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Transition-metal-promoted reactions of boron hydrides. 5. Palladium-catalyzed pentaborane(9)-olefin coupling reactions: a new, mild synthetic route to alkenylpentaboranes

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of three major products: Ph_3PBH_3, **2**, and the desired cobaltacarborane **3** in about 20% yield. The identity of **3**, a dull yellow, fairly air-stable compound as 3,4,5,6-$(C_6H_5)_4$-1,3,4,5,6-$(\eta^5\text{-}C_5H_5)CoC_4BH$, was determined by comparison of its spectroscopic properties[11] with those of the known pentaphenyl derivative.[12] Although **3** is a member of the isolobal, pseudoisoelectronic series[13] shown in Chart I,[14] it may also be considered an organometallic complex with a η^5-borocycle ligand.

Mechanistically, one can speculate that, following loss of the triphenylphosphine ligand, BH_3 adds to a double bond with the transfer of a hydrogen atom to cobalt. Reductive elimination of H_2 with rearrangement would lead to **3**. Note that an expected isomer with BH in an apical position is not found and, if formed, may well rearrange under the present reaction conditions to **3**.

The metallacarborane **3** is a new derivative, and some interest lies in examining the properties of the BH fragment in such an environment; i.e., few metallacarboranes of this type have boron substituted with hydrogen.[4] However, the significance of this work lies in the demonstration that metallacycles provide a viable route to metallacarboranes. Considering the variety in the type of metallacycles known,[8] this particular method may potentially lead to some unusual compounds.

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Registry No. **1**, 12124-09-3; **2**, 1278-02-0; **3**, 87281-37-6; BH_3, 13283-31-3.

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[11] High-resolution MS: *m/e* 492.1459 (P^+) (calcd 492.1460), *m/e* 491.1484 ($P - 1^+$) (calcd 491.1496); ratio ($P - 1^+/P^+$) = 0.25, ($P + 1^+/P^+$) = 0.39, ($P + 2^+/P^+$) = 0.07. ^1H FT NMR (C_6H_6): δ 4.45 (5, s, C_5H_5), 7.03–7.44 (20, m, C_6H_5). $^{11}B\{^1H\}$ FT NMR (C_6D_6): δ 17 (bd s). IR (BH): 2540 cm^{-1}.

[12] Herberich, G. E.; Buller, B.; Hessner, B.; Oschmann, W. *J. Organomet. Chem.* **1980**, *195*, 253.

[13] Hoffmann, R. *Science (Washington, D.C.)* 1981, 995.

[14] Derivatives of all three of these compounds are known.

Transition-Metal-Promoted Reactions of Boron Hydrides. 5.[1] Palladium-Catalyzed Pentaborane(9)–Olefin Coupling Reactions: A New, Mild Synthetic Route to Alkenylpentaboranes

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Summary: The reactions of pentaborane(9) with various olefins including ethylene, propylene, and 1-butene, in the presence of catalytic amounts of palladium dibromide, have been found to give excellent yields of 1- and 2-substituted alkenylpentaboranes under mild conditions. Although palladium-promoted olefin substitution reactions are well-known, the reactions described herein are the first such reactions to be reported that are catalytic in the absence of an additional oxidizing agent.

We have previously reported[3–5] the development of transition-metal-catalyzed synthetic routes to boron-substituted alkenylboranes and -carboranes. Many of these compounds have potentially important uses, and, indeed, we have already demonstrated[3,4] that alkenylpentaboranes can be thermally converted in high yields to monocarbon carboranes. As a result, we have been actively investigating the development of new, high-yield synthetic routes to alkenylboranes.

Our previous syntheses of alkenylpentaboranes employed transition-metal complexes, such as $Ir(CO)Cl(PPh_3)_2$ and $(R_2C_2)Co_2(CO)_6$, to activate the reactions of pentaborane(9) with acetylenes. Naturally, the use of acetylenes as starting materials in these reactions provides a number of serious practical and safety problems when large scale syntheses are envisioned. In addition, although the reactions with these complexes were shown to be catalytic, the yields of alkenylpentaborane products were found to be limited by two factors. First, the temperatures (55–125 °C) required for reaction with these complexes, although mild when compared to conventional borane–alkyne reactions, are still high enough to cause product decomposition or polymerization; and second, other dissociable ligands on these complexes, such as carbon monoxide or phosphines, were found to attack the pentaborane(9) cage and cause decomposition. In an effort to circumvent these problems, we have now investigated the use of palladium(II) salts to promote borane–olefin coupling reactions. We report here that the reactions of pentaborane(9) with various olefins including ethylene, propylene, and 1-butene in the presence of catalytic amounts of palladium(II) dibromide give excellent yields of alkenylpentaboranes under milder conditions than previously employed.

In a typical reaction, 0.1331 g (0.50 mmol) of $PdBr_2$ powder (Aldrich) was stirred in vacuo with 40 mmol of pentaborane(9) and 40 mmol of propylene at 0 °C in an 88-mL Parr bomb. The reaction was stopped after 2 h and fractionated through a −63 °C trap using standard vacuum line techniques. The material passing this trap was then recondensed in the Parr flask and the reaction continued for a total reaction time of 10 h with removal of product by vacuum line fractionation as above, at 2-h intervals. The material retained in the −63 °C trap was then further purified by fractionation through a −23 °C trap. Gas chromatographic[6] separation of the material passing the −23 °C trap (423 mg) followed by spectral analysis (NMR, mass, and IR spectroscopy) indicated that this material contained three propenylpentaborane products: 2-(*trans*-1-propenyl)pentaborane,[4] I, 46.8%, 1-(*trans*-1-propenyl)pentaborane,[7] II, 36.4%, and 1-(*cis*-1-propenyl)pentaborane,[8] III, 9.5%.

The yield of alkenylpentaborane products (3.8 mmol) was 87% based on the amount of B_5H_9 consumed. This corresponds to 7.6 equiv of alkenylpentaboranes/equiv of

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[1] For part 4, see: Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.

[2] Alfred P. Sloan Foundation Fellow.

[3] Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857.

[4] Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955.

[5] Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506.

[6] Tricresyl phosphate (TCP) 6% on 60–80 mesh Chromosorb P, 65 °C; $R_v(B_5H_9) = 1.0$, $R_v(I) = 11.6$, $R_v(II) = 10.5$, and $R_v(III) = 12.9$.

[7] ^{11}B NMR (ppm, C_6D_6): −13.8 (d, 4, B_{2-5}, $J_{B-H} = 161$ Hz, $J_{B_{apex}-B_{base}} = 19.4$ Hz), −43.3 (s, B_1). ^1H NMR (δ, C_6D_6, ^{11}B spin decoupled): 6.06 (d, of m, $J_{H_A-H_B} = 17.7$ Hz, $J_{CH_3-H_B} = 6.1$ Hz, CH_B), 5.73 (d of m, $J_{H_A-H_B} = 17.7$ Hz, $J_{CH_3-H_A} \approx 1.2$ Hz, CH_A), 2.48 (B_{2-5}–H), 1.79 (d, $J_{CH_3-H_B} = 6.1$ Hz, CH_3), −2.36 (BHB).

[8] ^{11}B NMR (ppm, C_6D_6): −13.1 (d, 4, B_{2-5}, $J_{B-H} = 162$ Hz, $J_{B_{apex}-B_{base}} = 19.7$ Hz), −45.9 (s, B_1). ^1H NMR (δ, C_6D_6, ^{11}B spin decoupled) 6.32 (d of m, $J_{H_A-H_B} = 14.0$ Hz, $J_{CH_3-H_B} = 8.2$ Hz, CH_B), 5.81 (d of m, $J_{H_A-H_B} = 14.0$ Hz, $J_{CH_3-H_A} \approx 1.5$ Hz, CH_A), 2.50 (B_{2-5}–H), 1.82 (d of d, $J_{CH_3-H_B} = 8.2$ Hz, $J_{CH_3-H_A} \approx 1.5$ Hz, CH_3), −2.35 (BHB).

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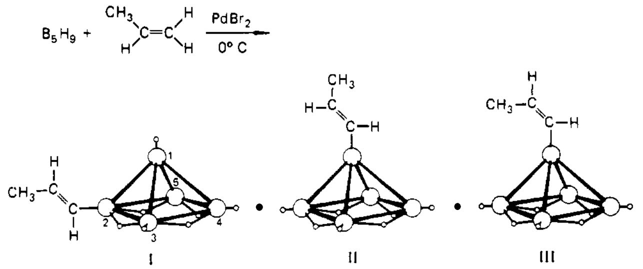

$PdBr_2$. Also isolated in smaller quantities were 2-propylpentaborane (4.7%) and 1-propylpentaborane (2.6%). No hydrogen was produced in the reaction, but GC analysis[9] of the higher volatile materials from the reaction revealed that 10.7 mmol of propylene had been consumed and that 5.5 mmol of propane had been produced. Also produced in the reaction was a small amount of lower volatile material which has not yet been characterized.

$PdBr_2$ was also found to catalyze the reactions of ethylene and 1-butene with pentaborane(9) under mild conditions to give good yields of alkenylpentaboranes: ethylene, 10 h, 0 °C, 43% 2-vinylpentaborane,[4] 13% 2-ethylpentaborane,[10] 2.3 equiv of vinylpentaboranes/$PdBr_2$; 1-butene, 8 h, 0 °C, 2-(*trans*-1-but-1-enyl)pentaborane[11] (50.4%),[12] 1-(*trans*-1-but-1-enyl)pentaborane[13] (26.9%), 2-(*trans*-1-but-2-enyl)pentaborane[14] (21.7%), 2-butylpentaborane (1%), 5.1 equiv of butenylpentaboranes/$PdBr_2$.

The procedures outlined above provide a number of significant improvements over our previously reported metal-catalyzed syntheses of alkenylboranes, in terms of higher yields, avoidance of side reactions, and ease of product separation and purification. Although the reaction gives a mixture of 1-alkenyl- and 2-alkenyl-substituted pentaboranes, we have now shown[15] that pyrolysis of the unseparated reaction products, using conditions similar to those previously described,[3,4] gives monocarbon carborane products based on the $2\text{-}CB_5H_9$ cage system in high yields. Thus, separation of the alkenylpentaborane isomers before the conversion to monocarbon carboranes is not necessary.

Palladium salts have of course been used as stoichiometric reagents for arene–olefin coupling reactions[16] which can be made pseudocatalytic in the presence of a suitable oxidant, such as oxygen or cupric chloride. The reactions described above with pentaborane(9) were found to be *catalytic* in the absence of an additional oxidant and are to our knowledge the first examples of transition-metal-catalyzed olefin substitution reactions. The mechanism of this reaction is at present unknown; however, the formation of nearly equivalent amounts of alkenylpentaboranes and propane in the propylene reaction suggests that the hydrogenation of a second equivalent of olefin is an important step in the catalytic cycle. In addition, the formation of both 1-alkenyl- and 2-alkenyl-substituted pentaboranes suggest the possibility that two different reaction pathways, involving either oxidative addition of a basal B–H unit (2-position) of pentaborane(9) to the palladium or electrophilic attack of the metal reagent at the apex boron (1-position) in pentaborane(9), may be important in the reaction. Indeed, we have previously proposed[1] similar types of reactivities to account for the platinum bromide catalyzed dehydrodimerization of pentaborane(9) which leads to the selective formation of the boron–boron coupled compound $1{:}2'\text{-}[B_5H_8]_2$. Further studies are now in progress aimed at elucidating the mechanism(s) of these unique reactions.

In conclusion, we feel it is significant that alkenylboranes can now be prepared from olefins, rather than more difficult to handle acetylenes, and that these reactions can be carried out by using mild, low-temperature conditions. Furthermore, these palladium-promoted reactions appear to have great potential for the large scale syntheses of alkenylboranes and -carboranes and we are presently investigating the production of a variety of such species using these procedures.

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Registry No. I, 78837-93-1; II, 87261-36-7; III, 87261-37-8; $PdBr_2$, 13444-94-5; pentaborane(9), 19624-22-7; propylene, 115-07-1; 2-vinylpentaborane, 78837-91-9; 2-ethylpentaborane, 23753-62-0; 2-(*trans*-1-but-1-enyl)pentaborane, 87281-27-4; 1-(*trans*-1-but-1-enyl)pentaborane, 87308-13-2; 2-(*trans*-1-but-2-enyl)pentaborane, 87281-28-5; ethylene, 74-85-1; 1-butene, 106-98-9.

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[9] Durapak phenyl isocyanate/Poracil C, 80–100 mesh, ambient temperature.

[10] Onak, T.; Dunks, G. B.; Searcy, I. W.; Spielman, J. *Inorg. Chem.* **1967**, *6*, 1465.

[11] ^{11}B NMR (ppm, C_5H_{12}, C_6D_6): 1.2 (s, B_2), −13.5 (d, 2, $B_{3,5}$, J_{B-H} = 153 Hz), −18.2 (d, B_4, J_{B-H} = 161 Hz), −51.6 (d, B_1, J_{B-H} = 165 Hz). ^1H NMR (δ, C_6D_6, ^{11}B spin decoupled) 6.00 (m, C–H), 5.40 (d of m, C–H, J = 17.5 Hz), 2.50 (br q, 3, B_{3-5}–H), 1.90 (m, 2, CH_2), 0.80 (t, 3, CH_3), −1.50 (br s, BHB), −2.60 (br s, BHB).

[12] Only relative yields are given for the 1-butene reaction owing to the difficulty in quantitatively separating 1-butene from pentaborane(9).

[13] ^{11}B NMR (ppm, C_5H_{12}, C_6D_6): −12.8 (d, 4, B_{2-5}, J_{B-H} = 166 Hz, $J_{B_{apex}-B_{base}}$ = 20 Hz), −45.2 (s, B_1). ^1H NMR (δ, C_6D_6, ^{11}B spin decoupled): 6.20 (m, C–H), 5.84 (d of m, C–H, J = 19.5 Hz), 2.40 (br q, 4, B_{2-5}–H), 2.10 (m, 2, CH_2), 1.00 (t, 3, CH_3), −2.40 (br s, BHB).

[14] ^{11}B NMR (ppm, C_5H_{12}, C_6D_6): 2.5 (s, B_2), −13.5 (d, 2, $B_{3,5}$, J_{B-H} = 153 Hz), −18.2 (d, B_4, J_{B-H} = 161 Hz), −51.6 (d, B_1, J_{B-H} = 165 Hz). ^1H NMR (δ, C_6D_6, ^{11}B spin decoupled): 5.40 (m, 2, C–H), 2.40 (br q, 3, B_{3-5}–H), 1.60 (d, 3, CH_3), 1.10 (m, 2, CH_2), −2.10 (br s, BHB), −2.80 (br s, BHB).

[15] Davan, T.; Corcoran, E. W., Jr.; Sneddon, L. G., to be submitted for publication.

[16] (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518. (b) Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *Ibid.* **1969**, *91*, 7166. (c) Shue, R. S. *J. Catal.* **1972**, *26*, 117.

Hydrogen Peroxide Oxidation of the Silicon–Carbon Bond in Organoalkoxysilanes[1]

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Summary: The silicon–carbon bond in organoalkoxysilanes is readily cleaved by 30% H_2O_2, with retention of configuration at carbon, to give the corresponding alcohols. The new methodology is applicable to one-pot synthesis of anti-Markownikoff alcohols from terminal olefins and of ketones from acetylenes via a sequence of hydrosilylation with $HSiMe(OEt)_2$ and oxidation.

Described herein is the first successful result on the oxidative cleavage of the silicon–carbon bond with 30%

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[1] Silafunctional Compounds in Organic Synthesis. 20. For part 19, see: (a) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120. For part 18, see: (b) Tamao, K.; Akita, M.; Kumada, M. *J. Organomet. Chem.*, in press. For part 17, see: ref 5. The present series title has been numbered consecutively from the former series "Organofluorosilicates in Organic Synthesis".

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