both **1a** and **2b** the pyrone ring is planar or very nearly so. However, the bond lengths and bond angles in the 2-pyrone rings of **1a**, as compared to those in **2b**, are reflective of a significant delocalization of π-electron density over the metal-attached $C-CO_2$ fragments. This feature is indicated by the shorter C(7)–C(6) and C(7)–O(3) bonds and longer C(7)–O(4) bond in complex **1a**. This delocalization is probably a manifestation of the positive charge extant in the pyrone ring and is similar in magnitude to that exhibited by the related lactone complexes.[22] The key information gained in each case is that the crystallographic analyses of **1a** and **2b** confirm the existence of the isolated pyrone complex as only one of two possible regioisomers with respect to the formation of the pyrone ring (vide supra). This regioselectivity is important synthetically since it allows for selective functionalization of the 5- and 6-positions of the 2-pyrone moiety.

The analytical and spectroscopic data for all isolated pyrone complexes are collected in Tables I and II. The salts **1a–c** are green, air-stable solids which are soluble in polar solvents such as THF, CH_2Cl_2, and acetone. The neutral complexes **2a–c**, on the other hand, are brown, air-stable solids which display the expected solubility in less polar solvents such as Et_2O and benzene. The spectroscopic properties of complexes **1a–c** and **2a–c** are unremarkable and are fully consistent with the complexes possessing molecular structures similar to those established crystallographically for **1a** and **2b** and retaining these structures in solutions.

The generality of the reactions outlined in Scheme I remains to be established. For example, it may be feasible to incorporate other heteroatoms into the organic ring, with lactams and thiolactones being possible products. It should be possible to extend the condensations effected by the $[Cp^*M(NO)_2]^+$ cations to encompass acetylene esters other than methyl propiolate and to effect the removal of the assembled 2-pyrone from the metal center with a variety of reagents (e.g. HCl, Me_3SiCl, etc.). Also feasible is the insertion of electrophiles of the type NE^+ (E = O, p-$O_2NC_6H_4N$, S) into the Cr–C bond of complex **2a** or its analogues, since such insertions into Cr–C σ bonds have precedent in these systems.[24] It remains to be seen if the selectivity of formation of the pyrone ring can be maintained without the presence of a phenyl group, but if so, this could allow for the formation of 2-pyrone molecules with selective functionalization of the pyrone ring at all four available ring positions. At present, no known synthetic route leading to 2-pyrones allows for such selective substitution.[6a]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and postgraduate scholarships to W.S.M. and E.G.V.

Registry No. **1a**, 141526-55-8; **1b**, 141508-00-1; **1c**, 141508-02-3; **2a**, 141508-03-4; **2b**, 141508-04-5; **2c**, 141508-05-6; **3a**, 141507-97-3; **3b**, 141507-98-4; $[Cp^*Cr(NO)_2]BF_4$, 124921-16-0; $[Cp^*Mo(NO)_2]BF_4$, 124921-20-6; $[Cp^*W(NO)_2]BF_4$, 124921-24-0; $Cp^*Cr(NO)_2Cl$, 110681-76-0; $HC{\equiv}CCO_2Me$, 922-67-8; $EtC{\equiv}CPh$, 622-76-4; $MeC{\equiv}CPh$, 673-32-5; I_2, 7553-56-2.

Supplementary Material Available: Tables of fractional atomic coordinates and isotropic temperature factors for the remaining atoms and remaining bond distances and angles for $[Cp^*Cr(NO)_2C{=}C(H)C(Et){=}C(Ph)OC{=}OMe]BF_4$ (**1a**) and torsion angles, H atom coordinates and isotropic temperature factors, and anisotropic thermal parameters for $Cp^*Mo(NO)_2C{=}C(H)C(Me){=}C(Ph)OC{=}O$ (**2b**) (9 pages). Ordering information is given on any current masthead page.

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A Silyl Carborane Containing the *closo*-1,10-$C_2B_8H_8$ Fragment

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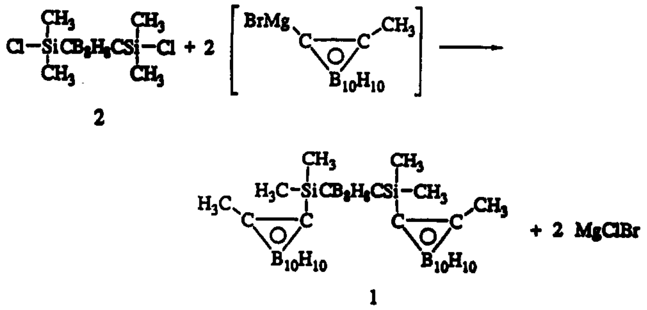
Summary: When 1,10-$(Si(CH_3)_2Cl)_2$-*closo*-1,10-$C_2B_8H_8$ was reacted with 2 equiv of 1-CH_3-2-MgBr-*closo*-1,2-$C_2B_{10}H_{10}$, 1,10-(1′-$Si(CH_3)_2$-2′-CH_3-*closo*-1′,2′-$C_2B_{10}H_{10})_2$-*closo*-1,10-$C_2B_8H_8$ (**1**) was isolated in 51% yield. The molecular structure of **1** was determined by single-crystal X-ray diffraction techniques. Compound **1** crystallized in the monoclinic space group $P2_1/c$: a = 13.1739 (9), b = 7.2412 (5), and c = 18.886 (1) Å; β = 107.905 (2)°; V = 1714 Å^3; and Z = 2 (two centrosymmetric molecules, achieved by disordering the C_2B_8 moiety). Data were collected on a Huber diffractometer constructed at UCLA, using Mo Kα radiation, to a maximum 2θ = 50°, giving 3028 unique reflections. The structure was solved by direct methods (SHELX86). The final discrepancy index was R = 0.074, R_w = 0.097 for 2022 independent reflections with $I > 3\sigma(I)$.

Scheme I



Silyl derivatives of the isomers of *closo*-$C_2B_{10}H_{12}$ have been known since the 1960s.[1-4] However, although a large

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number of polymeric siloxanes have been prepared,[5] only one report[4] on polymeric, silyl carboranes containing a carborane unit, the *closo*-1,7-$C_2B_{10}H_{10}$ unit, in the backbone of the polymer has appeared in the literature. We have recently begun to explore the use of *closo*-1,10-$C_2B_8H_{10}$ as a precursor to boron carbide, B_4C, and in the preparation of precursors to silicon carbide–boron carbide, SiC–B_4C, composites. The reaction of 1,10-($Si(CH_3)_2Cl)_2$-*closo*-1,10-$C_2B_8H_8$ (**2**) with 1-CH_3-2-MgBr-*closo*-1,2-$C_2B_{10}H_{10}$ (Scheme I) has been investigated for the purpose of developing routes to silicon-linked carborane units in species which might be employed as precursors to SiC–B_4C composites.

Experimental Section

Unless otherwise stated, all manipulations were performed under an atmosphere of purified nitrogen by employing standard Schlenk techniques. Solvents were dried and distilled in an inert atmosphere prior to use.[6] The literature procedures were used to prepare 1-CH_2Br-*closo*-1,2-$C_2B_{10}H_{11}$[7] and *closo*-1,10-$C_2B_8H_{10}$.[8] Thermal gravimetric analysis (TGA) was performed in an inert atmosphere on a Perkin-Elmer TGS-2, at a heating rate of 10 °C/min.

Synthesis. 2. To 4.3 g (36 mmol) of *closo*-1,10-$C_2B_8H_{10}$ in 125 mL of diethyl ether at 0 °C was added 36 mL of butyllithium (2.0 M, 72 mmol). This mixture was allowed to stir for 2 h and added via a cannula to 46 mL (380 mmol) of dichlorodimethylsilane in 50 mL of diethyl ether. The reaction was stirred for 12 h and filtered through a $^1/_4$-in. bed of Celite. The diethyl ether was removed under dynamic vacuum; the solid was then dissolved in hexane. The hexane solution was cooled to ~−15 °C (ice–acetone) to yield a white precipitate. The hexane was decanted from the white solid via a cannula. The solid thus obtained was placed in a sublimation apparatus and 3.5 g (11 mmol, 31% based upon *closo*-1,10-$C_2B_8H_{10}$ employed) of **2** collected on a 0 °C cold finger. Characterization. ^1H NMR: ($CDCl_3$, TMS, 25 °C, 200.132 MHz) 0.85 ppm (s, CH_3). ^{11}B NMR: (toluene, $BF_3{\cdot}O(C_2H_5)_2$, 25 °C, 160.463 MHz) −8.4 ppm (d, J = 164 Hz). IR: 2967, 2596, 1257, 1207, 1013, 931, 969, 841, 820, 793, 691, 683, 500 cm^{-1}. Mp: 102–103 °C. Anal. Calcd for $C_6H_{20}B_8Cl_2Si_2$: C, 23.56; H, 6.61; B, 28.28; Cl, 23.18; Si, 18.37. Found: C, 23.42; H, 6.69; B, 28.15.

1. The Grignard reagent, 1-CH_3-2-MgBr-*closo*-1,2-$C_2B_{10}H_{10}$, was prepared in THF from 0.538 g (2.27 mmol) of 1-CH_2Br-*closo*-1,2-$C_2B_{10}H_{11}$ and an excess of magnesium (0.072 g, 2.96 mmol). The Grignard solution was added to a THF solution of **2** (prepared as above, 0.341 g, 1.12 mmol). This solution was refluxed for 6 h, and the THF was removed under dynamic vacuum. To the solids was added diethyl ether (~20 mL), and this mixture was stirred for ~30 min, then exposed to the atmosphere, and extracted 3 times with water. The diethyl ether layer was dried over magnesium sulfate and filtered and the solvent removed on a rotary evaporator. The solid was eluted through a silica gel column with a 50:50 mixture of toluene and methylene chloride. After removal of solvent from the fraction that was collected, a waxy solid (0.460 g) was obtained. This waxy solid was placed in a sublimation apparatus and the 1-CH_3-*closo*-1,2-$C_2B_{10}H_{11}$ present as an impurity was sublimed away at 90 °C, under vacuum, over a period of 6 h. Solid **1** remained unsublimed (0.311 g, 0.566 mmol, 51% based upon **2** employed). Characterization. ^1H NMR: ($CDCl_3$, TMS, 25 °C, 200.132 MHz) 2.16 (s, CH_3, carboranyl), 0.78 ppm (s, CH_3, silyl group). Integration 1.00:2.06, respectively, in good agreement with the theoretical values of 1:2. MS: parent ion obsd 553.6, calcd parent 554. ^{11}B NMR: (toluene, $BF_3{\cdot}O(C_2H_5)_2$, 25 °C, 160.463 MHz) 1.4 (d, J = 141), −4.6 (d, J = 148), −7.9 (not resolved), −8.7 (d, J = 160), −10.3 ppm (d, J = not resolved). IR: 2966, 2593, 2559, 1447, 1405, 1388, 1260, 1195, 1107, 1050, 1009, 926, 865, 838, 820, 803, 730, 700, 677 cm^{-1}. Anal. Calcd for $C_{12}H_{46}B_{28}Si_2$: C, 26.23; H, 8.46; B, 55.09; Si, 10.22. Found: C, 26.22; H, 8.43.

Table I. Crystallographic Data for 1

formula	$C_{12}H_{46}B_{28}Si_2$
fw	549.44
space group	$P2_1/c$
λ/Å	0.7107
a/Å	13.1739 (9)
b/Å	7.2412 (5)
c/Å	18.886 (1)
β/deg	107.905 (2)
V/Å^3	1714
Z	2
T/K	298
ρ_{calcd}/g cm^{-3}	1.1
μ/cm^{-1}	1.1
R, R_w, GOF[a]	0.074, 0.097, 2.89

[a] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Crystallography. Collection and Reduction of X-ray Data for 1. A colorless crystal, obtained from a toluene–hexane–pentane solution, was mounted on a fiber on a Huber diffractometer constructed at UCLA. Systematic absences were found for 0*k*0, $k = 2n + 1$, and for *h*0*l*, $l = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 36 accurately centered reflections ($9.4 < 2\theta < 20.4°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table I. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections (02-5, 033, 60-6) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay and had a maximum fluctuation of ±3.2% during the course of the experiment (63.7 h). Of the 3028 unique reflections measured, 2022 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis and Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; SHELX76 and SHELX86 (Sheldrick) crystal structure and solution packages; and ORTEP (Johnson).

Solution and Refinement of the Structure of 1. Atoms were located by use of direct methods (SHELX86). All calculations were performed on the VAX 3100 computer of the J. D. McCullough X-ray Crystallography Laboratory. With the exception of the C_2B_8 moiety, all non-hydrogen atoms were refined anisotropically. Although the C_2B_8 cage cannot be centrosymmetric, the remainder of the molecule was centrosymmetric and the eight boron atoms of the C_2B_8 cage were disordered in the crystal structure. Therefore the eight boron atoms of the C_2B_8 moiety were refined at half-occupancy with isotropic thermal parameters. All methyl H were included in calculated positions as members of rigid CH_3 groups, with H–C–H angles 109.5° and C–H distances 1.0 Å. Carboranyl H were included in located positions. H atoms were assigned u values based approximately on the u value of the attached atom. Scattering factors for H were obtained from Stewart et al.[9] and for other atoms were taken from ref 10. Anomalous dispersion terms were applied to the scattering of Si. The larger peaks on a final difference electron density map were 0.4 e/Å^3. Final positional and thermal parameters for non-hydrogen atoms are given in Table II.

Results and Discussion

When the reaction outlined in the scheme is carried out, **1** is formed in 51% yield. Compound **1** contains three carboranyl units linked in a chain via two dimethylsilyl

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Table II. Final Non-Hydrogen Positional and Thermal Parameters for 1

atom	*x*	*y*	*z*	$U_{eq}/Å^2$
Si(1)	0.25495 (8)	0.1015 (2)	0.13300 (6)	0.055
C(11)	0.2798 (4)	0.3492 (7)	0.1211 (3)	0.085
C(12)	0.3517 (4)	−0.0454 (8)	0.1042 (3)	0.089
C(1)	0.2729 (3)	0.0480 (5)	0.2358 (2)	0.052
C(2)	0.2112 (3)	0.1588 (6)	0.2883 (2)	0.066
C(2M)	0.1321 (6)	0.3096 (10)	0.2526 (3)	0.129
B(3)	0.1755 (5)	−0.0600 (9)	0.2639 (3)	0.086
B(4)	0.2960 (8)	−0.1731 (9)	0.2681 (4)	0.116
B(5)	0.3992 (5)	−0.0081 (13)	0.2915 (3)	0.106
B(6)	0.3422 (5)	0.2030 (9)	0.3018 (3)	0.089
B(7)	0.1884 (5)	0.0192 (9)	0.3546 (3)	0.079
B(8)	0.2457 (9)	−0.1930 (9)	0.3425 (4)	0.127
B(9)	0.3833 (9)	−0.1578 (16)	0.3598 (5)	0.158
B(10)	0.4113 (5)	0.0749 (16)	0.3814 (3)	0.131
B(11)	0.2891 (5)	0.1819 (9)	0.3776 (3)	0.082
B(12)	0.3139 (6)	−0.0437 (11)	0.4127 (3)	0.102
C(1′)	0.1173 (3)	0.0432 (5)	0.0697 (2)	0.05
B(2′)	−0.0032 (9)	0.002 (2)	0.0811 (6)	0.08
B(3′)	0.0195 (9)	0.198 (2)	0.0288 (6)	0.07
B(4′)	0.0929 (7)	0.055 (1)	−0.0171 (4)	0.04
B(5′)	0.0706 (8)	−0.149 (1)	0.0330 (6)	0.06
B(6′)	−0.1092 (9)	0.087 (2)	0.0026 (7)	0.08
B(7′)	−0.0414 (8)	0.128 (1)	−0.0660 (6)	0.06
B(8′)	−0.0052 (7)	−0.117 (1)	−0.0638 (5)	0.05
B(9′)	−0.0712 (9)	−0.158 (2)	0.0059 (6)	0.07

Table III. Selected Angles (deg) in 1

C(11)–Si(1)–C(12)	110.8 (2)	C(11)–Si(1)–C(1)	110.3 (2)
C(11)–Si(1)–C(1′)	108.1 (2)	C(12)–Si(1)–C(1)	107.2 (2)
C(12)–Si(1)–C(1′)	107.3 (2)	C(1)–Si(1)–C(1′)	113.0 (2)
Si(1)–C(1)–C(2)	124.9 (3)	Si(1)–C(1)–B(3)	122.1 (3)
Si(1)–C(1)–B(4)	120.2 (3)	Si(1)–C(1)–B(5)	117.5 (3)
Si(1)–C(1)–B(6)	118.3 (3)	Si(1)–C(1′)–B(2′)	135.6 (5)
Si(1)–C(1′)–B(3′)	125.8 (4)	Si(1)–C(1′)–B(4′)	119.9 (4)
Si(1)–C(1′)–B(5′)	129.7 (4)		

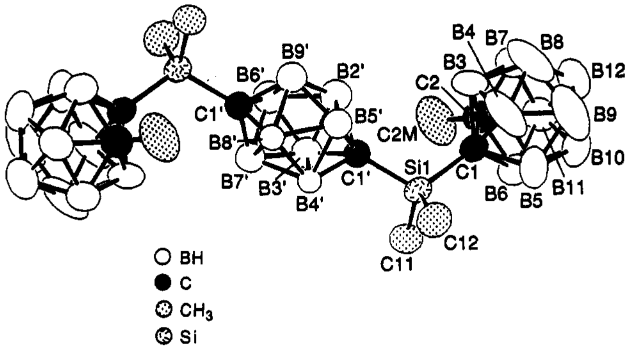

Figure 1. Molecular structure of 1 with thermal ellipsoids drawn at 50% probability. The terminal hydrogen atoms have been omitted for clarity. Only one of the disordered $C_2B_8H_8$ fragments is shown.

Table IV. Selected Interatomic Distances (Å) within 1

Si(1)–C(11)	1.849 (5)	Si(1)–C(12)	1.865 (5)
Si(1)–C(1)	1.921 (4)	Si(1)–C(1′)	1.887 (4)
C(1)–C(2)	1.668 (6)	C(1)–B(3)	1.720 (7)
C(1)–B(4)	1.707 (8)	C(1)–B(5)	1.721 (7)
C(1)–B(6)	1.717 (7)	C(2)–C(2M)	1.517 (8)
C(2)–B(3)	1.676 (8)	C(2)–B(6)	1.696 (7)
C(2)–B(7)	1.706 (7)	C(2)–B(11)	1.691 (7)
C(1′)–B(2′)	1.693 (12)	C(1′)–B(3′)	1.704 (12)
C(1′)–B(4′)	1.573 (9)	C(1′)–B(5′)	1.590 (11)
C(1′)–B(6′)[a]	1.635 (13)	C(1′)–B(7′)[a]	1.580 (11)
C(1′)–B(8′)[a]	1.542 (9)	C(1′)–B(9′)[a]	1.601 (12)

[a] Positions are related to the listed positions in Table II by −*x*, −*y*, −*z*.

groups. The molecular structure of 1, Figure 1, determined via X-ray diffraction techniques reveals a zig-zag arrangement of carborane polyhedra. The $-(Si(CH_3)_2CB_8H_8CSi(CH_3)_2)-$ core is rodlike and the $-2'-CH_3-1',2'-C_2B_{10}H_{10}$ fragments orient themselves in a "trans" arrangement about this core. The C(1)–Si(1)–C(1′) angle, 113.0 (2)°, is the largest of the angles about silicon, illustrating that steric repulsion between adjacent carborane polyhedra exists, but is minimal. Other selected angles within 1 are presented in Table III. The interatomic distances between Si(1) and C(11), C(12), C(1′), and C(1) are 1.849 (5), 1.865 (5), 1.887 (4), and 1.921 (4) Å, respectively. These distances reveal an increase in the Si–C interatomic distances with an increase in the steric requirements of the carbon substituent. The interatomic distances within the carborane polyhedra are within the normal range for *closo*-$C_2B_8H_{10}$ and *closo*-$C_2B_{10}H_{12}$ carboranes.[11] Selected interatomic distances within 1 are given in Table IV.

The Si–C distances can be compared to those in 1-Si$(CH_3)_3$-2-CH_3-*closo*-1,2-$C_2B_{10}H_{10}$[12a] and 1-Si$(CH_3)_3$-*closo*-1,2-$C_2B_{10}H_{11}$.[12b] In these two carboranes the Si–methyl carbon distances are 1.867 (4), 1.852 (3), 1.852 (3),[12a] and 1.849 (4) Å.[12b] The Si–C carborane distances are 1.937 (3)[12a] and 1.922 (4) Å.[12b] A projection down the Si(1)–C(1) carborane bond of 1, perpendicular to the CB(4) plane closely resembles the corresponding projection for 1-Si$(CH_3)_3$-2-CH_3-*closo*-1,2-$C_2B_{10}H_{10}$. One methyl group lies between B(4) and B(5) in each projection. In 1 the C_2B_8 carborane carbon (C(1′)) lies over B(3). The C_2B_{10} carborane C–C distance is 1.669 (4),[12a] 1.660 (3),[12b] and 1.668 (6) Å, in the two trimethylsilyl compounds and in 1, respectively. In the three compounds, C(1)–B distances range from 1.717 (4) to 1.727 (3),[12a] 1.709 (4) to 1.729 (4),[12b] and 1.707 (8) to 1.721 (7) Å in 1. The C(2)–B distances range from 1.711 (3) to 1.716 (4),[12a] 1.698 (4) to 1.716 (4),[12b] and 1.676 (8) to 1.706 (7) Å in 1.

Since 1 did not sublime at 90 °C in vacuo, a TGA experiment was conducted to determine if 1, itself, might be a suitable precursor to SiC–B_4C composites. Heating a sample of 1 revealed that weight loss began at 400 °C and was essentially complete (98%) by 472 °C (heating rate 10 °C/min). Total loss of weight was observed by 580 °C. This complete loss of weight is presumed to be due to the great thermal stability of 1 and its subsequent sublimation. This observation suggests that silyl carboranes of relatively high molecular weight, such as oligomers or true polymers, should be employed if SiC–B_4C composites are to be obtained by this route.

Acknowledgment. The support of this work by the National Science Foundation (Grant DMR 9014487) is gratefully acknowledged.

Supplementary Material Available: Complete tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for 1 (6 pages). Ordering information is given on any current masthead page.

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