Formation of Two Isomeric *closo*-[(η^5-C_5H_5)Fe$PC_2B_8H_{10}$] Phosphadicarbaborane Analogues of Ferrocene via Isolable η^1-Bonded Complexes of the [7-{(η^5-C_5H_5)Fe(CO)$_2$}-(η^1-*nido*-$PC_2B_8H_{10}$)] Type

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Abstract: The reaction of *nido*-[7,8,9-$PC_2B_8H_{11}$] (**1**) with [{CpFe(CO)$_2$}$_2$] (Cp = η^5-$C_5H_5^-$) in benzene (reflux, 3 days) gave an η^1-bonded complex [7-Fp-(η^1-*nido*-7,8,9,-$PC_2B_8H_{10}$)] (**2**; Fp = CpFe(CO)$_2$; yield 38%). A similar reaction at elevated temperatures (xylene, reflux 24 h) gave the isomeric complex [7-Fp-(η^1-*nido*-7,9,10-$PC_2B_8H_{10}$)] (**3**; yield 28%) together with the fully sandwiched complexes [1-Cp-*closo*-1,2,4,5-Fe$PC_2B_8H_{10}$] **4a** (yield 30%) and [1-Cp-*closo*-1,2,4,8-Fe$PC_2B_8H_{10}$] **4b** (yield 5%). Compounds **2** and **3** are isolable intermediates along the full η^5-complexation pathway of the phosphadicarbaborane cage; their heating (xylene, reflux, 24 h) leads finally to the isolation of compounds **4a** (yields 46 and 52%, respectively) and **4b** (yields 4 and 5%, respectively). Moreover, compound **3** is isolated as a side product from the heating of **2** (yield 10%). The structure of compound **4a** was determined by an X-ray structural analysis and the constitution of all compounds is consistent with the results of mass spectrometry and IR spectroscopy. Multinuclear (^{1}H, ^{11}B, ^{31}P, and ^{13}C), two-dimensional [^{11}B–^{11}B]-COSY, and ^{1}H{^{11}B(selective)} magnetic resonance measurements led to complete assignments of all resonances and are in excellent agreement with the structures proposed.

Keywords: boron · boranes · ferraphosphadicarbaboranes · heteroboranes · iron · metallaphosphacarboranes

Introduction

One of our groups has recently been interested in the synthesis and chemistry of the phosphacarborane analogues of tricarbollides (11-vertex *nido* tricarbaboranes).[1] In this field we have already reported on the synthesis of the *nido* phosphadicarbaboranes [7,8,11-$PC_2B_8H_{11}$] and [7,8,11-$PC_2B_8H_{10}$]$^-$ based on the reaction between [6,9-$C_2B_8H_{10}$]$^{2-}$ and PCl_3.[2] Also treatment of the dicarbaborane *nido*-[5,6-$C_2B_8H_{12}$] with PCl_3 has recently led to the isolation of other *nido* phosphadicarbaborane isomers, [7,8,9-$PC_2B_8H_{11}$] and [7,8,9-$PC_2B_8H_{11}$]$^-$.[3] Owing to the isolobal relation between CH and P cluster vertices, the neutral [7,8,9-$PC_2B_8H_{11}$] phosphadicarbaborane is an analogue of the neutral tricarbollide [7,8,9-$C_3B_8H_{12}$], and the corresponding [7,8,9-$PC_2B_8H_{10}$]$^-$ ion is analogous to the tricarbollide anion [7,8,9-$C_3B_8H_{11}$]$^-$.[4] All these eleven-vertex cluster systems are also regarded as Cp analogues[1b] as they are monoanionic and contain an open pentagonal face, and the radicals donate five electrons for η^5-coordination to metal center. To demonstrate this analogy, we report herein on the complexation of *nido*-[7,8,9-$PC_2B_8H_{11}$], which results ultimately in the synthesis of two complexes of general structure [1-Cp-*closo*-Fe$PC_2B_8H_{10}$]. These compounds are the first phosphadicarbaborane ana-

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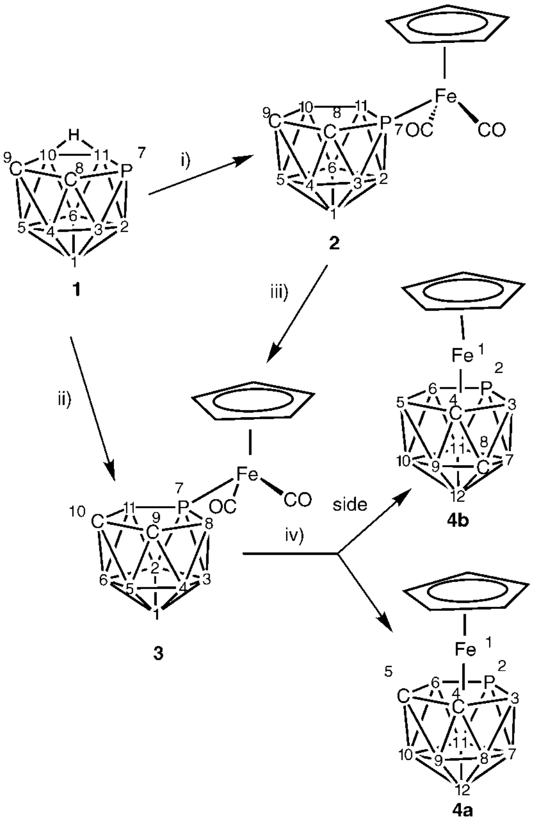
logues of ferrocene, and it is also demonstrated that their formation proceeds via isolable η^1-bonded, P-substituted complexes of the general formulation [7-Fp-(η^1-*nido*-$PC_2B_8H_{10}$)]. Unmarked vertices in Scheme 1 denote cluster BH units, and the numbering system used in this work is outlined in Scheme 1.

Results and Discussion

Syntheses: The straightforward structural analogy between the parent tricarbollide [7,8,9-$C_3B_8H_{12}$] and the phosphadicarbaborane [7,8,9-$PC_2B_8H_{11}$] (**1**) has suggested that complexation of the open pentagonal face in **1** might be achieved by reaction with the [{$CpFe(CO)_2$}$_2$] dimer at elevated temperatures.[5] As shown in Scheme 1, the reaction between the dimer and compound **1** is not that simple as in the case of the tricarbollide analogue.[5] Prolonged heating of the [{$CpFe(CO)_2$}$_2$] dimer with compound **1** in benzene at reflux for three days (Scheme 1, path i) and Equation (1), resulted in the isolation of a light-orange product which was identified by NMR spectroscopy as [7-Fp-(η^1-*nido*-7,8,9-$PC_2B_8H_{10}$)] (**2**).

$$\mathbf{1} + 0.5[CpFe(CO)_2]_2 \longrightarrow \underset{\mathbf{2}}{[7\text{-}Fp\text{-}7,8,9\text{-}PC_2B_8H_{10}]} + 0.5H_2 \quad (1)$$

The net result of the reaction of Equation (1) carried out under relatively mild conditions is, instead of the expected η^5-complexation, substitution of the cage P atom by the Fp group at the exoskeletal position. Compound **2** is thus isostructural with the [7-R-7,8,9-$PC_2B_8H_{10}$] (where R = Me and Ph) compounds (P-substituted derivatives of **1**) isolated by Sneddon's group.[6]



Scheme 1. Complexes isolated along the complexation pathway leading to [1-Cp-*closo*-1,2,4,5-$FePC_2B_8H_{10}$] (**4a**) and [1-Cp-*closo*-1,2,4,8-$FePC_2B_8H_{10}$] (**4b**). i)[$CpFe(CO)_2$]$_2$, benzene, reflux three days. ii) [{$CpFe(CO)_2$}$_2$], xylene, reflux 24 h. iii), iv) xylene, reflux 24 h.

As shown in Scheme 1 (paths ii and iv), the course of the same reaction is, however, different at elevated temperatures. Refluxing the reaction mixture in xylene for 24 h led to two main products, which were isolated by repeated chromatographic separation on silica gel. These were identified by NMR spectroscopy as the complexes [7-Fp-(η^1-*nido*-7,9,10-$PC_2B_8H_{10}$)] (**3**; yield 28 %, dark red) and [1-Cp-*closo*-1,2,4,5-$FePC_2B_8H_{10}$] (**4a**; yield 30 %, dark orange). A side product isolated from this reaction is the isomeric compound [1-Cp-*closo*-1,2,4,8-$FePC_2B_8H_{10}$] (**4b**; yield 5 %, orange). Compound **3** is a cage isomer of **2**, while the complexes **4a** and **4b** are sandwich compounds in which the [η^5-7,9,10-$PC_2B_8H_{10}$]$^-$ and [η^5-7,4,9-$PC_2B_8H_{10}$]$^-$ ions, respectively, act as sandwich ligands.

There is no doubt that η^1-bonded *nido* complexes **2** and **3** have to be considered as isolable intermediates of the fully η^5-complexed *closo* complexes **4a** and **4b**, which would be formed upon elimination of two CO molecules. This fact is also reflected in the mass spectra of **2** and **3**, both of which show a molecular ion consistent with the $[M-2CO]^+$ fragmentation and formation of sandwiches of type **4** under the conditions of the experiment. This proposal has been further confirmed by two independent experiments [Eq. (2)].

$$\mathbf{2} \longrightarrow \mathbf{3} \longrightarrow \underset{\mathbf{4a}\text{ and }\mathbf{4b}}{[1\text{-}Cp\text{-}FePC_2B_8H_{10}] + 2CO} \quad (2)$$

Heating of either **2** or **3** in xylene at reflux for 24 h led ultimately to the isolation of **4a** (yields 46 and 52 %, respectively) and **4b** (yields 4 and 5 %, respectively, see also paths iii and iv of Scheme 1). Moreover, complex **3** is formed in this reaction as a side product (yield 10 %) by heating of **2**; the formation is consistent with a rearrangement of the P-vertex within the open pentagonal face of the phosphacarborane core in **2**. This type of rearrangement is well established in the structurally similar eleven-vertex *nido* dicarbaborane[7] and tricarbaborane[8, 9] series. Inspection of Scheme 1 additionally suggests that the fully complexed compound **4a** is formed from **3** by transfer of the Fp group from the exoskeletal site into the endoskeletal position above the center of the pentagonal open face upon elimination of both carbonyl ligands. The insertion of a CpFe fragment of an *exo*-framework Fp group is precedented in metallaborane chemistry, albeit driven by photons.[10]

Structural studies: Even though we were able to grow well-shaped crystals of complexes **2** and **3**, the structure determination was unsuccessful owing to problems encountered during structure solution. As demonstrated graphically in Figure 1 by simplified stick diagrams, the ^{11}B NMR spectrum of compound **2** consists of eight doublets (range 36.2 ppm) and is very similar to that of the structurally related phosphadicarbaborane [7-Me-7,8,9-$PC_2B_8H_{10}$] (**5**),[6] except that two resonances in the spectrum of **2** coincidentally

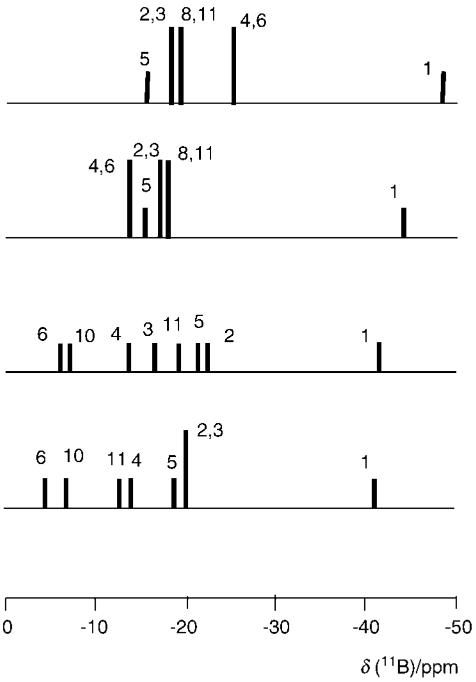


Figure 1. Simplified stick diagrams comparing the ^{11}B chemical shifts and relative intensities for structurally related couples [7-Fp-(η^1-*nido*-7,8,9,-$PC_2B_8H_{10}$)] (**2**)/*nido*-[7-Me-7,8,9-$PC_2B_8H_{10}$] (**5**; data from reference [6]) and [7-Fp-(η^1-*nido*-7,9,10-$PC_2B_8H_{10}$)] (**3**) /*nido*-[7,8,10-$C_3B_8H_{11}$]$^-$ (**6**; data from reference [4b]).

overlap. The ^1H NMR spectrum of **2** shows three resonances with relative intensities of 5:1:1, which are assigned to Cp and two nonequivalent cage CH(9) and CH(8) resonances, respectively. The CH(8) resonance shows a distinct doublet ^2J(P,H), because the CH(8) vertex is adjacent to the cage P atom. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows five resonances with relative intensities of 1:1:5:1:1, which are assigned to the two nonequivalent CO groups, one Cp ligand, and to the two nonequivalent C(9) and C(8) cage carbon atoms. All the ^{13}C resonances, except for the C(9) singlet, are split into doublets due to ^1J(C,P) or ^2J(C,P) coupling. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a single singlet resonance, and the IR spectrum contains two very strong ν(CO) absorptions. These data are consistent with the asymmetrical C_1-structure for **2** shown in Scheme 1 with a piano-stool configuration of the two CO ligands and the P atom of the asymmetrical cluster around the Fe center. A similar structure is adopted, for example, by numerous analogous complexes containing the Fp fragment.[11] The η^1-bonded [7,8,9-$PC_2B_8H_{10}$] ligand in **2** contributes one electron to the 18-electron shell configuration around the central Fe atom.

Figure 1 also shows that the ^{11}B NMR spectrum of compound **3** consists of five doublets of relative intensities 2:1:2:2:1 (range 30.2 ppm) and is very similar to that of the isostructural tricarbollide anion *nido*-[7,8,10-$C_3B_8H_{11}$]$^-$ (**6**)[4b] (range 32.6 ppm), except that the spectrum of **3** is shifted downfield by about 7 ppm. The $^1H\{^{11}B\}$ NMR spectrum of **3** shows two resonances with relative intensities of 5:2, which are assigned to Cp and two equivalent CH(9,10) units, respectively. The $^{13}C\{^1H\}$ NMR spectrum of **3** shows three resonances with relative intensities of 2:5:2, which are assigned to two equivalent pairs of CO, Cp, and to the two equivalent cage C(9,10) units, respectively. A single P-vertex is indicated by the presence of only one high-field resonance in the $^{31}P\{^1H\}$ NMR spectrum of **3**. The IR spectrum contains two, very strong ν(CO) absorptions. These data are consistent with the C_s structure of **3** shown in Scheme 1 with a symmetry plane intersecting the Fe, P(7), B(1), and B(5) atoms. The configuration of ligands around the central Fe^{II} atom is similar to that in compound **2**, except that the η^1-bonded [7,9,10-$PC_2B_8H_{10}$] ligand is symmetrical.

The structure of **4a** was determined unambiguously by an X-ray structure analysis (Figure 2; for selected crystallographic parameters see Table 1 and Table 2). The carbon atoms of the Cp ring are disordered, in contrast with the positions of the twelve-vertex $FePC_2B_8H_{10}$ cluster. The Fe–C(cage) and Fe–P distances are 2.018(2) Å (mean) and 2.2515(6) Å, respectively, other intracluster C–B, P–B, and B–B distances approximate those found crystallographically[12] for the phosphacarbollide complex [Fe(9-CH_3-9,7-PCB_9H_{10})$_2$]. The structure determination also confirms a symmetrical arrangement of the Fe, C, and P heteroatoms within the 12-vertex *closo* cage with a C_s symmetry plane

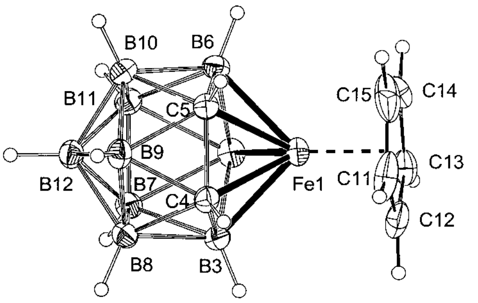


Figure 2. Molecular structure of [1-(η^5-Cp)-*closo*-1,2,4,5-$FePC_2B_8H_{10}$] (**4a**, ORTEP representation; the second position of the Cp ring was omitted for clarity. The thermal ellipsoids are drawn at 30% probability level).

Table 1. Crystal data and structure refinement for **4a**.

empirical formula	$C_7H_{15}B_8FeP$
M_r	272.49
λ [Å]	0.71073
crystal system	monoclinic
space group	$P2_1/c$ (no 14.)
a [Å]	6.94600 (10)
b [Å]	9.7980 (3)
c [Å]	18.1510 (5)
β [°]	90.8300 (17)
V [Å^3]	1235.17 (5)
Z	4
ρ_{calcd} [Mg m^{-3}]	1.465
μ [mm^{-1}]	1.309
F(000)	552
θ range [°]	3–27.5
h, k, l collected	−8,8; −12,12; −23,23
no. of reflections collected	17719
no. of independent reflections	2811 (R_{int} = 0.028)
completeness to θ = 27.5° [%]	99.8
data/parameters	2811/180
GoF on F^2	1.049
final R indices [$I > 2\sigma(I)$]	0.036
wR indices (all data)	0.096
extinction coefficient	0.018(2)
$\Delta\rho$, max/min [e Å^{-3}]	0.48/−0.41

Table 2. Selected intracluster bond lengths [Å] and angles [°] for **4a**.

bond lengths			
Fe1–C5	2.020(2)	Fe1–C4	2.016(2)
Fe1–B6	2.110(2)	Fe1–B3	2.117(3)
Fe1–P2	2.2514(6)	P2–B3	2.041(3)
P2–B11	2.049(3)	P2–B6	2.049(3)
P2–B7	2.049(3)	B3–C4	1.690(3)
C4–C5	1.622(3)	C5–B6	1.693(3)
bond angles			
B6-Fe1-P2	55.92(7)	B3-Fe1-P2	55.62(7)
B3-P2-B11	93.01(10)	B3-P2-B6	93.45(10)
B11-P2-B6	53.49(11)	B3-P2-B7	53.66(10)
B11-P2-B7	52.64(10)	B6-P2-B7	92.94(11)
B3-P2-Fe1	58.84(7)	B11-P2-Fe1	102.88(8)
B6-P2-Fe1	58.55(7)	B7-P2-Fe1	103.14(8)
C4-B3-P2	109.75(14)	C5-C4-B3	113.58(17)
C4-C5-B6	113.68(17)	C5-B6-P2	109.38(14)

bisecting the C–C bond and intersecting the P2, B9, and B12 atoms. This structure is also in agreement with all NMR data for **4a**. The ^{11}B NMR spectrum of **4a** consists of five doublets with relative intensities of 1:2:1:2:2 (range 16.8 ppm). The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **4a** show two singlet resonances of relative intensities 5:2, which are assigned to Cp and two equivalent CH(4,5) units, respectively, and the mass spectrum shows the expected molecular ion.

In agreement with the asymmetrical structure, the ^{11}B NMR spectrum of **4b** consists of eight doublets of equal intensities (range 22.7 ppm). The ^{1}H{^{11}B} NMR spectrum of **4b** shows three singlet resonances with relative intensities of 5:1:1, which are assigned to Cp and two nonequivalent CH(4,8) units, respectively, and the mass spectrum shows the expected molecular ion.

Conclusion

It was demonstrated that the straightforward structural similarities between the tricarbaborane [7,8,9-$C_3B_8H_{12}$][4] and compound **1**[3] are also reflected in the formation of ferraphosphatricarbollide complexes, the counterparts of ferratricarbollides.[5, 13] We have also proved in this work that the ultimate η^5-complexation of the anionic *nido*-[7,9,10-$PC_2B_8H_{10}$]$^-$ ligand by the CpFe group proceeds via two isolable η^1-bonded P-substituted complexes **2** and **3**. As far as we are aware, this is a rare case in the area of cluster borane chemistry in which the intermediates along the η^5-complexation pathway have been isolated and characterized. As in the case of the isostructural tricarbaborane [7,8,9-$C_3B_8H_{12}$], [5] the η^5-complexation of **1** is accompanied by rearrangement of the cluster CH and P units, but no transient η^1 complexes have been isolated thus far in the corresponding tricarbaborane series. As the analogous tricarbollide anions of the *nido*-[$C_3B_8H_{11}$]$^-$ type[5, 13] the complexing anion *nido*-[7,9,10-$PC_2B_8H_{10}$]$^-$ is an analogue of Cp^-, as it contains a bare pentagonal face and is monoanionic, and complexes **4a** and **4b** are then analogues of ferrocene. From the viewpoint of cluster borane chemistry, both complexes **4a** and **4b** contain four heteroatom vertices in different positions of a twelve-vertex *closo* cage, and there is no doubt that other isomeric structures will be possible. Relevant experiments on various thermal rearrangement reactions of these compounds in with the aim of isolating isomeric species are in progress.

Experimental Section

General procedures: All reactions were carried out by using standard vacuum or inert-atmosphere techniques as described by Shriver and Drezdon,[14] although some operations, such as column liquid chromatography, were carried out in air. The starting phosphacarborane **1** was prepared according to reference [3]. Dichloromethane, cyclohexane, hexane, and aromatic solvents (Fluka) were dried over CaH_2 and freshly distilled before use. Other chemicals were reagent or analytical grade and were used as purchased. Column chromatography was carried out using silica gel (Aldrich, 130–270 mesh) as the stationary phase. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (silica gel on aluminum foil; detection by diiodine vapor, followed by 2% aqueous $AgNO_3$ spray). Melting points were measured in sealed capillaries under argon and are uncorrected. Low-resolution mass spectra were obtained by using a Finnigan MAT MAGNUM ion trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basel, Switzerland (70 eV, EI ionization). Proton (^{1}H) and boron (^{11}B), and phoshorus (^{31}P) NMR spectroscopy was performed at 11.75 and 5.88 Tesla on Varian XL-500, and ARX 250 instruments, and the ^{13}C NMR spectra were measured on a Bruker DRX 500 spectrometer, equipped for heteronuclear ^{13}C{^{1}H,^{11}B} triple resonance experiments. The [^{11}B–^{11}B]-COSY[15] and ^{1}H-{^{11}B(selective)}[16] NMR experiments were carried out as described in other related papers from our laboratories.[17] Chemical shifts are given in ppm to high-frequency (low field) of $X = 32.083971$ MHz (nominally $F_3B \cdot OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm), $X = 25.145004$ MHz ($SiMe_4$) for ^{13}C (quoted ±0.5 ppm), $X = 40.4807477$ MHz (H_3PO_3) for ^{31}P (quoted ±0.5 ppm), and $X = 100$ MHz ($SiMe_4$) for ^{1}H (quoted ±0.05 ppm), X being defined as in reference [18]. Solvent resonances were used as internal secondary standards. Coupling constants $^{1}J_{B,H}$ are taken from Gauss-enhanced ^{11}B spectra and are given in Hz (±8 Hz). The ^{11}B and ^{1}H NMR spectra of all phosphacarborane compounds discussed in this work can be easily assigned by using two-dimensional [^{11}B–^{11}B]-COSY spectroscopy[15] combined with ^{1}H{^{11}B(selective)}[16] measurements. Moreover, all ^{1}H{^{11}B} resonances of individual BH and CH vertices adjacent to the cluster P vertex are mostly split into doublets due to ^{2}J(P,H) coupling, which faciliates the assignment of all cluster resonances. IR spectra were obtained on a EU 9512 Pye-Unicam Fourier transform spectrometer.

[7-Fp-(η^1-*nido*-7,8,9-$PC_2B_8H_{10}$)] (2): A solution of compound **1** (342 mg, 2.24 mmol) in benzene (30 mL) was treated with [{$CpFe(CO)_2$}$_2$](850 mg, 2.40 mmol) and the mixture was heated under reflux for three days. The benzene was removed by evaporation, the residue dissolved in CH_2Cl_2 (20 mL), and this solution was filtered through a short silica gel column. The eluted solution was evaporated, and the residual mixture was separated on a silica gel column (30 × 2.5 cm) by using a mixture of CH_2Cl_2 and cyclohexane (10:3, v/v) as the mobile phase. The main yellow band of $R_f = 0.3$ was collected and evaporated to dryness to isolate a light yellow solid (yield 320 mg, 38%). The product was obtained as light yellow needles by diffusion of hexane vapors into a toluene solution. For **2**: m.p. 170 °C, ^{11}B NMR (160.4 MHz, CD_2Cl_2, 25 °C): $\delta = -4.7$ (d, ^{1}J(B,H) = 131 Hz, 1B; B6), −7.0 (d, ^{1}J(B,H) = 124 Hz, 1B; B10), −13.1 (d, 1B; B11), −14.2 (d, 1B; B4), −18.5 (d, 1B; B5), −19.4 (d, 2B; B2,3), −40.9 ppm (d, ^{1}J(B,H) = 146 Hz, 1B; B1), all theoretical [^{11}B–^{11}B]-COSY crosspeaks observed, except for B2–B11, B5–B10, and B6–B11; ^{1}H{^{11}B}NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 5.32$ (s, 5H; Cp), 2.38 (s, 1H; H9), 2.06 (s, 2H; H4,6), 1.96 (d, ^{2}J(P,H) = 13.1 Hz, 1H; H8), 1.93 (s, 1H; H10), 1.84 (d, ^{2}J(P,H) = 14.2 Hz, 1H; H2 or 3), 1.44 (s, 1H; H5), 1.30 (d, ^{2}J(P,H) = 26 Hz, 1H; H11), 1.27 (s, 1H; H2 or 3), 0.98 ppm (s, 1H; H1); ^{13}C{^{1}H }NMR (125.7 MHz, CD_2Cl_2, 25 °C): $\delta = 208.6$ (d, ^{2}J(C,P) = 20.6 Hz, 1C; CO), 208.4 (d, ^{2}J(C,P) = 18 Hz, 1C; CO), 87.1 (d, ^{2}J(C,P) = 2.4 Hz, 5C; Cp), 48.4 (d, ^{1}J(C,P) = 23.4 Hz, 2C; C8), 37.8 ppm (d, ^{2}J(C,P) = 1.7 Hz, 1C; C9); ^{31}P{^{1}H }NMR (202.4 MHz, CD_2Cl_2, 25 °C): $\delta = -51.8$ ppm (s, 1P; P7); IR (KBr): $\tilde{\nu} = 3111$ (CH(Cp)), 3045, 3032 (CH(cage)) 2510, 2545, 2575, 2596, 2625 (BH), 2057, 2014 (CO), 1427, 1420, 1115 (CC(Cp)), 1013

(δ(CH(Cp))), 810 (γ(CH(Cp))) cm^{-1}; MS (70 eV, EI): *m/z* (%): 275 (6) [$M - 2$CO]$^+$, 273 (85) [$M - 2$CO $- 2$H]$^+$; elemental analysis calcd (%) for $C_9H_{15}B_8O_2PFe$ (328.57): C 32.90, H 4.60; found: C 34.05, H 4.88.

Complexation of *nido*-[7,8,9-PC$_2$B$_8$H$_{11}$] (1) with [{CpFe(CO)$_2$}$_2$]: A solution of compound **1** (270 mg, 1.75 mmol) in xylene (20 mL) was treated with [{CpFe(CO)$_2$}$_2$] (850 mg, 2.40 mmol) and the mixture was heated under reflux for 24 h. The xylene was removed by evaporation, the residue dissolved in CH_2Cl_2 (20 mL), and this solution was filtered through a short silica gel column. The eluted solution was evaporated and the residual mixture was separated on a silica gel column (30 × 2.5 cm) by using hexane as the mobile phase. The purity of individual fractions was checked by analytical TLC and ^{11}B NMR spectroscopy. After repeated chromatographic purification, the following compounds were isolated after evaporation and vacuum drying at ambient temperature: dark orange **4a** (crystallized from CH_2Cl_2, yield 143 mg, 30%) orange **4b** (crystallized by slow evaporation of a concentrated hexane solution, yield 24 mg, 5%) and dark red **3** (crystallized by diffusion of hexane vapors into a toluene solution, yield 162 mg, 28%). **3**: R_f (hexane) 0.10; m.p. 140 °C; ^{11}B NMR (160.4 MHz, $CDCl_3$, 25 °C): $\delta = -13.25$ (d, 2B; B4,6), -14.5 (d, 1B; B5), -16.2 (d, 2B; B2,3), -16.7 (d, 2B; B8,11), -43.5 ppm (d, ^1J(B,H) = 146 Hz, 1B; B1), all theoretical [^{11}B–^{11}B]-COSY cross-peaks observed. ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 5.18$ (s, 5H; Cp), 2.24 (s, 2H; H9,10), 2.15 (s, 1H; H5), 1.88 (s, 2H; H2,3), ~1.80 (s, 2H; H8,11), 1.74 ppm (s, 2H; H4,6); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 208.6$ (d, ^2J(C,P) = 20.5 Hz, 2C; CO), 88.5 (s, 5C; Cp), 46.1 ppm (d, ^1J(C,P) = 47.4 Hz, 2C; C9,10); ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 25 °C): $\delta = -103.2$ ppm (s, 1P; P7); IR (KBr): $\tilde{\nu} = 3112$ (CH(Cp)), 2552 (BH), 2056, 2020 (CO), 1420, 1108 (CCCp), 1010 (δ(CH(Cp))), 846 (δ(CH(Cp))) cm^{-1}; MS (70 eV, EI): *m/z* (%): 275 (10) [$M - 2$CO]$^+$, 273 (50) [$M - 2$CO $-$ 2H]$^+$; elemental analysis calcd (%) for $C_9H_{15}B_8O_2PFe$ (328.57): C 32.90, H 4.60; found: C 33.21, H 4.81.

4a: R_f (hexane) 0.43; m.p. 175 °C; ^{11}B NMR (160.4 MHz, $CDCl_3$, 25 °C): $\delta = -3.1$ (d, ^1J(B,H) = 150 Hz, 1B; B12), -12.4 (d, ^1J(B,H) = 162 Hz, ^1J(B,P) = 38 Hz, 2B; B3,6), -14.0 (d, ^1J(B,H) ≈ 154 Hz, 1B; B9), -14.8 (d, ^1J(B,H) ≈ 140 Hz, 2B; B7,11), -19.85 ppm (d, ^1J(B,H) = 162 Hz, 2B; B8,10), all theoretical [^{11}B–^{11}B]-COSY cross-peaks observed; ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 4.95$ (s, 5H; Cp), 3.30 (s, 1H; H12), 2.56 (d, ^2J(P,H) = 23.0 Hz, 2H; H3,6), 2.20 (s, 1H; H9), 1.65 (s, 2H; H8,10), 1.55 (s, 2H; H4,5), 1.53 (d, ^2J(P,H) = 27.0 Hz, 2H; H7,11); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 79.2$ (s, 5C; Cp), 50.0 (s, 2C; C4,5); ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 25 °C): $\delta = -14.5$ (s, 1P; P2); IR (KBr): $\tilde{\nu}$2924 (CH), 2552 (BH) cm^{-1}; MS (70 eV, EI): *m/z* (%): 275 (5) [M]$^+$, 273 (55) [$M - 2$H]$^+$; elemental analysis calcd (%) for $C_7H_{15}B_8PFe$ (272.54): C 30.85, H 5.55; found: C 31.20, H 5.61.

4b: R_f (hexane) 0.40; m.p. 178 °C; ^{11}B NMR (160.4 MHz, $CDCl_3$, 25 °C): $\delta = -0.8$ (d, ^1J(B,H) = 140 Hz, 1B; B6), -6.3 (d, ^1J(B,H) ≈ 160 Hz, 1B; B5), -7.6 (d, ^1J(B,H) = 177 Hz, 1B; B12), -10.5 (d, ^1J(B,H) = 169 Hz, 1B; B9), -12.5 (d, ^1J(B,H) ≈ 150 Hz, ^1J(B,P) = 46 Hz, 2B; B3,11), -13.4 (d, ^1J(B,H) ≈ 145 Hz, 1B; B10), -23.5 ppm (d, ^1J(B,H) = 169 Hz, ^2J(B,P) = 42 Hz, 1B; B7), all theoretical [^{11}B–^{11}B]-COSY cross-peaks observed; ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 4.86$ (s, 5H; Cp), 3.47 (s, 1H; H4 or 8), 3.38 (s, 1H; H5), 3.17 (s, 1H; H12), 2.77 (s, 1H; H4 or 8), ~2.58 (s, ^2J(P,H) = 20 Hz, 2H; H3,11), 2.25 (d, ^2J(P,H) = 28 Hz, 1H; H6), 1.99 (s, 1H; H10), 1.76 ppm (d, ^2J(P,H) = 22 Hz, 1H; H7); ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 25 °C): $\delta = -34.3$ (s, 1P; P2); IR (KBr): $\tilde{\nu} = 2928$ (CH), 2549 (BH) cm^{-1}; MS (70 eV, EI): *m/z* (%): 275 (6) [M]$^+$, 273 (60) [$M - 2$H]$^+$; elemental analysis calcd (%) for $C_7H_{15}B_8PFe$ (272.54): C 30.85, H 5.55; found: C 31.24, H 5.70.

Thermal decomposition of [7-Fp-(η^1-*nido*-7,8,9-PC$_2$B$_8$H$_{10}$)] (2): A solution of compound **2** (132 mg, 0.4 mmol) in xylene (10 mL) was heated at reflux for 24 h. The xylene was then evaporated and the residue subjected to column (1 × 40 cm) chromatography on a silica gel support. Repeated elution with hexane gave finally three fractions of R_f 0.43 (orange), 0.40 (orange), and 0.10, from which compounds **4a** (50 mg, 46%), **4b** (5 mg, 4%), and **3** (7 mg, 10%) were isolated on evaporation and drying in vacuo at ambient temperature, and identified by ^{11}B NMR spectroscopy.

Thermal decomposition of [7-[Fp]-η^1-*nido*-7,9,10-PC$_2$B$_8$H$_{10}$] (3): A solution of compound **3** (66 mg, 0.2 mmol) in xylene (10 mL) was heated at reflux for 24 h. The xylene was then evaporated and the residue subjected to column (1 × 40 cm) chromatography on a silica gel support. Repeated elution with hexane gave finally two fractions of R_f 0.43 (orange) and 0.40 (orange), from which compounds **4a** (28 mg, 52%) and **4b** (3 mg, 5%) were isolated on evaporation and drying in vacuo at ambient temperature, and identified by ^{11}B NMR spectroscopy.

X-ray crystallography: A colorless crystal of compound **4a** of dimensions 0.30 × 0.2 × 0.15 mm was mounted on a glass capillary with epoxy glue and measured on a Nonius KappaCCD diffractometer using monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. The absorption was neglected. The crystallographic details are summarized in Table 1 and selected interatomic distances are in Table 2. The structure was solved by direct methods (SIR93)[19] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97).[20] The cyclopentadienyl carbon atoms are disordered at least into two positions mutually rotated by about 20° and restricted in idealized geometry during refinement. Cage hydrogen atoms were localized on a difference Fourier map and refined isotropically. The final difference map had no peaks of chemical significance. Scattering factors were those implemented in the SHELXL97. CCDC-199900 contains the supplementary crystallographic data for this paper. These can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033 or: deposit@ccdc.cam.ac.uk).

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