THE FIRST METALLACARBORANE TRIPLE-DECKER COMPLEXES WITH A BRIDGING PENTAPHOSPHOLYL LIGAND

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Dedicated to Professor Bohumil Štíbr on the occasion of his 70th birthday in recognition of his outstanding contributions to boron chemistry.

Visible light irradiation of cations $[(Carb)Fe(\eta\text{-}C_6H_6)]^+$ in the presence of $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$ affords the μ-pentaphospholyl triple-decker complexes $[(Carb)Fe(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$ (Carb = 9-SMe_2-7,8-$C_2B_9H_{10}$ (**3a**) and 1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$ (**3b**)). Structures of **3a**- and **3b**$[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]$ were determined by X-ray diffraction. Bonding in **3a**, **3b** and mononuclear building blocks was analyzed by energy decomposition analysis.
Keywords: Boranes; Metallacarboranes; Iron; Sandwich compounds; Triple-decker complexes.

We have described previously the first examples of metallacarborane triple-decker complexes with a bridging cyclopentadienyl ligand $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Ni(\mu\text{-}\eta\text{:}\eta\text{-}Cp)NiCp]^+$ and $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Ni(\mu\text{-}\eta\text{:}\eta\text{-}Cp)\text{-}Ni(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^+$ [1]. A number of similar complexes were also synthesized with boron-containing heterocycles, borole C_4BH_5 [2], diborolyl $C_3B_2H_5$ [3], and triborole $C_2B_3H_5$ [4], which are capable to strong bifacial bonding with two metal atoms due to favorable balance of donor and acceptor properties. Phosphorus heterocycles also possess high propensity to bifacial coordination. In particular, reactions of pentaphosphametallocenes $Cp^*M(\eta\text{-}cyclo\text{-}P_5)$ with fragments $[M'Cp]^+$ (M, M′ = Fe, Ru) give the triple-

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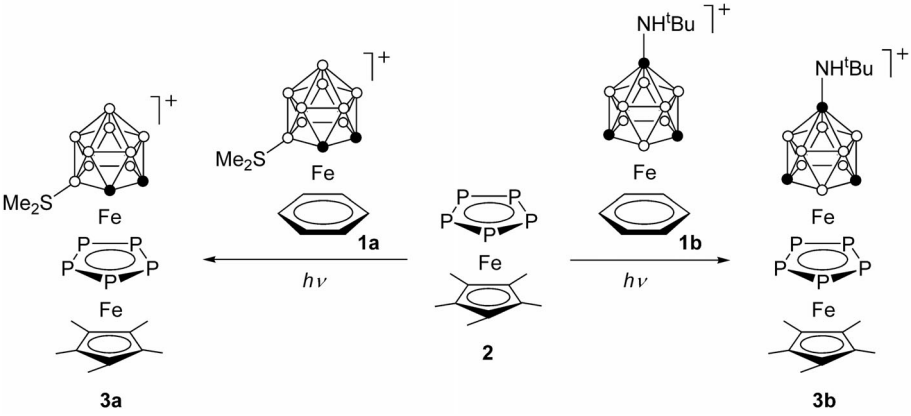
decker cations $[Cp^*M(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)M'Cp]^+$ [5]. Herein we report the synthesis and structures of the first metallacarborane triple-decker complexes with a bridging pentaphospholyl ligand *cyclo*-P_5. These compounds contain monoanionic carborane ligands, charge-compensated dicarbollide or tricarbollide. Basic chemistry of the latter was developed by Stibr in cooperation with others[6].

RESULTS AND DISCUSSION

Recently, we have shown that visible light irradiation of benzene complexes $[(Carb)Fe(\eta\text{-}C_6H_6)]^+$ (Carb = 9-SMe_2-7,8-$C_2B_9H_{10}$ (**1a**) and 1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$ (**1b**)) leads to the replacement of benzene by other ligands, such as isonitriles, phosphites, arenes and carborane anions[2c,7]. In the present work, we found that photochemical reactions of **1a** and **1b** with pentaphosphaferrocene $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$ (**2**) afford the cationic triple-decker complexes $[(Carb)Fe(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$ (**3a**, **3b**)[8] (Scheme 1).



SCHEME 1

Salts **3a**- and **3b**PF_6 are stable in air only for short periods of time and lose solubility after prolonged storage due to oxidation. In solutions in coordinating solvents (e.g. Me_2CO and MeCN) they undergo nucleophilic degradation with elimination of the $[Fe(Carb)]^+$ fragment giving **2**. Noteworthy, the carborane complexes **3a** and **3b** are more reactive than the cyclopentadienyl analogue $[CpFe(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$ (**4**), e.g. they are destroyed by acetonitrile within 24 h at room temperature, while degradation of **4** proceeds only at 80 °C.

The structures of **3a**- and **3b**[Co(η-7,8-$C_2B_9H_{11})_2$] were determined by X-ray diffraction. Two iron atoms are located between three cyclic frames (C_2B_3, P_5 and C_5) (Figs 1 and 2). In **3a** the P_5 cycle is disordered over three sites with site occupancies 0.40:0.35:0.25 due to rotation in plane around Fe1···Fe2 axis.

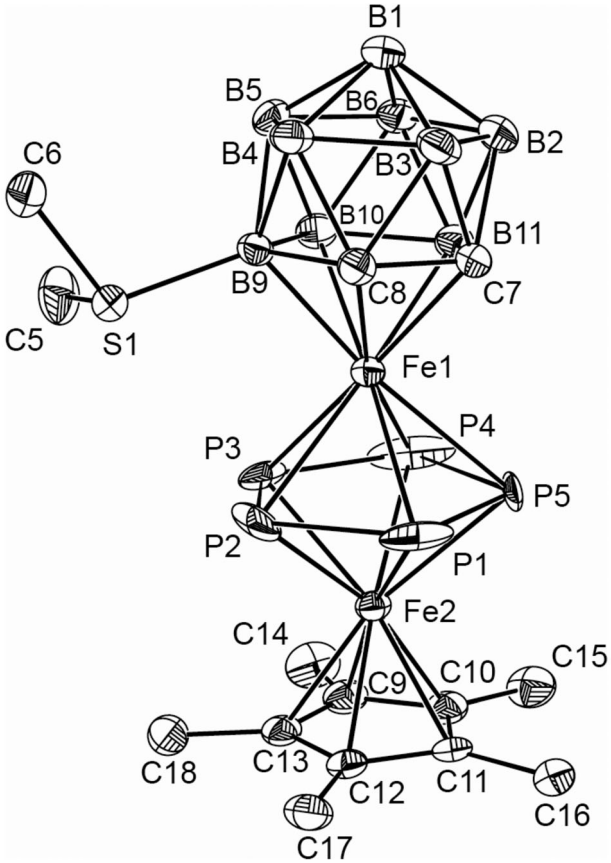


FIG. 1

Structure of cation **3a** (the first conformation of the disordered P_5-ring). Ellipsoids are shown at the 50% level. Selected bond lengths (in Å): Fe1–B9 2.132(2), Fe1–B10 2.185(2), Fe1–B11 2.126(2), Fe1–C7 2.089(2), Fe1–C8 2.097(2), Fe1–P2 2.396(9), Fe1–P3 2.404(9), Fe1–P4 2.379(10), Fe2–P2 2.330(12), Fe2–P3 2.304(7), Fe2–P5 2.348(7), Fe2–C9 2.097(2), Fe2–C10 2.100(2), Fe2–C11 2.093(2), Fe2–C12 2.088(2), Fe2–C13 2.100(2), P1–P2 2.09(3), P2–P3 2.10(3), P3–P4 2.092(15), P4–P5 2.107(12), P5–P1 2.21(2), C7–C8 1.607(3), B9–S1 1.928(2)

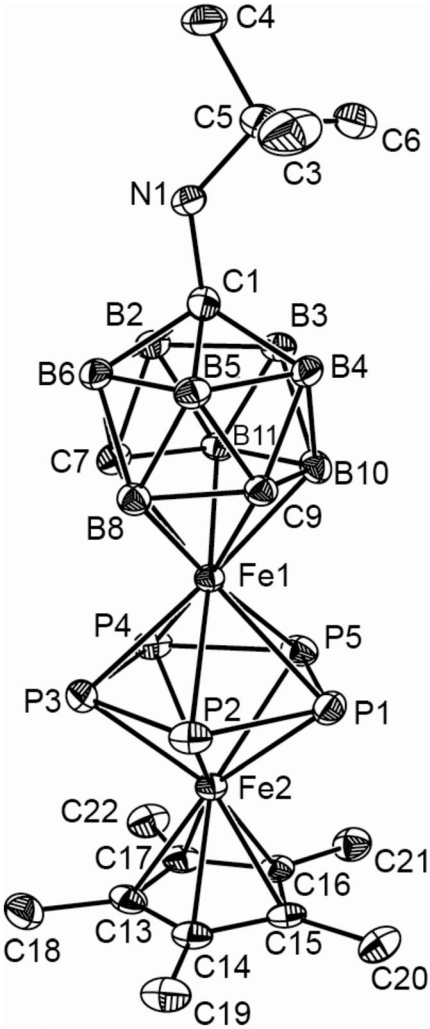


FIG. 2

Structure of cation **3b**. Ellipsoids are shown at the 50% level. Selected bond lengths (in Å): Fe1–B8 2.088(3), Fe1–B10 2.121(3), Fe1–B11 2.099(3), Fe1–C7 2.115(3), Fe1–C9 2.128(3), Fe1–P1 2.4259(8), Fe1–P2 2.4416(8), Fe1–P3 2.4172(8), Fe1–P4 2.4041(8), Fe1–P5 2.3937(8), Fe2–P1 2.3827(8), Fe2–P2 2.3906(8), Fe2–P3 2.3641(8), Fe2–P4 2.3611(8), Fe2–P5 2.3752(8), Fe2–C13 2.102(3), Fe2–C14 2.099(3), Fe2–C15 2.101(3), Fe2–C16 2.095(3), Fe2–C17 2.096(3), P1–P2 2.140(1), P2–P3 2.136(1), P3–P4 2.145(1), P4–P5 2.140(1), P5–P1 2.139(1), C1–N1 1.399(3)

The metal-to-ring Fe1···P_5 distances (av. 1.597 Å in **3a**, 1.589(8) Å in **3b**) are longer than Fe2···P_5 (av. 1.520 and 1.525(8) Å), suggesting weaker bonding of the *cyclo*-P_5 ligand with $[Fe(Carb)]^+$ fragments than with $[FeCp^*]^+$. This correlates with elimination of the $[Fe(Carb)]^+$ fragment upon nucleophilic degradation. In addition, the Fe1···P_5 distances in cations **3a** and **3b** are longer than Fe(Cp)···P_5 in the cyclopentadienyl analog $[CpFe(\mu\text{-}\eta\text{:}\eta\text{-}cyclo\text{-}P_5)Fe(\eta\text{-}C_5Me_4Et)]^+$ (av. 1.534 Å)[9] in accordance with higher reactivity of the carborane complexes **3a** and **3b** towards MeCN as compared with **4**.

Earlier, we have shown that the P–P bonds in μ-pentaphospholyl triple-decker complexes are longer than corresponding bonds in pentaphosphametallocenes by ca. 0.05 Å [5b]. However, in **3a** and **3b** these bonds (av. 2.115 Å in **3a**, 2.140 Å in **3b**) are close to those in $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$ (av. 2.120 Å)[10] in accordance with the weaker bonding of $[Fe(Carb)]^+$ fragments versus $[MCp]^+$ (vide infra).

Bonding Analysis

Bonding in the triple-decker complexes **3a**, **3b**, **4** and the corresponding mononuclear building blocks LFe(*cyclo*-P_5) were analyzed using energy decomposition analysis (EDA)[11]. According to the EDA method, the interaction energy between the bonding fragments ΔE_{int} can be divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb},$$

where ΔE_{elstat} is the electrostatic interaction energy between the fragments with a frozen electron density distribution, ΔE_{Pauli} presents the repulsive four-electron interactions between occupied orbitals (Pauli repulsion), and ΔE_{orb} refers to the stabilizing orbital interactions. The ratio $\Delta E_{elstat}/\Delta E_{orb}$ indicates the electrostatic/covalent character of the bond. The bond dissociation energy:

$$D_e = -(\Delta E_{int} + \Delta E_{prep}),$$

where ΔE_{prep} (the fragment preparation energy) is the energy that is necessary to promote the fragments from their equilibrium geometry and electronic ground state to the geometry, and electronic state that they have in the optimized structure. This method has already proven its usefulness for

the analysis of the nature of metal–ligand bonding in ferrocene and some other sandwich compounds[7c,12].

The EDA data for complexes **3a**, **3b** and **4** in terms of interactions $[Fe(L)]^+$ + (*cyclo*-P_5)FeCp* or $[FeCp^*]^+$ + (*cyclo*-P_5)Fe(L) (corresponding to the first and second bonds) are given in Table I. In complexes **3a** and **3b**, the interaction energy (ΔE_{int}) between the ferracarborane cations $[Fe(Carb)]^+$ and pentaphosphaferrocene **2** is lower than between $[FeCp^*]^+$ and (*cyclo*-P_5)Fe(L) by 6–7 kcal mol^{-1}. The dissociation energy (D_e) of the first bond is lower by ca. 11 kcal mol^{-1} than that of the second one. The larger difference between D_e values is caused by higher preparation energies in the case of the bond with ferracarborane fragments. This correlates with elimination of the $[Fe(Carb)]^+$ fragment upon nucleophilic degradation and longer Fe1···P_5 distances than Fe2···P_5 (vide supra). Interestingly, the attractive orbital interaction (ΔE_{orb}) is almost equal for both bonds. The lower ΔE_{int} value for the first bond results from the difference in the electrostatic attraction (ΔE_{elstat}) and the Pauli repulsion (ΔE_{Pauli}).

The ΔE_{int} and D_e values for the first bond in the metallacarborane complexes **3a** and **3b** are lower than those in the cyclopentadienyl analog **4** by ca. 20 and 25–29 kcal mol^{-1}, respectively. This correlates with easier nucleophilic degradation of cations **3a** and **3b**, and elongation of the

TABLE I
Results of EDA (energy values in kcal mol^{-1}) for complexes **3a**, **3b** and **4** using $[Fe(L)]^+$ + (*cyclo*-P_5)FeCp* or $[FeCp^*]^+$ + (*cyclo*-P_5)Fe(L) as interacting fragments at BP86/TZ2P

Complex	$[Fe(L)]^+$ + (*cyclo*-P_5)FeCp*			$[FeCp^*]^+$ + (*cyclo*-P_5)Fe(L)		
	3a	**3b**	**4**	**3a**	**3b**	**4**
ΔE_{int}	–109.04	–109.57	–128.94	–114.81	–116.99	–113.28
ΔE_{Pauli}	224.21	210.25	195.97	210.97	212.48	208.38
ΔE_{elstat} [a]	–152.20 (45.67%)	–142.58 (44.58%)	–139.48 (42.93%)	–144.93 (44.49%)	–150.75 (45.76%)	–142.32 (44.25%)
ΔE_{orb} [a]	–181.04 (54.33%)	–177.24 (55.42%)	–185.42 (57.07%)	–180.86 (55.51%)	–178.72 (54.24%)	–179.34 (55.75%)
ΔE_{prep}	13.78	11.05	4.93	8.24	7.14	7.14
D_e	–95.26	–98.52	–124.01	–106.57	–109.85	–106.14

[a] The values in parentheses give the percentage contribution to the total attractive interactions.

Fe1···P_5 distance (vide supra). Finally, the energy partitioning suggests that the attractive interactions between $[Fe(L)]^+$ and (*cyclo*-P_5)Fe(L′) fragments are ca. 55% covalent and 45% electrostatic.

The EDA data for the mononuclear complexes (L)Fe(*cyclo*-P_5) in terms of interactions $[Fe(cyclo\text{-}P_5)]^+ + L^-$ or $[Fe(L)]^+ + [cyclo\text{-}P_5]^-$ are given in Table II. The ΔE_{int} and D_e values for the first bond in the metallacarborane complexes **5a** and **5b** (Chart 1) are lower than in the cyclopentadienyl analogs **2** and CpFe(*cyclo*-P_5). Interestingly, the bonding of the charge-compensated dicarbollide is stronger than that of the tricarbollide. All contributions (ΔE_{elstat}, ΔE_{Pauli} and ΔE_{orb}) are also higher (by absolute magnitude) for $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. The ΔE_{int} and D_e values for the second bond are also lower than those in **2** and CpFe(*cyclo*-P_5). For cations [Fe(η-9-SMe_2-

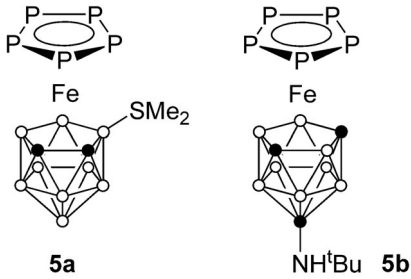


CHART 1

TABLE II
Results of EDA (energy values in kcal mol^{-1}) for (L)Fe(*cyclo*-P_5) complexes using $[Fe(cyclo\text{-}P_5)]^+ + L^-$ or $[Fe(L)]^+ + [cyclo\text{-}P_5]^-$ as interacting fragments at BP86/TZ2P

Complex	$[Fe(cyclo\text{-}P_5)]^+ + L^-$				$[Fe(L)]^+ + [cyclo\text{-}P_5]^-$			
	5a	**5b**	**2**	CpFe(*cyclo*-P_5)	**5a**	**5b**	**2**	CpFe(*cyclo*-P_5)
ΔE_{int}	–223.18	–213.78	–249.87	–237.43	–194.90	–192.54	–199.29	–214.95
ΔE_{Pauli}	279.52	269.06	225.37	235.45	214.97	201.93	198.46	185.15
ΔE_{elstat} [a]	–274.26 (54.56%)	–264.84 (54.85%)	–253.56 (53.35%)	–260.94 (55.41%)	–217.07 (52.96%)	–201.29 (51.03%)	–211.60 (53.20%)	–207.11 (51.76%)
ΔE_{orb} [a]	–228.45 (45.44%)	–218.00 (45.15%)	–221.68 (46.65%)	–209.95 (44.59%)	–192.79 (47.04%)	–193.19 (48.97%)	–186.16 (46.80%)	–192.99 (48.24%)
ΔE_{prep}	27.92	25.42	15.03	13.10	13.85	11.39	6.81	5.09
D_e	–195.26	–188.36	–234.84	–224.33	–181.05	–181.15	–192.48	–209.86

[a] The values in parentheses give the percentage contribution to the total attractive interactions.

7,8-$C_2B_9H_{10}$)]$^+$ and [Fe(η-1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$)]$^+$, the total interaction is almost equal. Both ΔE_{elstat} and ΔE_{Pauli} are higher for [Fe(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]$^+$, however ΔE_{orb} is practically the same as for [Fe(η-1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$)]$^+$. The same pattern is observed in the case of bonding of the ferracarborane cations with **2** (Table I). The attractive interactions of [Fe(*cyclo*-P_5)]$^+$ with the carborane anions are ca. 45% covalent and 55% electrostatic, being slightly more electrostatic compared with interactions between [Fe(L)]$^+$ and [*cyclo*-P_5]$^-$.

Recently, based on electrostatic potentials at iron and carbon nuclei in series of the related ferracarborane and cyclopentadienyl complexes with

TABLE III
Electrostatic potentials at nuclei (*E* in a.u.) for [(L)Fe(*cyclo*-P_5)FeCp*]$^+$ and (L)Fe(*cyclo*-P_5) complexes[a]

Complex	E_{Fe}[b]	E_p av.
3a	–115.563 (–115.566) *–117.396 (–117.398)*	–54.040 *–54.347*
3b	–115.563 (–115.568) *–117.398 (–117.400)*	–54.043 *–54.350*
4	–115.552 (–115.561) *–117.384 (–117.393)*	–54.035 *–54.341*
5a	–115.665 *–117.497*	–54.165 *–54.470*
5b	–115.666 *–117.498*	–54.168 *–54.172*
CpFe(*cyclo*-P_5)	–115.666 *–117.494*	–54.169 *–54.471*
2	–115.681 *–117.513*	–54.180 *–54.485*
CpFe(9-SMe_2-7,8-$C_2B_9H_{10}$)[c]	–115.703 *–117.540*	–
CpFe(1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$)	–115.704 *–117.541*	–
$FeCp_2$[c]	–115.715 *–117.549*	–
CpFeCp*	–115.725 *–117.563*	–

[a] Values at BP86/def2-TZVPP//BP86/TZ2P are given in normal type and at BP86/TZ2P in italics. [b] Values for the FeCp* iron atom are given in parentheses. [c] Ref.[7c]

carbocyclic ligands (Cp, C_6H_6, cyclohexadienyl) we have shown that the carborane anions [η-9-L-7,8-$C_2B_9H_{10}$]$^-$ (L = SMe_2, NMe_3) are stronger donors than Cp$^-$ in cationic complexes but weaker donors in neutral derivatives[7c].

In cations **3a** and **3b**, electrostatic potentials (*E*) at the Fe and P nuclei are higher (by absolute magnitude) than those in **4** indicating stronger donor ability of the carborane anions [9-SMe_2-7,8-$C_2B_9H_{10}$]$^-$ and [1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$]$^-$ compared with Cp$^-$ (Table III). Interestingly, in neutral complexes **5a** and **5b**, the E_{Fe} and E_P values are close to those in the cyclopentadienyl analog CpFe(*cyclo*-P_5) but lower than those in the pentamethylated derivative **2** suggesting that the carborane anions are weaker donors than [Cp*]$^-$ but close in donor ability with Cp$^-$, in contrast to previously analyzed complexes with carbocyclic ligands[7c]. This difference is explained by strong acceptor character of the pentaphospholyl ligand[13,14]. Much stronger acceptor ability of [*cyclo*-P_5]$^-$ compared with Cp$^-$ and the carborane anions is clearly indicated by lower E_{Fe} values for CpFe(*cyclo*-P_5) and **5a**, **5b** than those for the corresponding Cp analogs. At the same time, comparison of the neutral complexes CpFe(9-SMe_2-7,8-$C_2B_9H_{10}$) and CpFe(η-1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$) with ferrocene suggests weaker donor ability of the carborane anions, as in other neutral complexes with carbocyclic ligands.

CONCLUSION

We may conclude that the benzene complexes [(Carb)Fe(η-C_6H_6)]$^+$ (Carb = 9-SMe_2-7,8-$C_2B_9H_{10}$, 1-*t*-BuNH-1,7,9-$C_3B_8H_{10}$) can be used as syntons of cationic ferracarborane fragments [Fe(Carb)]$^+$ for the synthesis of triple-decker complexes. The ferracarborane triple-decker cations **3a** and **3b** more easily undergo nucleophilic degradation by MeCN than the cyclopentadienyl analog **4**. X-ray diffraction data suggest weaker bonding of the Cp*Fe(*cyclo*-P_5) moiety with the ferracarborane cations [Fe(Carb)]$^+$ compared with [Fe(C_5R_5)]$^+$. It was further evidenced by DFT calculations.

EXPERIMENTAL

General Methods

The reactions were carried out under an inert atmosphere in dry solvents. The isolation of products was conducted in air. Starting complexes **1a**PF_6 [7c], **1b**PF_6 [7b], and **2** [5b] were prepared as described in the literature. ^{1}H, ^{11}B{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker Avance-400 spectrometer operating at 400.13, 128.38, and 161.98 MHz, respectively. Chemical shifts are given in ppm (δ-scale).

Synthesis of Triple-Decker Complexes **3a**PF_6 and **3b**PF_6

Dichloromethane (7 ml) was added to a mixture of **1a**PF_6 or **1b**PF_6 (0.062 mmol) and **2** (25 mg, 0.072 mmol) in a Schlenk tube. In the case of **1a**PF_6, which is poorely soluble in CH_2Cl_2, it is better to use a mixture of CH_2Cl_2 (2.5 ml) and $MeNO_2$ (0.5 ml) as a solvent. The reaction mixture was irradiated using mercury luminescent lamps with a total power of 650 W for 1 h. Both the Schlenk tube and the lamps were placed into a vessel of an appropriate volume; cooling was accomplished by running water. The solvent was removed in vacuo, and the residue was eluted through the silica gel column (15 × 1 cm) with CH_2Cl_2/acetone (10:1). The second dark-grey band was collected and the solution was concentrated up to 1 ml. Then ether was added, the green precipitate was filtered off and dried in vacuo.

3aPF_6: yield 31 mg (65%). ^{1}H NMR (acetone-d_6): 3.87 (s, 1 H, CH), 3.00 (s, 1 H, CH), 2.94 (s, 3 H, SMe_2), 2.73 (s, 3 H, SMe_2), 1.29 (s, 15 H, Cp*). ^{11}B{^{1}H} NMR (acetone-d_6): –1.3 (1 B), –4.7 (1 B), –7.9 (1 B), –10.0 (1 B), –12.6 (2 B), –20.1 (1 B), –21.8 (1 B), –25.1 (1 B). ^{31}P{^{1}H} NMR (acetone-d_6): 0.3 (s, 5 P, *cyclo*-P_5), –144.3 (sept., 1 P, PF_6^-). For $C_{14}H_{31}B_9F_6Fe_2SP_6$ (740.30) calculated: 22.72% C, 4.22% H, 13.14% B; found: 22.40% C, 4.02% H, 13.30% B.

3bPF_6: yield 32 mg (68%). ^{1}H NMR (acetone-d_6): 3.48 (s, 2 H, CH), 1.27 (s, 15 H, Cp*), 0.90 (s, 9 H, *t*-Bu). ^{11}B{^{1}H} NMR (acetone-d_6): –13.1 (3 B), –16.6 (2 B), –17.2 (1 B), –20.3 (2 B). ^{31}P{^{1}H} NMR (acetone-d_6): –2.4 (s, 5 P, *cyclo*-P_5), –144.3 (sept., 1 P, PF_6^-). For $C_{17}H_{35}B_8F_6Fe_2NP_6$ (751.46) calculated: 27.17% C, 4.69% H, 11.51% B, 1.86% N; found: 27.09% C, 4.64% H, 11.60% B, 1.91% N.

Salts **3a**- and **3b**[Co(η-7,8-$C_2B_9H_{11})_2$] were prepared in a similar way using **1a**- and **1b**[Co(η-7,8-$C_2B_9H_{11})_2$] instead of **1a**- and **1b**PF_6.

X-ray Diffraction Study

Crystals of **3a**- and **3b**[Co(η-7,8-$C_2B_9H_{11})_2$] were grown up by slow diffusion in two-layer system, ether and a solution of the complex in CH_2Cl_2.

Crystal data for **3a**[Co(η-7,8-$C_2B_9H_{11})_2$]: $C_{18}H_{53}B_{27}CoFe_2P_5S$, orthorhombic, space group $Pna2_1$, a = 12.8843(7) Å, b = 17.7764(10) Å, c = 18.2742(11) Å, V = 4185.5(4) Å^3, Z = 4, d_{calc} = 1.458 g cm^{-3}, μ = 1.337 mm^{-1}, crystal size 0.54 × 0.45 × 0.30 mm, F(000) = 1864, T_{min}/T_{max} 0.4728/0.6766, *R1* = 0.0286 (from 9868 unique reflections with $I > 2\sigma(I)$) and *wR2* = 0.0613 (from all 11056 unique reflections).

Crystal data for **3b**[Co(η-7,8-$C_2B_9H_{11})_2$]: $C_{21}H_{57}B_{26}CoFe_2NP_5$, monoclinic, space group $P2_1/n$, a = 13.7368(6) Å, b = 11.8950(6) Å, c = 26.7068(12) Å, β = 98.7320(10)°, V = 4313.3(3) Å^3, Z = 4, d_{calc} = 1.432 g cm^{-3}, μ = 1.253 mm^{-1}, crystal size 0.50 × 0.35 × 0.20 mm, F(000) = 1896, T_{min}/T_{max} 0.593/0.775, *R1* = 0.0412 (from 6611 unique reflections with $I > 2\sigma(I)$) and *wR2* = 0.1035 (from all 8345 unique reflections).

X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 120 K. The absorption correction was applied semiempirically using SADABS program. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms of the BH groups were found in the difference Fourier synthesis, and the positions of other hydrogen atoms were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.5 $U_{eq}(C_i)$ for methyl groups and to 1.2 $U_{eq}(C_{ii})$

and 1.2 $U_{eq}(B_i)$ for other atoms, were $U_{eq}(B)$ and $U_{eq}(C)$ are the equivalent thermal parameters of the atoms to which the corresponding H atoms are bound.

CCDC 775543 (for **3a**[Co(η-7,8-$C_2B_9H_{11})_2$]) and 775544 (for **3b**[Co(η-7,8-$C_2B_9H_{11})_2$]) contain the supplementary crystallographic data for this paper. These data 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 336033; or deposit@ccdc.cam.ac.uk).

Computational Details

The geometries have been optimized without constraints at the gradient corrected DFT level of theory using the exchange functional of Becke[15] and the correlation functional of Perdew[16] (BP86). Uncontracted Slater-type orbitals were employed as basis functions for the SCF calculations[17]. Scalar relativistic effects were considered using the zero-order regular approximation (ZORA)[18]. All-electron ZORA relativistic valence triple-ζ basis set augmented by two polarization functions TZ2P was used. The bonding interactions were studied by means of Morokuma–Ziegler energy decomposition analysis[19]. The calculations were carried out using the ADF 2006.01 program package[20].

Electrostatic potentials at nuclei were calculated with the Gaussian 98 program[21] for the BP86/TZ2P optimized structures using the BP86 functional and a basis set of triple-ζ quality with two polarization functions def2-TZVPP [22]. They were also calculated at BP86/TZ2P. The ChemCraft program[23] was used for molecular modeling and visualization.

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