$(CH_3)_2NNH_2$ does not appear to be moisture-sensitive (the ^1H NMR spectrum of a material exposed to laboratory atmosphere for 24 h was identical with that of a freshly prepared product), but the adduct is thermally fairly unstable. Decomposition to the individual components was observed to occur near 100 °C under vacuum. The complex $(-BC_6H_5O-)_3 \cdot 2(CH_3)_2NNH_2$ was also isolated; it is thermally quite unstable and, after melting, begins to decompose into the individual components. The room-temperature ^{11}B NMR data for both the 1:1 and the 1:2 complex are essentially identical.

$(-BC_6H_5O-)_3 \cdot CH_3NNHCH_3$ is extremely hygroscopic and thermally not very stable. When heated under atmospheric pressure, it loses hydrazine even before melting. No other adduct composition between the two agents was observed.

B-Triphenylboroxin and hydrazine interact in both 1:1 and 1:2 molar ratios. Of these adducts, the 1:1 molar complex does not readily decompose on melting but decomposes to the components on heating to 90–100 °C under vacuum. The 1:2 species loses hydrazine just above its melting point (48–52 °C) and under atmospheric pressure. Thereafter the thermal behavior is analogous to that of the 1:1 complex.

Discussion

Hydrazines interact readily with *B*-triorganylboroxins to form 1:1 molar complexes. The room-temperature ^{11}B NMR data show that these complexes are fluxional, and all three boron atoms of the boroxin are involved in the bonding. At low temperatures, however, the N-to-B coordination is localized at only one boron atom, rendering it be sp^3 hybridized, whereas the other two boron atoms are in an sp^2 environment. These observations also imply that the hydrazines function exclusively in monodentate fashion when interacting with boroxins. Otherwise, the observed ratio of the ^{11}B NMR signals for three-coordinate vs. four-coordinate boron should be in the reverse order to show bidentate intramolecular coordination, or the hydrazines should form 1:2 molar complexes with the boroxins, which is not the case. On the other hand, it is possible that more than one hydrazine molecule coordinates to a single boroxin ring. However, such additional interaction is very weak and may be viewed as solvation rather than coordination. This interpretation is supported by the ready loss of excess (as compared to a 1:1 molar ratio) of the hydrazine. There is little if any difference in the ambient-temperature ^{11}B NMR spectra of the 1:1 complexes and the solvated species.

It is worth noting that such solvated complexes were observed only in cases where the hydrazine contained at least one NH_2 group. This suggests that the NH_2 grop of *N,N*-dimethylhydrazine is the more likely donor site in this 1:1 complexes. Coordination of the sterically least hindered donor site is also in consonance with some infrared data. Furthermore, a steric effect is also suggested by the different thermal stabilities of the various species; i.e., with increasing steric crowding (either at boron or at nitrogen) the thermal stabilities of the adducts decrease. However, the different thermal stabilities are not reflected by the room-temperature ^{11}B NMR data, since all compounds exhibit a (single) signal in the 20–24 ppm range. The 70-eV mass spectra of all of these complexes exhibit only the fragmentation patterns of the individual components. Very weak parent ion clusters of the 1:1 molar complexes could be observed in some cases in the 14-eV spectra.

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Organotransition-Metal Metallacarboranes. 11.[1] Chromium Tricarbonyl η^6-Complexes of *nido*-2,3-$(PhCH_2)_2C_2B_4H_6$: Metal Complexation and Oxidative Fusion

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The consequences of η^6-phenyl coordination of $Cr(CO)_3$ groups on the chemistry of the *C,C'*-dibenzylcarborane *nido*-2,3-$(PhCH_2)_2C_2B_4H_6$ (**1**) were investigated. The monochromium species $[(CO)_3Cr](PhCH_2)_2C_2B_4H_6$ (**2**) underwent bridge (B–H–B) deprotonation by NaH in THF, and the resulting anion, on treatment with $FeCl_2$, formed $[[(CO)_3Cr](PhCH_2)_2C_2B_4H_4]_2FeH_2$ (not isolated); subsequent oxidation with O_2 gave two isomers of $[(CO)_3Cr]_2(PhCH_2)_4C_4B_8H_8$ (**7A,B**), which were characterized spectroscopically. Reaction of the tetracarbon carborane $(PhCH_2)_4C_4B_8H_8$ (**5**) with $Cr(CO)_6$ gave dichromium products identical with **7A,B** but no other isomers. An attempted analogous sequence with $[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_6$ (**3**) proceeded only as far as bridge deprotonation with KH; the resulting anion on treatment with $FeCl_2/O_2$ did not undergo fusion, nor was fusion observed with other transition metals. An attempted mixed-ligand fusion of the anions of **1** and **3** gave only **5** and the original substrate **3**. Deprotonation of **3** was shown to proceed cleanly, via deuteriation of the anion to produce monodeuteriated **3**. The resistance of **3** to oxidative fusion is discussed in terms of steric and electronic effects.

Introduction

The *nido*-dibenzylcarborane 2,3-$(PhCH_2)_2C_2B_4H_6$ (**1**), an air-stable nonvolatile liquid,[2] has three active sites for metal π-complexation, specifically the C_2B_3 ring (following bridge deprotonation) and the two phenyl groups. A fourth site can be created, in ferracarborane derivatives of **1**, by "decapitation" (apex-BH removal) to form a second C_2B_3 face.[2] This multifold controlled reactivity toward metal coordination makes **1** a highly versatile reagent in the emerging area of organotransition metal–carborane chemistry. We have described elsewhere[1] the synthesis and structure of the mono- and bis(chromium tricarbonyl) π-complexes $[(CO)_3Cr]_n(PhCH_2)_2C_2B_4H_6$ (**2**, $n = 1$; **3**, $n = 2$). Since the uncomplexed carborane **1** (in common with most known *nido*-2,3-$R_2C_2B_4H_6$ species where R = alkyl[3] or arylalkyl[1]) undergoes bridge deprotonation by NaH or KH, followed by complexation with Fe^{2+} to form $[(PhCH_2)_2C_2B_4H_4]_2FeH_2$ (**4**), and oxidative fusion of the latter to generate $(PhCH_2)_4C_4B_8H_8$ (**5**),[1] we were interested in exploring the effects of the coordinated $Cr(CO)_3$ groups in **2** and **3** on this well-established carborane reaction sequence.

Results and Discussion

Deprotonation and Metal-Promoted Fusion of $[(CO)_3Cr](PhCH_2)_2C_2B_4H_6$ (2). Scheme I illustrates the previously demonstrated[1] conversion of **1** to the bis(dibenzylcarboranyl)iron

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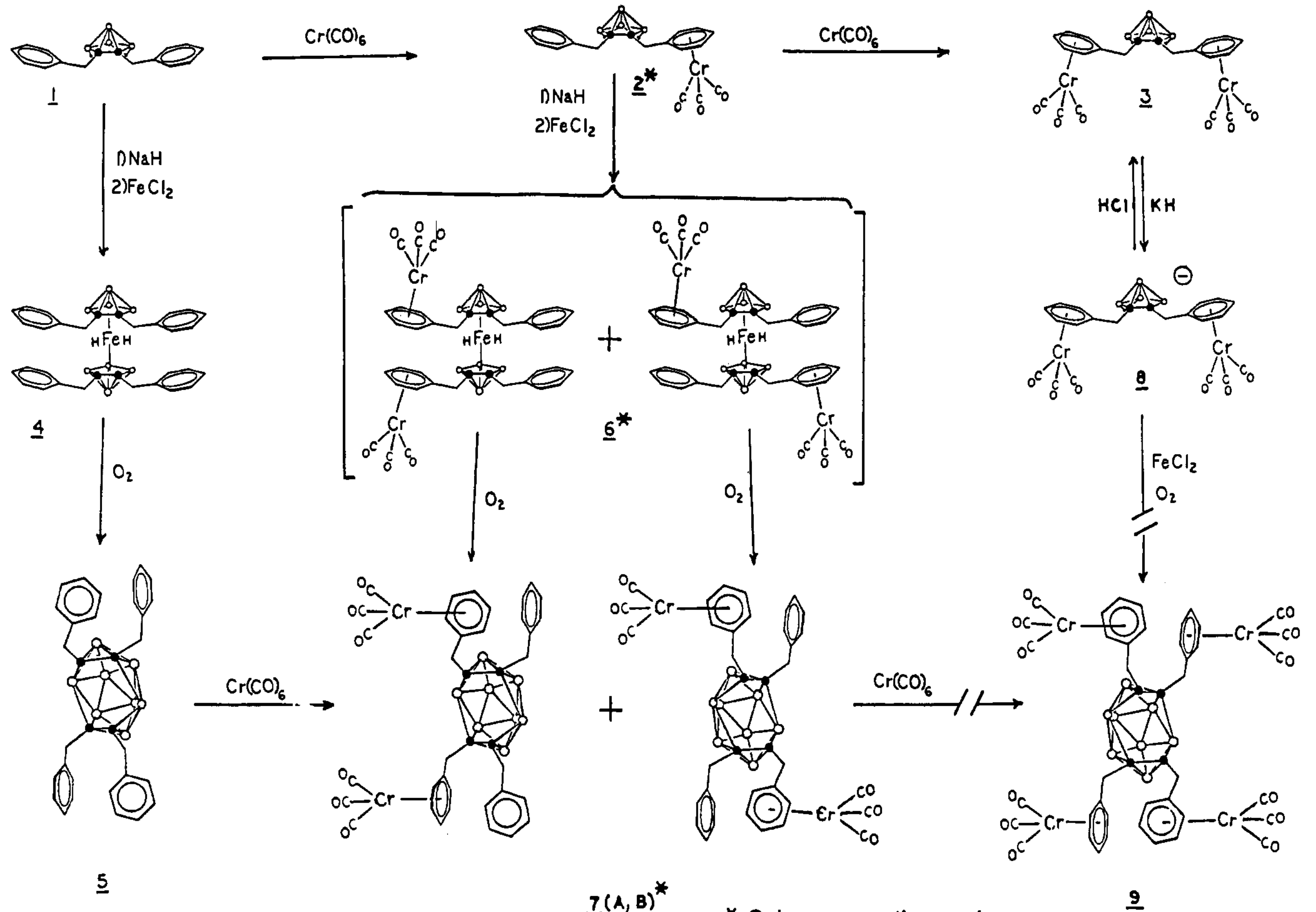
(1) Part 10: Spencer, J. T.; Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* **1987**, *6*, 335.

(2) Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 328.

0020-1669/87/1326-3116$01.50/0

Scheme I[a]



* Only one enantiomer shown for each isomer

[a] Key: ●, C; ○, BH.

complex **4** and the fusion of the latter to give the tetracarbon carborane **5**. In the present work, a corresponding sequence was investigated with the monochromium species **2**,[1] a pale yellow solid. Deprotonation of **2** was achieved with NaH in cold THF solution, producing H_2 and the deep yellow $[Cr(CO)_3](PhCH_2)_2C_2B_4H_5^-$ ion. On addition of anhydrous $FeCl_2$ at −78 °C and subsequent stirring, no color change was observed, but treatment of the solution with O_2 for several hours, and subsequent workup, gave an orange product characterized as $[(CO)_3Cr]_2Ph_4C_4B_8H_8$ (**7**), which on preparative-layer chromatography was resolved into two isomers, **7A**,**B**. There is no evidence of other products. Both isomers are moderately air- and light-sensitive in the solid state but rapidly decompose in solution, in contrast to the uncomplexed carborane **5**, which is an air-stable colorless solid.[1] The ferracarborane intermediates **6** depicted in Scheme I were not isolated, but their formation is inferred from the oxidation products **7** and via analogy with known fusion reactions of $(R_2C_2B_4H_4)_2FeH_2$ species (vide supra).[1,3]

The isomers of **7** were characterized from their IR, ^{11}B NMR, and positive and negative ion mass spectra, which support their formulation as $Cr(CO)_3$ complexes of the structurally defined[1] tetraphenyl carborane **5**. Although the electron-impact mass spectra (identical for the two isomers) exhibit only a very weak parent peak, with more intense groups corresponding to the loss of CO and $Cr(CO)_3$ units, the positive and negative ion chemical ionization spectra contain strong parent groupings whose patterns conform closely to the calculated intensities based on natural isotope abundances. In the negative ion spectra, the parent group is the most intense in the spectrum (typical for metallacarboranes), and the only significant fragments are at *m/z* 645 and 509, corresponding to loss of one and two $Cr(CO)_3$ units. The ^{11}B spectra of **7A**,**B** are very similar to each other and to the spectrum of the uncomplexed compound **5**[1] [δ −2.88 and −12.86 (J = 134 Hz), area ratio 3:1, in CH_2Cl_2]. The small influence of the $Cr(CO)_3$ moieties on the ^{11}B shifts in **7A**,**B** contrasts interestingly with the spectra of the chromium tricarbonyl complexes of $(PhCH_2)_2C_2B_4H_6$ (**2** and **3**); as was shown earlier,[1] in the latter compounds the ^{11}B resonances of the *basal* boron atoms are shifted significantly to high field (ca. 1.3 ppm) compared to the uncomplexed carborane **1**. [The ^{11}B shifts for the dichromium complex **3** are incorrectly reported in ref 1 (compound **6** in that paper); the correct values are −1.64, −3.91 (J = 154), and −47.92 (J = 186) ppm, with coupling constants in Hz given in parentheses]. The observation that complexation by $Cr(CO)_3$ produces somewhat smaller shifts in the $(PhCH_2)_4C_4B_8H_8$ spectrum is indicative of rather substantial differences in electronic structure between the *nido*-C_2B_4 and C_4B_8 carborane systems. Possibly ring currents in the basal ring of the C_2B_4 cage transmit electronic effects more efficiently than is the case in the C_4B_8 framework. As anticipated, the infrared spectra of isomers **7A**,**B** exhibit strong B–H and carbonyl C–O stretching frequencies in the regions 2500 and 1900 cm^{-1}, respectively.

The fact that two (and apparently only two) isomers of **7** are produced is in agreement with the proposed formation of **7** via oxidative fusion of the formal $(CO)_3Cr(PhCH_2)_2C_2B_4H_4^{2-}$ ligands in **6**. Since **2** and its deprotonated ions are necessarily chiral, face-to-face fusion to give **7** can occur between identical ligands (*d*,*d*, and *l*,*l*) and between enantiomers (*d*,*l*); in the former case the $[(CO)_3Cr]_2(PhCH_2)_4C_4B_8H_8$ product has its $Cr(CO)_3$ units

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(3) (a) Grimes, R. N. *Acc. Chem. Res.* **1983**, *16*, 22. (b) *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55 and references therein. (c) Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983 and references therein. (d) Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 323.

in a trans arrangement, while the *d,l* combination generates a cis product (Scheme I).[4] The cis and trans forms are, of course, geometric isomers (diastereomers) and hence physically separable, as observed; on the basis of the established structure of **5**, each must consist of a racemic mixture of enantiomers, which have not been resolved.[5] If the *d,d*/*l,l* and *d,l* combinations of ligands are statistically equally probable, as would be the case in the absence of directive effects, one expects to find the cis and trans forms of **7** formed in equal amounts. This is essentially what is observed, which we take as an indication that there is, indeed, no large interligand steric interaction in the intermediate **6** or during the fusion process.

If more than one stable C_4B_8 cage geometry were present, additional isomers might be found; moreover, migration of $Cr(CO)_3$ units could conceivably generate a third distinct isomer, similar to **7A,B** but with the two $(CO)_3CrPhCH_2$ groups attached to adjacent cage carbon atoms. Again, the absence of evidence for more than two isomers of **7** suggests that neither of these possibilities has occurred. Moreover, the ^{11}B NMR spectra of **7A,B**, like that of the uncomplexed tetraphenylcarborane **5**,[1] are invariant over time, showing that there is no cage fluxionality of the kind previously observed[6] and that the C_4B_8 framework in **7** is locked into an open configuration. This is in sharp contrast to $R_4C_4B_8H_8$ species where R = Me, Et, or *n*-Pr, which in solution manifest two cage isomers in equilibrium.[6]

Reaction of $(PhCH_2)_4C_4B_8H_8$ (5) with $Cr(CO)_6$. In the absence of crystallographic proof of the structures of **7A,B**, it occurred to us that these same species ought to be obtainable via direct attack of $Cr(CO)_3$ groups on the tetraphenyl carborane (**5**), if our proposed formualations of **7A,B** were correct. Accordingly, **5** was treated with excess $Cr(CO)_6$ in refluxing 9:1 dibutylether/THF, affording an orange product, which was isolated and shown to be a mixture of **7A,B** in yields of 21 and 23%, respectively. Comparison of NMR, IR, and mass spectra confirmed the identity of these products with those obtained from $(CO)_3Cr(PhCH_2)_2C_2B_4H_8$ (**2**) via fusion, as described above. Since the geometry of **5** itself has been established,[1] this result supports, to a high degree of confidence, the structural characterizations of **7A,B** as shown. One problem, however, remains: which isomer is which? Although one could construct rationalizations based on the small spectral differences between the two isomers, this question appears unresolvable at present. The ^{11}B NMR spectra of **7A,B** are clearly too little affected by the $(CO)_3CrPhCH_2$ substituents to provide useful structural information. We also have no convincing explanation for the absence of the hypothetical "third isomer" [having both $Cr(CO)_3$ units on adjacent *C*-benzyl units] in the products obtained directly from **5**. It is probable that the initial $Cr(CO)_3$ exerts an electronic directive effect on further chromium complexation in the C_4B_8 system, but it is to be noted that such effects do not prevent addition of a second $Cr(CO)_3$ to **2**, forming **3**.[1]

Treatment of **7** (combined isomers) with $Cr(CO)_6$, $Cr(NH_3)_3(CO)_3$, or $Cr(CH_3CN)_3(CO)_3$ in an effort to coordinate chromium to the uncomplexed phenyl groups, gave no evidence of reaction.

Deprotonation and Attempted Complexation and Fusion of $[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_6$ (3). The foregoing discussion suggests that fusion of the bis(chromium tricarbonyl) carborane **3** via metal complexation of its anion should give a single product, $[(CO)_3Cr]_4(PhCH_2)_4C_4B_8H_8$ (**9**), which would have four identical chromium tricarbonylbenzyl ligand units (Scheme I). The first step in the sequence, bridge deprotonation, was achieved only with difficulty, as **3** reacts very slowly with NaH in THF at room temperature but more rapidly with KH, to give the blood red $[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_7^-$ ion (**8**). To confirm that this reaction involved only deprotonation according to eq 1, the solution of **8** was treated with excess DCl, quantitatively generating yellow-orange $[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_7D$.

$$\underset{\textbf{3};\ \text{yellow-orange}}{[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_6} \xrightarrow[-H_2]{H^-} \underset{\textbf{8};\ \text{deep red}}{[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_5^-} \quad (1)$$

In contrast to the behavior of the anion of the monochromium species **2** described above, addition of $FeCl_2$ to a solution of **8** followed by prolonged treatment with O_2 gave no evidence of the fused carborane **9** (or any other characterizable product) and only the original carborane complex **3** was recovered. Moreover, the fusion of **3** via its anion was attempted with several other transition-metal halides and under a variety of reaction conditions, with the same result. Hence it appears that fusion in this case is blocked by the presence of two $Cr(CO)_3$ units on the carborane substrate. In a further probe of this presumed steric effect, we attempted the mixed-ligand fusion of **1** and **3** via their deprotonated anions; such a process, if it occurred, should give the unknown third isomer of **7** having both $Cr(CO)_3$ units of the same C_2B_4 half-cage. However, exposure of an equimolar mixture of the anions of **1** and **3** to $FeCl_2$ and O_2 gave only the "homogeneous" fusion product **5** plus recovered **3** in 40 and 50% yields, respectively. Thus we conclude that the dichromium complex **3** is, at the least, strongly resistant to oxidative fusion.

The failure of **3** to undergo fusion is reminiscent of recent findings in our laboratory with other *nido*-$R_2C_2B_4H_6$ carboranes where R is a bulky group, e.g., indenylmethyl or fluorenylmethyl.[7] These species behave similarly to **3**, undergoing bridge deprotonation with NaH or KH only slowly, and giving no evidence of fusion on treatment with metal ions and O_2 (in the case of the bis(indenylmethyl) carborane, we do know that at least metal complexation occurs[7] with Fe^{2+}).

It is tempting to conclude simply that fusion in these cases is sterically blocked by the large substituents. However, there are also indications that electronic effects in the $Cr(CO)_3$ complexes may play a role. We note that reaction of the tetrabenzylcarborane **5** with a large excess of $Cr(CO)_6$ produces only dichromium products, with no evidence of further metal complexation (vide supra). Since the attack of $Cr(CO)_3$ on the remaining uncomplexed phenyl rings of **7** should be relatively unhindered, we can only infer that those rings have been deactivated (with respect to complexation) by the $Cr(CO)_3$ units already present. If the boron framework in **3** were similarly deactivated (i.e. by electron withdrawal by the $Cr(CO)_3$ groups), this could at least partially account for its inability to complex with Fe^{2+} and/or to undergo fusion. The fact that the anion of **3** will not fuse even with that of the uncomplexed carborane **1** is consistent with this idea, since steric crowding in this case is surely no more severe than in the observed fusion of the monochromium complex **2** with itself. In summary, at this point it appears that the nonfusion of **3** is a consequence of both steric crowding and electron withdrawal induced by the $Cr(CO)_3$ units. As noted earlier, the observation of other "nonfusable" $R_2C_2B_4H_6$ carboranes[7] should help to illuminate this problem.

Experimental Section

Materials. $(PhCH_2)_4C_4B_8H_8$, $(CO)_3Cr(PhCH_2)_2C_2B_4H_6$, and $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ were prepared as previously reported.[1] $Cr(NH_3)_3(CO)_3$ and $Cr(CH_3CN)_3(CO)_3$ were prepared by literature methods.[8,9] All solvents used were degassed with a dry nitrogen stream and stored over 4-Å molecular sieves prior to use. Deuteriated solvents were purchased from the Aldrich Chemical Co. The following reagents

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(4) The terms "cis" and "trans" designate the isomers of **7** shown left and right, respectively, in Scheme I.

(5) In principle, a second type of trans isomer (not shown in Scheme I) can occur, in which both $(CO)_3CrPhCH_2$ groups are attached to the high-coordinate cage carbons on the C_4B_8 framework. However, the two possible trans geometries differ only slightly; in solution they undoubtedly undergo rapid low-energy interconversion involving a small movement of cage atoms, which would be undetectable via NMR spectroscopy.

(6) Venable, T. L.; Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 6187.

(7) Fessler, M. E.; Spencer, J. T.; Grimes, R. N., manuscript in preparation.

(8) Rausch, M. D.; Moser, G. A.; Zaiko, E. J.; Lipman, A. L., *J. Organomet. Chem.* **1970**, *23*, 185.

(9) Knox, G. R.; Leppard, P. G.; Paulson, P. L.; Watts, W. E. *J. Organomet. Chem.* **1974**, *71*, 347.

were used as received: butyl ether (Aldrich, 99+%), NaH (Aldrich, 60% in mineral oil), KH (aldrich, 35% in mineral oil), and chromium hexacarbonyl (Strem). NaH and KH were washed twice with anhydrous hexane prior to use.

Instrumentation. ^{11}B (115.8 MHz) high-resolution pulse Fourier transform NMR spectra were obtained on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and data manipulation utilized standard Nicolet software with a 1280/293B data system. Broad-band heteronuclear decoupling was employed. Unit resolution mass spectral measurements of deuteriated **3** and of **7** were recorded on a Finnigan MAT-4500 GC/MS spectrometer with perfluorotributylamine (FC43) as a calibration standard. The negative ion mass spectra of these compounds exhibited strong parent envelopes (the most intense in the spectrum), and intensity profiles in the parent region were consistent with calculated spectra based on natural isotope distributions. Negative and positive ion spectra were generated together by using pulse positive ion/negative chemical ionization (PPINICI)[10] with reagent grade methane. Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer and were referenced to the 1601.8-cm^{-1} band of polystyrene. Column chromatography was conducted on silica gel 60 (Merck) and preparative thin-layer chromatography was carried out on precoated silica gel plates (Merck).

Conversion of $(CO)_3Cr(PhCH_2)_2C_2B_4H_6$ (2) to $[(CO)_3Cr]_2(PhCH_2)_4C_4B_8H_8$ (7). A solution of $Na^+(CO)_3Cr(PhCH_2)_2C_2B_4H_5^-$ was prepared from the reaction of 0.360 g (0.918 mmol) of **2** and 25 mg (1.04 mmol) of NaH in 50 mL of anhydrous THF by using an apparatus similar to that described elsewhere.[11] The reactants were combined in vacuo at liquid-nitrogen temperature and allowed to warm to room temperature, during which time hydrogen evolution was observed and the color changed from pale yellow to very deep yellow. After being stirred at room temperature for 30 minutes, the solution was filtered onto 59 mg (0.465 mmol) of anhydrous $FeCl_2$ in a 100-mL flask immersed in a dry ice–acetone slush bath. The reaction mixture was slowly warmed to room temperature and stirred at this temperature for 4 h, during which time no noticeable color change was observed. The solvent was removed in vacuo and the flask filled with dry nitrogen at 1 atm and opened to the air. The contents were dissolved in 50 mL of methylene chloride, and O_2 gas was bubbled through the solution for 8 h, during which the solution turned a brown color. The solution was filtered through 2 cm of silica gel and washed with methylene chloride until the washings were colorless. The yellow/orange filtrate was concentrated and chromatographed by using 30% methylene chloride–hexane as eluent. Two distinct bands were collected; the first, yellow (R_f 0.50), was starting material (72 mg, 20% recovery). The second band was orange $(CO)_6Cr_2(PhCh_2)_4C_4B_8H_8$ (**7**), yield 0.110 g (30%). Further separation of **7** by thin-layer chromatography in the same eluent afforded two isomers, **7A** [R_f 0.40, 56 mg (16%)] and **7B** [R_f 0.38, 52 mg (14%)]. Negative ion mass spectra of **7A,B**: strong parent group with cutoff at *m/z* 781 [$^{52}Cr_2{}^{11}B_8{}^{13}C^{12}C_{37}{}^{16}O_6{}^{1}H_{36}{}^{+}$], and less intense fragments with local cutoffs at *m/z* 696 (P – 3CO), 644 (P – $Cr(CO)_3$), 612 (P – 6CO), 560 (base peak, P – $Cr(CO)_6$), and 508 (P – $Cr_2(CO)_6$). Exact mass: calcd for $^{52}Cr_2{}^{11}B_6{}^{10}B_2{}^{12}C_{38}{}^{16}O_6{}^{1}H_{36}{}^{+}$, 778.2139; found, 778.2175. ^{11}B NMR in CH_2Cl_2 [δ relative to $BF_3{\cdot}OEt_2$ (*J*, Hz)]: **7A**, –3.11 (132), –13.90 (unres. doublet), area ratio 3:1; **7B**, –3.02 (133) –13.58 (unres. doublet), area ratio 3:1. IR (cm^{-1}, KBr): **7A**, 3104 sh, 3078 m, 3044 s, 2976 sh, 2944 vs, 2866 s, 2585 vs, 1967 vs, 1894 vs, br, 1716, w, br, 1601 s, 1581 m, 1495 vs, 1454 vs, 1416 m, 1377 w, 1258 w, 1155 w, 1076 m, 1027 m, 1011 m, 910 w, 876 w, 802 w, 746 m, 700 s, 661 s, 626 s, 531 w; **7B**, 3104 sh, 3078 m, 3044 s, 2976 sh, 2944 vs, 2866 s, 2585 vs, 1967 vs, 1894 vs, br, 1716 w, br, 1601 s, 1581 m, 1495 vs, 1454 vs, 1416 m, 1377 w, 1258 w, 1155 w, 1076 m, 1027 m, 1011 m, 910 w, 876 w, 802 w, 746 m, 700 s, 661 s, 626 s, 531 w.

Reaction of $(PhCH_2)_4C_4B_8H_8$ (5) with $Cr(CO)_6$. $(PhCh_2)_4C_4B_8H_8$ [0.210 g (0.413 mmol)] and 0.900 g (4.09 mmol) of $Cr(CO)_6$ were placed in a 250-mL round-bottom flask equipped with a condenser and magnetic stirrer. Anhydrous dibutyl ether (90 mL) and 10 mL of anhydrous THF were added, and the mixture was refluxed under dry nitrogen for 18 h, during which time the solution gradually changed from colorless to deep orange. The reactor was cooled to room temperature and the solvent removed in vacuo, the orange residue was dissolved in a minimum of methylene chloride, and the solution was chromatographed with 50% methylene chloride–hexane as eluent. A single yellow/orange band [$(CO)_6Cr_2(PhCH_2)_4C_4B_8H_8$, (**7**)] was collected; yield 0.146 g (45%). Further purification of **7** by thin-layer chromatography afforded two isomers, **7A** (68 mg, 21%) and **7B** (76 mg, 23%), whose R_f values and IR, ^{11}B NMR and mass spectra were identical with those of **7** obtained in the preceding synthesis.

Attempts were made to coordinate additional chromium to the uncoordinated phenyl rings of **7**, via separate reactions of **7** with $Cr(CO)_6$, $Cr(NH_3)(CO)_3$, or $Cr(CH_3CN)_3(CO)_3$ following the same procedure as in the reaction of **5** with $Cr(CO)_6$. In all cases, only starting materials were recovered.

Deprotonation of *nido*-$[(CO)_3Cr]_2(PhCH_2)_2C_2B_4H_6$ (3). To a solution of **3** (0.210 g, 0.398 mmol) in 50 mL of anhydrous THF was added 20 mg (0.50 mmol) of KH at room temperature. After 1 h, during which the color changed from light orange to blood red, the solution was filtered onto 26 mg (0.205 mmol) of anhydrous $FeCl_2$ in a 100-mL flask. Following the same workup as in the oxidative fusion of $(CO)_3Cr(PhCH_2)_2C_2B_4H_6$ described above, the only isolated boron-containing compound was starting material (0.102 g, 49% recovery). Similar attempts at fusion of the red anion employing $CoCl_2$ and $NiCl_2$ gave no isolable boron-containing products, with recovery of up to 50% of neutral **3**.

Reaction of $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_5^-$ with DCl. A solution of $K^+(CO)_6Cr_2(PhCH_2)_2C_2B_4H_5^-$ (**8**) was prepared from 0.102 g (0.193 mmol) of **3**, 15 mg (0.375 mmol) of KH, and approximately 50 mL of anhydrous THF, in the manner described earlier. The blood red solution was filtered into an empty 100-mL flask immersed in liquid nitrogen. DCl (0.4 mmol) was condensed into the reaction mixture, and the mixture was slowly warmed to room temperature. On warming, the color changed rapidly from blood red to yellow-orange. After the mixture was stirred for 1 h, the solvent was removed in vacuo and the flask was filled with dry nitrogen and opened to the air. The contents were dissolved in a minimum of methylene chloride, and the solution was thin-layer chromatographed with methylene chloride–hexane, giving one orange band (R_f 0.28), characterized as $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_5D$ (0.100 g, 98%). The mass spectrum closely resembled that of **3**[1] with the parent grouping displaced one mass unit higher (cutoff at *m/z* 530 corresponding to $^{52}Cr_2{}^{11}B_4{}^{13}C^{12}C_{21}{}^{16}O_6{}^{2}H^{1}H_{19}{}^{+}$) with fragments at *m/z* 445 (P – 3CO), 361 (P – 6CO), and 309 (P – $Cr(CO)_6$).

Attempted Fusion of $(PhCH_2)_2C_2B_4H_5^-$ and $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_5^-$. A solution of $K^+(CO)_6Cr_2(PhCH_2)_2C_2B_4H_5^-$ (**8**) was prepared in vacuo from 0.205 g (0.388 mmol) of $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (**3**) and 0.016 g (0.4 mmol) of KH in 50 mL of dry THF as in the preceding reaction, employing a three-flask apparatus described elsewhere.[12] After being stirred at room temperature for 30 min, the solution was filtered into 51 mg (0.401 mmol) of anhydrous $FeCl_2$ in a 250-mL flask immersed in an acetone–dry ice bath, and was warmed to room temperature and stirred for 1 h. In the manner described earlier[1] a solution of $(PhCH_2)_2C_2B_4H_5^-$ was prepared from 0.100 g (0.391 mmol) of $(PhCH_2)_2C_2B_4H_6$ (**1**) and 10 mg (0.417 mmol) of NaH in 50 mL of anhydrous THF. This solution was added slowly (over 3 h) to the solution of **8**. The combined reactant mixture was stirred at room temperature for 12 h, during which time the color changed from yellow to deep purple. The solvent was removed in vacuo, and the flask was filled with dry nitrogen and opened to the air. The contents were dissolved in methylene chloride and O_2 was bubbled through the solution for 12 h. The contents were then filtered, concentrated, and chromatographed on silica gel preparative TLC plates with 30% methylene chloride–hexane. Two bands were collected, the first of which was 40 mg (40%) of colorless $(PhCH_2)_4C_4B_8H_8$, while the second was orange $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (**3**); yield 0.102 g (50% recovery).

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(12) Borodinsky, L.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1921, Figure 6.