Polyhedral-Based Nonlinear Optical Materials. 3.[1] Synthetic Studies of Cyclopentadiene- and Cycloheptatriene-Substituted Polyhedral Compounds: Synthesis of 1,12-[(C_7H_7)$C_2B_{10}H_{10}$($C_5H_3Me_2$)] and Related Species

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The synthesis and characterization of a series of new olefin-substituted *closo*-1,12-[$C_2B_{10}H_{12}$] compounds is described. The reaction of deprotonated *closo*-1,12-dicarbadodecaborane with 7-methoxycycloheptatriene yields the cycloheptatriene-substituted carborane compound, *closo*-[1-(1-C_7H_7)-12-(H)-$C_2B_{10}H_{10}$] (**3**). Deprotonation of **3** with butyllithium and subsequent reaction with 3,4-dimethyl-2-cyclopenten-1-one was found to yield the bis-olefin-substituted carbinol compound [1-(1-C_7H_7)-12-(C_5H_4-1-(OH)-3,4-(CH_3)$_2$)-$C_2B_{10}H_{10}$] (**5**) in good yield. Acidic dehydration of **5** quantitatively converted it into the simple bis-olefin cage compound [1-(1-C_7H_7)-12-(C_5H_3-3,4-(CH_3)$_2$)-$C_2B_{10}H_{10}$] (**6**). Finally, thermal treatment of **6** in refluxing toluene was employed to prepare the isomerized cycloheptatriene compound [1-(4-C_7H_7)-12-(C_5H_3-3,4-(CH_3)$_2$)-$C_2B_{10}H_{10}$] (**7**) in high yield. These compounds represent the first metal-free cyclopentadiene and bis-olefin large cluster species reported in which the C_5 ring is attached directly to the cage. The complete characterization of products by multinuclear NMR (^{1}H, ^{11}B, and ^{13}C), infrared, UV−visible, and mass spectroscopic analyses is presented. The X-ray crystal structures of **3** and **7** are also reported. X-ray data for **3**: triclinic system, space group $P\bar{1}$ with cell constants $a = 6.6807(3)$ Å, $b = 10.2939(3)$ Å, $c = 10.3962(4)$ Å, $\alpha = 89.342(2)°$, $\beta = 74.610(2)°$, $\gamma = 83.373(2)°$, $Z = 2$, R1 = 0.0487 (wR2 (all data) = 0.1272). X-ray data for **7**: monoclinic system, space group $P2_1/c$ with cell constants $a = 7.7207(7)$ Å, $b = 15.8730(14)$ Å, $c = 15.5493(13)$ Å, $\beta = 99.146(2)°$, $Z = 4$, R1 = 0.0761 (wR2 (all data) = 0.2050).

Introduction

The development of new molecular nonlinear optical (NLO) materials for a variety of photonic applications has recently received a great deal of attention.[1−4] The discovery of new molecular compounds and solid-state materials with enhanced photonic properties bears directly on the viability of a number of valued technological applications including optical communications, optical switching, and dynamic image processing. While new enhanced materials have been recently reported, significantly better materials are yet required for these applications.

Most current molecular NLO materials employ electron donor−acceptor substituents bridged by an organic π-delocalized structure.[3] Serious limitations, however, of this conventional approach to generate technologically useful new materials have arisen. Fundamental to the design of new compounds with large first hyperpolarizabilities (β) is the application of chemical strategies that increase intramolecular electronic polarization and transfer integrals.[5] In the previous papers in this series, we have suggested through detailed calculational studies that several new families of molecules that are based on boron polyhedral compounds coupled with charged aromatic donor−acceptor substituents should provide significantly enhanced NLO responses.[1]

Thus far, relatively little work has been directed toward the study of the NLO properties of molecular boron polyhedral compounds.[1] Three studies have been previously reported in which the first hyperpolarizabilities of polyhedral clusters have been considered.[6−8] In the previous papers in this series,[1] however, we have reported that the calculated NLO responses for several new classes of cluster-based molecules are particularly large. These new species employ boron-based polyhedra, especially the *closo*-icosahedral carborane cage [$C_2B_{10}H_{10}$], substituted by charged organic aromatic subunits, specifically the tropylium [C_7H_7]$^+$ and cyclopentadienide [C_5H_5]$^-$ groups

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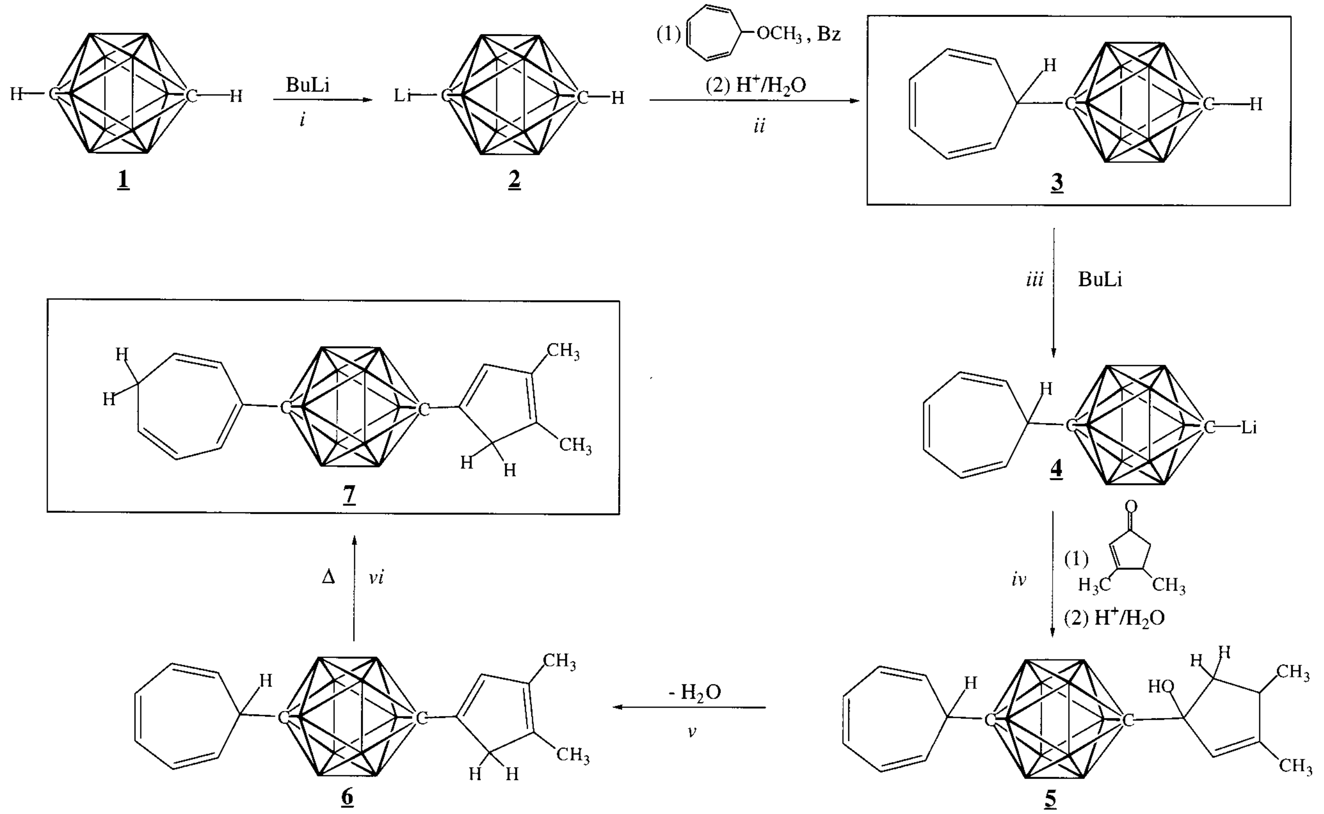
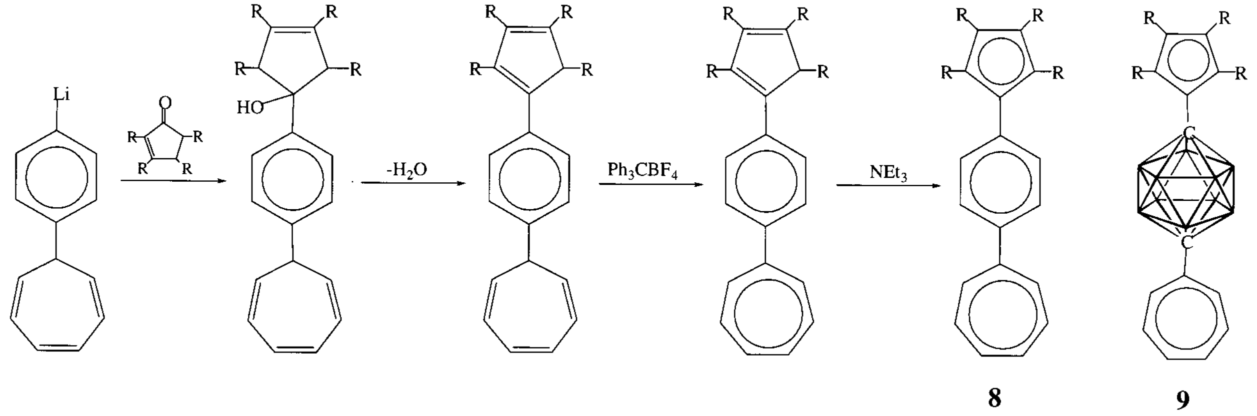
Scheme 1. Synthetic Scheme for Preparation of Cycloheptatriene- and Cyclopentadiene- Bis-substituted *closo*-1,12-[$C_2B_{10}H_{10}$] Polyhedron, **7**[a]



[a] Cage and olefinic ring hydrogen atoms have been omitted from the structures for clarity with the boxes indicating compounds for which X-ray crystallographic characterization has been completed

Scheme 2. Literature Synthetic Route to **8**[9,10] and Its Comparison to the Target Bis-substituted *closo*-1,12-[$C_2B_{10}H_{10}$] Cluster, **9**



(Schemes 1and 2). These molecules are interesting both because of their large calculated NLO responses and their synthetic viability. If the *closo*-icosahedral [$C_2B_{10}H_{12}$] carborane unit is viewed as chemically similar to the organic two-dimensional π-aromatic species benzene,[1] a useful comparison can be made between the analogous organic [5.6.7]quinarene system (**8**) and our ultimate synthetic target cluster molecule (**9**), as illustrated in Scheme 2.[9,10] Indeed, there is quite a large amount of data in the literature to suggest that this comparison between *closo*-[$C_2B_{10}H_{12}$] and benzene is quite reasonable both from electronic and reactivity considerations.[1,11] Among other similarities, both are electron-delocalized species, both undergo predominantly electrophilic substitution reactions and not addition reactions, and both are very stable species. One major difference between the two analogues that impacts their intramolecular polarization, however, is that the bridging benzene unit is known to provide facile electronic communication between the tropylium and

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cyclopentadienide units leading to a fully delocalized system, while the carborane bridge should significantly restrict this electronic redistribution, potentially leading to a highly polarized cluster molecule.[1,4] While derivatives of **8** have been prepared in the literature by the synthetic pathway shown in Scheme 2,[9,10] the cluster analogue species is unknown.

In this paper, we describe our synthetic efforts to prepare the molecular precursors required for the ultimate formation of the first prototypes of these new classes of polyhedral-based NLO compounds. In particular, we report here the complete synthesis and characterization of the [1-(4-C_7H_7)-12-(C_5H_3-3,4-$(CH_3)_2$)-$C_2B_{10}H_{10}$] cluster compound (**7**). While organometallic-substituted *o*-carborane species have been reported, for example, from the reaction of ethynyl ferrocene with decaborane,[12] the preparation of **7** represents the first synthesis of a metal-free cyclopentadiene-substituted icosahedral borane cluster in which the C_5 ring is attached directly to the cluster and also the first bis-olefin large cluster species.

Experimental Section

Physical Measurements. All NMR spectra were recorded on samples dissolved in $CDCl_3$ in 5-mm (o.d.) tubes. The boron (^{11}B) spectra were recorded on a Brücker DPX-300 NMR spectrometer operating at 96.3 MHz. Spectra were referenced to BBr_3 at +40.0 ppm (relative to $BF_3 \cdot Et_2O$ $\delta = 0.0$ ppm, with positive chemical shifts indicating downfield resonances). Typical ^{11}B NMR acquisition parameters employed were a relaxation delay of 0.1 ms and a 90° pulse of 10 μs. Proton (^1H) NMR spectra were recorded on a Brücker DPX-300 spectrometer operating at 300.15 MHz with chemical shifts referenced to residual $CHCl_3$ at $\delta = 7.27$ ppm. Carbon (^{13}C) NMR were obtained on a Brücker DPX-300 NMR spectrometer operating at 77.47 MHz. The spectrometer was operated in the FT mode while locked on the deuterium resonance of the $CDCl_3$ solvent. The reference was set relative to tetramethylsilane from the known chemical shifts of the $CDCl_3$ carbon atom. High-resolution mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences. The 70-VSE mass spectrometer was purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648). Unit resolution mass spectra were obtained on a Hewlett-Packard model 5989B gas chromatograph−mass spectrometer (GC−MS) using an ionization potential of between 11 and 70 eV. FT-IR in the range of 400−4000 cm^{-1} were measured on a Mattson Galaxy 2020 spectrometer and were referenced to the 1602.8 cm^{-1} band of polystyrene. UV−vis spectral data were collected on a Cary 1 UV−vis spectrophotometer in a quartz cell.

Materials. All solvents were reagent grade or better. Benzene was distilled from potassium metal prior to use. 7-Methoxycycloheptatriene (tropenyl methyl ether) was prepared as previously described.[13] *n*-BuLi was purchased from Aldrich Chemical Co. as a 1.6 M solution in hexanes. The 3,4-dimethyl-2-cyclopenten-1-one was prepared as previously described.[14] 1,12-[$C_2B_{10}H_{10}$] was purchased from Katchem, Inc. and used as received. Thin-layer chromatography (TLC) plates were purchased from Aldrich Chemical Co. All other commercially available reagents were used as received.

[1-(1-C_7H_7)-12-(H)-$C_2B_{10}H_{10}$] (3). In an inert atmosphere, 437 mg (3.03 mmol) of 1,12-[$C_2H_2B_{10}H_{10}$] was placed in a dry Schlenk flask. To the carborane solid was added 10 mL of dry benzene. A 1.6 M hexane solution of *n*-BuLi, 2.5 mL (3.94 mmol), was slowly syringed into the carborane solution at room temperature. This mixture was heated to 60 °C for 6 h and then cooled to room temperature. The tropenyl methyl ether[13] was placed in a dry Schlenk flask and dissolved in 5 mL of dry benzene. This tropenyl methyl ether solution was then added by cannula to the deprotonated carborane solution and stirred at room temperature for 12 h. The reaction mixture was then hydrolyzed with 25 mL of 0.2 M HCl. The aqueous layer was washed with diethyl ether, and the organic layers were combined. The organic layer was washed twice with water and dried over $MgSO_4$, and the solvent was removed in vacuo. The unreacted 1,12-[$C_2H_2B_{10}H_{10}$] was sublimed out of the reaction mixture at room temperature and 0.05 T. The mixture was placed on a silica gel TLC plate and eluted with hexanes. The top band ($R_f = 0.53$) was collected and sublimed. Pure **3** was collected as white crystals, suitable for X-ray crystallography, in 41% yield. Complete NMR (^1H, ^{11}B, and ^{13}C), IR, mass, and electronic spectral data for **3** are given in Tables 1 and 2, respectively. Crystallographic and structural data for **3** are given in Tables 3 and 4.

[1-(1-C_7H_7)-12-(C_5H_4-1-(OH)-3,4-$(CH_3)_2$)-$C_2B_{10}H_{10}$] (5). To a dry Schlenk flask containing 181 mg (0.77 mmol) of **3** was added 10 mL of dry benzene. To this solution was added 0.58 mL (0.93 mmol) of 1.6 M *n*-BuLi by syringe at room temperature. This mixture was heated to 70 °C under an N_2 atmosphere for 3 h. After being cooled to room temperature, 101 mg (0.927 mmol) of 3,4-dimethyl-2-cyclopenten-1-one,[14] dissolved in 5 mL of dry benzene and placed in a dry dropping funnel, was slowly added dropwise to the carborane solution. The combined mixture was stirred at room temperature for 0.5 h. The mixture was then hydrolyzed with 30 mL of 0.1 M HCl, and the aqueous layer was washed with diethyl ether. The organic layers were combined, washed twice with water, and dried over $MgSO_4$, and the solvents were removed in vacuo. The mixture was then eluted on a preparative silica gel TLC plate with benzene. The second band was collected ($R_f = 0.56$) and extracted from the silica gel with diethyl ether to yield ***5***. Pure ***5*** was obtained by the slow evaporation of a hexane solution at −15 °C to yield 125 mg of product (48% yield). Complete NMR (^1H, ^{11}B, and ^{13}C), IR, mass, and electronic spectral data for ***5*** are given in Tables 1 and 2, respectively.

[1-(1-C_7H_7)-12-(C_5H_3-3,4-$(CH_3)_2$)-$C_2B_{10}H_{10}$] (6). To a Schlenk flask containing 69 mg (0.020 mmol) of **5** was added 5 mL of 95% ethanol, and the mixture was heated to reflux. A dropping funnel containing 1.5 mL of 12 M HCl was employed to add the HCl dropwise to the hot solution of **5**. The reaction mixture was refluxed for 1 h, during which time a white precipitate formed. After the reaction cooled to room temperature, 20 mL of water was added, and the solution was cooled to 0 °C and filtered. The solid was washed with water and dried under vacuum. The solid was then chromatographed and eluted from a silica gel TLC plate with hexanes. Pure **6** ($R_f = 0.40$) was extracted from the silica gel with diethyl ether to obtain 62 mg (95% yield) of product. Complete NMR (^1H, ^{11}B, and ^{13}C), IR, mass, and electronic spectral data for **6** are given in Tables 1 and 2, respectively.

[1-(4-C_7H_7)-12-(C_5H_3-3,4-$(CH_3)_2$)-$C_2B_{10}H_{10}$] (7). To a round-bottom flask containing 131 mg (0.401 mmol) of **6** was added 15 mL of toluene. This solution was then heated to reflux for 5 days. After the reaction cooled to room temperature, the solvent was removed by rotary evaporation. The remaining solid was eluted with hexanes from a silica gel TLC plate. The product was collected ($R_f = 0.40$) and extracted with diethyl ether to yield 107 mg (82% yield) of pure **7**. Suitable crystals for X-ray crystallography were grown from slow evaporation of a diethyl ether solution at room temperature. Complete NMR (^1H, ^{11}B, and ^{13}C), IR, mass, and electronic spectral data for **7** are given in Tables 1 and 2, respectively. Crystallographic and structural data for **7** are given in Tables 3 and 5.

X-ray Crystallographic Studies of 3 and 7. Suitable crystals for **3** and **7** were selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[15] All data sets were collected using a Siemens SMART X-ray diffraction system, complete with 3-circle goniometer and CCD detector operating at −54 °C. The data sets were collected at 95 and 91 K, respectively, employing graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of

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Table 1. NMR Data for Compounds[a]

compd	^{11}B NMR[b]	^{1}H NMR[c]	^{13}C NMR[d]
3	−12.5 (d, B(2,3,4,5,6), J_{BH} = 180.7 Hz), −14.5 (d, B(7,8,9,10,11), J_{BH} = 182.4 Hz)	6.67 (t, 2H, C_7H_7, 4,5-C*H*), 6.10 (m, 2H, C_7H_7, 3,6-C*H*), 5.12 (dd, 2H, C_7H_7, 2,7-C*H*), 2.80 (s, 1H, cage C*H*), 1.41 (t, 1H, C_7H_7, 1-C*H*)	131.22 (C_7H_7, *C*H), 123.90 (C_7H_7, *C*H), 122.21 (C_7H_7, *C*H), 86.55 (cage-C), 60.40 (cage-CH), 45.47 (C_7H_7, *C*H)
5	−13.0 (d, 10B, J_{BH} = 163.4 Hz)	6.64 (t, 2H, C_7H_7, 4,5-C*H*), 6.08 (m, 2H, C_7H_7, 3,6-C*H*), 5.09 (dd, 2H, C_7H_7, 2,7-C*H*), 1.44 (m, 2H, $C_5(OH)(CH_3)_2H_4$, 2-CH*H* and C_7H_7, 1-C*H*), 5.12 (s, 1H, $C_5(OH)(CH_3)_2H_4$, 5-C*H*), 2.45 (m, 2H, $C_5(OH)(CH_3)_2H_4$, 2-C*H*H and 3-C*H*CH$_3$), 1.75 (s, 1H, $C_5(OH)(CH_3)_2H_4$, 1-O*H*), 1.67 (s, 3H, $C_5(OH)(CH_3)_2H_4$, 4-C*H*$_3$), 1.02 (d, 3H, $C_5(OH)(CH_3)_2H_4$, 3-CHC*H*$_3$)	149.2 ($C_5(OH)(CH_3)_2H_4$, *C*CH$_3$), 131.2 (C_7H_7, *C*H), 129.6 ($C_5(OH)(CH_3)_2H_4$, *C*H), 123.9 (C_7H_7, *C*H), 122.4 (C_7H_7, *C*H), 91.2 (cage-C), 84.0 (cage-C), 68.9 (C_7H_7, *C*OH), 49.6 ($C_5(OH)(CH_3)_2H_4$, *C*H$_2$), 44.6 (C_7H_7, *C*H), 41.9 ($C_5(OH)(CH_3)_2H_4$, *C*HCH$_3$), 19.5 ($C_5(OH)(CH_3)_2H_4$, CH*C*H$_3$), 14.6 ($C_5(OH)(CH_3)_2H_4$, C*C*H$_3$)
6	−12.7 (dd, B(2,3,4,5,6), J_{BH} = 151.8 Hz), −12.0 (dd, B(7,8,9,10,11), J_{BH} = 153.5 Hz)	6.67 (t, 2H, C_7H_7, 4,5-C*H*), 6.11 (m, 2H, C_7H_7, 3,6-C*H*), 5.13 (dd, 2H, C_7H_7, 2,7-C*H*), 1.44 (t, 1H, C_7H_7, 1-CH), 6.04 (s, 1H, $C_5(CH_3)_2H_3$, 2-C*H*), 2.73 (m, 2H, $C_5(CH_3)_2H_3$, 5-C*HH*), 1.84 (s, 3H, $C_5(CH_3)_2H_3$, 4-C*H*$_3$), 1.77 (s, 3H, $C_5(CH_3)2H_3$, 3-C*H*$_3$)	139.4 ($C_5(CH_3)_2H_3$, cage-C), 136.5 ($C_5(CH_3)_2H_3$, *C*CH$_3$), 135.2 ($C_5(CH_3)_2H_3$, *C*H), 134.3 ($C_5(CH_3)_2H_3$, *C*CH$_3$), 131.2 (C_7H_7, *C*H), 132.9 (s, C_7H_7, *C*H), 122.4 (C_7H_7, *C*H), 81.1 (cage-C), 80.6 (cage-C), 48.1 ($C_5(CH_3)_2H_3$, *C*H$_2$), 44.7 (C_7H_7, *C*H), 13.2 ($C_5(CH_3)_2H_3$, *C*H$_3$), 12.5 ($C_5(CH_3)_2H_3$, *C*H$_3$)
7	−12.1 ppm (d, 10B, J_{BH} = 164.5 Hz)	6.59 (d, 1H,C_7H_7, 2-C*H*), 6.07 (dd, 1H, C_7H_7, 3-C*H*), 5.98 (d, 1H, C_7H_7, 7-C*H*), 5.44 (m, 1H, C_7H_7, 4-C*H*), 5.27 (m, 1H,C_7H_7, 6-C*H*), 2.09 (t, 2H, C_7H_7, 5-C*H*$_2$), 6.02 (s, 1H, $C_5(CH_3)_2H_3$, 2-C*H*), 2.71 (m, 2H, $C_5(CH_3)_2H_3$, 5-C*H*$_2$), 1.83 (s, 3H, $C_5(CH_3)_2H_3$, 4-C*H*$_3$), 1.75 (s, 3H, $C_5(CH_3)_2H_3$, 3-C*H*$_3$)	139.5 ($C_5(CH_3)_2H_3$, cage-C), 138.9 (C_7H_7, cage-C), 136.5 ($C_5(CH_3)_2H_3$, *C*CH$_3$), 135.2 ($C_5(CH_3)_2H_3$, *C*H), 134.3 ($C_5(CH_3)_2H_3$, *C*CH$_3$), 130.5 (C_7H_7, *C*H), 126.4 (C_7H_7, *C*H), 125.7 (C_7H_7, *C*H), 123.2 (C_7H_7, *C*H), 120.0 (C_7H_7, *C*H), 82.9 (cage-C), 80.0 (cage-C), 48.0 ($C_5(CH_3)_2H_3$, *C*H$_2$), 27.7 (C_7H_7, *C*H$_2$), 13.2 ($C_5(CH_3)_2H_3$, *C*H$_3$), 12.5 ($C_5(CH_3)_2H_3$, *C*H$_3$)

[a] Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet. [b] Relative to BBr_3 (40.0 ppm) in $CDCl_3$. [c] Relative to TMS (0.0 ppm) in $CDCl_3$. Assignments were made from analysis of ^{1}H−^{1}H COSY NMR experiments. [d] Relative to TMS (0.0 ppm) in $CDCl_3$.

exposures, each with a different φ angle and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. No decay was observed. Absorption corrections were applied utilizing the program SADABS.[16] The crystal structures were solved by direct methods included in the SHELX program package.[17] Missing atoms were located in subsequent difference Fourier cycles and included in the refinement. The structures were refined by full-matrix least-squares refinement on F^2 (SHELXL-96).[17] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms on the boron cage and in the organic ring systems were found in difference Fourier maps and refined with U_{iso} constrained at $1.2U_{eq}$ of the carrier atom. The hydrogen atoms of the methyl groups were placed geometrically and refined using a riding model with $U_{iso} = 1.5U_{eq}$ of the carrier atom. The crystallographic programs used for structure solution and refinement were installed on a PC clone and a Silicon Graphics Indigo R10000 high impact computer system. Scattering factors were those provided with the SHELX program.[17]

Results and Discussion

The key compound in the formation of the new cluster-based NLO compounds, such as **9** (Scheme 2), is the formation of the bis-olefin-substituted *closo*-[$C_2B_{10}H_{10}$] cage system, **7** (Scheme 1). The complete synthetic pathway leading to this new species **7** is shown in Scheme 1. Relatively little synthetic work has been done with the 1,12-derivative of *closo*-C_2B_{10} in comparison with the 1,2- and 1,7-isomers, and the extension of 1,12-cluster chemistry is of interest in itself. The choice of the 1,12-isomer was dictated here, however, by the desire for NLO properties that are maximized in this isomer.

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Table 2. Infrared, Mass Spectral, and Electronic Data for Compounds

compd	IR (cm^{-1})^{a,b}	mass spectral data^c	electronic spectra (nm)^d
3	2930 (w),^{a} 2613 (s), 2864 (w), 1545 (w)	high resolution calcd, found (amu): 236.2339, 236.2346. nominal mass (found, calcd; envelope): 231 (41, 8; P$^+$), 232 (59, 28; P$^+$), 233 (83, 65; P$^+$), 234 (100, 100; P$^+$; $^{12}C_9{}^1H_{18}{}^{10}B_2{}^{11}B_8$), 235 (82, 93; P$^+$), 236 (41, 42; P$^+$), 91 (base peak, C_7H_7 fragment)	202.3, 252.3
5	3606 (sp),^{a} 2962 (m), 2922 (m), 2861 (w), 2611 (s), 1656 (w)	high resolution calcd, found (amu): 346.3071, 346.3063. nominal mass (found, calcd; envelope): 343 (67, 64; P$^+$), 344 (100, 100; P$^+$; $^{12}C_{16}{}^1H_{28}{}^{10}B_2{}^{11}B_8{}^{16}O$), 345 (94, 96; P$^+$), 346 (45, 48; P$^+$), 327 (rel int 5; P$^+$ − OH; $^{12}C_{16}{}^1H_{27}{}^{10}B_2{}^{11}B_8$), 91 (base peak, C_7H_7 fragment)	202.2, 252.3
6	2966 (m),^{b} 2899 (m), 2855 (m), 2611 (m)	high resolution calcd, found (amu): 328.2965, 328.2972 nominal mass (found, calcd; envelope): 322 (6, 2; P$^+$), 323 (13, 8; P$^+$), 324 (35, 27; P$^+$), 325 (70, 64; P$^+$), 326 (100, 100; P$^+$; $^{12}C_{16}{}^1H_{26}{}^{10}B_2{}^{11}B_8$), 327 (94, 96; P$^+$), 328 (48, 47; P$^+$), 329 (7, 7; P$^+$), 311 (rel int 15; P$^+$ − CH_3; $^{12}C_{15}{}^1H_{23}{}^{10}B_2{}^{11}B_8$), 91 (base peak, C_7H_7 fragment)	202.2, 277.4
7	2970 (s),^{b} 2931 (s), 2841 (s), 2610 (m)	high resolution calcd, found (amu): 328.3038, 328.3030. nominal mass (found, calcd; envelope): 322 (6, 2; P$^+$), 323 (13, 8; P$^+$), 324 (34, 27; P$^+$), 325 (64, 64; P$^+$), 326 (100, 100; P$^+$; $^{12}C_{16}{}^1H_{26}{}^{10}B_2{}^{11}B_8$), 327 (93, 96; P$^+$), 328 (47, 47; P$^+$), 329 (7, 7; P$^+$), 311 (rel int 36; P$^+$ − CH_3; $^{12}C_{15}{}^1H_{23}{}^{10}B_2{}^{11}B_8$), 91 (base peak, C_7H_7 fragment)	207.3, 230.7

[a] KBr plates with CCl_4 solvent. Abbreviations: s = strong, m = moderate, w = weak, sp = sharp. [b] KBr plates with Nujol. [c] Relative intensities are given with the largest peak in the envelope normalized to 100.0%. The calculated values are based on the natural isotopic abundances of the elements, which are normalized to the most intense peak in the envelope. [d] Solvent: CH_3CN.

Table 3. Crystallographic Data for **3** and **7**

	3	**7**
empirical formula	$C_9H_{18}B_{10}$	$C_{16}H_{26}B_{10}$
fw	234.33	326.47
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	6.6807(3)	7.7207(7)
b (Å)	10.2939(3)	15.8730(14)
c (Å)	10.3962(4)	15.5493(13)
α (deg)	89.342(2)	90
β (deg)	74.610(2)	99.146(2)
γ (deg)	83.373(2)	90
V (Å^3)	684.57(5)	1881.4(3)
Z	2	4
λ (Å)	0.71073	0.71073
T (°C)	−181(2)	−178(2)
ρ_{calc} (g/cm^3)	1.137	1.153
μ (cm^{-1})	0.53	0.57
2θ range (deg)	3.98−56.56	3.70−47.98
no. of reflns collected	5270	9325
no. of reflns with [$I > 2\sigma(I)$]	3138	2949
no. of params	244	295
final R indices	R1 = 0.0487, wR2 = 0.1272	R1 = 0.0761, wR2 = 0.2050
largest diff peak and hole (e-/Å^3)	0.370 and −0.221	0.580 and −0.578

In the first portion of the synthesis of **7**, the steps leading from 1,12-[$C_2B_{10}H_{12}$] to the formation of **3** are related to those successfully employed in the high yield synthesis of the related 1,2-[$(C_7H_7)(CH_3)C_2B_{10}H_{10}$] cluster.[18] While the initial synthesis of the 1,2- and 1,7-cycloheptatriene-substituted icosahedral carborane clusters were first reported over 30 years ago, neither their complete spectroscopic and structural characterization nor the synthesis of the related 1,12-substituted species, **3**, has been reported.[18]

The complete characterization of **3** has been accomplished by multinuclear NMR (^{1}H, ^{11}B, ^{13}C), infrared, UV−visible, mass spectral, and X-ray diffraction studies. Complete spectroscopic data are given in Tables 1 and 2. The ^{11}B NMR spectrum for **3** shows a 1:1 pattern arising from the two inequivalent belts of boron atoms in the icosahedron. The ^{1}H NMR spectrum displays a pattern very typical for monosubstituted cycloheptatriene carbocycles with four resonances observed at 6.67, 6.10, 5.12, and 1.41 ppm in a 2:2:2:1 relationship, respectively. The expected connection of the sp^3 carbocyclic ring carbon directly to the cage (1-isomer) is supported by the observed multiplicity (triplet) and chemical shift (1.41 ppm) of this resonance. The resonance for the single remaining CH cage hydrogen in **3** was observed at 2.80 ppm, very similar to the observed chemical shift of 2.75 ppm for the parent *closo*-1,12-$C_2B_{10}H_{12}$. The ^{13}C data show resonances for the two inequivalent cage carbons (86.55 and 60.40 ppm), the olefinic C_7 ring carbons (131.22, 123.90, and 122.21 ppm), and the sp^3 ring carbon (45.47 ppm),

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(18) (a) Harmon, K. M.; Harmon, A. B.; Thompson, B. C.; Spix, C. L.; Coburn, T. T.; Ryan, D. P.; Susskind, T. Y. *Inorg. Chem.* **1974**, *13*, 862. (b) Harmon, K. M.; Nelson, T. E.; Stachowski, B. M. *J. Mol. Struct.* **1995**, *350*, 135. (c) Harmon, K. M.; Harmon, A. B.; Thompson, B. C. *J. Am. Chem. Soc.* **1967**, *89*, 5309. (d) Harmon, A. B.; Harmon, K. M. *J. Am. Chem. Soc.* **1966**, *88*, 4093. (e) Harmon, K. M.; Harmon, A. B.; MacDonald, A. A. *J. Am. Chem. Soc.* **1969**, *91*, 323.

Table 4. Selected Bond Distances and Angles for **3**

Selected Bond Distances

	distance		distance		distance
C(1)−C(21)	1.5457(17)	B(5)−B(6,9)	1.775(2)	B(11)−C(12)	1.712(2)
C(1)−B(4)	1.7154(18)	B(7)−C(12)	1.7047(19)	C(21)−C(27)	1.5067(17)
C(1)−B(2)	1.7201(18)	B(7)−B(8,11)	1.783(2)	C(21)−C(22)	1.5088(17)
C(1)−B(3)	1.7263(18)	B(8)−C(12)	1.7079(19)	C(22)−C(23)	1.3423(18)
C(1)−B(5)	1.7273(18)	B(8)−B(9)	1.780(2)	C(23)−C(24)	1.4477(18)
C(1)−B(6)	1.7274(18)	B(9)−C(12)	1.7083(19)	C(24)−C(25)	1.357(2)
B(2)−B(3,6,7)	1.7813(2)	B(9)−B(10)	1.786(2)	C(25)−C(26)	1.4483(19)
B(3)−B(4,7)	1.773(2)	B(10)−C(12)	1.7073(19)	C(26)−C(27)	1.3436(18)
B(4)−B(5)	1.785(2)	B(10)−B(11)	1.785(2)		

Selected Bond Angles

atoms	angle	atoms	angle
C(21)−C(1)−B(2,3,4,6)	117.51(10)	C(22)−C(21)−C(1)	114.98(10)
B(3)−B(2)−B(6)	108.17(10)	C(27)−C(21)−H(21)	107.5(9)
B(2)−B(3)−B(4)	107.74(10)	C(23)−C(22)−C(21)	119.97(11)
B(3)−B(4)−B(5)	108.22(10)	C(22)−C(23)−C(24)	124.58(12)
B(6)−B(5)−B(4)	107.91(9)	C(25)−C(24)−C(23)	125.21(12)
B(5)−B(6)−B(2)	107.95(10)	C(24)−C(25)−C(26)	125.31(12)
C(27)−C(21)−C(22)	106.10(10)	C(27)−C(26)−C(25)	124.63(12)
C(27)−C(21)−C(1)	115.62(10)	C(26)−C(27)−C(21)	119.79(12)

Table 5. Selected Bond Distances and Angles for **7**

Selected Bond Distances

	distance		distance		distance
C(1)−C(2)	1.491(5)	B(3)−B(4)	1.779(6)	B(11)−C(12)	1.721(5)
C(1)−B(2−6)	1.726(5)	B(4)−B(5)	1.781(6)	C(12)−C(13)	1.523(5)
C(2)−C(3)	1.385(5)	B(5)−B(6)	1.781(6)	C(13)−C(14)	1.350(5)
C(2)−C(6)	1.462(5)	B(7)−C(12)	1.732(5)	C(13)−C(19)	1.469(5)
C(3)−C(4)	1.482(5)	B(7)−B(8,11)	1.784(5)	C(14)−C(15)	1.451(5)
C(4)−C(5)	1.338(5)	B(8,9)−C(12)	1.736(5)	C(15)−C(16)	1.347(5)
C(4)−C(7)	1.504(5)	B(8)−B(9)	1.787(6)	C(16)−C(17)	1.482(5)
C(5)−C(6)	1.494(5)	B(9)−B(10)	1.779(6)	C(17)−C(18)	1.497(5)
C(5)−C(8)	1.503(5)	B(10)−C(12)	1.725(5)	C(18)−C(19)	1.332(5)
B(2)−B(3,6)	1.783(6)	B(10)−B(11)	1.775(6)		

Selected Bond Angles

atoms	angle	atoms	angle
C(3)−C(2)−C(6)	108.5(3)	B−B−B (cage) av	108.1(3)
C(3)−C(2)−C(1)	127.3(3)	C(14)−C(13)−C(19)	123.1(3)
C(6)−C(2)−C(1)	124.2(3)	C(14)−C(13)−C(12)	119.6(3)
C(2)−C(3)−C(4)	108.2(3)	C(19)−C(13)−C(12)	116.6(3)
C(5)−C(4)−C(3)	108.8(3)	C(13)−C(14)−C(15)	126.3(3)
C(5)−C(4)−C(7)	127.6(3)	C(16)−C(15)−C(14)	124.1(4)
C(3)−C(4)−C(7)	123.6(3)	C(15)−C(16)−C(17)	122.3(3)
C(4)−C(5)−C(6)	109.3(3)	C(16)−C(17)−C(18)	107.1(3)
C(4)−C(5)−C(8)	129.4(3)	C(19)−C(18)−C(17)	122.0(3)
C(6)−C(5)−C(8)	121.3(3)	C(18)−C(19)−C(13)	123.7(3)
C(2)−C(6)−C(5)	105.1(3)		

consistent with the proposed structure. Mass spectral data for **3** shows a strong parent envelope displaying the characteristic boron isotopic distribution (Table 2) with the base peak at 91 *m*/*e* arising from loss of the C_7 ring fragment.[19] The IR and UV−vis spectral data given in Table 2 are also fully consistent with the proposed structure and compare well with the reported data for the related cycloheptatriene-substituted 1,2-cage species.

A single-crystal X-ray analysis of **3** confirmed the proposed structure shown in Scheme 1. A drawing of the molecular structure of **3** is given in Figure 1 while selected bond distance and bond angle data are presented in Table 4. The overall geometry, bond lengths, and bond angles within the carborane cage of **3** are consistent with other known structures, which incorporate the *closo*-icosahedral cage unit.[11] As anticipated, a clear alternation between long (1.448 Å av) and short (1.348 Å av) bond lengths is observed in the cycloheptatriene unit with the longest bond lengths associated with sp^3 carbon (1.508 Å av). The structure also confirms the spectroscopic assignment of the sp^3 ring carbon as the point of attachment to the carborane cage with the associated hydrogen atom directed toward the B3 cage boron atom. The geometry of the cycloheptatriene ring system shows a *pseudo*-boat geometry, as illustrated in Figure 2, which is symmetric around the mirror plane incorporating the C21−C1 bond and the midway point of the C24−C25 bond.

The reaction of butyllithium with **3** was found to provide a high yield pathway to the lithiated intermediate **4**. Subsequent treatment of **4** with 3,4-dimethyl-2-cyclopenten-1-one followed by acid hydrolysis yielded the key intermediate cage-substituted carbinol **5** in which both cycloheptatriene and hydroxycyclo-

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(19) Ditter, J. F.; Gerhart, F. J.; Williams, R. E. *Mass Spectrometry of Inorganic Compounds*; ACS Monograph 7L; American Chemical Society: Washington, DC, 1968; p 191.

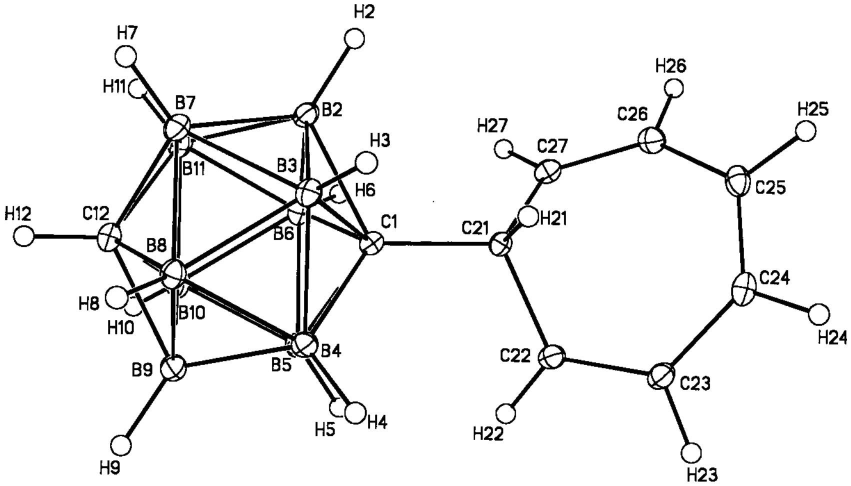

Figure 1. Drawing of the molecular structure of **3** showing the atom-labeling scheme (thermal ellipsoids are shown at the 30% probability level with hyrdogen atoms not shown by ellipsoids).

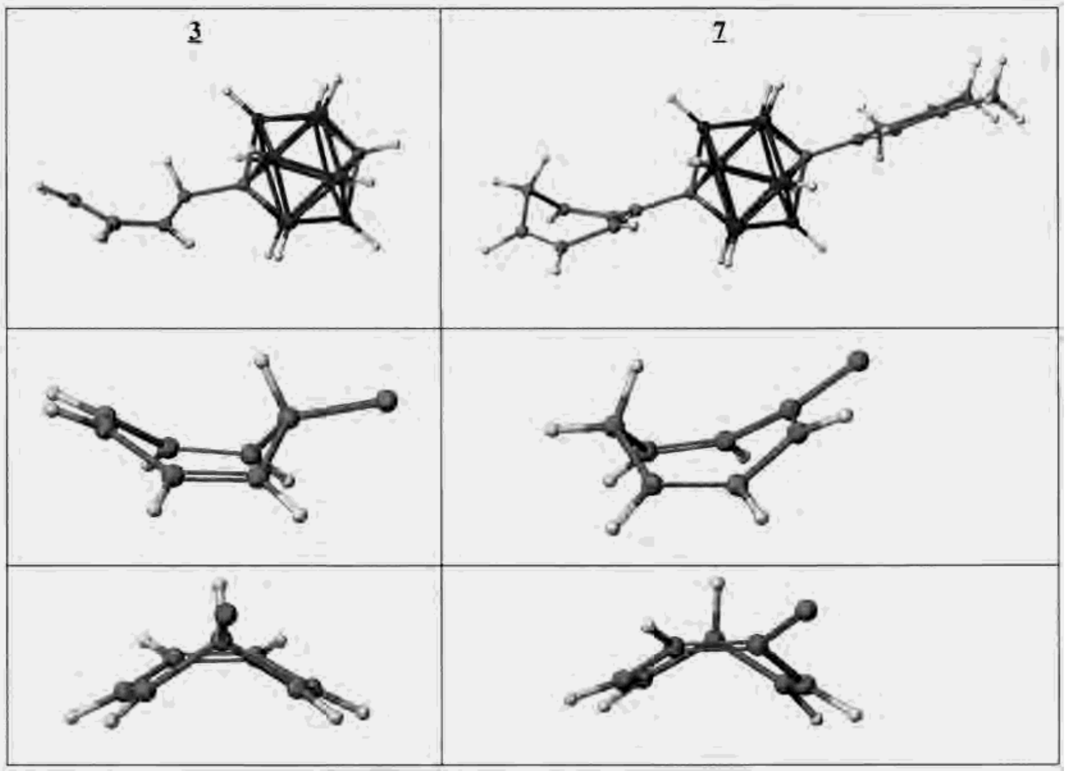

Figure 2. Structures of **3** (left) and **7** (right) illustrating the conformation of the triene and diene subunits (the carborane cage carbon atom attached to the olefin is shown in the lower two drawings of **3** and **7** to illustrate the point of attachment to the carbocycle). The lower two drawings show the conformation of the C_7 ring for each compound from side (middle drawing) and end-on (bottom) orientations.

pentene units are substituted onto the carborane framework. The reaction of **4** with 3,4-dimethyl-2-cyclopenten-1-one is directly analogous to both the known reaction of 2-cyclopenten-1-one with *p*-tropylphenyllithium to yield the tropylphenylcyclopentadienyl carbinol, structurally related to **5** as seen in Scheme 2,[9] and the reaction of *o*-carborane with ketones and aldehydes to yield the acyclic cage carbinol-substituted carboranes.[20] The preferential site of lithiation is at the cage C—H site, rather than at cycloheptatriene sites, which is fully consistent with calculational data that shows that the cage C—H proton is the only appreciably acidic hydrogen in **3**. In addition, this cage C—H lithiation site specificity is also consistent with both the literature synthesis of the direct organic analogue *p*-tropylphenyllithium (Scheme 2) and the known stability of the tropyl hydrogens in tropylcyclopentadienyl benzene derivatives toward lithiation by *n*-butyllithium.[9,10]

Complete spectroscopic data for **5** are given in Tables 1 and 2. The ^{11}B NMR spectrum of **5** shows only one signal for all the boron atoms, suggesting that the two olefinic units provide rather similar chemical environments for the two formally inequivalent belts of cage boron atoms. This single resonance pattern is similar to that observed for the alkyl and cycloheptatriene bis-substituted 1,2-[$(C_7H_7)(CH_3)C_2B_{10}H_{10}$] species, although these two species differ in their symmetry.[18b] The ^{1}H NMR spectrum, however, clearly shows resonances typical for the hydroxycyclopentene group (at 1.44, 2.45, 5.12, and 1.75

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(20) Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1167.

ppm), the methyl groups substituted on the cyclopentene ring system (at 1.67 and 1.02 ppm), and the cycloheptatriene unit (at 6.64, 6.08, 5.09, and 1.44 ppm). Confirmation of the assignment of the OH resonance at 1.75 ppm was obtained through D_2O addition studies. Cage CH proton signals were not observed in the ^1H spectrum. Resonances typical for cage, cycloheptatriene, and hydroxycyclopentene were also observed in the ^{13}C NMR data. Mass spectral data for **5** showed a strong parent envelope displaying the characteristic boron isotopic distribution (Table 2) with strong peaks observed at 327 (envelope) and 91 *m*/*e*, corresponding to OH loss and the C_7 ring fragment, respectively.[19] Infrared data further support structural assignment, including an OH stretching vibration observed at 3606 cm^{-1}.

Dehydration of the hydroxycyclopentene ring system in **5** by hot ethanolic acidification quantitatively provided the cage-substituted cyclopentadiene species **6**. Complete spectroscopic data for **6** are given in Tables 1 and 2. As observed for **3**, the ^{11}B NMR spectrum for **6** shows two closely spaced resonances (-12.68 and -11.97 ppm) assigned to the two inequivalent belts of the icosahedron. The main differences observed in the ^1H NMR spectrum between the starting **5** and the new **6** were the disappearances of the OH resonance at 1.75 ppm and the C_5 ring 3-CH resonance at 2.45 ppm. The ^1H NMR also clearly shows typical resonances for the 1-cycloheptatriene ring. Mass spectral data showed the parent enveloped at 328 *m*/*e* (for $^{12}C_{16}{}^1H_{26}{}^{11}B_{10}$) with an envelope at 311 *m*/*e* corresponding to the loss of CH_3 and a peak at 91 *m*/*e* for the C_7 ring fragment. The infrared spectrum of **6** also showed the disappearance of the OH stretching vibration observed in **5**.

Finally, the prolonged thermal treatment of **6** in refluxing toluene was found to convert **6** in very high yield into the isomerized cycloheptatriene compound, **7**. This reaction, consistent with similar rearrangements reported by Harmon for 1,2-$[(1\text{-}C_7H_7)C_2B_{10}H_{11}]$ and related compounds,[18] produces the 4-cycloheptatriene isomer. As observed for **5**, the ^{11}B NMR spectrum for **7** showed a single resonance, again supporting the idea that the two cage-substituted olefins provide very similar chemical environments for the cage boron atoms. The ^1H NMR spectrum, however, showed a modified pattern for the cycloheptatriene unit with peaks observed at 6.59, 6.07, 5.98, 5.44, 5.27, and 2.09 ppm. These data are very similar to the observed chemical shifts and splitting patterns for other known 4-cycloheptatriene species.[18,21] The ^1H resonances for the cyclopentadiene ring in **7** (6.02, 2.71, 1.83, and 1.75 ppm) are essentially identical to those found in **6**. Additionally, as observed for **6**, the mass spectral data for **7** showed a strong parent enveloped at 328 *m*/*e* with an envelope at 311 *m*/*e* arising from the loss of CH_3 and a peak at 91 *m*/*e* for the C_7 ring fragment.

The structural assignment of **7** as an icosahedral *closo*-carborane unit bridging between cycloheptatriene and cyclopentadiene ring systems has been confirmed by single-crystal X-ray analysis. A drawing of the molecular structure of **7** is given in Figure 3 while selected bond distance and bond angle data are presented in Table 5. As observed in the crystal structure of **3**, all of the bond distances and angles within the *closo*-icosahedral cluster are typical of those found in other structures. Both the cycloheptatriene and cyclopentadiene rings showed the anticipated long (C_7 av of 1.460 Å and C_5 av of 1.479 Å) and short (C_7 av of 1.343 Å and C_5 av of 1.362 Å) bond length alternation with the sp^3 carbons located at the 4-cycloheptatriene ring and cyclopentadiene ring positions. The geometry of the C_7 ring system in **7** showed a distorted boat conformation, as illustrated in Figure 2. The connection of the 4-C_7 ring to the cage, however, removes the mirror plane observed in **3**. The C_5 ring system is planar, despite the presence of the sp^3 carbon in the ring. In addition, the plane composed of the C13, C14, and C19 atoms in the C_7 ring is essentially coplanar with the plane of the five ring carbons of the C_5 ring system, C2−C6, with an interplane dihedral angle of 7.00° (0.17).

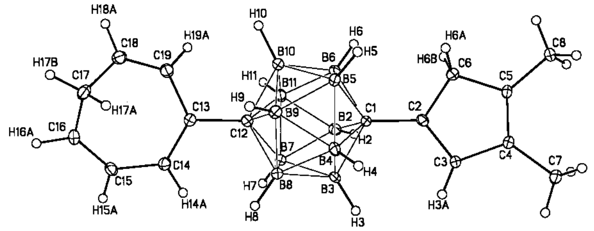

Figure 3. Drawing of the molecular structure of **7** showing the atom-labeling scheme (thermal ellipsoids are shown at the 30% probability level with hydrogen atoms not shown by ellipsoids).

Conclusions

The synthesis of **7** illustrates the preparation of an interesting new class of bis-olefin-substituted cage systems. These olefin-substituted compounds are remarkably stable and are prepared in relatively high yields. This synthesis opens up pathways to a variety of potentially interesting organometallic derivatives through either direct coordination of an organometallic fragment to the olefins or deprotonation to directly yield new sandwich compounds. Our current work is focused upon the deprotonation and hydride abstraction reactions of **7** to prepare the tropylcyclopentadienyl-substituted *closo*-1,12-$[C_2B_{10}H_{10}]$ cluster, particularly interesting for its potential NLO properties.

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Supporting Information Available: Tables giving complete crystallographic experimental details, bond distances and angles, positional parameters for all atoms, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for both **3** and **7** with figures showing their thermal ellipsoid plots. Structure in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Harmon, K. M. In *Carbonium Ions*; Olah, G. A., Ed.; Interscience Publishers: New York, 1973; Vol. 4, p 1579.