Tetrabutylammonium Fluoride Promoted Novel Reactions of *o*-Carborane: Inter- and Intramolecular Additions to Aldehydes and Ketones and Annulation via Enals and Enones

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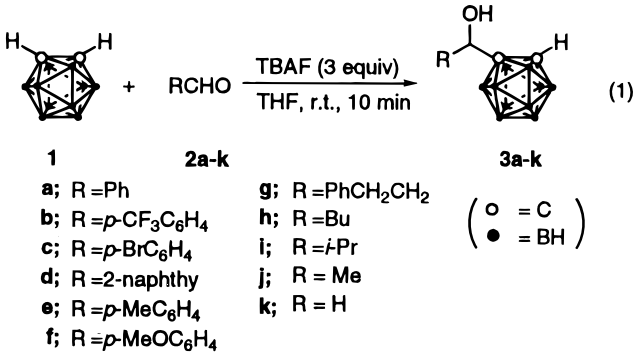
Abstract: The addition of *o*-carborane (**1**) to aldehydes **2** proceeded very smoothly in the presence of aqueous tetrabutylammonium fluoride (TBAF; 3 equiv) at room temperature, giving the corresponding carbinols **3** in high yields. The TBAF-mediated reaction was applied to the intramolecular cycloaddition of *o*-carboranyl aldehydes and ketones **4**, and the corresponding five-, six-, and seven-membered carboracycles were obtained in good-to-high yields. Further, [3 + 2] annulation between *o*-carborane (dianionic C_2 synthons) and α,β-unsaturated aldehydes and ketones (dicationic C_3 synthons) proceeded very smoothly in the presence of TBAF to give the corresponding five-membered carbocycles in good-to-high yields. Detailed mechanistic studies revealed that the [3 + 2] annulation proceeded through kinetically controlled 1,2-addition and thermodynamically controlled 1,4-addition.

Introduction

The addition of *o*-carborane to electrophiles is one of the most important reactions to synthesize carboranes containing organic functional groups, which could be useful as multifunctional molecules for material science[1] and/or as boron carriers for boron neutron capture therapy.[2] Lithiocarboranes, which are readily prepared from butyllithium with carboranes, are widely utilized for C−C bond formation of various functional groups with carboranes.[3,4] We have developed the addition reactions of stannyl-[5] and silylcarboranes[6,7] to various electrophiles, which proceed under very mild conditions and therefore are potentially useful for synthesizing biologically active functionalized carboranes sensitive to strong basic or acidic conditions.[8]

On the other hand, it is known that a carborane framework involves three-center two-electron bonding and is thus an electron-deficient cluster.[3a] Therefore, the C−H bond of carborane is highly activated. Shatenshtein reported that the pK_a value of this proton is 23.[9] It occurred to us that a proton attached to the carbon of *o*-carborane could be deprotonated easily by a weak base and the resulting carbanion could react with electrophiles. Actually, we have found that *o*-carborane undergoes an addition reaction to carbonyl compounds in the presence of tetrabutylammonium fluoride (TBAF). In this paper, we report the first direct addition of *o*-carborane to carbonyl compounds without using any metalated carborane species; the reaction of *o*-carborane (**1**) with aldehydes **2** in the presence of TBAF in THF at room temperature gave the corresponding *o*-carboranyl carbinols **3** in high-to-good yields (eq 1). The intramolecular cycloadditions of *o*-carboranes



containing carbonyl moieties proceeded very smoothly by treatment with TBAF to give the corresponding five-, six-, and seven-membered carboracycles **5** (eq 2). *o*-Carborane underwent a facile annulation reaction with various α,β-unsaturated enals and enones in the presence of aqueous TBAF, giving the

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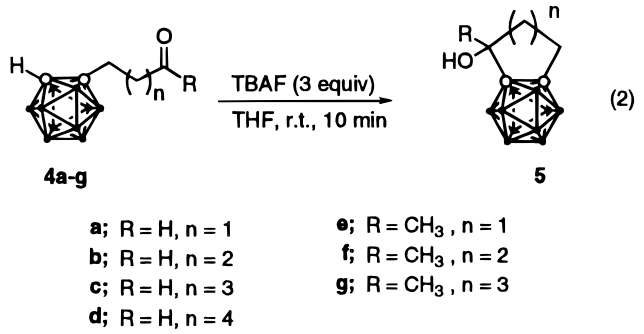
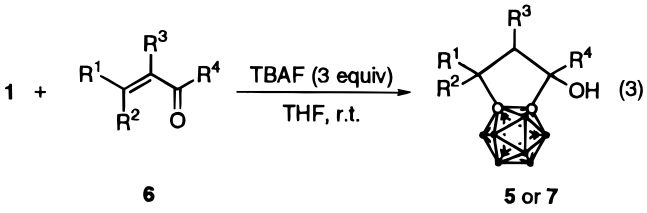


corresponding five-membered carboracyclic products **7** in high-to-good yields (eq 3).



Results and Discussion

Addition of Nonmetalated *o*-Carborane to Aldehydes. The addition of **1** to aldehydes **2** proceeded very smoothly in the presence of aqueous TBAF (3 equiv) at room temperature, giving the corresponding carbinols **3** in high yields (eq 1). The results are summarized in Table 1. The reaction of **1** with benzaldehyde **2a** was complete within 10 min and the carbinol **3a** was obtained in 88% yield (entry 1). The use of less than or greater than 3 equiv of TBAF resulted in lower yields. Other ammonium salts, such as tetraethylammonium iodide, tetrabutylammonium chloride, and tetrabutylammonium hydroxide, did not give the desired product. Not only aromatic aldehydes **2a**−**f** (entries 1−6) but also aliphatic aldehydes **2g**−**j** (entries 7−10) underwent the addition reaction, affording the corresponding carbinols **3a**−**f** and **3g**−**j**, respectively, in high yields. This addition reaction proceeded very smoothly even in an aqueous medium. The reaction of **1** with aqueous formaldehyde (37% w/w in water) gave *o*-carboranylmethanol (**3k**) in 86% yield (entry 11). No double addition of **2a** to **1** was observed even when excess amounts of **2a** and TBAF were used. Selective monolithiation of **1** is not necessarily easy, and in certain cases, double-addition products are obtained in addition to the desired monoadducts, since the facile disproportionation of the monolithio species takes place. Therefore, the present TBAF method is quite useful for the selective formation of monoadducts.[10]

Intramolecular Cycloaddition of *o*-Carboranes Bearing Carbonyl Groups. The intramolecular cycloaddition of *o*-carboranyl aldehydes and ketones **4** via the traditional lithiocarborane method is difficult since the carbonyl groups are reactive toward lithium organometallics which are needed to produce the lithiocarboranes. We examined the TBAF-mediated intramolecular cycloaddition of **4** and found that the five-, six-, and seven-membered carboracycles **5** can be synthesized in good-to-high yields (eq 2). The results are summarized in Table 2. 3-Carboranylpropanal (**4a**; $n = 1$) underwent the cycloaddition reaction by treatment with TBAF (3 equiv) in THF, giving the corresponding five-membered cyclic product **5a** in 49% yield (entry 1). Very interestingly, the six- and seven-membered-ring products **5b** and **5c** ($n = 2, 3$) were obtained in higher yields from the corresponding aldehydes **4b** and **4c**, respectively (entries 2 and 3). However, in the case of **4d**, the eight-membered cyclic product **5d** was not obtained. The cycloaddition of carbonyl ketones **4e**−**g** was also examined. The reaction of **4e** and **4f** gave the corresponding five- and six-membered carboracycles **5e** and **5f** in 79% and 82% yields, respectively (entries 5 and 6). However, the seven-membered-ring product **5g** was not obtained from **4g** but the reduced product (6-(*o*-carboranyl)-2-hexanol) was obtained in 35% yield (entry 7).

Table 1. 1,2-Addition of *o*-Carborane **1** to Aldehydes **2** in the Presence of TBAF

entry	aldehyde **2**	R	product **3**	yield,[a] %
1	**2a**	Ph	**3a**	88
2	**2b**	*p*-$CF_3C_6H_4$	**3b**	88
3	**2c**	*p*-BrC_6H_4	**3c**	96
4	**2d**	2-naphthyl	**3d**	76
5	**2e**	*p*-MeC_6H_4	**3e**	71
6	**2f**	*p*-$MeOC_6H_4$	**3f**	48
7	**2g**	$PhCH_2CH_2$	**3g**	76
8	**2h**	Bu	**3h**	93
9	**2i**	*i*-Pr	**3i**	>99
10	**2j**	Me	**3j**	86
11[b]	**2k**	H	**3k**	86

[a] Yields of isolated products. [b] Formaldehyde contained 37% w/w in water was used.

Table 2. Intramolecular Cycloaddition of Carboranes **4** Prompted by TBAF

entry	carboranes **4**	cyclic products **5**	yield,[a] %
1	**4a**	**5a**	49[b]
2	**4b**	**5b**	99
3	**4c**	**5c**	99
4	**4d**	**5d**	0[c]
5	**4e**	**5e**	79[b]
6	**4f**	**5f**	82
7	**4g**	**5g**	0[c]

[a] Yield of isolated products. [b] Yields were determined by ^{1}H NMR using *p*-xylene as an internal standard, since these products were synthesized by the different procedures developed in our laboratory (ref 7), and their structures were determined unambiguously. [c] In the cases of entries 4 and 7, the complex mixtures were obtained including the reduced products, 6-(*o*-carboranyl)hexanol and 6-(*o*-carboranyl)-2-hexanol, in 17% and 35% yield, respectively.

[3 + 2] Annulation Reaction of *o*-Carborane with Enals and Enones. Next we examined the TBAF-promoted addition to α,β-unsaturated enals and enones and found that *o*-carborane underwent a [3 + 2] annulation reaction with conjugated carbonyl compounds.[7] A [3 + 2] annulation is one of the most efficient methods for the construction of five-membered carbocyclic rings.[11] Perhaps the most widely utilized strategy in this regard is one in which dipolar C_3 synthons are utilized in conjunction with electron-deficient olefins (dipolar C_2 synthons) to achieve [3 + 2] annulation (Scheme 1a).[11,12] However, [3 + 2] annulations between dianionic C_2 synthons and dicationic C_3 synthons are less common than the dipolar annulations.[13] The coupling reaction of the 1,3-dihalides or β-haloesters with the doubly charged succinate anions[14] or tetraethoxycarbonylethyl anions[15] has been investigated in the latter approach. We found that [3 + 2] annulation between *o*-carborane (dianionic C_2 synthons) and α,β-unsaturated aldehydes and ketones (dicationic C_3 synthons) gave the corresponding five-membered carbocycles (Scheme 1b). *o*-Carborane underwent a facile annulation reaction with various α,β-unsaturated carbonyl

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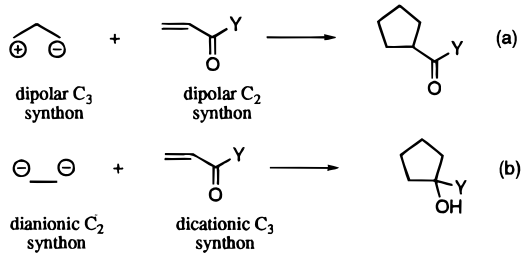
(11) Reviews: *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, pp 240−314.

Scheme 1



compounds under aqueous TBAF-promoted conditions, giving the corresponding five-membered carboracyclic products **7** (or **5**) (eq 3).

The results are summarized in Table 3. The reaction of **1** with crotonaldehyde **6a** gave carboracyclopentane **7a** in 90% yield with a 52:48 mixture of syn and anti diastereomers (entry 1). The syn configuration of the major diastereoisomer of **7a** was confirmed unambiguously by X-ray analysis (Figure 1). Enals with bulky groups on the β-position such as **6b** underwent a facile annulation to give the corresponding cyclic product **7b** in 77% yield (entry 2). The reaction of cinnamaldehyde **6c** gave **7c** in 74% yield with a syn/anti ratio of 63:37 (entry 3). The configuration of the major isomer of **7c** was determined by comparison with the chemical shifts of ^{1}H NMR of the major isomer of **7a**. The reaction of acrolein **6d** gave **5a** in 40% yield (entry 4) and that of methacrolein **6e** gave **7e** in 65% yield with a syn/anti ratio of 20:80 (entry 5). The stereochemistry of the major isomer of **7e** was determined by NOE experiments. Since NOEs were observed between CH_3 protons and H^b but not between H^b and H^a, the configuration of the major isomer was anti. The stereochemistry of the minor isomer (syn) was also determined by NOE experiments. The yields in the reactions with 3-substituted aldehydes (**6a**−**c**) were higher than those with 3-unsubstituted aldehydes (**6d** and **6e**). The reactions of α,β-unsaturated ketones were also examined. The reaction of enone **6f** gave the corresponding cyclic adduct **7f** in 42% yield with a syn/anti ratio of 40:60 (entry 6). NOEs were obtained between H^a and H^b and between H^c and the protons of CH_3 attached to the OH-substituted C atom of **7f**, thus indicating that the configuration of the major isomer was anti (see **7f**). A phenyl group at the β-position of the enone led to higher diastereoselectivity (syn/anti = 26/74, entry 7), although the substituent groups at the β-position of the enals did not affect the diastereoselectivity (entries 1 and 3). 3-Unsubstituted enone **6h** underwent the annulation, giving the corresponding product **5e** in lower yield (entry 8).

Table 3. [3 + 2] Annulation of **1** with **6**

entry	enones and enals **6**	carbocycles [a] **5** or **7**	yield,[b] %
1	**6a**	**7a**	90 (52:48)
2	**6b**	**7b**	77
3	**6c**	**7c**	74 (63:37)
4	**6d**	**5a**	40
5	**6e**	**7e**	65 (20:80)
6[c]	**6f**	**7f**	42 (40:60)
7	**6g**	**7g**	72 (26:74)
8[c]	**6h**	**5e**	54

[a] When the stereochemistry of **7** was determined unambiguously, that of a major isomer is shown in the column. [b] Yield of isolated products. Syn:anti ratios determined by ^{1}H NMR are shown in parentheses. [c] The reactions did not complete within 40 min.

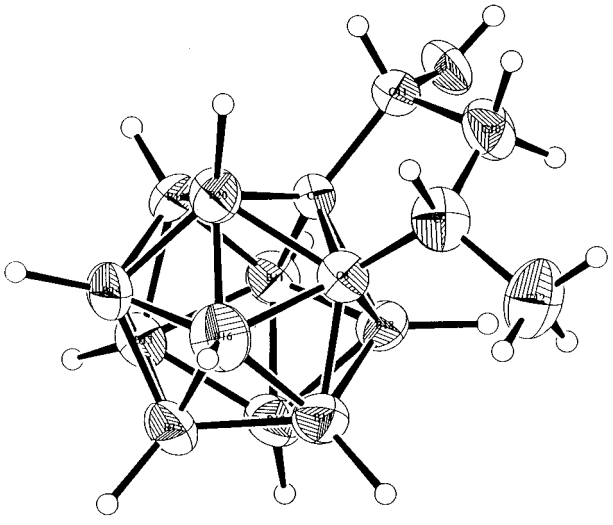


Figure 1. X-ray structure of cyclic adduct **7a**.

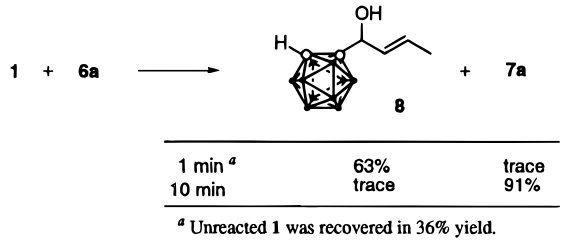
(12) (a) Allylic transition-metal complexes: Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. Calligaris, M.; Carturan, G.; Nardin, G,; Scrivanti, A.; Wojcicki, A. *Organometallics* **1983**, *2*, 865. Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002. (b) Allylic silane: Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. (c) Trimethylenemethane: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6432. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (d) Cyclopropenone ketal: Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1984**, *106*, 805. (e) Nitrones: Stevens, R. V.; Christensen, C. G.; Cory, R. M.; Thorsett, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 914. Funk, R. L.; Bolton, G. L.; Daggett, J. U.; Hansen, M. M.; Horcher, L. H. M. *Tetrahedron* **1985**, *41*, 3479. Oppolzer, W.; Siles, S.; Snowden, R. L.; Bakker, B. H.; Petrzilka, M. *Tetrahedron* **1985**, *41*, 3497. Padwa, A.; Kline, D. N.; Koehler, K. F.; Matzinger, M.; Venkatramanan, M. K. *J. Org. Chem.* **1987**, *52*, 3909. Curran, D. P.; Fenk, C. J. *Tetrahedron. Lett.* **1986**, *27*, 4865.

(13) The reaction between dicationic substrates (⊕−⊕) and dianionic synthons (⊖ & ⊖) has been reported. Molander, G. A.; Shubert, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 4683.

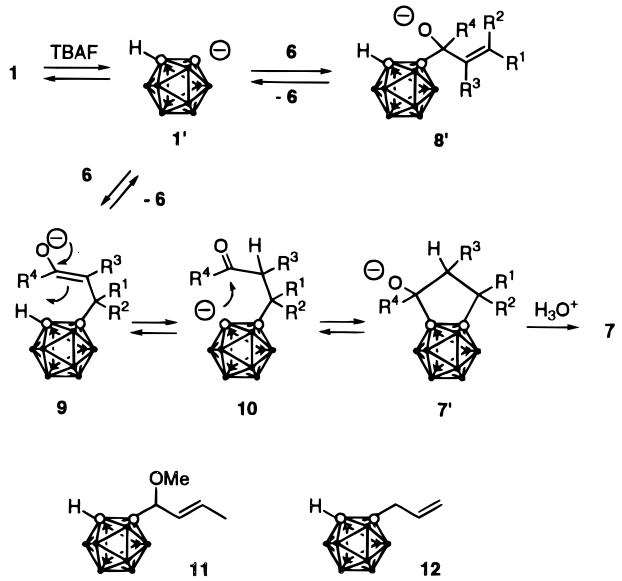
(14) Misumi, A.; Iwanaga, K.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 3343. Furuta, K.; Misumi, A.; Mori, A.; Ikeda, N.; Yamamoto, H. *Tetrahedron Lett.* **1984**, *25*, 669. Misumi, A.; Furuta, K.; Yamamoto, H. *Tetrahedron Lett.* **1984**, *25*, 671.

(15) Ibuka, T.; Aoyagi, T.; Yoneda, F.; Yamamoto, Y. *J. Organomet. Chem.* **1985**, *287*, C18.

Scheme 2



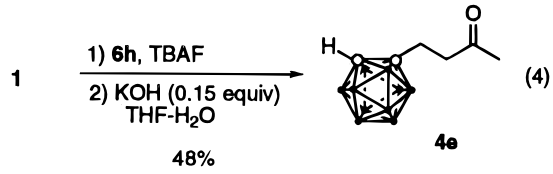
Scheme 3



Mechanism. To clarify the mechanism of the annulation reaction, we monitored the reaction of **1** with crotonaldehyde **6a** by ^{1}H NMR (Scheme 2). When the reaction was quenched after 1 min, the 1,2-adduct **8** was obtained in 63% yield along with the recovery of *o*-carborane in 36% yield. However, the cyclic product **7a** was obtained exclusively after 10 min. Furthermore, the cyclic product **7a** was also obtained in 58% yield by the treatment of allylic alcohol **8**, which was synthesized independently by the 1,2-addition reaction of lithiocarborane and enal **6a**, with TBAF (3 equiv).

Based upon these observations, it was considered that the [3 + 2] annulation would proceed through kinetically controlled 1,2-addition followed by a thermodynamically controlled cyclization process. According to a possible mechanism for this unprecedented annulation reaction (Scheme 3), an anionic intermediate **1′**, which would produce by the reaction of **1** with TBAF (or from 1,2-adduct **8′**), would undergo addition to **6** either in a 1,2- or in a 1,4-manner to give the 1,2-adduct **8′** or 1,4-adduct **9**, respectively. There would be an equilibrium between **8′** and **9**, and the formation of **8** would be a kinetically controlled process as is apparent from the result of Scheme 2. The thermodynamically favored **9** would undergo proton exchange to afford the *o*-carborane anion **10**, which would give **7** via an intramolecular ring closure.[16] The methylated 1,2-adduct analogue **11** and allylcarborane **12** did not undergo the [3 + 2] annulation reaction by treatment with TBAF. These results support that a hydroxy group at the allylic position is essential for the equilibrium between **1** and 1,2-adduct **8** and for the annulation reaction.[17]

Pseudo-1,4-addition of *o*-Carborane to the Enone. 1,4-Addition of *o*-carborane to conjugated carbonyl compounds is an attractive reaction to synthesize the carboranes containing a carbonyl moiety, which are very useful for the synthesis of functionalized carborane compounds since further functionalization is possible via the manipulation of the carbonyl group. There are few examples of the 1,4-addition of carboranes to conjugated carbonyl compounds. The α,β-unsaturated ketones substituted by bulky groups, such as phenyl and *tert*-butyl at the α' position, underwent 1,4-addition with *o*-carborane.[18] It was thought that the carbocyclic products derived from enones, if a hydroxy proton is deprotonated, would undergo the retro cyclization via the equilibration process (**7′** → **10** → **9**) and the 1,4-addition products might be obtained under certain reaction conditions. This hypothesis proved to be practical. Accordingly, even in the case of less bulky methyl vinyl ketone, the 1,4-addition of *o*-carborane is possible by the two-step sequential reaction. The reaction of **1** with **6h** in the presence of TBAF in THF, followed by the retro 1,2-addition by the treatment with catalytic amounts of KOH (0.15 equiv) in THF−H_2O (100:1), gave the corresponding 1,4-adduct **4e** in 48% yield (eq 4).[17]



Conclusion

We have developed a new method for the C−C bond formation between *o*-carborane and carbonyl compounds. A selective monoaddition reaction of **1** to aldehydes **2** is accomplished by treating the two substrates with TBAF at room temperature: the corresponding carbinols **3** are obtained in high yields even in aqueous medium. Intramolecular cycloaddition of *o*-carborane containing carbonyl moieties is also accomplished by the treatment with TBAF. Further, [3 + 2] annulation between *o*-carborane and α,β-unsaturated aldehydes and ketones proceeds in the presence of TBAF to give the corresponding five-, six-, and seven-membered carboracycles. Finally, pseudo-1,4-addition of *o*-carborane to a less hindered enone is demonstrated as an extension of the annulation reaction. We are now in a position to synthesize a variety of carborane derivatives, some of which are difficult to synthesize via the previously known methods.

Experimental Section

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX-270 spectrometer. The chemical shifts are reported in δ units relative to internal tetramethylsilane. IR spectra were recorded on a Shimadzu FTIR-8200A spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-HX110. Most commercially supplied chemicals were distilled and stored over molecular sieves.

Addition to Aldehydes. A typical procedure for the TBAF-promoted addition is as follows. To a solution of *o*-carborane **1** (290 mg, 2.01 mmol) and hydrocinnamaldehyde **2g** (290 μL, 2.2 mmol) in THF (10 mL) was added TBAF (1.0 M in THF, 6 mL) under Ar atmosphere, and the mixture was stirred at room temperature for 30 min. The reaction was quenched by saturated aqueous NH_4Cl, and the mixture was extracted with ether, washed with saturated aqueous

(16) The mechanism of this reaction involving a 1,4-addition−proton exchange−addition sequence is quite similar to that of 2,3-bis(phenylsulfonyl)-1,3-butadiene with activated methylenes: Padwa, A.; Murphree, S. S.; Ni, Z.; Watterson, S. H. *J. Org. Chem.* **1996**, *61*, 3829.

(17) Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 780.

(18) (a) Zakharkin, L. I.; Kazantsev, A. V. *Zh. Obshch. Khim.* **1967**, *37*, 554. (b) *Carboranes*: Grimes, R. N., Ed.; Academic: New York, 1970; p 102 and references therein.

NaCl, dried over anhydrous $MgSO_4$, and then concentrated. Purification by silica gel column chromatography (hexane:ethyl acetate = 15:1) gave the carbinol **3g** in 76% yield (423 mg, 1.52 mmol).

The structure of **3k** were determined unambiguously by comparison with an authentic sample, prepared by the literature procedure.[10] Spectral data of compounds **3f**−**j** are given in the supporting information.

1-(*o*-Carboranyl)benzyl Alcohol (3a). Colorless solid: mp 70 °C. IR (KBr) 3550, 3100, 2550, 1490, 1460, 1100, 1040, 770, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.36 (m, 5 H), 5.27 (d, J = 3.5 Hz, 1 H), 3.81 (br s, 1 H), 2.56 (d, J = 3.5 Hz, 1 H). MS (EI) m/z 250 (M^+), 233 (M^+ − OH), 108 (M^+ − carborane), 77 (Ar). Anal. Calcd for $C_9H_{18}OB_{10}$: C, 43.18; H, 7.25. Found: C, 42.98; H, 7.09.

1-(*o*-Carboranyl)-*p*-(trifluoromethyl)benzyl Alcohol (3b). Colorless solid: mp 70 °C. IR (KBr) 3674, 3549, 3444, 3087, 2937, 2900, 2582, 1622, 1419, 1384, 1325, 1247, 1168 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 8.0 Hz, 2 H), 5.34 (d, J = 3.0 Hz, 1 H), 3.94 (br s, 1 H), 2.73 (d, J = 3.0 Hz, 1 H). HRMS (EI) Calcd for $C_{10}H_{17}OB_{10}F$: m/z 320.2162. Found: m/z 320.2152. Anal. Calcd for $C_{10}H_{17}OB_{10}F$; C, 37.7; H, 5.38. Found: C, 38.1; H, 5.21.

1-(*o*-Carboranyl)-*p*-bromobenzyl Alcohol (3c). White solid. IR ($CHCl_3$) 3600, 3500−3150, 3050, 2570, 1600, 1480, 1400, 1090, 1070, 1010 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 2 H), 7.22 (d, J = 8.5 Hz, 2 H), 5.25 (d, J = 3.5 Hz, 1 H), 3.88 (br s, 1 H), 2.61 (d, J = 3.5 Hz, 1 H). MS (EI) m/z 329 (M^+), 249 (M^+ − Br), 157 (BrPh), 143 (carborane). HRMS (EI) Calcd for $C_9H_{17}OB_{10}Br$: m/z 330.1393. Found: m/z 330.1405.

1-(*o*-Carboranyl)-2-naphthylmethanol (3d). Colorless solid. IR (KBr) 3585, 3086, 2633, 2603, 2580, 1356, 1315, 1247, 1184, 1166, 1083, 1020 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.87 (m, 3 H), 7.78 (s, 1 H), 7.54 (m, 2 H), 7.45 (m, 1 H), 5.44 (d, J = 3.5 Hz, 1 H), 3.84 (br s, 1 H), 2.72 (d, J = 3.5 Hz, 1 H). HRMS (EI) Calcd for $C_{13}H_{20}OB_{10}$: m/z 302.2445. Found: m/z 302.2450. Anal. Calcd for $C_{13}H_{20}OB_{10}$: C, 51.9; H, 6.71. Found: C, 51.7; H, 6.41.

1-(*o*-Carboranyl)-*p*-methylbenzyl Alcohol (3e). Liquid. IR ($CHCl_3$) 3600, 3500−3150, 3150−2800, 2570, 1730, 1650, 1610, 1095, 1010, 900 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.20 (s, 4 H), 5.23 (d, J = 3.0 Hz, 1 H), 3.77 (br s, 1 H), 2.51 (d, J = 3.0 Hz, 1 H), 2.37 (s, 3 H). MS (EI) m/z 264 (M^+), 143 (carborane), 121 (M^+ − carborane), 93 (MePh). HRMS (EI) Calcd for $C_{10}H_{20}OB_{10}$: m/z 266.2445. Found: m/z 266.2448.

Intramolecular Cycloaddition of 4. *o*-Carboranyl aldehydes and ketones **4a**−**g** were prepared from the corresponding ynals and ynones by using the standard Lewis base promoted addition of decaborane to acetylene derivatives. Spectral data of compounds **4b**−**d**, **4f**, and **4g** are given in the supporting information.

3-(*o*-Carboranyl)propanal (4a). White solid. IR (KBr) 3057, 2842, 2578, 1724, 727 cm^{-1}. ^1H NMR ($CDCl_3$) δ 9.74 (s, 1 H), 3.67 (br s, 1 H), 2.74 (t, J = 7.0 Hz, 2 H), 2.55 (t, J = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 198.54, 73.86, 61.73, 42.98, 30.07. HRMS (EI) Calcd for $C_5H_{16}OB_{10}$: m/z 202.2132. Found: m/z 202.2130. Anal. Calcd for $C_5H_{16}OB_{10}$: C, 29.98; H, 8.05. Found: C, 29.76; H, 7.90.

4-(*o*-Carboranyl)-2-butanone (4e). White solid. IR (KBr) 3055, 2956, 2923, 2850, 2597, 1712 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.72 (br s, 1 H), 2.68 (t, J = 7.0 Hz, 2 H), 2.51 (t, J = 7.0 Hz, 2 H), 2.19 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 205.64, 74.38, 61.77, 42.53, 31.30, 29.69. HRMS (EI) Calcd for $C_6H_{18}OB_{10}$: m/z 216.2289. Found: m/z 216.2294.

A typical procedure for the TBAF-promoted intramolecular cycloaddition of **4c** is as follows. To a solution of **4c** (99 mg, 0.43 mmol) in THF (5 mL) was added TBAF (1.0 M solution in THF, 1.3 mL), and the mixture was stirred at room temperature for 35 min. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with ether, washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated. Purification by silica gel column chromatography (hexane:ethyl acetate = 5:1) gave the cyclic product **5e** in 99% yield (98 mg, 0.429 mmol).

1,2-Carboracyclopentan-3-ol (5a). White solid. IR (KBr) 3317, 2954, 2592, 1444, 1350, 1315, 1163, 1099 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.79 (m, 1 H), 2.84−2.70 (m, 1 H), 2.59−2.12 (m, 4 H). HRMS (EI) Calcd for $C_5H_{16}OB_{10}$: m/z 202.2132. Found: m/z 202.2125. Anal. Calcd for $C_7H_{20}OB_{10}$: C, 29.98; H, 8.05. Found: C, 29.54; H, 7.83.

1,2-Carboracyclohexan-3-ol (5b). White solid. IR (KBr) 3303, 2962, 2933, 2873, 2580, 1743, 1452, 1346, 1178, 1147 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.35 (dd, J = 10.0, 5.0, Hz, 1 H), 2.38 (m, 2 H), 2.30 (d, J = 5.0 Hz, 1 H), 1.96−1.52 (m, 4 H). ^{13}C NMR ($CDCl_3$) δ 68.76, 32.88, 28.22, 17.19. HRMS (EI) Calcd for $C_6H_{18}OB_{10}$: m/z 216.2289. Found: m/z 216.2280.

1,2-Carboracycloheptan-3-ol (5c). White solid. IR (KBr) 3452, 2931, 2866, 2648, 2580, 1446, 1112, 1060 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.37 (m, 1 H), 2.64−2.45 (m, 2 H), 2.26 (d, J = 4.8 Hz, 1 H), 2.08−1.68 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 82.59, 74.26, 38.76, 33.66, 30.32, 25.92, 24.07. HRMS (EI) Calcd for $C_7H_{20}OB_{10}$: m/z 230.2445. Found: m/z 230.2427. Anal. Calcd for $C_7H_{20}OB_{10}$: C, 36.82; H, 8.83. Found: C, 37.12; H, 8.90.

3-Methyl-1,2-carboracyclopentan-3-ol (5e). White solid. IR (KBr) 3583, 3467, 2991, 2956, 2592, 1452, 1379 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.33−2.63 (m, 4 H), 2.08 (s, 1 H), 1.62 (s, 1 H). Anal. Calcd for $C_6H_{18}OB_{10}$: C, 33.63; H, 8.47. Found: C, 33.50; H, 8.81.

3-Methyl-1,2-carboracyclohexan-3-ol (5f). White solid. IR (KBr) 3469, 2952, 2873, 2578, 1452, 1380, 1132 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.49 (m, 1 H), 2.32 (m, 1 H), 2.13 (s, 1 H), 1.87−1.73 (m, 2 H), 1.62−1.50 (m, 2 H), 1.52 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 70.18, 35.16, 33.69, 32.57, 17.10. HRMS (EI) Calcd for $C_7H_{20}OB_{10}$: m/z 230.2445. Found: m/z 230.2444.

[3 + 2]Annulation of 1 with 6. A typical procedure for the TBAF-promoted [3 + 2] annulation is as follows. To a solution of **1** (74 mg, 0.51 mmol) and 3-methyl-2-butanal (**6b**. 46 μL, 0.48 mmol) in THF (10 mL) was added TBAF (1.0 M in THF, 1.5 mL) under Ar atmosphere, and the mixture was stirred at room temperature for 10 min. The reaction was quenched by saturated aqueous NH_4Cl, and the mixture was extracted with ether, washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and then concentrated. Purification by silica gel column chromatography (hexane:ethyl acetate = 4:1) gave the annulated product **7b** in 77% yield (84 mg, 0.37 mmol). Spectral data of compounds **7e**−**g** are given in the supporting information.

5-Methyl-1,2-carboracyclopentan-3-ol (7a). White solid. IR (KBr) 3325, 2976, 2586, 1458, 1384, 1342, 1166, 731 cm^{-1}. ^1H NMR ($CDCl_3$) syn isomer δ 4.72 (m, 1 H), 2.82 (m, 2 H), 2.24 (d, J = 5.5 Hz, 1 H), 1.71 (m, 1 H), 1.17 (d, J = 6.0 Hz, 3 H), anti isomer δ 4.65 (m, 1 H), 3.01 (m, 1 H), 2.36 (m, 1 H), 2.25 (m, 1 H), 2.05 (d, J = 5.0 Hz, 1 H), 1.13 (d, J = 6.0 Hz, 3 H). Anal. Calcd for $C_6H_{18}OB_{10}$: C, 33.63; H, 8.47. Found: C, 33.98; H, 8.41.

5,5-Dimethyl-1,2-carboracyclopentan-3-ol (7b). White solid. IR (KBr) 3367, 2978, 2596, 1334, 1074 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.67 (ddd, J = 8.0, 5.1, 5.0 Hz, 1 H), 2.54 (dd, J = 14.8, 8.0 Hz, 2 H), 2.18 (d, J = 5.0 Hz, 1 H), 2.02 (dd, J = 14.8, 5.1 Hz, 1 H), 1.37 (d, J = 5.0 Hz, 3 H), 1.32 (d, J = 5.0 Hz, 3 H). HRMS (EI) Calcd for $C_7H_{20}OB_{10}$: m/z 230.2445. Found: m/z 230.2443. Anal. Calcd for $C_7H_{20}OB_{10}$: C, 36.82; H, 8.83. Found: C, 36.45; H, 8.95.

5-Phenyl-1,2-carboracyclopentan-3-ol (7c). White solid. IR (CCl_4) 3583, 3413, 2586, 1748, 1074, 794 cm^{-1}. ^1H NMR ($CDCl_3$) syn isomer δ 7.15−7.34 (m, 5 H), 4.82 (m, 1 H), 4.16 (dd, J = 9.5, 9.0 Hz, 1 H), 2.83−3.05 (m, 1 H), 2.39−2.53 (m, 1 H), 2.10 (d, J = 3.0 Hz, 1 H), anti isomer δ 7.15−7.34 (m, 5 H), 4.82 (m, 1 H), 3.92 (dd, J = 9.0, 8.5 Hz, 1 H), 2.83−3.05 (m, 1 H), 2.39−2.53 (m, 1 H), 2.10 (d, J = 3.0 Hz, 1 H). HRMS (EI) Calcd for $C_{11}H_{20}OB_{10}$: m/z 278.2452. Found: m/z 278.2452. Anal. Calcd for $C_{11}H_{20}OB_{10}$: C, 47.80; H, 7.29. Found: C, 47.95; H, 7.30.

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Supporting Information Available: Spectral data for compounds **3f**−**j**, **4b**−**d**, **4f**, **4g**, and **7e**−**g**, NMR spectra for compounds **3c**, **3e**, **3g**, **3h**, **4b**−**g**, **5b**, and **5f**, and X-ray crystallographic data for compound **7a** (25 pages). See any current masthead page for ordering and Internet access instructions.

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