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Reactions of Anionic Carborane Nucleophiles with Chromium-Coordinated Haloarenes

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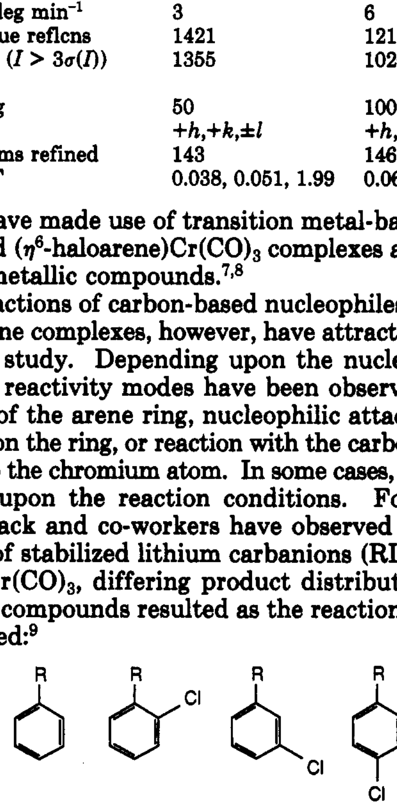
Summary: Lithiated *C*-methyl-*o*-carborane, $LiC_2B_{10}H_{10}(CH_3)$, reacts with the complexes (η^6-arene)$Cr(CO)_3$ to yield *C*-methyl-*C'*-aryl-substituted carboranes. With the complexes (η^6-*o*-$C_6H_4X_2$)$Cr(CO)_3$, the carborane displaces either a hydrogen atom (X = Cl) or a halide (X = F) from the arene ring to give 1-(1'-*closo*-2'-CH_3-1',2'-$C_2B_{10}H_{10}$)-2,3-$Cl_2C_6H_3$ (**1**) or 1-(1-*closo*-2'-CH_3-1',2'-$C_2B_{10}H_{10}$)-2-FC_6H_4 (**2**), respectively. Reaction of 2 equiv of $LiC_2B_{10}H_{10}(CH_3)$ with (η^6-p-$C_6H_4F_2$)$Cr(CO)_3$ results in the displacement of both fluoride atoms on the arene ring to yield the *p*-phenylene compound 1,4-(1'-*closo*-2'-CH_3-1',1'-$C_2B_{10}H_{10}$)$_2C_6H_4$ (**3**). Compounds **1** and **3** have been characterized by X-ray crystallography. **1** crystallized in the monoclinic space group $P2_1$ with $a = 7.2516$ (7), $b = 7.7424$ (8), and $c = 13.4028$ (13) Å; $\beta = 97.389$ (3)°; $V = 750$ Å^3; and $Z = 2$. Data were collected at 128 K on a modified Picker FACS-1 diffractometer, using Mo Kα radiation, to a maximum $2\theta = 50°$, giving 1421 unique reflections, and the structure was solved by direct methods. The final discrepancy index was $R = 0.038$, $R_w = 0.051$ for 1355 independent reflections with $I > 3\sigma(I)$. The C–C bond in the carborane is unusually long, 1.706 (5) Å, but it is the shortest interatomic distance within the icosahedron. **3** crystallized in the monoclinic space group $P2_1/n$ with $a = 7.024$ (1), $b = 13.764$ (4), and $c = 12.335$ (4) Å; $\beta = 90.99$ (1)°; $V = 1192$ Å^3; and $Z = 2$. Data were collected on a modified Syntex P$\bar{1}$ diffractometer, using Cu Kα radiation, to a maximum $2\theta = 100°$, giving 1219 unique reflections, and the structure was solved by direct methods. The final discrepancy index was $R = 0.061$, $R_w = 0.086$ for 1020 independent reflections with $I > 2\sigma(I)$. The molecule is centrosymmetric. The C–C bond in the carborane is rather long, 1.684 (5) Å, but it is the shortest interatomic distance in the icosahedron.

It has been known for many years that the arene ligands in the complexes (η^6-arene)$Cr(CO)_3$ exhibit greatly enhanced electrophilicity relative to free arenes because of the electron-withdrawing properties of the $Cr(CO)_3$ unit. The π-bonded organometallic moiety has thus been compared to the highly electron-withdrawing nitro substituent in aromatic systems. In the same manner as in S_NAr displacements, good leaving groups on the arene ring in (η^6-arene)$Cr(CO)_3$ complexes can be displaced by introduced nucleophiles. The new arene can then be cleaved from the chromium under mild oxidative conditions. Oxygen-, nitrogen-, and sulfur-based nucleophiles have been extensively explored in these reactions;[1-6] recent studies have made use of transition metal-based nucleophiles and (η^6-haloarene)$Cr(CO)_3$ complexes as a route to heterobimetallic compounds.[7,8]

Table I. Details of Crystallographic Data Collection

compd	1	3
temp/K	128	25
cryst size/mm	0.32 × 0.32 × 0.32	0.1 × 0.2 × 0.22
normal to faces	001, 100, $0\bar{1}1$	$01\bar{1}$, 011, 100
appearance	cut colorless parallelepiped	colorless plate
radiation (graphite monochromator)	Mo Kα	Cu Kα
wavelength/Å	0.7107	1.5418
space group	$P2_1$	$P2_1/n$
a/Å	7.2516 (7)	7.024 (2)
b/Å	7.7424 (8)	13.764 (4)
c/Å	13.4028 (13)	12.335 (4)
β/deg	97.389 (3)	90.99 (1)
v/Å^3	750	1192
Z	2	2
ρ(calcd)/g cm^{-3}	1.35	1.09
μ/cm^{-1}	4.1	2.7
scan width		
below $K\alpha_1$	1.3	1.3
above $K\alpha_2$	1.6	1.6
scan rate/deg min^{-1}	3	6
no. of unique reflcns	1421	1219
no. of obsd ($I > 3\sigma(I)$) reflcns	1355	1020
2θ max/deg	50	100
data collcd	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of params refined	143	146
R, R_w, GOF	0.038, 0.051, 1.99	0.061, 0.086, 2.98

The reactions of carbon-based nucleophiles with chromium arene complexes, however, have attracted the most intensive study. Depending upon the nucleophile, the following reactivity modes have been observed: deprotonation of the arene ring, nucleophilic attack and substitution on the ring, or reaction with the carbonyl ligands bonded to the chromium atom. In some cases, the product depends upon the reaction conditions. For example, Semmelhack and co-workers have observed that in the reaction of stabilized lithium carbanions (RLi) with (η^6-C_6H_5Cl)$Cr(CO)_3$, differing product distributions of the following compounds resulted as the reaction conditions were varied:[9]



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(2) (a) Brown, D.; Raju, J. R. *J. Chem. Soc. A* **1966**, 40. (b) Brown, D.; Raju, J. R. *J. Chem. Soc. A* **1966**, 1617.

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(6) Semmelhack, M. F. *J. Organomet. Chem. Libr.* **1976**, *1*, 361, and references therein.

(7) (a) Heppert, J. A.; Thomas, M. E.; Swepston, P. N.; Extine, M. W. *J. Chem. Soc., Chem. Commun.* **1988**, 280. (b) Heppert, J. A.; Thomas-Miller, M. E.; Scherubel, D. M.; Takusagawa, F.; Morgenstern, M. A.; Shaker, M. R. *Organometallics* **1989**, *8*, 1199.

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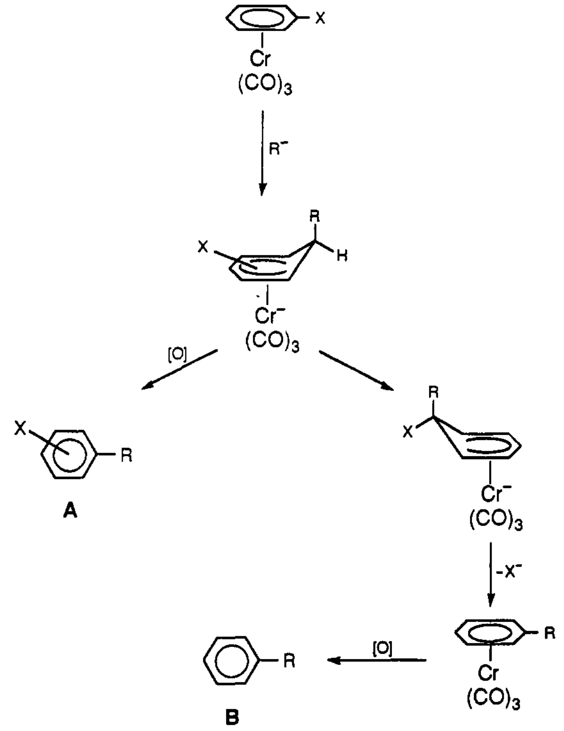
Semmelhack has proposed the following explanation for these observations:[10]



Depending upon whether the arene group is cleaved from the metal before or after the migration of R to displace X, the H-substituted or X-substituted product (**A** or **B**, respectively) will result.

As part of our continuing interest in the chemistry of carbon–boron clusters ("carboranes"), we were interested in methods of attaching functionalized aryl groups to these compounds. The chemistry detailed in the above scheme (with **R** being a carborane anion) seemed a logical approach to aryl-substituted carboranes (or, alternatively, carborane-substituted benzenes). To our knowledge, only one study has been reported regarding the reactions of lithiated carboranes with chromium-bound haloarenes,[11] and in that work, the free, substituted arenes were not isolated. We describe here the reactions of lithiated methylcarborane, *closo*-1-Li-2-CH$_3$-1,2-C$_2$B$_{10}$H$_{10}$, with several compounds of the (η^6-haloarene)Cr(CO)$_3$ type.

Experimental Section

Reaction solvents were dried and distilled immediately before use. Unless otherwise noted, all operations were carried out under nitrogen with the use of standard Schlenk techniques. Melting points were determined in sealed tubes and are uncorrected. *C*-Methyl-*o*-carborane, C$_2$B$_{10}$H$_{11}$(CH$_3$), was synthesized as previously described.[12] Hexane solutions of *n*-butyllithium were obtained from Aldrich and used as received. The complexes (η^6-haloarene)Cr(CO)$_3$ were prepared by literature methods.[5] ^{1}H NMR spectra were recorded at 200 MHz on a Bruker AF-200 spectrometer; chemical shifts were referenced to residual solvent protons (acetone-d_6, δ 2.04).

Table II. Positional and Isotropic Thermal Parameters for Non-Hydrogen Atoms of 1[a]

atom	*x*	*y*	*z*	equiv U^2/Å^2 [b]
C(01)	0.69798 (43)	0.47903 (51)	0.74599 (24)	0.0192
C(02)	0.79281 (48)	0.51107 (49)	0.63739 (25)	0.0215
C(21)	0.78429 (55)	0.69058 (53)	0.59340 (28)	0.0283
C(11)	0.60282 (45)	0.62927 (46)	0.79095 (25)	0.0190
C(12)	0.67513 (47)	0.71578 (50)	0.88019 (26)	0.0226
C(13)	0.57354 (51)	0.85162 (53)	0.91637 (27)	0.0262
C(14)	0.40407 (51)	0.90443 (51)	0.86660 (29)	0.0276
C(15)	0.33406 (49)	0.82116 (56)	0.78047 (31)	0.0290
C(16)	0.43056 (49)	0.68512 (55)	0.74340 (27)	0.0269
Cl(12)	0.88381 (12)	0.66622	0.95111 (6)	0.0297
Cl(13)	0.66193 (14)	0.96082 (19)	1.02447 (7)	0.0389
B(03)	0.9359 (5)	0.4807 (6)	0.7482 (3)	0.021 (1)*
B(04)	0.8224 (5)	0.3247 (6)	0.8167 (3)	0.021 (1)*
B(05)	0.6077 (6)	0.2732 (6)	0.7443 (3)	0.025 (1)*
B(06)	0.5901 (6)	0.3951 (6)	0.6312 (3)	0.024 (1)*
B(07)	0.9843 (5)	0.3837 (6)	0.6351 (3)	0.024 (1)*
B(08)	1.0041 (6)	0.2618 (6)	0.7476 (3)	0.024 (1)*
B(09)	0.8009 (6)	0.1322 (6)	0.7445 (3)	0.026 (1)*
B(10)	0.6548 (5)	0.1761 (6)	0.6300 (3)	0.024 (1)*
B(11)	0.7712 (6)	0.3324 (6)	0.5625 (3)	0.025 (1)*
B(12)	0.9014 (6)	0.1684 (7)	0.6323 (3)	0.025 (1)*

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. Isotropic values are $1/8\pi^2$ times the "equivalent *B* value".[20] [b] The asterisk denotes an atom refined isotropically.

Synthesis of 1-(1′-*closo*-2′-CH$_3$-1′,2′-C$_2$B$_{10}$H$_{10}$)-2,3-Cl$_2$C$_6$H$_3$ (1). A diethyl ether solution of C$_2$B$_{10}$H$_{11}$(CH$_3$) (0.258 g, 1.63 mmol) was treated with 1.0 mL of 1.6 M *n*-BuLi (1.6 mmol) in hexane at 0 °C. To this solution was added an ether solution of (η^6-*o*-C$_6$H$_4$Cl$_2$)Cr(CO)$_3$ (0.223 g, 0.788 mmol). The reaction mixture was stirred at 0 °C for 6 h, then allowed to warm to room temperature, and stirred overnight. Iodine (1.5 g) was added to oxidize the chromium, and the resulting mixture was stirred for 2 days. The organic phase was washed with 50 mL of 10% NaCl, while the aqueous phase was extracted with 50 mL of ether. The organic fractions were combined and taken to dryness under vacuum. The oily yellow residue was dissolved in acetone; slow evaporation of this solution in air precipitated white crystals of product. A fragment of one crystal was used for X-ray diffraction studies, which conclusively demonstrated the 1,2,3-trisubstituted benzene structure: *closo*-1-CH$_3$-2-(2′,3′-Cl$_2$C$_6$H$_3$)-1,2-C$_2$B$_{10}$H$_{10}$. ^{1}H NMR (acetone-d_6): δ 1.84 (s, 3 H, CH$_3$), 7.53 (t, 1 H, H$_b$), 7.85 (dd, 1 H, H$_c$), 8.19 (dd, 1 H, H$_a$); J_{ac} = 1.3 Hz, J_{ab} = 8.4 Hz, J_{bc} = 7.9 Hz. EI-MS: *m/z* 302 (M$^+$). Mp: 161–163 °C.

1,4-(1′-*closo*-2′-CH$_3$-1′,2′-C$_2$B$_{10}$H$_{10}$)$_2$C$_6$H$_4$ (3). A THF solution of C$_2$B$_{10}$H$_{11}$(CH$_3$) (0.420 g, 2.65 mmol) was treated with 1.0 mL of 2.5 M *n*-BuLi (2.5 mmol) in hexane at room temperature. To this solution was added a THF solution of (η^6-*p*-C$_6$H$_4$F$_2$)Cr(CO)$_3$ (0.353 g, 1.41 mmol). This solution was refluxed overnight. Iodine (0.93 g) was added, and the resulting mixture was stirred at room temperature overnight. The organic phase was then washed with 50 mL of 10% NaCl, while the aqueous phase was extracted with 50 mL of ether. The organic fractions were combined and taken to dryness under vacuum, and the residue was washed with pentane. The resulting solid was dissolved in acetone and crystallized by slow evaporation in air. Yield: 47.1 mg, 9%. Crystals were obtained by slow evaporation of an acetone/heptane solution in air. ^{1}H NMR (acetone–d_6): δ 1.79 (s, 6 H, CH$_3$), 7.90 (s, 4 H, phenyl H). EI-MS: *m/Z* 394 (M$^+$). Mp: >280 °C.

Collection and Reduction of X-ray Data for 1 and 3. Colorless crystals of 1 and 3 were mounted on fibers. All data were collected in the θ–2θ scan mode and were corrected for Lorentz and polarization effects and for secondary extinction but not for absorption. Programs used in this work are included in the UCLA Crystallography Package. All calculations were performed on the VAX 3100 computer of the J. D. McCullough X-ray Crystallography Laboratory. Scattering factors for H were obtained from Stewart et al.[13] and for other atoms were taken from ref 14. Atoms were located by use of direct methods (MULTAN80).

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[9] (a) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7091. (b) Semmelhack, M, F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7092. (c) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.* **1979**, *101*, 217.

[10] Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. L.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957.

[11] Zakharkin, L. I.; Zhigareva, G. G. *J. Gen. Chem. USSR (Engl. Transl.)* **1983**, *53*, 841.

[12] *Inorganic Syntheses*; McGraw Hill: New York, 1967; Vol X, p 104.

[13] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table III. Positional and Isotropic Thermal Parameters for Non-Hydrogen Atoms of 3[a]

atom	x	y	z	equiv U^2/Å^2 [b]
B(03)	0.7928 (6)	0.2550 (3)	0.3636 (3)	0.046
B(04)	0.9599 (6)	0.2085 (3)	0.4611 (3)	0.051
B(05)	1.1903 (6)	0.2336 (3)	0.4127 (3)	0.051
B(06)	1.1673 (6)	0.2954 (3)	0.2884 (3)	0.047
B(07)	0.8438 (6)	0.1301 (3)	0.3667 (3)	0.054
B(08)	0.8224 (6)	0.1912 (3)	0.2419 (3)	0.049
B(09)	1.0533 (6)	0.2164 (3)	0.1943 (3)	0.050
B(10)	1.2207 (6)	0.1704 (3)	0.2904 (4)	0.053
B(11)	1.0917 (7)	0.1161 (3)	0.3966 (4)	0.057
B(12)	1.0077 (6)	0.1052 (3)	0.2621 (3)	0.054
C(01)	1.0068 (5)	0.3125 (2)	0.3905 (3)	0.040
C(02)	0.9269 (5)	0.3014 (2)	0.2615 (3)	0.045
C(11)	1.0016 (5)	0.4104 (2)	0.4456 (3)	0.043
C(12)	0.8412 (5)	0.4420 (3)	0.4983 (3)	0.063
C(16)	1.1616 (5)	0.4691 (3)	0.4487 (3)	0.064
C(21)	0.8547 (6)	0.3929 (3)	0.2051 (3)	0.071

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. Isotropic values are $1/8\pi^2$ times the "equivalent B value".[20] [b] The asterisk denotes an atom refined isotropically

Cell dimensions and other parameters, including conditions of data collection, are summarized in Table I. Final positional and thermal parameters for nonhydrogen atoms are given in Tables II and III for 1 and 3, resepctively.

A crystal of 1, obtained from a CH_3COCH_3 solution, was placed on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for 0k0 reflections for which $k \neq 2n$. Unit cell parameters were determined from a least-squares fit of 37 accurately centered reflections ($9.3 < 2\theta < 20.5°$). Data were collected at 128 K. Three intense reflections (204, 3,1,−4, 120) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 4% during the course of the experiment (26.4 h). Of the 1421 unique reflections measured, 1355 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis.

A crystal of 3, obtained from a methyl ethyl ketone/acetone solution, was placed on a Syntex P$\bar{1}$ diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for 0k0 reflections for which $k \neq 2n$ and for h01 reflections for which $h + 1 \neq 2n$. Unit cell parameters were determined from a least-squares fit of 14 accurately centered reflections ($15.9 < 2\theta < 35.8°$). Data were collected at 25 °C. Three intense reflections (2,−1,0, 0,2,−2, 111) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (12.9 h). Of the 1219 unique reflections measured, 1020 were considered observed ($I > 2\sigma(I)$) and were used in the subsequent structure analysis.

Solution and Refinement of the Structure of 1. All boron atoms were refined with isotropic parameters. All other nonhydrogen atoms were refined with anisotropic parameters. For both 1 and 3 all methyl H were included in calculated positions as members of rigid groups; C–H = 1.0 Å H–C–H = 109.5°. All other H were included in located positions. H atoms were assigned isotropic displacement values of 0.04 and 0.03 Å^2 for methyl and all other H, respectively. The maximum and minimum peaks on a final difference electron density map were 0.3 e Å^{-3}.

Solution and Refinement of the Structure of 3. All nonhydrogen atoms were refined with anisotropic parameters. H on the carborane ligand and on the benzene ring were kept in located positions. H atoms of methyl groups and other H atoms were assigned isotropic displacement values of 0.09 and 0.06 Å^2, respectively. The maximum and minimum peaks on a final difference electron density map were 0.2 e Å^{-3}.

Results and Discussion

The complexes (η^6-haloarene)$Cr(CO)_3$ react with the lithiated carborane $LiC_2B_{10}H_{10}(CH_3)$ under mild conditions

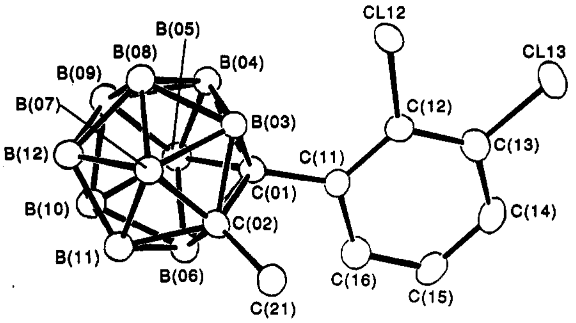

Figure 1. Molecular structure of 1-(1′-*closo*-2′-CH_3-1′,2′-$C_2B_{10}H_{10}$)-2,3-$Cl_2C_6H_3$ (1). Hydrogen atoms have been omitted for clarity.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for 1

C(01)–C(02)	1.706 (5)	C(01)–B(03)	1.722 (5)	C(01)–B(04)	1.709 (6)
C(01)–B(05)	1.722 (6)	C(01)–B(06)	1.758 (5)	C(01)–C(11)	1.516 (5)
C(02)–C(21)	1.508 (6)	C(02)–B(03)	1.715 (5)	C(02)–B(06)	1.715 (6)
C(02)–B(07)	1.707 (6)	C(02)–B(11)	1.704 (6)	B(03)–B(04)	1.781 (6)
B(03)–B(07)	1.767 (6)	B(03)–B(08)	1.766 (7)	B(04)–B(05)	1.771 (6)
B(04)–B(08)	1.773 (6)	B(04)–B(09)	1.773 (6)	B(05)–B(06)	1.776 (6)
B(05)–B(09)	1.776 (6)	B(05)–B(10)	1.779 (6)	B(06)–B(10)	1.760 (7)
B(06)–B(11)	1.766 (6)	B(07)–B(08)	1.769 (6)	B(07)–B(11)	1.762 (6)
B(07)–B(12)	1.770 (7)	B(08)–B(09)	1.779 (6)	B(08)–B(12)	1.780 (6)
B(09)–B(10)	1.782 (6)	B(09)–B(12)	1.776 (6)	B(10)–B(11)	1.787 (6)
B(10)–B(12)	1.786 (6)	B(11)–B(12)	1.776 (6)	C(12)–Cl(12)	1.724 (4)
C(13)–Cl(13)	1.728 (4)				

C(02)–C(01)–C(11)	118.8 (3)		
B(03)–C(01)–C(11)	119.6 (3)	B(04)–C(01)–C(11)	123.4 (3)
B(06)–C(01)–C(11)	117.2 (3)	B(05)–C(01)–C(11)	121.6 (3)
C(21)–C(02)–B(03)	117.1 (3)	C(01)–C(02)–C(21)	117.8 (3)
C(21)–C(02)–B(07)	121.2 (3)	C(21)–C(02)–B(06)	118.2 (3)
C(01)–C(11)–C(12)	124.2 (3)	C(21)–C(02)–B(11)	121.4 (3)
C(12)–C(11)–C(16)	116.9 (3)	C(01)–C(11)–C(16)	118.8 (3)
C(11)–C(12)–Cl(12)	124.5 (3)	C(11)–C(12)–C(13)	119.6 (3)
C(12)–C(13)–C(14)	121.8 (3)	C(13)–C(12)–Cl(12)	116.0 (3)
C(14)–C(13)–Cl(13)	118.1 (3)	C(12)–C(13)–Cl(13)	120.1 (3)

[a] Units of esd, in parentheses, are those of the least significant digit of the corresponding value.

to give a variety of aryl-substituted carboranes following oxidative workup. The chemical shift of the CH_3 group of methylcarborane derivatives proved to be a reliable indicator to determine if the aryl group had bonded to the carborane: the resonance of the unsubstituted carborane, at δ 2.11 (acetone-d_6), shifted significantly upfield, to δ 1.8–1.9. No attempts were made to isolate the presumed intermediates (η^6-carboranylarene)$Cr(CO)_3$. In all reactions, large quantities of $C_2B_{10}H_{11}(CH_3)$ were recovered after the oxidative workup; this observation may result from the reprotonation of $LiC_2B_{10}H_{10}(CH_3)$ by the relatively acidic ring hydrogens of (η^6-haloarene)$Cr(CO)_3$. Although the reaction of $LiC_2B_{10}H_{10}(CH_3)$ with (η^6-C_6H_5Cl)$Cr(CO)_3$ is reported to give (η^6-$C_6H_5C_2B_{10}H_{10}$-(CH_3))$Cr(CO)_3$ in reasonable yield,[11] we were unable to isolate any of the aryl-substituted carborane after oxidation with I_2. The same was true for the attempted reaction of $LiC_2B_{10}H_{10}(CH_3)$ with (η^6-C_6H_5F)$Cr(CO)_3$.

When $LiC_2B_{10}H_{10}(CH_3)$ is allowed to react with the dihaloarene complex (η^6-*o*-$C_6H_4Cl_2$)$Cr(CO)_3$, however, an unexpected reaction takes place. Instead of displacing one or both chlorides—even in the presence of less than 0.5 equiv of dichloroarene complex—the carborane anion formally substitutes for one of the arene ring hydrogens to give 1-(1′-*closo*-2′-CH_3-1′,2′-$C_2B_{10}H_{10}$)-2,3-$Cl_2C_6H_3$ (1). The 1,2-dichloro-3-carboranyl structure was determined by X-ray crystallography and is shown in Figure 1. In 1, the C–C bond in the carborane is unusually long, 1.706 (5) Å, but it is the shortest interatomic distance within the icosahedron. B–B distances range from 1.760 (7) to 1.787 (6) Å. C–C distances to substituents on the carborane are

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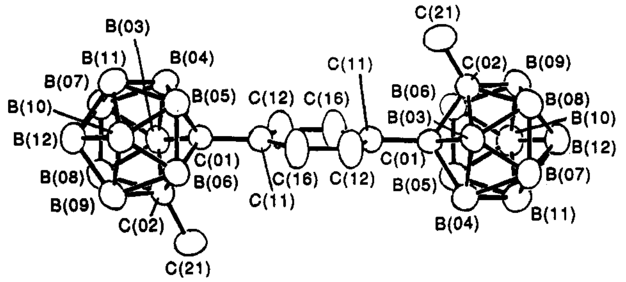

Figure 2. Molecular structure of 1,4-bis(1′-*closo*-2′-CH_3-1′,1′-$C_2B_{10}H_{10})_2C_6H_4$ (**3**). Hydrogen atoms have been omitted for clarity.

1.516 (5) and 1.508 (6) Å for phenyl and methyl carbon. Bond lengths and angles are collected in Table IV.

This type of reactivity, while previously observed with monohaloarene complexes and carbon-based anions,[9b,c] is unprecedented for dihaloarene complexes. For example, Barrett et al. have shown that $(\eta^6$-*o*-$C_6H_4Cl_2)Cr(CO)_3$ reacts cleanly with 2 equiv of KCN to give $(\eta^6$-*o*-$C_6H_4(CN)_2)Cr(CO)_3$.[15] In another study, Baldoni and coworkers have demonstrated that when $(\eta^6$-*o*-$C_6H_4Cl_2)Cr(CO)_3$ is treated with stabilized carbanions, substitution of one chloride occurs.[16] In neither case reported was evidence for hydrogen displacement obtained. It should be noted, however, that chloride is a strong ortho and meta director in the reaction of lithiated carbanions with $(\eta^6$-$C_6H_5Cl)Cr(CO)_3$;[9b,c] in compound **1**, the carboranyl moiety is ortho to one chlorine atom and meta to the other. The ortho- and meta-directing tendencies of ring-bound alkoxides have also been noted; Semmelhack observed that $(\eta^6$-*o*-$C_6H_4(OMe)_2)Cr(CO)_3$ reacts with lithiated carbanions to give the 1,2,3-trisubstituted benzene.[17] In this case, as in that presented here, the product A, of the unrearranged intermediate in the scheme above has been isolated.

Since fluoride ion is known to be a better leaving group than chloride in nucleophilic aromatic substitutions,[18] we decided to compare the reactivity of $(\eta^6$-*o*-$C_6H_4F_2)Cr(CO)_3$ to that of $(\eta^6$-*o*-$C_6H_4Cl_2)Cr(CO)_3$ with $LiC_2B_{10}H_{10}(CH_3)$. We found that the carborane anion displaced one fluorine from the ring, as indicated by mass spectrometry (m/z 254 for the parent ion) and ^1H NMR spectrometry (the upfield shift of the methyl resonance on the carborane, as mentioned above). Unfortunately, the product 1-(1-*closo*-2′-CH_3-1′,2′-$C_2B_{10}H_{10}$)-2-FC_6H_4 (**2**) could not be satisfactorily purified. Substitution of both fluorines could not be achieved, even under forcing conditions.

On the assumption that the ortho disubstitution of fluorines was sterically blocked, we then allowed $LiC_2B_{10}H_{10}(CH_3)$ to react with the *p*-difluoro analogue, $(\eta^6$-*p*-$C_6H_4F_2)Cr(CO)_3$, in refluxing THF. After oxidative workup, we obtained a small amount of the bis(carborane)-substituted benzene, 1,4-(1′-*closo*-2′-CH_3-1′,2′-$C_2B_{10}H_{10})_2C_6H_4$ (**3**). The para-disubstituted configuration was suggested by the simple aryl ^1H NMR pattern (one signal) and was confirmed in the solid state by X-ray crystallography. The structure of **3** is shown in Figure 2; selected interatomic distances and bond angles are listed in Table V. An interesting feature of this structure is that, because of crystallographic inversion at the center of the benzene ring, the methyl groups on the carboranes are constrained to lie on opposite sides of the ring. No extremely long B–B distances are found in this compound. The range is 1.754 (6)–1.785 (6) Å. The C–C bond in the carborane is rather long, 1.684 (5) Å, but it is the shortest interatomic distance in the icosahedron. The carboranyl C-methyl and C-phenyl carbon distances are not unusual, 1.522 (5) and 1.510 (4) Å, respectively.

Table V. Selected Interatomic Distances (Å) and Angles (deg) for 3

B(03)–B(04)	1.785 (6)	B(03)–B(07)	1.757 (6)	B(03)–B(08)	1.754 (6)
B(03)–C(01)	1.726 (5)	B(03)–C(02)	1.709 (5)	B(04)–B(05)	1.769 (6)
B(04)–B(07)	1.776 (6)	B(04)–B(11)	1.770 (6)	B(04)–C(01)	1.711 (5)
B(05)–B(06)	1.759 (6)	B(05)–B(10)	1.758 (6)	B(05)–B(11)	1.768 (6)
B(05)–C(01)	1.705 (5)	B(06)–B(09)	1.772 (6)	B(06)–B(10)	1.762 (6)
B(06)–C(01)	1.721 (5)	B(06)–C(02)	1.717 (5)	B(07)–B(08)	1.759 (6)
B(07)–B(11)	1.784 (7)	B(07)–B(12)	1.778 (6)	B(08)–B(09)	1.769 (6)
B(08)–B(12)	1.774 (6)	B(08)–C(02)	1.700 (5)	B(09)–B(10)	1.772 (6)
B(09)–B(12)	1.776 (6)	B(09)–C(02)	1.694 (5)	B(10)–B(11)	1.771 (6)
B(10)–B(12)	1.774 (6)	B(11)–B(12)	1.759 (6)	C(01)–C(02)	1.684 (5)
C(01)–C(11)	1.510 (4)	C(02)–C(21)	1.522 (5)	C(11)–C(12)	1.380 (5)
C(11)–C(16)	1.384 (5)	C(12)–C(16)	1.388 (5)		

B(03)–C(01)–C(11)	117.9 (3)		
B(04)–C(01)–C(11)	120.7 (3)	B(05)–C(01)–C(11)	121.3 (3)
C(02)–C(01)–C(11)	119.8 (3)	B(06)–C(01)–C(11)	118.2 (3)
B(08)–C(02)–C(21)	122.2 (3)	B(03)–C(02)–C(21)	117.5 (3)
B(09)–C(02)–C(21)	121.4 (3)	B(06)–C(02)–C(21)	116.5 (3)
C(01)–C(11)–C(12)	121.3 (3)	C(01)–C(02)–C(21)	117.3 (3)
C(12)–C(11)–C(16)	118.2 (3)	C(01)–C(11)–C(16)	120.5 (3)

[a] Units of esd, in parentheses, are those of the least significant digit of the corresponding value.

Substitution of two fluorides on a benzene ring coordinated to $Cr(CO)_3$ has precedent. Hamilton and Mahaffy[19] have described the reaction of three isomers of difluoroaniline (in which the fluorides were ortho, meta, and para to each other) with methoxide ion to yield amino ethers. To our knowledge, however, nothing as massive as a carborane has been attached to a benzene ring by this procedure.

It appears that a number of factors govern the reactivity of $LiC_2B_{10}H_{10}(CH_3)$ with chromium-coordinated haloarenes. The high basicity of the carborane anion is probably responsible for the low yields of aryl-substituted product relative to the amount of recovered methylcarborane. The use of fluoride as the leaving group is required for halide substitution in these reactions; if chloride is employed, hydrogen substitution (as in **1**) or no reaction is observed. Furthermore, the steric bulk of the carborane must play a role. If *o*-difluorobenzene is used with carborane as anion, substitution of only one fluoride is observed (whereas with methoxide as nucleophile both fluorides are displaced); however, if *p*-difluorobenzene is used, both fluorides can be substituted by carboranes.

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Supplementary Material Available: Listings of positional and thermal parameters and bond distances and angles for 1 and 3 (15 pages). Ordering information is given on any current masthead page.

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