

Phosphadiborababorane Analogues of Ferrocene: New Isomers of [*closo*-(η^5 -C₅H₅)FePC₂B₈H₁₀]

Bohumil Štíbr,^{*,[a]} Josef Holub,^[a] Mario Bakardjiev,^[a] Ivan Pavlík,^[b] Oleg L. Tok,^[c] and Bernd Wrackmeyer^[c]

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Thermal isomerisation of the ferraphosphadiborababorane [1-Cp-*closo*-1,2,4,5-FePC₂B₈H₁₀] (**1a**; Cp = η^5 -C₅H₅⁻) at elevated temperatures (180–350 °C) leads to the formation of three new isomeric complexes. These were characterized by multinuclear (¹H, ¹¹B, ³¹P, and ¹³C) NMR spectroscopy and mass spectrometry as [1-Cp-*closo*-1,2,3,8-FePC₂B₈H₁₀] (**1b**), [1-Cp-*closo*-1,10,2,4-FePC₂B₈H₁₀] (**1c**), and *closo*-[1,2,4,10-FePC₂B₈H₁₀] (**1d**). The formation of **1b** is accompanied by an unusual agglomeration of the P and C heteroatoms. Com-

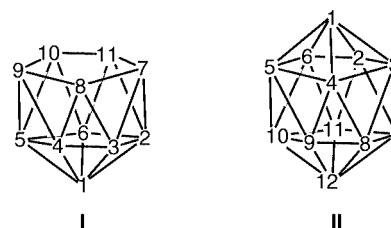
plexes **1b** and **1c** have also been isolated as side products from the direct reaction between *nido*-[7,8,9-PC₂B₈H₁₁] (**2**) and [CpFe(CO)₂]₂ in refluxing mesitylene, and **1a** and **1b** from the pyrolysis of [7-Fp-(η^1 -*nido*-7,9,10-PC₂B₈H₁₀)] (**3**; Fp = CpFe(CO)₂) at 350 °C. NMR intercomparisons of all five [1-Cp-*closo*-FePC₂B₈H₁₀] isomers thus far isolated have been made.

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Introduction

We have recently been interested in the synthesis and chemistry of the eleven-vertex *nido* phosphadiboraboranes (phosphadiborabollides), which are analogues of tricarbollides.^[1] In this field of boron cluster chemistry we have reported the synthesis of the two isomeric neutral compounds 7,8,11-PC₂B₈H₁₁ and 7,8,9-PC₂B₈H₁₁.^[2,3] Deprotonation of these compounds gave the corresponding anions [7,8,11-PC₂B₈H₁₀]⁻ and [7,8,9-PC₂B₈H₁₀]⁻.^[2,3] These anions can be regarded as Cp analogues as they are monoanionic and contain an open pentagonal face^[1] capable of donating five electrons in an η^5 -type coordination to metal fragments. This analogy was demonstrated just recently by the complexation of *nido*-7,8,9-PC₂B₈H₁₁ with [CpFe(CO)₂]₂ resulting ultimately in the synthesis of the first two representatives of the [1-Cp-*closo*-FePC₂B₈H₁₀] series (compounds

1a and **1e**). These compounds are the first phosphadiboraborane analogues of ferrocene. It was demonstrated that their formation proceeds via two isolable η^1 -bonded, P-substituted complexes of general formula [Fp-*nido*-(η^1 -PC₂B₈H₁₀)].^[4] By analogy with dicarbollide^[5] and tricarbollide complexes,^[6] the complexes **1a** and **1e** were expected to undergo cluster rearrangement by migration of the heteroatomic CH and P cage units at higher temperatures to form further [1-Cp-*closo*-FePC₂B₈H₁₀] isomers. We report in this paper several variations of reactions from which we have isolated another three isomers of this constitution. The numbering system for the eleven-vertex *nido* and twelve-vertex *closo* skeletons used in this work is shown in structures **I** and **II**. These structures are presented in a simplified manner; unmarked vertices in the schemes stand for cluster BH units, while C and P denote CH and bare phosphorus vertices, respectively. For convenience, the Fe atom in structures of type **1** is numbered first, followed by P and C vertexes.



[a] Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic (Research Center for New Inorganic Compounds and Advanced Materials, University of Pardubice), 25068 Rez, Czech Republic
Fax: (internat.) + 420-220/941-502
E-mail: stibr@iic.cas.cz

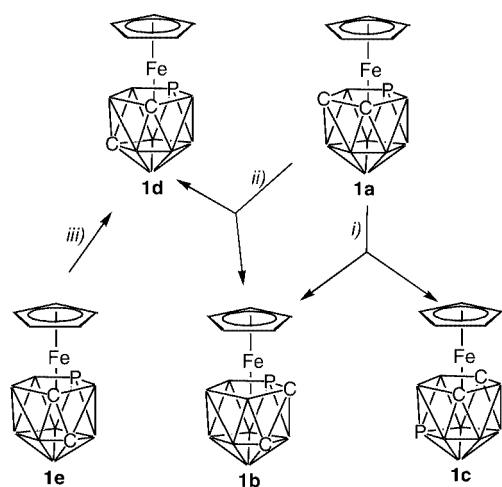
[b] University of Pardubice, Department of General and Inorganic Chemistry (Research Center for New Inorganic Compounds and Advanced Materials), 53210 Pardubice, Czech Republic
Fax: (internat.) + 420-4/603-7068
E-mail: koanch.fcht@upce.cz

[c] Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 101251, 95440 Bayreuth
Fax: (internat.) + 49-921/552-157
E-mail: B.Wrack@uni-bayreuth.de

Results and Discussion

Syntheses

As shown in path i) of Scheme 1, prolonged heating of **1a** in mesitylene at reflux temperature produces the complexes [1-Cp-*closo*-1,2,3,8-FePC₂B₈H₁₀] (**1b**) and [1-Cp-*closo*-1,10,2,4-FePC₂B₈H₁₀] (**1c**) in yields of 15 and 13%, respectively. The conversion is, however, very slow and incomplete, and compound **1a** was recovered in 60% yield. The formation of **1b** from **1a** is very unusual as it is associated with the migration of one of the cage carbon atoms from the original *m*-position to the *o*-position with respect to the P center. Moreover, the second carbon atom is moved into the lower structural belt, to form a contiguous P–C–C string with a P–C bond in the pentagonal belt adjacent to the Fe center. The formation of **1c** from **1a** is associated with a migration of the P-vertex into an *m*-position with respect to the Fe center and *m*-separation of the C-vertices within the pentagon adjacent to the Fe atom to achieve a maximum space separation of the P and C vertices, a feature encountered in the isoelectronic [1-Cp-*closo*-1,2,4,10-FeC₃B₈H₁₁] tricarbollide series.^[7] A different type of maximum separation of the C and P heteroatoms is encountered in the isomer [1-Cp-*closo*-1,2,4,10-FePC₂B₈H₁₀] (**1d**). As shown in path ii) of Scheme 1, this complex was isolated in a yield of 23%, together with the isomer **1b** (yield 52%), from thermal rearrangement of **1a** at 350 °C. The result of the **1a** → **1d** rearrangement is a movement of the one of the C vertices into an *m*-position with respect to both C and P atoms in the lower belt near B(12). Moreover, isomer **1d** was additionally obtained in a yield of 51% by the thermolysis of **1e**^[4] at 350 °C (see path iii) of Scheme 1), the rearrangement being associated with a migration of one carbon vertex into or within the pentagonal belt connected to the B(12) atom.



Scheme 1. i) mesitylene, reflux, 3 hours. ii), iii) 350 °C, 2 hours

Complexes **1b** and **1c** can also be obtained directly from the phosphadecarborane **2** by treatment with [CpFe(CO)₂]₂ in refluxing mesitylene (two days). The main products isolated from this reaction were, however, the pre-

viously reported^[4] compounds **1a** (yield 33%) and **3** (yield 28%); nevertheless, the reaction is accompanied by the formation of the isomeric complexes **1b** and **1c** (yields 10 and 7%, respectively). Alternatively, complex **1b** was also generated (yield 23%), together with compound **1a**^[4] (yield 52%), by heating the *nido* compound **3**^[4] at 350 °C in vacuo. It is obvious that complexes **1b** and **1c** in these experiments have been formed by rearrangement of **1a** as in path i) of Scheme 1. All the new isomeric complexes **1b–1d** are orange or dark orange compounds that are remarkably stable in air.

Structural Studies

Even though we were able to grow crystals of almost all new complexes of type **1**, the structural determinations of these species were unsuccessful owing to disorder problems encountered during structure solution. Nevertheless, the constitution of all new isomers **1b–1d** could be easily derived from multinuclear NMR (¹H, ¹¹B, ³¹P, and ¹³C) and two-dimensional [¹¹B-¹¹B]-COSY NMR measurements^[8] combined with ¹H{¹¹B(selective)} experiments,^[9] and the interpretation of the data led to complete assignments of all resonances to individual BH, CH, and P vertices. The mass spectra of compounds **1b–1d** exhibit the same molecular cut-off at *m/z* = 275, as expected for the identical molecular formulation. Some absorption bands in the IR spectra have been assigned to BH and CH vibrations.

The ¹¹B NMR spectra of all five isomers of general constitution **1** thus far isolated are depicted graphically in Figure 1 as simplified stick diagrams indicating the ¹¹B chemical shifts and relative intensities. The ¹¹B resonances fall within a relatively narrow span (ca. 20 ppm), which corresponds well to that of the isostructural [1-Cp-*closo*-FeC₃B₈H₁₁] compounds and their amino derivatives (also ca. 20 ppm).^[1,7] The ¹¹B resonances of the BH units adjacent to the P vertex are generally either split into a doublet or at least broadened owing to unresolved ³¹P-¹¹B scalar coupling. As shown in Figure 2, the ³¹P resonances are very sensitive to structural changes among individual isomers of general formula **1**. The ³¹P resonances of the isomers containing the Fe–P bond (**1a**, **1b**, **1d**, and **1e**) fall within a range of ca. δ = +20 to –45 ppm, while the ³¹P(10) resonance in **1c** is shifted to low frequency (δ³¹P = –166 ppm), to a range typical of phosphorus in polyhedral boranes with a *closo* structure.^[10] Therefore, the ³¹P NMR signals at higher frequencies in the range of δ = +20 to –55 ppm are a consequence of Fe–P bonding. As expected, the ¹H and ¹³C{¹H} NMR chemical shifts associated with the Cp ring are not significantly affected by structural changes in the phosphadecarborane cage.

As shown in Figure 1, the ¹¹B NMR spectra of the C_s-symmetric isomers **1a**^[4] and **1c** consist of 1:2:1:2:2 patterns of doublets, which is consistent with a plane of symmetry intersecting the Fe(1), B(or P)(10), and B(12) vertices. The spectra of **1a**^[4] and **1c** are very similar to those of their tricarbollide congeners [1-Cp-*closo*-1,2,4,5-FeC₃B₈H₁₁] (**4a**)^[11] and [1-Cp-*closo*-1,2,4,10-FeC₃B₈H₁₁] (**4b**),^[7] except that the spectra of the ferraphosphadecarborallides are shifted

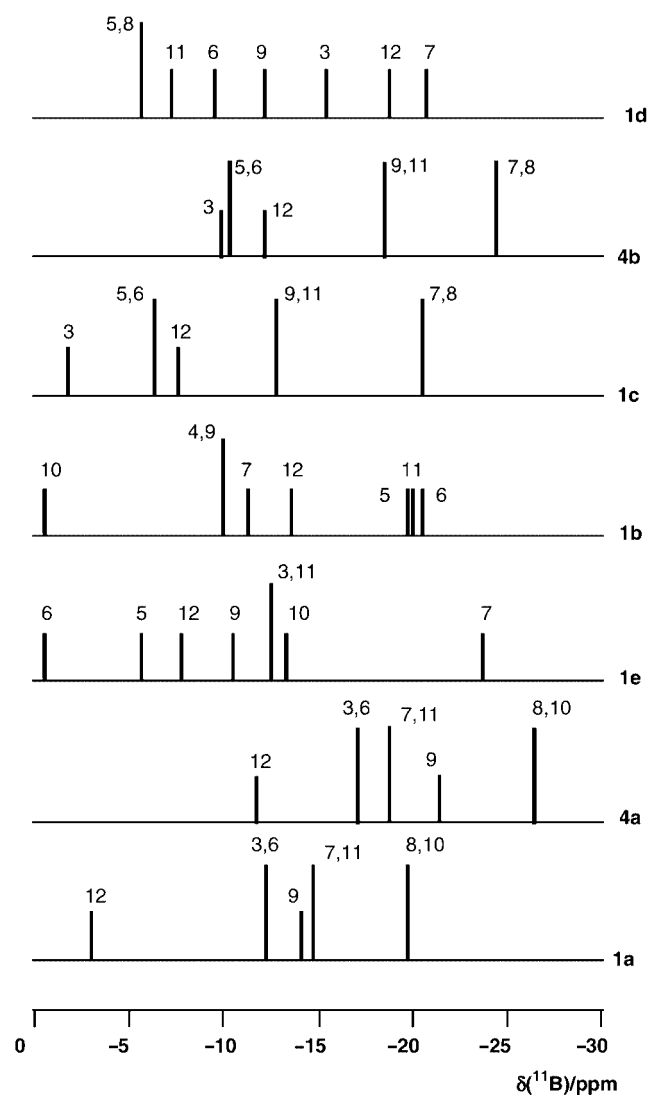


Figure 1. Simplified stick diagrams showing intercomparison of the ^{11}B NMR chemical shifts and relative intensities for all known ferraphosphadecarbollide $[1\text{-Cp-closo-FePC}_2\text{B}_8\text{H}_{10}]$ (**1**) isomers with those for selected isostructural ferratricarbollides $[1\text{-Cp-closo-FeC}_3\text{B}_8\text{H}_{11}]$ (**4**); data for **1a** and **1e** from ref.^[4] and data for **4a** and **4b** from refs.^[7,11]

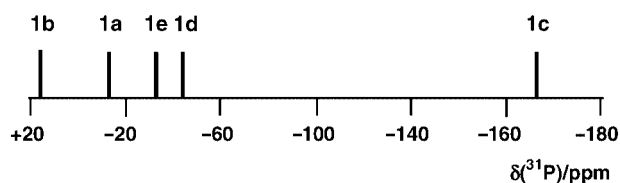


Figure 2. Stick representation of the ^{31}P NMR chemical shifts for all known ferraphosphadecarbollide $[1\text{-Cp-closo-FePC}_2\text{B}_8\text{H}_{10}]$ (**1**) isomers; data for **1a** and **1e** from ref.^[4]

downfield ($\Delta\delta = \text{ca. } 5 \text{ ppm}$). In agreement with the existence of the symmetry plane, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1c** show two singlet resonances of integral intensities 5:2, assigned to Cp and two equivalent CH(2,4) units, respectively. As expected for the asymmetric derivatives **1b**, **1d**, and **1e**,^[4] their ^{11}B NMR spectra are characterized by eight different resonances some of which overlap. The ^1H

and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these asymmetrical isomers contain three resonances of relative areas 5:1:1 attributed to Cp and two different cage CH units. In the case of **1b**, which is a single isomer containing a P–C bond, one of the CH resonances shows distinct $^2J_{\text{P,H}}$ and $^1J_{\text{P,C}}$ doublet splittings.

Conclusions

We have demonstrated that another three structurally diverse isomers of general *closo* ferraphosphadecarbollide structure **1** can be isolated from various high-temperature reactions involving – directly or indirectly – the previously reported isomer **1a**.^[4] There is no doubt that the separation of carbon atoms is not the only driving force responsible for the observed rearrangements, as the isomer **1b**, containing a contiguous P–C–C string, is formed as the main kinetic product. This fact is in sharp contrast to the rearrangements of the structurally related ferratricarbollide complexes^[6,7] and to those of the $[\text{CpCoC}_2\text{B}_9\text{H}_{11}]$ cobaltadecarbollides as well.^[5] The isomerisations leading to **1b–1d** can be explained by the triangular-face rotation mechanism,^[12] although the participation of other mechanisms (diamond-square-diamond,^[13] pyramidal rotation,^[14] and Lipscomb's hybrid^[15]), cannot be excluded. It should also be noted that all the complexes isolated contain at least one heteroatom on the coordinating face and, in comparison with complexes of the $[\text{CpCoC}_2\text{B}_9\text{H}_{11}]$ series,^[5] no $[\text{CpFePC}_2\text{B}_8\text{H}_{10}]$ isomer containing P or C heteroatoms in position 12 (*para* with respect to the Fe center) has been formed. These will probably be formed at temperatures higher than 400–500 °C; application of such severe conditions led to complete decomposition. The isomeric complexes of structure **1** are expected to undergo various substitution reactions either on the cluster atoms or the Cp ring, which might generate interesting substitution derivatives. Also, application of boron or carbon degradation reactions is expected to lead to other structurally interesting smaller-cage ferraphosphacarborane systems. These and related reactions aimed at establishing reactivity systemization within a series of phosphacarborane analogues of ferrocene are in progress.

Experimental Section

General Procedures: All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,^[16] although some operations, such as column LC, were carried out in air. The starting compounds **1a**, **1e**, **2**, and **3** were prepared according to the literature.^[3,4] Dichloromethane, hexane, and mesitylene (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 iodine vapor, followed by 2% aqueous AgNO_3 spray). Melting points were measured in sealed capillaries under argon and are un-

corrected. Multinuclear (^1H , ^{11}B , ^{31}P , and ^{13}C) NMR and IR spectroscopy, and mass spectrometry have been performed essentially with the instrumentation described in other related papers from our laboratories.^[4,17]

[1-Cp-1,2,3,8-FePC₂B₈H₁₀] (1b) and [1-Cp-1,10,2,4-FePC₂B₈H₁₀] (1c): a) A solution of compound **1a** (100 mg, 0.36 mmol) in mesitylene (20 mL) was heated under reflux for three days. Most of the mesitylene was removed by evaporation and the mixture was then worked up by repeated chromatography on a silica gel column (40 × 1.5 cm) using hexane as a mobile phase to collect three main fractions of R_f (hexane) 0.60, 0.50, and 0.43, from which complexes **1c** (13 mg, 13%), **1b** (15 mg, 15%), and the starting compound **1a** (60 mg, 60%) were isolated, respectively, by evaporation of the solvent and identified by ^{11}B NMR spectroscopy.

1c: R_f (hexane) 0.60. M.p. 80 °C. $^1\text{H}\{^{11}\text{B}\}$ NMR (CDCl_3): δ = 4.81 (s, 5 H, Cp), 3.14 (d, $^2J_{\text{P,H}}$ = 24 Hz, 2 H, H_{5,6}), 2.82 (d, $^2J_{\text{P,H}}$ = 23 Hz, 1 H, H₁₂), 2.50 (s, 2 H, H_{2,4}), 1.72 (s, 2 H, H_{7,8}), 1.70 (d, $^2J_{\text{P,H}}$ = 23 Hz, 2 H, H_{9,11}) ppm. ^{11}B NMR (CDCl_3): δ = -2.0 (d, $^1J_{\text{B,H}}$ = 166 Hz, 1 B, B₃), -6.4 (d, $^1J_{\text{B,H}}$ ≈ 160, $^1J_{\text{B,P}}$ = 35 Hz, 2 B, B_{5,6}), -7.5 (d, $^1J_{\text{B,H}}$ ≈ 160 Hz, 1 B, B₁₂), -15.4 (d, $^1J_{\text{B,H}}$ = 165 Hz, 2 B, B_{9,11}), -21.1 (d, $^1J_{\text{B,H}}$ = 161 Hz, 2 B, B_{7,8}) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = -166.2 (s, 1 P, P₁₀) ppm. IR (KBr): $\tilde{\nu}$ = 2924 (CH), 2580 (BH) cm^{-1} . MS (70 eV, EI), m/z (%) = 275 (5) [M]⁺, 273 (85) [$\text{M} - 2\text{H}$]⁺. C₇H₁₅B₈FeP (272.54): calcd. C 30.85, H 5.55; found C 30.98, H 5.70.

1b: R_f (hexane) 0.50. M.p. 180 °C. $^1\text{H}\{^{11}\text{B}\}$ NMR (CDCl_3): δ = 4.99 (s, 5 H, Cp), 4.21 (s, 1 H, H_{4 or 9}), 3.46 (s, 1 H, H₈), 3.41 (s, 1 H, H₁₀), 2.29 (s, 1 H, H_{4 or 9}), 2.23 (d, $^2J_{\text{P,H}}$ = 26 Hz, 1 H, H₇), 1.76 (s, 1 H, H₁₂), 1.52 (s, 1 H, H₅), 1.44 (d, $^2J_{\text{P,H}}$ = 26 Hz, 1 H, H₁₁), 1.94 (d, $^2J_{\text{P,H}}$ = 18 Hz, 1 H, H₃), 1.35 (d, $^2J_{\text{P,H}}$ = 15 Hz, 1 H, H₆) ppm. ^{11}B NMR (CDCl_3): δ = -0.9 (d, $^1J_{\text{B,H}}$ = 150 Hz, 1 B, B₁₀), -9.9 (d, $^1J_{\text{B,H}}$ ≈ 160 Hz, 2 B, B_{4,9}), -12.0 (d, $^1J_{\text{B,H}}$ = 162, $^1J_{\text{B,P}}$ = 36 Hz, 1 B, B₇), -13.7 (d, $^1J_{\text{B,H}}$ = 162 Hz, 1 B, B₁₂), -19.7 (d, $^1J_{\text{B,H}}$ = 162 Hz, 1 B, B₅), -20.0 (d, $^1J_{\text{B,H}}$ ≈ 160 Hz, 1 B, B₁₁), -21.6 (d, $^1J_{\text{B,H}}$ ≈ 160 Hz, 1 B, B₆) ppm. $^{13}\text{C}\{^1\text{H}, ^{11}\text{B}\}$ NMR (CDCl_3): δ = 80.4 (s, 5 C, Cp), 58.6 (s, 1 C, C₈), 45.8 (s, $^1J_{\text{C,P}}$ = 74 Hz, 1 C, C₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 17.7 (s, 1 P, P₂) ppm. IR (KBr): $\tilde{\nu}$ = 2925 (CH), 2548 (BH) cm^{-1} . MS (70 eV, EI), m/z (%) = 275 (5) [M]⁺, 273 (85) [$\text{M} - 2\text{H}$]⁺. C₇H₁₅B₈FeP (272.54): calcd. C 30.85, H 5.55; found C 31.20, H 5.73.

b) A solution of compound **2** (500 mg, 3.25 mmol) in mesitylene (20 mL) was treated with [CpFe(CO)₂]₂ (1500 mg, 4.23 mmol) and the mixture was heated under reflux for 24 h. Most of the mesitylene was removed by evaporation and the mixture was then worked up by repeated chromatography on a silica gel column (40 × 2.5 cm) using hexane as a mobile phase to isolate (ordered by decreasing R_f values) compounds **1c** (58 mg, 7%), **1b** (82 mg, 10%), **1a** (294 mg, 33%), and **3** (318 mg, 28%), which were identified by ^{11}B NMR spectroscopy.

c) Compound **3** (0.063 g, 0.19 mmol) was heated at 350 °C in an evacuated ampoule for 2 h. The melt was then cooled to ambient temperature and extracted with CH₂Cl₂ (2 × 10 mL). The extract was filtered, the solvents evaporated to dryness and the solid residue was separated by chromatography on silica gel in hexane. Two orange fractions of R_f = 0.50 and 0.43 were collected from which compounds **1b** (12 mg, 23%) and **1a**^[4] (27 mg, 52%) were isolated, respectively, after evaporation of the solvents and drying in vacuo at ambient temperature and identified by ^{11}B NMR spectroscopy.

[1-Cp-1,2,4,10-FePC₂B₈H₁₀] 1d: a) Compound **1a** (100 mg, 0.36 mmol) was heated at 350 °C in an evacuated ampoule for 2 h. The melt was then cooled to ambient temperature and extracted with CH₂Cl₂ (2 × 10 mL). The extract was filtered, the solvents

evaporated to dryness and the solid residue was separated by chromatography on silica gel in hexane. Two orange fractions of R_f = 0.60 and 0.50 were collected, from which compounds **1d** (12 mg, 23%) and **1b** (27 mg, 52%) were isolated, respectively, on evaporation of the solvents and drying in vacuo at ambient temperature.

1d: R_f (hexane) 0.60. M.p. 80 °C. $^1\text{H}\{^{11}\text{B}\}$ NMR (CDCl_3): δ = 4.84 (s, 5 H, Cp), 3.53 (s, 1 H, H_{5 or 8}), 3.27 (s, 1 H, H_{5 or 8}), 2.99 (s, 1 H, H_{4 or 10}), 2.81 (d, $^2J_{\text{P,H}}$ = 23 Hz, 1 H, H₁₁), 2.73 (s, 1 H, H₉), 2.36 (s, 1 H, H_{4 or 10}), 1.91 (d, $^2J_{\text{P,H}}$ = 18 Hz, 1 H, H₃), 1.85 (s, 1 H, H₁₂), 1.84 (d, $^2J_{\text{P,H}}$ = 16 Hz, 1 H, H₆), 1.58 (d, $^2J_{\text{P,H}}$ = 22 Hz, 1 H, H₇) ppm. ^{11}B NMR (CDCl_3): δ = -6.4 (d, $^1J_{\text{B,H}}$ ≈ 160 Hz, 2 B, B_{5,8}), -7.3 (d, $^1J_{\text{B,H}}$ ≈ 160 Hz, 1 B, B₁₁), -8.6 (d, 1 B, B₆), -12.1 (d, $^1J_{\text{B,H}}$ = 169 Hz, 1 B, B₉), -15.7 (d, $^1J_{\text{B,H}}$ = 166, $^1J_{\text{B,P}}$ = 31 Hz, 1 B, B₃), -18.2 (d, $^1J_{\text{B,H}}$ = 161 Hz, 1 B, B₁₂), -21.1 (d, $^1J_{\text{B,H}}$ = 158 Hz, 1 B, B₇) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 79.8 (s, 5 C, Cp), 49.5 (s, 1 C, C₁₀), 46.5 (s, 1 C, C₄). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = -41.3 (s, 1 P, P₂) ppm. IR (KBr): $\tilde{\nu}$ = 2924 (CH), 2580 (BH) cm^{-1} . MS (70 eV, EI), m/z (%) = 275 (5) [M]⁺, 273 (100) [$\text{M} - 2\text{H}$]⁺. C₇H₁₅B₈FeP (272.54): calcd. C 30.85, H 5.55; found C 31.25, H 5.69.

b) Compound **1e** (20 mg, 0.07 mmol) was heated at 350 °C in an evacuated ampoule for 2 h. The melt was then cooled to ambient temperature and extracted with CH₂Cl₂ (2 × 5 mL). The extract was filtered, the solvents evaporated to dryness and the solid residue was separated by chromatography on silica gel in hexane to isolate the main orange band of R_f = 0.60, from which compound **1d** (10.2 mg, 51%) was isolated after evaporation of the solvents and drying in vacuo at ambient temperature; it was identified by NMR spectroscopy.

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