of anhydrous dibutyl ether and 25 mL of anhydrous THF under a dry nitrogen atmosphere. The mixture was refluxed for 24 h during which time the colorless mixture became bright yellow-orange. The solution was cooled to room temperature, opened to the air, and filtered and the solvent removed in vacuo. The residue was chromatographed on a 2.5 × 60 cm silica gel column eluted with 20% methylene chloride–hexane. The colorless unreacted fluorene was eluted from the column first near the solvent front. This was followed by a yellow band which yielded 2.84 g (18.8%) of $(C_{13}H_{10})Cr(CO)_3$. This complex was isolated as a yellow-orange, moderately air-stable, crystalline solid which was stored in the dark under nitrogen prior to use.

Preparation of $[2\text{-}((CO)_3CrPhCH_2)\text{-}3\text{-}PhCH_2\text{-}2,3\text{-}C_2B_4H_4]Fe(C_8H_{10})$ (7) and $[((CO)_3CrPhCH_2)_2C_2B_4H_4]Fe(C_8H_{10})$ (8). A 0.230-g (0.553-mmol) sample of 2 and 1.216 g (5.53 mmol) of $Cr(CO)_6$ were placed in a 250-mL round-bottom flask equipped with a condenser and magnetic stirrer. Anhydrous dibutyl ether (100 mL) and 10 mL of anhydrous THF were added, and the mixture was refluxed under dry nitrogen for 48 h, during which time the color gradually changed from colorless to 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 by using 30% CH_2Cl_2–hexane as eluent. Two distinct orange bands were collected. The first band (R_f 0.49) produced 0.132 g (43.1%) of 7 as an orange, crystalline, moderately air-stable solid. The second band (R_f 0.24) yielded 0.065 g (17.2%) of 8, again as a moderately air-stable, orange crystalline solid.

Complex 8 was also prepared directly from 7. In a typical experiment, 0.100 g (0.181 mmol) of 7 and 0.398 g (1.81 mmol) of $Cr(CO)_6$ were placed in a 250-mL round-bottom flask, equipped as described above, and 100 mL of dibutyl ether and 10 mL of THF were added. The mixture was refluxed for 48 h, after which it was cooled to room temperature and the solvent removed in vacuo to give an orange residue. This material was purifed as described to yield 0.065 g (52.1%) of 8.

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Registry No. **1**, 105472-14-8; **2**, 105472-15-9; **3**, 105472-16-0; **4**, 105472-17-1; **5**, 105500-99-0; **6**, 105472-18-2; **7**, 105472-19-3; **8**, 105501-00-6; B_5H_9, 19624-22-7; $FeCl_2$, 7758-94-3; $P(OCH_2)_3CCH_3$, 1449-91-8; $Cr(CO)_6$, 13007-92-6; *trans*-2,3-dibromo-2-butene, 21285-46-1; *trans*-2,3-dibromo-1,4-diphenyl-2-butene, 105456-31-3; 1,4-diphenyl-2-butyne, 33598-23-1; 1,4-butynediol, 110-65-6; 1,4-dichlorobutyne, 821-10-3; cyclooctatetraene, 629-20-9; [2.2]-paracyclophane, 1633-22-3; 9,10-dihydroanthracene, 613-31-0; fluorene, 86-73-7; (η^3-fluorene)chromium tricarbonyl, 33635-16-4.

Organotransition-Metal Metallacarboranes. 10. π-Complexation of *nido*-$(PhCH_2)_2C_2B_4H_6$ at the C_2B_3 and C_6 Rings. Synthesis and Crystal Structures of *nido*-2,3-$[(CO)_3Cr(\eta^6\text{-}C_6H_5)CH_2]_2$-2,3-$C_2B_4H_6$ and $(PhCH_2)_4C_4B_8H_8$, a Nonfluxional C_4B_8 Cluster[1]

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Reaction of the *C,C′*-dibenzyl-*nido*-carborane $(PhCH_2)_2C_2B_4H_6$ (1) with NaH in THF followed by $FeCl_2$ forms a red complex, $[(PhCH_2)_2C_2B_4H_4]_2FeH_2$ (2), which on treatment with O_2 generates a tetrabenzyl tetracarbon carborane, $(PhCH_2)_4C_4B_8H_8$ (3). Compound 3 is nonfluxional in solution, in contrast to previously studied $R_4C_4B_8H_8$ species where R = Me, Et, or *n*-Pr, and an X-ray diffraction study of 3 disclosed that the C_4B_8 cage is locked into an open-cage geometry as a consequence of severe intramolecular crowding of the benzyl groups. Reaction of 2 with $CpCo(CO)_2$ generates $[(PhCH_2)_2C_2B_4H_4]_4FeCoCp$ (4), for which a wedged structure is proposed. Treatment of 1 with $Cr(CO)_6$ produces the mono- and dichromium complexes $(CO)_3Cr(PhCH_2)_2C_2B_4H_6$ (5) and $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (6) as moderately air-sensitive solids which were characterized from NMR, IR, and mass spectra and an X-ray crystallographic investigation of 6. Crystal data for 3: M_r 507, space group $P2_1/c$, $Z = 4$, $a = 10.007$ (2) Å, $b = 22.681$ (6) Å, $c = 13.692$ (2) Å, $\beta = 110.18$ (2)°, $V = 2917$ Å^3, $R = 0.053$ for 3813 reflections having $F_o^2 > 3\sigma(F_o)^2$. Crystal data for 6: M_r 521, space group *Pnam*, $Z = 4$, $a = 11.914$ (2) Å, $b = 6.927$ (1) Å, $c = 28.729$ (6) Å, $V = 2371$ Å^3, $R = 0.044$ for 1678 reflections having $F_o^2 > 3\sigma(F_o)^2$.

The carborane derivative *nido*-2,3-dibenzyl-2,3-dicarbahexaborane $(PhCH_2)_2C_2B_4H_6$ (1) with its multifunctional capability for π-coordination to transition metals has considerable potential for exploitation in organometallic synthesis. As described elsewhere,[1] the conjugate base anion of 1, $(PhCH_2)_2C_2B_4H_5^-$, in combination with transition-metal ions and arene ligands forms isolable, stable mixed-ligand sandwich complexes. Here we are concerned with somewhat different aspects of dibenzylcarborane chemistry, namely, the formation of bis(dibenzylcarboranyl)metal complexes and their oxidative fusion properties and the reactivity of the benzyl groups in 1 itself toward metal complexation. Our primary purpose in this study was to explore the steric and/or electronic influence

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[1] Part 9: Spencer, J. T.; Grimes, R. N. *Organometallics*, second of three papers in this issue.

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of the benzyl groups on the properties of the $R_2C_2B_4H_6$ *nido*-carborane cage. Heretofore, investigations of this carborane system, though extensive,[3,4] have been limited mainly to derivatives in which R is relatively inactive[5] (e.g., H or alkyl). The present work was considerably aided by the accessibility of 1 on a multigram scale as an air- (and water-!)stable liquid reagent.[1]

Results and Discussion

Preparation of $[(PhCH_2)_2C_2B_4H_4]_2FeH_2$ and Conversion to $(PhCH_2)_4C_4B_8H_8$. The synthesis of $(R_2C_2B_4H_4)_2MH_x$ complexes (R = alkyl; M = Fe, x = 2; M = Co, x = 1) and the formation of $R_4C_4B_8H_8$ carboranes via oxidative fusion of the $R_2C_2B_4H_4^{2-}$ ligands is well established as a general reaction.[6] Metal-promoted fusion has been widely observed not only with carboranes[6,7] but also with metallacarboranes,[6] boranes,[8,9] and metallaboranes.[8] In particular the conversion of two $R_2C_2B_4H_4^{2-}$ ligands to $R_4C_4B_8H_8$ has been extensively studied,[7] and the C_4B_8 cages are known to be fluxional, existing in solution as equilibrium mixtures of "open" and "closed" isomers.[10] When R = CH_3, the quasi-icosahedral or "closed" form is predominant at room temperature, while larger R groups (C_2H_5, *n*-C_3H_7) tend to favor the more open cage geometry. The availability of the dibenzylcarborane 1 presented us with an opportunity to examine the effects of very large R groups on both the fusion of $R_2C_2B_4H_4^{2-}$ units and the stereochemistry of the $R_4C_4B_8H_8$ product(s). Indeed it was not certain, a priori, that fusion of $(PhCH_2)_2C_2B_4H_4^{2-}$ ligands would occur at all, given the large steric demands of the benzyl substituents. It was also conceivable that fusion, if it did take place, would occur in "backwards" fashion to give an edge-bonded $(R_2C_2B_4H_4)_2$ cluster with the R–C–C–R moieties at opposite ends of the molecule. This latter mode of cage fusion has recently been observed[9] in the formation of $B_{12}H_{16}$ from the $B_6H_9^-$ anion (a structural analogue of $R_2C_2B_4H_4^{2-}$) and is attributed to the presence of several B–H–B bridges on the open faces of the hexaborane ligands (in this instance, less is known about the fusion process itself because the metallaborane intermediate has not been isolated).

In this study, 1 was bridge-deprotonated with NaH and allowed to react with $FeCl_2$ in THF to give orange, moderately air-sensitive $[(PhCH_2)_2C_2B_4H_4]_2FeH_2$ (2), characterized from its ^{11}B and ^{1}H NMR, infrared, and mass spectra (Tables I–IV). The spectral data on 2 closely resemble, in general, those of its tetra-*C*-alkyl counterparts,[6,10,11] $(R_2C_2B_4H_4)_2FeH_2$ (R = Me, Et, *i*-Pr), and 2 is assumed to adopt a similar bis(carboranyl)iron sandwich structure. Of course, the relative conformation of the two carborane ligands may or may not be identical with that previously established in $(Me_2C_2B_4H_4)_2FeH_2$, whose ligands are rotated by 90° relative to an eclipsed orientation.[12]

Table I. 115.8-MHz ^{11}B FT NMR Data[a]

compd	δ (J_{BH}, Hz)[b]	rel areas
$(PhCH_2)_2C_2B_4H_6$ (1)	−0.43 (219), −2.53 (149), −46.37 (180)	1:2:1
$[(PhCH_2)_2C_2B_4H_4]_2FeH_2$ (2)	−1.46 (127), −3.75 (138), −47.18 (184)	1:2:1
$(PhCH_2)_4C_4B_8H_8$ (3)	−2.88,[c] −12.86 (134)	3:1
$[(PhCH_2)_2C_2B_4H_4]_2FeCo(C_5H_5)$ (4)	−1.47,[c] −2.31,[c] −3.72 (152), −12.25 (129), −47.31 (177), −92.70[c]	1:1:3:1:1:1
$(CO)_3Cr(PhCH_2)_2C_2B_4H_6$ (5)	−1.61,[c] −4.06 (146), −47.65 (176)	1:2:1
$(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (6)	−8.91,[c] −10.79 (132), −54.9 (178)	1:2:1

[a] CH_2Cl_2 solution. [b] Shifts relative to $BF_3{\cdot}Et_2O$, positive value downfield. [c] Unresolved doublet.

Table II. 360-MHz ^{1}H FT NMR Data

compd	δ[a,b]	rel areas
1	7.28 m (C_6H_5), 2.68 m (BH),[c] 2.31 m (CH_2), 1.32 m (BHB)	5:2:2:1
2	7.25 m (C_6H_5), 1.28 m (CH_2), −10.51 s (FeH)	10:4:1
3	7.21 m (C_6H_5), 1.28 m (CH_2)	5:2
5	7.30 m, br (C_6H_5), 2.42 m (BH), 2.18 m (CH_2), 1.27 m (BHB)	5:4:2:1
6	7.38 m (C_6H_5), 2.46 m (BH), 2.25 m (CH_2), 1.18 m (BHB)	5:4:2:1

[a] $CDCl_3$ solution. [b] Shifts relative to Me_4Si. Legend: br = broad, m = multiplet, s = singlet. [c] Terminal B–H quartets are broad and in most cases are partially or wholly obscured by C–H signals.

Table III. Infrared Absorptions (cm^{-1}, KBr Pellets)[a]

compd	absorptions
1[b]	3165 sh, 3100 m, 3080 s, 3022 s, 2972 sh, 2938 s, 2864 s, 2608 vs, 1948 m, 1610 s, 1592 sh, 1501 vs, 1460 vs, 1388 w, 1115 m, br, 1082 m, 1037 sh, 987 m, 960 m, 921 w, 892 sh, 855 m, 822 w, 794 m, 752 s, 732 s, 704 vs
2	3105 w, 3084 m, 3050 m, 2944 s, 2868 m, 2622 s, 2600 s, 1611 w, 1505 m, 1462 m, 1082 m, 1038 m, 988 w, 755 w, 730 w, 708 m, 480 w
3	3062 w, 3040 w, 3005 w, 2900 m, 2881 w, 2838 m, 2580 m, 2562 m, 2536 s, 2502 m, 1590 m, 1482 s, 1440 s, 1422 m, 1379 w, 1294 m, 1174 w, 1142 w, 1068 m, 1018 m, 1002 m, 990 w, 979 w, 958 w, 872 m, 742 m, 712 m, 688 s, 628 w, 530 w, 449 w
5	3104 w, 3084 w, 3050 w, 2942 vs, 2878 vs, 2622 vs, 1958 vs, br, 1898 vs, br, 1614 w, 1508 m, 1468 m, 1390 w, 1088 w, 1038 w, 758 w, 742 w, 738 w, 710 m, 675 m, 640 m, 542 m, 488 w
6	3115 m, 2920 m, 2618 s, 2608 m, 2600 m, 1920 vs, br, 1742 vs, br, 1460 m, 1431 m, 1168 w, 980 w, 950 w, 858 w, 836 w, 812 w, 770 w, 750 w, 691 w, 668 s, 637 s, 538 s, 482 m, 400 w, 312 m

[a] Legend: sh = shoulder, m = medium, s = strong, v = very, w = weak, br = broad. [b] Neat sample.

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(5) The asymmetric derivatives 2-Ph$(CH_2)_n$-2,3-$C_2B_4H_7$ (n = 2, 3) do have active phenylalkyl substituents and form complexes in which the phenyl and carborane rings are coordinated to the same metal ion: Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1985**, *4*, 890.

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Table IV. Selected Mass Spectroscopic Data

compd	*m/e*	rel intensity[a]	assignt
1	257	16.2	$^{13}C^{12}C_{15}{}^{11}B_4{}^1H_{20}{}^+$
	178	18.9	parent − C_6H_6
	91	88.5	$C_6H_5CH_2{}^+$
2	567	0.3 (1.1)	$^{13}C^{12}C_{31}{}^{11}B_8{}^{56}Fe^1H_{38}{}^+$
	556	2.9 (3.7)	parent envelope
	565	5.4 (5.4)	
	564	5.6 (4.3)	
	563	4.7 (2.2)	
	562	1.5 (0.8)	
	561	0.8 (0.2)	
	508	7.9 (10.7)	$C_{32}B_8H_{36}{}^+$ envelope
	507	15.6 (15.6)	
	506	15.1 (11.9)	
	505	11.1 (5.4)	
	255	100.0	$(C_6H_5CH_2)_2C_2B_4H_5{}^+$
	176	97.2	
	91	68.6	$C_6H_5CH_2{}^+$
3	509	6.2 (6.7)	$^{13}C^{12}C_{31}{}^{11}B_8{}^1H_{36}{}^+$
	508	23.3 (24.3)	parent envelope
	507	35.4 (35.4)	
	506	28.8 (27.1)	
	505	14.9 (12.4)	
	504	6.2 (3.8)	
	255	5.2	$(C_6H_5CH_2)_2C_2B_4H_5{}^+$
	91	100.0	$C_6H_5CH_2{}^+$
4	688	4.6 (3.2)	$^{12}C_{37}{}^{11}B_8{}^{56}Fe^{59}Co^1H_{41}{}^+$
	687	9.9 (9.9)	parent envelope
	686	19.4 (13.9)	
	685	14.1 (10.8)	
	684	5.6 (5.5)	
	683	3.0 (2.0)	
	509	27.3 (18.9)	$C_{32}B_8{}^1H_{36}{}^+$ envelope
	508	54.3 (68.6)	
	507	100.0 (100.0)	
	506	79.3 (76.6)	
	505	64.8 (35.0)	
	255	47.6	$(C_6H_5CH_2)_2C_2B_4H_5{}^+$
	91	100.0	$C_6H_5CH_2{}^+$
5	393	0.7 (0.6)	$^{13}C^{12}C_{18}{}^{11}B_4{}^{16}O_3{}^{52}Cr^1H_{20}{}^+$
	392	2.1 (2.1)	parent envelope
	391	1.8 (1.7)	
	390	1.2 (0.7)	
	389	0.3 (0.2)	
	308	11.4	parent − 3 CO envelope
	307	13.7	
	306	9.1	
	305	2.6	
	255	100.0	parent − $Cr(CO)_3H$
	91	100.0	$C_6H_5CH_2{}^+$
6	529	10.3 (10.2)	$^{13}C^{12}C_{21}{}^{11}B_4{}^{16}O_6{}^{52}Cr_2{}^1H_{20}{}^+$
	528	23.8 (23.8)	parent envelope
	527	22.2 (18.8)	
	526	10.5 (8.3)	
	525	4.2 (2.7)	
	445	10.6	parent − 3CO envelope
	444	26.7	
	443	26.6	
	442	17.5	
	441	8.9	
	360	14.8	parent − 6CO
	358	100.0	
	308	36.8	parent − $Cr(CO)_6$
	91	98.9	$C_6H_5CH_2{}^+$

[a] Values in parentheses are calculated intensities for the parent (or other) group, based on natural isotope abundances and normalized to the most intense observed peak in the group.

Table V. Experimental Parameters and Crystal Data on $(PhCH_2)_4C_4B_8H_8$ (3)

M_r	507	*D*(calcd), g cm^{-3}	1.155
space group	$P2_1/c$	2θ range, deg	1–116
a, Å	10.007 (2)	reflctns obsd	4501
b, Å	22.681 (6)	reflctns refined	3813
c, Å	13.692 (2)	*R*	0.053
β, deg	110.18 (2)	R_w	0.056
V, $Å^3$	2917	esd unit wt	1.1
μ, cm^{-1}	4.5	*Z*	4
		radiation	Cu

In contrast to the corresponding methyl-, ethyl-, and *n*-propylcarborane iron complexes, which react with atmospheric O_2 within minutes to give $R_4C_4B_8H_8$, **2** survives exposure to air for 1–2 h with little change. This is in line with the expectation (vide supra) that oxidative fusion would be sterically impeded by the benzyl groups. However, solutions of **2** in CH_2Cl_2 or benzene on standing overnight in air gave the tetra-*C*-benzyl carborane $(PhCH_2)_4C_4B_8H_8$ (**3**) in 48% yield as colorless nonvolatile air-stable crystals (Scheme I). From its ^{11}B and ^1H NMR and mass spectra, **3** was identified as a C_4B_8 cluster of the same class as the crystallographically characterized species $Me_4C_4B_8H_8$[13] and $Et_4C_4B_8H_8$.[10] The ^{11}B spectrum of **3** is particularly suggestive of an open-type geometry as found in the tetraethyl derivative; since the detailed cage geometry is of interest for reasons mentioned earlier, an X-ray structure determination was undertaken.

Solid-State Structure of $(PhCH_2)_4C_4B_8H_8$ (3). Tables V–VIII list crystallographic data collection parameters, final positional parameters, bond distances, and bond angles, with corresponding lengths in $Et_4C_4B_8H_8$ included for comparison (tables of thermal parameters and calculated mean planes and a packing diagram are available as supplementary material). The C_4B_8 cage structure, depicted in Figure 1, is of type "B"[10] and surprisingly is virtually identical with that of the tetraethyl derivative, as shown by comparison of bond distances (Table VII). A further point of comparison is given by the dihedral angle formed by the C2–C3–B4–B5–B6 and C7–C8–B9–B10–B11 planes, which is 27.4° in **3** and 28.2° in $Et_4C_4B_8H_8$.

The phenyl rings in **3** are planar within experimental error, but their orientation in the crystal is worthy of comment. As can be seen in Figure 1, each pair of benzyl groups (those bonded to adjacent cage carbon atoms) is positioned such that its phenyl rings are roughly perpendicular to each other, with a C–H bond on one ring directed approximately toward the center of the other ring of the pair. This appears to be a crystal packing effect since the closest inter-ring contacts within each pair of benzyl groups correspond to van der Waals distances or greater (Table XIII, supplementary material).

Solution Behavior of $(PhCH_2)_4C_4B_8H_8$. As noted above, $R_4C_4B_8H_8$ carboranes in which R = CH_3, C_2H_5, or *n*-C_3H_7 exhibit cage fluxionality in solution (essentially independent of solvent), with "open" (B) and "closed" (A) structures present in equilibrium in each case. The ΔH values for A → B conversion are quite small (ca. 1–2 kcal mol^{-1}), but the equilibrium is shifted toward the open form as the size of the R groups increases.[10] It was of interest to see whether such behavior is maintained in the tetrabenzyl derivative **3**, and accordingly we examined the ^{11}B and ^1H NMR spectra as a function of time. In both experiments there is no evidence of change on a time scale of weeks at room temperature, nor do the spectra give any indication of more than one isomer. Hence we conclude

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[13] (a) Freyberg, D. P.; Weiss, R.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 1847. (b) Grimes, R. N.; Maxwell, W. M.; Maynard, R. B.; Sinn, E. *ibid.* **1980**, *19*, 2981.

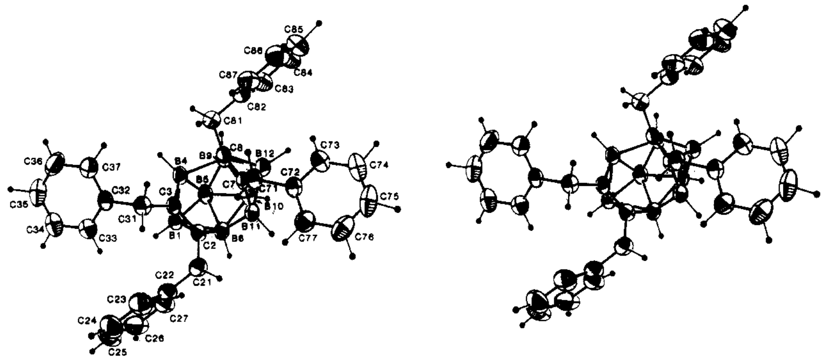
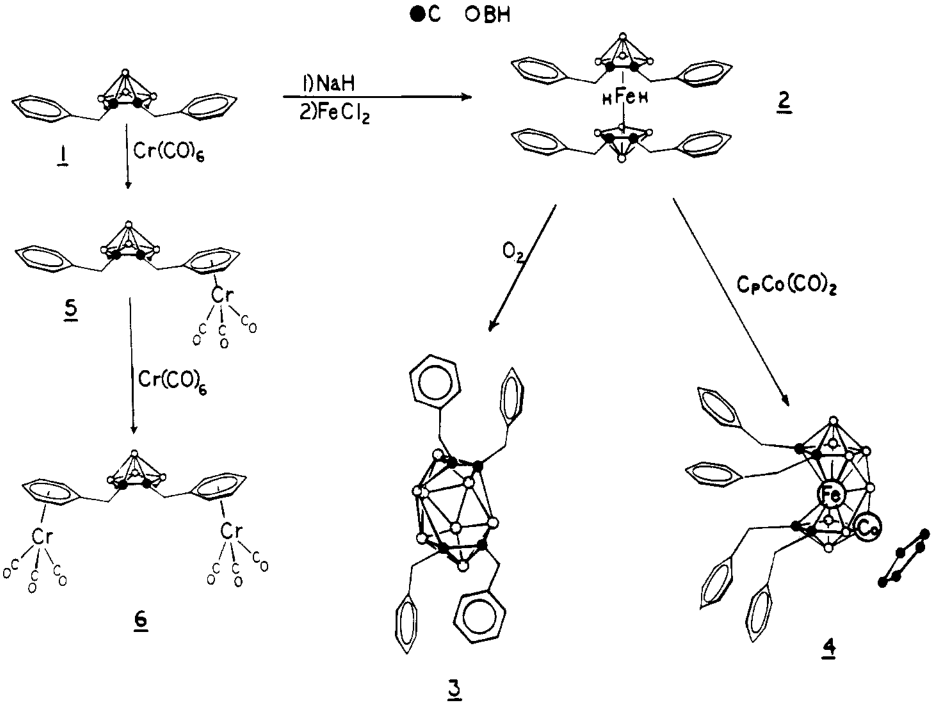


Figure 1. Stereoview of $(PhCH_2)_4C_4B_8H_8$ (*3*).

Scheme I



that 3 is nonfluxional, in contrast to the tetraalkyl derivatives studied previously (it should be noted that $(Me_3Si)_2C_4B_8H_{10}$, prepared by Hosmane and co-workers,[14] is also apparently nonfluxional). The solution properties of 3 may to some extent reflect the electronic influence of the benzyl groups on the C_4B_8 framework; however, such an effect must be relatively minor in view of the nearly identical solid-state cage structures of 3 and its tetraethyl counterpart.[10] Consequently, we attribute the nonfluxionality of 3 primarily to the steric interaction of the benzyl substituents which effectively "freeze" the cage into an open configuration. Examination of models supports this conclusion, since it is apparent that "closure" of the cage via formation of a C3–C7 bond (as in the methyl, ethyl, and propyl analogues)[10] would, in the case of 3, produce substantially increased crowding of the benzyl units. We anticipate further testing of this effect as other $R_4C_4B_8H_8$ species with bulky R groups are examined.

The 360-MHz ^1H NMR spectrum of 3 indicates that the four benzyl units are equivalent on the NMR time scale, implying that the ordering of the phenyl rings in the crystal is not maintained in solution and, as suggested earlier, is strictly a solid-state feature.

Reaction of 2 with $(\eta^5\text{-}C_5H_5)Co(CO)_2$. Given that the bulky benzyl substituents in 2 do not prevent formation of the C_4B_8 carborane 3 via ligand fusion, it was of interest to examine the reactivity of 2 toward metal-inserting reagents. The tetra-*C*-methyl counterpart of 2, $(Me_2C_2B_4H_4)_2FeH_2$, is known to react photolytically with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ to insert $(C_5H_5)Co$ into the cage;[15] in this work, similar treatment of 2 with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ gave a single isolable product which was characterized as $[(PhCH_2)_2C_2B_4H_4]_2FeCo(\eta^5\text{-}C_5H_5)$ (4). From its ^{11}B, ^1H, and mass spectra, 4 was deduced to be structurally analogous to the compound $(Me_2C_2B_4H_4)_2FeCo(\eta^5\text{-}C_5H_5)$, which exhibits a "wedged" geometry in which the iron atom is sandwiched between C_2B_4 and CoC_2B_3 ligands with a BH unit located in the interligand crevice (Scheme I).[16] This observation further underlines the impression that the general reactions established for *nido*-$R_2C_2B_4H_6$ carboranes proceed even when R is as sterically demanding (and

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Table VI. Positional Parameters for $(PhCH_2)_4C_4B_8H_8$ (3)

atom	*x*	*y*	*z*
C2	0.390292	0.332768	−0.029765
C3	0.265173	0.366172	−0.072751
C7	0.198551	0.252455	−0.011955
C8	0.108623	0.296261	0.006048
C21	0.484625	0.312598	−0.089948
C22	0.564933	0.361439	−0.119030
C23	0.544253	0.373396	−0.223448
C24	0.618517	0.420228	−0.248152
C25	0.708727	0.454662	−0.172493
C26	0.733052	0.442554	−0.069209
C27	0.660594	0.395892	−0.043194
C31	0.201903	0.383443	−0.186498
C32	0.175892	0.449020	−0.204094
C33	0.286473	0.486285	−0.198971
C34	0.262134	0.546032	−0.219968
C35	0.128430	0.568244	−0.243916
C36	0.017070	0.532089	−0.247972
C37	0.040452	0.471596	−0.228242
C71	0.146543	0.205008	−0.095508
C72	0.195234	0.143443	−0.057077
C73	0.127944	0.112248	−0.000536
C74	0.167391	0.055017	0.031950
C75	0.277638	0.029095	0.008578
C76	0.347392	0.059383	−0.047287
C77	0.306362	0.116865	−0.079715
C81	−0.051499	0.299488	−0.050083
C82	−0.135460	0.250610	−0.023978
C83	−0.137218	0.244871	0.077765
C84	−0.215836	0.199438	0.101813
C85	−0.293545	0.160089	0.024806
C86	−0.295288	0.166873	−0.076044
C87	−0.216296	0.211784	−0.100462
B1	0.381872	0.399597	0.031451
B4	0.192073	0.382948	0.009035
B5	0.333207	0.377152	0.136473
B6	0.455734	0.331412	0.098558
B9	0.178693	0.333000	0.115679
B10	0.354798	0.301637	0.172416
B11	0.357784	0.258633	0.060328
B12	0.211244	0.254993	0.113508
H1	0.444381	0.441216	0.031349
H4	0.102260	0.416399	−0.009202
H5	0.358363	0.410701	0.200886
H6	0.576581	0.329696	0.137424
H9	0.097366	0.349341	0.148947
H10	0.412586	0.291348	0.255727
H11	0.445902	0.225019	0.072208
H12	0.167141	0.219596	0.157908
H211	0.546573	0.284851	−0.052741
H212	0.425587	0.290578	−0.157485
H23	0.481529	0.349109	−0.272730
H24	0.603003	0.428378	−0.323585
H25	0.762910	0.485164	−0.184446
H26	0.819176	0.463301	−0.018762
H27	0.671449	0.387420	0.027005
H311	0.267125	0.370184	−0.223026
H312	0.105221	0.362694	−0.218330
H33	0.381713	0.470201	−0.180718
H34	0.348327	0.571000	−0.215264
H35	0.106949	0.616789	−0.263439
H36	−0.068557	0.548795	−0.252783
H37	−0.044328	0.441284	−0.229915
H711	0.031123	0.204314	−0.130902
H712	0.181248	0.215992	−0.153893
H73	0.049912	0.129815	0.011864
H74	0.097920	0.030777	0.068382
H75	0.317562	−0.015697	0.030824
H76	0.437941	0.038409	−0.064466
H77	0.361931	0.141437	−0.118486
H811	−0.089586	0.341138	−0.038071
H812	−0.068721	0.300553	−0.118570
H83	−0.084578	0.280063	0.136066
H84	−0.236082	0.199404	0.183917
H85	−0.368650	0.126489	0.043336
H86	−0.350971	0.137747	−0.133682
H87	−0.207720	0.216582	−0.179418

Table VII. Bonded and Nonbonded Distances (Å) in 3

	$(PhCH_2)_4C_4B_8H_8$ (3)	$Et_4C_4B_8H_8$[a]
	Bond Distances	
C2–C3	1.407 (1)	1.362 (6)
C2–C21	1.522 (2)	1.506 (7)
C2–B1	1.748 (2)	1.732 (8)
C2–B6	1.650 (2)	1.627 (6)
C2–B11	2.175 (3)	2.181 (6)
C3–C31	1.516 (3)	1.554 (5)
C3–B1	1.681 (3)	1.669 (6)
C3–B4	1.581 (2)	1.603 (8)
C7–C8	1.418 (1)	1.408 (7)
C7–C71	1.525 (2)	1.502 (7)
C7–B11	1.565 (2)	1.574 (6)
C7–B12	1.679 (3)	1.656 (7)
C8–C81	1.521 (2)	1.530 (6)
C8–B4	2.131 (2)	2.145 (7)
C8–B9	1.647 (2)	1.672 (7)
C8–B12	1.747 (2)	1.763 (6)
B1–B4	1.855 (2)	1.859 (7)
B1–B5	1.746 (2)	1.737 (8)
B1–B6	1.820 (2)	1.825 (7)
B4–B5	1.832 (2)	1.832 (6)
B4–B9	1.889 (2)	1.878 (6)
B5–B6	1.813 (2)	1.867 (9)
B5–B9	1.781 (3)	1.788 (6)
B5–B10	1.775 (2)	1.809 (7)
B6–B10	1.790 (2)	1.790 (7)
B6–B11	1.899 (3)	1.859 (6)
B9–B10	1.808 (2)	1.857 (7)
B9–B12	1.801 (2)	1.840 (8)
B10–B11	1.827 (2)	1.744 (8)
B10–B12	1.742 (2)	1.712 (7)
B11–B12	1.850 (3)	1.804 (9)
C21–C22	1.501 (2)	
C22–C23	1.399 (2)	
C23–C24	1.403 (2)	
C24–C25	1.361 (1)	
C25–C26	1.377 (1)	
C26–C27	1.397 (2)	
C27–C22	1.385 (3)	
C31–C32	1.515 (3)	
C32–C33	1.375 (2)	
C33–C34	1.389 (2)	
C34–C35	1.360 (3)	
C35–C36	1.369 (2)	
C36–C37	1.402 (2)	
C37–C32	1.378 (3)	
C71–C72	1.512 (3)	
C72–C73	1.383 (2)	
C73–C74	1.385 (3)	
C74–C75	1.382 (2)	
C75–C76	1.383 (3)	
C76–C77	1.393 (2)	
C77–C72	1.391 (3)	
C81–C82	1.507 (2)	
C82–C83	1.405 (3)	
C83–C84	1.403 (2)	
C84–C85	1.395 (3)	
C85–C86	1.384 (2)	
C86–C87	1.399 (2)	
C87–C82	1.394 (2)	
	Nonbonded Distances	
C2–C7	2.717 (1)	2.743 (7)
C3–C7	2.858 (1)	2.886 (2)
C3–C8	2.703 (1)	2.702 (7)

[a] Reference 10.

electronically active) as benzyl. However, current work in our laboratory indicates that still larger R groups have a more pronounced effect on the properties of $R_2C_2B_4H_6$ carboranes, in some cases even preventing formation of a $(R_2C_2B_4H_4)_2FeH_2$ complex altogether.[17]

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(17) Spencer, J. T.; Fessler, M. E.; Grimes, R. N., to be submitted for publication.

Table VIII. Selected Bond Angles (deg) in 3

C3–C2–C21	124.3 (2)	C25–C26–C27	119.3 (3)
C3–C2–B1	63.3 (1)	C22–C27–C26	131.4 (3)
C3–C2–B6	115.1 (2)	C3–C31–C32	113.9 (2)
C3–C2–B11	111.6 (2)	C31–C32–C33	120.3 (2)
C21–C2–B1	131.4 (2)	C31–C32–C37	120.2 (2)
C21–C2–B6	118.6 (2)	C33–C32–C37	119.4 (2)
C21–C2–B11	108.5 (2)	C32–C33–C34	120.6 (2)
B1–C2–B6	64.7 (1)	C33–C34–C35	119.9 (3)
B1–C2–B11	110.9 (1)	C34–C35–C36	120.5 (2)
B6–C2–B11	57.6 (1)	C35–C36–C37	119.9 (3)
C2–C3–C31	124.4 (2)	C32–C37–C36	119.7 (3)
C2–C3–B1	68.3 (1)	C7–C71–C72	113.9 (2)
C2–C3–B4	113.3 (2)	C71–C72–C73	120.4 (2)
C31–C3–B1	132.6 (2)	C71–C72–C77	120.6 (2)
C31–C3–B4	122.3 (2)	C73–C72–C77	119.0 (2)
B1–C3–B4	69.3 (2)	C72–C73–C74	121.3 (3)
C8–C7–C71	123.5 (2)	C73–C74–C75	119.1 (3)
C8–C7–B11	113.3 (2)	C74–C75–C76	128.8 (2)
C8–C7–B12	68.1 (1)	C75–C76–C77	119.5 (3)
C71–C7–B11	123.2 (2)	C72–C77–C76	120.3 (2)
C71–C7–B12	132.6 (2)	C8–C81–C82	114.9 (2)
B11–C7–B12	69.4 (2)	C81–C82–C83	120.1 (2)
C7–C8–C81	124.5 (2)	C81–C82–C87	120.9 (2)
C7–C8–B4	112.4 (2)	C83–C82–C87	118.9 (2)
C7–C8–B9	114.6 (2)	C82–C83–C84	120.0 (3)
C7–C8–B12	63.1 (1)	C83–C84–C85	120.3 (3)
C81–C8–B4	107.6 (2)	C84–C85–C86	119.7 (3)
C81–C8–B9	118.6 (2)	C85–C86–C87	120.4 (3)
C81–C8–B12	131.4 (2)	C82–C87–C86	120.7 (2)
B4–C8–B9	58.3 (1)	C2–C21–C22	114.2 (2)
B4–C8–B12	111.4 (2)	C3–B4–C8	92.2 (1)
B9–C8–B12	64.0 (1)	C3–B4–B5	105.3 (2)
C23–C22–C27	118.5 (2)	B4–B5–B6	98.3 (2)
C23–C22–C21	120.7 (2)	C2–B6–B5	103.6 (2)
C27–C22–C21	120.8 (2)	C8–B9–B10	103.8 (2)
C22–C23–C24	119.3 (3)	B9–B10–B11	98.3 (2)
C23–C24–C25	121.2 (3)	C2–B11–C7	91.7 (1)
C24–C25–C26	120.2 (3)	C7–B11–B10	105.7 (2)

Reaction of 1 with Chromium Hexacarbonyl. The ability of the phenyl rings in 1 to adopt η^6-coordination with $Cr(CO)_3$ was examined by refluxing the carborane with $Cr(CO)_6$ in tetrahydrofuran–dibutyl ether, forming two orange crystalline products, **5** and **6**, which were isolated in 51% total yield. Characterization by NMR, IR, and mass spectroscopy supported by an X-ray study of **6**, identified the new compounds as a monochromium complex, 2-[$(CO)_3Cr(\eta^6$-$C_6H_5)CH_2$]-3-($PhCH_2$)-2,3-$C_2B_4H_6$ (**5**), and a dichromium species, 2,3-[$(CO)_3Cr(\eta^6$-$C_6H_5)CH_2]_2$-2,3-$C_2B_4H_6$ (**6**). The latter compound was also produced by reaction of **5** with $Cr(CO)_6$ (Scheme I).

The 115.5-MHz ^{11}B NMR spectra of **1**, **5**, and **6** are similar, each exhibiting three signals in a 1:2:1 area ratio (typical of *nido*-$R_2C_2B_4H_6$ derivatives). In the spectra of the metalated species **5** and **6**, all three resonances exhibit upfield shifts relative to uncomplexed **1**; the effect is particularly evident in the dimetallic species **6** where the signals are found ca. 8 ppm to high field of **1**. The high-resolution proton NMR spectra of the three compounds are almost identical, with little shift (0.02–0.10 ppm) detectable in the chromium-complexed phenyl rings relative to the parent carborane; in contrast, the complexation of arenes with $Cr(CO)_3$ normally causes an upfield shift of 1.5–2.5 ppm.[18] The virtual absence of such an effect in **5** and **6** indicates that the C_2B_4 carboranyl unit essentially neutralizes the influence of the $Cr(CO)_3$ groups on the phenyl rings (implying substantial carborane–phenyl electronic interaction). Moreover, it is likely that the effects of metalation are buffered by electron delocalization across the large dibenzylcarborane system.

Table IX. Experimental Parameters and Crystal Data on $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (6)

M_r	521	2θ range, deg	4–55
space group	*Pnam*	reflctns obsd	3979
a, Å	11.914 (2)	reflctns refined	1678
b, Å	6.927 (1)	*R*	0.044
c, Å	28.729 (6)	R_w	0.048
V, Å^3	2371 (1)	esd unit wt	1.4
μ, cm^{-1}	9.283	*Z*	4
D(calcd), g cm^{-3}	1.458	radiatn	Mo Kα

In contrast to the parent carborane **1**, complexes **5** and **6** are air-sensitive in solution and revert to **1**; however, in the solid state both compounds appear to change only very slowly on prolonged exposure to light, air, and moisture. These properties are fairly typical of arene–chromium tricarbonyl complexes as a class.

X-ray Crystallographic Study of 6. Perhaps surprisingly given the extensive synthetic effort in this area, no crystal structure of a simple (σ-bonded only) derivative of *nido*-2,3-$C_2B_4H_8$ has been reported since the original X-ray investigations of the parent molecule and 2,3-Me_2-2,3-$C_2B_4H_6$ by Lipscomb and co-workers more than 20 years ago.[19] (Structures of the bridged complexes μ(4,5)-X-2,3-$R_2C_2B_4H_5$ where X = $(Et_3P)_2PtH$[20] and $(C_5H_5)Co(Me_2C_2B_4H_3)$[21] have been reported, and the geometry of 2-Me_3Si-2,3-$C_2B_4H_7$ has been studied by gas-phase electron diffraction.[22]) In view of the paucity of detailed structural information on uncomplexed $R_2C_2B_4H_6$ carboranes and also in order to examine the consequences of η^6-metal coordination at the phenyl rings, we undertook an X-ray diffraction investigation of the dichromium complex **6**.

The parameters of data collection, atomic coordinates, and bond distances and angles are given in Tables IX–XII, and drawings of the molecular structure of **6** are given in Figure 2; tables of thermal parameters and calculated mean planes are available as supplementary material. The molecule has crystallographically imposed mirror symmetry and is consistent with the structure indicated from NMR data. The C_2B_4 cage structure is closely comparable to those of the parent and dimethyl species,[19] there being no significant differences in framework bond distances. The phenyl ring is planar within experimental error and the C_6H_5–$Cr(CO)_3$ group displays bond lengths and angles within the normal ranges for monosubstituted arene–chromium tricarbonyl complexes,[23] but the orientation of the $Cr(CO)_3$ unit is staggered with respect to the attached phenyl ring. This observation runs counter to the usual prediction based on electronic considerations for monosubstituted (η^6-arene)$Cr(CO)_3$ complexes, in which one normally finds the carbonyls eclipsing three of the ring carbons.[23] Undoubtedly the departure of **6** from this rule is related to the large steric bulk of the –CH_2–carborane substituent, an effect that has been noted in a few previously studied complexes (e.g., $[(C_6H_5)Cr(CO)_3]_2$[24]), where intramolecular contacts force the molecule to adopt a staggered conformation. There is also evidence of an

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Table X. Positional Parameters for $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (6)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cr	0.17471 (4)	0.12975 (8)	0.09438 (2)	B6	0.3294 (4)	−0.4126 (6)	0.2027 (1)
O1	0.0178 (2)	0.2952 (5)	0.02354 (9)	B5	0.3761 (7)	−0.555 (1)	0.250
O2	0.3293 (2)	0.4588 (4)	0.0737 (1)	B1	0.4013 (6)	−0.312 (1)	0.250
O3	0.0646 (3)	0.3679 (5)	0.16816 (9)	HB6	0.355 (3)	−0.429 (5)	0.169 (1)
C1R	0.2302 (3)	−0.0821 (5)	0.1475 (1)	HB5	0.435 (4)	−0.684 (7)	0.250
C2R	0.3166 (3)	−0.0530 (5)	0.1161 (1)	H2R	0.376 (2)	−0.017 (4)	0.1266 (9)
C3R	0.2986 (3)	−0.0778 (6)	0.0677 (1)	H3R	0.354 (3)	−0.050 (5)	0.051 (1)
C4R	0.1965 (4)	−0.1330 (6)	0.0513 (1)	HB1	0.476 (4)	−0.226 (7)	0.250
C5R	0.1084 (3)	−0.1631 (6)	0.0822 (1)	H4R	0.181 (3)	−0.156 (5)	0.018 (1)
C6R	0.1255 (3)	−0.1392 (5)	0.1298 (1)	H5R	0.044 (3)	−0.196 (5)	0.071 (1)
C(M)	0.2468 (4)	−0.0536 (6)	0.1990 (1)	H6R	0.065 (2)	−0.151 (4)	0.148 (1)
C2	0.2732 (3)	−0.2388 (5)	0.2252 (1)	HB56	0.296 (3)	−0.576 (5)	0.218 (1)
C11	0.0772 (3)	0.2300 (6)	0.0510 (1)	HM1	0.179 (3)	−0.004 (5)	0.211 (1)
C12	0.2690 (3)	0.3317 (5)	0.0818 (1)	HM2	0.292 (3)	0.064 (5)	0.206 (1)
C13	0.1073 (3)	0.2756 (6)	0.1396 (1)				

Table XI. Interatomic Distances (Å) in 6

Cr–C1R	2.219 (3)	C1R–C6R	1.404 (5)	C(M)–HM2	1.00 (4)
Cr–C2R	2.203 (3)	C1R–C(M)	1.506 (4)	C2–B6	1.521 (5)
Cr–C3R	2.199 (4)	C2R–C3R	1.419 (5)	C2–B1	1.760 (7)
Cr–C4R	2.216 (4)	C2R–H2R	0.81 (3)	C2–C2′	1.424 (5)
Cr–C5R	2.205 (4)	C3R–C4R	1.359 (5)	C6–B5	1.468 (6)
Cr–C6R	2.202 (4)	C3R–H3R	0.83 (3)	C6–B1	1.750 (6)
Cr–C11	1.840 (3)	C4R–C5R	1.390 (5)	B6–HB6	1.02 (3)
Cr–C12	1.830 (4)	C4R–H4R	0.98 (4)	B6–HB56	1.28 (4)
Cr–C13	1.831 (4)	C5R–C6R	1.391 (5)	B5–B1	1.704 (9)
O1–C11	1.152 (3)	C5R–H5R	0.86 (3)	B5–HB5	1.13 (5)
O2–C12	1.160 (4)	C6R–H6R	0.89 (3)	B5–HB56	1.33 (3)
O3–C13	1.158 (4)	C(M)–C2	1.520 (5)	B1–HB1	1.08 (5)
C1R–C2R	1.383 (5)	C(M)–HM1	0.95 (3)		

Table XII. Selected Bond Angles (deg) in 6

C11–Cr–C12	88.0 (2)	C1R–C(M)–HM2	113 (2)
C11–Cr–C13	89.7 (1)	C2–C(M)–HM1	108 (2)
C12–Cr–C13	89.3 (1)	C2–C(M)–HM2	118 (2)
Cr–C1R–C(M)	128.9 (2)	HM1–C(M)–HM2	95 (3)
C2R–C1R–C(M)	121.6 (4)	C(M)–C2–B6	123.4 (4)
C6R–C1R–C(M)	120.6 (4)	C(M)–C2–B1	128.7 (4)
C2R–C1R–C6R	117.8 (3)	C2′–C2–B6	115.1 (3)
C1R–C2R–C3R	120.6 (3)	C2–B6–B5	104.6 (3)
C2R–C3R–C4R	120.6 (3)	B6–B5–B6′	100.4 (3)
C3R–C4R–C5R	119.8 (3)	B6–HB56–B5	85 (2)
C4R–C5R–C6R	119.9 (4)	Cr–C11–O1	178.6 (3)
C1R–C6R–C5R	121.3 (3)	Cr–C12–O2	179.5 (3)
C1R–C(M)–C2	113.7 (2)	Cr–C13–O3	180.00 (0)
C1R–C(M)–HM1	107 (2)		

electronic effect by the $-CH_2-$carborane group on the C_6 ring, in that a smaller internal C–C–C angle is found on the substituted ring carbon C1R [117.8 (3)°] than on the remaining ring atoms [mean value 120.4 (1)°].

The chemical properties of the mono- and dimetalated complexes **5** and **6** are of particular interest, since they offer an opportunity to study the consequences of coordinating strongly electron-withdrawing $Cr(CO)_3$ units to the dibenzylcarborane **1**. An investigation of these and related complexes is in progress.

Conclusions

This work demonstrates that the *C,C′*-dibenzyl-*nido*-carborane **1**, like its alkylated analogues $R_2C_2B_4H_6$ (R = CH_3, C_2H_5, or *n*-C_3H_7),[4] can be converted to a complex $(R_2C_2B_4H_4)_2FeH_2$ which in turn undergoes oxidative fusion to form the tetra-*C*-benzyltetracarbon carborane **3**; the insertion of $(\eta^5\text{-}C_5H_5)Co$ into the framework of **1** also parallels earlier observations,[15] generating a wedged dimetallacarborane **5**. However, effects arising from the presence of the four *C*-benzyl substituents are clearly evident in the cage nonfluxionality of **3** and also in the relatively sluggish fusion (compared to its alkyl analogues) of **2** to give **3**. These findings suggest that substituents larger than benzyl might produce more dramatic effects, such as failure of the fusion reaction altogether. Current studies in our laboratory involving carboranes with attached indenylmethyl and fluorenylmethyl groups tend to support this idea and will be described later.

Experimental Section

Materials. Except as noted, all reagents and solvents used were as given in an accompanying paper.[3a] *nido*-2,3-Dibenzyl-2,3-dicarbahexaborane(8) (**1**) was prepared as described elsewhere.[1] Cyclopentadienylcobalt dicarbonyl and chromium hexacarbonyl were used as received from Strem Chemicals, Inc.

Instrumentation. The instruments and procedures employed in this work have been described previously.[3a]

Preparation of $[(PhCH_2)_2C_2B_4H_4]_2FeH_2$ (2). A solution of $(PhCH_2)_2C_2B_4H_5^-$ was prepared from the reaction of 0.68 g (2.7 mmol) of **1** and 0.15 g (6.3 mmol) of NaH in 35 mL of anhydrous THF at 0 °C by using the procedure previously given[1] and employing an apparatus similar to that described elsewhere.[25] After being stirred at room temperature for 1 h, this solution was filtered into 0.18 g (1.4 mmol) of anhydrous $FeCl_2$ in a 100-mL flask immersed in a dry ice–acetone slush bath. The reaction mixture was stirred for 2 h at this temperature and then slowly warmed to room temperature followed by stirring for an additional 15 min. The solvent was quickly removed in vacuo, and the resulting dark red residue was transferred to a glovebox under dry N_2 and dissolved in 40 mL of dry benzene. This solution was filtered through a 2-cm layer of silica gel on a sintered glass frit and washed with additional benzene until the washings were colorless. The benzene was removed in vacuo and the residue sublimed at 70 °C and 10^{-5} torr. The red compound, which was collected on a cold finger at −78 °C, gave 0.54 g (0.96 mmol, 72% yield) of **2** as an air-sensitive, red solid.

Conversion of 2 to $(PhCH_2)_4C_4B_8H_8$ (3). In an apparatus similar to that previously described,[25] 0.78 g (1.38 mmol) of **2** was

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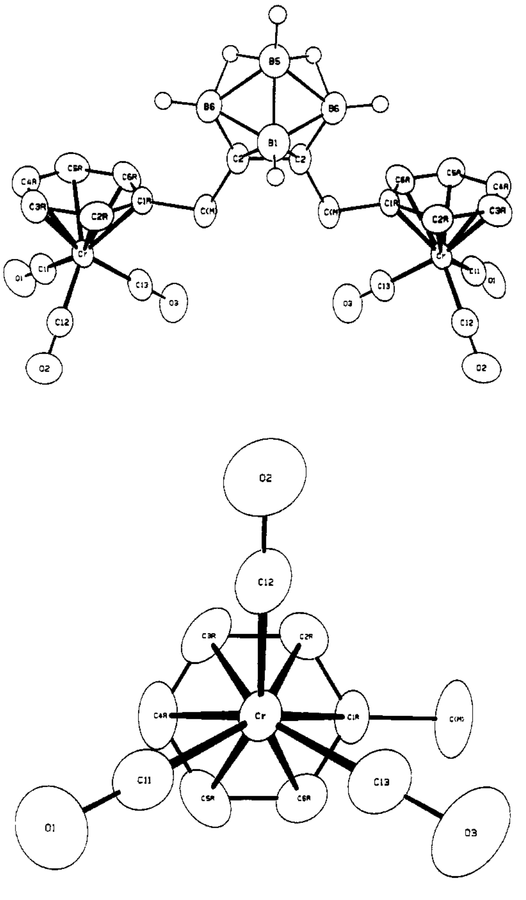

Figure 2. Views of $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (6): top, molecular structure; bottom, $(CO)_3Cr(\eta^6-C_6H_5)CH_2$ group normal to plane of C_6 ring.

dissolved in 40 mL of methylene chloride and O_2 gas was bubbled through the solution for 30 min. After subsequent exposure to air for 12 h, the solution was filtered in air and the solvent removed by rotary evaporation. The white residue was recrystallized from methylene chloride to give 0.70 g (48% yield) of 3 as air-stable, colorless crystals.

$[(PhCH_2)_2C_2B_4H_4]_2FeCo(\eta^5-C_5H_5)$ (4). A 0.62-g (1.1-mmol) sample of 2 and 0.31 g (1.7 mmol) of $(\eta^5-C_5H_5)Co(CO)_2$ were dissolved in 100 mL of dry degassed benzene, and the solution was placed in an Ace Glass Co. quartz photochemical reactor employing a 450-W mercury vapor lamp. Under a dry nitrogen atmosphere, the solution was irradiated for 5 h with constant stirring. The reactor was opened to the atmosphere and the solution filtered through silica gel, washing with methylene chloride. The solvent was removed by rotary evaporation to yield a dark orange solid, which was chromatographed on silica gel TLC plates and developed with 95:5 CH_2Cl_2–hexane to give 0.19 g (28% yield) of dark red crystalline 4 (R_f 0.80).

Preparation of $(CO)_3Cr(PhCH_2)_2C_2B_4H_6$ (5) and $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (6). Into a 250-mL round-bottom flask equipped with a condenser and magnetic stirrer were placed 0.572 g (2.23 mmol) of $(C_6H_5CH_2)_2C_2B_4H_6$ and 2.47 g (11.2 mmol) of chromium hexacarbonyl. Anhydrous dibutyl ether (45 mL) and 5 mL of anhydrous tetrahydrofuran (THF) were added, and the reaction mixture was refluxed under dry N_2 for 18 h. The reactor was cooled to room temperature and filtered and the solvent removed in vacuo. The residue was extracted with methylene chloride and chromatographed on silica gel preparative TLC plates with a 2:3 CH_2Cl_2–hexane solution. Two orange bands were collected, the first of which (R_f 0.51 in 2:3 CH_2Cl_2–hexane) gave 0.283 g (32.4% yield) of 5. The second band (R_f 0.28) provided 0.219 g (18.6% yield) of 6. Both complexes are orange, crystalline, moderately air-stable materials, decomposing only slowly on exposure to the air.

The dimetallic complex 6 was also prepared by the reaction of 5 with a 10:1 excess of $Cr(CO)_6$ in 10:1 refluxing dibutyl ether–THF solution under dry nitrogen. In a typical experiment, 0.374 g (0.954 mmol) of 5 was refluxed for 30 h with 2.09 g (9.50 mmol) of $Cr(CO)_6$ in 90 mL of anhydrous dibutyl ether and 10 mL of anhydrous THF. The product was chromatographically purified as previously described to yield 0.364 g of 6 (72.3% based on 2 employed).

X-ray Structure Determination on $(PhCH_2)_4C_4B_8H_8$ (3). Data were collected on a single crystal grown from CH_2Cl_2 solution and mounted on a glass fiber, using standard methods on a Nicolet P3 four-circle diffractometer to determine cell dimensions and space group data. The θ–2θ scan technique was employed as previously described[26,27] to record the intensities for all nonequivalent reflections within the 2θ range given in Table V.

The intensities of three standard reflections showed no greater fluctuations during data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects but not for absorption. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($p = 0.03$),[28] were used in the final refinement of the structural parameters.

The direct methods program MULTAN 74 was used to determine the non-hydrogen atom positions, and full-matrix least-squares refinement was carried out as previously described.[29] Anisotropic temperature factors were introduced for the non-hydrogen atoms. Further Fourier difference functions permitted location of all the hydrogen atoms, which were included in the least-squares refinement for several cycles and then held fixed. The model converged to the final R and R_w values given in Table V, where $R = \sum||F_o - F_c|| / \sum F_o$ and $R_w = (\sum w(F_o)^2 / \sum w F_o^2)^{1/2}$. Tables of observed and calculated structure factors and thermal parameters are available as supplementary material.

X-ray Structure Determination on $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$ (6). A single crystal of dimensions 0.2 × 0.3 × 0.4 mm, grown from CH_2Cl_2 solution, was mounted in a random orientation on the end of a glass fiber with epoxy cement and the fiber fixed to an aluminum pin with sealing wax and mounted on a goniometer head. Crystal data were obtained by standard procedures[30] on a Nicolet P3m microprocessor-controlled diffractometer. Systematic absences of type $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$, $h0l$, $h = 2n + 1$, and $0kl$, $k + l = 2n + 1$, indicated possible space groups as $Pna2_1$ or $Pnam$ (a nonstandard setting of Pnma). Data was collected by standard methods[31] within the range 4° < 2θ < 55°.

Solution and Refinement. The structure was solved by direct methods using a modified version of MULTAN 80, initially in the noncentric space group $Pna2_1$. Positions of the two chromium atoms were located in an E map calculated from the highest combined figure of merit, and all subsequent non-hydrogen atoms were found from subsequent difference Fourier syntheses. At this point, careful analysis of chemically equivalent bond lengths indicated discrepancies, indicating that the centric space group *Pnam* was the correct choice. Positional parameters for the unique half-molecule were then transformed to correspond to this space group. Subsequent refinement followed by difference Fourier syntheses revealed the positions of all hydrogen atoms. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. In view of the regular shape of the crystal and the small value for the absorption coefficient, no absorption corrections were applied.

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(31) Programs used are part of the SDP-Plus Crystallographic Computing package supplied with the TEXRAY 234 Crystallographic Computing System. This is based on a PDP 11/73 computer with 1 megabyte of core storage, a Kennedy 800/1600 bpi magnetic tape drive, a SKYMNK array processor, an Envision color graphics terminal, an Envision color printer/plotter, and PDP 220 terminals.

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Registry No. 1, 105472-14-8; 2, 105472-94-4; 3, 105472-95-5; 4, 105501-04-0; 5, 105472-92-2; 6, 105472-93-3; (η^5-C_5H_5)Co(CO)$_2$, 12078-25-0; Cr(CO)$_6$, 13007-92-6.

Supplementary Material Available: Tables of structure factors, thermal parameters and calculated mean planes for compounds 3 and 6, a stereo diagram of unit cell packing for 3, and a table of short inter- and intramolecular nonbonded contacts in 3 (9 pages); listings of observed and calculated structure factors for 3 and 6 (34 pages). Ordering information is given on any current masthead page.

Variable-Temperature NMR Study of Dynamic Exchange in Sodium (μ-Fluoro)bis(triethylaluminate)

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Variable-temperature ^{13}C studies and ^1H and ^{27}Al NMR studies have been carried out on mixtures of Na[Al_2Et_6F] and Al_2Et_6. We observe that Na[Al_2Et_6F] undergoes facile exchange of $AlEt_3$ with Al_2Et_6 in contrast to previously published work. The exchange process has been shown to involve a dissociative mechanism. A ΔH^* of 20.4 kcal mol^{-1} (85.4 kJ mol^{-1}) and ΔS^* of 18.7 eu were determined. The value of ΔH^* closely approximates the bond dissociation energy for the Al–F bond in $Et_3Al{-}F{-}AlEt_3$. This is the first reported bond dissociation energy for the Al–F bond in this unusual class of compounds.

M[Al_2R_6X] complexes[2] (where M is alkali metal or tetraalkylammonium ion; X is halide, pseudohalide, or oxo anion; and R is an alkyl group) are of interest from the point of view of structure,[3] electronic properties,[4] thermal behavior,[5] and utilization in separating triethylaluminum from α-olefins[6] and as "liquid clathrates".[7] However, little, if any, fundamental thermodynamic bond data or kinetic data are available to aid in understanding the chemistry of these materials.

In this paper, we report the ^1H, ^{13}C, and ^{27}Al NMR characterization of Na[Al_2Et_6F]. Unexpectedly, we find that Na[Al_2Et_6F] exchanges with Al_2Et_6 in toluene solution. The mechanism of exchange has been found to involve dissociation of Na[Al_2Et_6F] to Na[$AlEt_3F$] and $AlEt_3$. Examination of the activation energy for the exchange reaction yields a value for the $Et_3Al{-}F$ bond dissociation energy for this complex.

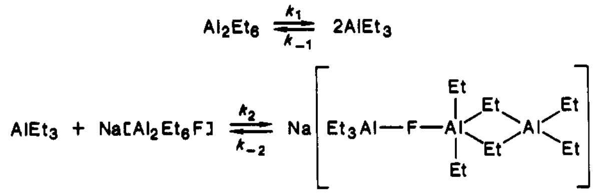
Neat mixtures of Na[Al_2Pr_6F] and Al_2Et_6 show little, if any exchange by ^{27}Al NMR to form Na[Al_2Et_6F] and Al_2Pr_6 at 120 °C.[8] However, in toluene-d_8 at room temperature, we observed by ^1H NMR the characteristic averaging of ethyl resonances, indicative of rapid exchange when Al_2Et_6 was mixed with M[Al_2Et_6X] complexes. Exchange was demonstrated by plotting the ^1H chemical shift of the methyl resonance in mixtures of Al_2Et_6 and Na[Al_2Et_6F] vs. the mole fraction of Na[Al_2Et_6F]. A linear dependence was observed (Figure 1).

Scheme I

$$\mathrm{Na[Al_2Et_6F]} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Na[AlEt_3F]} + \mathrm{AlEt_3}$$

$$\mathrm{Al_2Et_6} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{2AlEt_3}$$

Scheme II



The exchange process is of interest from a mechanistic point of view. We have considered two possible mechanisms for the exchange process. The first involves dissociation of M[Al_2Et_6X] to form M[$AlEt_3X$] plus $AlEt_3$ (Scheme I). The second involves a bimolecular associative mechanism to form an alkyl-bridged complex with five-coordinate aluminum (Scheme II). Both mechanisms have precedence in the literature.[9]

A variable-temperature ^{13}C NMR study was carried out by using a mixture of Al_2Et_6 (0.23 g) and Na[Al_2Et_6F] (0.27

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