Articles

(Tetramethylcyclobutadiene)cobalt Complexes with Phosphacarborane Ligands†

Elena V. Mutseneck,‡ Dmitry S. Perekalin,‡ Josef Holub,§ Zoya A. Starikova,‡
Pavel V. Petrovskii,‡ Piero Zanello,⊥ Maddalena Corsini,⊥ Bohumil Štíbr,§ and
Alexander R. Kudinov*,‡

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow,
Russian Federation, Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic,
250 68 Řež, Czech Republic, and Dipartimento di Chimica, Università di Siena, 53100 Siena, Italy*

Received July 29, 2005

Reactions of the 11-vertex phosphadicarbollide anions $[10\text{-R-}7,8,9\text{-PC}_2B_8H_9]^-$ (R = H (**1a**) and Cl (**1b**)) and $[9\text{-Cl-}7,8,11\text{-PC}_2B_8H_9]^-$ (**7**) with $[Cb^*Co(MeCN)_3]PF_6$ or $[Cb^*Co(C_6H_6)]PF_6$ ($Cb^* = C_4Me_4$) give the expected cobaltaphosphadicarbollides $1\text{-}Cb^*\text{-}5\text{-R-}1,2,3,4\text{-CoPC}_2B_8H_9$ (R = H (**2a**) and Cl (**2b**)) and $1\text{-}Cb^*\text{-}4\text{-Cl-}1,2,3,6\text{-CoPC}_2B_8H_9$ (**5b**), respectively. **2a** rearranges to a mixture of $1\text{-}Cb^*\text{-}1,2,4,5\text{-CoPC}_2B_8H_{10}$ (**4a**) and $1\text{-}Cb^*\text{-}1,2,3,6\text{-CoPC}_2B_8H_{10}$ (**5a**) at 110 °C and further to $1\text{-}Cb^*\text{-}1,2,3,5\text{-CoPC}_2B_8H_{10}$ (**6a**) at 160 °C. Heating of the Cl-substituted derivative **2b** at 65 °C results in $1\text{-}Cb^*\text{-}5\text{-Cl-}1,2,4,8\text{-CoPC}_2B_8H_9$ (**3b**). Both **2b** and **5b** rearrange at 160 °C, giving $1\text{-}Cb^*\text{-}5\text{-Cl-}1,2,3,10\text{-CoPC}_2B_8H_9$ (**8b**) as a main product. The observed rearrangement sequence of $Cb^*CoPC_2B_8H_{10}$ isomers correlates well with the relative stabilities of their nonmethylated analogues estimated by DFT calculations. Reaction of the diphosphacarbollide anion $[7,8,10\text{-P}_2CB_8H_9]^-$ (**11**) with $Cb^*Co(CO)_2I$ at 160 °C affords the nonrearranged complex $1\text{-}Cb^*\text{-}1,2,3,5\text{-CoP}_2CB_8H_9$ (**12**). The structures of **2a**, **3b**, and **4a** were determined by X-ray diffraction. The electrochemical study revealed that phosphadicarbollide ligands are stronger acceptors compared with tricarbollide $[C_3B_8H_{11}]^-$ and charge-compensated dicarbollide $[9\text{-L-}7,8\text{-C}_2B_9H_{10}]^-$.

Introduction

In 1968, Todd et al. described manganese, iron, and cobalt complexes of phosphacarbollide dianion $[7,9\text{-PCB}_9H_{10}]^{2-}$.[2] Complexation of its methylated derivative $[7\text{-Me-}7,9\text{-PCB}_9H_{10}]^-$ was also studied.[3] Unfortunately, coordination chemistry of phosphacarborane ligands was forgotten for a long time, unlike the explosive development of chemistry of dicarbollide derivatives. The renaissance of this field was initiated by the synthesis of monoanionic triheteroborane ligands $[PC_2B_8H_{10}]^-$ and $[P_2CB_8H_9]^-$.[4,5] The isomeric iron phosphadicarbollides $CpFePC_2B_8H_{10}$ have been prepared by reaction of the neutral carborane $7,8,9\text{-PC}_2B_8H_{11}$ with $[CpFe(CO)_2]_2$.[6] Heating of $[P_2CB_8H_9]^-$ with $CpFe(CO)_2I$ gives diphosphacarbollide $CpFeP_2CB_8H_9$.[7]

We are presently developing (tetramethylcyclobutadiene)cobalt chemistry.[8] Using $Cb^*Co(CO)_2I$, $[Cb^*Co(C_6H_6)]^+$, and $[Cb^*Co(MeCN)_3]^+$ as synthons of the Cb*Co fragment, sandwich,[9] half-sandwich,[10] and cluster[1,11] derivatives have been prepared. In particular, complexes with tricarbollide $[7,8,9\text{-C}_3B_8H_{11}]^-$ and charge-compensated dicarbollide $[9\text{-L-}7,8\text{-C}_2B_9H_{10}]^-$ ligands have been synthesized. Herein we report the reactions of the same synthons with $[PC_2B_8H_{10}]^-$ anions, giving cobaltaphosphadicarbollides and their further polyhedral rearrangements. Similar reaction of anion $[P_2CB_8H_9]^-$ is also described.

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† (Tetramethylcyclobutadiene)cobalt Complexes. 5. Part 4: see ref 1.

* To whom correspondence should be addressed. E-mail: arkudinov@ineos.ac.ru.

‡ Russian Academy of Sciences.

§ Academy of Sciences of the Czech Republic.

⊥ Università di Siena.

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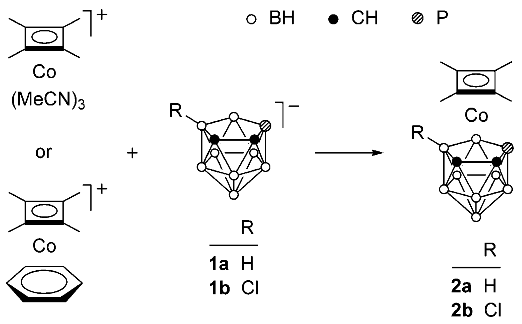
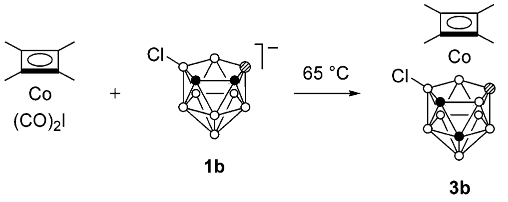
10.1021/om050653u CCC: $33.50

Scheme 1



Scheme 2



Results and Discussion

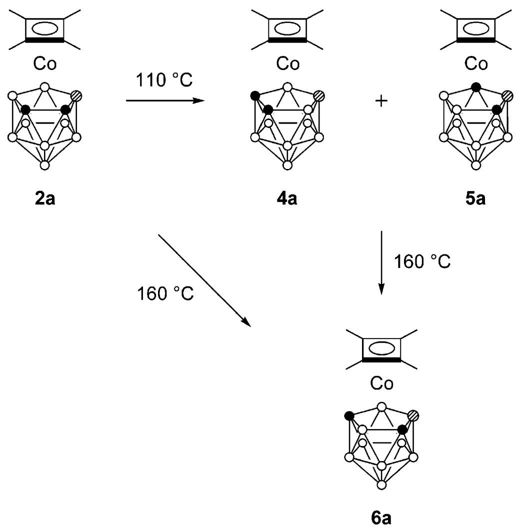
Synthesis of Cobaltaphosphadicarbollides. In the present work complexation reactions of carbons-adjacent and carbons-apart phosphadicarbollide anions were studied. The room-temperature reactions of the carbons-adjacent anions [10-R-7,8,9-$PC_2B_8H_9$]$^-$ (R = H (**1a**) and Cl (**1b**)) with [Cb*Co-(MeCN)$_3$]$^+$ (THF) or [Cb*Co(C_6H_6)]$^+$ ($h\nu$, CH_2Cl_2) lead to cobaltaphosphadicarbollides 1-Cb*-5-R-1,2,3,4-$CoPC_2B_8H_9$ (R = H (**2a**) and Cl (**2b**)) (Scheme 1). It should be emphasized that the arrangement of the cage P and C atoms is retained, in contrast to the reaction of 7,8,9-$PC_2B_8H_{11}$ with [CpFe(CO)$_2$]$_2$ at 140 °C, which is accompanied by polyhedral rearrangement.[6a]

Anions **1a** and **1b** also react with the (dicarbonyl)iodide complex Cb*Co(CO)$_2$I (THF, 65 °C); however the product structure depends on the substituent at the boron atom. In the case of the parent anion, the nonrearranged isomer **2a** (yield 23%) is formed as a main product (the contents of other isomers is ca. 3%). On the contrary, a similar reaction with the 10-Cl-substituted anion **1b** is accompanied by polyhedral rearrangement, selectively giving 1-Cb*-5-Cl-1,2,4,8-$CoC_2B_8H_9$ (**3b**) (Scheme 2). Thus, chlorine substitution considerably facilitates the isomerization process.

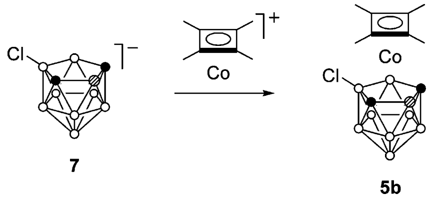
As outlined in Scheme 3, the isomerization of **2a** proceeds with considerable rate at temperatures over 100 °C. For instance, refluxing of **2a** in toluene affords a mixture of complexes 1-Cb*-1,2,4,5-$CoPC_2B_8H_{10}$ (**4a**, yield 39%) and 1-Cb*-1,2,3,6-$CoPC_2B_8H_{10}$ (**5a**, yield 13%), which were separated by thin-layer chromatography. Noteworthy, the isomer ratio does not depend on the reaction time, suggesting that they are formed as a result of two independent processes. Refluxing of either **2a** itself or a mixture of **4a** and **5a** in diglyme leads to the thermodynamically more stable isomer 1-Cb*-1,2,3,5-$CoPC_2B_8H_{10}$ (**6a**).

The reaction of the chlorinated carbons-apart anion **7** with any [Cb*Co]$^+$ precursor, i.e., [Cb*Co(MeCN)$_3$]$^+$ (THF, 20 °C), [Cb*Co(C_6H_6)]$^+$ ($h\nu$, CH_2Cl_2, 20 °C), or Cb*Co(CO)$_2$I (THF, 65 °C), yields the expected complex 1-Cb*-4-Cl-1,2,3,6-$CoPC_2B_8H_9$ (**5b**) (Scheme 4). It should be emphasized that the reaction of **7** with the (dicarbonyl)iodide in refluxing THF proceeds without rearrangement, in contrast to anion **1b** (see Scheme 2).

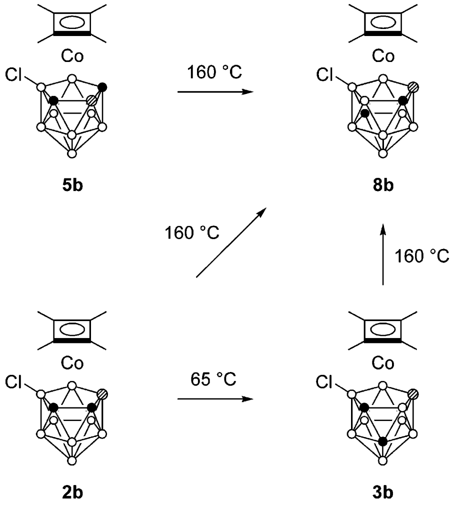
Scheme 3



Scheme 4



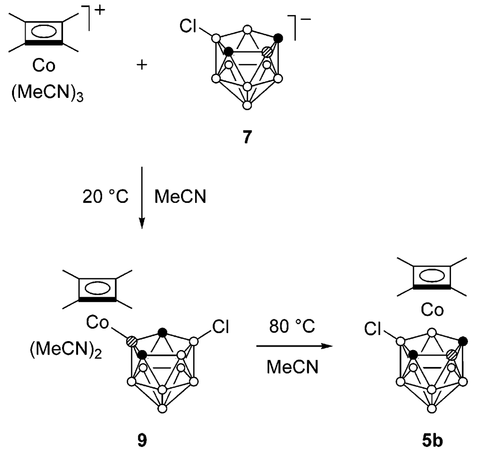
Scheme 5



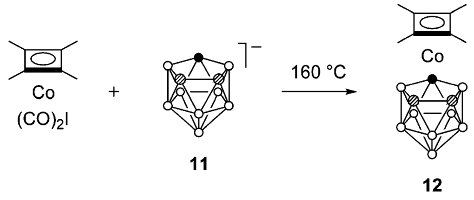
Scheme 5 summarizes rearrangement pathways for Cl-substituted phosphadicarbollide isomers. Complex **5b** undergoes polyhedral rearrangement in refluxing diglyme to give isomer 1-Cb*-5-Cl-1,2,3,10-$CoPC_2B_8H_9$ (**8b**) as a main product. As mentioned above, the carbons-adjacent analogue **2b** rearranges at much lower temperature (65 °C), giving **3b**, which is apparently connected with the electrostatic repulsion of the neighboring carbon atoms. Refluxing of **2b** or **3b** in diglyme affords **8b**. Thus, the chlorine substitution not only facilitates the rearrangement but also changes the process pathway, forcing migration of one of two carbon atoms into the second layer of the carborane ligand.

It should be noted that the phosphorus lone pair can complicate the formation of the π-complex. This can be illustrated by the reaction of anion **7** with [Cb*Co(MeCN)$_3$]$^+$. As mentioned above, carring out this reaction in THF at room temperature gives directly complex **5b** (see Scheme 4). How-

Scheme 6



Scheme 7



ever, the same reaction in MeCN is stopped at the stage of σ-complex 7-Cb*Co(MeCN)$_2$-9-Cl-*nido*-7,8,11-PC$_2$B$_8$H$_9$ (**9**) (Scheme 6). Further refluxing of **9** in MeCN results in transformation into π-complex **5b**. The formation of the related iron σ-complexes, 7-CpFe(CO)$_2$-7,8,9-PC$_2$B$_8$H$_{10}$ and 7-CpFe-(CO)$_2$-7,9,10-PC$_2$B$_8$H$_{10}$, has been described earlier.[6a]

The present study clearly demonstrates that the most characteristic feature of phosphadicarbollide derivatives is their much greater ability to undergo cluster rearrangements compared with dicarbollide analogues. Similar behavior was observed for cobaltatricarbollides Cb*Co(C$_3$B$_8$H$_{11}$).[1]

Synthesis of Cobaltadiphosphacarbollide. It was shown earlier that isomeric anions [7,8,9-P$_2$CB$_8$H$_9$]$^-$ (**10**) and [7,8,-10-P$_2$CB$_8$H$_9$]$^-$ (**11**) react with CpFe(CO)$_2$I (mesitylene, 165 °C), giving ferradiphosphacarbollides.[7] We studied reactions of these anions with the [Cb*Co]$^+$ fragment. Treatment of anion **11** with Cb*Co(CO)$_2$I or [Cb*Co(MeCN)$_3$]$^+$ in refluxing THF does not lead to any isolable complexes. Nevertheless, it reacts with the (dicarbonyl)iodide under more drastic conditions (diglyme, 160 °C), giving the nonrearranged complex 1-Cb*-1,2,3,5-CoP$_2$-CB$_8$H$_9$ (**12**) (Scheme 7). Unfortunately, the isomeric anion **10** does not form π-complexes even at 160 °C. Apparently, the presence of two phosphorus lone pairs complicates π-complexation to a greater extent than in the case of phosphadicarbollide.

X-ray Diffraction Study. Structures of complexes **2a**, **3b**, and **4a** were confirmed by X-ray diffraction (Figures 1−3). The Cb* ring is nearly ideal square with a side length 1.435−1.465 Å, approximating that for other cobaltacarborane complexes.[1,11b] The carbon atoms of the Cb* methyl groups are deviated from the ring plane by 0.12−0.23 Å away from the cobalt atom. For all compounds studied the metal-bonding ligand planes are essentially coplanar, the dihedral angles being 1.3−2.7°.

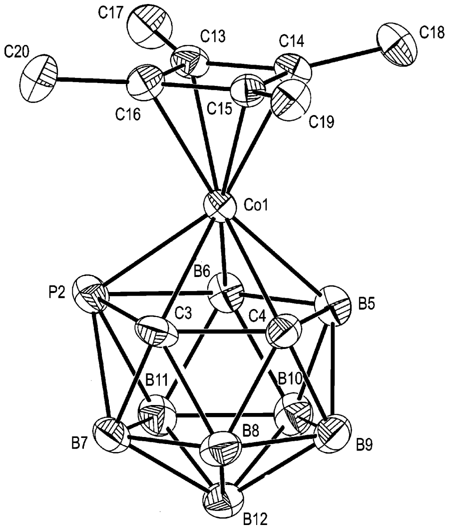


Figure 1. Molecular structure of 1-Cb*-1,2,3,4-CoPC$_2$B$_8$H$_{10}$ (**2a**). Ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (deg): Co1−P2 2.2014(16), Co1−C3 2.046(4), Co1−C4 2.041(4), Co1−B5 2.1058(6), Co1−B6 2.142(4), P2−C3 2.006(4), C3−C4 1.651(6), C4−B5 1.819(4), B5−B6 1.754(4), B6−P2 2.011(5), B6−P2−C3 93.20(19), P2−C3−C4 115.0(3), C3−C4−B5 110.8(3), C4−B5−B6 106.94(18), B5−B6−P2 113.4(2).

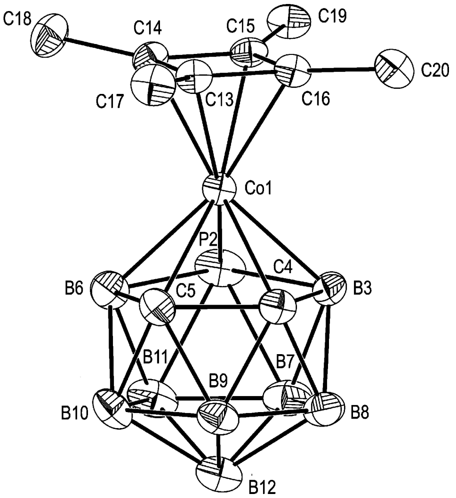


Figure 2. Molecular structure of 1-Cb*-1,2,4,5-CoPC$_2$B$_8$H$_{10}$ (**4a**). Ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (deg): Co1−C5 2.039(2), Co1−C4 2.030(2), Co1−B3 2.109 (2), Co1−B6 2.118 (2), Co1−P2 2.2389 (9), P2−B3 2.038(2), P2−B6 2.051(3), B3−C4 1.726(3), B6−C5 1.682(3), C4−C5 1.635(3), B3−P2−B6 93.96(10), C4−B3−P2 109.06(14), C5−B6−P2 110.02 (14), C4−C5−B6 113.66 (15), C5−C4−B3 113.17(15).

The Co···Cb* distances in the phosphadicarbollide complexes **2a** (1.724 Å), **4a** (1.719 Å), and **3b** (1.724 and 1.733 Å for two independent molecules) are the longest in a series of complexes with monoanionic ligands Cb*Co(η-C$_5$H$_4$COMe) (1.683 Å),[9a] 1-Cb*-4-SMe$_2$-1,2,3-CoC$_2$B$_9$H$_{10}$ (**13a**, 1.712 Å), 1-Cb*-4-py-1,2,3-CoC$_2$B$_9$H$_{10}$ (**13c**, 1.711 Å),[11b] and 1-Cb*-1,2,3,4-CoC$_3$B$_8$H$_{11}$ (**14**, 1.696 Å),[1] suggesting the strongest acceptor ability of phosphadicarbollide ligands. This conclusion correlates well with electrochemical data (vide infra).

Complexes **2a**, **3b**, and **4a** have a distorted icosahedral structure. The PC$_2$B$_2$ bonding faces in **2a** and **4a** are nonplanar,

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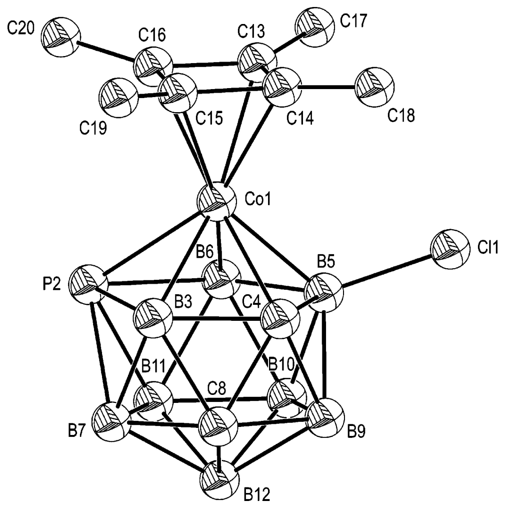
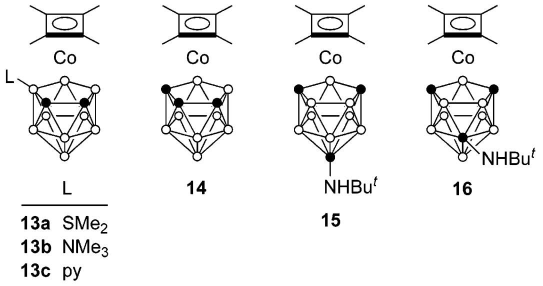


Figure 3. Molecular structure of 1-Cb*-5-Cl-1,2,4,8-$CoPC_2B_8H_9$ (**3b**). Ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg) for two independent molecules: Co1−C4 1.975(4), 1.983(4); Co1−B3 2.034(5), 2.045(5); Co1−P2 2.2188(13), 2.2235(12); Co1−B6 2.140(4), 2.134(4); Co1−B5 2.059(5), 2.033(5); P2−B3 2.066(5), 2.063(5); B5−B6 1.799(6), 1.801(6); C4−B5 1.723(6), 1.703(6); C4−B3 1.703(6), 1.722(6); P2−B6 2.061(5), 2.070(5); C4−C8 1.672(6), 1.676(6); B5−Cl1 1.817(5), 1.821(5); B3−P2−B6 94.57(18), 94.51(18); P2−B6−B5 111.1(3), 110.4(3); B6−B5−C4 107.9(3), 109.3(3); B5−C4−B3 116.1(3), 115.1(3); C4−B3−P2 110.0(3), 110.2(3).

Chart 1



the P atom being deviated from the C_2B_2 plane by 0.150 Å for **2a** and 0.084 Å for **4a** toward the cobalt atom. The PCB_3 bonding face in **3b** is also nonplanar, the P atom being deviated from the CB_3 plane by 0.106 Å in the same direction. It is noteworthy that in the phospholyl complex Cb*Co(C_4Me_4P) the phosphorus atom is deviated from the C_4 plane in the opposite direction. Accordingly, the Co−P bonds in **2a** (2.202 Å), **4a** (2.239 Å), and **3b** (2.221 Å) are shorter than that in Cb*Co(C_4Me_4P) (2.276 Å),[9a] suggesting stronger Co−P bonding in the case of phosphadicarbollide complexes.

Electrochemistry. The redox activity of the cobaltaphosphadicarbollides and recently prepared tricarbollide analogues **14**−**16** (Chart 1) was studied by electrochemical techniques. The formal electrode potentials are compiled in Table 1.

Figure 4 compares the cyclic voltammetric behavior of cobaltatricarbollide **14** with that of the corresponding phosphadicarbollide **2a** in CH_2Cl_2 solution. Complex **14** undergoes a completely irreversible oxidation process (no directly associated return peak could be detected even at the scan rate of 51.2 V s^{-1}), whereas the oxidation of complex **2a**, which occurs at notably higher potential values, is accompanied by an associated minor peak in the backscan. In both cases controlled potential coulometry failed in determining the number of electrons involved. In fact, electrode poisoning effects took place in the case of **14** (the electrolysis current abruptly decayed after the consumption of 0.3 electron/molecule), whereas the high potential value of **2a** probably triggered oxidation of the solvent too (the electrolysis current continued to flow slowly also after the consumption of more than 2 electrons/molecule). Nevertheless, in both cases comparison with the cyclic voltammetric response of equimolar amounts of decamethylferrocene (which has a comparable molecular weight) supports their one-electron nature (at least on the cyclic voltammetric time scale). This speculatively implies that [**2a**]$^+$ looks to be slightly more stable than [**14**]$^+$.

Table 1. Formal Electrode Potentials (V, vs SCE) for the Oxidation Processes of Cb*Co Complexes with Monoanionic Carborane Ligands

complex	ligand	$E^{\circ\prime}_{Co(I)/Co(II)}$	ΔE_p	i_{pc}/i_{pa}
2a[a]	7,8,9-$PC_2B_8H_{10}$	+1.14	270	~0.1
4a[a]	7,9,10-$PC_2B_8H_{10}$	+1.14	182	0.3
6a[a]	7,8,10-$PC_2B_8H_{10}$	+1.25	260	0.3
2b[b]	10-Cl-7,8,9-$PC_2B_8H_9$	+1.25		
3b[c]	8-Cl-10,2,7-$PC_2B_8H_9$	+1.21	82	0.5
5b[b]	9-Cl-7,8,11-$PC_2B_8H_9$	+1.26		
13a[d,e]	9-SMe_2-7,8-$C_2B_9H_{10}$	+0.57	80	1.0
13b[d,e]	9-NMe_3-7,8-$C_2B_9H_{10}$	+0.50	78	1.0
13c[d,e]	9-py-7,8-$C_2B_9H_{10}$	+0.54	91	1.0
14[b]	7,8,9-$C_3B_8H_{11}$	+0.74		
15[c]	1-NHBu^t-1,7,9-$C_3B_8H_{10}$	+0.73	89	1.0
16[c]	2-NHBu^t-2,8,10-$C_3B_8H_{10}$	+0.82	84	1.0

[a] Measured at 20.48 V s^{-1}. [b] Peak-potential for irreversible processes; measured at 0.2 V s^{-1}. [c] Measured at 0.1 V s^{-1}. [d] Measured at 0.05 V s^{-1}. [e] From refs 11b, 13.

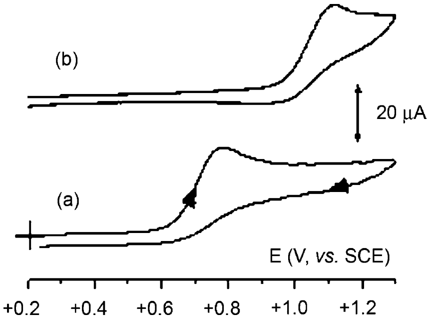


Figure 4. Cyclic voltammetric responses recorded at a platinum electrode in CH_2Cl_2 solution of (a) **14** (2.1×10^{-3} mol dm^{-3}) and (b) **2a** (1.6×10^{-3} mol dm^{-3}). $[NBu_4]PF_6$ (0.2 mol dm^{-3}) is the supporting electrolyte. Scan rate: 0.2 V s^{-1}.

Figure 5, which shows the cyclic voltammetric behavior of complex **4a**, i.e., an isomeric species of **2a**, even better points out the aspect connected with the lifetime of the monocations of the present complexes. At low scan rate, it exhibits a quite irreversible oxidation, but the increase of the scan rate causes the progressive appearance of the directly associated return peak, indicating that the kinetics of the chemical complication accompanying the generation of the monocation lie in the intervention times of cyclic voltammetry. A similar behavior holds for complex **6a**. A rough evaluation of the lifetime of monocations [**2a**]$^+$, [**4a**]$^+$, and [**6a**]$^+$ is on the order of a few milliseconds.

A quite significant stability is conferred to the tricarbollide monocations by the presence of the NHBu^t substituent. As a matter of fact, Figure 6 shows the cyclic voltammetric behavior of complex **15**. It undergoes an oxidation process with features of chemical reversibility on the cyclic voltammetric time scale. Also in this case, however, exhaustive electrolysis failed because of electrode adsorption phenomena (the current flow suddenly stops after about 0.2 electron/molecule, and the relative cyclic

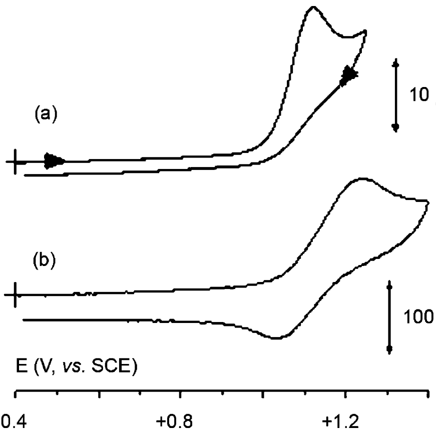


Figure 5. Cyclic voltammetric responses recorded at a gold electrode in CH_2Cl_2 solution of **4a** (1.1×10^{-3} mol dm^{-3}). $[NBu_4]PF_6$ (0.2 mol dm^{-3}) is the supporting electrolyte. Scan rates: (a) 0.2 V s^{-1}; (b) 20.5 V s^{-1}.

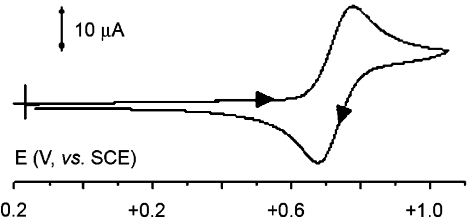


Figure 6. Cyclic voltammetric response recorded at a platinum electrode in CH_2Cl_2 solution of **15** (1.2×10^{-3} mol dm^{-3}). $[NBu_4]PF_6$ (0.2 mol dm^{-3}) is the supporting electrolyte. Scan rate: 0.2 V s^{-1}.

voltammogram remains substantially unchanged with respect to the original one), but once again comparison with decamethylferrocene suggests a one-electron process. As a matter of fact, analysis of the cyclic voltammograms with scan rates varying from 0.02 to 2.00 V s^{-1} is diagnostic for a chemically reversible, but electrochemically quasireversible, one-electron process, in that (i) the current ratio i_{pc}/i_{pa} is constantly equal to 1; (ii) the current function $i_{pa}/v_{1/2}$ decreases by about 10% for a 10 times increase of the scan rate; and (iii) the peak-to-peak separation progressively increases from 85 mV at the lowest scan rate to 145 mV at the highest scan rate.[12] A quite similar redox activity is exhibited by isomer **16**. It is noteworthy that the redox activity of cobaltatricarbollides **15** and **16** is qualitatively similar to that of the related charge-compensated dicarbollides **13b** and **13c**.[11b,13]

Let us finally proceed to the chlorinated phosphadicarbollides **2b**, **3b**, and **5b**. It is noted that complexes **2b** and **5b**, in which three heteroatoms lie on the metal-bonding face, undergo oxidation processes coupled to very fast chemical complications, as proved by the lack of return peak in cyclic voltammetry at the highest scan rates. In contrast, as illustrated in Figure 7, complex **3b** exhibits a partially reversible oxidation (for instance, $i_{pc}/i_{pa} = 0.6$ at the scan rate 0.2 V s^{-1}). The different response of **3b** with respect to those of **2b** and **5b** looks to be a noteworthy result, but confirmation of the role of the carbon atom position (on the metal-bonding face or in the second layer) needs further evidence for a wide series of metallacarboranes.

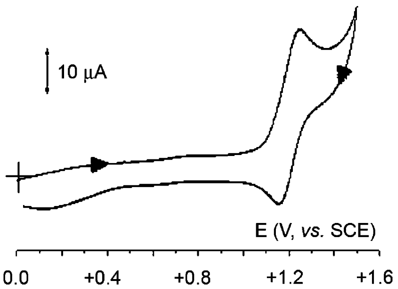


Figure 7. Cyclic voltammogram recorded at a platinum electrode in CH_2Cl_2 solution of **3b** (1.1×10^{-3} mol dm^{-3}). $[NBu_4]PF_6$ (0.2 mol dm^{-3}) is the supporting electrolyte. Scan rate: 0.2 V s^{-1}.

Finally, looking at Table 1, it is noted that phosphadicarbollides **2a**, **4a**, and **6a** as well as the chlorinated isomers **2b**, **3b**, and **5b** oxidize at potential values notably higher than tricarbollides **14**, **15**, and **16**, which in turn look to be more difficult to oxidize than the charge-compensated cobaltadicarbollide analogues **13a**−**c**. This suggests that the acceptor properties of carborane ligands increase in the following order: $[9\text{-L-}7,8\text{-}C_2B_9H_{10}]^- < [C_3B_8H_{11}]^- < [PC_2B_8H_{10}]^-$.

DFT Calculations. Recently, it was shown that DFT calculations of metallacarboranes provide reliable geometry, energy, and spectral data.[14−16] To estimate the thermodynamic stability and ^{11}B NMR spectra of the cobaltaphosphadicarbollide isomers **2a**, **4a**, **5a**, and **6a**, we carried out DFT calculations (at the B3LYP/6-31G* level) for their nonmethylated analogues $(C_4H_4)CoPC_2B_8H_{10}$ (**2a′**, **4a′**, **5a′**, and **6a′**), respectively.[17]

Complex **2a′** was proved to be the least stable. Isomers **5a′**, **4a′**, and **6a′** are more stable than **2a′** by 2.6, 12.8, and 15.9 kcal/mol, respectively. Thus, the observed rearrangement sequence **2a** → **4a** + **5a** → **6a** correlates with the stepwise increase of the thermodynamic stability of their nonmethylated analogues. Similarly, the CpFe congeners of **5a′**, **4a′**, and **6a′** are 3.1, 12.2, and 15.5 kcal/mol more stable than $1\text{-Cp-}1,2,3,4\text{-FePC}_2B_8H_{10}$.[16] This indicates that the relative stability of the isomers is mainly determined by the arrangement of carbon and phosphorus atoms and practically independent of the metal vertex, similar to tricarbollide derivatives.[1]

The stability of metallaphosphadicarbollide isomers can be rationalized on the basis of the relative electronegativity (EN) of the heteroatoms. Indeed, both carbon (EN = 2.6) and phosphorus (EN = 2.1) atoms are electron acceptors relative to the boron (EN = 2.0) framework.[18] Therefore they possess partial negative charge and tend to occupy the most distant positions owing to Coulomb repulsion. At the same time, they tend to be closer to the positively charged metal center (EN = 1.9 and 1.8 for Co and Fe, respectively). Both effects are much stronger for carbon than for phosphorus. As a consequence, the most stable isomer, **6a**, contains carbons and phosphorus atoms adjacent to cobalt, the carbon atoms being separated to minimize the unfavorable interactions. This explanation correlates with both Williams' heteroatom placement rules[19] and the structural increments scheme by Kiani and Hofman.[16]

The calculated ^{11}B NMR chemical shifts (Table 2) for isomers **2a′**, **4a′**, **5a′**, and **6a′** are in good agreement with the experimental values for the methylated congeners **2a**, **4a**, **5a**, and **6a**

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[17] The primed compound numbers correspond to derivatives with an unsubstituted cyclobutadiene ring.

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Table 2. Experimental and Calculated ^{11}B NMR Chemical Shifts for Phosphadicarbollide Isomers

complex	δ (ppm)							
	B5	B6	B12	B10	B9	B11	B8	B7
2a expt[a]	0.0	−4.6	−7.7	−8.6	−9.5	−11.7	−20.9	−25.3
2a′ calcd	0.6	−4.2	−4.3	−6.4	−8.4	−8.9	−22.0	−24.5
	B12	B7,11	B3,6	B9	B8,10			
4a expt[a]	−9.9	−11.2	−13.0	−11.2	−18.9			
4a′ calcd	−6.7	−10.0	−10.5	−12.5	−19.3			
	B4,5	B9	B12	B8,10	B7,11			
5a expt[a]	−0.2	−4.1	−6.5	−14.0	−23.7			
5a′ calcd	−0.3	0.0	−1.5	−13.9	−23.1			
	B12	B9	B6	B4	B10	B11	B7	B8
6a expt[a]	−7.6	−8.6	−9.6	−9.9	−12.8	−18.2	−19.5	−19.5
6a′ calcd	−3.3	−7.4	−10.0	−10.7	−13.2	−16.9	−17.6	−19.1

[a] In $CDCl_3$.

(av deviation 1.1 ppm), thus providing an additional confirmation of their structures. The only significant deviation (3−5 ppm) is constantly observed for the signal of the B12 atom owing to the approximation of the Cb* ligand with C_4H_4.[1] Such a strong influence of an antipodal vertex on the ^{11}B NMR shift is well established for heteroboranes.[20]

Unfortunately, the calculated ^{11}B NMR spectra for the chlorine-substituted cobaltacarborane isomers $(C_4H_4)CoPC_2B_8H_9$-Cl significantly differ from the experimental data, even in the case of the structurally characterized complex **3b**. The biggest deviation (5−8 ppm) was found for the signal of the boron atom connected with chlorine. The deviations for other atoms amount to 1−5 ppm. Increasing the theory level up to B3LYP/6-31+G* gives no improvement. Similarly, large deviations were observed previously for the calculation of 10-Cl-7,8,9-$PC_2B_8H_{10}$ at the HF/II//MP2/6-31G* level.[4b] Therefore, the structures of **2b**, **5b**, and **8b** were based only on the COSY {^{11}B−^{11}B}.

Conclusion

As a result of this study, the first cobaltaphosphadicarbollides were prepared. Mild reaction conditions resulted in complexes with nonrearranged ligands. Their most interesting feature is the ability to undergo polyhedral rearrangements under relatively mild conditions. Chlorine substitution at the boron atom facilitates the rearrangement and changes its pathway.

The electrochemical and X-ray diffraction study revealed that phosphadicarbollide ligands are the strongest acceptors among monoanionic carborane ligands.

Experimental Section

General Remarks. All reactions were carried out under argon in anhydrous solvents, which were purified and dried using standard procedures. The isolation of products was conducted in air. Starting materials were prepared as described in the literature: Cb*Co-$(CO)_2I$, [Cb*Co(C_6H_6)]PF_6, [Cb*Co(MeCN)$_3$]PF_6,[9a,10] H[**1a**], H[**1b**], H[**7**],[4] and Ph_4P[**11**].[21] Solutions of the sodium salts Na[**1a**], Na-[**1b**], and Na[**7**] were obtained by room-temperature reaction of the corresponding phosphadicarborane with NaH in THF, similar to Na[9-L-7,8-$C_2B_9H_{10}$].[11b] Irradiation was conducted in a Schlenck tube using a high-pressure mercury vapor lamp with a phosphor-coated bulb (400 W). Both the tube and the lamp were placed into a vessel of an appropriate volume covered inside with aluminum foil; cooling was accomplished by running water. Column chromatography was performed on silica gel L 100/400 (0.5 × 10 cm) using CH_2Cl_2/petroleum ether (1/5) as an eluent. TLC was performed on silica gel 230/400 (18 × 25 cm) using the same solvent mixture. All complexes prepared are yellow-orange solids. The ^{1}H, ^{31}P, and ^{11}B NMR spectra were recorded with a Bruker AMX 400 spectrometer operating at 400.13, 31.1, and 128.38 MHz, respectively. Materials and apparatus for electrochemistry have been described elsewhere.[22] Potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at $E^{\circ\prime} = +0.39$ V.

Preparation of Cb*Co(phosphadicarbollide) Complexes. Method A (Starting from [Cb*Co(MeCN)$_3$]PF_6). 1-Cb*-1,2,3,4-$CoPC_2B_8H_{10}$ (2a). A solution of Na[**1a**] (0.25 mmol) in THF (ca. 3 mL) was added to a frozen (−78 °C) solution of [Cb*Co(MeCN)$_3$]-PF_6 (100 mg, 0.23 mmol) in THF (5 mL). The temperature was allowed to rise to ambient, and stirring was continued overnight. The solvent was removed in a vacuum, and the residue was extracted with CH_2Cl_2/petroleum ether (1/1). Filtration and evaporation left a crude product, which was purified by column chromatography followed by washing with pentane (ca. 0.5 mL). Yield: 50 mg (68%). ^{1}H NMR ($CDCl_3$): δ 2.79 (s, 1H, CH), 2.33 (d (15.0, PH), 1H, CH), 1.73 (s, 12H, Cb*). ^{31}P{^{1}H} NMR: δ 7.70. Anal. Calcd for $C_{10}H_{22}B_8CoP$: C, 37.69; H, 6.96; B, 27.14; P, 9.72. Found: C, 38.08; H, 6.96; B, 27.19; P, 9.56. The following compounds were prepared in a similar way.

1-Cb*-5-Cl-1,2,3,4-$CoPC_2B_8H_9$ (2b). Yield: 54 mg (67%) from Na[**1b**]. ^{1}H NMR ($CDCl_3$): δ 3.26 (s, 1H, CH), 2.17 (d (14.7, PH), 1H, CH), 1.74 (s, 12H, Cb*). ^{31}P{^{1}H} NMR: δ −5.68. ^{11}B NMR: δ 9.0 (s, 1B, B5), −6.2 (d (135), 2B, B6,10), −7.2 (d (124), 1B, B9), −9.9 (d (161), 1B, B12), −11.2 (d (181), 1B, B11), −20.8 (d (174), 1B, B8), −29.6 (d (166), 1B, B7). Anal. Calcd for $C_{10}H_{21}B_8$-ClCoP: C, 34.01; H, 6.00; B, 24.49; P, 8.77. Found: C, 33.99; H, 6.02; B, 24.48; P, 8.57.

1-Cb*-4-Cl-1,2,3,6-$CoPC_2B_8H_9$ (5b). Yield: 47 mg (58%) from Na[**7**]. ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 12H, Cb*), 1.43 (d (19.3, PH), 1H, CH), 0.83 (d (19.2, PH), 1H, CH). ^{31}P{^{1}H} NMR: δ −2.84. ^{11}B NMR: δ 8.3 (s, 1B, B4), −2.1 (d (116), 1B, B5), −2.8 (d (135), 1B, B9), −8.2 (d (150), 1B, B12), −11.1 (d (160), 1B, B8), −13.9 (d (160), 1B, B10), −23.9 (d (160), 1B, B7), −28.1 (d (168), 1B, B11). Anal. Calcd for $C_{10}H_{21}B_8ClCoP$: C, 34.01; H, 6.00; B, 24.49; P, 8.77. Found: C, 34.33; H, 6.02; B, 24.65; P, 8.56.

The reaction with Na[**7**] in MeCN results in σ-complex 7-Cb*Co-(MeCN)$_2$-9-Cl-*nido*-7,8,11-$PC_2B_8H_9$ (**9**), which was identified by ^{31}P{^{1}H} and ^{11}B NMR spectroscopy. ^{31}P{^{1}H} NMR (CD_3CN): δ −53.40. ^{11}B NMR: δ −2.0 (d (149), 1B), −4.4 (s, 1B, B9), −5.4 (d (185), 1B), −14.3 (d (148), 1B), −15.4 (d (141), 1B), −17.5 (d (144), 1B), −20.9 (d (141), 1B), −43.1 (d (158), 1B, B1). Further refluxing of **9** in MeCN for 5 h affords π-complex **5b**. Yield: 62%. Alternatively, dissolution of **9** in THF or acetone affords **5b** within several minutes.

Method B (Starting from [Cb*Co(C_6H_6)]PF_6). 1-Cb*-1,2,3,4-$CoPC_2B_8H_{10}$ (2a). A solution of Na[**1a**] (0.14 mmol) in THF (ca. 3 mL) was added to solution of [Cb*Co(C_6H_6)]PF_6 (50 mg, 0.13 mmol) in CH_2Cl_2 (15 mL), and the mixture was irradiated for 6 h. The solvent was removed in a vacuum, and the residue was extracted with CH_2Cl_2/petroleum ether (1/1). Filtration and evaporation left a crude product, which was purified by column chromatography followed by washing with pentane (ca. 0.5 mL). Yield: 17 mg (42%). The following compounds were prepared in a similar way.

1-Cb*-4-Cl-1,2,3,6-$CoPC_2B_8H_9$ (5b). Yield: 25 mg (55%) from Na[**7**].

1-Cb*-5-Cl-1,2,3,4-$CoPC_2B_8H_9$ (2b). Yield: 20 mg (44%) from Na[**1b**].

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Table 3. Crystallographic Data and Structure Refinement Parameters for 2a, 3b, and 4a

	2a	**4a**	**3b**
empirical formula	$C_{10}H_{22}B_8CoP$	$C_{10}H_{22}B_8CoP$	$C_{10}H_{21}B_8ClCoP$
molecular weight	318.66	318.66	353.10
cryst color, habit	orange plate	orange plate	orange plate
cryst size (mm)	0.2 × 0.3 × 0.45	0.2 × 0.3 × 0.5	0.25 × 0.30 × 0.45
diffractometer	Syntex $P2_1$	Smart CCD	Smart CCD
scan type	$\theta/2\theta$	ω	ω
T, K	163	120	120
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1ca$
a (Å)	7.176(2)	7.313(3)	15.223(2)
b (Å)	16.922(4)	16.804(6)	16.348(2)
c (Å)	13.252(3)	13.480(5)	13.230(1)
β (deg)	101.582(17)	103.694(7)	90
V (Å^3)	1576.4(6)	1609.4(10)	3292.4(6)
Z (Z')	4(1)	4(1)	8(1)
D_{calcd} (g cm^{-3})	1.343	1.315	1.425
F(000)	656	656	1440
μ(Mo Kα) (mm^{-3})	11.68	11.44	12.83
θ range (deg)	2.81−26.00	1.97−28.00	1.25−28.00
no. of collected reflns	3108	12 278	25 954
indep reflns (R_{int})	2840 (0.0365)	3673 (0.0382)	7749 (0.0391)
no. of obsd reflns ($I > 2\sigma(I)$)	2451	3204	6315
no. of parameters	182	181	380
R_1 (on F for obsd reflns)[a]	0.0324	0.0353	0.0440
wR_2 (on F^2 for all reflns)[b]	0.0732	0.0715	0.0973
GOF	1.020	1.033	1.010
largest diff peak and hole (e Å^{-3})	0.374/−0.415	0.654/−0.552	0.935/−0.383

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$ for observed reflections. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$ for all reflections.

Method C (Starting from Cb*Co(CO)$_2$I). 1-Cb*-4-Cl-1,2,3,6-CoPC$_2$B$_8$H$_9$ (5b). A mixture of Cb*Co(CO)$_2$I (100 mg, 0.29 mmol) and Na[7] (0.35 mmol) in THF (20 mL) was stirred under reflux for 13 h. The solvent was removed in a vacuum, and the residue was extracted with CH_2Cl_2/petroleum ether (1/1). Filtration and evaporation left a crude product, which was purified by column chromatography followed by washing with pentane (ca. 1 mL). Yield: 23 mg (22%). The following compounds were prepared in a similar way.

1-Cb*-5-Cl-1,2,4,8-CoPC$_2$B$_8$H$_9$ (3b). Yield: 25 mg (24%) from Na[**1b**]. ^{1}H NMR (CDCl$_3$): δ 3.28 (s, 1H, CH), 2.99 (s, 1H, CH), 1.70 (s, 12H, Cb*). ^{31}P{^{1}H} NMR: δ −53.60. ^{11}B NMR: δ 4.8 (s, 1B, B5), −0.7 (dd (141, BH; 9.1, BP), 1B, B6), −8.0 (d (173), 1B, B10), −11.5 (d, (151), 2B, B9,11), −12.9 (dd (200, BH; 9.4, BP), 1B, B3), −14.4 (d (175), 1B, B12), −26.1 (dd (178, BH; 10.3, BP), 1B, B7). Anal. Calcd for $C_{10}H_{21}B_8ClCoP$: C, 34.01; H, 6.00; B, 24.49; P, 8.77. Found: C, 34.09; H, 6.02; B, 24.15; P, 8.31.

1-Cb*-1,2,3,5-CoP$_2$CB$_8$H$_9$ (12). Yield: 27 mg (28%) from Ph$_4$P[**11**] in refluxing diglyme (13 h). ^{1}H NMR (CDCl$_3$): δ 3.21 (s, 1H, CH), 1.75 (s, 12H, Cb*). ^{31}P{^{1}H} NMR: δ 1.82. ^{11}B NMR: δ 0.1 (d (163), 1B, B12), −1.2 (d (150), 2B, B4,6), −2.1 (d (129), 2B, B9,10), −11.3 (d (163), 1B, B7), −13.4 (d (161), 2B, B8,11). Anal. Calcd for $C_9H_{21}B_8CoP_2$: C, 32.11; H, 6.29. Found: C, 32.24; H, 6.34.

Thermal Rearrangements of Cb*Co(phosphadicarbollide) Complexes. Preparation of 1-Cb*-1,2,4,5-CoPC$_2$B$_8$H$_{10}$ (4a) and 1-Cb*-1,2,3,6-CoPC$_2$B$_8$H$_{10}$ (5a). A solution of **2a** (100 mg, 0.31 mmol) in toluene (5 mL) was refluxed for 12 h. The solvent was removed in a vacuum, and the residue was dissolved in CH_2Cl_2/petroleum ether (1/5) and filtered through a short layer of silica gel (ca. 2 cm). Evaporation left a mixture of **4a** and **5a**, which were separated by TLC.

4a. $R_f \approx 0.75$. Yield: 39 mg (39%). ^{1}H NMR (CDCl$_3$): δ 3.22 (s, 2H, CH), 1.69 (s, 12H, Cb*). ^{31}P{^{1}H} NMR: δ −33.23. Anal. Calcd for $C_{10}H_{22}B_8CoP$: C, 37.69; H, 6.96; B, 27.14; P, 9.72. Found: C, 37.98; H, 7.07; B, 26.98; P, 9.44.

5a. $R_f \approx 0.68$. Yield: 13 mg (13%). ^{1}H NMR (CDCl$_3$): δ 1.74 (s, 12H, Cb*), 1.01 (d (20.6, PH), 2H, CH). ^{31}P{^{1}H} NMR: δ 9.73. Anal. Calcd for $C_{10}H_{22}B_8CoP$: C, 37.69; H, 6.96; P, 9.72. Found: C, 37.89; H, 7.01; P, 9.62.

Preparation of 1-Cb*-1,2,3,5-CoPC$_2$B$_8$H$_{10}$ (6a). Complex **6a** was prepared by refluxing **2a** or a mixture of **4a** and **5a** (50 mg, 0.16 mmol) in diglyme (3 mL) for 20 h. Yield: 27 mg (54%). ^{1}H NMR (CDCl$_3$): δ 2.63 (s, 1H, CH), 1.70 (s, 12H, Cb*), 1.40 (d (16.9, PH), 1H, CH). ^{31}P{^{1}H} NMR: δ −3.67. Anal. Calcd for $C_{10}H_{22}B_8CoP$: C, 37.69; H, 6.96; B, 27.14; P, 9.72. Found: C, 37.74; H, 7.04; B, 26.90; P, 9.60.

Preparation of 1-Cb*-5-Cl-1,2,3,10-CoPC$_2$B$_8$H$_9$ (8b). A solution of **2b** or **5b** (50 mg, 0.14 mmol) in diglyme (3 mL) was refluxed for 20 h. The solvent was removed in a vacuum, and the residue was dissolved in CH_2Cl_2/petroleum ether (1/5) and filtered through a short layer of silica gel (ca. 2 cm). Complex **8b** was separated by TLC. $R_f \approx 0.55$. Yield: 16 mg (32%). ^{1}H NMR (CDCl$_3$): δ 2.47 (s, 1H, CH), 1.71 (s, 12H, Cb*), 1.65 (d (16.4, PH), 1H, CH). ^{31}P{^{1}H} NMR: δ 16.11. ^{11}B NMR: δ −6.5 (s, 1B, B5), −7.7 (dd (146, BH; 54, BP), 1B, B6), −9.4 (d (161), 1B, B4), −9.9 (d (159), 1B, B12), −10.7 (dd (170, BH; 38, BP), 1B, B11), −12.0 (d (163), 1B, B8), −17.4 (d (164), 2B, B7,9). Anal. Calcd for $C_{10}H_{21}B_8ClCoP$: C, 34.01; H, 6.00; B, 24.49; P, 8.77. Found: C, 34.05; H, 5.88; B, 24.40; P, 8.51. The fraction with $R_f \approx 0.62$ (6 mg, 10%) was also separated. This fraction is a mixture of two isomers, which were not identified.

Computational Details. All calculations were performed using Gaussian 98 (revision A.7) software[23] at the B3LYP/6-31G* level. The structures of **2a′**, **4a′**, **5a′**, and **6a′** were optimized using tightened SCF convergence criteria (SCF = tight option). The frequency calculations were performed to confirm the global minimum and include ZPE corrections to the energy. The ^{11}B NMR

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[23] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

shifts were calculated using the GIAO method by subtraction of calculated isotropic shielding values from that of B_2H_6 (93.50 at B3LYP/6-31G*). The experimental chemical shift of B_2H_6 was assigned as 16.6 ppm.[24]

X-ray Crystallography. Crystals of **2a** and **4a** suitable for X-ray diffraction were grown by evaporation of toluene solutions at 0 °C in air. Crystals of **3b** were grown by petroleum ether gas diffusion into CH_2Cl_2 solution. The structures of **2a**, **4a**, and **3b** were solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The analysis of the Fourier density synthesis has revealed that the phosphorus atom in the polyhedron of **2a** is disordered by two positions relative to a pseudoplane passing through the B6, B8, and B12 atoms. All polyhedron hydrogen atoms were located from the Fourier density synthesis and refined in isotropic approximation. Crystal data and structure refinement parameters for **2a**, **4a**, and **3b** are given in Table 3. All calculations were performed using the SHELXTL software.[25] Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 279629 for **2a**, CCDC 279631 for **3b**, and CCDC 279630 for **4a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgment. This work was supported by the Division of Chemistry and Material Sciences of the Russian Academy of Sciences (Grant No. 01). B.Š. acknowledges the Grant Agency (Grant No. 203/05/2646) and Ministry of Education (Grant No. LC523) of the Czech Republic. P.Z. gratefully acknowledges the financial support of the University of Siena (PAR 2005). Z.A.S. thanks the Scientific School Program (Grant No. 1060.2003.3). D.S.P. thanks INTAS for a Young Scientist Fellowship (Grant No. 04-83-3848).

Supporting Information Available: Details of crystallographic experiments for complexes **2a**, **3b**, and **4a** (tables of crystal data collection, refinement parameters, atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles) and details of DFT calculations for compounds **2a′**, **4a′**, **5a′**, and **6a′** (atomic coordinates for optimized geometry, energy data, summary of natural population analysis, and GIAO NMR shielding parameters). This material is available free of charge via the Internet at http://pubs.acs.org.

OM050653U

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