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Article

Ruthenium-Catalyzed Metathesis Reactions of *ortho*- and *meta*-Dialkenyl-Carboranes: Efficient Ring-Closing and Acyclic Diene Polymerization Reactions

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The ruthenium-catalyzed metathesis reactions of dialkenyl-substituted *ortho*- and *meta*-carboranes provide excellent routes to both cyclic-substituted *o*-carboranes and new types of main-chain *m*-carborane polymers. The adjacent positions of the two olefins in the 1,2-(alkenyl)$_2$-*o*-carboranes strongly favor the formation of ring-closed (RCM) products with the reactions of 1,2-(CH$_2$=CHCH$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**1**), 1,2-(CH$_2$=CH(CH$_2$)$_3$CH$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**2**), 1,2-(CH$_2$=CHSiMe$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**3**), 1,2-(CH$_2$=CHCH$_2$SiMe$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**4**), and 1,2-[CH$_2$=CH(CH$_2$)$_4$SiMe$_2$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**5**) affording 1,2-(−CH$_2$-CH=CHCH$_2$−)-C$_2$B$_{10}$H$_{10}$ (**10**), 1,2-[−CH$_2$(CH$_2$)$_3$CH=CH(CH$_2$)$_3$CH$_2$−]-1,2-C$_2$B$_{10}$H$_{10}$ (**11**), 1,2-[−SiMe$_2$CH=CHSiMe$_2$−]-1,2-C$_2$B$_{10}$H$_{10}$ (**12**), 1,2-[−SiMe$_2$CH$_2$CH=CHCH$_2$SMe$_2$−]-C$_2$B$_{10}$H$_{10}$ (**13**), and 1,2-[−SiMe$_2$(CH$_2$)$_4$CH=CH(CH$_2$)$_4$SiMe$_2$−]-C$_2$B$_{10}$H$_{10}$ (**14**), respectively, in 72−97% yields. On the other hand, the reaction of 1,2-(CH$_2$=CHCH$_2$OC(=O))$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**6**) gave cyclo-[1,2-(1′,8′-C(=O)OCH$_2$CH=CHCH$_2$OC(=O))-1,2-C$_2$B$_{10}$H$_{10}$]$_2$ (**15a**) and polymer **15b** resulting from intermolecular metathesis reactions. The nonadjacent positions of the alkenyl groups in the 1,7-(alkenyl)$_2$-*m*-carboranes, 1,7-(CH$_2$=CHCH$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (**7**), 1,7-(CH$_2$=CH(CH$_2$)$_3$CH$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (**8**), and 1,7-(CH$_2$=CHCH$_2$SiMe$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (**9**), disfavor the formation of RCM products, and in these cases, acyclic diene metathesis polymerizations (ADMET) produced new types of main chain *m*-carborane polymers. The structures of **3**, **9**, **11**, **12**, **13**, and **15a** were crystallographically confirmed.

Introduction

Metal catalyzed olefin metathesis reactions, using either early transition-metal-based "Schrock-type" M(NAr)(=CHR)(OR′)$_2$L, M = Mo, W, or late transition-metal-based "Grubbs-type" Cl$_2$Ru(=CHPh)(PCy$_3$)L, L = PCy$_3$ (**I**) or H$_2$IMes (**II**) catalysts, have been shown to be versatile and powerful tools for molecular and polymeric syntheses.[1] We have previously demonstrated[2] that the ruthenium-catalyzed homo- and cross-metathesis reactions of monoalkenyl−polyboranes enable the efficient syntheses of a wide variety of functionalized decaborane and carborane derivatives. We have also shown[3] that the ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) of 6-(norbornenyl)-decaborane provides a route to important new types of organopolyborane preceramic polymers with pendant decaborane units. In this paper, we report the first studies of the metal-catalyzed metathesis reactions of

dialkenyl−polyboranes and demonstrate that the ruthenium-catalyzed reactions of dialkenyl-substituted *ortho*- and *meta*-carboranes provide excellent routes to cyclic-substituted *o*-carboranes and new types of main-chain *m*-carborane polymers.

Experimental Procedures

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver and Drezdzon.[4]

Materials. The 1,2-C$_2$B$_{10}$H$_{12}$ (*o*-carborane) and 1,7-C$_2$B$_{10}$H$_{12}$ (*m*-carborane) (Katchem) were sublimed in vacuo prior to use. *n*-Butyl-lithium, allyl bromide, 4-bromo-1-butene, 6-bromo-1-hexene, 2-chloroethylvinylether, allylchloroformate, and Cl$_2$Ru(=CHPh)(PCy$_3$)$_2$ (Grubbs **II** catalyst) (Aldrich); 3-chloro-2-methylpropene and chlorodimethylvinylsilane (Alfa Aesar); and chlorodimethylallylsilane (Gelest) were used as received. Diethylether and CH$_2$Cl$_2$ were dried by passage through an alumina column prior to use. ACS grade hexanes, anhydrous magnesium sulfate, and 230−400 mesh silica gel (Fisher) were used as received. Thin-layer chromatography (TLC) was conducted on 0.5 mm silica gel F-254 plates (Merck-5744), which were then stained with a basic KMnO$_4$ solution to visualize the carborane derivatives. CDCl$_3$ (D, 99.8%; Cambridge Isotope Laboratories) was stored over 4 Å molecular sieves prior to use.

Physical Measurements. ^{1}H NMR spectra at 500.4 MHz and ^{11}B NMR spectra at 160.1 MHz were obtained on a Bruker

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(1) For some recent reviews, see: (a) Schrock, R. R.; Czekelius, C. *Adv. Synth. Catal.* **2007**, *349*, 55–77. (b) Schrock, R. R. *J. Mol. Catal., A* **2004**, *213*, 21–30. (c) Schrock, R. R; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592–4633. (d) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746–1787. (e) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117–7140. (f) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243–251.

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AMX 500 spectrometer. ^{1}H NMR spectra at 400.1 MHz and ^{11}B NMR spectra at 128.4 MHz were obtained on a Bruker DMX 400 spectrometer. All ^{11}B NMR chemical shifts are referenced to external BF$_3$·O(C$_2$H$_5$)$_2$ (0.00 ppm), with a negative sign indicating an upfield shift. All ^{1}H chemical shifts were measured relative to residual protons in the lock solvent and are referenced to Me$_4$Si (0.00 ppm). High and low resolution mass spectra (HRMS and LRMS) using negative chemical ionization (NCI) techniques were recorded on a Micromass Autospec spectrometer. Low resolution mass spectra (LRMS) using electrospray ionization (ESI) techniques were recorded on an Agilent LC-MS platform. Infrared spectra were recorded on a Perkin-Elmer 1430 FT-IR Spectrometer using NaCl plates or on a Perkin-Elmer 2000 FT-IR Spectrometer using KBr pellets. Elemental analyses were performed at Robertson Microlit Laboratories, Madison, New Jersey. Melting points were obtained on a standard melting point apparatus and are uncorrected.

Polymer molecular weights were determined by gel permeation chromatography (GPC) using an SEC-GPC instrument consisting of a Rainin HPXL solvent delivery system connected to Shodex GPC KF-801, KF-803, and KF-805 columns maintained at 45 °C. Two in-line detectors were connected in series, a Wyatt Technology mini-Dawn Tristar multiangle laser light scattering detector with a 690-nm solid-state laser and a Wyatt Technology Optilab DSP interferometric refractivemeter operating at 690 nm. Tetrahydrofuran (THF) was used as the mobile phase. The flow rate was 1 mL/min, and polymer solutions were prepared at a concentration of ~1 mg/mL. The signals from the in-line detectors were analyzed using Astra 4.9.08 software from Wyatt Technology Corp. The dn/dc values were calculated according to literature methods[5] and then confirmed using the Wyatt dndc kit along with DNDC software 5.90.03 from Wyatt Technology Corp.

Syntheses of o- and m-Dialkenyl−Carboranes. The 1,2-R$_2$-1,2-C$_2$B$_{10}$H$_{10}$ and 1,7-R$_2$-1,7-C$_2$B$_{10}$H$_{10}$ starting compounds, 1,2-(CH$_2$=CHCH$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**1**), 1,2-(CH$_2$=CH(CH$_2$)$_3$CH$_2$)$_2$-1,2-C$_2$-B$_{10}$H$_{10}$ (**2**), 1,2-(CH$_2$=CHSiMe$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**3**), 1,2-(CH$_2$=CHCH$_2$SiMe$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**4**), 1,2-[CH$_2$=CH(CH$_2$)$_4$SiMe$_2$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**5**), 1,2-(CH$_2$=CHCH$_2$OC(=O))$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**6**), 1,7-(CH$_2$=CHCH$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (**7**), 1,7-(CH$_2$=CH(CH$_2$)$_3$-CH$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (**8**), and 1,7-(CH$_2$=CHCH$_2$SiMe$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (**9**), were synthesized via literature methods[6] using the reaction of a 2-fold excess of n-butyl-lithium and a slight excess of halo-olefin in diethyl ether with either o- or m-carborane. A detailed description of the synthesis and characterization of **1** is given below. Synthetic details and characterization data for **2**−**9** can be found in the Supporting Information, and crystallographic data collection and structural refinement information can be found in Table 1.

1,2-(CH$_2$=CHCH$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (1). A 1.01 g (7.0 mmol) sample of o-carborane was lithiated with 6.1 mL (15.3 mmol) of n-BuLi at −78 °C in 75 mL of diethyl ether in a 250 mL three-neck flask. The solution was allowed to warm to room temperature, and after 1−2 h of reaction, the solution was cooled in an ice bath and 2.93 mL (34.7 mmol) of allyl bromide added. After returning to room temperature, the reaction mixture was refluxed at ~80 °C overnight. LiBr was extracted with ~50 mL of deionized water. The ether layer was dried with MgSO$_4$ and filtered. Column chromatography with dichloromethane eluent afforded 1.42 g (6.3 mmol, 91% yield) of **1** as a colorless oil. For **1**: NCI-HRMS (m/e) calcd. for ^{12}C$_8$^{11}-B$_{10}$^{1}H$_{20}$: 226.2495. Found: 226.2504. Anal. Calcd: C, 42.83; H, 8.99. Found: C, 42.53; H, 8.74. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz): −5.2 (d, 2B, J 147), −11.2 (d, 8B, J 155). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz): 5.79 (m, 2H, =CH), 1.73 (d, 4H, J 7.5, =CHCH$_2$), 2.97 (d, 4H, J 8.3, CH$_2$). FT-IR (NaCl plate, cm^{-1}): 3085 (m), 2985 (m), 2925 (s), 2854 (m), 2585 (vs), 1860 (w), 1644 (m),

1435 (s), 1418 (s), 1316 (w), 1295 (m), 1260 (m), 1162 (m), 1122 (m), 1067 (m), 1029 (s), 993 (s), 928 (s), 812 (m), 729 (s), 701 (m), 666 (w), 619 (w).

Metathesis Reactions of 1,2-(Alkenyl)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ Carboranes (1−6). 1,2-(CH$_2$=CHCH$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (1). A mixture of 0.82 g (3.7 mmol) of **1** and 8 mg (0.01 mmol) of **II** was refluxed in 2 mL of CH$_2$Cl$_2$ in vacuo at 45 °C overnight. Column chromatography with hexane eluent afforded 0.66 g (3.4 mmol, 92% yield) of 1,2-(−CH$_2$CH=CHCH$_2$−)-1,2-C$_2$B$_{10}$H$_{10}$ (**10**) as white crystals. The spectral data for **10** matched the literature values.[7]

1,2-[CH$_2$=CH(CH$_2$)$_4$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (2). A 0.42 g (1.4 mmol) sample of **2** and 58 mg (0.07 mmol) of **II** were refluxed in 5 mL of CH$_2$Cl$_2$ in vacuo for 2 days. Column chromatography with n-pentane eluent afforded 0.374 g (1.3 mmol, 97% yield) of 1,2-[−CH$_2$-(CH$_2$)$_3$CH=CH(CH$_2$)$_3$CH$_2$−]-1,2-C$_2$B$_{10}$H$_{10}$ (**11**) as white crystals. For **11**: NCI-HRMS (m/e) calcd for ^{12}C$_{12}$^{11}B$_{10}$^{1}H$_{28}$: 282.3121. Found: 282.3109. Anal. Calcd: C, 51.39; H, 10.06. Found: C, 51.63; H, 10.04. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz) −5.7 (d, 2B, J 144), −11.1 (d, 8B, J 147). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz): 5.32 (m, 2H, =CH), 2.15 (m, 8H, CH$_2$), 1.51 (m, 8H, CH$_2$). FTIR (KBr pellet, cm^{-1}): 2934 (s), 2859 (s), 2640 (s), 2590 (vs), 1455 (s), 1425 (m), 1364 (w), 1349 (w), 1312 (w), 1163 (m), 1067 (w), 1027 (s), 978 (s), 943 (m), 915 (m), 833 (w), 814 (w), 780 (w), 729 (s), 692 (m), 670 (m), 650 (w).

1,2-[CH$_2$=CHSiMe$_2$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (3). A 0.50 g (1.6 mmol) sample of **3** and 68 mg (0.08 mmol) of **II** was refluxed in 5 mL of CH$_2$Cl$_2$ in vacuo overnight. Column chromatography with n-pentane eluent afforded 0.45 g (1.6 mmol, 72.1% yield) of 1,2-[−SiMe$_2$CH=CHSiMe$_2$−]-1,2-C$_2$B$_{10}$H$_{10}$ (**12**) as white needles. For **12**: mp = 91−92 °C. NCI-HRMS (m/e) calcd for ^{12}C$_8$^{28}Si$_2$^{11}B$_{10}$^{1}-H$_{24}$: 286.2346. Found: 286.2353. Anal. Calcd: C, 33.77; H, 8.50. Found: C, 34.00; H, 8.31. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz): 0.3 (d, 2B, J 147), −5.5 (d, 2B, J 134), −10.2 (d, 4B, J 162), −13.3 (d, 2B, J 169). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz): 6.75 (s, 2H, =CH), 0.34 (s, 12H, CH$_3$). FT-IR (KBr pellet, cm^{-1}): 2959 (w), 2942 (w), 2924 (w), 2589 (vs), 2549 (s), 1402 (w), 1337 (w), 1248 (s), 1089 (m), 1073 (m), 983 (w), 910 (w), 870 (s), 843 (s), 817 (vs), 792 (s), 742 (w), 705 (w), 681 (w), 667 (w), 629 (m), 598 (w), 562 (w), 481 (w).

1,2-(CH$_2$=CHCH$_2$SiMe$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (4). A 0.68 g (2.0 mmol) sample of **4** and 7 mg (0.01 mmol) of **II** were refluxed in 2 mL of CH$_2$Cl$_2$ in vacuo overnight. Column chromatography with hexane eluent followed by recrystallization in cold hexanes afforded 0.60 g (1.9 mmol, 97% yield) of 1,2-(−SiMe$_2$CH$_2$CH=CHCH$_2$-SiMe$_2$−)-1,2-C$_2$B$_{10}$H$_{10}$ (**13**) as white needles. For **13**: mp = 123−125 °C. NCI-HRMS (m/e) calcd for ^{12}C$_{10}$^{28}Si$_2$^{11}B$_{10}$^{1}H$_{28}$: 314.2660. Found: 314.2659. Anal. Calcd: C, 38.42; H, 9.03. Found: C, 38.87; H, 9.50. ^{11}B NMR (160.1 MHz, CDCl$_3$, ppm, J= Hz): −0.1 (d, 2B, J 146), −7.9 (d, 2B, J 150), −11.0 (d, 4B, J 160), −12.9 (d, 2B, J 174). ^{1}H NMR (500.4 MHz, CDCl$_3$, ppm, J = Hz): 5.38 (t, 2H, J 7.1, =CH), 1.73 (d, 4H, J 7.3, =CHCH$_2$), 0.34 (s, 12H, CH$_3$). FT-IR (KBr pellet, cm^{-1}): 3020 (s), 2979 (m), 2928 (m), 2901 (m), 2581 (vs), 1649 (m), 1419 (s), 1259 (s), 1249 (s), 1184 (m), 1162 (m), 1102 (m), 1088 (m), 1061 (m), 1020 (w), 976 (w), 928 (m), 904 (w), 845 (s), 810 (s), 798 (s), 778 (m), 764 (m), 745 (m), 695 (w), 647 (m), 620 (m), 597 (m), 555 (w), 502 (w).

1,2-[CH$_2$=CH(CH$_2$)$_4$SiMe$_2$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (5). A 0.20 g (0.4 mmol) sample of **5** and 23 mg (0.02 mmol) of **II** were refluxed in 3 mL of CH$_2$Cl$_2$ in vacuo overnight. Column chromatography with hexane eluent afforded 0.16 g (0.4 mmol, 86% yield) of 1,2-[−SiMe$_2$(CH$_2$)$_4$CH=CH(CH$_2$)$_4$SiMe$_2$−]-1,2-C$_2$B$_{10}$-H$_{10}$ (**14**) as a waxy white oil. For **14**: NCI-HRMS (m/e) calcd for ^{12}C$_{16}$^{28}Si$_2$^{11}B$_{10}$^{1}H$_{40}$: 398.3599. Found: 398.3604. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J= Hz): 1.2 (d, 2B, J 140), −6.3 (d, 2B, J 149), −9.5 (d, 4B, J 168), −11.7 (d, 2B, J 150). ^{1}H NMR (500.4 MHz, CDCl$_3$, ppm): 5.38 (m, 2H, =CH), 2.04 (m, 4H, =CHCH$_2$),

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Table 1. Crystallographic Data Collection and Structural Refinement Information for Compounds **3**, **9**, **11**, **12**, **13**, and **15a**

	3	**9**	**11**	**12**
formula	$C_{10}B_{10}H_{28}Si_2$	$C_{12}B_{10}H_{32}Si_2$	$C_{12}B_{10}H_{28}$	$C_8B_{10}H_{24}Si_2$
fw	312.60	340.66	280.44	284.55
cryst class	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$ (#14)	$P2_1/m$ (#11)	$P2_1/n$ (#14)	$Pnma$(#62)
Z	4	2	4	4
a, Å	9.1097(11)	6.8286(8)	7.6883(15)	9.5811(9)
b, Å	13.6428(14)	23.243(2)	14.060(2)	15.0297(15)
c, Å	15.6055(19)	7.3086(8)	16.047(3)	12.0455(12)
V, Å^3	1906.0(4)	1050.7(2)	1732.2(6)	1734.6(3)
β, deg	100.666(3)	115.078(19)	93.052(5)	
μ, cm^{-1}	1.72	1.61	0.51	1.83
cryst size, mm	$0.42 \times 0.38 \times 0.28$	$0.38 \times 0.25 \times 0.01$	$0.30 \times 0.22 \times 0.15$	$0.38 \times 0.36 \times 0.01$
D_{calc}, g/cm^3	1.089	1.077	1.075	1.090
$F(000)$	664	364	600	600
radiation	Mo K$_\alpha$	Mo K$_\alpha$	Mo K$_\alpha$	Mo K$_\alpha$
2θ angle, deg	5.32−50.04	6.16−49.94	5.08−50.06	5.42−50.04
temp, K	143	143	153	143
hkl collected	$-10 \leq h \leq 8$	$-8 \leq h \leq 7$	$-7 \leq h \leq 9$	$-10 \leq h \leq 11$
	$-16 \leq k \leq 16$	$-27 \leq k \leq 24$	$-16 \leq k \leq 16$	$-17 \leq k \leq 17$
	$-18 \leq l \leq 15$	$-7 \leq l \leq 8$	$-17 \leq l \leq 19$	$-12 \leq l \leq 14$
no. reflns measured	11781	6208	14356	9505
no. of unique reflns	3348, $R_{int} = 0.0171$	1878, $R_{int} = 0.0210$	3028, $R_{int} = 0.0305$	1589, $R_{int} = 0.0188$
no. obsd reflns ($F > 4\sigma$)	3089	1463	2447	1426
no. reflns used in refinement	3348	1878	3028	1589
no. params	244	118	240	150
R indices ($F > 4\sigma$)	$R_1 = 0.0380$	$R_1 = 0.0372$	$R_1 = 0.0691$	$R_1 = 0.0351$
	$wR_2 = 0.1017$	$wR_2 = 0.1026$	$wR_1 = 0.1812$	$wR_1 = 0.0937$
R indices (all data)	$R_1 = 0.0406$	$R_1 = 0.0484$	$R_1 = 0.0834$	$R_1 = 0.0388$
	$wR_2 = 0.1040$	$wR_2 = 0.1102$	$wR_2 = 0.1961$	$wR_2 = 0.0986$
GOF	1.091	1.055	1.069	1.026
final difference peaks, e/Å^3	+0.663, −0.221	+0.415, −0.195	+0.821, −0.277	+0.215, −0.250

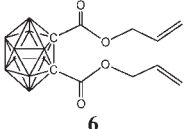|	**13**	**15a**
formula	$C_{10}B_{10}H_{28}Si_2$	$C_{16}H_{32}B_{20}O_8$
fw	312.60	568.62
cryst class	orthorhombic	monoclinic
space group	$Pnma$ (#62)	$C2/c$ (#15)
Z	4	4
a, Å	11.252(3)	16.7641(8)
b, Å	11.200(3)	12.7268(7)
c, Å	15.266(5)	13.6400(8)
V, Å^3	1923.9(10)	2879.5(3)
β, deg		98.327(4)
μ, cm^{-1}	1.70	0.83
cryst size, mm	$0.32 \times 0.20 \times 0.005$	$0.39 \times 0.05 \times 0.04$
D_{calc}, g/cm^3	1.079	1.312
$F(000)$	664	1168
radiation	Mo K$_\alpha$	Mo K$_\alpha$
2θ angle, deg	5.34−50.66	4.04−50.04
temp, K	143	143
hkl collected	$-12 \leq h \leq 13$	$-19 \leq h \leq 19$
	$-13 \leq k \leq 11$	$0 \leq k \leq 15$
	$-17 \leq l \leq 18$	$0 \leq l \leq 15$
no. reflns measured	10361	21497
no. unique reflns	1855 $R_{int} = 0.0727$	2515 $R_{int} = 0.0436$
no. of obsd reflns ($F > 4\sigma$)	1398	1845
no. reflns used in refinement	1855	2515
no. params	106	209
R indices ($F > 4\sigma$)	$R_1 = 0.1007$	$R_1 = 0.0533$
	$wR_1 = 0.2673$	$wR_1 = 0.1406$
R indices (all data)	$R_1 = 0.1246$	$R_1 = 0.0781$
	$wR_2 = 0.2944$	$wR_2 = 0.1500$
GOF	1.120	1.067
final difference peaks, e/Å^3	+1.315, −0.397	+0.561, −0.233
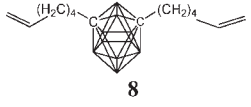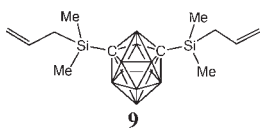
1.60 (m, 4H, CH_2), 1.33 (m, 4H, CH_2), 0.78 (m, 4H, CH_2), 0.30 (s, 12H, CH_3). FT-IR (NaCl plate, cm^{-1}): 3020 (s), 2905 (m), 2665 (vs), 2640 (vs), 1660 (w), 1440 (w), 1420 (w), 1395 (m), 1340 (w), 1325 (w), 1240 (vs), 1170 (w), 1070 (s), 1040 (m), 1020 (w), 1005 (s), 895 (w), 840 (m), 795 (m), 765 (m), 720 (w), 680 (w), 630 (w).

1,2-(CH_2=$CHCH_2OC$(=O))$_2$-1,2-$C_2B_{10}H_{10}$ (6). A 1.83 g (58.3 mmol) sample of **6** and 0.249 g (0.29 mmol) of **II** were

refluxed in 100 mL of CH_2Cl_2 under nitrogen overnight. The mixture was exposed to air, and ethylvinylether was added to deactivate the catalyst.[8] Crystals were physically separated from the product mixture and then further purified by thin layer

(8) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.

Table 2. Polymerization Data

(Alkenyl)$_2$-C$_2$B$_{10}$H$_{10}$	Polymer	M_w M_n	DP[a] PDI
6	15b	1.1×10^4 4.3×10^3	39 2.4
7	16	1.8×10^4 1.1×10^4	80 1.7
8	17	7.6×10^3 4.0×10^3	30 1.9
9	18a	4.7×10^3 3.3×10^3	14 1.4
	18b	2.5×10^3 1.6×10^3	7 1.7

[a] Degree of polymerization based on M_n.

chromatography in dichloromethane to give 0.45 g (1.6 mmol, 27.0% yield) of cyclo-[1,2-(1',8'-C(=O)OCH$_2$CH=CHCH$_2$OC-(=O))-1,2-C$_2$B$_{10}$H$_{10}$]$_2$ (**15a**) as white crystals, thereby allowing its crystallographic characterization. Polymer **15b** was obtained and isolated as a clear oil, 0.95 g (3.3 mmol, 57.1% yield). For **15a**: mp = 227−229 °C. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz): −2.4 (d, J 146), −9.7 (d, overlapped), −11.5 (d, overlapped). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz): 5.82 (m, 2H, =CH), 4.72 (m, 4H, CH_2). FT-IR (KBr pellet, cm^{-1}): 2925 (s), 2855 (m), 2609 (s), 1754 (s), 1457 (w), 1262 (vs), 1121 (m), 1012 (m), 945 (m), 803 (m), 728 (w). For **15b**, ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz): −2.7 (d, J 149), −9.9 (d, overlapped), −11.7 (d, overlapped). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz): 5.83 (m, 2H, =CH), 5.41 (m, small), 4.74 (m, 4H, CH_2). GPC data for **15b** are in Table 2.

Metathesis Reactions of 1,7-(Alkenyl)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ Carboranes (7−9). **ADMET Polymerization of 1,7-(CH$_2$=CHCH$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (7).** A 0.208 g (0.92 mmol) sample of **7** was reacted with 7.9 mg (0.01 mmol) of **II** in 10 mL of CH$_2$Cl$_2$ at 45 °C for 7 days under a nitrogen atmosphere. The mixture was exposed to air and ethylvinylether added to deactivate the catalyst.[8] Column chromatography with dichloromethane eluent yielded 0.13 g (0.63 mmol, 68.2% yield) of polymer **16**, [CH$_2$=CHCH$_2$−C$_2$B$_{10}$H$_{10}$-CH$_2$-CH=]$_2$[CHCH$_2$−C$_2$B$_{10}$H$_{10}$-CH$_2$CH=]$_n$, as a whitish paste. For **16**, Anal. Found: C, 48.31; H, 960. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz): −7.7 (d, 2B, J 151), −11.6 (d, 6B, J 159), −14.2 (d, 2B, J 159). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz): 5.37 (broad, 2H, =CH), 2.57 (broad, 4H, CH_2). FT-IR (NaCl plate, cm^{-1}): 2960 (vs), 2925 (vs), 2854 (s), 2597 (s), 1639 (w), 1615 (w), 1457 (m), 1377 (m), 1322 (m), 1261 (s), 1200 (s), 1096 (s), 1028 (s), 924 (w), 872 (w), 816 (s), 738 (w), 703 (w). GPC data are in Table 2.

ADMET Polymerization of 1,7-(CH$_2$=CH(CH$_2$)$_3$CH$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (8). A 0.41 g (1.3 mmol) sample of **8** was reacted with 11.3 mg (0.01 mmol) of **II** in 15 mL of CH$_2$Cl$_2$ at 45 °C for 7 days. Thin layer chromatography with pentane eluent yielded 0.32 g (1.1 mmol, 85.2% yield) of **17**, [CH$_2$=CH(CH$_2$)$_4$-C$_2$B$_{10}$H$_{10}$-(CH$_2$)$_4$-CH=]$_2$[CH(CH$_2$)$_4$-C$_2$B$_{10}$H$_{10}$-(CH$_2$)$_4$CH=]$_n$, as a white/clear oil. For **17**, Anal. Found: C, 52.96; H, 9.88. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz) −4.7 (d, small, J 148), −8.1 (small, broad), −11.6 (d, overlapped, J 143), −14.3 (d, overlapped, J 157), −16.5 (d, overlapped). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz) 5.34 (t, 2H, J 4.87, =CH), 1.91 (m, 8H, CH_2). FT-IR (NaCl plate,

cm^{-1}): 2927 (s), 2856 (s), 2597 (vs), 1462 (s), 1371 (w), 1309 (w), 1261 (m), 1179 (m), 1137 (w), 1086 (m), 1027 (s), 967 (s), 937 (w), 921 (w), 804 (m), 732 (s), 692 (w), 659 (w). GPC data are in Table 2.

ADMET Polymerization of 1,7-(CH$_2$=CHCH$_2$SiMe$_2$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (9). A 0.426 g (1.25 mmol) sample of **9** was reacted with 1 mol %, 10.8 g (0.01 mmol), of **II** in 10 mL of CH$_2$Cl$_2$ at 45 °C for 7 days. Column chromatography with dichloromethane eluent yielded 0.30 g (1.0 mmol, 77.8% yield) of **18a**, [CH$_2$=CHCH$_2$-SiMe$_2$-C$_2$B$_{10}$H$_{10}$-SiMe$_2$CH$_2$CH=]$_2$[CHCH$_2$SiMe$_2$-C$_2$B$_{10}$H$_{10}$-SiMe$_2$CH$_2$CH=]$_n$, as a colorless oil. For **18a**, Anal. Found: C, 40.03; H, 8.65. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm, J = Hz): −3.4 (d, broad), −8.2 (d, broad), −10.4 (d, overlapped, J 151), −14.6 (d, broad, J 147). ^{1}H NMR (400.1 MHz, CDCl$_3$, ppm, J = Hz): 5.31 (m, 1H, =CH), 5.18 (m, 1H, =CH), 1.53 (broad, 4H, CH_2), 0.12 (s, 12H, CH_3). FT-IR (NaCl plate, cm^{-1}): 3006 (m), 2961 (s), 2926 (s), 2853 (s), 2602 (vs), 1620 (m), 1442 (m), 1399 (s), 1377 (m), 1314 (w), 1255 (vs), 1156 (s), 1100 (vs), 999 (s), 962 (m), 913 (s), 899 (s), 881 (m), 780 (vs), 690 (m), 656 (w), 645 (w), 573 (w). A second reaction using 0.402 g (1.18 mmol) of **9** and 29.9 mg (0.03 mmol) of **II**, yielded **18b** after 7 days. Polymer **18b** was synthesized in a similar fashion, but employed 3 mol % catalyst. GPC data for **18a** and **18b** are in Table 2.

Crystallographic Data for Compounds 3, 9, 11, 12, 13 and 15a. Single crystals were grown from room temperature n-pentane solutions of **3** (UPenn #3302), **9** (UPenn #3260), **11** (UPenn #3345), and **12** (UPenn #3307) and a hexanes solution of **13** (UPenn # 3220). Crystals of **15a** (UPenn #3350) were grown from dichloromethane at 0 °C.

Collection and Reduction of the Data. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo K$_\alpha$ (λ = 0.71069 Å for **13** and 0.71073 Å for the others) radiation at a temperature of 143 K. Indexing was performed from a series of 12 0.5° rotation images with exposures of 30 s with a crystal-to-detector distance of 36 mm for **13** and 35 mm for the others. Oscillation images were processed using CrystalClear,[9] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the Crystal-Structure program package[10] for further processing and structure solution on a Dell Pentium III computer. The intensity data were corrected for Lorentz and polarization effects and for absorption for **13**.

For **15a**, X-ray intensity data were collected on a Bruker APEX2 DUO CCD area detector employing graphite-mono-chromated Mo K$_\alpha$, as indicated above. Indexing was performed on a series of rotation images, collected with a crystal-to-detector distance of 50 mm, a 2θ swing angle of 28°, rotation widths of 0.5°, and exposures of 60 s; three ø scans were performed over a total rotation of 586°. Rotation images were processed using SAINT/XPREP, producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL program package for further processing and structure solution.

Solution and Refinement of the Structures. The structures were solved by direct methods (SIR97).[11] Refinements were by full-matrix least-squares based on F^2 using SHELXL-97.[12] All reflections were used during refinement (F^2's that were experimentally negative were replaced by F^2 = 0). Non-hydrogen atoms were refined anisotropically; the cage hydrogen atoms for **3**, **11**, and **12** were refined isotropically. All other hydrogens were refined using a "riding" model.

(9) *CrystalClear*; Rigaku Corporation: Tokyo, Japan, 1999.
(10) *CrystalStructure: Crystal Structure Analysis Package*, Rigaku Corporation: Tokyo, Japan, 2002.
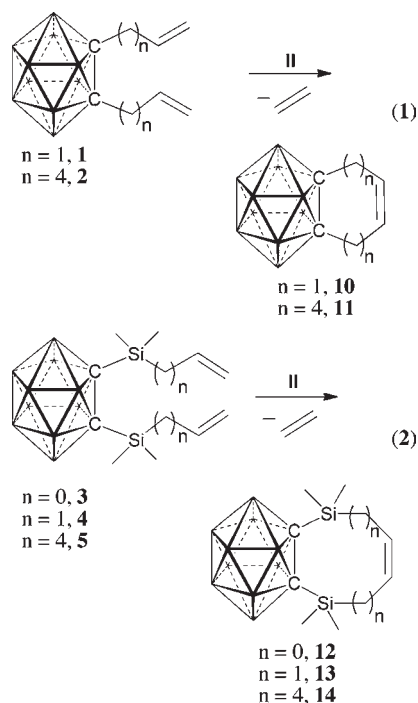(11) SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.
(12) *SHELXL-97: Program for the Refinement of Crystal Structures*; Sheldrick, G. M., Ed.; University of Göttingen: Göttingen, Germany, 1997.
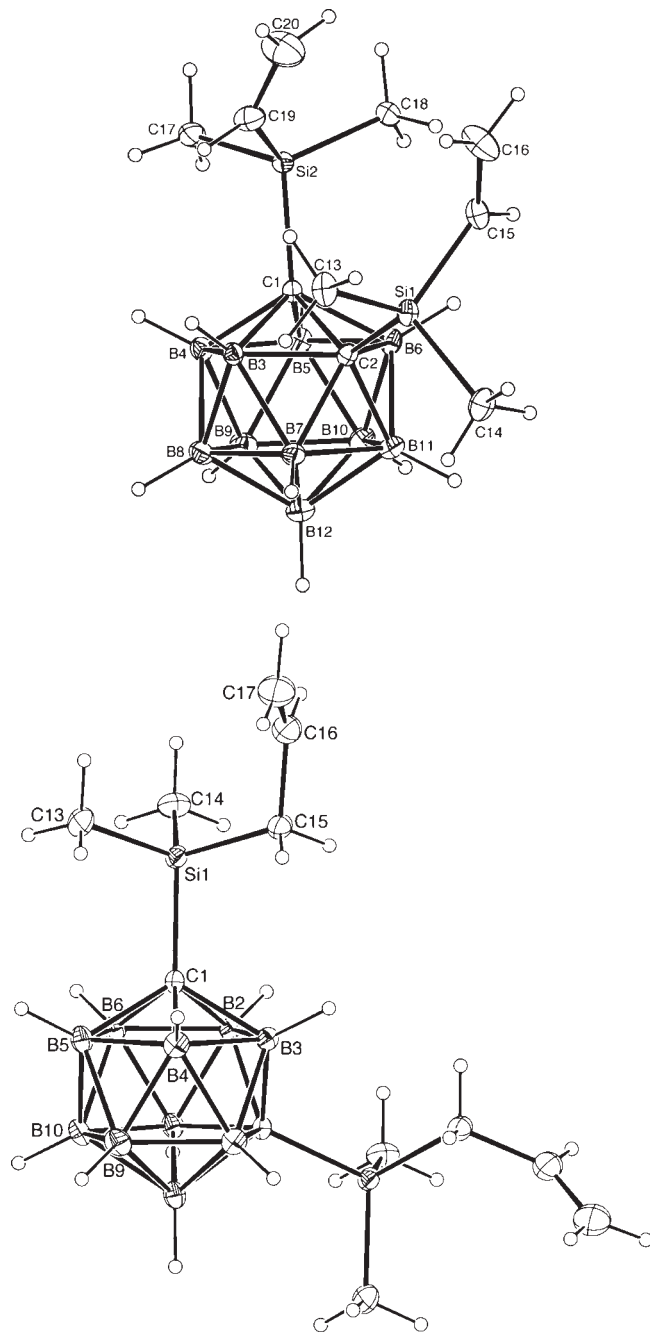
Results and Discussion

The dialkenyl *ortho*- and *meta*- carborane starting materials were synthesized in yields ranging from 54 to 97% via literature methods[6] involving reactions of the dilithiated carboranes with a large excess of the appropriate alkenyl-halide reagents. While most of the dialkenyl-carboranes were liquids, 1,2-(CH_2=CH-SiMe$_2$)$_2$-1,2-$C_2B_{10}H_{10}$ (**3**) and 1,7-(CH_2=CHCH$_2$SiMe$_2$)$_2$-1,7-$C_2B_{10}H_{10}$ (**9**) were obtained as crystalline solids, allowing crystallographic confirmations of their structures (Figure 1). The observed intracage distances and angles (Figure 1 caption) for both compounds fall in the normal ranges.[13]

Ruthenium-Catalyzed Metathesis Reactions of 1,2-(Alkenyl)$_2$-1,2-$C_2B_{10}H_{10}$ Carboranes. Either ring closing metathesis (RCM) or acyclic diene metathesis (ADMET) reactions are possible for acyclic dienes in the presence of a metathesis catalyst.[1] As can be observed in Figure 1 for the structure of **3**, the adjacent positions of the two olefins in the 1,2-(alkenyl)$_2$-*o*-carboranes should strongly favor the formation of RCM products, and thus reactions with these derivatives were expected to provide efficient routes to cyclic substituted *o*-carboranes. As shown in eqs 1 and 2, when 1,2-(CH_2=CHCH$_2$)$_2$-1,2-$C_2B_{10}H_{10}$ (**1**), 1,2-(CH_2=CH(CH$_2$)$_3$CH$_2$)$_2$-1,2-$C_2B_{10}H_{10}$ (**2**), 1,2-(CH_2=CHSiMe$_2$)$_2$-1,2-$C_2B_{10}H_{10}$ (**3**), 1,2-(CH_2=CHCH$_2$SiMe$_2$)$_2$-1,2-$C_2B_{10}H_{10}$ (**4**), and 1,2-[CH_2=CH(CH$_2$)$_4$SiMe$_2$]$_2$-1,2-$C_2B_{10}H_{10}$ (**5**) were treated with the Grubbs **II** catalyst in refluxing CH_2Cl_2 under a vacuum, efficient ring closing metathesis reactions occurred to afford compounds 1,2-(−CH$_2$CH=CHCH$_2$−)-$C_2B_{10}H_{10}$ (**10**), 1,2-[−CH$_2$(CH$_2$)$_3$CH=CH(CH$_2$)$_3$CH$_2$−]-1,2-$C_2B_{10}H_{10}$ (**11**), 1,2-[−SiMe$_2$CH=CHSiMe$_2$−]-1,2-$C_2B_{10}H_{10}$ (**12**), 1,2-[−SiMe$_2$CH$_2$CH=CHCH$_2$SMe$_2$−]-$C_2B_{10}H_{10}$ (**13**), and 1,2-[−SiMe$_2$(CH$_2$)$_4$CH=CH(CH$_2$)$_4$SiMe$_2$−]-$C_2B_{10}H_{10}$ (**14**) in 72−97% yields.

(1)

n = 1, **1**
n = 4, **2**

n = 1, **10**
n = 4, **11**

(2)

n = 0, **3**
n = 1, **4**
n = 4, **5**

n = 0, **12**
n = 1, **13**
n = 4, **14**

The reactions were carried out in dilute (∼0.01 M) CH_2Cl_2 solutions, since low diene concentrations have

(13) Llop, J.; Viñas, C.; Oliva, J. M.; Teixidor, F.; Flores, M. A.; Kivekäs, R.; Sillanpää, R. *J. Organomet. Chem.* **2002**, *657*, 232–238.

Figure 1. Crystallographically determined structures of (top) 1,2-(CH_2=CHSiMe$_2$)$_2$-1,2-$C_2B_{10}H_{10}$ (**3**) (top) and (bottom) 1,7-(CH_2=CHCH$_2$SiMe$_2$)$_2$-1,7-$C_2B_{10}H_{10}$ (**9**). Selected distances (Å) and angles (deg): (**3**) C15−C16, 1.317(3); Si1−C15, 1.854(2); Si1−C14, 1.863(2); Si1−C13, 1.860(2); C2−Si1, 1.933(2), C1−C2, 1.717(2); Si2−C18, 1.853(2); C19−C20, 1.286(3); Si2−C17, 1.865(2); C1−Si2, 1.937(2); C16−C15−Si1, 123.3(2); C20−C19−Si2, 125.1(2); Si2−C1−C2, 126.65(10); C1−C2−Si1, 127.02(10). (**9**) B3−C1, 1.709(2); B2−C1, 1.717(2); C1−Si1, 1.912(2); Si1−C13, 1.857(2); Si1−C14, 1.856(2); Si1−C15, 1.876(2); C15−C16, 1.507(3); C16−C17, 1.282(3); B3−C1−Si1, 118.26(12); B2−C1−Si1, 118.95(12); B4−C1−Si1, 118.11(11); B5−C1−Si1, 119.67(11); B6−C1−Si1, 119.45(11); C1−Si1−C13, 109.01(9); C1−Si1−C14, 109.28(8); C1−Si1−C15, 107.76(7); C13−Si−C14, 110.71(10); C13−Si1−C15, 109.93(9); C14−Si1−C15, 110.10(10); Si1−C15−C16, 112.54(13); C15−C16−C17, 125.8(2).

been proposed to favor intramolecular metathesis to produce RCM products, while high diene concentrations favor intermolecular ADMET reactions.[1,14] The reactions were determined to be complete when the terminal olefinic resonances of the starting dienes disappeared in

Figure 2. Comparison of the ^{1}H NMR spectra of **3** (top) and **12** (bottom).

the ^{1}H NMR spectra of the reaction mixtures. The RCM products were then purified via column chromatography. Recrystallization afforded **10**, **11**, **12**, and **13** as white crystalline solids, but **14** was isolated as a viscous oil. All compounds were stable in the air and were soluble in nonpolar and polar solvents including hexanes, benzene, toluene, dichloromethane, chloroform, and ethylacetate.

Compounds **10** and **12**−**14** each showed ^{11}B NMR spectra characteristic of a disubstituted *o*-carborane consisting of four doublets of relative intensities 2:2:4:2 in the narrow chemical shift range between 1 and −13 ppm. Compound **11** showed only two doublets in a 2:8 ratio owing to overlapping resonances.

As illustrated in Figure 2 for the conversion of **3** to **12**, the ^{1}H NMR spectra of **10**, **12**, and **13** each showed that the three olefinic resonances of the starting dienes (**1**, **3**, and **4**) had been replaced by a single internal olefinic resonance.

Matteson et al. originally reported the synthesis of **10** in 42% yield by reaction of $ClCH_2CH=CHCH_2Cl$ with 1,2-Li_2-1,2-$C_2B_{10}H_{10}$.[7] Vdovin et al. later synthesized **10** via a RCM reaction with WCl_6/Me_4Sn and $WOCl_4/Me_4Sn$ catalysts, but in only 12% and 30% yields.[15] The 92% yield of **10** attained by the ruthenium-catalyzed RCM reaction reported herein is a significant synthetic improvement.

The previous crystallographic characterization[16] of **10** and the structural determinations of **12** and **13** shown in Figures 3 and 4 confirm the formation of six-membered (**10** and **11**) and eight-membered (**13**) ring structures with one *cis*-olefin

(14) As pointed out by a reviewer, dilute solutions may not always be necessary since recent work has shown that large and medium ring RCM products can also be obtained in high yields from concentrated solutions when longer reaction times are employed that allow a backbiting reaction of any ADMET produced oligomers. See: Conrad, J. C.; Eelman, M. D.; Duarte Silva, J. A.; Monfette, S.; Parnas, H. H.; Snelgrove, J. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2007**, *129*, 1024–1025.
(15) Vdovin, V. M.; Bespalova, N. B.; Bovina, M. A.; Kalinin, V. N.; Zakharkin, L. I. *Russ. Chem. Bull.* **1984**, *33*, 441.
(16) Copley, R. C. B.; Fox, M. A.; Gill, W. R.; Howard, J. A. K.; MacBride, J. A. H.; Peace, R. J.; Rivers, G. P.; Wade, K. *Chem. Commun.* **1996**, 2033–2034.
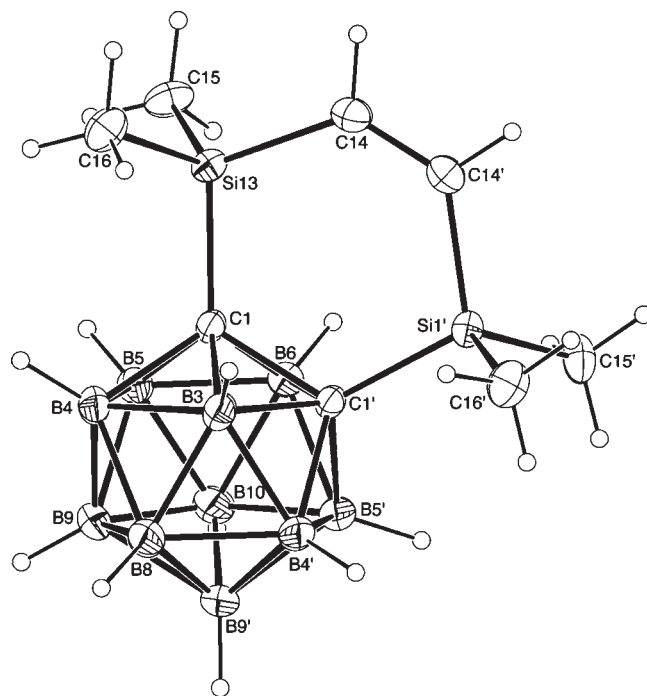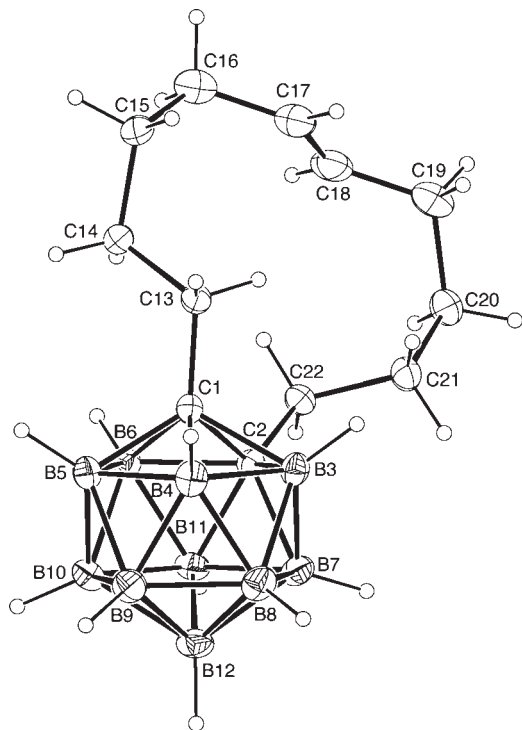

Figure 3. Crystallographically determined structure of 1,2-[$SiMe_2CH=CHSiMe_2$]-1,2-$C_2B_{10}H_{10}$ (**12**). Selected distances (Å) and angles (deg): C14−C14′, 1.333(3); C14−Si13, 1.8505(17); Si13−C15, 1.8566(18); Si13−C16, 1.8559(18); Si13−C1, 1.9134(14); C1−C1′, 1.692(3); C14′−C14−Si13, 128.92(5); C16−Si13−C16, 108.89(9); C14−Si13−C1, 110.12(7); C15−Si1−C1, 108.41(8); C16−Si13−C1, 108.89(8); C14−Si13−C15, 111.25(9); Si13−C1−C1′, 120.93(4).
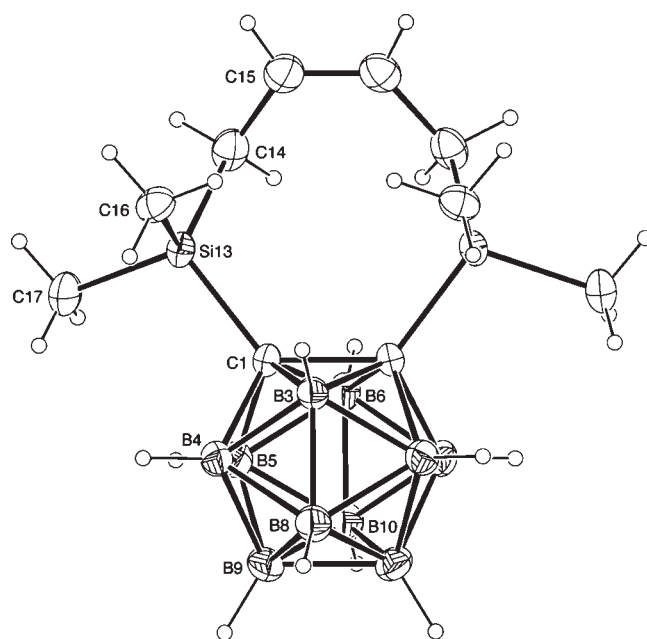
Figure 4. Crystallographically determined structure of 1,2-($SiMe_2CH_2$-CH=CHCH_2SiMe_2$)-1,2-$C_2B_{10}H_{10}$ (**13**). Selected distances (Å) and angles (deg): C1−C1′, 1.719(8); C1−B4, 1.709(6); C1−B5, 1.726(6); C1−B6, 1.726(7); C1−Si13, 1.929(4); Si13−C17, 1.869(5); Si13−C16, 1.843(5); Si13−C14, 1.876(5); C14−C15, 1.503(7); C15−C15′, 1.341(10); C1′−C1−Si13, 127.71(12); C1−Si13−C17, 106.9(2); C1−Si13−C16, 109.1(2); C1−Si13−C14, 112.6(2); C17−Si13−C16, 109.0(3); Si13−C14−C15, 112.8(3); C14−C15−C15′, 124.7(3).

constituent. The C=C bond lengths in the three compounds are similar, **10** (1.326(2) Å), **12** (1.333(3) Å), and

Figure 5. Crystallographically determined structure of 1,2-[CH$_2$-(CH$_2$)$_3$CH=CH(CH$_2$)$_3$CH$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (**11**). Selected distances (Å) and angles (deg): C1−C2, 1.679(3); C1−C13, 1.524(3); C13−C14, 1.518(3); C14−C15, 1.535(3); C15−C16, 1.530(4); C16−C17, 1.461(4); C17−C18, 1.364(4); C18−C19, 1.470(4); C19−C20, 1.527(3); C20−C21, 1.538(3); C21−C22, 1.521(3); C22−C2, 1.530(3). C2−C1−C13, 117.9(2); C1−C13−C14, 118.2(2); C13−C14−C15, 112.4(2); C15−C16−C17, 115.1(3); C17−C18−C19, 121.1(3); C18−C19−C20, 115.8(2); C−20−C21−C22, 112.1(2); C21−C22−C2, 117.1(2); C22−C2−C1, 118.0(2).

13 (1.341(10) Å). The six-membered rings in both **10** and **12** are planar with the six ring angles summing to 720°. The eight-membered ring of **13** has a puckered (C1−Si13−C14, 112.6(2)°; Si13−C14−C15, 112.8(3)°) chair-type conformation with the C1−C1′ and C15−C15′ bonds being parallel, but on opposite sides of the Si13−Si13′−C14−C14′ plane. The more acute Si13−C1−C1′ angle (120.93(4)°) in **12** relative to the Si13−C1−C1′ angle (127.71(12)°) in **13** and the Si2−C1−C2 (126.65(10)° and S1−C2−C1 (127.02(10)°) angles in **3** is consistent with the geometric requirements of its six-membered ring. Although their intracage carborane C−C bond lengths all fall in the normal range of *o*-carborane derivatives,[13] the carborane C−C lengths in **10** (1.662(2) Å) and **12** (1.692(3) Å) are shorter than those in **13** (1.719(8) Å) and **3** (1.718(2) Å) perhaps again as a consequence of the six-membered ring structures of **10** and **12**.

The formation of a *trans*-double bond would be too energetically and sterically demanding within either a six- or an eight-membered ring. However, such conformations are possible in larger rings since the ring strain is not significantly different in either of the *cis* or *trans* conformations. As shown in Figure 5, the crystallographic determination of **11** (1,2-[−CH$_2$(CH$_2$)$_3$CH=CH(CH$_2$)$_3$-CH$_2$−]-1,2-C$_2$B$_{10}$H$_{10}$) confirmed a 12-membered puckered-ring structure that is, in fact, closed with a *trans*-C17−C18 (1.364(4) Å) double bond. Likewise, **14**, which has a 14-membered ring, showed two sets of olefinic

resonances in a 3.3:1 ratio in its ^{1}H NMR spectrum, indicating the presence of both *trans* and *cis* double bond isomers.
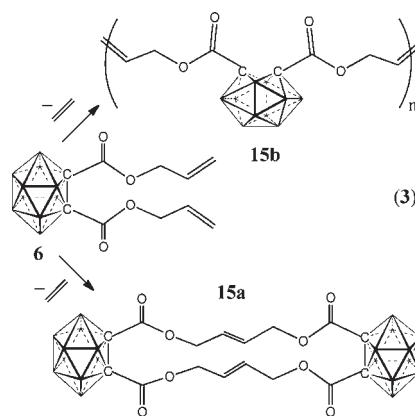

While the reactions with **1**−**5** gave exclusively cyclic products resulting from intramolecular RCM reactions, the comparable reaction with **6** gave two products resulting from intermolecular metathesis reactions (eq 3). Crystals of **15a** were physically separated from the major oily polymer product **15b** and then further purified by thin layer chromatography. The crystallographic determination of **15a** revealed the cyclo-[1,2-(1′,8′-C(=O)OCH$_2$-CH=CHCH$_2$OC(=O))-1,2-C$_2$B$_{10}$H$_{10}$]$_2$ structure shown in Figure 6 where intermolecular metathesis reactions of the two arms resulted in the loss of two equivalents of ethylene and formation of a dimeric structure composed of a 20-membered ring joined by the two *transoid* double bonds at C17−C17′ (1.341(5) Å) and C22−C22′ (1.322(6) Å). Both the ^{11}B and ^{1}H NMR spectra of **15a** showed the expected resonances. The ^{11}B NMR spectrum of polymer **15b** was similar to that of **15a**, showing three broad, overlapped resonances, but its ^{1}H NMR spectrum showed two resonances in the olefinic region, indicating the presence of both *cis* and *trans* double bonds. The GPC analysis of **15b** indicated the formation of oligomeric species with $M_n = 4.3 \times 10^3$ and $M_w = 1.1 \times 10^4$ corresponding to a degree of polymerization of ~39 (based on M_n) for a reaction employing 1 mol % catalyst.

Ruthenium-Catalyzed Metathesis Reactions of 1,7-(Alkenyl)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ Carboranes. As illustrated by the structure of **9** given in Figure 1, the nonadjacent positions of the alkenyl groups in the 1,7-(alkenyl)$_2$-*m*-carboranes disfavor the formation of RCM products for derivatives with short or medium length arms. In these cases, acyclic diene metathesis polymerization (ADMET[17]) should be favored. As shown in the examples in Table 2, the Grubbs **II** catalyst induced the ADMET polymerization of the 1,7-(alkenyl)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ monomers to produce new types of main-chain *m*-carborane polymers.

In a typical reaction, a monomer was syringed into a flask previously charged with 1 mol % Grubbs **II** catalyst

(17) For some recent examples of metal catalyzed ADMET syntheses of inorganic polymers, see: (a) Matloka, P. P.; Wagener, K. B. *J. Mol. Catal., A: Chemical* **2006**, *257*, 89–90. (b) Church, A. C.; Pawlow, J. H.; Wagener, K. B. *Macromolecules* **2002**, *35*, 5746–5751. (c) Church, A. C.; Pawlow, J. H.; Wagener, K. B. *Macromol. Chem. Phys.* **2003**, *204*, 32–39. (d) Baughman, T. W.; Wagener, K. B. *Adv. Polym. Sci.* **2005**, *176*, 1–42. (e) Allcock, H. R.; Kellam, E. C., III; Hofmann, M. A. *Macromolecules* **2001**, *34*, 5140–5146.
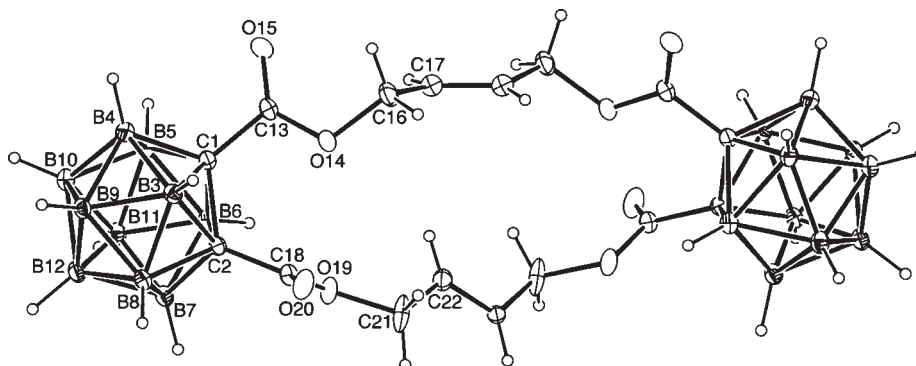
Figure 6. Crystallographically determined structure of cyclo-[1,2-(1′,8′-C(=O)OCH$_2$CH=CHCH$_2$OC(=O))-1,2-C$_2$B$_{10}$H$_{10}$]$_2$ (**15a**). Selected distances (Å) and angles (deg): C17−C17′, 1.341(5); C16−C17, 1.456(4); C16−O14, 1.474(3); O14−C13, 1.335(3); C13−O15, 1.188(3); C1−C13, 1.513(3); C1−C2, 1.660(3); C2−C18, 1.522(3); C18−O20, 1.198(3); C18−O19, 1.320(3); O19−C21, 1.462(3); C21−C22, 1.574(5); C22−C22′, 1.322(6); C22−C21−O19, 111.7(3); C21−O19−C18, 116.66(18); O19−C18−O20, 126.4(2); O19−C18−C2, 110.74(19); O20−C18−C2, 122.8(2); C18−C2−C1, 120.75(18); C2−C1−C13, 121.24(19); C1−C13−O15, 121.5(2); C1−C13−O14, 111.70(19); C13−O14−C16, 115.75(18); O14−C16−C17, 112.2(2); C16−C17−C17′, 121.8(3).
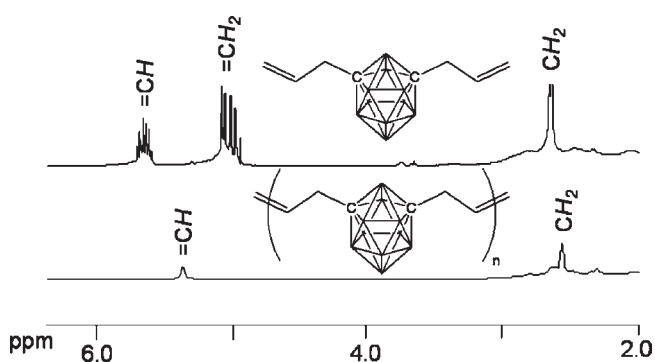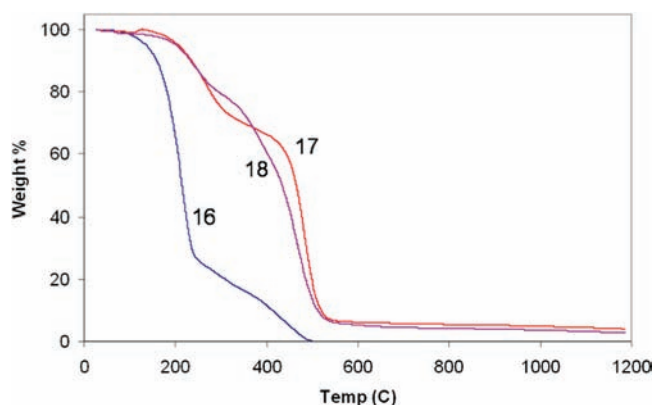

Figure 7. ^{1}H NMR spectrum of **7** (top) and **16** (bottom).

Figure 8. TGA curves of *m*-carborane polymers **16**−**18**.

and ∼5 mL of dichloromethane. An increased (∼1 M) monomer concentration, relative to the RCM reactions, was used to promote intermolecular reactions. Reactions were carried out at reflux for prolonged periods. The polymers were then separated from the catalyst using column chromatography with CH$_2$Cl$_2$ eluent.

The ^{11}B NMR spectra of the polymers were essentially identical to their monomers, but much broader. However, the olefinic regions of their ^{1}H NMR spectra, as illustrated in Figure 7 for the conversion of monomer **7** to **16**, clearly showed the absence of the monomer terminal olefinic resonances.

Depending upon the monomer, molecular weights (M_n) in the range of 4700 to 11 000 with PDIs ranging from 1.4 to 2.4 were attained when using 1 mol % catalyst. When the catalyst loading for the polymerization of monomer **9** was increased from 1 mol % to 3 mol %, the M_n decreased from 4700 (**18a**) to 2500 (**18b**).

The elemental analyses for polymers **17** and **18a** were in the expected ranges for their proposed [CH$_2$=CH(CH$_2$)$_4$-C$_2$B$_{10}$H$_{10}$-(CH$_2$)$_4$CH=]$_2$[CH(CH$_2$)$_4$-C$_2$B$_{10}$H$_{10}$-(CH$_2$)$_4$CH=]$_n$ (**17**) and [CH$_2$=CHCH$_2$SiMe$_2$-C$_2$B$_{10}$H$_{10}$-SiMe$_2$CH$_2$CH=]$_2$[CHCH$_2$SiMe$_2$-C$_2$B$_{10}$H$_{10}$-SiMe$_2$CH$_2$-CH=]$_n$ (**18a**) compositions. The elemental analyses for **16** showed higher than expected carbon for [CH$_2$=CH-CH$_2$-C$_2$B$_{10}$H$_{10}$-CH$_2$CH=]$_2$[CHCH$_2$−C$_2$B$_{10}$H$_{10}$-CH$_2$-CH=]$_n$, suggesting solvent retention in the oily polymer. Supporting this conclusion, the TGA analyses showed (Figure 8) that, while **17** and **18a** had excellent thermal

stability to greater than 250 °C, **16** exhibited an initial mass loss at a much lower temperature consistent with solvent evaporation. As evidenced by their ultimate zero char yields, all three polymers had completely depolymerized by 500 °C.

High boron content polyborane polymers and oligomers are of great interest[18] for their potential ceramic precursor,[19] boron neutron cancer therapy (BNCT),[20] and/or optical and electronic properties.[21] While main-chain siloxane−carborane polymers[22] have been extensively studied, the syntheses and properties of the corresponding

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(19) For example, see: (a) ref 2 above. (b) Sneddon, L. G.; Pender, M.; Forsthoefel, K.; Kusari., U.; Wei, X. *J. Eur. Ceram. Soc.* **2005**, *25*, 91–97. (c) Guron, M. M.; Wei, X.; Welna, D.; Krogman, N.; Kim, M. J.; Allcock, H. R.; Sneddon, L. G. *Chem. Mater.* **2009**, *21*, 1708–1715.

(20) See, for example: (a) Sivaev, I. B.; Bregadze, V. V. *Eur. J. Inorg. Chem.* **2009**, 1433–1450. (b) Armstrong, A. F.; Valliant, J. F. *Dalton Trans.* **2007**, 4240–4251. (c) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950–984. (d) Barth, R. F.; Soloway, A. H.; Fairchild, R. G. *Sci. Am.* **1990**, 100–107. (e) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515–1562.

(21) For example, see: (a) Kokado, K.; Chujo, Y. *Macromolecules* **2009**, *42*, 1418–1420. (b) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 2925–2930. (c) Kokado, K.; Tokoro, T.; Chujo, Y. *Macromolecules* **2009**, *42*, 9238–9242.

(22) (a) Mayes, N.; Green, J.; Cohen, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **1967**, *5*, 365. (b) Patel, M.; Swain, A. C.; Skinner, A. R.; Mallinson, L. G.; Hayes, G. F. *Macromol. Symp.* **2003**, *202*, 47–58.

main-chain organo–carborane polymers[23,24] and cyclic oligomers have been less well developed. The work described herein has demonstrated that metal-catalyzed RCM and ADMET reactions of (alkenyl)$_2$-o-carboranes and -m-carboranes, and potentially other dialkenylpolyboranes,[25] can provide versatile new synthetic routes to such materials. These metal-catalyzed pathways should now provide a new method that will enable the systematic tuning of the properties needed for use of these types of materials in many of the potential applications described above.

Supporting Information Available: Synthetic procedures and characterization data for dialkenyl-carboranes **1**−**9**. X-ray crystallographic data for the structural determinations of **3**, **9**, **11**, **12**, **13**, and **15a** (CIF). These materials are available free of charge via the Internet at http://pubs.acs.org.

(23) For some early examples of main-chain organocarborane polymers, see:(a) Green, J.; Mayes, N.; Cohen, M. S. *J. Poly. Sci., Part A: Polym. Chem.* **1964**, *2*, 3113–3133. (b) Green, J.; Cohen, M. S.; Kotloby, A. P.; Mayes, N. *J. Polym. Sci., Part A: Polym. Chem.* **1964**, *2*, 3135-3146. (b)

(24) For some recent examples of main-chain organocarborane polymers, see:(a) ref 20 above. (b) Peterson, J. J.; Simon, Y. C.; Coughlin, E. B.; Carter, K. R. *Chem. Commun.* **2009**, 4950–4952. (c) Peterson, J. J.; Were, M.; Simon, Y. C.; Coughlin, E. B.; Carter, K. R. *Macromolecules* **2009**, *42*, 8594–8598. (d) Colquhoun, H. M.; Herbertson, P. L.; Wade, K.; Baxter, I.; Williams, D. J. *Macromolecules* **1998**, *31*, 1694–1696. (e) Colquhoun, H. M.; Lewis, D. F.; Daniels, J. A.; Herbertson, P. L.; MacBride, J. A. H.; Stephenson, I. R.; Wade, K. *Polymer* **1997**, *38*, 2447–2453. (f) Korshak, V. V.; Bekasova, N. I.; Komarova, N. G.; Komarova, L. G.; Vagin, V. V. *Acta Polym.* **1989**, *40*, 439–442.

(25) For example, dialkenyldecaboranes, see: Chatterjee, S.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **2010**, *49*, 3095–3097.