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# Reaction of *nido*-7,8-$C_2B_9H_{13}$ with Dicobalt Octacarbonyl: Crystal Structures of the Complexes [$Co_2(CO)_2(\eta^5$-7,8-$C_2B_9H_{11})_2$], [$Co_2(CO)(PMe_2Ph)(\eta^5$-7,8-$C_2B_9H_{11})_2$], and [$CoCl(PMe_2Ph)_2(\eta^5$-7,8-$C_2B_9H_{11})$]†

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The compounds [$Co_2(CO)_8$] and *nido*-7,8-$C_2B_9H_{13}$ react in $CH_2Cl_2$ to give a complex mixture of products consisting primarily of two isomers of the dicobalt species [$Co_2(CO)_2(\eta^5$-7,8-$C_2B_9H_{11})_2$] (**1**), together with small amounts of a mononuclear cobalt compound [$Co(CO)_2(\eta^5$-10-CO-7,8-$C_2B_9H_{10})$] (**5**) and a charge-compensated carborane *nido*-9-CO-7,8-$C_2B_9H_{11}$ (**6**). In solution, isomers **1a** and **1b** slowly equilibrate. However, column chromatography allows a clean separation of **1a** from the mixture, and a single-crystal X-ray diffraction study revealed that each metal atom is ligated by a terminal CO molecule and in a pentahapto manner by a *nido*-$C_2B_9H_{11}$ cage framework. The two $Co(CO)(\eta^5$-7,8-$C_2B_9H_{11})$ units are linked by a Co−Co bond [2.503(2) Å], which is supported by two three-center two-electron B−H $\rightharpoonup$ Co bonds. The latter employ B−H vertices in each cage which lie in α-sites with respect to the carbons in the $\overline{\mathrm{CC}B\mathrm{BB}}$ rings bonded to cobalt. Addition of $PMe_2Ph$ to a $CH_2Cl_2$ solution of a mixture of the isomers **1**, enriched in **1b**, gave isomers of formulation [$Co_2(CO)(PMe_2Ph)(\eta^5$-7,8-$C_2B_9H_{11})_2$] (**2**). Crystals of one isomer were suitable for X-ray diffraction. The molecule **2a** has a structure similar to that of **1a** but differs in that whereas one B−H $\rightharpoonup$ Co bridge involves a boron atom in an α-site of a $\overline{\mathrm{CC}B\mathrm{BB}}$ ring coordinated to cobalt, the other uses a boron atom in the *β*-site. Reaction between **1b** and an excess of $PMe_2Ph$ in $CH_2Cl_2$ gave the complex [$CoCl(PMe_2Ph)_2(\eta^5$-7,8-$C_2B_9H_{11})$] (**3**), the structure of which was established by X-ray diffraction. Experiments indicated that **3** was formed through a paramagnetic $Co^{II}$ species of formulation [$Co(PMe_2Ph)_2(\eta^5$-7,8-$C_2B_9H_{11})$]. Addition of 2 molar equiv of $CNBu^t$ to solutions of either **1a** or **1b** gave a mixture of two isomers of the complex [$Co_2(CNBu^t)_2(\eta^5$-7,8-$C_2B_9H_{11})_2$] (**4**). NMR data for the new compounds are reported and discussed.

## Introduction

We have recently shown that reactions under mild conditions between [$Ru_3(CO)_{12}$] and the carboranes *nido*-7,8-$R_2$-7,8-$C_2B_9H_{11}$ (R = H[1] or Me[2]) or *nido*-7-$NH_2Bu^t$-7-$CB_{10}H_{12}$[3] afford mono- or triruthenacarborane carbonyl complexes in good yield. We have extended this methodology for preparing metallacarboranes by investigating the reaction between [$Co_2(CO)_8$] and *nido*-7,8-$C_2B_9H_{13}$ with the results described herein. Transition element complexes having metal centers ligated in a pentahapto manner by $C_2B_9$ or $CB_{10}$ *nido*-icosahedral cage systems and in which the metals are also coordinated exopolyhedrally by carbonyl ligands are important because of their formal relationship with metallacyclopentadienyl carbonyl complexes. Thus the complex [$Ru(CO)_3(\eta^5$-7,8-$C_2B_9H_{11})$][1] is isolobal with the very extensively studied species [$Mn(CO)_3(\eta^5$-$C_5H_5)$]. With some 80% of all known organometallic complexes of the transition elements containing cyclopentadienyl ligands,[4] it is not surprising that the chemistry of the metallacyclopentadienyl carbonyls is very extensive. In contrast, relatively little is known about the reactivity patterns of their metallacarborane analogs. This is partly due to a lack of suitable synthetic methods for obtaining this class of compound. Hence the possibility of obtaining metallacarboranes having carbonyl groups attached to the metal vertices directly from reactions between metal carbonyls and *nido*-carboranes is attractive.

## Results and Discussion

The compounds [$Co_2(CO)_8$] and *nido*-7,8-$C_2B_9H_{13}$ react in $CH_2Cl_2$ at room temperature or below to afford a complicated mixture of products. The major reaction products are two isomers of formulation [$Co_2(CO)_2(\eta^5$-7,8-$C_2B_9H_{11})_2$] (**1**), which equilibrate slowly in solution. These species were characterized by microanalysis and IR and NMR spectroscopies (Tables 1 and 2). One isomer (**1a**) could be separated free of the other by column chromatography, and crystals suitable for X-ray diffraction were obtained. The second isomer **1b** was never isolated entirely free of **1a** (Chart 1).

The molecular structure of **1a** is shown in Figure 1, and selected internuclear separations and angles are listed in Table 3. The molecule consists of two $Co(CO)(\eta^5$-7,8-$C_2B_9H_{11})$ fragments joined by a Co−Co bond. The latter is supported by two B−H $\rightharpoonup$ Co linkages. The two-electron three-center

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[†] In the compounds described in this paper cobalt atoms and *nido*-$C_2B_9$ cages form *closo*-1,2-dicarba-3-cobaltadodecaborane structures. Use of this numbering scheme leads to a complicated nomenclature for the metal complexes reported; hence as in earlier papers we treat the cage as a *nido* 11-vertex ligand with numbering as for an icosahedron from which the 12th vertex has been removed. This has the added convenience of relating the metallacarborane complexes to similar species with $\eta^5$-$C_5H_5$ ligands.

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**Table 1.** Analytical and Physical Data

| | compd | color | $\nu_{max}$(CO) (cm$^{-1}$)[a] | yield (%) | anal.[b] C | anal.[b] H |
|---|---|---|---|---|---|---|
| **1a** | $[Co_2(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ α,α-isomer | brown | 2086 s, 2066 s | 20[c] | 16.6 (16.4) | 4.9 (5.1) |
| **1b** | $[Co_2(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ α,$\beta$-isomer | brown | 2088 s, 2070 s | 10[c] | 16.7 (16.4) | 4.6 (5.1) |
| **2a** | $[Co_2(CO)(PMe_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ α,$\beta$-isomer | red-brown | 2056 s, 2028 w* | 59 | 27.7 (28.5) | 6.0 (6.1) |
| **3** | $[CoCl(PMe_2Ph)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ | purple | | 63 | 43.0 (43.0) | 6.7 (6.6) |
| **4** | $[Co_2(CNBu^t)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ α,α- and α,$\beta$-isomers | brown | 2190 br,[d] 2180 br | 64[e] | 30.8[f] (30.6) | 7.7 (7.3) |
| **5** | $[Co(CO)_2(\eta^5\text{-}10\text{-}CO\text{-}7,8\text{-}C_2B_9H_{10})]$[g] | light brown | 2156 br, 2040 s, 1990 s | 4 | | |
| **6** | *nido*-9-CO-7,8-$C_2B_9H_{11}$ | colorless[h] | 2152 s | 5 | 22.7 (22.4) | 6.4 (6.9) |

[a] Measured in $CH_2Cl_2$ unless otherwise stated, all compounds show broad medium-intensity bands in their infrared spectra at ca. 2550 cm$^{-1}$ due to B−H absorptions. Peak marked with an asterisk is due to a minor isomer. [b] Calculated values are given in parentheses. [c] Approximate values, because these two compounds always occur as a mixture, and because even repeated chromatography cannot remove traces of one from the other. Total yield of two isomers is ca. 30%. [d] $\nu_{max}$(NC), measured in petroleum ether. [e] Yield 52% when prepared from **1b**. [f] N 4.7 (5.1). [g] Microanalysis unavailable. Positive-ion EI mass spectrum: *m/z* 275.08, $[Co(CO)_2(\eta^5\text{-}10\text{-}CO\text{-}7,8\text{-}C_2B_9H_{10})]^+$ (calcd 275.08); 247.09 (−CO × 1); 219.09 (−CO × 2); 190.10 (−CO × 3). [h] Solutions may be stained pale brown by trace impurities of **5**.

**Table 2.** Hydrogen-1, Carbon-13, and Boron-11 NMR Data[a]

| compd | $^1$H ($\delta$)[b] | $^{13}$C ($\delta$)[c] | $^{11}$B ($\delta$)[d] |
|---|---|---|---|
| **1a** | −11.45 (q br, 2 H, B−H ⇀ Co, $J_{BH}$ = 92), 3.38, 3.65 (s × 2, 4 H, CH) | 196.0 (br, CO), 43.1 (vbr, CH) | 15.4 (2 B, B−H ⇀ Co, $J_{HB}$ = 92), 3.7 (2 B), −0.3 (2 B), −3.8 (2 B), −7.3 (2 B), −11.7 (2 B), −16.9 (2 B), −17.5 (2 B), −18.7 (2 B) |
| **1b** | −12.98 (q br, 1 H, B−H ⇀ Co, $J_{BH}$ = 79), −11.39 (q br, 1 H, B−H ⇀ Co, $J_{BH}$ = 91), 3.55, 3.62, 3.75, 3.96 (s × 4, 4 H, CH) | 195.8, 193.5 (br, CO), 58.3, 55.3, 43.8, 37.5, (br, CH) | 24.7 (1 B, B−H ⇀ Co, $J_{HB}$ = 79), 16.6 (1 B, B−H ⇀ Co, $J_{HB}$ = 91), 3.5 (1 B), −0.5 (1 B), −3.0 (1 B), −3.5 (1 B), −5.5 (1 B), −7.6 (1 B), −9.4 (2 B), −11.5 (1 B), −11.9 (1 B), −13.7 (1 B), −14.7 (1 B), −16.4 (1 B), −17.6 (1 B), −18.5 (1 B), −26.2 (1 B) |
| **2a**[e] | −15.01 (q br, 1 H, B−H ⇀ Co, $J_{BH}$ = 79), −10.47 (q br, 1 H, B−H ⇀ Co, $J_{BH}$ = 85), 1.62, 1.76 (d × 2, 6 H, PMe, $J_{PH}$ = 10, 10), 2.25, 2.33, 3.57, 3.88 (s × 4, 4 H, CH), 7.44−7.78 (m, 5 H, Ph) | 198.0 (br, CO), 131.3−129.5 (Ph), 54.0, 54.2, 48.9, 34.5 (CH), 17.4, 12.0 (d × 2, PMe, $J_{PC}$ = 24, 26) | 18.1 (1 B, B−H ⇀ Co, $J_{HB}$ = 79), 14.9 (1 B, B−H ⇀ Co, $J_{HB}$ = 85), 14.3* (1 B, B−H ⇀ Co), 10.6* (1 B, B−H ⇀ Co, $J_{HB}$ = 82), 0.0 (1 B), −0.1 (1 B), −2.6 (2 B), −4.5 (2 B), −7.2 (1 B), −9.3 (1 B), −11.1 (1 B), −13.3 (2 B), −15.9 (1 B), −19.5 (3 B), −26.2 (1 B) |
| **3**[f] | 1.52 (AXX′, 6 H, PMe, *N* = 5[g]), 1.91 (AXX′, 6 H, PMe, *N* = 6[g]), 3.49 (s, 2 H, CH), 7.39−7.76 (m, 10 H, Ph) | 138.8−128.9 (Ph), 53.1 (CH), 17.2 (AXX′, PMe, *N* = 38[g]), 17.1 (AXX′, PMe, *N* = 34[g]) | 5.1 (1 B), −5.3 (3 B), −5.7 (2 B), −8.3 (1 B), −16.5 (2 B) |
| **4** | −13.72[h],* (q br, 1 H, B−H ⇀ Co, $J_{BH}$ = 79), −11.54 (q br, 2 H, B−H ⇀ Co, $J_{BH}$ = 89), 1.48* (s, 9 H, Me), 1.54 (s, 18 H, Me), 1.57* (s, 9 H, Me), 2.80 (s, 2 H, CH), 3.08* (s, 1 H, CH), 3.31 (s, 2 H, CH), 3.49* (s br, 2 H, CH), 3.66* (s, 1 H, CH) | 144.1,[h],* 142.9 (br, *C*NCMe$_3$), 59.0, 58.9,* 58.8* (CN*C*Me$_3$), 55.3,* 50.4,* 46.7, 40.8,* 36.1, 35.4* (CH), 30.4,* 30.3,* 30.2 (CNC*Me*$_3$) | 19.0* (1 B, B−H ⇀ Co, $J_{HB}$ = 79), 13.0* (1 B, B−H ⇀ Co, $J_{HB}$ = 89), 12.3 (2 B, B−H ⇀ Co, $J_{HB}$ = 89), −2.2 (2 B), −4.1 (2 B), −6.8 (2 B), −9.4 (2 B), −12.3 (2 B), −13.7* (1 B), −14.6* (1 B), −15.4* (1 B), −19.5 (2 B), −20.4 (2 B), −22.2 (2 B), −27.5* (1 B) |
| **5** | 3.43 (s, 2 H, CH) | 197.0 (br, CO), 172.0 (q br, BCO, $J_{BC}$ = 85), 44.0 (CH) | −4.1 (1 B), −11.1 (2 B), −15.7 (2 B), −17.1 (1 B), −18.6 (2 B), −23.9 (1 B, BCO) |
| **6** | −2.74 (br, 1 H, B−H−B), 2.81, 3.12 (s × 2, 2 H, CH) | 171.7 (q br, BCO, $J_{BC}$ = 84), 57.5 (q br, CH, $J_{BC}$ = 43), 46.6 (q br, CH, $J_{BC}$ = 32) | −0.1 (2 B), −14.2 (1 B), −17.3 (1 B), −18.4 (1 B), −19.5 (1 B), −24.1 (1 B, *B*−H−B, $J_{HB}$ = 40, 147), −30.5 (1 B, BCO), −31.5 (1 B) |

[a] Chemical shifts in ppm, coupling constants in hertz, measurements in $CD_2Cl_2$ at room temperature. Peaks marked with an asterisk are due to a minor isomer (see text). [b] Resonances for terminal BH protons occur as broad unresolved signals in the range $\delta$ ca. −2 to 3. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). B−H ⇀ Co, BCO, and *B*−H−B assignments are made from fully coupled $^{11}$B spectra. Many peaks due to minor isomers may be masked by peaks due to the major counterpart; only distinct peaks due to minor isomers are noted. [e] $^{31}P\{^1H\}$ NMR: $\delta$ 4.1 (br), with a weak resonance at $\delta$ 7.4 attributed to an isomer, see text. [f] $^{31}P\{^1H\}$ NMR: $\delta$ 5.2 (br). [g] Insufficient resolution prevents full analysis of coupling constants; $N = |J_{AX} + J_{AX'}|$. [h] A second similar resonance should be observed for the minor isomer, but is presumably hidden by peak due to corresponding nucleus in the major isomer.

bonds involve boron atoms, B(13) and B(23), respectively. These atoms lie in the α-sites with respect to the carbons in the pentagonal $\overline{\mathrm{CC}B\mathrm{BB}}$ faces of the *nido*-$C_2B_9$ fragments ligating the cobalt atoms. We therefore designate **1a** as the α,α-isomer. Each cobalt atom in **1a** carries a CO group, which is terminally bound (Co−C−O average angle = 177.8°). Thus the dimetal species is electronically saturated since it has 34 valence electrons with each $C_2B_9H_{11}$ cage formally contributing six electrons to the system and the carbonyl ligands four electrons.

The Co−Co separation [2.503(2) Å] is similar to those found in many polynuclear cobalt complexes[5] and may be compared with the Co−Co bond distances in the two isomers of $[Co_2(\mu\text{-}CO)\{\mu\text{-}B_{10}H_8(SEt_2)_2\}(CO)_4]$ [average 2.489(2) Å][6] and in $[WCo_2(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ [2.502(3) Å].[7] The agostic B−H ⇀ Co linkages in **1a** are very common structural features for dimetal complexes in which a metal atom M in an icosahedral *closo*-3,1,2-$MC_2B_9$ framework forms an exopolyhedral bond to another metal center.[8] Clear evidence for the presence of the hydrogen atoms H(13) and H(23) in **1a** came from the NMR spectra, discussed later, but these atoms were located and refined in the analysis of the diffraction data.

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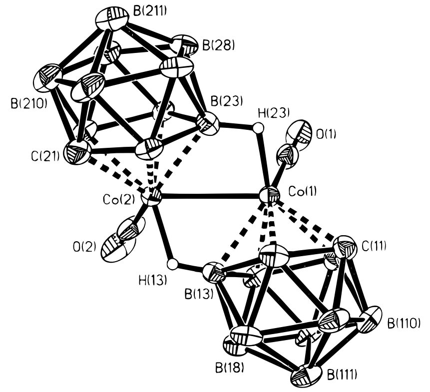
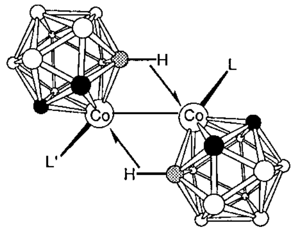
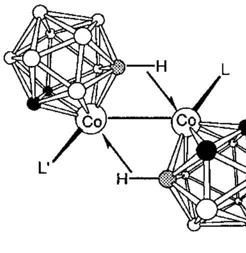


**Figure 1.** Molecular structure of the α,α-isomer $[Co_2(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**1a**) showing the crystallographic atom-labeling scheme. Thermal ellipsoids are shown at the 40% probability level. Only the agostic hydrogen atoms are shown for clarity.

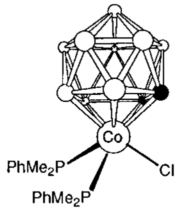
**Chart 1**



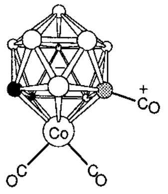
| | L | L' |
|---|---|---|
| **1a** | CO | CO |
| **2c** | CO | $PMe_2Ph$ |
| **4a** | $CNBu^t$ | $CNBu^t$ |



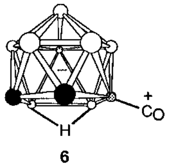
| | L | L' |
|---|---|---|
| **1b** | CO | CO |
| **2a** | CO | $PMe_2Ph$ |
| **2b** | $PMe_2Ph$ | CO |
| **4b** | $CNBu^t$ | $CNBu^t$ |



**3**



**5**



**6**

● CH ○ BH ◍ B

As expected, the atoms B(13) and B(23) unsymmetrically bridge the Co$-$Co bond [Co(1)$-$B(13) = 2.049(7) Å and Co(1)$-$B(23) = 2.138(8) Å; Co(2)$-$B(13) = 2.134(8) Å and Co(2)$-$B(23) = 2.056(7) Å]. The cobalt atoms, the midpoints of the cage C$-$C connectivities, and CO ligands do not all lie in a plane, but adopt a more twisted configuration, as revealed by the C(1)$-$Co(1)$-$Co(2)$-$C(2) dihedral angle of 56.1°. This is reminiscent of the crystal structure of the complex $[Ni_2(CO)_2(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)_2]$,[9] which contains two $Ni(CO)(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)$ units linked by a long Ni···Ni connectivity and two agostic B$-$H $\rightharpoonup$ Ni groups in a very similar manner to that observed in **1a**. The disposition of the carbon atoms in both the cages of **1a** is *anti* to the carbonyl groups. While it is ostensibly possible to generate isomers by disposing these carbon atoms *syn* to the carbonyl ligands in one or both cages, there is no structural precedent for this in our work or in similar dimeric metallacarborane structures where $B_\alpha-H \rightharpoonup M$ contacts are formed.[10]

Successive chromatographic procedures yielded solutions of sufficiently pure **1a** and **1b** to be able to record accurate IR and NMR measurements for both complexes, and the data are listed in Tables 1 and 2, respectively. The IR spectrum of **1a** shows two strong $\nu_{max}$(CO) peaks at 2086 and 2066 $cm^{-1}$. The $^{11}B\{^1H\}$ NMR spectrum revealed a pattern of nine singlet signals (each integrating to two boron nuclei) consistent with two identical cages in a molecule with axial $C_2$ molecular symmetry, as found in the X-ray structure, with the $C_2$ axis lying perpendicular to the Co$-$Co bond. One of the signals ($\delta$ 15.4) becomes a doublet in the fully coupled spectrum, with a diminished $J_{HB}$ coupling of 92 Hz, indicative of an agostic B$-$H $\rightharpoonup$ Co system. Though this coupling lies at the high end of the range expected for B$-$H $\rightharpoonup$ M groups,[8b] the presence of the equivalent B$-$H $\rightharpoonup$ Co hydrogen atoms was confirmed by the above-discussed X-ray results and also by the $^1H$ NMR spectrum, with the appearance of a broad quartet at $\delta$ $-$11.45 ($J_{BH}$ = 92 Hz). The latter spectrum also showed two cage CH resonances at $\delta$ 3.38 and 3.65, in accordance with the structure and symmetry of the molecule. The $^{13}C\{^1H\}$ NMR spectrum revealed, as expected, one resonance due to the CO nuclei at $\delta$ 196.0, but only one broad peak due to the CH carbon nuclei ($\delta$ 43.1), which must be due to partial overlap of two signals.

The IR spectrum of complex **1b** was almost identical with that of **1a**, with strong $\nu_{max}$(CO) absorptions at 2088 and 2070 $cm^{-1}$. The complete lack of molecular symmetry manifests itself in the $^{11}B\{^1H\}$ NMR spectrum as a collection of 17 distinguishable signals (one peak being due to fortuitous overlap of two resonances). Two of these signals ($\delta$ 24.7 and 16.6) were, as determined by deduction from the fully coupled spectrum, due to inequivalent B$-$H $\rightharpoonup$ Co boron nuclei, with $J_{HB}$ coupling constants of 79 and 91 Hz, respectively. Correspondingly, in the $^1H$ NMR spectrum, two broad quartets were observed at $\delta$ $-$12.98 ($J_{BH}$ = 79 Hz) and $-$11.39 ($J_{BH}$ = 91 Hz). As expected, all four CH nuclei gave rise to separate resonances ($\delta$ 3.55, 3.62, 3.75, and 3.96) and this was also the case in the $^{13}C\{^1H\}$ NMR spectrum ($\delta$ 58.3, 55.3, 43.8, and 37.5). In this latter spectrum, two resonances are seen for the inequivalent CO ligands at $\delta$ 195.8 and 193.5. There is little doubt from these spectroscopic data that **1b** is the α,β-isomer, where one of the cages involves a $B_\beta-H \rightharpoonup Co$ linkage and where the cage carbon atoms in the α-system almost certainly lie *anti* to the carbonyl groups.

It should be noted that, even allowing for some flexibility of the molecules in solution in the form of a partial rotation or "wiggling" about the Co$-$Co bond, the overall molecular symmetry and, therefore, the number of signals expected in the NMR spectra of **1a** and **1b** remains the same. Complete rotation about the Co$-$Co bond could only be facilitated by breaking the B$-$H $\rightharpoonup$ Co contacts, and this was indeed observed to be happening, but at a very slow rate. If a solution of pure **1a** was left to stir in $CH_2Cl_2$ at room temperature, then the formation of **1b** was monitored over a period of 24$-$48 h, until an equilibrium ratio of 5:2 (**1a**:**1b**) was achieved. Solutions

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**Table 3.** Selected Internuclear Distances (Å) and Angles (deg) for $[Co_2(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ α,α-Isomer (**1a**) with Estimated Standard Deviations in Parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co(1)−C(1) | 1.784(7) | Co(1)−C(12) | 2.031(6) | Co(1)−B(13) | 2.049(7) | Co(1)−C(11) | 2.090(6) |
| Co(1)−B(14) | 2.109(7) | Co(1)−B(15) | 2.112(7) | Co(1)−B(23) | 2.138(8) | Co(1)−Co(2) | 2.503(2) |
| Co(2)−C(2) | 1.779(7) | Co(2)−C(22) | 2.053(6) | Co(2)−B(23) | 2.056(7) | Co(2)−C(21) | 2.082(7) |
| Co(2)−B(25) | 2.097(7) | Co(2)−B(24) | 2.101(7) | Co(2)−B(13) | 2.134(8) | C(1)−O(1) | 1.137(8) |
| C(2)−O(2) | 1.124(9) | Co(1)−H(23) | 1.66(6) | Co(2)−H(13) | 1.58(8) | B(13)−H(13) | 0.88(8) |
| B(23)−H(23) | 1.04(6) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| C(1)−Co(1)−C(12) | 163.5(3) | C(1)−Co(1)−B(13) | 138.5(3) | C(12)−Co(1)−B(13) | 49.4(3) |
| C(1)−Co(1)−C(11) | 117.4(3) | C(12)−Co(1)−C(11) | 46.1(3) | B(13)−Co(1)−C(11) | 83.8(3) |
| C(1)−Co(1)−B(14) | 93.4(3) | C(12)−Co(1)−B(14) | 84.4(3) | B(13)−Co(1)−B(14) | 51.6(3) |
| C(11)−Co(1)−B(14) | 83.3(3) | C(1)−Co(1)−B(15) | 84.0(3) | C(12)−Co(1)−B(15) | 82.0(3) |
| B(13)−Co(1)−B(15) | 87.4(3) | C(11)−Co(1)−B(15) | 47.2(3) | B(14)−Co(1)−B(15) | 50.6(3) |
| C(1)−Co(1)−B(23) | 93.6(3) | C(12)−Co(1)−B(23) | 99.4(3) | B(13)−Co(1)−B(23) | 98.1(3) |
| C(11)−Co(1)−B(23) | 130.4(3) | B(14)−Co(1)−B(23) | 135.4(3) | B(15)−Co(1)−B(23) | 173.9(3) |
| C(1)−Co(1)−Co(2) | 106.7(2) | C(12)−Co(1)−Co(2) | 89.3(2) | B(13)−Co(1)−Co(2) | 54.8(2) |
| C(11)−Co(1)−Co(2) | 134.6(2) | B(14)−Co(1)−Co(2) | 84.0(2) | B(15)−Co(1)−Co(2) | 134.2(2) |
| B(23)−Co(1)−Co(2) | 51.9(2) | C(2)−Co(2)−C(22) | 163.4(3) | C(2)−Co(2)−B(23) | 139.5(4) |
| C(22)−Co(2)−B(23) | 49.9(3) | C(2)−Co(2)−C(21) | 117.8(3) | C(22)−Co(2)−C(21) | 45.7(3) |
| B(23)−Co(2)−C(21) | 83.4(3) | C(2)−Co(2)−B(25) | 84.4(3) | C(22)−Co(2)−B(25) | 82.5(3) |
| B(23)−Co(2)−B(25) | 87.6(3) | C(21)−Co(2)−B(25) | 47.5(3) | C(2)−Co(2)−B(24) | 94.4(3) |
| C(22)−Co(2)−B(24) | 85.3(3) | B(23)−Co(2)−B(24) | 51.5(3) | C(21)−Co(2)−B(24) | 83.8(3) |
| B(25)−Co(2)−B(24) | 51.1(3) | C(2)−Co(2)−B(13) | 93.1(3) | C(22)−Co(2)−B(13) | 98.8(3) |
| B(23)−Co(2)−B(13) | 98.1(3) | C(21)−Co(2)−B(13) | 130.0(3) | B(25)−Co(2)−B(13) | 173.7(3) |
| B(24)−Co(2)−B(13) | 135.0(3) | C(2)−Co(2)−Co(1) | 107.1(3) | C(22)−Co(2)−Co(1) | 89.4(2) |
| B(23)−Co(2)−Co(1) | 54.9(2) | C(21)−Co(2)−Co(1) | 134.1(2) | B(25)−Co(2)−Co(1) | 134.6(2) |
| B(24)−Co(2)−Co(1) | 83.8(2) | B(13)−Co(2)−Co(1) | 51.7(2) | O(1)−C(1)−Co(1) | 177.2(7) |
| O(2)−C(2)−Co(2) | 178.4(8) | | | | |

containing an initially high proportion of **1b** took slightly less time to equilibrate (<12 h). There are in theory a maximum of six isomers of **1** which could form,[10b] but no others, in particular a *β*,*β*-isomer, were observed, either after the workup of the original preparation or after the solutions were stirred at room temperature and above.

Such interconversion between $B_\alpha$−H $\rightharpoonup$ M and $B_\beta$−H $\rightharpoonup$ M systems has been observed in spectroscopic studies on solutions of the complex $[WIr(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$.[11] In this case an equilibrium exists between three isomers, one where the *closo*-3,1,2-$WC_2B_9$ core utilizes a boron atom in the α-site in the $\overline{\mathrm{CC}\mathit{B}\mathrm{BB}}$ coordinating face of the cage to form a B−H $\rightharpoonup$ Ir bond, a second isomer using a boron in the *β*-position, and a third isomer where no B−H $\rightharpoonup$ Ir group is present. The intermediacy of the latter is believed to provide the route between the other two, since in this isomer the $\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$ cage can rotate to allow either $B_\alpha$−H or $B_\beta$−H bonds to come into position for bonding to iridium. It is this kind of interconversion that, as will be discussed later, can have a significant influence on the reactivity pattern of the compounds **1**.

As mentioned above, **1b** was not obtained entirely free of **1a**, and thus crystals for an X-ray diffraction study were not obtained. However, treatment of mixtures enriched in **1b** with 1 equiv of $PMe_2Ph$ gave isomers of formulation $[Co_2(CO)(PMe_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**2**). Crystals of the major isomer (**2a**) suitable for X-ray analysis were obtained after careful chromatography and recrystallization, thus allowing establishment of its molecular structure.

The molecular structure is shown in Figure 2, and selected bond distances and angles are listed in Table 4. Apart from the replacement of a CO ligand by a $PMe_2Ph$ molecule, the structure of **2a** is similar to that of **1a**. It differs, however, in the disposition of the two B−H $\rightharpoonup$ Co groups. Whereas in **1a** both groups involve boron atoms in the α-sites in the two $\overline{\mathrm{CC}\mathit{B}\mathrm{BB}}$ rings, in **2a** one linkage involves the boron atom B(13), thus forming a $B_\alpha$−H $\rightharpoonup$ Co bond, while the other bridge employs the boron atom B(24), hence forming a $B_\beta$−H $\rightharpoonup$ Co bond. This mode of unsymmetrical exopolyhedral B−H vertex bridge-bonding by two $\eta^5$-7,8-$C_2B_9H_{11}$ groups across a metal−metal bond has been previously seen in the dirhodium complex $[Rh_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$.[10] In both the latter rhodium complex and in **2a** the carbon atoms in the α-cage systems occupy the usual positions *anti* to the carbonyl and phosphine groups, respectively. The Co−Co bond in **2a** [2.5480(9) Å] is slightly longer than that in **1a** but within the customary range of such distances.[5] Several complexes with Co−$PMe_2Ph$ groups have been studied by X-ray crystallography, and the Co−P bond distances are in the range 2.174−2.242 Å.[12] The Co−P bond of 2.269(1) Å in **2a** is somewhat longer.

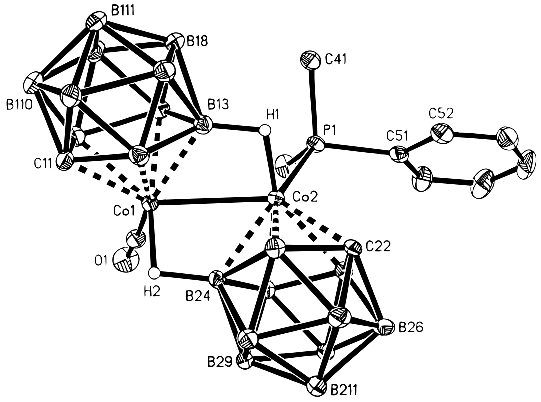

**Figure 2.** Molecular structure of the α,*β*-isomer $[Co_2(CO)(PMe_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**2a**) showing the crystallographic atom-labeling scheme. Thermal ellipsoids are shown at the 40% probability level. Only the agostic hydrogen atoms are shown for clarity.

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**Table 4.** Selected Internuclear Distances (Å) and Angles (deg) for $[Co_2(CO)(PMe_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ α,*β*-Isomer (**2a**) with Estimated Standard Deviations in Parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co(1)−C(1) | 1.783(5) | Co(1)−C(12) | 2.020(4) | Co(1)−B(13) | 2.046(5) | Co(1)−C(11) | 2.102(4) |
| Co(1)−B(15) | 2.121(5) | Co(1)−B(14) | 2.126(5) | Co(1)−B(24) | 2.161(5) | Co(1)−Co(2) | 2.5480(9) |
| Co(2)−B(24) | 2.075(5) | Co(2)−C(21) | 2.075(4) | Co(2)−B(23) | 2.101(5) | Co(2)−B(25) | 2.102(5) |
| Co(2)−C(22) | 2.105(4) | Co(2)−B(13) | 2.159(5) | Co(2)−P(1) | 2.2691(14) | C(1)−O(1) | 1.132(5) |
| P(1)−C(31) | 1.809(5) | P(1)−C(41) | 1.821(5) | P(1)−C(51) | 1.826(4) | C(51)−C(56) | 1.380(6) |
| C(51)−C(52) | 1.407(6) | C(52)−C(53) | 1.383(7) | C(53)−C(54) | 1.387(8) | C(54)−C(55) | 1.375(8) |
| C(55)−C(56) | 1.378(7) | Co(1)−H(2) | 1.59(4) | Co(2)−H(1) | 1.58(4) | B(13)−H(1) | 1.23(4) |
| B(24)−H(2) | 1.24(4) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| C(1)−Co(1)−C(12) | 164.4(2) | C(1)−Co(1)−B(13) | 139.4(2) | C(1)−Co(1)−C(11) | 118.7(2) |
| C(1)−Co(1)−B(15) | 86.7(2) | C(1)−Co(1)−B(14) | 96.0(2) | C(1)−Co(1)−B(24) | 97.1(2) |
| C(1)−Co(1)−Co(2) | 106.3(2) | C(12)−Co(1)−Co(2) | 89.26(12) | B(13)−Co(1)−Co(2) | 54.75(14) |
| C(11)−Co(1)−Co(2) | 134.43(13) | B(15)−Co(1)−Co(2) | 135.52(14) | B(14)−Co(1)−Co(2) | 84.58(14) |
| B(24)−Co(1)−Co(2) | 51.48(13) | B(24)−Co(2)−C(21) | 82.9(2) | B(24)−Co(2)−P(1) | 148.24(14) |
| C(21)−Co(2)−P(1) | 89.10(13) | B(23)−Co(2)−P(1) | 156.79(14) | B(25)−Co(2)−P(1) | 101.45(14) |
| C(22)−Co(2)−P(1) | 112.38(12) | B(13)−Co(2)−P(1) | 96.33(14) | B(24)−Co(2)−Co(1) | 54.59(13) |
| C(21)−Co(2)−Co(1) | 130.00(12) | B(23)−Co(2)−Co(1) | 89.51(14) | B(25)−Co(2)−Co(1) | 82.75(13) |
| C(22)−Co(2)−Co(1) | 134.51(12) | B(13)−Co(2)−Co(1) | 50.70(13) | P(1)−Co(2)−Co(1) | 112.62(4) |
| C(12)−B(13)−Co(1) | 63.8(2) | B(18)−B(13)−Co(1) | 120.0(3) | B(17)−B(13)−Co(1) | 117.1(3) |
| B(14)−B(13)−Co(1) | 66.8(2) | C(12)−B(13)−Co(2) | 111.2(3) | B(18)−B(13)−Co(2) | 145.6(3) |
| B(17)−B(13)−Co(2) | 145.1(3) | B(14)−B(13)−Co(2) | 105.8(3) | Co(1)−B(13)−Co(2) | 74.5(2) |
| B(29)−B(24)−Co(2) | 118.7(3) | B(28)−B(24)−Co(2) | 118.3(3) | B(25)−B(24)−Co(2) | 65.1(2) |
| B(23)−B(24)−Co(2) | 65.0(2) | B(29)−B(24)−Co(1) | 140.9(3) | B(28)−B(24)−Co(1) | 150.1(3) |
| B(25)−B(24)−Co(1) | 101.8(3) | B(23)−B(24)−Co(1) | 111.4(3) | Co(2)−B(24)−Co(1) | 73.9(2) |
| O(1)−C(1)−Co(1) | 177.9(4) | C(31)−P(1)−Co(2) | 114.8(2) | C(41)−P(1)−Co(2) | 120.0(2) |
| C(51)−P(1)−Co(2) | 111.90(14) | | | | |

The IR and NMR spectroscopic data for **2** may now be addressed. The IR spectrum revealed, as expected, one CO absorption at 2056 $cm^{-1}$ for **2a**, with a small but discernible peak at 2028 $cm^{-1}$ arising from a minor isomer. The $^{11}B\{^1H\}$ NMR spectrum (Table 2) showed the expected number of peaks for the major product **2a**, with resonances of note in the fully coupled spectrum at $\delta$ 18.1 and 14.9 ($J_{HB} = 79$ and 85 Hz, respectively), due to the inequivalent $B{-}H \rightharpoonup Co$ boron nuclei. In addition, two weak signals arising from the minor isomer were seen at $\delta$ 14.3 and 10.6 with only the higher field resonance showing a discernible $J_{HB}$ coupling (82 Hz). Peaks due to the minor isomer, apart from in the $^{31}P\{^1H\}$ NMR spectrum, were not observed elsewhere because of its low concentration. This latter spectrum was simple, displaying one large singlet for **2a** at $\delta$ 4.1, with a much weaker resonance at $\delta$ 7.4 for the minor isomer. The $^1H$ NMR spectrum shows two resonances due to the $B{-}H \rightharpoonup Co$ protons at $\delta$ −15.01 and −10.47 with $J_{BH} =$ 79 and 85 Hz, respectively. There were two doublet resonances for the diastereotopic PMe groups ($\delta$ 1.62 and 1.76, both with $J_{PH} = 10$ Hz) and four peaks for the CH protons ($\delta$ 2.25, 2.33, 3.57, and 3.88), in accordance with the lack of molecular symmetry. The $^{13}C\{^1H\}$ NMR spectrum revealed a single resonance due to the CO group ($\delta$ 198.0), and the remaining signals are in agreement with the established structure.

Although the experimental procedure for the synthesis of **2a** from **1b** produced small amounts (<10%) of a minor isomer, **2a** was clearly the major product. The proportion of the minor isomer was somewhat variable and depended on the chromatographic procedure. Curiously, if the synthesis was attempted using pure **1a**, an intractable mixture of **2a**, the minor isomer, and other compounds was produced. The nature of this minor isomer is uncertain, and we rule out multiple substitution by $PMe_2Ph$ to give a complex with no CO ligands, as will be discussed momentarily, particularly as this species appears to display a CO band (2028 $cm^{-1}$) in the IR spectrum. Two possibilities present themselves, which are plausible on the basis of the work discussed so far. The first is an α,*β*-isomer (**2b**) with the same cage $B{-}H \rightharpoonup Co$ configuration as in **2a**, but with the $PMe_2Ph$ carried by the other Co atom. The second is an α,α-isomer (**2c**), similar to **1a** in its cage arrangements, where it would make no difference to which Co atom the $PMe_2Ph$ ligand is attached. In both of these we suggest that the carbon atoms in the α-cage ligands lie *anti* to the carbonyl and phosphine ligands, as has been consistently observed in **1a**, **2a**, and previous structural studies.[10b] Unfortunately we can only speculate, as the NMR spectra for **2b** and **2c** would likely be very similar due to both complexes lacking in any kind of symmetry, and our studies have not allowed us to discriminate between the two. Of course, in the reaction of $PMe_2Ph$ with **1a**, where numerous products are formed, both **2b** and **2c** could be present, and we cannot rule out the formation of species where the α-system cage carbon atoms are *syn* to the carbonyl and phosphine ligands.

Unlike the compounds **1** NMR spectroscopic studies of **2a** showed no tendency for it to equilibrate with its minor isomer(s) in solution, and indeed, traces of the minor isomer detected in the original preparation could be completely removed. Therefore $B_{\alpha/\beta}{-}H \rightharpoonup Co$ interconversion does not appear to be a significant process with the monosubstituted phosphine complexes **2**.

In an attempt to substitute the remaining CO ligand in **2a**, reaction of **1b** with $PMe_2Ph$ was repeated employing 2 equiv of the phosphine in $CH_2Cl_2$. However, only **2a** was recovered from this reaction in any quantity, and no disubstituted product could be isolated. When the reaction was repeated in $CH_2Cl_2$ with a 5-fold excess of $PMe_2Ph$, then the complex $[CoCl(PMe_2Ph)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ (**3**) was formed. While there is a fairly extensive family of compounds known of the type $[Co(\eta^5\text{-}C_5R_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R'_2)]$ and $[Co(\eta^5\text{-}C_2B_9H_9R'R'')_2]^{n-}$ (R = H, Me; R′, R″ = H, alkyl, aryl, halide, $2e^-$ donor ligands; $n = 0, 1$),[13] very few mononuclear cobaltacarborane species containing other inorganic ligands coordinated to the cobalt have been reported. For this reason and because the presence of the chloride ligand was not ascertained from the original NMR measurements, single crystals of compound **3** were obtained and subjected to X-ray analysis. The molecular structure is shown in Figure 3, and selected bond distances and angles are listed in Table 5.

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**Table 5.** Selected Internuclear Distances (Å) and Angles (deg) for [CoCl(PMe$_2$Ph)$_2$($\eta^5$-7,8-C$_2$B$_9$H$_{11}$)] (**3**) with Estimated Standard Deviations in Parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co-C(1) | 2.077(5) | Co-C(2) | 2.092(5) | Co-B(3) | 2.157(6) | Co-B(4) | 2.192(5) |
| Co-B(5) | 2.136(6) | Co-Cl(1) | 2.292(1) | Co-P(1) | 2.271(2) | Co-P(2) | 2.262(2) |
| P(1)-C(11) | 1.820(5) | P(1)-C(12) | 1.817(5) | P(1)-C(13) | 1.821(5) | P(2)-C(21) | 1.818(5) |
| P(2)-C(22) | 1.820(5) | P(2)-C(23) | 1.824(5) | | | | |

| | | | | | |
|---|---|---|---|---|---|
| C(1)-Co-C(2) | 45.5(2) | C(1)-Co-B(3) | 80.4(2) | C(2)-Co-B(3) | 46.2(2) |
| C(1)-Co-B(4) | 81.9(2) | C(2)-Co-B(4) | 81.2(2) | B(3)-Co-B(4) | 49.9(2) |
| C(1)-Co-B(5) | 47.7(2) | C(2)-Co-B(5) | 80.5(2) | B(3)-Co-B(5) | 83.8(2) |
| B(4)-Co-B(5) | 49.0(2) | C(1)-Co-Cl(1) | 95.4(1) | C(2)-Co-Cl(1) | 86.9(1) |
| B(3)-Co-Cl(1) | 115.9(2) | B(4)-Co-Cl(1) | 165.7(2) | B(5)-Co-Cl(1) | 136.7(2) |
| C(1)-Co-P(1) | 99.7(1) | C(2)-Co-P(1) | 143.6(1) | B(3)-Co-P(1) | 157.9(2) |
| B(4)-Co-P(1) | 108.1(2) | B(5)-Co-P(1) | 80.3(2) | Cl(1)-Co-P(1) | 86.2(1) |
| C(1)-Co-P(2) | 160.7(1) | C(2)-Co-P(2) | 115.7(1) | B(3)-Co-P(2) | 81.5(2) |
| B(4)-Co-P(2) | 91.3(2) | B(5)-Co-P(2) | 136.1(2) | Cl(1)-Co-P(2) | 86.6(1) |
| P(1)-Co-P(2) | 99.5(1) | Co-P(1)-C(11) | 120.3(2) | Co-P(1)-C(12) | 116.0(2) |
| C(11)-P(1)-C(12) | 101.0(2) | Co-P(1)-C(13) | 111.5(2) | C(11)-P(1)-C(13) | 99.8(2) |
| C(12)-P(1)-C(13) | 106.2(2) | Co-P(2)-C(21) | 112.9(2) | Co-P(2)-C(22) | 119.1(2) |
| C(21)-P(2)-C(22) | 101.7(3) | Co-P(2)-C(23) | 117.5(2) | C(21)-P(2)-C(23) | 101.8(2) |
| C(22)-P(2)-C(23) | 101.2(2) | | | | |

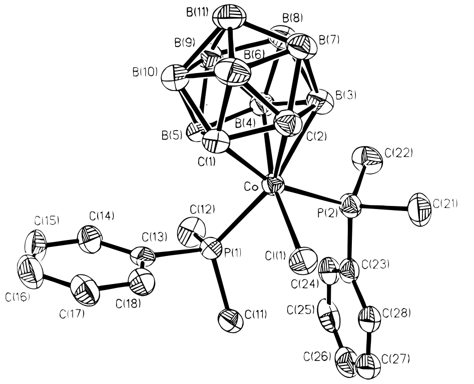

**Figure 3.** Molecular structure of [CoCl(PMe$_2$Ph)$_2$($\eta^5$-7,8-C$_2$B$_9$H$_{11}$)] (**3**) showing the crystallographic atom-labeling scheme. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

The cobalt is ligated in an $\eta^5$ fashion by the $\overline{\mathrm{CC}B\mathrm{BB}}$ face of the cage [Co−C(1) = 2.077(5) Å, Co−C(2) = 2.092(5) Å, Co−B(3) = 2.157(6) Å, Co−B(4) = 2.192(5) Å, Co−B(5) = 2.136(6) Å]. The Co−P bond lengths in **3** (average 2.267 Å) are similar to the Co−P distance observed in complex **2a** [2.269(1) Å] and are again perceptibly longer than those in the other cobalt complexes containing PMe$_2$Ph ligands.[12] The Co−Cl bond [2.292(1) Å] is only slightly longer than the mean Co−Cl distance of 2.260 Å quoted for a range of six-coordinate Co$^{III}$ complexes.[14]

The NMR spectroscopic data for **3** are as expected and reflect the presence in the molecule of a mirror plane that includes the cobalt and chlorine atoms and the midpoint of the C−C connectivity in the cage, with the PMe$_2$Ph ligands sitting symmetrically on either side of this plane. Thus the $^{31}$P{$^1$H} NMR spectrum shows just one signal at $\delta$ 5.2 for the equivalent phosphorus nuclei, and the $^1$H NMR spectrum reveals one resonance for the cage CH protons at $\delta$ 3.49. The latter spectrum shows two virtual triplet signals for the PMe groups ($\delta$ 1.52 and 1.91), as expected for $C_s$ molecular symmetry in solution.

Of interest in the formation of **3** is the origin of the chloride ligand. It is almost certainly derived from the CH$_2$Cl$_2$ solvent used, and examples where metallacarborane complexes have abstracted chlorine atoms from CH$_2$Cl$_2$ are documented.[15,16] We believe that compound **1b** and an excess of PMe$_2$Ph in solution produces an equilibrium mixture (Scheme 1) of a 34e$^-$ diamagnetic Co$_2$ species **A** and a mononuclear 17e$^-$ Co$^{II}$ moiety **B**. The latter then readily abstracts a chlorine atom from the solvent to give the product **3**. If the reaction of PMe$_2$Ph with **1b** is repeated in THF, an extremely air-sensitive yellow-brown solution is produced. A $^{31}$P{$^1$H} NMR spectrum in THF-$d_8$ of the oily product from this reaction shows a very broad resonance at $\delta$ ca. −37 ($\nu_{1/2}$ = 1953 Hz) with a weaker less broad peak at $\delta$ ca. 35 ($\nu_{1/2}$ = 641 Hz) in 4:1 ratio, respectively. We tentatively attribute the smaller signal to diamagnetic complex **A** and the larger to paramagnetic species **B**. Furthermore, the $^{11}$B{$^1$H} NMR spectrum is dominated by very broad peaks due to complex **B** over a wide chemical shift range ($\delta$ −1.2, −82.9, −86.1, and −134.5), consistent with previously reported $^{11}$B NMR spectra of paramagnetic cobaltacarborane complexes.[17] Smaller, sharper peaks also appear in the $^{11}$B{$^1$H} NMR spectrum of the mixture at $\delta$ −7.8, −11.9, −12.9, and −20.1, which would be due to complex **A**. Because of the prevalence in the NMR spectra of peaks due to species **B**, the room temperature equilibrium in THF (Scheme 1) clearly lies well to the right. Variable temperature $^{31}$P{$^1$H} NMR spectra of the **A**−**B** mixture in THF-$d_8$ were therefore measured down to −90 °C. The spectrum at this temperature showed no resonance due to species **B**, but a much stronger sharper peak was observed at $\delta$ 35.3 ($\nu_{1/2}$ = 147 Hz) attributable to complex **A**. This result implies a reversal in the equilibrium position shown in Scheme

## Scheme 1

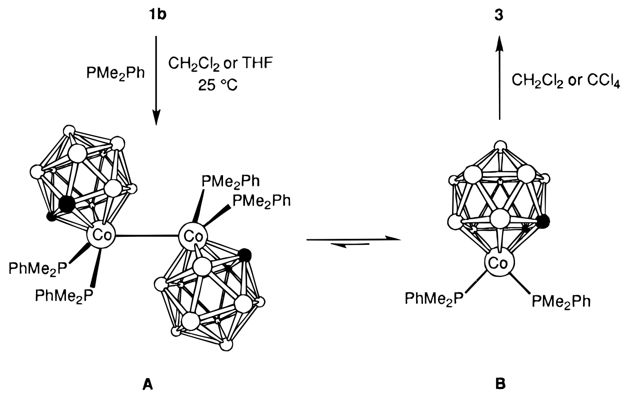

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**Table 6.** Crystallographic Data

| | **1a** | **2a** | **3** |
|---|---|---|---|
| formula | $C_6H_{22}B_{18}Co_2O_2$ | $C_{13}H_{33}B_{18}Co_2OP$ | $C_{18}H_{33}B_9ClCoP_2$ |
| $M_r$ | 438.68 | 548.80 | 503.1 |
| $T$ (K) | 173 | 173 | 292 |
| cryst syst | monoclinic | triclinic | monoclinic |
| space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 15.842(7) | 10.364(3) | 11.8998(13) |
| $b$ (Å) | 9.597(4) | 12.073(3) | 12.973(2) |
| $c$ (Å) | 12.946(4) | 12.251(3) | 16.470(3) |
| α (deg) | | 103.901(12) | |
| $\beta$ (deg) | 91.35(3) | 111.342(12) | 98.468(14) |
| $\gamma$ (deg) | | 104.563(11) | |
| $V$ (Å$^3$) | 1967.7(13) | 1284.9(6) | 2514.9(7) |
| Z | 4 | 2 | 4 |
| $d_{calcd}$ (g cm$^{-3}$) | 1.481 | 1.418 | 1.329 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 1.685 | 1.362 | 0.919 |
| $F$(000) (e) | 872 | 556 | 1040 |
| cryst dimens (mm) | 0.60 × 0.20 × 0.05 | 0.10 × 0.10 × 0.05 | 0.31 × 0.16 × 0.16 |
| crystal color, shape | brown plate | brown prism | purple parallelepiped |
| no. of reflcns measd | 8665 | 4933 | 2633 |
| no. of independent reflcns | 3436 | 3504 | 2333[a] |
| $2\theta$ range (deg) | 5.0−50.1 | 3.7−46.5 | 3.0−40.0 |
| reflcns limits | | | |
| $h$ | −17 to +18 | −11 to +9 | 0 to +11 |
| $k$ | −8 to +11 | −6 to +13 | 0 to +12 |
| $l$ | −15 to +15 | −13 to +13 | −15 to +15 |
| refinement method | full-matrix least-squares on all $F^2$ data | full-matrix least-squares on all $F^2$ data | full-matrix least-squares on observed $F$ data[a] |
| final residuals | $wR_2 = 0.176$[b] ($R_1 = 0.065$)[c] | $wR_2 = 0.096$[b] ($R_1 = 0.044$)[c] | $R = 0.356$ ($R' = 0.400$)[d] |
| weighting factors | $a = 0.0468$; $b = 12.3838$[b] | $a = 0.0000$; $b = 3.8365$[b] | $g = 0.0001$[e] |
| goodness of fit | 1.175 | 1.226 | 1.83 |
| final electron density diff features (max/min) (e Å$^{-3}$) | 1.03, −0.82 | 0.36, −0.31 | 0.80, −0.28 |

[a] 1948 observed reflections used in refinement with $F_o > 4\sigma(F_o)$. [b] Structure was refined on $F_o^2$ using all data: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + a(P)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] The value in parentheses is given for comparison with refinements based on $F_o$ with a typical threshold of $F_o > 4\sigma(F_o)$ and $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $w^{-1} = [\sigma^2(F_o) + gF_o^2]$. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R' = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$. [e] Weighting scheme of the form where $w^{-1} = [\sigma^2(F_o) + gF_o^2]$, where $\sigma^2(F_o)$ is the variance in $F_o$ due to counting statistics; $g$ was chosen so as to minimize variation in $\sum w(|F_o| - |F_c|)^2$ with $|F_o|$.

1, as one would expect since the process is a simple homolytic bond fission/formation reaction. If a few drops of $CCl_4$ are added to the THF solution of **A** and **B**, the color turns immediately purple and compound **3** is formed, identified by its NMR spectra.

Reaction of either **1a** or **1b** in $CH_2Cl_2$ with 2 equiv of $CNBu^t$ at room temperature, followed by column chromatography, produced the complex $[Co_2(CNBu^t)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**4**) in reasonable yield. While the IR spectrum of a petroleum ether solution of **4** showed only two strong, broad $\nu_{max}$(NC) bands at 2190 and 2180 cm$^{-1}$, it was evident from NMR spectroscopy that the compound existed as an inseparable mixture of two isomers, **4a** and **4b**. On the basis of NMR measurements of this and other complexes discussed herein, we can confidently assign the major component **4a** as the α,α-isomer, akin to **1a**, and **4b** as the α,$\beta$-complex, analogous to **1b**. Furthermore, **4a** and **4b** exist in $CH_2Cl_2$ solution in equilibrium in a 3:1 ratio, respectively.

In a fully coupled $^{11}$B NMR spectrum, a doublet peak at $\delta$ 12.3 ($J_{HB} = 89$ Hz) corresponds to the equivalent B−H $\rightharpoonup$ Co boron nuclei in **4a**, with two smaller peaks at $\delta$ 19.0 and 13.0 ($J_{HB} = 79$ and 89 Hz, respectively) due to inequivalent B−H $\rightharpoonup$ Co borons in **4b**. All of the peaks expected for **4a** were accounted for in this spectrum, the remaining signals being attributable to isomer **4b**. Two of the three quartet resonances expected for the B−H $\rightharpoonup$ Co protons in the isomer mixture were observed in the $^1$H NMR spectrum. These occur at $\delta$ −11.54 ($J_{BH} = 89$ Hz) for **4a** and at $\delta$ −13.72 ($J_{BH} = 79$ Hz) for **4b**, the other resonance for **4b** probably being masked by the strong signal due to **4a**. The remaining signals in the $^1$H NMR spectrum were as expected based on a $C_2$ molecular symmetry for **4a** and no symmetry for **4b**. The $^{13}C\{^1H\}$ NMR spectrum clearly revealed a broad resonance due to the *C*NBu$^t$ nuclei in **4a** at $\delta$ 142.9. This chemical shift is somewhat lower than that observed for the ligating isocyanide carbon atoms of the complex $[Co_2(CNBu^t)_8]$,[18] which displays three signals ($\delta$ 229.0, 182.0, and 177.7) in a toluene-$d_8$ solution at −90 °C. However, the chemical shift observed for **4a** is fairly similar in magnitude to the analogous peaks in the $^{13}C\{^1H\}$ NMR spectra of the complexes $[M(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (M = Ni, $\delta$ = 137.1; M = Pt, $\delta$ = 127.7).[9] The minor isomer **4b** shows one peak due to a *C*NBu$^t$ nucleus at $\delta$ 144.1; again it is believed that a second peak may be hidden by the stronger signal due to **4a**. All the remaining signals observed are in agreement with the proposed structures for **4a** and **4b**. It is assumed that the carbon atoms in the α-cage systems in **4a** and **4b** lie *anti* to the CNBu$^t$ ligands, similar to that found for **1a** and **2a**. Of course, only structural analysis by X-ray diffraction could prove this beyond doubt, but it was not possible to obtain X-ray quality crystals of either isomer of **4**.

That the reaction between either **1a** or **1b** and CNBu$^t$ produces a mixture of the isomers **4** at their equilibrium ratio within 1 h of the start of the reaction is interesting, when one considers that it was found that solutions of **1a** or **1b** only attained equilibrium proportions at times ≥12 h. This observation may provide some insight into the reaction mechanism. It is proposed that formation of **4** progresses through initial associa-

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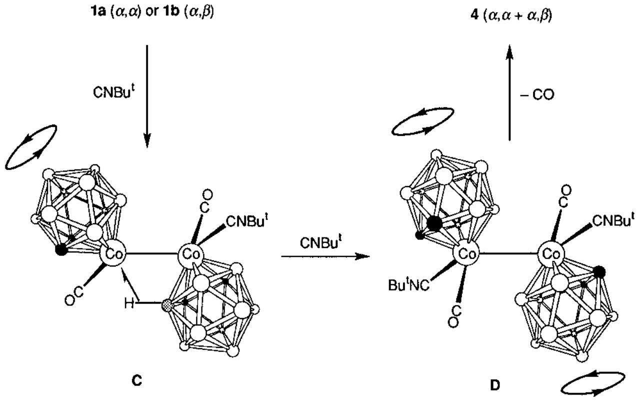
**Scheme 2**



tive steps (Scheme 2). This would involve addition of one or both equivalents of CNBu$^t$ to **1a** or **1b** to give molecules like **C** and **D**, respectively, and would involve a lifting of the B−H $\rightharpoonup$ Co contacts. Bands for CO groups appearing and then diminishing in the IR spectrum in the range 2029−1937 cm$^{-1}$ could correspond to such intermediate species. An opportunity is thus provided for both cages to rotate freely and interconvert the B$_\alpha$−H and B$_\beta$−H bonds used in the formation of the agostic B−H $\rightharpoonup$ Co contacts. Upon loss of CO, the complexes **4** are generated in their thermodynamically stable ratio.

A variable temperature $^{11}$B{$^1$H} NMR experiment was conducted on a toluene-$d_8$ solution of **4**, measuring the spectra at temperatures up to 90 °C to observe the effect on the equilibrium between isomers **4a** and **4b**. Only minimal change was observed when compared with room temperature $CD_2Cl_2$ solutions, there being a slight adjustment in the equilibrium position, with the peaks due to each isomer remaining as distinct as those recorded at ambient temperatures.

The compounds [Co(CO)$_2$($\eta^5$-10-CO-7,8-$C_2B_9H_{10}$)] (**5**) and *nido*-9-CO-7,8-$C_2B_9H_{11}$ (**6**) were minor products of the reaction between [$Co_2(CO)_8$] and *nido*-7,8-$C_2B_9H_{13}$. Both species were never observed other than in poor yield, which is disappointing because **5** is isolobal with the well-known reagent [Co(CO)$_2$($\eta^5$-$C_5H_5$)]. The cage ligand in **5** is zwitterionic and formally contributes five electrons to the metal. Such charge-compensated metallacarboranes are well-known.[19,20] The appearance of only one resonance in the $^1$H NMR spectrum of **5** for the cage CH protons ($\delta$ 3.43) is indicative of the structure shown, with the CO group at the $\beta$-site in the CCB*B*B ring ligating the metal atom. The observation in the $^{11}$B{$^1$H} NMR spectrum of six signals (1:2:2:1:2:1) is also in accord with a symmetrical cage structure. The peak at $\delta$ −23.9 is assigned to the BCO group since in a fully coupled $^{11}$B NMR spectrum it remains as a singlet. A CO stretching band in the IR spectrum at 2156 cm$^{-1}$ may be attributed to the BCO group, with strong bands at 2040 and 1990 cm$^{-1}$ arising from the cobalt carbonyl ligands. The carbonyl carbon nuclei are clearly visible in the $^{13}$C{$^1$H} NMR spectrum, with a broad singlet at $\delta$ 197.0 and a broad quartet at $\delta$ 172.0, the latter showing a $^{11}$B−$^{13}$C coupling of 85 Hz, allowing it to be assigned to the BCO group. It was not possible to obtain **5** in sufficient purity to procure an adequate microanalysis, chiefly because it is formed as an oily solid with unavoidable contamination by very small amounts of **6**. However, a positive-ion EI mass spectrum was obtained and this clearly shows a parent molecular ion peak at *m*/*z* 275 and peaks due to molecular ions resulting from consecutive loss of three CO ligands at 247, 219, and 190, respectively.

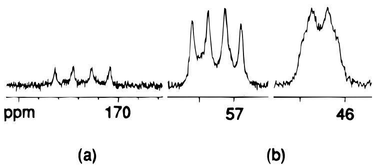


**Figure 4.** $^{13}$C{$^1$H} NMR spectrum showing the principal peaks for the *nido*-carborane **6**: (a) quartet at $\delta$ 171.7 due to the BCO carbon nucleus, (b) signals at $\delta$ 57.5 and 46.6 due to cage CH carbon nuclei.

The *nido*-carborane **6** is a new member of the well-established family of charge-compensated species of formulation *nido*-*n*-L-7,8-$C_2B_9H_{11}$ ($n$ = 9 or 10, L = $NEt_3$, $NMe_2Ph$, $NC_5H_5$, $NC_5H_4CO_2Me$-4, $NMe_2COMe$, THF, NCMe).[19,20] In these molecules a neutral donor molecule L has replaced hydride ($H^-$) on a boron vertex in the open pentagonal face of the cage. Such species have been described as asymmetric ($n$ = 9) or symmetric ($n$ = 10) according to the site occupied by the donor molecule in the face.[19c,21] The location of the proton in the face of the symmetric cage systems apparently does not lower the symmetry, probably because in solution there is rapid exchange between the two possible B$_\alpha$−B$_\beta$(L) bridge sites. The function of a CO molecule as a donor into a carborane cage is comparatively rare, but has been observed before in the related *nido*-icosahedral carborane *nido*-*n*-CO-7-$NMe_3$-7-$CB_{10}H_{10}$ ($n$ = 8 or 9).[22] In this molecule the CO ligand could be bound to either an α- or a $\beta$-site in the $CB_4$ face of the cage. A band in the IR spectrum of **6** at the relatively high frequency of 2152 cm$^{-1}$ is in accord with the presence of the BCO group and is similar to that observed for compound **5**. On the basis of its NMR spectra (Table 2), compound **6** is assigned an asymmetric structure with the CO group attached to a boron atom in the α-site in the CC*B*BB ring. The asymmetry is reflected in the appearance of two resonances at $\delta$ 2.81 and 3.12 in the $^1$H NMR spectrum for the cage CH protons. There is also a broad signal at $\delta$ −2.74 that may be ascribed to the *endo*-B−H−B group. The $^{11}$B{$^1$H} NMR spectrum is also indicative of asymmetry displaying eight peaks, with the relative intensity of one resonance ($\delta$ −0.1) corresponding to the fortuitous overlap of two signals. Importantly, a fully coupled $^{11}$B NMR spectrum revealed that the peak at $\delta$ −30.5 remained a singlet and thus may be assigned to the BCO group. The $^{13}$C{$^1$H} NMR spectrum was particularly informative, and the principal peaks are shown in Figure 4. In accordance with lack of symmetry in the molecule, two resonances are observed for the cage CH nuclei, one of these signals ($\delta$ 57.5) showing a fully resolved $^{11}$B−$^{13}$C coupling of 43 Hz and the other ($\delta$ 46.6) a broader less resolved coupling of ca. 32 Hz. Normally these peaks are broad and weak, and since both these carbon atoms are each bonded to three inequivalent boron atoms in the polyhedral cage framework, the nature of this coupling is unclear. Possibly the couplings are all of a very similar magnitude, especially so for the quartet at $\delta$ 57.5. Most important, though, is the observation of a quartet at $\delta$ 171.7 ($J_{BC}$ = 84 Hz) for the BCO carbon

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nucleus, which is very similar to that seen for the BCO group in compound **5**.

It is strongly believed that compound **6** derives from a cobalt species $[Co(CO)_2(\eta^5\text{-}9\text{-}CO\text{-}7,8\text{-}C_2B_9H_{10})]$ similar to complex **5**. This complex may then have decomposed, ejecting compound **6** possibly during chromatographic workup or even before. We have frequently found that unstable cobaltacarborane species can produce free cages among the decomposition products, though this is the first time a CO ligand from a transition metal moiety has been transferred directly to a $C_2B_9$ cage system. Attempts to synthesize compound **6** using a more logical route based on previous methods used to prepare compounds of the type *nido*-*n*-L-7,8-$C_2B_9H_{11}$ have so far been unsuccessful.

## Conclusions

The isomers **1** are as far as we are aware the first cobaltacarborane carbonyl complexes to be isolated since an early report of the existence of the unstable salt $[NMe_4][Co(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$.[23] Although not structurally similar, the compounds **1** are isolobal with the cylopentadienylnickel carbonyl $[Ni_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$. The reactions between **1** and $PMe_2Ph$ or $CNBu^t$, which afford the species **2**, **3**, and **4**, indicate that the species **1** will serve as useful precursors to other complexes in which a *closo*-3,1,2-$CoC_2B_9$ cage system is bonded via cobalt to other ligands. Although the charge-compensated *nido*-carborane **6** was only obtained in low yield, its existence is of interest in the context of the rarity shown by CO as a donor group to boron.

## Experimental Section

**General Considerations.** Solvents were freshly distilled from appropriate drying agents prior to use. Petroleum ether refers to that fraction of boiling point 40−60 °C. All reactions were performed under an atmosphere of dry nitrogen using Schlenk line techniques. Chromatography columns (ca. 15 cm in length and ca. 3 cm in diameter) were packed with silica gel (Aldrich, 70−230 mesh). Celite pads used for filtration were ca. 4 cm thick. The reagent *nido*-7,8-$C_2B_9H_{13}$ was prepared using a modified literature method.[24] The NMR measurements were recorded in $CD_2Cl_2$ at the following frequencies: $^1H$ at 360.13 MHz, $^{13}C\{^1H\}$ at 90.6 MHz, $^{11}B\{^1H\}$ at 115.3 MHz, and $^{31}P\{^1H\}$ at 145.8 MHz.

**Reaction between $[Co_2(CO)_8]$ and *nido*-7,8-$C_2B_9H_{13}$.** (i) A 500 mL jacketed round-bottom flask fitted with a 500 mL dropping funnel and a nitrogen bubbler was charged with a $CH_2Cl_2$ (150 mL) solution of $[Co_2(CO)_8]$ (2.00 g, 5.85 mmol) and cooled to 0 °C. A solution of *nido*-7,8-$C_2B_9H_{13}$ (1.60 g, 11.90 mmol) in $CH_2Cl_2$ (250 mL) was syringed into the dropping funnel and then added dropwise (ca. 2−3 $s^{-1}$). The mixture was slowly warmed to room temperature and stirred for 24 h. After filtration through a Celite pad, the volume of the solvent was reduced in vacuo to ca. 8 mL and the solution chromatographed at −30 °C. Elution with petroleum ether yielded initially a dark brown fraction containing **1b**. A second dark brown band containing **1a** was next removed using a $CH_2Cl_2$−petroleum ether (1:9) mixture. Further elution with $CH_2Cl_2$−light petroleum ether (2:3) gave a light brown band of **5**. Finally, a pale brown band containing **6** was eluted using $CH_2Cl_2$−petroleum ether (1:1). Solvent was removed from each fraction separately, and the complexes isolated by crystallizations from $CH_2Cl_2$−petroleum ether or petroleum ether as follows: $[Co_2(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**1a**) (0.51 g) from $CH_2Cl_2$−petroleum ether (1:9, 10 mL); $[Co_2(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**1b**) (0.25 g) from $CH_2Cl_2$−petroleum ether (1:9, 10 mL); $[Co(CO)_2(\eta^5\text{-}10\text{-}CO\text{-}7,8\text{-}C_2B_9H_{10})]$ (**5**) (0.13 g) from $CH_2Cl_2$−petroleum ether (1:9, 10 mL) at −78 °C; *nido*-9-CO-7,8-$C_2B_9H_{11}$ (**6**) (0.10 g) from petroleum ether (5 mL) at −78 °C. To achieve microanalytical purity, it was necessary to rechromatograph each fraction and repeat the crystallizations. Even this procedure failed for **5** which persisted as an oily product.

**Table 7.** Atomic Positional Parameters (Fractional Coordinates × $10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for the Atoms of **1a**

| atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Co(1) | 3302(1) | 756(1) | 6460(1) | 27(1) |
| Co(2) | 1737(1) | 987(1) | 6628(1) | 28(1) |
| C(1) | 3471(4) | −479(8) | 5456(6) | 41(2) |
| O(1) | 3596(4) | −1224(6) | 4795(5) | 63(2) |
| C(2) | 1322(5) | 1517(8) | 5400(6) | 50(2) |
| O(2) | 1043(4) | 1857(8) | 4635(5) | 77(2) |
| C(11) | 4346(4) | 1899(7) | 6999(5) | 35(1) |
| C(12) | 3466(4) | 2271(7) | 7542(5) | 33(1) |
| B(13) | 2669(5) | 2594(7) | 6666(5) | 28(1) |
| B(14) | 3158(5) | 2438(8) | 5422(5) | 33(2) |
| B(15) | 4234(5) | 1923(8) | 5702(6) | 34(2) |
| B(16) | 4260(5) | 3500(8) | 7587(6) | 38(2) |
| B(17) | 3194(5) | 3940(7) | 7368(6) | 35(2) |
| B(18) | 2998(5) | 4096(8) | 6012(5) | 34(2) |
| B(19) | 3970(5) | 3672(9) | 5409(6) | 41(2) |
| B(110) | 4738(5) | 3319(9) | 6397(6) | 40(2) |
| B(111) | 3973(5) | 4646(8) | 6573(5) | 39(2) |
| C(21) | 885(5) | 388(8) | 7744(5) | 43(2) |
| C(22) | 1853(4) | 331(7) | 8134(5) | 32(1) |
| B(23) | 2463(5) | −581(8) | 7267(5) | 31(2) |
| B(24) | 1734(5) | −1145(8) | 6258(6) | 32(2) |
| B(25) | 723(5) | −418(9) | 6600(6) | 40(2) |
| B(26) | 1128(6) | −672(9) | 8767(6) | 47(2) |
| B(27) | 2136(6) | −1315(8) | 8465(6) | 38(2) |
| B(28) | 2057(5) | −2280(8) | 7294(6) | 38(2) |
| B(29) | 974(5) | −2186(8) | 6864(6) | 39(2) |
| B(210) | 408(6) | −1181(9) | 7789(7) | 48(2) |
| B(211) | 1227(6) | −2355(9) | 8208(6) | 46(2) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Synthesis of $[Co_2(CO)(PMe_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$.** Compound **1b** (0.20 g, 0.46 mmol) in $CH_2Cl_2$ (20 mL) was treated dropwise with $PMe_2Ph$ (65 $\mu$L, 0.46 mmol), and the mixture was stirred for 6 h. Solvent was reduced in volume in vacuo to ca. 5 mL and the solution chromatographed at −30 °C. Elution with $CH_2Cl_2$−petroleum ether (1:1) removed a red-brown band, from which solvent was removed in vacuo. The residue was crystallized from $CH_2Cl_2$−petroleum ether (1:8, 10 mL) to yield $[Co_2(CO)(PMe_2Ph)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**2a**) (0.13 g).

**Synthesis of $[CoCl(PMe_2Ph)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$.** A solution of **1b** (0.18 g, 0.41 mmol) in $CH_2Cl_2$ (10 mL) was treated with $PMe_2Ph$ (0.30 mL, 2.11 mmol) dropwise and the mixture stirred at room temperature for 3 d. Solvent was removed in vacuo, and the residue was dissolved in $CH_2Cl_2$ (5 mL) and chromatographed at −30 °C. Elution with a $CH_2Cl_2$−petroleum ether mixture (2:3) removed a purple band. Solvent was removed in vacuo, and crystallization of the product from $CH_2Cl_2$−petroleum ether (1:5, 12 mL) gave purple microcrystals of $[CoCl(PMe_2Ph)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ (**3**) (0.26 g).

**Synthesis of $[Co_2(CNBu^t)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$.** Compound **1a** (or **1b**) (0.20 g, 0.46 mmol) was dissolved in $CH_2Cl_2$ (20 mL), and $CNBu^t$ (110 $\mu$L, 0.97 mmol) was added dropwise. The mixture was stirred for 1 h, after which the solution was reduced in volume in vacuo to ca. 5 mL and chromatographed at −30 °C. Elution with $CH_2Cl_2$−petroleum ether (1:1) afforded a brown fraction. Removal of solvent in vacuo and crystallization of the residue from $CH_2Cl_2$−petroleum ether (1:8, 10 mL) gave $[Co_2(CNBu^t)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$ (**4**) (0.16 g from **1a**, 0.13 g from **1b**).

**Crystal Structure Determinations and Refinements.** Crystals of **1a**, **2a**, and **3** were grown by diffusion of petroleum ether into $CH_2Cl_2$ solutions of the complexes. Low-temperature data sets were collected for **1a** and **2a** with the crystals mounted on a glass fiber. A crystal of **3a** was mounted in a glass capillary with data collection carried out at an ambient temperature.

Data for **1a** and **2a** were collected on a Siemens SMART CCD area-detector three-circle diffractometer using Mo Kα X-radiation, $\lambda$ =

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**Table 8.** Atomic Positional Parameters (Fractional Coordinates × $10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × $10^3$) for the Atoms of **2a**

| atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Co(1) | 2764(1) | 2693(1) | 838(1) | 17(1) |
| Co(2) | 4614(1) | 2295(1) | 2594(1) | 16(1) |
| C(11) | 1477(5) | 3793(4) | 780(4) | 22(1) |
| C(12) | 2230(5) | 3628(4) | 2102(4) | 21(1) |
| B(13) | 4139(6) | 3942(5) | 2632(5) | 20(1) |
| B(14) | 4555(6) | 4387(5) | 1465(5) | 22(1) |
| B(15) | 2744(6) | 4207(5) | 252(5) | 23(1) |
| B(16) | 1720(6) | 4873(5) | 2102(5) | 26(1) |
| B(17) | 3418(6) | 4978(5) | 3300(5) | 23(1) |
| B(18) | 4885(6) | 5525(5) | 2898(5) | 23(1) |
| B(19) | 4041(6) | 5694(5) | 1401(5) | 24(1) |
| B(110) | 2103(6) | 5293(5) | 958(5) | 27(1) |
| B(111) | 3416(6) | 6091(5) | 2570(5) | 26(1) |
| C(21) | 4913(5) | 670(4) | 2651(4) | 21(1) |
| C(22) | 4412(5) | 1217(4) | 3686(4) | 18(1) |
| B(23) | 2902(5) | 1568(5) | 3053(5) | 19(1) |
| B(24) | 2418(5) | 1114(4) | 1390(4) | 17(1) |
| B(25) | 3814(5) | 562(4) | 1175(5) | 20(1) |
| B(26) | 4082(6) | −325(5) | 3233(5) | 22(1) |
| B(27) | 2751(6) | 233(5) | 3449(5) | 23(1) |
| B(28) | 1453(6) | 134(5) | 1960(5) | 21(1) |
| B(29) | 2011(5) | −502(4) | 799(5) | 18(1) |
| B(210) | 3652(6) | −767(5) | 1613(5) | 21(1) |
| B(211) | 2184(6) | −1044(5) | 2058(5) | 22(1) |
| C(1) | 2873(5) | 1979(4) | −562(4) | 24(1) |
| O(1) | 2915(4) | 1542(3) | −1470(3) | 38(1) |
| P(1) | 6996(1) | 3101(1) | 2887(1) | 19(1) |
| C(31) | 7228(5) | 2713(5) | 1467(4) | 31(1) |
| C(41) | 8038(5) | 4756(4) | 3652(4) | 27(1) |
| C(51) | 8238(5) | 2551(4) | 3915(4) | 22(1) |
| C(52) | 8421(5) | 2837(4) | 5158(4) | 26(1) |
| C(53) | 9382(6) | 2476(5) | 5990(5) | 36(1) |
| C(54) | 10158(6) | 1815(5) | 5607(6) | 45(2) |
| C(55) | 9966(6) | 1527(5) | 4388(6) | 45(2) |
| C(56) | 9019(5) | 1890(5) | 3555(5) | 33(1) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table 9.** Atomic Positional Parameters (Fractional Coordinates × $10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × $10^3$) for the Atoms of **3**

| atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Co | 2439(1) | 1810(1) | 959(1) | 28(1) |
| C(1) | 1643(4) | 454(3) | 1231(3) | 36(2) |
| C(2) | 2471(4) | 285(4) | 550(3) | 37(2) |
| B(3) | 3783(5) | 726(4) | 849(4) | 37(2) |
| B(4) | 3785(5) | 1215(5) | 1894(3) | 37(2) |
| B(5) | 2355(5) | 1025(4) | 2088(3) | 36(2) |
| B(6) | 2082(5) | −791(5) | 1059(4) | 47(2) |
| B(7) | 3481(5) | −614(5) | 839(4) | 44(2) |
| B(8) | 4307(5) | −52(5) | 1705(3) | 42(2) |
| B(9) | 3403(5) | 125(5) | 2460(4) | 44(2) |
| B(10) | 2034(5) | −330(5) | 2056(4) | 45(2) |
| B(11) | 3260(5) | −991(5) | 1836(4) | 49(2) |
| Cl(1) | 1224(1) | 2149(1) | −225(1) | 42(1) |
| P(1) | 1401(1) | 2967(1) | 1570(1) | 31(1) |
| C(11) | 800(4) | 4095(4) | 1009(3) | 44(2) |
| C(12) | 2115(4) | 3558(4) | 2506(3) | 49(2) |
| C(13) | 108(4) | 2387(3) | 1832(3) | 31(2) |
| C(14) | −93(5) | 2266(4) | 2642(3) | 43(2) |
| C(15) | −1096(5) | 1823(4) | 2804(3) | 52(2) |
| C(16) | −1906(5) | 1492(4) | 2179(4) | 56(3) |
| C(17) | −1714(4) | 1605(4) | 1380(3) | 48(2) |
| C(18) | −723(4) | 2043(4) | 1206(3) | 41(2) |
| P(2) | 3670(1) | 2899(1) | 476(1) | 34(1) |
| C(21) | 3875(5) | 2609(4) | −572(3) | 52(2) |
| C(22) | 5127(4) | 2966(4) | 995(4) | 52(2) |
| C(23) | 3290(4) | 4262(4) | 401(3) | 34(2) |
| C(24) | 3678(4) | 4926(4) | 1040(3) | 41(2) |
| C(25) | 3389(5) | 5963(4) | 983(4) | 55(3) |
| C(26) | 2721(5) | 6336(5) | 291(4) | 58(3) |
| C(27) | 2354(4) | 5698(5) | −343(4) | 51(2) |
| C(28) | 2623(4) | 4658(4) | −289(3) | 41(2) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

0.710 73 Å. For three settings of $\phi$, narrow data "frames" were collected for 0.3° increments in $\omega$. In both cases 1321 frames of data were collected affording rather more than a hemisphere of data. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections. Crystals of **2a** were very small, and data frames were collected for 60 s per frame giving an overall data collection time of ca. 25 h. For **1a** data frames were collected for 20 s per frame. The data frames were integrated using SAINT,[25a] and the structures were solved by conventional direct methods. The structures were refined by full-matrix least squares on all $F^2$ data using Siemens SHELXTL version 5.03,[25b] and with anisotropic thermal parameters for all non-hydrogen atoms. For both **1a** and **2a** the agostic B−H ⇀ Co protons were located from final electron density difference syntheses, and their positions were refined. All other hydrogen atoms were included in calculated positions and allowed to ride on the parent boron or carbon atoms with isotropic thermal parameters ($U_{\mathrm{iso}} = 1.2 \times U_{\mathrm{iso\ equiv}}$ of the parent atom except for Me protons where $U_{\mathrm{iso}} = 1.5 \times U_{\mathrm{iso\ equiv}}$). All calculations were carried out on Silicon Graphics Iris, Indigo, or Indy computers.

The data set for **3** was collected on an Enraf-Nonius CAD4-F automated diffractometer operating in the $\omega-2\theta$ scan mode, using graphite-monochromated Mo Kα X-radiation. Data were collected at various scan speeds of 0.54−5.17° min$^{-1}$ in $\omega$ with a scan range of $1.15° + 0.34 \tan \theta$. No significant variations were observed in the intensities of the monitored check reflections (<1%). All observed data were corrected for Lorentz and polarization effects, after which an empirical absorption correction[26] based on nine high-angle $\psi$ scans was carried out. The structure was solved by direct methods, which located most of the non-hydrogen atoms, and successive Fourier difference syntheses were used to locate all remaining non-hydrogen atoms. Refinement was by full-matrix least squares on *F* using Siemens SHELXTL-PC version 4.1,[25c] with anisotropic thermal parameters for all non-hydrogen atoms. Methyl and phenyl hydrogen atoms were included in calculated positions (C−H 0.96 Å) and constrained to ride on their parent carbon atoms with fixed isotropic thermal parameters ($U_{\mathrm{iso}} = 0.08$ Å$^2$). Terminal B−H hydrogen atoms were also included in calculated positions (B−H 1.10 Å, $U_{\mathrm{iso}} = 0.06$ Å$^2$).[27] All calculations were performed on a VAX station. Atomic scattering factors were taken from the usual source.[28]

Final atomic positional parameters for non-hydrogen atoms with equivalent isotropic thermal parameters for complexes **1a**, **2a**, and **3** are listed in Tables 7, 8, and 9, respectively.

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**Supporting Information Available:** Complete tables of atom parameters, bond lengths and angles, and anisotropic thermal parameters for **1a**, **2a**, and **3** (36 pages). Ordering information is given on any current masthead page.

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