Palladium-Mediated Substitution Reactions of Polyhedral Borane Anions

Steve A. Jasper, Jr., Richard B. Jones, John Mattern, John C. Huffman, and Lee J. Todd*

Department of Chemistry and Molecular Structure Center, Indiana Univeristy, Bloomington, Indiana 47405

Received May 26, 1994[⊗]

Reaction of L_2PdCl_2 species (L = PMe_2Ph or Me_2S) with $Li_2[closo\text{-}B_{10}H_{10}]$ or $Li_2[closo\text{-}B_{12}H_{12}]$ at room temperature resulted in neutral L_2-substituted boranes. The following compounds were isolated chromatographically and characterized by multinuclear NMR spectroscopy: 1,10-$(PMe_2Ph)_2B_{10}H_8$ (**1**), 2,7(8)-$(PMe_2Ph)_2B_{10}H_8$ (**2**) (a mixture of enantiomers), 1,6-$(PMe_2Ph)_2B_{10}H_8$ (**3**), 1,7-$(PMe_2Ph)_2B_{12}H_{10}$ (**4**), 1,12-$(Me_2S)_2B_{12}H_{10}$ (**5**), and 1,7-$(Me_2S)_2B_{12}H_{10}$ (**6**). Compound **2** was characterized by an X-ray diffraction study. Colorless crystals were orthorhombic space group $P2_12_12_1$, with a = 8.917(3) Å, b = 9.601(3) Å, c = 26.525(12) Å, and Z = 4. The structure was determined by conventional methods and refined to a final value of R = 0.0591 (1886 reflections), R_w = 0.0522.

Introduction

The use of palladium reagents in synthetic organic chemistry is well-known.[1] The use of transition metals, particularly platinum and rhodium reagents, to promote various reactions in boranes and carboranes has also been described.[2−4] Known reaction types include: hydroboration, alkenyl cage substitution, acetylene insertion, multicage coupling, and cage closure. We wish to demonstrate the use of easily accessible palladium(II) reagents to effect cage substitution reactions. In these reactions, 2 electron neutral donor ligands transfer from palladium to a borane anion at 25 °C, substituting for one or more hydride ions resulting in a "charge-compensated"[5] species.

Numerous charge-compensated boranes and carboranes are known; indeed, several of the compounds described herein were originally made nearly 30 years ago.[6,7] There are also a fair number of metallaheteroboranes containing charge-compensated ligands. Methods of preparation include formal ligand rearrangement from the metal onto the cage,[8−10] reduction of a metallacarborane complex by a Lewis base,[11−13] addition of R_2S to a protonated metallocene-type sandwich complex,[14] and metallation of a charge-compensated carborane ligand.[5,15−18] It was during recent studies of palladadiarsaboranes[19] that we first realized that a general method for palladium assisted substitution of polyhedral borane anions was possible.

In this preliminary report we describe this synthetic method and characterize the products (including more detailed characterization of some compounds previously published), along with an X-ray structure of one enantiomer of a new diphosphine−borane.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.85 MHz (21 °C) with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3{\cdot}OEt_2$. Phosphorus (^{31}P) NMR spectra were obtained at 146.2 MHz (21 °C) and externally referenced to 85% H_3PO_4. Proton (^1H) spectra were obtained at 361.1 MHz (21 °C) and internally referenced to trace protonated solvent. In all NMR spectra, positive chemical shifts were downfield. Infrared spectra were obtained as KBr pellets and recorded on a Nicolet 510P Fourier transform spectrometer. Melting points were obtained in sealed, evacuated capillaries and are uncorrected.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5. Bis(trimethylammonium) decahydrodecaborate, $(Me_3NH)_2B_{10}H_{10}$ was prepared by previous literature methods.[20] Disodium Dodecahydrododecaborate, $Na_2B_{12}H_{12}$, was used as purchased from Callery Chemical Co., Pittsburgh, PA. Dibenzonitrilepalladium(II) chloride, $(PhCN)_2PdCl_2$, was made by the Kharasch method.[21] Bis(dimethylphenylphosphine) palladium(II) chloride was prepared by the method of Wild et al.[22] All other commercially available reagents were used as purchased.

$(Me_2S)_2PdCl_2$. Dibenzonitrilepalladium(II) chloride (767 mg, 2.00 mmol) was dissolved in 30 mL benzene in a three-neck round-bottom flask equipped with a septum and nitrogen inlet. Dimethyl sulfide (0.31

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

(1) (a) Heck, R. F. *Palladium reagents in organic syntheses*; Academic Press: London, 1985. (b) Tsuji, J. *Organic synthesis with palladium compounds*; Springer-Verlag: Berlin, 1980.
(2) Sneddon, L. G. *Pure Appl. Chem.* **1987**, *59*, 837.
(3) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175; and references therein.
(4) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179.
(5) Kang, H. C.; Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2024.
(6) Miller, H. C.; Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1456.
(7) Knoth, W. H.; Hertler, W. R.; Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 280.
(8) Miller, S. B.; Hawthorne, M. F. *J. Chem. Soc. Chem. Commun.* **1976**, 787.
(9) King III, R. E.; Miller, S. B.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3548.
(10) Greenwood, N. N.; Kennedy, J. D. *Pure Appl. Chem.* **1991**, *63*, 317.
(11) Jones, C. J.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 7633.
(12) Churchill, M. R.; Gold, K. *Inorg. Chem.* **1973**, *12*, 1157.
(13) Plesek, J.; Stibr, B.; Hermanek, S. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1492.
(14) Hawthorne, M. F.; Warren Jr., L. F.; Callahan, K. P.; Travers, N. F. *J. Am. Chem. Soc.* **1971**, *93*, 2407.
(15) Teller, R. G.; Wilczynski, J. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 472.
(16) Colquhoan, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc. Dalton Trans.* **1979**, 619.
(17) Young, D. C.; Howe, D. V.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 859.
(18) Kang, H. C.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 1716.
(19) Jasper, S. A., Jr.; Roach, S.; Stipp, J. N.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1993**, *32*, 3072.
(20) Hawthorne, M. F.; Pilling, R. L. *Inorg. Synth.* **1967**, *9*, 16.
(21) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.
(22) Roberts, N. K.; Skelton, B. W.; White, A. H.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1982**, 2093.

0020-1669/94/1333-5620$04.50/0

Table 1. ^{11}B NMR Data

cmpd	chem shift (ppm), rel intens, J_{B-H} (Hz)
1,10-$(PMe_2Ph)_2$-$B_{10}H_8$[a]	3.2, 2B, doublet, J_{B-P} 194 Hz; −22.0, 8B, 134
2,7(8)-$(PMe_2Ph)_2$-$B_{10}H_8$[a]	1.0, 2B, 151; −25.9, 2B, 137; −28.7, 6B, doublet, J_{B-P} 134 Hz
1,6-$(PMe_2Ph)_2$-$B_{10}H_8$[a]	10.3, 1B, 147; −5.6, 1B, doublet, J_{B-P} 197 Hz; −23.9, 3B; −24.7, 2B; −26.5, 2B; −28.4, 1B, doublet, J_{B-P} ca. 119 Hz
1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$[a]	−11.9, 4B; −13.6, 4B, 159; −15.3, 2B; −16.2, 2B, doublet, J_{B-P} 150 Hz
1,12-$(Me_2S)_2$-$B_{12}H_{10}$[b]	−7.7, 2B, singlet; −15.3, 10B, 136
1,7-$(Me_2S)_2$-$B_{12}H_{10}$[b]	−9.3, 2B, singlet; −13.3, 2B; −15.4, 6B; −16.9, 2B

[a] CH_2Cl_2 solvent. [b] THF solvent.

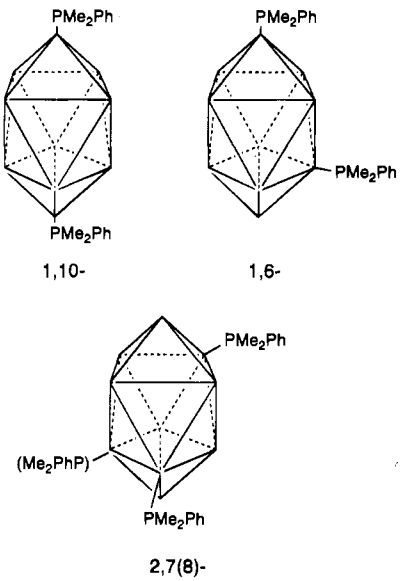

Figure 1. Geometries of $(PMe_2Ph)_2B_{10}H_8$ isomers.

Table 2. $^{31}P\{^1H\}$ NMR Data

cmpd[a]	chem shift (ppm), multiplicity, J_{B-P} (Hz)
1,10-$(PMe_2Ph)_2$-$B_{10}H_8$	−6.3, 1:1:1:1 quartet, 194
2,7(8)-$(PMe_2Ph)_2$-$B_{10}H_8$	−2.0, multiplet
1,6-$(PMe_2Ph)_2$-$B_{10}H_8$	−5.6, 1:1:1:1 quartet, 196; −3.6, 1:1:1:1 br quartet
1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$	−8.9, 1:1:1:1 quartet, 150

[a] $CDCl_3$ solvent.

mL, 4.2 mmol) was transferred to the solution via cannula, and the resulting solution allowed to stir for 3 h. Some of the benzene was rotary evaporated, and the product crystallized by addition of pentane to the point of turbidity. The yield was nearly quantitative.

$(PMe_2Ph)_2$-*closo*-$B_{10}H_8$. In a typical reaction scheme, $(Me_3NH)_2B_{10}H_{10}$ (1430 mg, 5.998 mmol) was placed in a round-bottom flask equipped with magnetic stir bar, and dissolved in 300 mL of H_2O. To this solution was added $LiOH{\cdot}H_2O$ (503 mg, 12.0 mmol). After stirring at room temperature overnight, the water was removed by rotary evaporation, and the resulting solid $Li_2B_{10}H_{10}$ pumped dry *in vacuo* (10^{-2} Torr) for 5 h. The solids were suspended in dry distilled CH_2Cl_2 (35 mL). In a separate flask, $(PMe_2Ph)_2PdCl_2$ (6803 mg, 15.00 mmol) was dissolved in dry distilled CH_2Cl_2 (30 mL), and then transferred via cannula to the stirring $Li_2B_{10}H_{10}$ suspension. An immediate color change to orange was observed. After reacting for 2 days, during which the color changed to brown, the CH_2Cl_2 was rotary evaporated. The resulting solids were extracted exhaustively with benzene, and the extract filtered through a coarse fritted funnel. An excess of $NaBH_4$ was added to the benzene solution to reduce all remaining palladium species to Pd^0. The solution was brought to reflux

Table 3. ^1H NMR Data

cmpd	chem shift (ppm), rel intens, assignt, multiplicity, $^2J_{H-P}$ (Hz)
1,10-$(PMe_2Ph)_2$-$B_{10}H_8$[a]	2.178, 12H, P*Me*$_2$, doublet, 12.1: 7.5−8.2, 10H, P*Ph*, mult
2,7(8)-$(PMe_2Ph)_2$-$B_{10}H_8$[a]	1.568, 6H, P*Me*$_2$, doublet, 12.0; 1.580, 6H, P*Me*$_2$, doublet, 12.0; 7.1−7.7, 10H, P*Ph*, multiplets
1,6-$(PMe_2Ph)_2$-$B_{10}H_8$[a]	1.583, 6H, P*Me*$_2$, equatorial doublet, 12.0; 2.115, 6H, P*Me*$_2$, apical doublet, 12.2; 7.4−8.1, 10H, P*Ph*, multiplets
1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$[a]	1.780, 12H, P*Me*$_2$, doublet, 12.2; 7.4−7.6, 10H, P*Ph*, mult
1,12-$(Me_2S)_2$-$B_{12}H_{10}$[b]	2.454, *Me*$_2$S
1,7-$(Me_2S)_2$-$B_{12}H_{10}$[b]	2.480, *Me*$_2$S

[a] $CDCl_3$ solvent. [b] CD_3CN solvent.

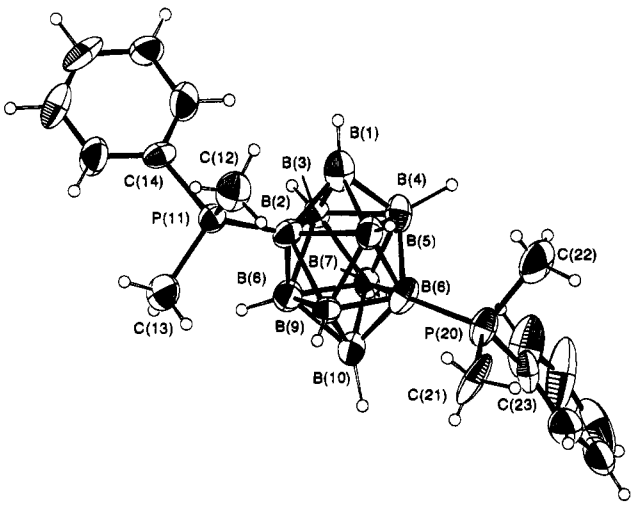

Figure 2. ORTEP diagram of 2,8-$(PMe_2Ph)_2B_{10}H_8$ (**2**).

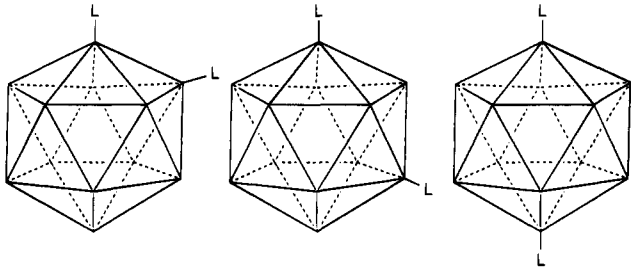

Figure 3. Geometries of possible $L_2B_{12}H_{10}$ isomers.

for 4 h. The mixture was filtered through a coarse fritted funnel to remove finely divided gray metal and unreacted $NaBH_4$ (*Caution*! the solid sometimes ignites spontaneously upon drying in air), resulting in a colorless filtrate. The benzene was removed by rotary evaporation, the remaining solids redissolved in CH_2Cl_2, and 2 g of silica gel (Merck grade 60, 230−400 mesh, 60 Å) was added. The CH_2Cl_2 was removed *in vacuo* and the solids were packed on a 35 cm × 2.4 cm silica gel chromatography column, and eluted with toluene, followed by 1:1 (v/v) toluene:CH_2Cl_2. There were four detectable bands, all colorless: band **I** had $R_f = 0.43$ by TLC (toluene mobile phase, I_2 development); band **II** had $R_f = 0.81$ (CH_2Cl_2 mobile phase); band **III** had $R_f = 0.66$; and band **IV** had $R_f = 0.50$. Band **I** was determined by ^{11}B NMR to be $(PMe_2Ph)BH_3$.[23] Band **II**, determined to be 1,10-$(PMe_2Ph)_2B_{10}H_8$ (**1**), is a white solid (221 mg, 9.38% yield). Mp: 188−193 °C. Exact mass measured for $^{12}C_{16}{}^1H_{30}{}^{11}B_{10}{}^{31}P_2$ 394.2758, calcd 394.2753. Band **III**, determined to be 2,7(8)-$(PMe_2Ph)_2B_{10}H_8$ (**2**), is a white solid (99

(23) Noeth, H. *Nuclear magnetic resonance spectroscopy of boron compounds*; Springer-Verlag: Berlin, 1978.

Table 4. Infrared Data

cmpd	ν_{max} (cm^{-1})
1,10-$(PMe_2Ph)_2$-$B_{10}H_8$	3058 (w), 2992 (w), 2919 (w), 2496 (vs), 1574 (w), 1489 (w), 1437 (s), 1416 (m), 1406 (m), 1314 (w), 1302 (m), 1289 (m), 1190 (w), 1159 (m), 1115 (s), 984 (w), 951 (vs), 920 (vs), 882 (m), 860 (m), 762 (m), 745 (s), 725 (s), 691 (s), 492 (m), 473 (m), 444 (vs), 422 (m)
2,7(8)-$(PMe_2Ph)_2$-$B_{10}H_8$	3063 (w), 2990 (w), 2913 (w), 2541 (s), 2502 (vs), 2471 (vs), 1489 (w), 1439 (m), 1412 (m), 1318 (w), 1302 (w), 1291 (m), 1188 (w), 1115 (m), 1074 (w), 1061 (w), 1013 (w), 999 (w), 947 (m), 936 (m), 912 (s), 895 (m), 860 (m), 835 (w), 750 (m), 723 (w), 693 (m), 681 (w), 476 (w), 432 (s)
1,7-$(PMe_2Ph)_2$-$B_{12}H_{10}$	3056 (w), 2990 (w), 2921 (w), 2537 (vs), 1489 (w), 1437 (s), 1418 (m), 1400 (m), 1343 (w), 1319 (w), 1304 (m), 1291 (m), 1119 (s), 1076 (m), 1059 (w), 1028 (w), 988 (w), 949 (s), 920 (s), 880 (w), 858 (m), 826 (w), 768 (m), 745 (s), 731 (s), 691 (s), 482 (s), 421 (m)
1,7-$(Me_2S)_2$-$B_{12}H_{10}$	2508 (s), 1426 (s), 1036 (m), 1003 (s), 966 (s), 808 (s), 727 (m)

mg, 4.2% yield). Mp: 128−134 °C. Band **IV** was determined to be 1,6-$(PMe_2Ph)_2$-$B_{10}H_8$ (**3**) (201 mg, 8.53% yield).

$(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$ (4). The preparation is similar to that for $(PMe_2Ph)_2B_{10}H_8$, except that THF was used as reaction solvent. Reaction of $Na_2B_{12}H_{12}$ (1.8031 g, 9.6012 mmol) with $(PMe_2Ph)_2PdCl_2$ (4.3553 g, 9.6012 mmol), followed by workup and chromatography, resulted in two principal bands, both colorless: band **I** had $R_f = 0.8$ by TLC (CH_2Cl_2 mobile phase, I_2 development); band **II** had $R_f = 0.6$. Band **I** was determined by ^{11}B NMR to be $(PMe_2Ph)BH_3$.[23] Band **II**, $(PMe_2Ph)_2$-$B_{12}H_{10}$, is a white solid (1.201 g, 30.14% yield). Mp: 202−206 °C.

$(Me_2S)_2$-*closo*-$B_{12}H_{10}$. The preparation is similar to that for $(PMe_2Ph)_2B_{10}H_8$, except that THF was used as reaction solvent. Reaction of $Li_2B_{12}H_{12}$ (606 mg, 3.89 mmol) with $(Me_2S)_2PdCl_2$ (2.346 g, 7.780 mmol), followed by workup and chromatography, resulted in three observable bands, all colorless: band **I** had $R_f = 0.96$ by TLC (CH_2Cl_2 mobile phase, I_2 development); band **II** had $R_f = 0.64$; and band **III** had $R_f = 0.50$. Band **I** was determined by ^{11}B NMR to be $(PMe_2Ph)BH_3$.[23] Band **II**, a white solid, was determined to be 1,12-$(Me_2S)_2B_{12}H_{10}$ (**5**) by ^{11}B NMR (see Table 1). Band **III** was determined to be 1,7-$(Me_2S)_2B_{12}H_{10}$ (**6**), a white solid. Mp: 276.5−278 °C.

Crystal Structure Determination. The diffractometer utilized for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator was interfaced to a Z80 microprocessor which was controlled by an RS232 serial port on an IBM PC microcomputer. Motors were slo-syn stepping motors, and a special top/bottom−left/right slit assembly was used to align the crystal. All computations were performed on IBM compatible microcomputer systems using DOS or OS/2 operating systems.

For 2,8-$(PMe_2Ph)_2$-*closo*-$B_{10}H_8$ (**2**), data were collected using a continuous theta, two-theta scan technique with fixed backgrounds at each extreme of the scan. A small well formed fragment with dimensions 0.25 × 0.25 × 0.45 mm of a larger colorless parallelepiped of **2** was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −173 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique orthorhombic space group $P2_12_12_1$. Subsequent solution and refinement confirmed this choice. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MULTAN78) and standard Fourier techniques. Most hydrogen atoms were clearly visible in a difference Fourier phased on the nonhydrogen atoms, and were included in the least squares refinement, although it was necessary to fix the thermal parameters of those associated with the organic ligand. The hydrogen atoms are not well defined, but are qualitatively correct. A final difference Fourier was essentially featureless, the largest peak being 0.34 e/Å^3. Additional information may be obtained from the Molecular Structure Center by reference to report No. 94104.

Results and Discussion

$(PMe_2Ph)_2$-*closo*-$B_{10}H_8$ Isomers. Reaction of *closo*-$B_{10}H_{10}^{2-}$ with $(PMe_2Ph)_2PdCl_2$ at ambient temperature afforded three isomers of $(PMe_2Ph)_2$-*closo*-$B_{10}H_8$, in low yields, eq 1. The fate

$$Li_2B_{10}H_{10} + (PMe_2Ph)_2PdCl_2 \rightarrow (PMe_2Ph)_2B_{10}H_8 + 2LiCl + [L_nPd] \quad (1)$$

of the palladium is not completely understood, as the $[L_nPd]$ product indicates. However, a significant quantity of gray insoluble material was always produced in the workup, upon treating the mixture with sodium borohydride, eq 2.

$$[L_nPd] + NaBH_4 \rightarrow Pd^0 + H_2 + (PMe_2Ph)BH_3 + Na^+ + \text{other} \quad (2)$$

The purpose of this set of reactions was to use palladium complexes to make charge-compensated boranes. Although the yields are relatively low, we are concerned at present with the generality of this synthetic method. Specifically, we believe it may be possible to choose from a wide variety of anionic boranes and palladium(II) species of the general formula L_2PdCl_2, where L = neutral $2e^-$ donor, to generate neutral L-substituted *closo*-boranes. We are now investigating the scope and limitations of this method.

This methodology was developed after it was noticed that charge-compensated metallaheteroborane complexes were formed while synthesizing nickel- and palladium-containing heteroboranes.[19] Thus, it was decided to employ palladium reagents to investigate this chemistry, since many L_2PdCl_2 compounds are known, and can be easily made. The analogous platinum reagents can also be made easily, but the charge-compensation reaction does not occur to an appreciable extent under the conditions employed here. This is perhaps to be expected, as third row transition metal complexes are well known to be less kinetically labile than first and second row transition metal complexes, and M-L bond strengths (and thus dissociation energies) generally increase going down a group.[24] However, it has recently been shown that charge compensation may occur by rearrangement of a platinacarborane, but only under thermolytic conditions.[25]

Previous $B_{10}H_{10}^{2-}$ chemistry shows a marked preference for reactivity at the two apical sites.[7] This preference is evident in the $(PMe_2Ph)_2B_{10}H_8$ case in that, of the products isolated, 42% is the 1,10-isomer, and 81% has at least one apical substituent (see Figure 1). The remaining products are the 2,7(8)- (all equatorial) isomers, which are statistically the most favored

(24) Collman, J. P.; Hegedus, L. S. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(25) Jones, J. H.; Stibr, B.; Kennedy, J. D.; Thornton-Pett, M. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2924.

Table 5. Selected Bond Distances (Å) for 2,8-$(PMe_2Ph)_2$-$B_{10}H_8$ (**2**)

B(2)−P(11)	1.901(13)	B(5)−B(8)	1.792(19)
B(8)−P(20)	1.886(11)	B(5)−B(9)	1.837(18)
B(1)−B(2)	1.696(20)	B(6)−B(7)	1.831(18)
B(1)−B(3)	1.691(20)	B(6)−B(9)	1.845(19)
B(1)−B(4)	1.710(21)	B(6)−B(10)	1.733(19)
B(1)−B(5)	1.668(20)	B(7)−B(8)	1.817(15)
B(2)−B(3)	1.788(17)	B(7)−B(10)	1.681(18)
B(2)−B(5)	1.829(17)	B(8)−B(9)	1.789(17)
B(2)−B(6)	1.800(18)	B(8)−B(10)	1.673(19)
B(2)−B(9)	1.797(16)	B(9)−B(10)	1.682(19)
B(3)−B(4)	1.803(16)	P(11)−C(12)	1.783(16)
B(3)−B(6)	1.824(18)	P(11)−C(13)	1.827(12)
B(3)−B(7)	1.812(18)	P(11)−C(14)	1.820(9)
B(4)−B(5)	1.849(20)	P(20)−C(21)	1.792(15)
B(4)−B(7)	1.828(19)	P(20)−C(22)	1.813(15)
B(4)−B(8)	1.801(20)	P(20)−C(23)	1.810(12)

Table 6. Crystallographic Data for 2,8-$(PMe_2Ph)_2$-$B_{10}H_8$ (**2**)

mol wt = 392.46	scan width = 2.0° + dispersion
cryst syst: orthorhombic,	single bkgd time at extremes
$P2_12_12_1$, $Z = 4$	of scan = 4 s
unit cell	aperture size = 3.0 × 4.0 mm
$a = 8.917(3)$ Å	collcn limit (2θ) = 6−45°
$b = 9.601(3)$ Å	tot. no. of reflcns: 1886
$c = 26.525(12)$ Å	no. of unique intens: 1737
$V = 2270.88$ Å^3	no. with $F > 0.0$: 1534
$\varrho_{calcd} = 1.148$ g cm^{-3}	no. with $F > 2.33*\sigma(F)$: 1174
$\lambda = 0.710\,69$ Å	R for averaging: 0.050
$\mu = 1.869$ cm^{-1}	final residuals
detector−sample dist = 22.5 cm	$R(F) = 0.0591$
sample−source dist = 23.5 cm	$R_w(F) = 0.0522$
takeoff angle = 2.0°	GOF for last cycle = 1.186
av ω scan width at	max Δ/σ for last cycle = 0.12
half-height = 0.25°	
scan speed = 8.0°/min	

of the observed products—yet they comprise only 19% of the observed products. Note steric factors may also be important in the determination of which isomers are formed, as no 1,2-, 2,3(5)-, or 2,6(9)-substitution was observed.

Note that ^{11}B and ^{31}P NMR of both 1,10-$(PMe_2Ph)_2B_{10}H_8$ and 1,6-$(PMe_2Ph)_2B_{10}H_8$ have recently been reported.[25] Our data are in good agreement, except for the magnitude of $J_{B(6)-P}$ (see Tables 1 and 2). This could not be determined precisely by either ^{11}B or ^{31}P NMR because of overlap with other resonances. Phosphorus-31 NMR clearly distinguishes between apically and equatorially substituted phosphines. While both are quartets, the apical signals are sharp and easily recognizable; the equatorial signals are considerably broader, perhaps due to partial thermal decoupling of ^{11}B from the ^{31}P signal.

The difference between apical and equatorial substitution is also apparent in the ^{1}H NMR, looking at the methyl groups on the phosphines (see Table 3). Apical substitution results in chemical shifts in the 2.1−2.2 ppm region; equatorial substitution results in chemical shifts in the 1.5−1.6 ppm region. This agrees with 1.71 ppm observed for 6-PMe_2Ph-1-CB_9H_9.[25] Particularly interesting is the ^{1}H NMR of 2,7(8)-$(PMe_2Ph)_2B_{10}H_8$, which shows a pair of doublets ($^2J_{H-P}$) due to molecular asymmetry. This is a similar result to the two resonances observed in 2,7(8)-$(Me_2S)_2B_{10}H_8$.[7] This data, in addition to the X-ray structure determination on 2,8-$(PMe_2Ph)_2B_{10}H_8$ (*vide infra*), confirms the regiochemistry of 2,7(8)-$(Me_2S)_2B_{10}H_8$, as previously reasoned. It also suggests the same regiochemical assignments for $(NMe_3)_2B_{10}H_8$[26] and $(NMe_2CH_2Cl)_2B_{10}H_8$,[27] as previously reasoned.

Structural Considerations. An X-ray structural determination of 2,7(8)-$(PMe_2Ph)_2B_{10}H_8$ (**2**) was undertaken to verify its regiochemistry (see Figure 2). NMR evidence indicates that both enantiomeric 2,7- and 2,8-isomers are present in solution. However, crystallization favors separation of the enantiomers, and the 2,8-enantiomer was the one chosen for structural determination. The compound has C_2 molecular symmetry, and therefore has five pairs of equivalent B atoms: positions (1,10), (2,8), (3,7), (4,6), and (5,9). Overall, the structural parameters of this molecule are fairly unexceptional. The two

(26) Hertler, W. R.; Raasch, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 3661.
(27) Hertler, W. R. *Inorg. Chem.* **1964**, *3*, 1195.

Table 7. Fractional Coordinates and Isotropic Thermal Parameters for 2,8-$(PMe_2Ph)_2$-$B_{10}H_8$ (**2**)[a]

atom	x	y	z	B_{iso}[b] (Å^2)
B(1)	5281(16)	3589(14)	4424(6)	41
B(2)	4317(14)	3959(12)	3889(5)	31
B(3)	6242(15)	4433(11)	3967(5)	32
B(4)	6739(17)	2692(13)	4159(6)	36
B(5)	4746(16)	2188(14)	4098(5)	35
B(6)	5457(15)	4218(15)	3337(5)	34
B(7)	7166(15)	3290(11)	3520(5)	31
B(8)	6082(14)	1713(11)	3623(6)	33
B(9)	4405(16)	2584(13)	3430(5)	33
B(10)	5990(16)	2625(13)	3087(6)	38
P(11)	2418(4)	4847(3)	3939(1)	30
C(12)	1177(16)	3798(15)	4304(7)	49
C(13)	1534(15)	5120(14)	3325(5)	47
C(14)	2447(14)	6539(10)	4248(4)	29
C(15)	1438(16)	7577(14)	4135(5)	46
C(16)	1527(17)	8840(13)	4384(6)	51
C(17)	2498(20)	9041(12)	4758(5)	48
C(18)	3493(18)	8052(12)	4881(5)	49
C(19)	3466(17)	6810(12)	4621(5)	53
P(20)	6494(3)	−212(3)	3591(1)	37
C(21)	4967(17)	−1138(13)	3307(7)	58
C(22)	6743(21)	−983(13)	4209(6)	60
C(23)	8200(13)	−610(12)	3250(5)	42
C(24)	9403(15)	254(15)	3332(7)	74
C(25)	10752(19)	−25(18)	3108(11)	99
C(26)	10888(21)	−1133(29)	2797(8)	90
C(27)	9699(23)	−2013(21)	2716(6)	70
C(28)	8322(17)	−1787(14)	2947(5)	51
H(1)	495(14)	383(12)	479(5)	84(25)
H(2)	691(8)	560(7)	405(3)	21(15)
H(3)	763(10)	205(8)	445(3)	40(16)
H(4)	403(9)	131(9)	426(3)	34(17)
H(5)	516(9)	516(9)	312(3)	41(17)
H(6)	834(12)	352(10)	338(3)	54(19)
H(7)	350(9)	216(7)	326(3)	26(15)
H(8)	625(14)	215(11)	267(4)	79(24)
H(9)	34(14)	396(15)	428(5)	57
H(10)	104(13)	284(13)	416(4)	57
H(11)	160(13)	364(12)	472(4)	57
H(12)	51(13)	548(12)	339(4)	56
H(13)	234(14)	561(11)	317(4)	56
H(14)	112(13)	403(12)	312(4)	56
H(15)	79(13)	751(13)	389(4)	55
H(16)	75(14)	942(14)	441(5)	60
H(17)	247(13)	983(12)	495(4)	59
H(18)	443(13)	824(11)	518(5)	58
H(19)	404(13)	608(13)	478(5)	63
H(20)	413(13)	−72(13)	352(5)	67
H(21)	474(15)	−90(14)	289(5)	67
H(22)	504(14)	−211(13)	337(5)	67
H(23)	583(15)	−62(15)	440(5)	68
H(24)	700(14)	−247(13)	413(4)	68
H(25)	747(15)	−41(13)	432(5)	68
H(26)	910(15)	129(14)	353(5)	82
H(27)	1170(18)	51(16)	317(6)	108
H(28)	1169(18)	−153(17)	264(6)	102
H(29)	996(20)	−280(15)	254(6)	79
H(30)	742(14)	−238(13)	293(4)	61

[a] Fractional coordinates are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. B_{iso} values are $\times 10$. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

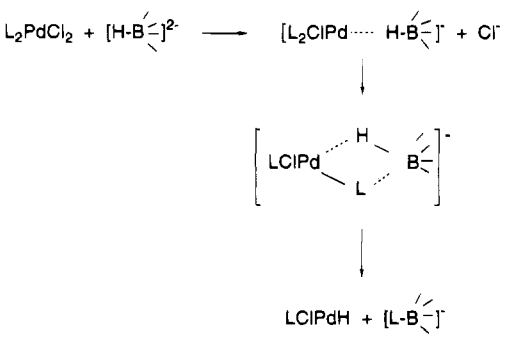

Figure 4. Possible mechanistic scheme for reaction of palladium reagents with boranes.

B−P distances, 1.901(13) and 1.886(11) Å, agree fairly well with values observed previously for phosphines substituted onto a boron hydride (1.900(5)−1.945(9) Å).[25,28] The average B−B distance in the molecule is 1.774 Å, which is completely usual; however, the two apical B atoms, which each have only four nearest B neighbors, have slightly smaller average distances, 1.691 Å and 1.692 Å.

1,7-$(PMe_2Ph)_2$-*closo*-$B_{12}H_{10}$. Reaction of *closo*-$B_{12}H_{12}^{2-}$ with $(PMe_2Ph)_2PdCl_2$ at ambient temperature yields a similar result to the $B_{10}H_{10}^{2-}$ reaction, except that only one isomer (of three possible, see Figure 3) predominates, eq 3. To our

$$Li_2B_{12}H_{12} + (PMe_2Ph)_2PdCl_2 \rightarrow 1,7\text{-}(PMe_2Ph)_2B_{12}H_{10} + 2LiCl + [L_nPd] \quad (3)$$

knowledge, this is the first reporting of this compound (however, the closely related $(PMe_3)_2$-*closo*-$B_{12}H_{10}$ has been reported)[6]. Although no X-ray structural determination has been undertaken to conclusively prove it, this isomer is most likely 1,7-$(PMe_2Ph)_2B_{12}H_{10}$ for the following reasons: assuming that the phosphines attach to the cage one at a time, a 1,2-disubstituted product would be sterically unfavored; a 1,12-disubstituted product is ruled out by ^{11}B NMR.

The B−P coupling constant, 150 Hz as determined by ^{31}P NMR, is within the range of values observed for phosphine-borane compounds (118−200 Hz).[28,29] The value could not be corroborated by ^{11}B NMR, however, because the doublet was not quite well enough resolved for accurate measurement.

$(Me_2S)_2$-*closo*-$B_{12}H_{10}$ Isomers. Reaction of *closo*-$B_{12}H_{12}^{2-}$ with $(Me_2S)_2PdCl_2$ at ambient temperature yielded the known[6] $(Me_2S)_2$-*closo*-$B_{12}H_{10}$ compound. Two isomers were isolated, which is consistent with Kaczmarczyk's TLC observations.[30] The 1,12-isomer was identified by the ^{11}B NMR spectrum (see Table 1), which indicates a high symmetry (D_{5h}) that excludes the 1,2- or 1,7-isomers as possibilities. The predominant isomer, by the same reasoning applied to $(PMe_2Ph)_2B_{12}H_{10}$, is most likely the 1,7-$(Me_2S)_2$-$B_{12}H_{10}$ isomer. The original synthesis of the compound does not address the issue of isomerism, and relatively little characterization was accomplished. However, the IR spectrum[6] (see Table 4) and ^1H NMR[30] (see Table 3) agree very well with those previously reported spectra. We therefore speculate that the original synthesis (by an independent route) resulted in the 1,7-isomer as well.

The stoichiometry of these reactions remains unoptimized. A variety of stoichiometries from 1 mol of cage:1 mol of Pd complex to 1 mol of cage:3 mol of Pd complex have been tried, with no great difference resulting. If the phosphine ligands are indeed attached to the cages one at a time, it should be possible to place only one ligand on a cage by carefully controlling the stoichiometry. However, it is not yet known whether one or two phosphines leave the palladium and attach to the cage. Further studies to determine this are in progress.

We have no formal mechanistic data for this metal-mediated ligand transfer from the metal to a borane. Nonetheless, we present one possible mechanistic pathway, partially based upon recent work of Hartwig et al.,[31] see Figure 4. It may be regarded as an example of B−H bond activation, with subsequent functionalization of the B atom, proceeding through a PdLBH four-centered intermediate. Two such cycles would be required to substitute a ligand L at two different BH sites.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, and intramolecular angles (7 pages). Ordering information is given on any current masthead page.

(28) Bould, J.; Brint, P.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2335.

(29) Ferguson, G.; Gallagher, J. F.; Sheehan, J. P.; Spalding, T. R.; Kennedy, J. D.; Macias, R. *J. Chem. Soc., Dalton Trans.* **1993**, 3147.

(30) Wright, J.; Kaczmarczyk, A. *Inorg. Chem.* **1973**, *6*, 1453.

(31) Hartwig, J. F.; Bhandari, S.; Rablen, P. R. *J. Am. Chem. Soc.* **1994**, *116*, 1839.