tablished by a single-crystal X-ray diffraction study (Figure 1). The structure consists of isolated neutral molecules of **3** in which the Sn atom is η^5 bonded to two $(i\text{-}Pr_2N)_2PC_5H_4$ ligands. The range of Sn–C bond lengths is typically large (2.53–2.81 Å), cf. in stannocene itself[11] (2.56 (2)–2.85 (3) Å), a situation often observed in bent-sandwich molecules.[12] The ring centroid–metal–ring centroid angle is 150.2° and thus slightly larger than that in stannocene (148.0° (molecule A) and 143.7° (molecule B)). The two $(i\text{-}Pr_2N)_2P$ moities adopt a mutually trans arrangement, and each nitrogen center is trigonal planar within experimental error.

Finally we note two aspects of the reaction of stannocene with 1 equiv of *n*-BuLi. First, the ^1H and ^{13}C NMR spectra show only single resonances, implying a time-averaged spectrum as a result of a fluxional process. Second, treatment of this solution with 1 equiv of Me_3SiCl affords **2** as the only isolable product. This result and others will be discussed in detail in a future paper.

Acknowledgment is made to the donors of the Petroleum Fund, administered by the American Chemical Society, for the support of this research.

Registry No. 1, 87050-55-3; 2, 87050-56-4; 3, 87050-57-5; $(\eta^5\text{-}C_5H_5)_2Sn$, 1294-75-3; $Me_3SiC_5H_4Li$, 76514-39-1; $(i\text{-}Pr_2N)_2PCl$, 56183-63-2.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond lengths, and bond angles and a listing of structure factor amplitudes for **3** (29 pages). Ordering information is given on any current masthead page.

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(9) Crystal data for 3: $C_{34}H_{64}N_4P_2Sn$; M_r = 708.36, triclinic, space group $P\bar{1}$ (No. 2)(by refinement), a = 9.209 (2) Å, b = 14.325 (3) Å, c = 14.726 (4) Å, α = 92.80 (2)°, β = 96.60 (2)°, γ = 92.62 (2)°, U = 1924.9 Å^3, D_{calcd} = 1.225 g cm^{-3}, Z = 2, λ(Mo Kα) (graphite monochromator) = 0.71069 Å, μ(Mo Kα) = 7.7 cm^{-1}. From a total of 6738 unique reflections, measured on an Enraf-Nonius CAD-4 diffractometer, 3382 ($I > 2.0\sigma(I)$) reflections were used to solve (Patterson and difference Fourier) and refine (full-matrix least-squares) the structure of 3. All non-hydrogen atoms were located and refined by using anisotropic thermal parameters although some carbon atoms showed a high degree of thermal motion. All unique hydrogen atoms were either located or calculated and allowed to refine positionally with a fixed isotropic temperature factor. Methyl hydrogens were neither located nor refined. This was the result of a low percentage of observed data as a result of poor crystal quality. Refinement with a weighting scheme[10] converged to give final residuals R = 0.0540, R_w = 0.0695, and GOF = 1.575.

(10) The weighting scheme used was of the form $w = (4F^2/\sigma^2(F^2) + P^2F^4)$ with P = 0.06.

(11) Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 925.

(12) See, for example: Lappert, M. F.; Riley, P. I.; Yarrow, P. I. W.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Dalton Trans.* **1981**, 814.

Preparation of a Carbon-Rich Metallacarborane from a Metallacycle

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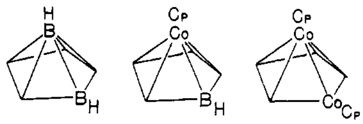
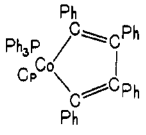
Summary: The reaction of $BH_3 \cdot THF$ with the cobaltacycle $(\eta^5\text{-}C_5H_5)[P(C_6H_5)_3]CoC_4(C_6H_5)_4$ produces the *nido*-cobaltacarborane 3,4,5,6-$(C_6H_5)_4$-1,3,4,5,6-$(\eta^5\text{-}C_5H_5)CoC_4BH$ in 20% yield. This result demonstrates a new route to carbon-rich metallacarboranes, i.e., organometallic compounds with polyhapto heterocyclic rings.

Chart I

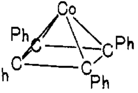


In a general sense, there are three, pair-wise routes to metallacarboranes, i.e., clusters containing a transition metal, carbon, and boron. The first involves reaction of a suitable carborane ligand with a metal fragment. The second is the reaction of a metallaborane with a source of carbon fragments. The final alternative is the reaction of a transition-metal hydrocarbon complex with a source of borane fragments. The first constitutes the major existing route to metallacarboranes and is well illustrated by the work of Hawthorne[1] and Grimes.[2] Examples of the second approach exist, but it has yet to be demonstrated that this is also a viable route to these systems.[3] Although there are notable exceptions[4] these two methods lead to compounds with cages containing high atom percents of boron whereas the third route leads naturally to carbon-rich cages. Indeed, the original synthesis of $(\eta^5\text{-}C_5H_5)Co(\eta^6\text{-}C_5H_5BC_6H_5)$ resulted from the insertion of a borane fragment into a C_5H_5 ring of cobaltacene.[5] We report here another example of the third route to metallacarboranes in which metallacycles are used as the metal–carbon source.

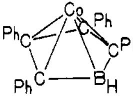
Some years ago we demonstrated the photochemical insertion of a borane fragment into $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ to yield the six-atom, nido cage $(CO)_3FeBC_4H_5$.[6] Although providing a demonstration of the third approach (above), yields were tiny and we have since sought other routes. As a nido cage can be viewed as a cyclic ligand bound to a capping BH,[4,7] we thought the reaction of a suitable metallacycle with a source of borane would provide a viable method. As many metallacycles contain metal-bound Lewis bases,[8] the use of $BH_3 \cdot THF$ provides for both a source of the borane fragment as well as a means of removing the free ligand, generated in activating the metallacycle, from the reaction. The thermolysis of (triphenylphosphine)cyclopentadienylcobalta-2,3,4,5-tetraphenylcyclopentadiene, **1**,[9] has already been shown to yield the cyclobutadiene complex **2**.[10] Presumably an unsaturated metallacycle intermediate is produced, and, thus, we chose this system to investigate initially.



1



2



3

Reflux of 0.1 mmol of **1** in toluene with 0.2 mmol of $BH_3 \cdot THF$ for 6 h, followed by hexane extraction and chromatography on silica gel, permitted the identification

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(1) Hawthorne, M. F. *J. Organomet. Chem.* **1975**, *100*, 97.

(2) Grimes, R. N. *Acc. Chem. Research* **1978**, *11*, 420.

(3) See for example: Weiss, R.; Bowser, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1522. Fehlner, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 3424.

(4) See: Grimes, R. N. *Coord. Chem. Rev.* **1979**, *28*, 47.

(5) Herberich, G. E.; Greiss, G.; Heil, H. F. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 905.

(6) Fehlner, T. P. *J. Am. Chem. Soc.* **1978**, *100*, 3250.

(7) Fehlner, T. P. In "Homoatomic Rings, Chains and Macromolecules of the Main-Group Elements"; Rheingold, A. L., Ed.; Elsevier: New York, 1977, Chapter 7, p 191.

(8) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739.

(9) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157.

(10) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1967**, *7*, 22.

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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.

Acknowledgment. The support of the National Science Foundation under Grant 81-09503 is gratefully acknowledged.

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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