Hydrophilically Augmented Glycosyl Carborane[1] Derivatives for Incorporation in Antibody Conjugation Reagents

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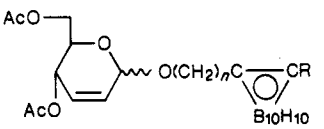
The synthesis of a series of *O*-glycosyl carboranes is described. The reactions of hydroxyalkyl carboranes and esterified carbohydrates, in the presence of a Lewis acid catalyst, proved to be stereoselective. Reactions of these carboranes with tri-*O*-acetyl-D-glucal or di-*O*-acetyl-D-xylal and a catalytic amount of BF_3·OEt_2 favored the formation of α anomers, while the β anomer was the major product of the $SnCl_4$-catalyzed reaction involving hydroxymethyl carborane and 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose. The ^1H and ^{13}C NMR spectra of 1-[(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (**3**) were analyzed by using several one-dimensional and two-dimensional techniques; the chemical shifts and coupling interactions of all atoms were unequivocally assigned.

Introduction

The application of the cytotoxic ^{10}B-neutron capture reaction [$^{10}B(n,\alpha)^7Li$] to the treatment of human tumors coupled with the use of antitumor antibodies as a vehicle for depositing boron-10 selectively in tumors has been discussed for at least 25 years.[2] The slow progress in this approach has been due, principally, to the difficulty in labeling antibodies with large quantities of boron while retaining immunoreactivity of the immunoglobulins and the lack of a truly specific tumor-localizing antibody for human studies. The latter problem has been overcome since the demonstration that tumor-associated antibodies, such as those to CEA, AFP, and HCG, can localize radioactivity selectively in tumors having the appropriate antigenic markers.[3] Mizusawa et. al have shown that it is possible to attach as many as 14 molecules of suitably functionalized carborane units to a single antibody molecule.[4] However, they also found that protein precipitation and loss of immunoreactivity are significant when as few as six carborane units are attached to each antibody molecules.[4] The extremely hydrophobic nature of the carboranes used in these studies led us to conclude that the addition of polar, hydrophilic functional groups had the potential of drastically reducing antibody precipitation. In an effort to increase the water solubility of the carborane-containing antibody conjugate, we have investigated the preparation of glycosyl carboranes.

Table I. Anomeric Ratios of a Series of O-Glycosyl Carboranes



compd	R	*n*	α:β
3	H	1	9.0:1.0
4	H	2	8.7:1.3
5	CH_3	2	8.2:1.8
6	H	3	8.2:1.8
7	CH_3	3	7.7:2.3

The reactions of simple alcohols with carbohydrates have been well-documented.[5] The need for non-ionic, water-soluble carborane derivatives has prompted us to apply this chemistry to the reactions of carboranyl alcohols with sugars. Here we describe the Lewis acid assisted reactions of hydroxyalkyl carboranes with 3,4,6-tri-*O*-acetyl-D-glucal,[6] 3,4-di-*O*-acetyl-D-xylal,[7] and 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose[6] as facile and efficient approaches to the synthesis of *O*-glycosyl carboranes.

Results and Discussion

O-Glycosylation of a derivatized furanose was accomplished by a $SnCl_4$-assisted reaction[5b] between 1-*O*-acetyl-2,3,5-*O*-benzoyl-β-D-ribofuranose and (hydroxymethyl)-*o*-carborane. Integration of the proton NMR spectrum and comparison of peak heights in the carbon-13 NMR spectrum showed that the α anomer comprised only 5–7% of the crude product. The pure β anomer was isolated by column chromatography. Neighboring group participation, illustrated in Figure 1, provided retention of the original configuration at the anomeric center of the resultant glycosyl carborane (**1**).

Hydroxymethyl carborane was found to undergo BF_3·OEt_2 catalyzed addition to di-*O*-acetyl-D-xylal, and the waxy white solid thus produced was isolated in 90% yield (Figure 2). In the same manner, several other hydroxyalkyl carboranes reacted with tri-*O*-acetyl-D-glucal to give

(1) Throughout this paper, the term carborane or 1,2-dicarba-*closo*-dodecaborane refers to an icosahedron with carbon at two adjacent vertices and boron at the remaining ten. Unsubstituted carborane has the formula $C_2B_{10}H_{12}$ with one hydrogen attached to each of the heavier atoms.

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(3) (a) Goldenberg, D. M.; DeLand, F.; Kim, E.; Bennett, S.; Primus, F. J.; van Nagell, J. R., Jr.; Estes, N.; DeSimone, P.; Rayburn, P. *New England J. Med.* **1978**, *298*, 1384. (b) Kim, E. E.; DeLand, F. H.; Casper, S.; Primus, F. J.; Goldenberg, D. M. *Cancer* **1980**, *45*, 1243. (c) Van Nagell, J. R., Jr.; Kim, E.; Casper, S.; Primus, F. J.; Bennett, S.; DeLand, F. H.; Goldenberg, D. M. *Cancer Res.* **1980**, *40*, 502. (d) Goldenberg, D. M.; Primus, F. J.; Kim, E.; Casper, S.; Corgan, R. L.; DeLand, F. *In The Clinical Biochemistry of Cancer*, Fleisher, M., Ed.; The Amer. Assoc. Clinic. Chem.: Winston-Salem, NC, 1979; pp 155–167. (e) Goldenberg, D. M.; Kim, E. E.; DeLand, F. H.; Bennett, S.; Primus, F. J. *Cancer Res.* **1980**, *40*, 2984. (f) Goldenberg, D. M.; Kim, E. E.; DeLand, F. H.; Spremulli, E.; Nelson, M. O.; Gockerman, J. P.; Primus, F. J.; Corgan, R. L.; Alpert, E. *Cancer* **1980**, *45*, 2500. (g) Goldenberg, D. M.; Kim, E. E.; DeLand, F. H.; van Nagell, J. R., Jr.; Javadpour, N. *Science (Washington, D.C.)* **1980**, *208*, 1284. (h) Javadpour, N.; Kim, E. E.; DeLand, F. H.; Salyer, J. R.; Shah, U.; Goldenberg, D. M. *J. Am. Med. Assoc.* **1981**, *246*, 45.

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(5) (a) Ferrier, R. J. *Methods in Carbohydrate Chemistry*; Whistler, R. L., BeMiller, J. N., Eds.; Academic: New York, 1967; Vol. VI, p 307. (b) Hanessian, S.; Banoub, J. *Carbohydr. Res.* **1977**, *59*, 261. (c) Wulff, G.; Röhle, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*(3), 157.

(6) Purchased from Aldrich Chemical Company, Inc., Milwaukee, WI.

(7) Prepared by a modification of the method described by: Weygand, F. *Methods in Carbohydrate Chemistry*; Whistler, R. L., Wolfrom, M. L., Eds.; Academic: New York, 1962; Vol. I, p 182.

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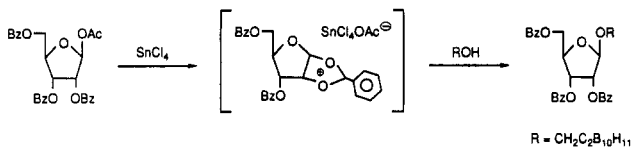


Figure 1. Mechanism of formation of a ribofuranosyl carborane (1).

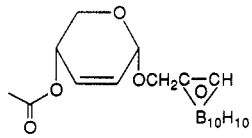
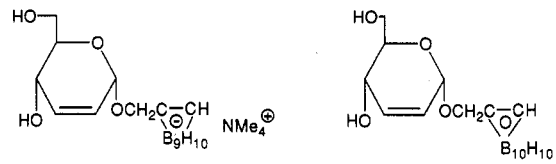


Figure 2. Structure of 1-[(4-*O*-acetyl-2,3-dideoxy-α,β-D-*erythro*-pent-2-enopyranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (2).

the corresponding 2,3-unsaturated pyranosides in good yield (70–90%). In agreement with previous reports,[5a] we found the α anomer to be the predominant product. The data presented in Table I show that this anomeric selectivity is dependent on the length of the alkyl chain which separates the hydroxyl group from the carborane cage. In this vein, (hydroxymethyl)-*o*-carborane reacts with tri-*O*-acetyl-D-glucal to give a crude product that is 90% α anomer while the relative predominance of the α anomer decreases to 77% in the product formed by the reaction of 1-(3-hydroxypropyl)-2-methyl-*o*-carborane. Previous work has shown that the relative amount of α anomer produced increases with increasing size of the alcohol. The trend we observed is consistent with the fact that the carborane cage is a large group, and its steric requirements should dominate reactions of the hydroxymethyl derivative to a greater extent than those of the 3-hydroxypropyl derivatives. In contrast to a procedure for the addition of simple alcohols to carbohydrate glycals described by Ferrier,[5a] we found that only a catalytic amount of $BF_3 \cdot OEt_2$ was required for the reactions described here. In fact, as little as 10 mol % of $BF_3 \cdot OEt_2$ led to significant addition of the hydroxyalkyl carborane across the double bond of the glycal.

The γ-gauche effect,[8] which has been observed in cyclohexanes and *C*-glycosides, is present to a limited extent in the 2,3-unsaturated pyranosides decribed here. The less shielded anomer is assigned the β (cis) configuration. In α-**4**, this carbon appears at 94.66 ppm in the ^{13}C NMR spectrum, while the anomeric carbon of the β anomer is found at 95.81 ppm. This chemical shift difference of ~1 ppm between the anomeric carbons of the two anomers is typical of the ^{13}C NMR spectra of compounds **2–7**.

Compound **8** was prepared by ethanolic potassium hydroxide degradation of **3**, and subsequent conversion to the tetramethylammonium salt, and is shown in Figure 3. In contrast to the tetramethylammonium salts of other *nido*-carborane monoanions,[9] **8** showed surprising water solubility, and 1.3 g was recrystallized from only 40 mL of hot H_2O. The acetyl groups of **3** were hydrolyzed during the cage degradation, and the resulting hydroxyl groups are presumed to be primarily responsible for increasing the relative water solubility of **8**. This hydrophilicity should play a critical role in increasing the water solubility of carborane-containing antibody conjugates. In addition to these expected reactions, epimerization at the anomeric



8 **9**

Figure 3. Structure of tetramethylammonium salt of 1-[(2,3-dideoxy-α-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarba-dodecahydroundecaborate(1–) ion (**8**) and 1-[(2,3-dideoxy-α-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (**9**).

Table II. Chemical Shifts and Coupling Interactions from ^1H and ^{13}C NMR Spectra of 3

^1H δ	$J_{H,H}$ (Hz)	^{13}C δ	assign[a]
5.78	10.3, 1.7, 1.5	130.35	2
5.49	10.3, 2.1, 2.7	125.89	3
5.22	9.8, 2.1, 1.6	64.89	4
4.61	2.6, 1.7	93.69	1
4.12	12.2, 2.4	62.73	6
4.08	12.2, 6.2	62.73	6
3.97	10.6	69.74	11
3.90	9.8, 6.1, 2.4	67.80	5
3.56	10.6	69.74	11
3.57		57.84	12
1.89		20.39	9[b]
1.85		20.30	10[b]
		170.15	7[c]
		169.67	8[c]

[a] See Figure 4. [b] These two assignments may be reversed without significantly affecting the spectral analysis. [c] These two assigments may be reversed without significantly affecting the spectral analysis.

carbon was also observed. While **3** was essentially 100% α anomer, **8** was approximately 57% α and 43% β anomers; the relative abundance of both anomers was confirmed by ^1H and ^{13}C NMR. We initially sought to prepare compound **9** (Figure 3) by treating **3** with $LiAlH_4$ in diethyl ether, but several such attempts resulted in repeated isolation of starting material. This compound was eventually prepared by K_2CO_3-catalyzed hydrolysis of the acetate groups in ethanol, at room temperature. As expected, **9** was more polar than the precursor **3**; it dissolved readily in ethanol and was recrystallized from chloroform, while **3** was quite soluble in chloroform. Particularly important is the fact that these acetyl groups were removed under mild conditions. This method of deprotection would provide maximum flexibility in the deprotection of the hydroxyl groups of glycosyl carborane containing antibody conjugates.

The ^1H and ^{13}C NMR spectra of compounds **3–7** are similar, since all of these compounds share the 4,6-di-*O*-acetyl-2,3-dideoxy-2-hexenopyranosyl subunit. To increase our understanding of these spectra, we chose to analyze the spectra of the least complex member of the series, **3**, more completely. Comparison of ^1H NMR spectra obtained from solvent mixtures of benzene and chloroform (5:95 $C_6D_6/CDCl_3$ to 55:45 $C_6D_6/CDCl_3$ as well as 100% C_6D_6 and 100% $CDCl_3$) showed that 45:55 $C_6D_6/CDCl_3$ gave the best separation of discrete proton signals in the critical 4.5–3.5 ppm region. Consequently, this solvent mixture was employed in further studies.

Comparison of the 200- and 500-MHz proton NMR spectra of **3**, combined with selective decoupling experiments, allowed us to determine coupling constants for all protons except the anomeric proton (4.61 ppm). These coupling constants are shown in Table II. Because each of the four protons above 4.5 ppm have two small coupling

(8) *Anomeric Effect—Origin and Consequences*; Szarek, W. A., Horton, D., Eds.; ACS Symposium Series 87; American Chemical Society; Press: Washington, D.C., 1979.
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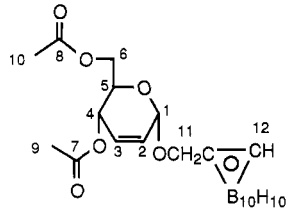

Figure 4. 1-[(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (3).

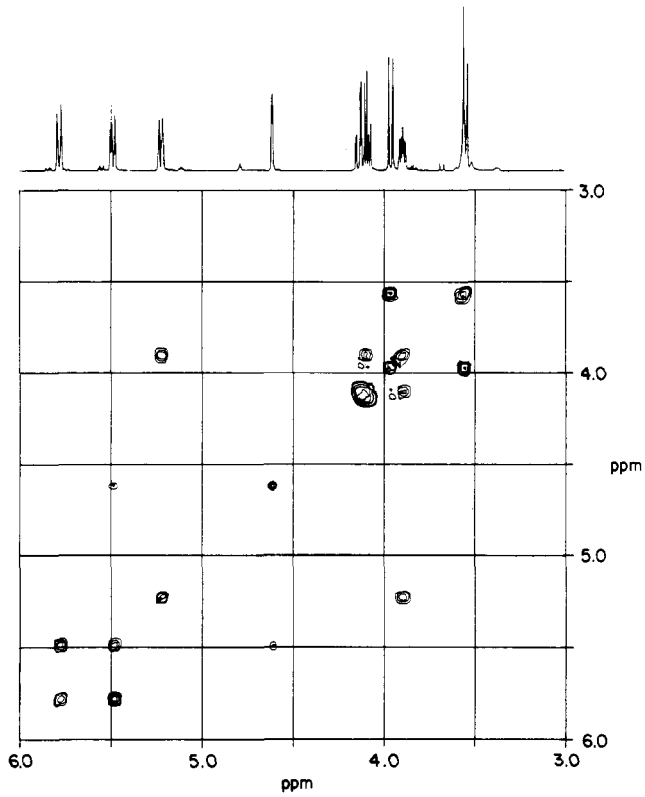

Figure 5. Partial 2D ^{1}H NMR COSY spectrum of 3.

constants (J < 3 Hz), unequivocal assignment of each coupling interaction based on these experiments was not possible. The anomeric proton appears as a broad singlet, while the signals at 5.78 and 5.49 ppm are apparent doublets of triplets. Homonuclear irradiation at the frequency of the anomeric proton produced a partially decoupled spectrum in which the signals at 5.78 and 5.49 ppm collapsed to doublets of doublets, J = 10.3, 1.5 and J = 10.3, 2.7, respectively.

In addition to the one-dimensional spectra, several two-dimensional (2D) spectra were obtained. A carbon–proton heteronuclear shift correlation experiment[10] allowed the determination of carbon–hydrogen connectivities in a straightforward manner. These connectivities are summarized in Table II. The spectra previously described made it possible to assign the resonance due to each atom, except the alkene carbons and hydrogens. Although we had determined that the carbon at δ 130.35 was bonded to the hydrogen at δ 5.78, final assignment of these resonances to either the 2- or 3-position (Figure 4) was not obvious.

Proton–proton coupling interactions (particularly those of the signals at δ 5.78, 5.49, 5.22, and 4.61) were further investigated in two 2D ^{1}H NMR COSY experiments. The first, a standard 2D ^{1}H NMR COSY,[11] confirmed much

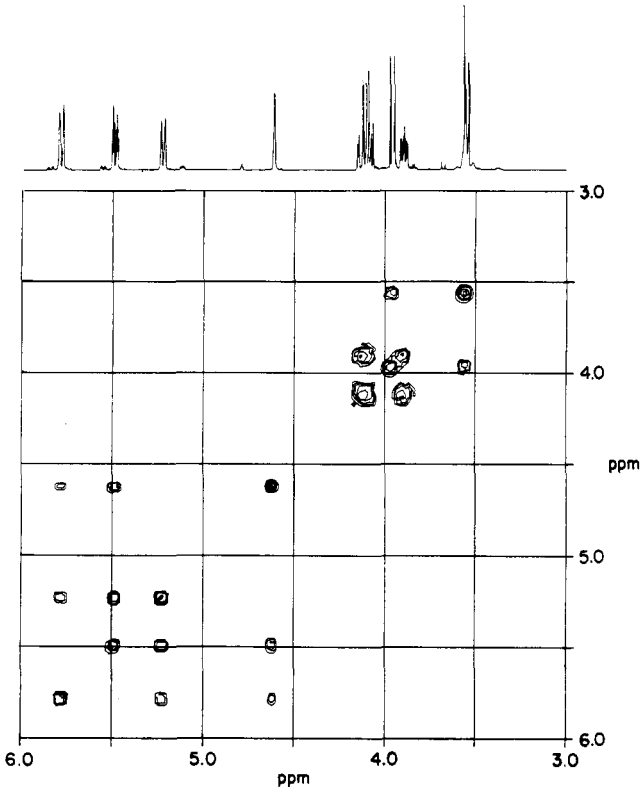

Figure 6. Partial 2D ^{1}H NMR COSY 45 spectrum of 3.

of the information found in the one-dimensional spectra (Figure 5). Strong coupling interactions were observed for the following pairs of signals: δ 5.78 and 5.49; δ 5.22 and 3.90; δ 4.12 and 4.08; δ 4.12 and 3.90; δ 4.08 and 3.90; δ 3.97 and 3.56. Weaker coupling interactions between the signals at δ 5.49 and 5.22 were also apparent. In addition, this spectrum showed a cross peak between the signals at δ 5.49 and 4.61 (anomeric proton).

A second 2D ^{1}H NMR COSY experiment, modified to enhance signals due to long-range coupling interactions[12] yielded some very useful information. Figure 6 shows that as expected, many of the cross peaks previously observed from two-bond or three-bond coupling interactions decreased in intensity or completely disappeared. This is dramatically apparent when the cross peaks between δ 5.22 and 3.90 or δ 5.78 and 5.49 in the two 2D ^{1}H NMR COSY spectra are compared. Cross peaks between the signals at δ 5.78 and 5.22, δ 5.78 and 4.61, and δ 5.49 and 5.22 were seen for the first time in this spectrum. With this information, we were able to assign coupling constants to the anomeric proton, even though these were not directly measured.

Finally, we used a second carbon–proton heteronuclear shift correlation experiment, which was designed to suppress one-bond C–H couplings and enhance long-range coupling interactions,[13] in order to assign the resonances due to the 2- and 3-positions. The information obtained from this spectrum is summarized in Table III. The crucial information concerns the long-range coupling interactions of H-1, H-2, and H-3. H-1, the anomeric proton, showed strong coupling to the carbon at δ 130.35 and weaker coupling to the signal at δ 125.89. H-2, δ 5.78, showed strong coupling to the anomeric carbon, while H-3,

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(11) Nagayama, K.; Kumar, A.; Wüthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321.

(12) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542.

(13) Kessler, H.; Griesinger, C.; Zarbok, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.

Table III. $^{2,3}J_{CH}$ Coupling Interactions As Observed by 2D NMR

positn of atom[a]		
H	C	peak intensity
1	2	strong
	3	weak
	11	weak
	5	strong
2	1	strong
	5	weak
3	1	weak
	4	strong
4	2	strong
	3	strong
	5	medium
	4	medium
	6	weak
5	5	medium
6 (H_a)	6	strong
6 (H_b)	6	weak
	5	weak
11 (H_a)	11	strong
11 (H_b)	11	strong

[a] See Figure 4.

Table IV. Calculated Chemical Shifts and Coupling Constants Using PANIC Spectral Simulation of a Partial ^{1}H NMR Spectrum of 3

chem shift (ppm)	assignm[a]	coupling consts (Hz)
5.78	2	J_{12} = 1.14; J_{23} = 10.25; J_{24} = −1.55
5.49	3	J_{13} = −2.04; J_{23} = 10.25; J_{34} = 2.99
5.22	4	J_{24} = −1.55; J_{34} = 2.99; J_{45} = 9.73
4.61	1	J_{12} = 1.14; J_{13} = −2.04

[a] See Figure 4.

δ 5.49, had a weak interaction with this carbon and strong coupling to C-4, δ 64.89.

All of the spectral information, from both 1-D and 2-D experiments, is thus consistent with the assignment alluded to in the previous paragraph; specifically, the two atoms at the 2-position resonate at δ 130.35 in the carbon spectrum and δ 5.78 in the proton spectrum, while the carbon and hydrogen at the 3-position appear at 125.89 and 5.49 ppm, respectively. As a final check of this assignment, the downfield portion of the ^{1}H NMR spectrum was subjected to PANIC spectral analysis.[14] Both the magnitudes and signs of the coupling constants generated as the calculated, theoretical PANIC spectrum are entirely consistent with the aforementioned assignments (Table IV).

Conclusion

The synthetic methods described here provide a simple and effective route to *O*-glycosyl carboranes. These methods are particularly attractive, since mild reaction conditions proceed cleanly to give high yields (70–90%) of the desired products. The enhanced water solubilities of many of these new carborane derivatives make them attractive candidates for inclusion in the structures of antibody modification reagents.

Experimental Section

General Data. Except as noted, all experiments were run in oven-dried glassware under a positive pressure of dry argon. Solvents were distilled under nitrogen from an appropriate drying agent: benzene from potassium and dichloromethane from phosphorus pentoxide. Ethanol was reagent grade, 95%. BF_3·OEt_2 was distilled once from commercial grade boron trifluoride etherate and redistilled only when discolored. Ethyl acetate, hexane, and acetonitrile were reagent grade (certified ACS), as supplied by Fisher. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. In many instances, these analyses were in close agreement with the theoretical values of the percentages of carbon and hydrogen present in the molecule, but consistently underestimated the relative amount of boron present, when compared with theoretical values. Nonetheless, all other physical characterization data obtained were consistent with the proposed structures. Infrared spectra were recorded on a Beckman 1100 FT-IR spectrometer. The following abbreviations are used to describe IR spectra: w, weak; m, medium; s, strong; v, very; b, broad.

Proton (^{1}H NMR) and carbon (^{13}C NMR) spectra were obtained on a Bruker AM 500, at 500.13 and 125.76 MHz, respectively. Additional proton spectra were obtained by using a Bruker AF 200 spectrometer at 200.13 MHz. Boron (^{11}B NMR) spectra were obtained at 160.46 MHz on a Bruker AM 500 spectrometer. Chemical shifts are reported in parts per million on the δ scale. Internal reference standard of Me_4Si (0.00) for the proton and carbon spectra was used, along with external reference to BF_3·OEt_2 (0.00) for the boron spectra. The following abbreviations are used to describe NMR signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The prefix br indicates a broad signal. Spin–spin coupling constants are reported in hertz (Hz).

Optical rotations were measured in a 1-dm cel of 5-mL capacity, using a Perkin-Elmer 241 MC polarimeter. Analytical thin-layer chromatography was performed on precoated silica gel 60 F_{254} plastic plates, 0.2 mm thickness, as obtained from Merck. TLC plates, usually precut to 2 × 6.6 cm, were visualized by dipping the plate in an aqueous $AgNO_3$ solution, rinsing with distilled water, and drying in air. Column chromatography was performed by using Merck Kiesegel 60, (63-200 μm). Isocratic gravity elution was used in all cases. Peaks were visualized by TLC, as previously described.

All solvent evaporation was accomplished by using a Buchi-Brinkman rotary evaporator at or below 40 °C. Removal of solvent in vacuo refers to evaporation at or below 5 mmHg. The solvent system used for chromatography is (A) 20:80 ethyl acetate/hexane.

Compounds 3–7 were synthesized by the following general procedure: A solution of the carboranyl alcohol in benzene was prepared (usually ~0.1 M). Tri-*O*-acetyl-D-glucal was added to this solution. After the solution was stirred for 10–15 min, 15–25 μL of BF_3·OEt_2 was added. The reaction was stirred at room temperature for 30–45 min. Anhydrous $NaHCO_3$ (0.5–1.0 g) was added and the mixture stirred for 10–15 min. The reaction was then filtered and concentrated in vacuo.

1-[(2,3,5-Tri-*O*-benzoyl-D-ribofuranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (1). A modification of the general procedure for O-glycosylation, described by Hanessian,[5b] was employed. A 0.1 M solution of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (2.18 g, 4.0 mmol) in dichloromethane was chilled to 5 °C. After addition of $SnCl_4$ (0.47 mL), the solution was stirred at room temperature for 10 min. 1-(Hydroxymethyl)-1,2-dicarba-*closo*-dodecaborane (0.7 g, 4.0 mmol) was added, and the mixture stirred an additional 2 h at room temperature. The reaction was diluted with 50 mL of CH_2Cl_2 and poured into a separatory funnel containing 100 mL of saturated aqueous sodium bicarbonate. The aqueous layer was further washed with two 60-mL portions of CH_2Cl_2. The organic portions were combined, dried over $MgSO_4$, and concentrated to give a syrup. This syrup was purified by column chromatography. Removal of solvent in vacuo produced a waxy, white solid (2.00 g, 81%): mp 57–59 °C; $[\alpha]^{23}_D$ +21.3° (*c* 10, $CHCl_3$). IR (neat melt): 3065 (m), 2951 (w), 2591 (s), 1726 (vs), 1601 (m), 1585 (w), 1452 (m), 1316 (m), 1265 (vs), 1177 (m), 1118–1104 (vs br), 1069 (s), 1025 (s), 969 (m br), 878 (w), 805 (w), 711 (s), 686 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.20–8.00 (6 H, m), 7.75–7.43 (9 H, m), 5.89 (1 H, dd, *J* = 5.6), 5.81 (1 H, d, *J* = 1.5), 5.23 (1 H, s), 4.84 (2 H, m), 4.67 (1 H, dd, *J* = 6.13), 4.30 (1 H, d, *J* = 11), 4.06 (1 H, d, *J* = 11), 3.96 (1 H, br s, whh = 7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.09, 165.42, 165.22, 133.79, 133.67, 133.50, 129.78, 129.71, 129.68, 129.60, 129.57, 128.74,

(14) The 86.3004 version of PANIC, as supplied by Bruker Instruments, was used for spectral simulation of ^{1}H NMR spectra which were obtained on a Bruker AM500 spectrometer.

128.71, 128.58, 128.48, 105.79 (anomeric carbon), 80.02, 75.15, 71.83, 69.43, 64.18, 58.27. Anal. Calcd for $B_{10}C_{29}H_{34}O_8$: C, 56.30; H, 5.50; B, 17.49. Found: C, 57.00; H, 5.55; B, 18.10.

1-[(4-*O*-Acetyl-2,3-dideoxy-α,β-D-*erythro*-pent-2-enopyranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (2). 3,4-Di-*O*-acetyl-D-xylal (1.75 g, 8.75 mmol) was added to a solution of 1-(hydroxymethyl)-1,2-dicarba-*closo*-dodecaborane (1.39 g, 7.95 mmol) in benzene, followed by 15 μL of BF_3·OEt_2. The resulting syrup (α:β = 8.0:2.0) was purified by column chromatography to give a syrup which solidified in vacuo to give a white solid (2.25 g, 90.0%), mp 86.5–90 °C. IR (film): 3080 (m), 3060 (m), 2938 (w), 2925 (w), 2887 (w), 2591 (vs), 1736 (s), 1448 (w), 1406 (m), 1372 (m), 1236 (vs), 1193 (m), 1112 (m), 1061 (s), 1045 (s), 1007 (s), 983 (s), 960 (s), 723 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.08 (1 H, dd, J = 10.1, 5.4), 5.91 (1 H, dd, J = 10.1, 3.0), 4.95–4.86 (2 H, m), 4.11 (1 H, d, J = 10.9), 3.95 (1 H, dd, J = 12.9, 2.8), 3.89 (1 H, dd, J = 10.9, 2.3), 3.83 (1 H, br s), 3.80 (1 H, br d, J = 12.9), 2.10 (3 H, s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.49, 129.06, 126.20, 93.21 (anomeric carbon), 68.93, 62.66, 61.74, 57.83, 21.01 (α anomer). Resonances assigned to the β-anomer are δ 130.38, 127.33, 94.18 (anomeric carbon), 64.46, 60.44, and 20.94. Anal. Calcd for $B_{10}C_{10}H_{22}O_4$: C, 38.21; H, 7.05; B, 34.38. Found: C, 38.13; H, 7.05; B, 32.60.

1-[(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarba-*closo*-dodecaborane (3). Tri-*O*-acetyl-D-glucal (2.45 g, 9.0 mmol) was added with stirring to a solution of 1-(hydroxymethyl)-1,2-dicarba-*closo*-dodecaborane (1.5 g, 8.6 mmol) in 60 mL of benzene. Upon complete dissolution, BF_3·OEt_2 (20 μL) was added. The solution was filtered and concentrated to give a colorless syrup (α:β = 9:1). Chromatography (solvent A) gave a colorless syrup that solidified when residual solvent was removed (2.99 g, 90%). Recrystallization from hot *n*-hexane gave white prismatic crystals: mp 74–76 °C; $[\alpha]^{23}_D$ +36.3° (*c* 10, EtOH). IR (neat melt): 3066 (m), 2950 (w), 2929 (w), 2587 (vs), 1743 (vs), 1371 (s), 1229 (vs), 1047 (vs br), 1011 (s br), 911 (m), 725 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.95 (1 H, br d, J = 10.2), 5.78 (1 H, ddd, J = 10.2, 2.2, 2.7), 5.27 (1 H, ddd, J = 9.8, 2.2, 2.8), 4.99 (1 H, br s, whh = 6 Hz), 4.22 (1 H, d, J = 10.6), 4.23–4.14 (2 H, m), 3.99–3.96 (1 H, m), 3.94 (1 H, d, J = 10.6), 2.11 (3 H, s), 2.10 (3 H, s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.66, 170.14, 130.62, 126.03, 94.01 (anomeric carbon), 69.03, 67.85, 65.02, 62.89, 57.78, 20.93, 20.77. ^1H NMR (45:55 C_6D_6/$CDCl_3$): δ 5.78 (1 H, ddd, J = 10.3), 5.49 (1 H, ddd, J = 10.3), 5.22 (1 H, ddd, J = 9.8, 2.1, 1.6), 4.61 (1 H, br s), 4.12 (1 H, dd, J = 12.2, 2.4), 4.08 (1 H, dd, J = 12.2, 6.2), 3.97 (1 H, d, J = 10.6), 3.90 (1 H, ddd, J = 9.8, 6.2, 2.4), 3.56 (1 H, d, J = 10.6), 3.57 (1 H, br s), 1.89 (3 H, s), 1.85 (3 H, s). $^{13}C\{^1H\}$ NMR (45:55 C_6D_6/$CDCl_3$): δ 170.152, 169.666, 130.349, 125.878, 93.694 (anomeric carbon), 68.744, 67.799, 64.887, 62.725, 57.644, 20.386, 20.297. $^{11}B\{^1H\}$ NMR (H_3CCOCH_3): δ −2.71 (1 B, d), −4.69 (1 B, d), −9.06 (2 B, d), −11.09 (2 B, d), −12.70 (4 B). Anal. Calcd for $B_{10}C_{13}H_{26}O_6$: C, 40.36; H, 6.78; B, 24.84. Found: C, 39.60; H, 6.73; B, 23.97.

All two-dimensional ^1H NMR and ^{13}C NMR experiments were carried out on a Bruker AM500, using standard software and equipment. The 2D ^1H NMR COSY experiment[11] was performed by using a spectral width of 4032 Hz, and eight scans were acquired for each of 256 experiments. Zero-filling in the F1 dimension gave a 1K × 512W data matrix. This experiment employed the following pulse sequence: RD–90°–τ_1–90°–τ_2–FID. The ^1H NMR COSY45 experiment[12] also had a spectral width of 4032 Hz. A total of 256 experiments, each consisting of eight scans, were acquired by using the pulse sequence RD–90°–τ_1–45°–τ_2–FID, where τ_2 was optimized for coupling constants of 6 Hz.

The two $^{13}C\{^1H\}$ heteronuclear shift correlation experiments were carried out with spectral widths in the F1 and F2 dimensions of 2001 and 21 739 Hz, respectively. Zero-filling in the F1 dimension produced data matrices of 4K × 512W. The experiment that identified $^1J_{CH}$ couplings used the following pulse sequence:[10]

^1H RD–90–τ–180–τ–τ_2–90–τ_3–BB

^{13}C RD–90–τ–180–τ–τ_2–90–τ_3–FID

A modification of this pulse sequence, in which τ_2 and τ_3 were optimized for $J \approx 6.0$ Hz, was used in a second heteronuclear shift correlation experiment, to investigate long-range ($^2J_{CH}$ and $^3J_{CH}$) coupling interactions.[13]

1-[(4,6-Di-*O*-acetyl-2,3-dideoxy-α,β-D-*erythro*-hex-2-enopyranosyl)ethyl]-1,2-dicarba-*closo*-dodecaborane (4). A solution of 1-(2-hydroxyethyl)-1,2-dicarba-*closo*-dodecaborane (1.6 g, 4.0 mmol) in benzene was prepared. 3,4,6-Tri-*O*-acetyl-D-glucal (1.56 g, 5.7 mmol) was added to this solution, followed by 15 μL of BF_3·OEt_2. The resulting syrup (α:β ≅ 8.7:1.3) was purified by column chromatography, without separation of anomers, to give a colorless syrup (1.60 g, 83%). IR (film): 3060 (m), 2952 (m), 2941 (m), 2890 (m), 2593 (vs), 1734 (vs), 1653 (w), 1430 (m), 1371 (m), 1229 (vs br), 1187 (m), 1104 (s), 1071 (vs br), 1048 (vs br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.91 (1 H, d, J = 10.2), 5.77 (1 H, d, J = 10.2), 5.28 (1 H, d, J = 9.2), 4.98 (1 H, br s, whh = 5 Hz), 4.24–4.17 (2 H, m), 3.99–3.89 (2 H, m), 3.83 (1 H, br s), 3.61–3.58 (1 H, m), 2.60–2.49 (2 H, m), 2.11 (3 H, s), 2.10 (3 H, s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.71, 170.19, 129.88, 126.89, 94.66 (anomeric carbon), 72.88, 67.56, 66.39, 65.12, 62.97, 60.32, 37.61, 20.95, 20.79 (α anomer). Resonances that are assigned to the β anomer are δ 129.30, 128.04, 95.81 (anomeric carbon), 73.05, 65.38, 64.20, 37.46, and 20.79. Anal. Calcd for $B_{10}C_{14}H_{28}O_6$: C, 41.99; H, 7.05; B, 27.09. Found: C, 41.98; H, 7.01; B, 25.38.

1-[(4,6-Di-*O*-acetyl-2,3-dideoxy-α,β-*erythro*-hex-2-enopyranosyl)ethyl]-2-methyl-1,2-dicarba-*closo*-dodecaborane (5). 3,4,6-Tri-*O*-acetyl-D-glucal (0.91 g, 3.4 mmol) was added to a solution of 1-(2-hydroxyethyl)-2-methyl-1,2-dicarba-*closo*-dodecaborane (0.56 g, 2.8 mmol) in benzene, followed by the addition of 20 μL of BF_3·OEt_2. The resulting syrup (α:β = 8.2:1.8) was purified by column chromatography without the separation of anomers to give a colorless syrup (0.80 g, 70.0%). IR (film): 3018 (w), 2948 (m), 2889 (m), 2583 (vs), 1742 (vs), 1670 (w), 1432 (s), 1370 (s), 1229 (vs br), 1048 (vs br), 977 (s br), 910 (m), 756 (m), 730 (m), cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.90 (1 H, d, J = 10.1), 5.80 (1 H, dd, J = 1.9, 10.2), 5.29 (1 H, d, J = 9.7), 5.02 (1 H, br s), 4.24–4.17 (2 H, m), 4.07–4.03 and 3.98–3.96 (2 H, m), 3.64–3.62 (1 H, m), 2.56–2.51 (2 H, m), 2.12 (3 H, s), 2.10 (3 H, s), 2.08 (3 H, s) (α anomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.74, 170.20, 129.64, 127.21, 94.65 (anomeric carbon), 75.40, 74.76, 72.98, 67.36, 66.75, 65.20, 63.04, 35.06, 23.29, 20.95, 20.83 (α anomer). Resonances assigned to the β anomer are δ 127.07, 95.66 (anomeric carbon), 66.25, 64.18, 63.26, 62.56, 34.96, and 20.80. Anal. Calcd for $B_{10}C_{15}H_{30}O_6$: C, 43.47; H, 7.29; B, 26.08. Found: C, 43.37; H, 7.08; B, 23.77.

1-[(4,6-Di-*O*-acetyl-2,3-dideoxy-α,β-D-*erythro*-hex-2-enopyranosyl)propyl]-1,2-dicarba-*closo*-dodecaborane (6). A solution of 1-(3-hydroxypropyl)-1,2-dicarba-*closo*-dodecaborane (1.01 g, 5.0 mmol) in benzene was prepared. 3,4,6-Tri-*O*-acetyl-D-glucal (1.52 g, 5.6 mmol) was added, followed by 15 μL of BF_3·OEt_2. The resulting syrup (α:β = 8.2:1.8) was chromatographed without separation of anomers to give a colorless syrup (1.6 g, 77%). IR (film): 3059 (m), 2956 (m), 2935 (m), 2588 (vs), 1743 (vs), 1450 (m), 1437 (m), 1413 (w), 1371 (s), 1337 (w), 1240 (vs), 1188 (m), 1101 (s), 1048 (vs), 1018 (vs), 984 (m), 909 (w), 805 (w), 725 (m), 604 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.90 (1 H, br d, J = 10.2), 5.80 (1 H, ddd, J = 10.2), 5.31 (1 H, ddd, J = 9.6, 1.5, 3.0), 4.97 (1 H, br s), 4.26 (1 H, dd, J = 12.0, 5.4), 4.17–4.12 (1 H, m), 4.05–3.96 (1 H, m), 3.78–3.70 (1 H, m), 3.62 (1 H, br s), 3.54–3.40 (1 H, m), 2.37–2.28 (2 H, m), 2.10 (6 H, s), 1.86–1.72 (2 H, m). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.70, 170.22, 129.43, 127.36, 94.45 (anomeric carbon) 67.13, 67.03, 65.28, 63.01, 61.40, 35.24, 21.94, 20.97, 20.82 (α anomer). Anal. Calcd for $B_{10}C_{15}H_{30}O_6$: C, 43.47; H, 7.29; B, 26.08. Found: C, 43.62; H, 7.55; B, 25.04.

1-[(4,6-Di-*O*-acetyl-2,3-dideoxy-α,β-D-*erythro*-hex-2-enopyranosyl)propyl]-2-methyl-1,2-dicarba-*closo*-dodecaborane (7). A solution of 1-(3-hydroxypropyl)-2-methyl-1,2-dicarba-*closo*-dodecaborane (0.52 g, 2.40 mmol) in benzene was prepared. 3,4,6-Tri-*O*-acetyl-D-glucal (0.72 g, 2.64 mmol) was added to this solution, followed by 15 μL of BF_3·OEt_2. The resulting syrup (α:β = 7.7:2.3) was purified by column chromatography, without separation of anomers to give a colorless syrup (0.80 g, 78%). IR (film): 3071 (w), 3055 (w), 2949 (m), 2895 (m), 2886 (m), 2584 (vs), 1743 (vs), 1650 (w), 1449 (m), 1370 (s), 1229 (vs br), 1187 (m), 1102 (s), 1033 (s), 990 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.90 (1 H, br d, J = 10.1), 5.80 (1 H, dt, J = 10.1), 5.31 (1 H, dd, J = 9.6, 1.4), 5.00 (1 H, br s), 4.27 (1 H, dd, J = 12.2, 5.1), 4.20–4.13 (1 H, dd, J = 12.2, 2.4), 4.07–3.99 (1 H, m), 3.86–3.75 (1 H, m), 3.55–3.44 (1 H, m). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.69, 170.22, 129.39, 127.44, 94.46, (anomeric carbon) 67.32, 67.08, 65.26, 63.00, 32.32,

29.81, 23.13, 20.96, 20.81 (α anomer). The resonances assigned to the β anomer is δ 95.51. Anal. Calcd for $B_{10}C_{16}H_{32}O_6$: C, 44.85; H, 7.53; B, 25.23. Found: C, 45.10; H, 7.42; B, 25.20.

1-[(2,3-Dideoxy-*erythro*-hex-2-enopyranosyl)methyl]-1,2-dicarbadodecahydroundecaborate(1-) ion (8). The potassium salt of this monoanion was prepared by a general degradation procedure.[9] **3** (1.14 g, 2.95 mmol) was refluxed in ethanolic KOH (0.45 g, 0.5 M) for 20 h. The potassium salt was dissolved in water and converted to the tetramethylammonium salt by the addition of an excess of Me_4NCl. This salt was recrystallized from water to give white plates (0.79 g, 73%). IR (Nujol mull): 3480-3460 (br m), 2525 (vs), 1088 (w), 1035 (s), 1020 (s br), 949 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 5.88 (1 H, br d, J = 10.2), 5.68 (1 H, br d, J = 10.2), 5.00 and 4.90 (1 H, 2 br s), 4.10-4.01 (2 H, m), 3.82-3.56 (6 H, m), 3.45 (12 H, s), 3.35 (1 H, s), -2.6 (1 H, br s). ^{13}C NMR (MeOH-d_4): δ 132.79, 132.68, 125.79, 125.76, 92.96, 92.31, 75.47, 74.65, 71.71, 71.68, 62.39, 60.85, 60.81, 54.36, 54.33, 54.30. ^{11}B NMR (acetone): δ -9.91 (4 B, d, J = 135), -10.69 (1 B, d), -11.01 (1 B, d), -14.38 (1 B, d, J = 167), -22.48 (2 B, d, J = 147), -32.82 (2 B, d, J = 121), -37.15 (2 B, d, J = 137). MS: cluster of peaks between m/e 289 and 294, with most intense peak at m/e 292. This m/e corresponds to $^{10}B_1{}^{11}B_8C_9H_{22}O_4$.

1-[(2,3-Dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-methyl]-1,2-dicarba-*closo*-dodecaborane (9). K_2CO_3 (1.60 g, 11.6 mmol) was dissolved in 50 mL of 90% EtOH, with gentle heating. After the solution was cooled to room temperature, 2.01 g (5.20 mmol) of **3** was added. This solution was stirred overnight and concentrated in vacuo. The solid thus produced was washed with 3 × 15 mL H_2O and recrystallized from chloroform (0.97 g, 62%): mp 143-144.5 °C. IR (Nujol mull): 3330-3274 (br s), 3080 (m), 3060 (m), 2591-2569 (br s), 1409 (w), 1326 (m), 1305 (m), 1245 (w), 1180 (w), 1124 (m), 1095 (w), 1046 (s), 989 (m), 984 (m), 959 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 5.97 (1 H, br d, J = 10.1), 5.70 (1 H, ddd, J = 10.1), 5.03 (1 H, br s), 4.30 (1 H, d, J = 11.4), 4.12 (1 H, d, J = 11.4), 4.01 (1 H, m), 3.86-3.76 (2 H, m), 3.65-3.61 (2 H, m), 2.81 (2 H, br s, exchanges with D_2O). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 135.28, 124.08, 93.41, 74.39, 73.25, 68.22, 62.17, 61.06, 60.64. Anal. Calcd for $B_{10}C_9H_{22}O_4$: C, 35.77; H, 7.27; B, 35.77. Found: C, 35.31; H, 7.29; B, 35.42.

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Registry No. 1, 117162-37-5; α-**2**, 117162-38-6; β-**2**, 117162-39-7; α-**3**, 117162-40-0; β-**3**, 117162-41-1; α-**4**, 117162-42-2; β-**4**, 117183-74-1; α-**5**, 117162-43-3; β-**5**, 117162-44-4; α-**6**, 117162-45-5; β-**6**, 117162-46-6; α-**7**, 117162-47-7; β-**7**, 117162-48-8; **8**, 91946-38-2; **9**, 117162-49-9; $HOCH_2$-*o*-$C_2B_{10}H_{10}$-H, 19610-34-5; $HOCH_2CH_2$-*o*-$C_2B_{10}H_{10}$-H, 23835-95-2; $HOCH_2CH_2$-*o*-$C_2B_{10}H_{10}$-CH_3, 20644-51-3; $HO(CH_2)_3$-*o*-$C_2B_{10}H_{10}$-H, 23835-93-0; $HO(CH_2)_3$-*o*-$C_2B_{10}H_{10}$-CH_3, 17815-32-6; 1-*o*-acetyl-2,3,5-tri-*o*-benzoyl-β-D-ribofuranose, 6974-32-9; 3,4-di-*O*-acetyl-D-xylal, 3152-43-0; tri-*O*-acetyl-D-glucal, 2873-29-2.

Transition-Metal-Substituted Silanes. Hydrosilylation of Phenylacetylene Using $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H]$ and $[(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2R]$ (R = Me, $SiMe_3$)[1]

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The complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H]$ ($FpSiPh_2H$, I) has been synthesized and characterized. Treatment of I with *i*-Pr_2NLi (LDA) followed by MeI or Me_3SiCl produces the silyl migration products $[(\eta^5\text{-}C_5H_4SiPh_2H)Fe(CO)_2R]$ (R = Me (IIa), $SiMe_3$ (IIb)). Addition of the Si-H bonds to phenylacetylene using chloroplatinic acid yields exceptionally high yields of the appropriate α products. The hydrosilylation products of I may be transformed into those of II by treatment with LDA followed by MeI or Me_3SiCl. The *trans*-β-silylstyrene hydrosilylation products were synthesized independently by the reaction of $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]^-Na^+$ (R = H, $SiMe_3$) with *trans*-$Ph_2Si(Cl)CH{=}CHPh$.

Introduction

Transition-metal complexes containing a Si-H bond are relatively uncommon compared to those with halogen, alkyl, or aryl groups bonded to silicon; however, those complexes that are reported exhibit much unusual chemistry.[2-4] For example, the silicon-hydrogen bond of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2H]$ ($FpSiMe_2H$), exhibits a low Si-H stretching frequency and is readily transformed into a silicon-chlorine bond upon treatment with CCl_4;[5] bridging metal-hydrogen-silicon systems are known,[6,7] and (dimethylsilyl)methyl groups readily rearrange to trimethylsilyl groups, e.g. $[(\eta^5\text{-}C_5H_5)M(CO)_nCH_2SiMe_2H] \rightarrow [(\eta^5\text{-}C_5H_5)M(CO)_nSiMe_3]$.[8,9] Given the interesting chemistry it is surprising that the most studied reaction of organosilicon hydrogen bonds, namely, hydrosilylation, has

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