4.59 (s, Cp), 4.20–3.75 (m, 4 H, OCH_2), 3.70–2.85 (m, 4 H, NCH_2), 1.98 (b s, 3 H, $FeCCH_3$), 1.64 (b d, $^3J_{H\text{-}Me}$ = 6.4 Hz, 3 H, $=CHCH_3$). ^{13}C NMR ($CDCl_3$ or C_6D_6): δ 141.4 (d, $J_{C,P}$ = 47 Hz, FeC), 131.9 (s, $CH{=}C$), 84.0 (s, Cp), 69.3, 68.9 (d,d, $J_{C,P}$ = 4 Hz, OCH_2), 54.5 (b s, NCH_2), 30.8 (s, CH_3C), 17.2 (b s, $J_{C,P} \le 2$ Hz, CH_3CH). The CO resonance could not be located. This assignment was further confirmed by a ^{13}C off-resonance NMR spectrum.

Registry No. **7a** (bicyclic), 103794-48-5; **7a** (phosphine), 103794-53-2; **7b** (bicyclic), 103794-49-6; **7b** (phosphine), 103794-54-3; **7c** (bicyclic), 103794-50-9; **7c** (phosphine), 103794-55-4; **7d** (bicyclic), 103794-51-0; **7d** (phosphine), 103794-56-5; **8a**, 103794-41-8; **8b**, 103794-40-7; **8c**, 103816-39-3; **9a**, 103794-42-9; **9b**, 103794-43-0; **9c**, 103816-40-6; **9d**, 103794-44-1; **10a**, 103794-29-2; **10b**, 103794-39-4; **10d**, 103794-37-2; **11a**, 103794-35-0; **11b**, 89321-14-2; **11b′**, 103794-46-3; **11c**, 103794-31-6; **11d**, 103794-33-8; **11d′**, 103816-42-8; **12a**, 103816-33-7; **12b**, 103816-34-8; **12d**, 103816-38-2; **13a**, 103816-35-9; **13b**, 89321-12-0; **13c**, 103816-36-0; **13d**, 103816-37-1; **14b**, 89302-53-4; **14c**, 103794-47-4; $P(NEt_2)_3$, 2283-11-6; $CH_2{=}CHMgCl$, 3536-96-7; $CH_2{=}CHP(NEt_2)_2$, 89438-02-8; $C_6H_5CH_2P(NEt_2)_2$, 93633-48-8; $CH_2{=}CHCH_2P(NEt_2)_2$, 31480-07-6; (α-methylallyl)$P(NEt_2)_2$, 103794-52-1; η^5-$CpMo(CO)_3Cl$, 12128-23-3; η^5-$CpFe(CO)_2Br$, 12078-20-5; diethanolamine, 111-42-2.

Communications

Reaction of (Aminocarbene)iron Complexes with Alkynes. A Synthesis of 5-Aminofurans

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Received August 1, 1986

Summary: Alkynes react with ((dimethylamino)phenylmethylidene)tetracarbonyliron(0), compound **3**, with incorporation of CO to give 5-(dimethylamino)furans as the major products. Consistent with the mechanism proposed here and related to the mechanism proposed earlier for reactions of the corresponding (alkoxyalkylidene)iron complexes, the product distribution is CO-pressure-dependent, producing 6-(dimethylamino)-α-pyrones at the expense of furans under higher CO pressure. The regioselectivity in the addition of alkynes parallels that observed in the reactions of alkynes with (alkoxyalkylidene)chromium and -iron analogues. The 5-(dimethylamino)furans are relatively little studied; high reactivity toward oxygen and maleic anhydride is observed.

Chromium–carbene complexes such as **1** react with alkynes[1-4] and imines[5] in general processes to give potentially useful types of products,[1-3] although mechanistic features and the origin of selectivities are not well-defined. The iron analogues (e.g., **2**) react with alkynes to form 6-ethoxypyrones in a quite general way.[6] We now describe the reaction of alkynes with the corresponding amino derivatives **3**, leading generally to 2-aryl-5-aminofurans, in a process of preparative and mechanistic significance.[7]

Table I. Reaction of Alkynes with Aminocarbene Complex 3

entry	alkyne	solvt, atmosphere	products (% yield)
1	R_1, R_2 = Me	CH_2Cl_2, CO (55 psi)[c]	**6a** (47), **7a/8a** (13)
2	same	$ClCH_2CH_2Cl$, CO (650 psi)[d]	**6a** (20), **7a/8a** (47)
3	same	CH_2Cl_2, Ar (40 psi)[c]	**6a** (73), **9** (21)[b]
4	same	THF, Ar[e]	**6a** (62), **9** (4)[b]
5	R_1, R^2 = Et	$ClCH_2CH_2Cl$, Ar[e]	**6b** (74)[f]
6	same	THF, Ar[e]	**6b** (45)[f]
7	R_1, R_2 = CO_2Me	CH_2Cl_2, Ar (40 psi)[c]	**6c** (50)
8	same	$ClCH_2CH_2Cl$, Ar[e]	**6c** (35), **11c** (24)[b]
9	same	THF, Ar[e]	**6c** (16), **11** (13)[b]
10	R_1, R_2 = O-*t*-Bu	CH_2Cl_2, Ar (40 psi)[c]	**6d** (0), **13d** (5), **11d** (6)[b]
11	R_1 = Ph, R_2 = H	CH_2Cl_2, Ar (40 psi)[c]	**6e** (18)[g]
12	same	$ClCH_2CH_2Cl$, Ar[e]	**6e** (16), **13e** (30), **11e** (15)
13	same	THF, Ar[e]	**6e** (12), **10e** (13), **14e** (18), **11e** (13)
14	R_1 = *n*-C_3H_7, R_2 = H	$ClCH_2CH_2Cl$, Ar[e]	**6f** (64), **12f** (4)
15	R_1 = Me, R_2 = CO_2Me	$ClCH_2CH_2Cl$, Ar[e]	**6g** (73)

[a] Based on weighed samples purified by preparative layer chromatography or flash chromatography. [b] Based on alkyne at the start. [c] Glass pressure bottle. [d] Steel pressure vessel. [e] Conventional flask, under a small positive pressure of argon. [f] Based on oxidized product **20**. [g] Based on weight of adduct **21e** from addition of maleic anhydride.

Reaction of **2** with dimethylamine produced the known complex[9] **3** in 95% yield, mp 104–105 °C. A similar pro-

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(1) (a) Dötz, K. H. *Angew, Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689. (c) Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797.

(2) (a) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W. D.; Zask, A. *Tetrahedron* **1985**, *41*, 5803. (b) Semmelhack, M. F.; Bozell, J. J. *Tetrahedron Lett.* **1982**, 2931. (c) Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W. D.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* **1982**, *104*, 5850.

(3) (a) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060 and references therein. (b) Wulff, W. D.; Tang, D. C.; Chan, K.-S; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41* 5813.

(4) (a) Yamashita, A. *J.* Am. Chem. *Soc.* **1985**, *107*, 5823. (b) Yamashita, A.; Scahill, T. A.; Toy A. *Tetrahedron Lett.* **1985**, 2969.

(5) (a) Hegedus, *L. S.*; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc. 1984*, 106, 2680; (b) Hegedus, L. S. *Tetrahedron* **1985**, *41*, 5833.

(6) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *Tetrahedron* **1984**, *106*, 5363–5364.

(7) The corresponding *5-methoxyfurans* have been observed as minor products during reaction of alkynes with (methoxycarbene)chromium complexes 1.[1,2] In a recent paper, a synthesis of *2-alkoxyfurans* was reported from reaction of alkynes with cobalt–carbene complexes.[8]

(8) Wulff, W. D; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520–522.

(9) Fischer, E. O; Beck, H. J.; Kreiter, C. G.; Lynch, J.; Miller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.

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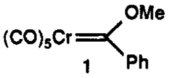
cedure to produce the *n*-butyl (**4**) and methyl (**5**) derivatives was less successful, probably due to base-induced rearrangement of the α-protons. Compound **4** was isolated in 10–15% yield after considerable purification; **5** has not been obtained in high purity.

Following a general procedure,[10] a series of alkynes combined with **3**. Typically 2-phenyl-5-(dimethylamino)furans (**6**) were the major products with 6-amino-α-pyrones (e.g., **7** and **8**) being detected in minor amounts. Other minor products from self-reaction of the alkyne without incorporation of the carbene unit were sometimes observed (**9–11**). In some cases, unexpected products (**12–14**) from incorporation of two alkynes, one carbene unit, and one CO ligand were isolated. The results are summarized in Table I.



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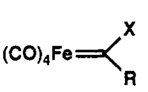
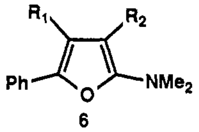


2: X = OEt, R = Ph
3: X = NMe$_2$, R = Ph
4: X = NMe$_2$, R = nBu
5: X = NMe$_2$, R = Me

$R_1—\equiv—R_2$

alkyne / product series:

a: R$_1$, R$_2$ = Me
b: R$_1$, R$_2$ = Et
c: R$_1$, R$_2$ = CO$_2$Et
d: R$_1$, R$_2$ = OtBu
e: R$_1$ = Ph, R$_2$ = H
f: R$_1$ = nPr, R$_2$ = H
g: R$_1$ = CO$_2$Me, R$_2$ = Me



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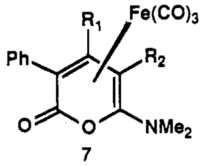

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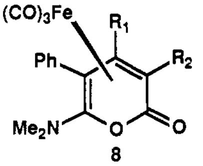

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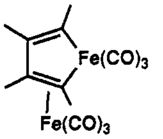

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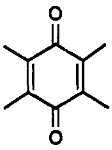

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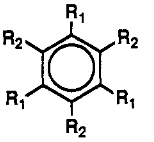

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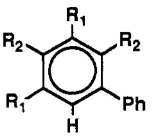

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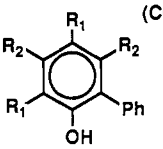

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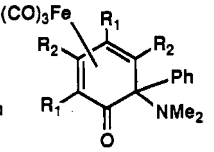
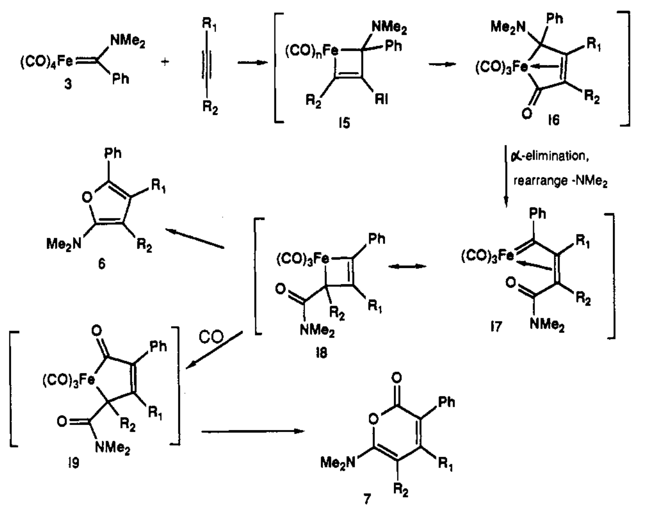


14

The alkynes were chosen to test generality and selectivity. The best conditions involve dichloromethane or dichloroethane solvent under argon pressure (entries 4, 5, 7, 14, 15). Added CO tends to favor formation of α-pyrones at the expense of furans; reaction of 2-butyne with **3** at higher pressure (650 psi of CO) given the α-pyrones **7a** and **8a** as the major products (entry 2). The electron-rich alkyne, di-tert-butoxyacetylene is relatively unreactive; the carbene complex decomposes while the alkyne slowly self-reacts (entry 10). Phenylacetylene is particularly prone to self-reaction, and furan synthesis is not efficient (entries 12–13). In three relevant examples, the regioselectivity is high (entries 11, 14, 15). The selectivity with monosubstituted alkynes (PhC≡CH; C$_3$H$_7$C≡CH) parallels that in the naphthoquinone synthesis from **1**[1,3] and α-pyrone synthesis from **2**;[8] the alkyne carbon bearing the smaller substituent attaches to the carbene carbon.

The formation of furans can be rationalized following a pathway at first identical with that proposed for the α-pyrone synthesis.[6] Initial formation of a ferracyclobutene (**15**) could allow migratory insertion of CO and give the ferracyclopentenone/vinylketene **16**.[11] Then α-elimination and rearrangement of the dimethylamino unit leads to a vinylcarbene complex (**17**), related to a ferracyclobutene (**18**). The latter representation reveals an iron–enolate unit; coupling of the enolate oxygen with the original carbene carbon produces the furan **6**. Insertion of a second CO ligand, favored by CO pressure, leads to a new iron enolate (**19**). Coupling of the enolate oxygen with the acyl unit leads to a mixture of pyrones **7**/**8**, with an Fe(CO)$_3$ unit attached. The byproducts such as **12**, **13**, and **14** presumably arise from incorporation of a second alkyne unit into one of the vinyl carbene intermediates, a process with some precedence.[13,14]



The furans are reactive toward oxygen and other electron acceptors.[15] Exposure to air at 25 °C for a few hours or during chromatographic separation leads to the oxida-

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[10] Reaction of complex **3** with 2-butyne as a exemplary procedure: Complex **3** (516 mg, 1.71 mmol) was weighed into a heavy-walled glass tube with a cap fitted with a pressure gauge and CO inlet ("Griffen-Worden" vessel, Kontes No. K-767100, borosilicate). For reactions at atmospheric pressure (less volatile alkynes, no CO pressure), a simple 50-mL pear-shaped flask sealed with a rubber septum was used. The system was evacuated and filled with argon at least three times, and dichloromethane (8 mL) and 2-butyne (0.30 mL, 4.9 molar equiv) were added rapidly by syringe. The system was closed, pressurized with CO to 55 psi, and heated in an oil bath at 60 °C for 1 h. The mixture was cooled and filtered through Celite, and the filtrate concentrated to leave a brown oil. On simple column chromatography (SiO$_2$; hexane/ether, 4:]), first eluted was a colorless oil, **6a** (174 mg, 47%), followed by the mixture **7a**/**8a** (84 mg, 13%), and duroquinone (**10**; 50 mg, 4% yield based on 2-butyne). Satisfactory spectral data have been obtained for **6a–c**, **6e–g**, **7a**, **7e**, **9**, **10**, **11c–e**, **12f**, **13d**, **13e**, **20a**, **20b**, **21a**, **21e–g**, **23e**, and **23g**. Combustion analyses were obtained for **6c**, **7a**, **20b**, **21a**, **23e**, and **23g**. The structure of **21f** was verified by X-ray diffraction; we thank Dr. D. Van Engen of the Princeton X-ray facility for this determination.

[11] The intermediacy of phenylvinylketene complexes has been proposed for the reaction of (carbene)chromium complexes with alkynes[1-4] and established for the parallel reactions of (carbene)cobalt complexes[8] and the (ethoxycarbene)iron complex, **2**.[12] Proposed intermediate **16** could not be detected during formation of furans.

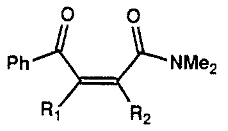
[12] Observations of M. F. Semmelhack, W. Schnatter, and M. Steigerwald, manuscript in preparation. The X-ray characterization of an analogue of **16a**, with ethoxy replacing dimethylamino, was carried out in collaboration with Professor J. Clardy at Cornell University.

[13] "Two-alkyne annulation" in related reactions of (carbene)chromium complexes has been observed and exploited as a preparative method. See: Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P.-C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

[14] Multiple alkyne insertion during reactions of carbene complexes is implicated in catalyzed polymerization of alkynes. For leading references, see: Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Che. Soc.* **1985**, *107*, 2182.

[15] Furans with 5-amino substituents are relatively rare and little studied.[16] This may be due to the extreme ease of air oxidation which hampers isolation procedures but suggests possibly valuable conversions for **6**.

tion products **20** in high yield.[16c,17] The furans can be trapped from the reaction mixture using maleic anhydride, giving the adducts **21**.[17] The diels–Alder adducts **22** were not observed,[16a,b] but formation of **21** can be rationalized via one mode of rearrangement from **22**. The products from elimination of H_2O from **22** were also detected in two cases (**23a,b**).[16a,b]



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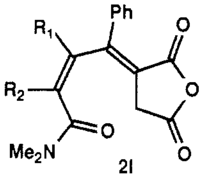

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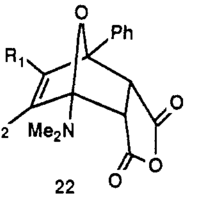

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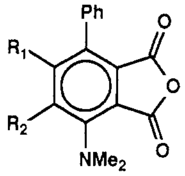

23

The general pathways available during reaction of (carbene)metal complexes with alkynes in the presence of CO are now clearer. While a simple series of steps can be written to rationalize formation of hydroquinones, pyrones, and furans, and factors which determine which product predominates in a given case are not evident.[18]

Registry No. **3**, 35797-88-7; **6a**, 104738-40-1; **6b**, 104738-41-2; **6c**, 104738-42-3; **6e**, 104738-43-4; **6f**, 104738-44-5; **6g**, 104738-45-6; **7a**, 104738-56-9; **8a**, 104738-57-0; **9**, 12245-44-2; **10**, 527-17-3; **11c**, 6237-59-8; **11d**, 104738-47-8; **11e**, 612-71-5; **12f**, 104738-48-9; **13d**, 104738-46-7; **13e**, 3140-01-0; **14e**, 104761-01-5; **20a**, 104738-55-8; **20b**, 104761-00-4; **21a**, 104738-49-0; **21e**, 104738-50-3; **21f**, 104738-51-4; **21g**, 104738-52-5; **23e**, 104738-53-6; **23g**, 104738-54-7; MeC≡CMe, 503-17-3; EtC≡CEt, 928-49-4; $EtO_2CC{\equiv}CCO_2Et$, 762-21-0; *t*-BuOC≡COBu-*t*, 66478-63-5; Ph≡CH, 536-74-3; *n*-PrC≡CH, 627-19-0; $MeC{\equiv}CCO_2Me$, 23326-27-4; maleic anhydride, 108-31-6.

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(16) (a) The parent 5-aminofuran appears to be unknown but has been implicated as a transient intermediate, disappearing by a Diels–Alder reaction and rearrangement of the adduct: Johnson, F.; Heeschen, J. P. *J. Org. Chem.* **1964**, *29*, 3252. (b) The 4-cyano-5-aminofuran derivatives have been isolated and converted to adducts related to 23 via a postulated Diels–Alder reaction: Gewald, K. *Chem. Ber*, **1966**, *99*, 1002. (c) oxidation products related to 20 from 2,3-diphenyl-5-(acylamino)furan have been reported: Ito, K.; yakushijin, K. *Heterocycles*, **1978**, 9.

(17) The oxidation products 20 and adducts 21 have been isolated and fully characterized.

(18) We wish to acknowledge financial support of this work by grants from the National Science Foundation and the National Institutes of Health.

New Synthetic Routes to the Small *closo*-Carboranes 2,3- and 2,4-$R_2C_2B_5H_5$

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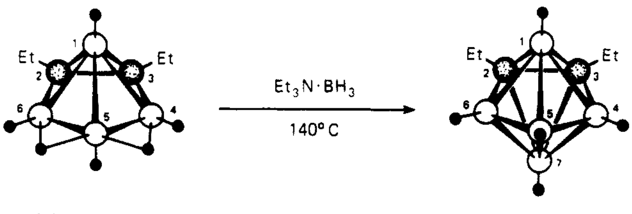
Received September 16, 1986

Summary: The reaction of *nido*-2,3-$Et_2C_2B_4H_6$ with triethylamine–borane at 140 °C has been found to result in the capping of the open face of the carborane, producing the *closo*-carborane 2,3-$Et_2C_2B_5H_5$ in good yields. Subsequent heating of 2,3-$Et_2C_2B_5H_5$ at ~320 °C results in the high yield isomerization of the carborane to *closo*-2,4-$Et_2C_2B_5H_5$.

Two different isomers of the small *closo*-carborane $C_2B_5H_7$ have previously been reported. The nonadjacent carbon compound 2,4-$C_2B_5H_7$ is formed by the thermolysis of *nido*-2,3-$C_2B_4H_8$[1] or in the complex pyrolytic reactions of pentaborane(9) with alkynes[2] and has been made on relatively large scales, although with poor selectivity. The 2,3-$R_2C_2B_5H_5$ isomer has previously been reported as a byproduct of the reaction of alkynes with B_8H_{12}[3] and has never been isolated in more than trace amounts. We report here the development of simple synthetic routes to both of these *closo*-$R_2C_2B_5H_5$ cage systems.

The synthesis of 2,3-$R_2C_2B_5H_5$ involves the reaction of the readily accessible[4] small carborane *nido*-2,3-$R_2C_2B_4H_6$ with triethylamine–borane at 140 °C. Thus, as is illustrated below, the reaction results in the capping of the open pentagonal face of the *nido*-carborane by a BH group derived from the amine–borane.



2,3-$Et_2C_2B_4H_6$ 2,3-$Et_2C_2B_5H_5$

In a typical reaction, 0.547 g (4.16 mmol) of 2,3-$Et_2C_2B_4H_6$ and 3.4 g (29.7 mmol) of $Et_3N{\cdot}BH_3$ were reacted in vacuo at 140 °C for a total of 96 h with periodic (~every 8 h) removal of evolved hydrogen and triethylamine. The volatile components were then separated by vacuum line fractionation through a −0, −45, and −196 °C trap series. Stopping in the −45 °C trap was 0.346 g (2.45 mmol) of 2,3-$Et_2C_2B_5H_5$, corresponding to a 58.9% yield. The material was determined to be pure by ^{11}B and ^1H NMR[5] and by gas chromatographic analysis.[6]

Similar capping reactions of larger cage polyhedral boranes and carboranes have previously been reported by using either Lewis base–borane complexes or diborane(6) as reagents. For example, the reaction[7] of decaborane(14)

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(5) ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 7.03 (d, B4,6, J_{BH} = 170 Hz), 2.54 (d, B5, J_{BH} = 152 Hz), −14.21 (d, B1, 7, J_{BH} = 168 Hz). ^1H NMR (200 MHz, ^{11}B spin-decoupled, δ, C_6D_6): 4.52 (s, BH4,6 and BH5), 2.14 (q, CH_2), 0.95 (t, CH_3), 0.18 (s, BH1,7). Mass spectrum: cutoff at *m/e* 142.1610, calcd for $^{12}C_6{}^{11}B_5{}^1H_{15}$ 142.1639.

(6) 6% Tricresyl phosphate on Chromosorb P, 60/80 mesh, 100 °C: 2,3-$Et_2C_2B_5H_5$, Rv = 2.4; 2,4-$Et_2C_2B_5H_5$, *R*v = 0.7; 2,3-$Et_2C_2B_4H_6$, Rv = 1.0.

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