, R = 0.059, wR_2 = 0.165, max. (min.) residual electron density 0.88 (−0.46) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of 8. The bis(phosphinimine) **2** (100 mg, 0.180 mmol, 1.0 equiv) was dissolved in dichloromethane (3 mL) and cooled to −78 °C. To this solution was added $HB(C_6F_5)_2$ (62.2 mg, 0.180 mmol, 1.0 equiv) in dichloromethane (3 mL), and the reaction mixture was stirred for two hours at −78 °C. After removing the solvent *in vacuo* at 0 °C, the reaction mixture was dissolved in toluene (5 mL) and heated for 26 h at 80 °C. Filtration over a Whatman filter and removal of the solvent under reduced pressure produced a residue, which was washed with pentane (30 mL) and dried *in vacuo* to yield a product mixture of **8** and **2** in a ratio of 7:1 [determined from the ^{31}P NMR spectrum] as a pale solid (118 mg, 0.116 mmol, 64%). Single crystals of **8** suitable for X-ray crystal structure analysis were obtained from a dimethylsulfoxide solution of **8** at room temperature. Mp (DSC): 166 °C. IR (KBr): $\tilde{\nu}$/cm^{-1} 3404, 3362 (ν(N−H), s), 2158 (ν(C≡N), s of **2**). Anal. Calcd for $C_{388}H_{255}B_7F_{70}N_{24}P_{16}$: C, 65.14; H, 3.59; N, 4.70. Found: C, 65.23; H, 2.82; N, 4.49 [for a mixture of **8** and **2** = 7 ($C_{50}H_{32}BF_{10}N_3P_2$):1 ($C_{38}H_{31}N_3P_2$)]. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 7.74 (m, 4H, *o*-Ph^{PN}), 7.61 (m, 2H, *p*-Ph^{PN}), 7.43 (m, 4H, *m*-Ph^{PN}), 7.27 (m, 2H, *p*-Ph^{P}), 7.23 (m, 2H, *m*-Ph^{N}), 7.19 (m, 4H, *m*-Ph^{P}), 7.14 (m, 1H, *p*-Ph^{N}), 6.97 (m, 4H, *o*-Ph^{P}), 6.93 (m, 1H, *p*-Ph^{NB}), 6.86 (m, 2H, *m*-Ph^{NB}), 6.77 (m, 2H, *o*-Ph^{NB}), 6.41 (m, 2H, *o*-Ph^{N}), 6.40 (br, 1H, =NH), 5.87 (br, 1H, NH^{Ph}). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 163.0 (d, $^2J_{PC}$ = 9.3 Hz, N=C), 147.8 (dm, $^1J_{FC}$ ≈ 239 Hz, *o*-C_6F_5), 142.4 (t, J = 2.4 Hz, *i*-Ph^{NB}), 139.4 (dm, $^1J_{FC}$ ≈ 247 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{FC}$ ≈ 243 Hz, *m*-C_6F_5), 136.5 (dd, $^1J_{PC}$ = 13.7 Hz, $^3J_{PC}$ = 8.6 Hz, *i*-Ph^{P}), 136.1 (d, $^4J_{PC}$ = 2.0 Hz, *i*-Ph^{N}), 134.2 (dd, $^2J_{PC}$ = 9.5 Hz, $^5J_{P'C}$ = 1.8 Hz, *o*-Ph^{PN}), 132.5 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Ph^{PN}), 131.8 (d, $^2J_{PC}$ = 17.8 Hz, *o*-Ph^{P}), 131.5 (br, *o*-Ph^{NB}), 130.1 (*m*-Ph^{N}), 129.6 (dm, $^1J_{PC}$ = 103.5 Hz, *i*-Ph^{PN}), 129.1 (d, $^3J_{PC}$ = 5.7 Hz, *m*-Ph^{P}), 128.6 (*p*-Ph^{P}), 128.4 (d, $^3J_{PC}$ = 12.6 Hz, *m*-Ph^{PN}), 128.2 (d, J = 1.7 Hz, *m*-Ph^{NB}), 126.7 (*p*-Ph^{N}), 126.0 (d, J = 2.2 Hz, *p*-Ph^{NB}), 124.8 (*o*-Ph^{N}), 42.8 (dd, $^1J_{PC}$ = 120.5 Hz, $^1J_{PC}$ = 27.9 Hz, P=C), n.o. (*i*-C_6F_5). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ ≈ −132.5 (m, 2F, *o*-C_6F_5), −160.0 (m, 1F, *p*-C_6F_5), −165.3 (m, 2F, *m*-C_6F_5) [$\Delta\delta(p,m)$ = 5.3]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ 37.6 (d, $^2J_{PP}$ = 170.1 Hz, 1P, *P*=N, $\nu_{1/2}$ = 5.1 Hz), −30.3 (d, $^2J_{PP}$ = 170.1 Hz, 1P, P, $\nu_{1/2}$ = 2.0 Hz). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ −4.1 ($\nu_{1/2}$ ≈ 50 Hz).

X-ray crystal structure analysis of **8**: formula $C_{50}H_{32}BF_{10}N_3P_2$, M = 937.54, colorless crystal 0.42 × 0.20 × 0.10 mm, a = 10.4591(4) Å, b = 11.6827(4) Å, c = 19.1693(9) Å, α = 101.833(2)°, β = 105.781(4)°, γ = 99.151(3)°, V = 2147.98(15) Å^3, ρ_{calc} = 1.450 g cm^{-3}, μ = 1.659 mm^{-1}, empirical absorption correction (0.543 ≤ T ≤ 0.852), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 28 040 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 7444 independent (R_{int} = 0.051) and 6595 observed reflections [$I \geq 2\sigma(I)$], 602 refined parameters, R = 0.042, wR_2 = 0.105, max. (min.) residual electron density 0.32 (−0.32) e Å^{-3}, hydrogen atom at N2 from difference Fourier calculations, the others calculated and refined as riding atoms.

■ ASSOCIATED CONTENT

Supporting Information. Text and figures giving further experimental and spectroscopic details and CIF files (**3**, **4**, **6**, **7**, **8**) giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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