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1:1 Adduct of 1,1′-Bis(dibromoboryl)ferrocene and 3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene

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Summary: The Lewis acid−base adduct between 1,1′-bis(dibromoboryl)ferrocene and 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene has been characterized by multinuclear variable-temperature NMR spectroscopy and single-crystal X-ray diffraction analysis. Irrespective of the crystallization conditions applied, the molecular structure of the adduct is that of an open-chain dinuclear complex featuring only one P−B bond.

Introduction

Metal-containing polymers are receiving increasing attention due to their useful properties, such as electrical conductivity and cooperative magnetic behavior.[1] Two classes of compounds have attracted particular interest during the last 20 years: (a) polyferrocenylenes, mainly derived from strained, ring-tilted *ansa*-ferrocenes by thermal or catalytic ring-opening polymerization,[2] and (b) low-dimensional solids comprised of coordinatively unsaturated metal complex fragments and ditopic bridging ligands.[3]

Our group is currently developing an alternative synthesis strategy to ferrocene-containing macromolecules which takes advantage of coordination polymer synthesis. Starting from 1,1′-diborylated ferrocene derivatives and aromatic diamines (e.g. 4,4′-bipyridine, pyrazine), we have already succeeded in the preparation of various boron−nitrogen bridged polymeric species (e.g. **A** in Figure 1).[4−6] In this specific example, the facile formation of boron−nitrogen adduct bonds provided a convenient way of connecting the mononuclear building blocks. The solid materials not only are reasonably stable toward air and moisture but also possess intense colors resulting from charge-transfer interactions between the ferrocene donors and the organic acceptor bridges.[4,7] To test the scope of our approach and to increase the number of metal atoms in the polymer chain, we decided to replace the diamine linkers by Lewis basic ferrocene derivatives. 1,1′-Dilithioferrocene appeared to be a well-suited building block, since this compound is readily available and provides two anionic sp^2-hybridized electron-pair donor sites as part of its cyclopentadienyl ligands. However, treatment of 1,1′-dilithioferrocene with 1,1′-bis(dimethylboryl)ferrocene did not lead to linear polymers but rather gave the cyclic dimer **B** (Figure 1), which is stable in solution and behaves as a highly efficient lithium scavenger.[8]

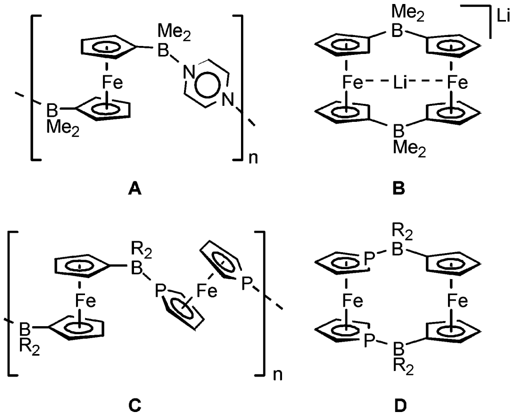

Figure 1. The B−N-bonded charge-transfer coordination polymer **A**, the B−C-bonded macrocyclic lithium scavenger **B**, and the structurally related hypothetical 1,1′-diphosphaferrocene adducts **C** and **D** (any substituents on 1,1′-diphosphaferrocene are omitted for clarity).

Given this background, it appeared to be worthwhile to explore the suitability of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene[9] as a difunctional organometallic Lewis base for the preparation of polymers **C** or macrocycles **D** (Figure 1). Even though numerous transition-metal complexes of monophosphaferrocenes and 1,1′-diphosphaferrocenes have been published up to now,[10,11] not much is known about the reactivity of these ligands toward main-group Lewis acids. Theoretical investigations indicate phosphaferrocene derivatives to be weakly σ-donating and strongly π-accepting ligands.[12] This is due to the fact that their electron lone pair(s) is (are) energetically low-lying and their LUMO possesses largely p_z character at the phosphorus atom(s). Since $d_\pi-p_\pi$

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[1] Pittman, C. U., Carraher, C. E., Zeldin, M., Sheats, J. E., Culbertson, B. M., Eds. *Metal-Containing Polymeric Materials*; Plenum Press: New York, 1996.

[2] Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515−1548.

[3] Archer, R. D. *Inorganic and Organometallic Polymers*; Wiley-VCH: Weinheim, Germany, 2001.

[4] Fontani, M.; Peters, F.; Scherer, W.; Wachter, W.; Wagner, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1998**, 1453−1465, 2087.

[5] Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, *18*, 4669−4672.

[6] Dinnebier, R. E.; Wagner, M.; Peters, F.; Shankland, K.; David, W. I. F. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1400−1405.

[7] Ding, L.; Fabrizi de Biani, F.; Bolte, M.; Zanello, P.; Wagner, M. *Organometallics* **2000**, *19*, 5763−5768.

[8] Scheibitz, M.; Winter, R. F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Angew. Chem.* **2003**, *115*, 954−957; *Angew. Chem., Int. Ed.* **2003**, *42*, 924−927.

[9] de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102,* 994−1000.

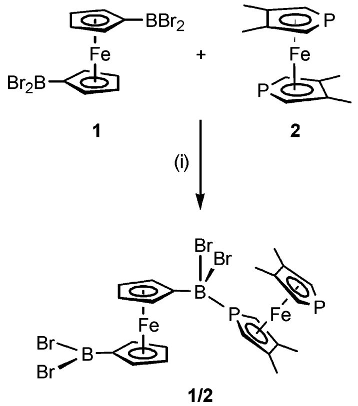
[10] Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1−52.

[11] Ganter, C. *J. Chem. Soc., Dalton Trans.* **2001**, 3541−3548.

[12] Frison, G.; Mathey, F.; Sevin, A. *J. Phys. Chem. A* **2002**, *106*, 5653−5659.

10.1021/om049707a CCC: $27.50

Scheme 1. Synthesis of the P−B Adduct 1/2[a]



[a] Legend: (i) −30 °C, toluene.

back-bonding is not possible for s- and p-block elements, adduct bonds between main-group compounds and phosphaferrocenes are expected to be weak. Nevertheless, Mathey[13] recently succeeded in the structural characterization of the ionic complex [octa-*n*-propyl-diphosphaferrocene/$GaCl_2$]$^+$[$GaCl_4$]$^-$, while Roberts and Silver[14] have gained NMR spectroscopic evidence for the existence of a 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene/BF_3 adduct in $CDCl_3$ solution. In the course of our own studies, we synthesized and structurally characterized adducts of 3,4-dimethyl-1-phosphaferrocene with boron tribromide on one hand and dibromoborylferrocene on the other.[15] The latter P−B complex can already be regarded as an important substructure of our target compounds **C** and **D**. With these encouraging results in hand, we focused on the reaction of 1,1′-bis(dibromoboryl)ferrocene (**1**) with 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**2**; Scheme 1). The purpose of this paper is to report on the structural characterization of the unexpected open-chain dinuclear complex **1**/**2**, which turned out to be the sole reaction product.

Results and Discussion

Synthesis and NMR Spectroscopic Characterization. For all NMR spectroscopic investigations, solutions of **1** and **2** in toluene-d_8 were mixed in equimolar proportions and sealed in an NMR tube. Similar to the 3,4-dimethyl-1-phosphaferrocene/dibromoborylferrocene system,[15] the ^{11}B, ^{13}C, and ^1H NMR spectra of **1**/**2** at 30 °C show only negligible differences from the NMR spectra of the individual components (Table 1). This is no longer true for the ^{31}P NMR spectrum (30 °C, toluene-d_8) of **2** compared to that of **1**/**2**. Even though the phosphorus chemical shifts of both species differ by as little as 2.7 ppm (**2**, $\delta(^{31}P)$ −68.1; **1**/**2**, $\delta(^{31}P)$ −65.4), the width at half-height increases considerably from $h_{1/2} = 14$ Hz (**2**) to $h_{1/2} = 100$ Hz (**1**/**2**), thereby indicating a dynamic association/dissociation equilibrium in the latter case. This result is in striking contrast to the work of Roberts and Silver,[14] who observed two ^{31}P NMR resonances for the complex **2**/BF_3 ($\delta(^{31}P)$ 31.0 and −62.2; room temperature, $CDCl_3$), one of them deshielded by 103 ppm with respect to the ^{31}P NMR signal of **2** ($\delta(^{31}P)$ −72.0; room temperature, $CDCl_3$). This leads to the conclusion that **2** forms a much weaker Lewis acid−base adduct with **1** than with BF_3. It is, however, important to note that even in the presence of excess $BF_3 \cdot OEt_2$ only the monoadduct **2**/BF_3 is formed,[14] which suggests that complexation of one phosphorus site deactivates the other. To gain further insight into the temperature dependence of the adduct equilibrium, variable-temperature ^{11}B and ^{31}P NMR spectra have been recorded. The results are summarized in Table 1. At 30 °C, the ^{11}B NMR signal appears at 52.5 ppm ($h_{1/2} = 210$ Hz). Lowering the sample temperature leads to an upfield shift of this resonance together with an increase of its width at half-height (e.g. $T = -30$ °C: $\delta(^{11}B)$ 38.1, $h_{1/2} = 890$ Hz). No signal is detectable in the ^{11}B NMR spectrum at −60 °C, which is most likely due to severe line broadening caused by decelerated exchange processes. The ^{31}P NMR resonance is shifted to lower field upon cooling, again accompanied by broadening of the signal. The ^{11}B and ^{31}P NMR data obtained at a given temperature represent average values of all components present in the reaction mixture. Our data therefore testify to an increase in the concentration of the adduct **1**/**2** at low temperatures. However, even at −30 °C, the absolute concentration of **1**/**2** is apparently not very high, since ^{11}B NMR shift values of stable boron−phosphorus adducts are typically observed in a range upfield of 10 ppm.[16]

Table 1. ^{11}B and ^{31}P Chemical Shift Values of an Equimolar Mixture of 1 and 2 in Toluene-d_8 at Various Temperatures

	T (°C)			
	30	0	−30	−60
$\delta(^{11}B)$	52.5[a] (210)[c]	49.8 (360)	38.1 (890)	n.o.[d]
$\delta(^{31}P)$	−65.4[b] (100)	−63.0 (90)	−48.5 (140)	−37.2 (950)

[a] Cf. **1**: $\delta(^{11}B)$ 53.3 (190). [b] Cf. **2**: $\delta(^{31}P)$ −68.1 (14). [c] $h_{1/2}$ values (Hz) given in parentheses. [d] n.o. = not observed.

X-ray Crystal Structure Determination. X-ray-quality crystals of **1**/**2** were grown (Scheme 1) at three different temperatures to maximize the chance of getting both the product of a *thermodynamically* controlled crystallization process and the product of a *kinetically* controlled process ($T_1 = 20$ °C, benzene, slow evaporation of the solvent; $T_2 = -30$ °C, toluene; $T_3 = -78$ °C, methylene chloride). In all three cases, crystals possessing identical cell parameters were obtained. Thus, only the result of the structure analysis of a crystal grown from toluene at −30 °C (triclinic space group $P\bar{1}$) is discussed here (Tables 2 and 3). Compound **1**/**2** establishes neither a polymeric nor a cyclic structure but, rather, forms an open-chain dinuclear complex in the solid state (Figure 2). Each of these complexes consists of a 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene together with a 1,1′-bis(dibromoboryl)ferrocene unit linked by one phosphorus−boron bond. The second BBr_2 substituent, which features a trigonal-planar boron center (sum of angles around boron 360°), and the second phosphorus atom are not engaged in intra- or

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[13] Sava, X.; Melaimi, M.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *New J. Chem.* **2002**, *26*, 1378−1383.

[14] Roberts, R. M. G.; Silver, J.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *119*, 165−169.

[15] Scheibitz, M.; Bats, J. W.; Bolte, M.; Wagner, M. *Eur. J. Inorg. Chem.* **2003**, 2049−2053.

[16] Nöth, H.; Wrackmeyer, B. Nuclear Magnetic Resonance Spectroscopy of Boron Compounds. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer: Berlin, Heidelberg, New York, 1978.

Table 2. Selected Crystallographic Data for 1/2

formula	$C_{22}H_{24}B_2Br_4Fe_2P_2$
fw	803.31
color, shape	red, block
cryst size (mm)	0.55 × 0.45 × 0.36
temp (K)	173(2)
radiation	Mo Kα, 0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	7.0864(7)
b (Å)	11.0523(11)
c (Å)	17.5153(18)
α (deg)	85.952(8)
β (deg)	83.493(8)
γ (deg)	73.518(8)
V (Å^3)	1305.9(2)
Z	2
D_{calcd} (g cm^{-3})	2.043
F(000)	776
μ (mm^{-1})	7.364
$2\theta_{\max}$ (deg)	53.08
no. of rflns collected	19 390
no. of indep rflns (R_{int})	5363 (0.0726)
no. of rflns obsd ($I > 2\sigma(I)$)	4548
no. of data/restraints/params	5363/0/294
GOF on F^2	1.023
R1, wR2 ($I > 2\sigma(I)$)	0.0373, 0.0899
R1, wR2 (all data)	0.0458, 0.0934
largest diff peak and hole (e Å^{-3})	0.905/−0.737

Table 3. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of 1/2

P(1)−B(2)	2.001(4)	B(1)−C(11)	1.493(7)
P(1)−Fe(2)	2.194(1)	B(2)−C(21)	1.572(5)
P(2)−Fe(2)	2.279(1)		
C(11)−B(1)−Br(11)	121.3(3)	C(32)−P(1)−C(35)	92.9(2)
C(11)−B(1)−Br(12)	122.7(3)	C(42)−P(2)−C(45)	88.1(2)
Br(11)−B(1)−Br(12)	116.1(3)	Br(21)−B(2)−Br(22)	110.7(2)
P(1)−B(2)−C(21)	104.5(3)	C(21)−B(2)−Br(21)	115.2(3)
P(1)−B(2)−Br(21)	105.5(2)	C(21)−B(2)−Br(22)	114.2(3)
P(1)−B(2)−Br(22)	105.6 (2)	COG−C(11)−B(1)[a]	161.9
C(12)−C(11)−B(1)−Br(12)	14.6(5)		
C(32)−P(1)−B(2)−C(21)	150.8(3)		
C(32)−P(1)−B(2)−Br(21)	29.0(3)		
C(32)−P(1)−B(2)−Br(22)	−88.3(3)		

[a] COG = centroid of the cyclopentadienyl ligand.

intermolecular bonding interactions (shortest intermolecular P⋯B distance 6.813 Å). The P−B bond of **1/2** (P(1)−B(2) = 2.001(4) Å) is slightly shorter than that of the related compound 3,4-dimethyl-1-phosphaferrocene/dibromoborylferrocene (P−B = 2.023(4) Å[15]) but somewhat longer than the P−B bond of the corresponding BBr_3 adduct (P−B = 1.972(9) Å[15]). The degree of pyramidalization of the tetracoordinate boron substituent is lower (C(21)−B(2)−Br(21) = 115.2(3)°, C(21)−B(2)−Br(22) = 114.2(3)°, Br(21)−B(2)−Br(22) = 110.7(2)°) than expected for a fully sp^3-hybridized boron atom with ideal tetrahedral geometry (R−B−R = 109.5°). This feature, together with the rather long P−B bond, points toward a weak acid−base interaction in **1/2**, as has already been concluded from our NMR spectroscopic studies (see above). P−B adduct formation nevertheless leads to remarkable structural changes at the boron-bound phospholyl ligand compared to the second phospholyl ring. Major differences lie in the lengths of the P−Fe bonds (P(1)−Fe(2) = 2.194(1) Å, P(2)−Fe(2) = 2.279(1) Å, Δ = 0.085 Å) as well as in the C−P−C angles (C(32)−P(1)−C(35) = 92.9(2)°, C(42)−P(2)−C(45) = 88.1(2)°, Δ = 4.8°). Qualitatively similar—but less pronounced—effects can be observed when the molecular structures of phosphaferrocene−transition-metal complexes are compared with those of the corresponding free phosphaferrocene ligands.[15] B−P acid−base pairing also has an impact on the second—uncomplexed—BBr_2 substituent of the dibromoborylferrocene fragment in **1/2**. It is known that three-coordinate boron groups attached to a ferrocene backbone tend to be bent out of the plane of the C_5H_4 ring toward the iron atom.[17] The dip angle $\alpha^* = 180° - \beta^*$ (β^* = B−C_{ipso}−COG; COG = centroid of the C_5H_4 ring) has been introduced as a measure of the degree of this distortion.[17] Large values of α^* are usually observed with strongly Lewis acidic boryl substituents (cf. $FcBBr_2$ with α^* = 17.7°/18.9° (two crystallographically independent molecules in the asymmetric unit)[17] and 1,1′-fc$(B(N^iPr_2)_2)_2$ with α^* = 0°;[18] Fc = $(C_5H_5)Fe(C_5H_4)$). Moreover, α^* tends to become smaller when additional boryl substituents are introduced into the ferrocene core (cf. $FcBBr_2$ with α^* = 17.7°/18.9°[17] and 1,1′-fc$(BBr_2)_2$ with α^* = 9.1°;[18] fc = $(C_5H_4)Fe(C_5H_4)$). Bending of the exocyclic BR_2 substituent(s) is likely due to electronic interactions between filled d-type orbitals at iron and the empty p orbital at boron.[17] In the case of **1/2**, a negligible dip angle α^* of 1.3° is found for the tetracoordinate B(2)Br(21)Br(22) group, since the p orbital at B(2) is filled by the P(1) lone pair. The C_5H_4−B(1)Br(11)Br(12) moiety, however, is bent by α^* = 18.1°, which is double the value observed for the free Lewis acid 1,1′-fc$(BBr_2)_2$ and equal to the dip angle exhibited by the monoborylated $FcBBr_2$. We may therefore assume that a delicate interplay exists between the individual BR_2 substituents in diborylated ferrocenes: satisfying the electron demand of one of the competing boryl groups by adduct formation with an external Lewis base promotes the electronic interaction between the remaining (and still three-coordinate) boryl substituent and the iron atom.

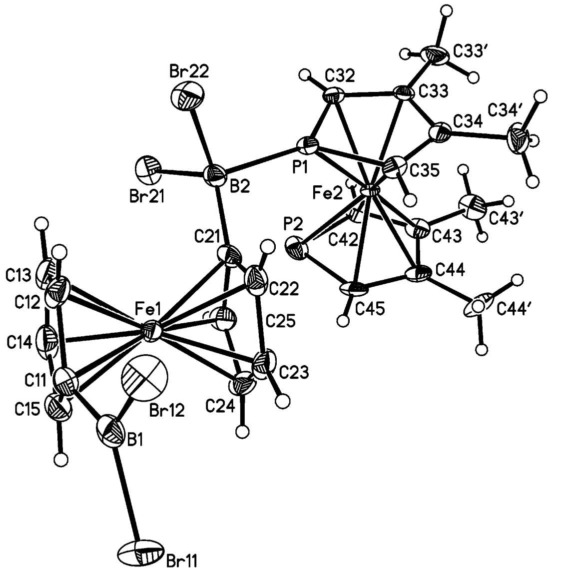

Figure 2. Molecular structure and numbering scheme of compound **1/2**. Thermal ellipsoids are shown at the 50% probability level.

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[17] Appel, A.; Jäkle, F.; Priermeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188−1194.

[18] Wrackmeyer, B.; Dörfler, U.; Milius, W.; Herberhold, M. *Polyhedron* **1995**, *14*, 1425−1431.

When the two phospholyl rings of free 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**2**) are projected on each other, the P atom of one ring superposes with a β-C atom of the other.[9] In contrast, the diphosphaferrocene unit of **1**/**2** adopts a staggered conformation in which P(1) and P(2) are more closely approaching each other (cf. P(1)−COG(1)−COG(2)−P(2) = 29.8°; COG(1), COG(2) = centroids of the two phospholyl rings). As a result, steric strain between the methyl groups of the P(2)-phospholyl ring and the ferrocene molecule is avoided. The relative position of the ferrocene and the diphosphaferrocene in **1**/**2** is characterized by the torsion angle C(32)−P(1)−B(2)−C(21) = 150.8(3)° and a dihedral angle of 99.3° between the C(21)C(22)C(23)C(24)C(25) ring and the P(1)-phospholyl ligand. The tilt angles between the two C_5H_4 rings are 2.9 and 2.3° between the two phospholyl ligands.

Conclusion

Even though P-bonded complexes between phosphaferrocenes and main-group Lewis acids were generally believed to be rather unstable, our group recently succeeded in the synthesis and structural characterization of P−B adducts between 3,4-dimethyl-1-phosphaferrocene and boron tribromide as well as dibromoborylferrocene. The existence of the latter aggregate in particular prompted us to investigate the suitability of 1,1′-diphosphaferrocenes and 1,1′-diborylferrocenes as building blocks for the synthesis of polymers or macrocycles via Lewis acid−base pairing. For practical reasons we chose 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**2**) as the base and treated it with 1,1′-bis(dibromoboryl)ferrocene (**1**), which is one of the most strongly Lewis acidic derivatives available. In contrast to a priori expectations, neither polymeric material nor a macrocycle was formed from **1** and **2** in solution or in the solid state. Rather, the compound obtained by crystallization consisted of the open-chain dinuclear complex **1**/**2**, featuring only one P−B adduct bond. This result was reproduced both at higher (T = 20 °C, benzene, slow evaporation of the solvent) and at lower crystallization temperatures (T = −78 °C, methylene chloride). As has already been mentioned by Roberts and Silver, who investigated the 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene/BF_3 couple in various stoichiometric ratios using ^{31}P NMR spectroscopy, P−B adduct formation at the first phosphorus atom apparently reduces the Lewis basicity of the second phosphorus donor to such an extent that it no longer forms stable dative bonds to boron Lewis acids. In our special case, the problem is aggravated by the fact that tetracoordination of the first boryl substituent in **1** likely leads to a decrease in the Lewis acidity of the second boryl group, which profits from the full electron density provided by the ferrocene backbone. Our results lead to the conclusion that 1,1′-diphosphaferrocenes are not suitable as organometallic bridging elements for the coordination polymerization of 1,1′-diborylferrocenes. In the future, we will therefore focus primarily on 1,1′-diazaferrocenes and 1,1′-dilithioferrocenes as alternative difunctional Lewis bases.

Experimental Section

General Remarks. All reactions were carried out under a nitrogen atmosphere using Schlenk tube techniques. Toluene-d_8 was freshly distilled under argon from Na/benzophenone. The starting materials **1**[19] and **2**[9] were prepared according to published procedures. NMR: Bruker DPX 250. Chemical shifts are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$), external H_3PO_3 ($^{31}P\{^1H\}$), or external $BF_3{\cdot}Et_2O$ ($^{11}B\ \{^1H\}$). Abbreviations: s = singlet; d = doublet; vtr = virtual triplet; n.o. = signal not observed.

Preparation of 1/2. 1,1′-fc(BBr_2)$_2$ (**1**; 56 mg, 0.11 mmol) and 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**2**; 30 mg, 0.11 mmol) were dissolved in 0.8 mL of toluene-d_8, the resulting mixture was sealed in an NMR tube and investigated by NMR spectroscopy.

^1H NMR (250.1 MHz, toluene-d_8, 303 K): δ 1.84 (s, 12H, CH_3), 3.59 (d, 4H, $^2J_{P,H}$ = 36.1 Hz, CH), 4.32, 4.38 (2 × vtr, 2 × 4H, $^3J_{H,H} = {}^4J_{H,H}$ = 1.7 Hz, C_5H_4). ^{13}C NMR (62.9 MHz, toluene-d_8, 303 K): δ 15.5 (CH_3), 79.0, 80.3 (C_5H_4), 81.6 (d, $^1J_{P,C}$ = 56.9 Hz, CH), 97.1 (d, $^2J_{P,C}$ = 6.4 Hz, CCH_3), n.o. (CB). ^{11}B NMR (80.3 MHz, toluene-d_8, 303 K): δ 52.5 ($h_{1/2}$ = 210 Hz). ^{31}P NMR (101.3 MHz, toluene-d_8, 303 K): δ −65.4 ($h_{1/2}$ = 100 Hz).

X-ray-quality crystals of **1**/**2** were grown (i) from a highly diluted benzene solution upon slow evaporation of the solvent at 20 °C, (ii) from toluene at −30 °C, and (iii) from methylene chloride at −78 °C (typical amounts of starting material used in the crystallization reactions are 68 mg, 0.13 mmol (**1**) and 36 mg, 0.13 mmol (**2**); yield of **1**/**2** 68 mg (65%)).

X-ray Crystal Structure Analysis of 1/2. A single crystal (red block; 0.55 × 0.45 × 0.36 mm) was analyzed with a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo Kα radiation. An empirical absorption correction was performed using the MULABS[20] option in PLATON;[21] the minimum and maximum transmissions were 0.1067 and 0.1769, respectively. The structure was solved by direct methods using the program SHELXS[22] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97.[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located by difference Fourier synthesis and refined using a riding model. CCDC reference number: 236748.

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Supporting Information Available: Crystallographic data of **1**/**2** in the Crystallographic Information File (CIF) format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Ruf, W.; Renk, T.; Siebert, W. *Z. Naturforsch.* **1976**, *31b*, 1028−1034.

(20) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.

(21) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

(22) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(23) Sheldrick, G. M. SHELXL-97: A Program for the Refinement of Crystal Structures, Universität Göttingen, Göttingen, Germany, 1997.