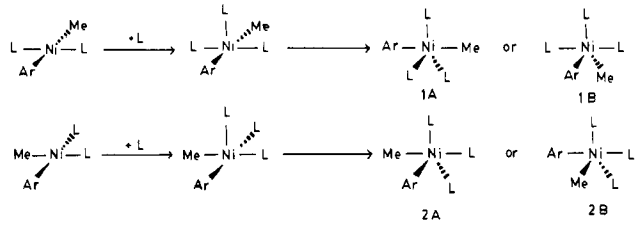
Scheme II. Five-Coordinate Intermediates in Reductive Elimination from *cis*- and *trans*-Arylmethylnickel Complexes



equatorial and apical positions in the trigonal bipyramid and thus reductive elimination is symmetry allowed,[13] whereas in 1A or 1B the aryl and the methyl ligands are either in the trans positions[14] or in the equatorial cis positions (1B), from which reductive elimination of the aryl and methyl ligands is not allowed.[13] Thus the reductive elimination from the trans complex may be forced to take another course, a dissociative pathway[7] through the formation of unsaturated three-coordinate species that may be isomerized by a polytopal rearrangement to the cis form, from which the methylarene can be reductively eliminated.[8]

In relation to the catalytic system, addition of aryl halide to the benzene or THF solution of **2** has some promotion effect on the reductive elimination, but the reaction is accompanied by formation of scrambled biaryls Ar–Ar, Ar′–Ar, and Ar′–Ar′ arising from NiArMe(dmpe) and the aryl halide Ar′X in agreement with the similar observation by Kochi concerning the reaction of **1** with aryl halides.[7] The accelerating effect of aryl halide, however, is much less pronounced than the effect of the tertiary phosphine addition to the cis complex **2**, and the *main* catlytic cross-coupling reaction may be proceeding by the phosphine-promoted reductive elimination pathway of the cis complex of type **2**.

Registry No. **1a**, 86823-38-3; **1b**, 86823-39-4; **1c**, 57811-74-2; **1d**, 52242-81-6; **1e**, 57811-73-1; **2a**, 86823-40-7; **2b**, 86823-41-8; **2c**, 86823-42-9; **2d**, 86823-43-0; **2e**, 86823-44-1; PPh_3, 603-35-0; $P(C_6H_4\text{-}p\text{-}F)_3$, 18437-78-0; $PPh_2(C_6H_4\text{-}p\text{-}OMe)$, 896-89-9; $P(C_6H_4\text{-}p\text{-}OMe)_3$, 855-38-9; PEt_3, 554-70-1; PCy_3, 2622-14-2; $P(OEt)_3$, 122-52-1; dmpe, 23936-60-9.

Supplementary Material Available: A table of yields and NMR data for compounds **2a–e** (1 page). Ordering information is given on any current masthead page.

(11) This assumption is not unreasonable since most of the ligand displacement reactions of the square-planar d^8 metal complexes take place with stereochemical retention of the initial configuration and are generally believed to proceed through trigonal-bipyramidal intermediates that do not rearrange to other isomers by the pseudorotation during the displacement reactions.[12]

(12) Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions", 2nd ed.; Wiley: New York, p 1967.

(13) (a) Tatsumi, K., private communication. Extended Hückel calculation revealed appropriate symmetry requirements for the reductive elimination and a higher energy barrier for interconversion between 1A and 2A (1B and 2B) than that for the symmetry-allowed reductive elimination in trigonal-bipyramid intermediates. The full paper will be published elswhere. (b) Akermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1979**, *188*, 59.

(14) The presence of stable, trigonal-bipyramidal, trans complexes of formula $NiMe_2L_3$ (L = PMe_3, PMe_2Ph) has been spectroscopically observed: (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1972**, *105*, 2628. (b) Jeffery, E. A. *Aust. J. Chem.* **1973**, *26*, 219.

General Synthesis of Alkylalkenylalkynylboranes via Haloboranes

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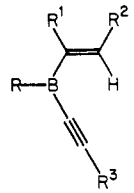
Summary: Methyl alkylalkenylborinates, obtained via hydroboration of alkynes with alkylbromoboranes, followed by methanolysis, react with alkynyllithium reagents in THF to form the corresponding "ate" complexes, which, on treatment with 1.33 equiv of $BF_3\cdot OEt_2$, produce the desired alkylalkenylalkynylboranes, thus providing a convenient and simple synthesis of these hitherto inaccessible organoboranes.

It has long been the dream of organoborane chemists to synthesize and study the chemistry of organoboranes containing three different groups on boron. Recently we have developed[2] a rational synthesis of mixed dialkylhaloboranes (**1**) and trialkylboranes (**2**), via stepwise hydroboration (eq 1), thus providing a solution to this

$$RBBr_2\cdot SMe_2 \xrightarrow{^1/_4LiAlH_4} \underset{\mathbf{3}}{RBHBr\cdot SMe_2} \xrightarrow{\text{alkene 1}} \underset{\mathbf{1}}{RR^1BBr} \xrightarrow[\text{MeOH}]{\text{NaOMe}} RR^1BOMe \xrightarrow[\text{alkene 2}]{^1/_3LiAlH_4} \underset{\mathbf{2}}{RR^1R^2B} \quad (1)$$

long-standing problem in organoborane chemistry. The synthesis of alkylalkenylalkynylboranes (**4**) constitutes



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another such unsolved long-standing problem in organoborane chemistry. A convenient synthesis of such valuable organoboranes would not only help in understanding the chemistry of those molecules but also further expand the scope and application of the versatile organoboranes. We herein report a general and simple synthesis of the hitherto inaccessible alkylalkenylalkynylboranes (**4**).

The importance of organoboranes in organic synthesis has been well documented, and a variety of methods via organoboranes are now becoming available for stereo- and regioconstruction of carbon–carbon bonds.[3,4] A general synthesis of thexyldiorganoboranes via the reaction of alkyl- or alkenyllithium reagents on thexylalkenylchloroboranes (eq 2) has recently been reported by Zweifel and Pearson.[5] Therefore, we first examined the utility of these

(1) (a) Postdoctoral research associate on Grant GM 10937-20 from the National Institutes of Health. (b) Postdoctoral research associate on Grant CHE 79-18881 from the National Science Foundation.

(2) Kulkarni, S. U.; Basavaiah, D.; Zaidlewicz, M.; Brown, H. C. *Organometallics* **1982**, *1*, 212.

(3) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(4) Brown, H. C. *Pure Appl. Chem.* **1976**, *47*, 49.

(5) Zweifel, G.; Pearson, N. R. *J. Am. Chem. Soc.* **1980**, *102*, 5919. For thexylallenic and thexylpropargylic borane intermediates, see: Zweifel, G.; Pearson, N. R. *J. Org. Chem.* **1981**, *46*, 829.

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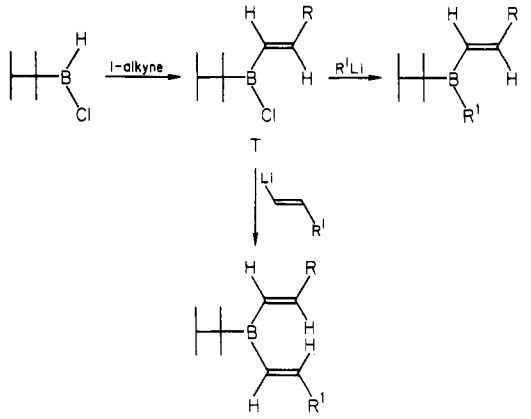
Table I. Preparation of Alkylalkenylalkynylboranes[a]

alkene for RBHBr[b]	alkyne for hydroboration by RBHBr	alkyne for alkynyllithium	product[c,d]	yield,[e] %	bp, °C (mm)	^{11}B NMR δ
thexylene[f]	1-octyne	1-hexyne	4a	>98[g]		63
cis-3-hexene	1-pentyne	*tert*-butylacetylene	4b	73	62-64 (0.01)	65
cyclopentene	1-pentyne	1-hexyne	4c	72	80-82 (0.03)	61
2-methyl-1-pentene	1-hexyne	1-pentyne	4d	72	78-80 (0.01)	62
propylene	1-pentyne	1-pentyne	4e	75	48-50 (0.01)	63
propylene	1-pentyne	1-hexyne	4f	73	59-61 (0.01)	63
ethylene	1-hexyne	1-pentyne	4g	73	58-60 (0.05)	62
propylene	3-hexyne	1-pentyne	4h	75	56-58 (0.01)	63

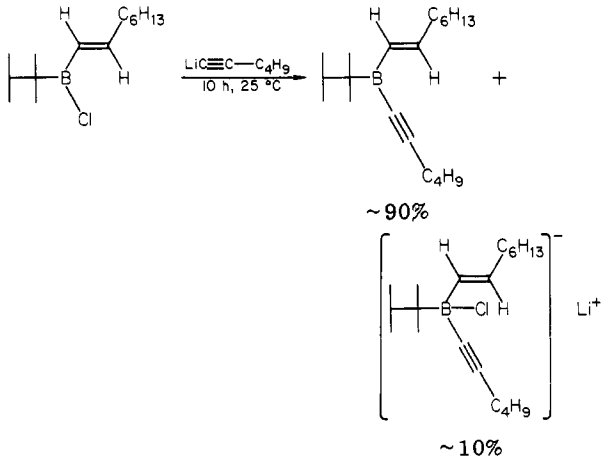
[a] All reactions were carried out on 30-mmol scale. [b] Alkylbromoboranes ($RBHBr\cdot SMe_2$)[2] were prepared by controlled hydridation of $RBBr_2\cdot SMe_2$.[12] [c] Distilled alkylalkenylborinates were utilized. [d] Chemical purities of all compounds are >98% by ^{11}B NMR. [e] Overall yields of the pure distilled products based on the starting alkenes. [f] Thexylchloroborane was prepared according to the known procedure.[13] [g] Yield of the undistilled product.



(2)

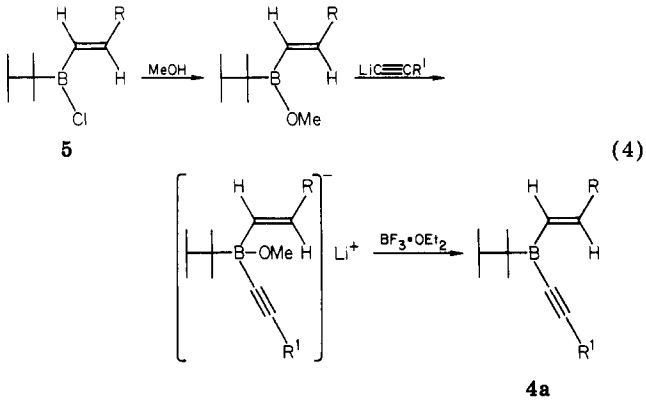
easily available thexylalkenylchloroboranes (**5**) for the synthesis of thexylalkenylalkynylboranes as a model reaction.

Unfortunately, we encountered difficulties. Reaction of thexyloctenylchloroborane with 1-hexynyllithium was inconveniently slow, requiring 10 h for 90% formation of the desired thexyloctenylhexynylborane (by ^{11}B NMR) in ether and pentane mixture as solvent at room temperature (eq 3). Changing the solvent from pentane and ether mixture to THF, ether, or pentane did not result in any significant change in the rate of reaction.



(3)

The reaction of alkynyllithium reagents with methyl dialkylborinates in THF followed by treatment with 1.33 equiv of $BF_3\cdot OEt_2$ has been reported to afford the corresponding *B*-alkynyldialkylboranes.[6] It appeared to us that the reaction of methyl thexylalkenylborinates with alkynyllithium, followed by a similar treatment with $BF_3\cdot OEt_2$, might provide the desired thexylalkenylalkynylboranes (eq 4). Indeed, we discovered that the reaction is quite clean,

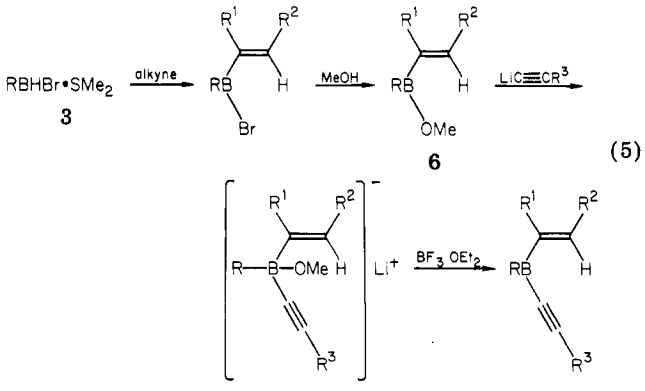


5 (4) **4a**

$R = n\text{-}C_6H_{13}$, $R^1 = n\text{-}C_4H_9$

providing thexyloctenylhexynylboranes (**4**) (^{11}B NMR δ 62.0) in almost quantitative yield (eq 4). Encouraged by this successful result, we then utilized the same strategy to prepare the alkylalkenylalkynylboranes.

Controlled hydridation[2] of alkyldibromoboranes with $LiAlH_4$ in ether produces the corresponding alkylbromoboranes (**3**). This intermediate hydroborates cleanly both terminal[7] and internal[8] alkynes to provide the corresponding alkylalkenylbromoboranes. Subsequent treatment with methanol results in the formation of the corresponding alkylalkenylborinates (**6**). These borinate es-



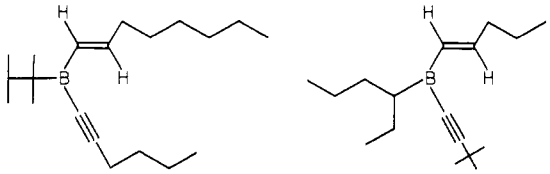
3 **6** (5) **7** **4**

(6) Brown, H. C.; Sinclair, J. A. *J. Organomet. Chem.* **1977**, *131*, 163.

(7) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 3806.
(8) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 5407.

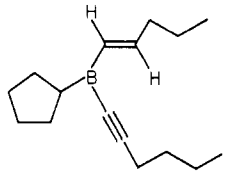
ters react with alkynyllithium reagents to generate the corresponding "ate" complexes (7), readily converted by 1.33 equiv of BF_3·OEt_2 to the desired alkylalkenylalkynylboranes in excellent yield (eq 5).

The variety of alkylalkenylalkynylboranes (**4a–h**) were prepared in excellent yields (Table I).

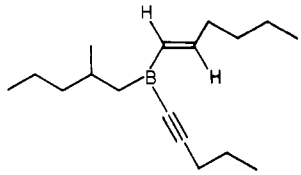


4a

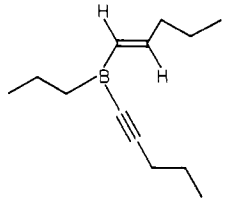
4b



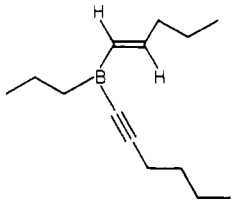
4c



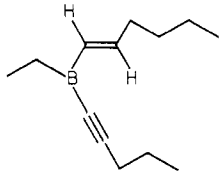
4d



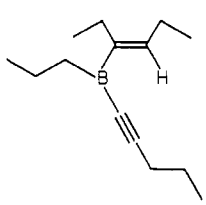
4e



4f



4g



4h

The following procedure for the preparation of ethyl((*E*)-1-hexenyl)(1-pentynyl)borane (**4g**) is representative. To 7.86 g of ethyldibromoborane–dimethyl sulfide[9] (30 mmol) were added 3 mL of SMe_2 and 20 mL of Et_2O, followed by a slow addition of $LiAlH_4$ in Et_2O (7.5 mmol) at 0 °C with stirring under nitrogen.[3] The reaction mixture was allowed to proceed for 3 h at 0 °C and 1 h at 25 °C. The resulting ethylbromoborane was slowly transferred to a solution of 1-hexyne (30 mmol) in Et_2O and stirred 1 h each at 0 and 25 °C. Then the reaction mixture was cooled to −10 °C and methanol (5 mL) was added. Stirring was continued for 0.25 h at −10 °C. ^{11}B NMR indicated that methyl ethylhexenylborinate was contaminated with 5–10% of diethyl ethylboronate.[10] Solvents were removed under reduced pressure, and careful distillation afforded 100% pure methyl ethyl ((*E*)-1-hexenyl)borinate (3.92 g, 25.5 mmol) in 85% yield: bp 64–66 °C (4.5 mm); ^{11}B NMR ($CDCl_3$, BF_3·OEt_2) δ 47.0.

To this distilled methyl ethylhexenylborinate (25.5 mmol) in THF at 0 °C was added 25.5 mmol of 1-pentynyllithium, prepared from 1-pentyne (25.5 mmol) and *n*-BuLi (25.5 mmol) in THF, and the mixture was immediately cooled to −78 °C. After 0.5 h, BF_3·OEt_2 (33.9 mmol) was added at −78 °C and stirred for an additional 0.5 h at −78 °C. The reaction mixture was then allowed to warm up to room temperature while the solvents were removed under reduced pressure. Pentane (25 mL) was added to the white solid and the mixture stirred for a few minutes. Pentane solution was decanted, the solid was washed with pentane (2 × 15 mL), and the pentane solution was combined. The pentane was removed under vacuum, and distillation afforded 4.17 g of 99% pure ethyl((*E*)-1-hexenyl)(1-pentynyl)borane (**4g**) (86%) (an overall yield of 73% based on ethyldibromoborane): bp 58–60 °C (0.05 mm); ^{11}B NMR ($CDCl_3$, BF_3·OEt_2) δ 62.0; ^1H NMR ($SiMe_4$) δ 0.7–2.00 (m, 17 H), 2.01–2.66 (m, 4 H), 6.0–7.33 (m, 2 H); IR ($CDCl_3$) 2171 (C≡C), 1612 cm^{-1} (C=C).

Thus, this procedure represents the first general synthesis of alkylalkenylalkynylboranes, valuable synthons, in excellent yields. We have successfully utilized thexylalkenylalkynylboranes for the synthesis of conjugated (*E*)-enynes.[11] We are presently exploring the possibilities of utilizing these fascinating organoboranes in organic transformations.

Registry No. **3** (R = thexyl), 86942-49-6; **3** (R = 3-hexyl), 86942-51-0; **3** (R = cyclopentyl), 86942-53-2; **3** (R = 2-methyl-1-pentyl), 86942-55-4; **3** (R = *n*-propyl), 86942-57-6; **3** (R = ethyl), 86942-59-8; (*E*)-**4a**, 86942-60-1; (*E*)-**4b**, 86942-61-2; (*E*)-**4c**, 86942-62-3; (*E*)-**4d**, 86942-63-4; (*E*)-**4e**, 86942-64-5; (*E*)-**4f**, 86942-65-6; (*E*)-**4g**, 86942-66-7; (*E*)-**4h**, 86942-67-8; (*E*)-**6** (R = thexyl, R^1 = H, R^2 = *n*-C_6H_{13}), 86942-68-9; (*E*)-**6** (R = 3-hexyl, R^1 = H, R^2 = *n*-C_3H_7), 86942-69-0; (*E*)-**6** (R = cyclopentyl, R^1 = H, R^2 = *n*-C_3H_7), 86942-70-3; (*E*)-**6** (R = 2-methyl-1-pentyl, R^3 = R^2 = *n*-C_4H_9), 86942-71-4; (*E*)-**6** (R = R^2 = *n*-C_3H_7, R^1 = H), 86942-72-5; (*E*)-**6** (R = Et, R^1 = R^2 = *n*-C_4H_9), 86942-73-6; (*E*)-**6** (R = *n*-C_3H_7, R^1 = R^2 = Et), 86942-74-7; LiC≡C-*n*-C_4H_9, 17689-03-1; LiC≡C-*t*-C_4H_9, 37892-71-0; LiC≡C-*n*-C_3H_7, 18643-50-0; $EtBBr_2$·SMe_2, 86942-75-8; 1-octyne, 629-05-0; 1-pentyne, 627-19-0; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4; diethyl ethylboronate, 53907-92-9.

(9) Ethyldibromoborane–dimethyl sulfide was prepared via redistribution of triethylborane with boron tribromide catalyzed by BH_3·SMe_2. For experimental details, see: Brown, H. C.; Basavaiah, D.; Bhat, N. G. *Organometallics*, in press.

(10) Diethyl ethylboronate (5–10%) was formed due to ether cleavage by $EtBBr_2$ during the hydridation step. For details, see ref 2.

(11) Brown, H. C.; Basavaiah, D.; Bhat, N. G., manuscript in preparation.

(12) Alkyldibromoboranes (except ethyl- and propyldibromoboranes) were prepared according to known procedure: Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384. Ethyl- and propyldibromoboranes were prepared as mentioned in ref 9.

(13) Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D. *J. Org. Chem.* **1982**, *47*, 863.

Evaluation by ESCA of the Electronic Effect of Methyl Substitution on the Cyclopentadienyl Ligand. A Study of Titanocenes, Zirconocenes, Hafnocenes, and Ferrocenes

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Summary: ESCA studies of a series of titanocenes, zirconocenes, hafnocenes, and ferrocenes have shown that substitution of methyls for hydrogens on the cyclopentadienyl ligand results in a dramatic electronic effect as reflected by the binding energies of the inner-shell

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