

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

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Supporting Information

Syntheses of *o*-Dialkenyl-Carboranes

1,2-(CH₂=CHCH₂)₂-1,2-C₂B₁₀H₁₀ (1). A 1.0049 g (7.0 mmol) sample of *o*-carborane was lithiated with 6.1 mL (15.3 mmol) of BuLi at -78 °C in 75 mL of diethyl ether in a 250 mL three-neck flask and allowed to warm to room temperature. After 1-2 h of reaction, the solution was cooled in an ice bath, and 2.93 mL (34.7 mmol) of allyl bromide was 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 resulting ether layer was dried with MgSO₄ 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 ¹²C₈¹¹B₁₀¹H₂₀: 226.2495, found: 226.2504. Anal. Calcd.: C, 42.83; H, 8.99. Found: C, 42.53; H, 8.74. ¹¹B NMR (128.4 MHz, CDCl₃, ppm, *J* = Hz): -5.2 (d, 2B, *J* 147), -11.2 (d, 8B, *J* 155). ¹H NMR (400.1 MHz, CDCl₃, ppm, *J* = Hz) 5.79 (m, 2H, =CH), 1.73 (d, 4H, *J* 7.5, =CHCH₂), 2.97 (d, 2H, *J* 8.3, CH₂). 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).

1,2-(CH₂=CH(CH₂)₃CH₂)₂-1,2-C₂B₁₀H₁₀ (2). A 1.5012 g (10.4 mmol) sample of *o*-carborane was lithiated with 9.2 mL (23.0 mmol) of BuLi and subsequently reacted with 4.5 mL (33.6 mmol) of 6-bromo-1-hexene. The product was purified using column chromatography with hexanes as eluent, then further purified by thin layer chromatography using dichloromethane as eluent. The reaction yielded 1.89 g (6.1 mmol, 58.9% yield) of **2** as an oil. For **2**: NCI-HRMS (m/e): calcd. for ¹²C₁₄¹¹B₁₀¹H₃₂: 310.3434, found: 310.3430. Anal. Calcd.: C, 54.50; H, 10.45. Found: C, 52.42; H, 10.39. ¹¹B NMR (128.4 MHz, CDCl₃, ppm, J = Hz) -5.6 (d, 2B, J 151), -11.4 (d, 8B, J 143). ¹H NMR (400.1 MHz, CDCl₃, ppm, J = Hz) 5.78 (m, 2H, =CH), 5.01 (d, 4H, J 8.0, =CH₂), 2.08 (m, 8H, CH₂), 1.44 (m, 8H, CH₂). FT-IR (NaCl plate, cm^{-1}): 3077 (m), 2933 (s), 2858 (m), 2585 (vs), 1641 (m), 1463 (m), 1439 (m), 1164 (w), 1032 (m), 992 (m), 913 (s), 800 (w), 731 (m), 639 (w).

1,2-(CH₂=CHCH₂OC(=O))₂-1,2-C₂B₁₀H₁₀ (6). As described for **1**, a 1.0060 g (7.0 mmol) sample of *o*-carborane was lithiated with 6.4 mL (16.0 mmol) of BuLi and subsequently reacted with 3.2 mL (30.5 mmol) of allylchloroformate. The product was purified using column chromatography with pentane as eluent to yield 1.75 g (5.6 mmol, 80.3% yield) of **6** as a reddish oil. For **6**: NCI-HRMS (m/e): calcd. for ¹²C₁₀¹¹B₁₀¹⁶O₄¹H₂₀: 314.2291, found: 314.2282. Anal. Calcd.: C, 38.45; H, 6.45. Found: C, 40.38; H, 6.66. ¹¹B NMR (128.4 MHz, CDCl₃, ppm, J = Hz) -2.9 (d, 2B, J 151), -10.0 (d, 2B, J 158), -11.9 (d, 6B, J 159). ¹H NMR (400.1 MHz, CDCl₃, ppm, J = Hz) 5.87 (m, 2H, =CH), 5.35 (m, 4H, =CH₂), 4.64 (d, 4H, J 5.6, CH₂). FT-IR (NaCl

plate, cm^{-1}): 3090 (w), 2960 (m), 2586 (vs), 1753 (vs), 1452 (m), 1425 (w), 1379 (w), 1362 (m), 1259 (vs), 1126 (s), 1012 (s), 993 (s), 941 (s), 837 (m), 777 (w), 722 (m), 554 (w).

1,2-(CH₂=CHSiMe₂)₂-1,2-C₂B₁₀H₁₀ (3). A 2.0076 g (13.9 mmol) sample of *o*-carborane was lithiated with 12.2 mL (30.5 mmol) of BuLi and subsequently reacted with 9.8 mL (71.7 mmol) of chlorodimethylvinylsilane. White crystals immediately emerged upon removal of solvent and required no further purification, yielding 4.34 g (8.9 mmol, 63.7% yield) of **3**. For **3**: mp = 75.0-75.4 °C. NCI-HRMS (*m/e*): calcd for ¹²C₁₀²⁸Si₂¹¹B₁₀¹H₂₈: 314.2659, found: 314.2670. Anal. Calcd.: C, 38.42; H, 9.03. Found: C, 38.36; H, 9.05. ¹¹B NMR (128.4 MHz, CDCl₃, ppm, *J* = Hz) 1.6 (d, 2B, *J* 146), -6.3 (d, 2B, *J* 149), -9.4 (d, 4B, *J* 160), -11.8 (d, 2B, *J* 161). ¹H NMR (400.1 MHz, CDCl₃, ppm, *J* = Hz) 6.14 (m, 4H, =CH₂), 5.78 (m, 2H, =CH), 0.38 (s, 12H, CH₃). FT-IR (KBr pellet cm^{-1}): 3060 (w), 2963 (m), 2618 (s), 2570 (s), 1939 (w), 1592 (m), 1402 (s), 1255 (s), 1084 (s), 1009 (m), 965 (s), 905 (w), 816 (s), 714 (m), 632 (m), 560 (w), 510 (m). Compounds 1,2-(CH₂=CHCH₂SiMe₂)₂-1,2-C₂B₁₀H₁₀ (**4**) and 1,2-[CH₂=CH(CH₂)₄SiMe₂]₂-1,2-C₂B₁₀H₁₀ (**5**) were synthesized in an analogous fashion via the reactions of the dilithio-1,2-carborane with chlorodimethylallylsilane and chlorodimethylhexenylsilane. Their ¹¹B NMR spectra were identical to those of **3**. Complete spectral data were not collected.

Syntheses of *m*-Dialkenyl-Carboranes

1,7-(CH₂=CHCH₂)₂-1,7-C₂B₁₀H₁₀ (7). A 1.0023 (6.9 mmol) sample of *m*-carborane was lithiated with 6.1 mL (15.3 mmol) of BuLi and subsequently reacted with 3.0 mL (35.5 mmol) of allyl bromide to yield 1.19 g (5.3 mmol, 76.1% yield) of **7** as a colorless oil after removal of solvent and LiBr. For **7**: NCI-LRMS (*m/e*): calcd. for ¹²C₈¹¹B₁₀¹H₂₀: 226, found: 226. Anal. Calcd.: C, 42.83; H, 8.99. Found: C, 42.59; H, 8.72. ¹¹B NMR (128.4 MHz, CDCl₃, ppm, *J* = Hz) -7.8 (d, 2B, *J* 159), -11.8 (d, 6B, *J* 149), -14.4 (d, 2B, *J* 151). ¹H NMR (400.1 MHz, CDCl₃,

ppm, J = Hz) 5.64 (m, 2H, =CH), 5.08 (m, 4H, =CH₂), 2.63 (d, 4H, J 7.0, CH₂). FT-IR (NaCl plate cm⁻¹): 2963 (s), 2907 (m), 2598 (s), 1642 (w), 1617 (m), 1470 (w), 1439 (m), 1414 (m), 1322 (m), 1260 (vs), 1201 (s), 1028 (vs), 925 (m), 864 (s), 819 (vs), 738 (w), 704 (m), 459 (m).

1,7-(CH₂=CH(CH₂)₃CH₂)₂-1,7-C₂B₁₀H₁₀ (8). As described for **1**, a 0.8045 g (5.6 mmol) sample of *m*-carborane was lithiated with 5.5 mL (13.8 mmol) of BuLi and subsequently reacted with 4.1 mL (30.7 mmol) of 6-bromo-1-hexene to give 1.67 g (5.4 mmol, 97.1% yield) of **8** as colorless oil. For **8**: NCI-LRMS (m/e): calcd. for ¹²C₁₄¹¹B₁₀¹H₃₂: 310, found: 310. Anal. Calcd.: C, 54.50; H, 10.45. Found: C, 54.75; H, 10.41. ¹¹B NMR (128.4 MHz, CDCl₃, ppm, J = Hz), -7.1 (d, 2B, overlapped), -11.2 (d, 6B, J 143), -13.8 (d, 2B, overlapped). ¹H NMR (400.1 MHz, CDCl₃, ppm, J = Hz) 5.76 (m, 2H, =CH), 4.96 (m, 4H, =CH₂), 1.93 (m, 8H, CH₂), 1.36 (m, 8H, CH₂). FT-IR (NaCl plate cm⁻¹): 3078 (w), 2929 (s), 2859 (s), 2598 (vs), 1641 (m), 1463 (m), 1440 (m), 1416 (w), 1260 (m), 1137 (w), 1072 (m), 1030 (m), 992 (m), 912 (s), 804 (m), 731 (m).

1,7-(CH₂=CHCH₂SiMe₂)₂-1,7-C₂B₁₀H₁₀ (9). The reaction was carried as described for **1**, except that 2:1 benzene:diethyl ether was used as the solvent. A 2.0014 g (13.9 mmol) sample of *m*-carborane was lithiated with 15.8 mL (39.5 mmol) of BuLi and subsequently reacted with 11.2 mL (76.7 mmol) of allylchlorodimethylsilane. The resulting yellow oil was dissolved in pentane and 3.36 g (9.86 mmol, 71.0% yield) of white crystals of **9** crashed out at -78 °C. For **9**: m.p. = 59.2-59.8 °C. NCI-HRMS (m/e): calcd for ¹²C₁₂²⁸Si₂¹¹B₁₀¹H₃₂: 342.2972, found: 342.2985. Anal. Calcd.: C, 42.31; H, 9.47. Found: C, 42.14; H, 9.19. ¹¹B NMR (128.4 MHz, CDCl₃, ppm, J = Hz) -3.3 (d, 2B, J 157), -8.2 (d, 2B, J 148), -10.4 (d, 4B, J 157), -14.7 (d, 2B, J 157). ¹H NMR (400.1 MHz, CDCl₃, ppm, J = Hz) 5.70 (m, 2H, =CH), 4.91 (m, 4H, =CH₂), 1.62 (d, 4H, J 7.9, CH₂), 0.13 (s, 12H, CH₃). FTIR (KBr pellet, cm⁻¹): 3080 (w), 2971 (m), 2957 (m), 2901

(w), 2646 (m), 2599 (s), 2562 (s), 1630 (m), 1420 (m), 1397 (m), 1254 (s), 1247 (s), 1197 (w),
1166 (s), 1105 (m), 1081 (m), 1070 (m), 1041 (m), 993 (s), 932 (w), 893 (s), 854 (s), 814 (s), 787
(s), 657 (m), 573 (m).