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nido-Metalloboranes Derived from $B_{10}H_{10}^{2-}$

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Anhydrous $K_2B_{10}H_{10}$ was found to react with $LLPtCl_2$ complexes where L = triphenylphosphine or LL = 1,2-bis(diphenylphosphino)ethane, diphos, in ethanolic chloroform to form isomeric ethoxy-substituted *nido*-metalloboranes, $LLPtB_{10}H_{11}OC_2H_5$. These complexes are derivatives of the $LLPtB_{10}H_{12}$ metalloboranes and arise from the polyhedral expansion of the *closo*-borane anion. This reaction is one of the few examples in which the $B_{10}H_{10}^{2-}$ skeleton is radically altered.

Introduction

The polyhedral borane anion, $B_{10}H_{10}^{2-}$, is prominent among the $B_nH_n^{2-}$ *closo*-borane dianions because of its extreme thermal, hydrolytic, and oxidative stability[1] coupled with its wide scope of derivative chemistry.[1] In the vast majority of its reactions, the boron framework of $B_{10}H_{10}^{2-}$ remains intact, and a formal hydride (H^-) is merely replaced by a substitutent. Prior to the chemistry reported here, only three reactions had been discovered in which the *closo*-$B_{10}H_{10}^{2-}$ framework was altered. Protonation of $B_{10}H_{10}^{2-}$ in acetonitrile with CF_3CO_2H resulted in the apparent formation of a *nido*-$B_{10}H_{11}^-$ ion as inferred from ^{11}B NMR spectroscopy.[2] Muetterties has reported[3] that upon careful dehydration of $(H_3O^+)_2B_{10}H_{10}^{2-}$, irreproducible yields of a volatile species, formulated as $B_{10}H_{12}OH_2$, were obtained. Finally, Marshall and coworkers[4] disclosed the important discovery that $B_{10}H_{10}^{2-}$ reacted with anhydrous HCl in diethyl sulfide solvent to produce the decaborane derivative, $B_{10}H_{12}[S(C_2H_5)_2]_2$.[5]

We now report the reaction of $B_{10}H_{10}^{2-}$ with two group 8c metal complexes which resulted in the expansion of this *closo*-borane dianion to form an 11-particle icosahedral fragment.

Discussion

Synthesis and Characterization. Reaction of *cis*-$(PPh_3)_2PtCl_2$ with $B_{10}H_{10}^{2-}$ in hot alcoholic chloroform resulted in the production of two isomeric complexes, Ia and Ib, formulated as $(PPh_3)_2PtB_{10}H_{11}(OC_2H_5)$. The same reaction utilizing $(diphos)PtCl_2$ yielded three isomers, IIa–c, formulated as $(diphos)PtB_{10}H_{11}(OC_2H_5)$. The reaction is depicted in Figure 1. Attempts to extend this chemistry to include the two remaining members of this triad (Ni, Pd) proved fruitless. These compounds contain an ethoxy-substituted $B_{10}H_{12}^{2-}$ ligand; the unsubstituted parent borane, $B_{10}H_{12}^{2-}$, has been reportedly isolated by Wilks and Carter[6] from the extended treatment of decaborane, $B_{10}H_{14}$, with sodium hydride. The parent complex $LLPtB_{10}H_{12}$[7] (L = triphenylphosphine, LL = diphos), III, was first prepared by reaction of the $B_{10}H_{13}^-$ ion with $(PPh_3)_2PtCl_2$. An X-ray diffraction study[8] of $[(B_{10}H_{12})_2Ni]^{2-}$, which contains two $B_{10}H_{12}^{2-}$ ligands fused through the transition metal atom, proved the heavy-atom arrangement of the $\{B_{10}H_{12}\}$ moiety to be that depicted in Figure 1.

The infrared spectra of Ia and b and IIa–c exhibited absorptions characteristic of terminal B–H vibrations, absorptions characteristic of the phenyl moiety, and strong and broad absorptions located at ca. 1250 cm^{-1} which were assigned to B–O stretching modes. Complete infrared data are presented in the Experimental Section.

The proton NMR spectra[9] (60, 100, or 251 MHz) of Ia and Ib displayed a complex pattern of resonances which were attributed to the phosphine ligands, in addition to resonances assigned to the ethoxy methylene protons and a triplet assigned to the ethoxy methyl protons. Integration of these spectra established the ratio of triphenylphosphine:ethoxy moieties as 2:1, thus supporting the analytical data.

The methylene protons always appeared as the AB portion of an ABX_3 pattern.[10] Evidently, the nonequivalence of the methylene protons was due to stereoelectronic influences exerted by the close proximity of the platinum–phosphine vertex and the open face of the icosahedral fragment such that one rotational configuration about the C–O bond is preferred over other configurations.[10] The 251-MHz proton NMR spectrum of Ia identified a resonance at τ 12.9 (B–H–B bridge proton region) and Ib exhibited a similar broad resonance at τ 12.7. The integral of these resonances was not considered to be accurate enough to establish the number of protons (i.e., 1 or 2) associated with this resonance.

The proton NMR spectra[9] of IIa–c contained resonances assigned to the diphosphine ligand, and similar to the spectra of Ia and b, resonances attributed to an ethoxy substituent were observed. Again, the methylene protons of the ethoxy group appeared as the AB portion of an ABX_3 system,[10] and the 251-MHz PMR spectra of all three isomers exhibited resonances attributable to B–H–B bridge protons. One B–H–B bridge proton resonance was located at τ 12.2 for IIa, while IIc exhibited a bridge proton resonance at τ 10.2. In contrast, IIb was the only complex to exhibit two identifiable bridge protons (τ 10.9 and 12.1).

The proton-decoupled 80.5-MHz ^{11}B NMR spectra of Ia and b and IIa–c are shown in Figure 2. Although the ^{11}B spectrum of III at 32 MHz was poorly resolved,[7] the proton-decoupled spectrum at 80.5 MHz was much more resolved and is included in Figure 2. Figure 1 suggests four unique boron atom pairs and two unique boron atom environments for III, and the spectrum of III is consistent with this prediction.

The ^{11}B spectra of Ia and b and IIa display eight unique resonances, whereas IIb and c displayed six or seven unique resonances and therefore established the absence of molecular symmetry in these metalloboranes. Ten unique boron environments exist in all five cases and resonances with integrals greater than 1 are the result of coincidental overlap. The possible positions of substitution in Ia and b and IIa–c,

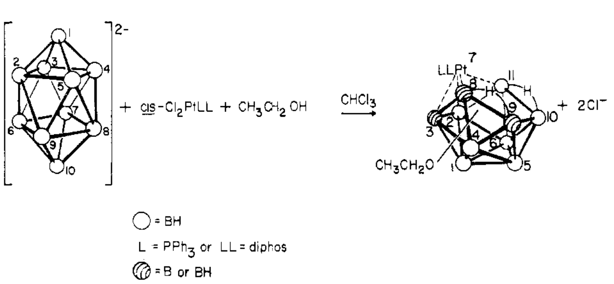

Figure 1. Reaction of $B_{10}H_{10}{}^{2-}$ with $LLPtCl_2$ in ethanolic chloroform showing proposed isomeric products.

Table I. ESCA and Molecular Weight Results

Compd	Pt($4f_{7/2}$)[a]	Mol wt	
		Found	Calcd
Ia	73.6	942[c]	884
Ib	73.6	870[c]	884
IIa	73.1	758[d]	758
IIb	73.6	745[c]	758
IIc	73.8	765[c]	758
III	73.2[b]		

[a] Binding energy from $4f_{7/2}$ peak, electron volts. [b] From ref 11. [c] As determined by the Signer method;[10] precision ±5%. [d] As determined by mass spectrometry.

consistent with the observed spectra, are at boron atoms 2, 3, 8, or 9 (equivalent to these are boron atoms 5, 6, 10, and 11, respectively).

Molecular weight measurements determined by the isothermal distillation method of Signer[11] confirmed a monomeric structure for Ia and b and IIb and c and the calculated molecular weight values are presented in Table I. Compound IIa was too insoluble to determine the molecular weight using this technique; however, mass spectrometry of IIa yielded reasonable results (cutoff *m*/*e* 758, corresponding to the $^{12}C_{28}{}^{1}H_{40}{}^{11}B_{10}{}^{16}O^{31}P_2{}^{195}Pt^+$ ion), although the observed isotopic distribution in the parent peak region was somewhat lower than the calculated distribution, presumably because of the loss of hydrogen.

Using the ESCA technique, Riggs[12] has determined the binding energies of the Pt($4f_{7/2}$) peak for a number of platinum-containing complexes, and the binding energies of this level were found to fall into distinct groups: d^{10} Pt^0, 71.6 eV; d^8 Pt^{2+}, 72.3–74.0 eV; d^6 Pt^{4+}, 75.9–76.1 eV. Table I lists the values found for Ia and b, IIa–c, and, for comparison, III. In all cases, the metal exhibited binding energies typical of formal d^8 Pt^{2+}.

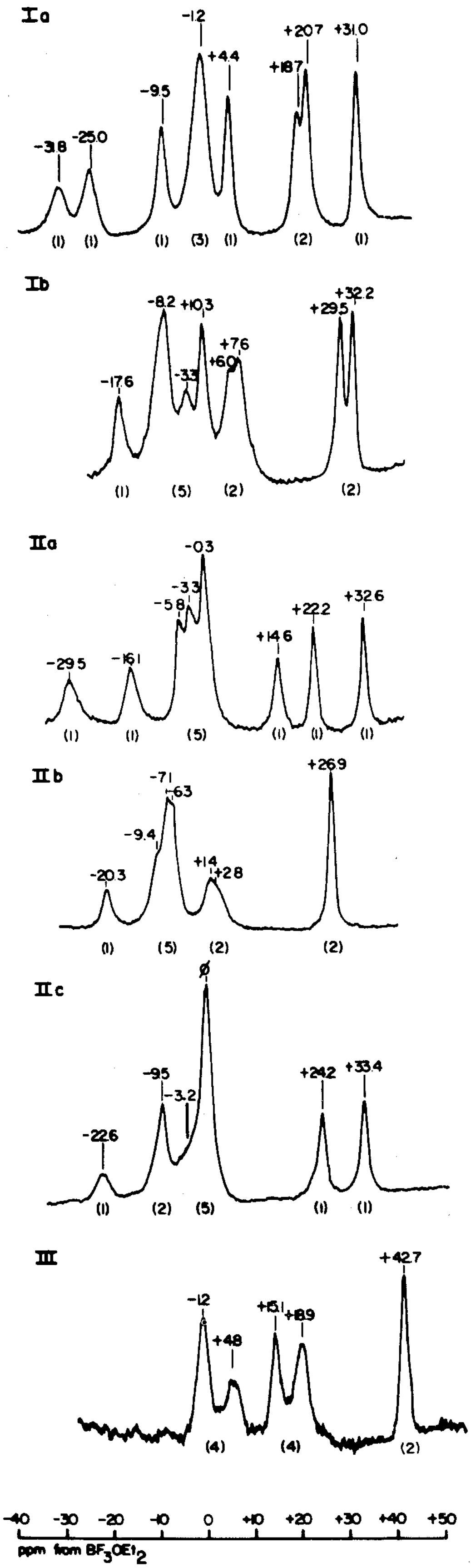

Figure 2. The 80.5-MHz, proton-decoupled ^{11}B NMR spectra of Ia and b, IIa–c, and III in methylene chloride. Chemical shifts are in ppm from external $BF_3 \cdot OEt_2$.

The solubility properties, location of ν(B–H) (2500 cm^{-1}) of the complexes, and molecular weight measurements established the metalloboranes Ia and b and IIa–c as neutral compounds. Coupled with the ESCA data, the borane moiety of the complexes therefore must function as a formal dianion. The reaction with ethanol and $LLPtCl_2$ evidently effected a two-electron reduction of *closo*-$B_{10}H_{10}{}^{2-}$ to form a substituted *nido*-$B_{10}H_{12}{}^{2-}$ dianion ($C_2H_5OB_{10}H_{11}{}^{2-}$). This dianion would contain two bridge hydrogen atoms, one presumably supplied by the boron atom which is ethoxy substituted and the other from ethanol. (It can be appreciated that simple protonation of $B_{10}H_{10}{}^{2-}$ with two protons would form the hypothetical neutral borane $B_{10}H_{12}$.) Two resonances consistent for nonequivalent B–H–B bridge hydrogen atoms were located in the 251-MHz PMR of IIb and, although only one B–H–B bridge proton resonance was located for Ia and b and IIa and c, to establish electronic neutrality in the complexes, *the other B–H–B bridge hydrogen atom must be present.* Since the bridge protons are magnetically nonequivalent, as indicated by the lack of symmetry in the ^{11}B spectra, either the B–H–B proton resonances must be accidentally coincidental in Ia and b and IIa and c or the missing B–H–B proton is sufficiently deshielded by the ethoxy oxygen to shift its resonance below

τ 10, where it would be lost among the terminal B–H proton resonances.

Mode of Formation. The past few years has seen the development of the polyhedral expansion reaction of carboranes[13] and metallocarboranes,[14] and it is obvious to extend this concept to the polyhedral expansion of the *closo*-borane anions ($B_nH_n^{2-}$). Use of lower valent metals, e.g., d^8 Pt(II) complexes, could effect the reduction of a *closo*-borane ($B_nH_n^{2-}$) with concomitant complexation to yield a formal *closo*-$\{Pt^{IV}B_nH_n\}$ polyhedral unit. However, an alternate reaction path was followed utilizing the $LLPtCl_2$ complexes in ethanolic solvent media.[15]

Marshall and coworkers,[4] postulated that the cage-opening process of $B_{10}H_{10}^{2-}$ in diethyl sulfide, which contained anhydrous HCl, was accomplished by the attack of a diethylsulfonium ion at the two apical sites of the dianion. Cage opening occurred with the formation of B–H–B bridge bonds between the 1,2 and 8,10 boron atoms[16] (apex to equatorial borons of $B_{10}H_{10}^{2-}$). (Attack of protons at this region of $B_{10}H_{10}^{2-}$ is consistent with the X-ray study of $Cu^I{}_2B_{10}H_{10}$ which showed coordination of the Cu^I cations along apical–equatorial edges[17]). The cage then "unzipped" between boron atoms 1 and 2, 2 and 5, 5 and 9, and 8 and 9 with coordination of the diethyl sulfide moieties at boron atoms 5 and 9.[18]

The compositions of Ia and b and IIa–c suggested that the cage-opening process during reaction with the platinum complexes followed a similar pathway. Initial complexation presumably involved a metathesis reaction in which 2 mol of KCl was produced[19] and the $B_{10}H_{10}^{2-}$ ion was attacked by a formal $\{LLPt^{2+}\}$ moiety along an apical–equatorial edge (1,2 borons [a]).[20] Bond rupture of boron atom sets 1,2; 2,5; 5,9; and 8,9 [a] then occurred with the subsequent attack of ethanol. The reverse attack sequence, i.e., initial attack by ethanol and then cage opening, could also have occurred, or in the limiting case, these processes could have been concurrent. In any situation, attack of ethanol would probably be at one of the boron atoms 1, 2, 5, 8, 9, or 10 [a] of the open face. Thus, ethoxy substitution would have occurred at boron 2, 3, 8, 11, 9, or 10 [b], resulting in the formation of three sets of positional isomers with each set containing a *d,l* enantiomeric pair. Substitution at any of these positions renders all 10 boron atoms of the product magnetically nonequivalent as was spectrally observed. The net reaction is shown in Figure 1.

Attempts to synthesize unsubstituted III directly from $B_{10}H_{10}^{2-}$ were unsuccessful. Various reducing agents, which are also proton sources (e.g., oxalic acid or hydroquinone), were allowed to react with $B_{10}H_{10}^{2-}$ and *cis*-$(PPh_3)_2PtCl_2$, but no tractable complexes were isolated. Although direct synthesis of III has not been accomplished from $B_{10}H_{10}^{2-}$, it was possible to prepare this complex in low yield from $B_{10}H_{12}{\cdot}2S(C_2H_5)_2$, and high yields of III (>90% based on borane or metal complex) could be obtained by reaction of decaborane and $Pt(PPh_3)_3$. The interrelation of these reactions is shown in Figure 3; in both reactions utilizing $Pt(PPh_3)_3$, the metal supplied the electrons necessary to reduce the borane to the formal $B_{10}H_{12}^{2-}$ ligand. The reaction route discovered by Klanberg, Wegner, Parshall, and Muetterties,[7] formed the $B_{10}H_{12}^{2-}$ ligand by disproportionation of $B_{10}H_{13}^-$ to form the $B_{10}H_{12}^{2-}$ dianion and $B_{10}H_{14}$.

Experimental Section

Reagents. Chloroform was dried over molecular sieves and distilled prior to use, and anhydrous ethanol was used without further purification. Triphenylphosphine was recrystallized three times from ethanol before use and $B_{10}H_{10}^{2-}$ was synthesized as described in the literature.[21] Prior to use, the potassium salt of this borane dianion was dried under high vacuum for 3 days at 100°. Bis(triphenylphosphine)metal dichlorides (M = Pt,[22a] Pd[22b] and Ni[22b]), (diphos)$PtCl_2$,[22c] and $Pt(PPh_3)_3$[22d] were synthesized as described in the literature. Diethyl sulfide was distilled from molecular sieves, and toluene and benzene were freshly distilled from CaH_2. Decaborane was purified by vacuum sublimation.

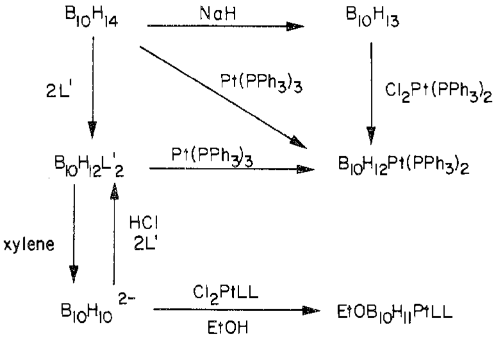

Figure 3. Interrelation of B_{10} borane reactions with platinum–phosphine complexes. In this scheme L = PPh_3 or LL = diphos for the LLPt complexes. The borane ligand L' = $S(C_2H_5)_2$, or, typically, in the preparation of $B_{10}H_{10}^{2-}$ from $B_{10}H_{14}$, L = $N(C_2H_5)_3$.

Physical Measurements. The 60-MHz ^1H NMR spectra were obtained using a Varian A-60D spectrometer and 100-MHz ^1H NMR spectra were obtained on a Varian HA-100 spectrometer. The 251-MHz ^1H NMR and 80.5-MHz ^{11}B NMR spectra were recorded using the cryogenic instrument designed and constructed by Professor F. A. L. Anet and Dr. C. H. Bradley of this department. Infrared spectra were obtained using a Perkin-Elmer 137F spectrometer. Analytical data were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Molecular weights for Ia and b and IIb and c were obtained by the method of Signer[11] in CH_2Cl_2 solution using *cis*-$(PPh_3)_2PtCl_2$ as a standard. Mass spectra were obtained on a CEC Model MS-9 mass spectrometer, and the ESCA data were obtained through the courtesy of Professor P. C. Maybury and Dr. W. E. Swartz, Jr., of the University of South Florida.

Reaction of *cis*-$(PPh_3)_2PtCl_2$ with $K_2B_{10}H_{10}$ in Alcoholic Chloroform. The *cis*-$(PPh_3)_2PtCl_2$ (1.0 g, 2.53 mmol) was placed in a 100-ml, three-necked flask equipped with a reflux condenser, stirring apparatus, and a 100-ml pressure-equalizing addition funnel. A nitrogen atmosphere was maintained in the system throughout the reaction. The flask was flushed with N_2 and 50 ml of N_2-saturated chloroform was added. The addition funnel was charged with 0.98 g (5.0 mmol) of powdered, anhydrous $K_2B_{10}H_{10}$, and approximately 20 ml of N_2-saturated ethanol was then added to the funnel. The chloroform solution was heated to the reflux temperature and the $K_2B_{10}H_{10}$ was added to the hot solution. The reaction mixture was heated at the reflux temperature for 6 hr, cooled to room temperature, and filtered through Celite which was washed with a small amount of chloroform; the solutions were combined and extracted with H_2O three times (100-ml aliquots). The chloroform phase was dried over anhydrous $MgSO_4$ and filtered. This solution was placed on a steam bath and concentrated while a slow stream of N_2 was bubbled through the solution. Heating was continued until crystallization was complete (more ethanol was occasionally added). The bright yellow crystals were collected, washed with ethanol, and air-dried to yield 0.61 g.

The crystals were then taken up in the minimum amount of CH_2Cl_2, the solution was stripped by rotary evaporation onto Florisil (ca. 20-ml dry volume), and this was placed atop a Florisil column (250-ml dry volume) packed in *n*-hexane. Gradually enriching the eluent in dichloromethane developed two bands; the first yellow band contained complex Ia (70 mg, 3.5% yield based on Pt) which was recrystallized from hexane–methylene chloride by slow evaporation in a N_2 atmosphere (mp 227–240° dec without melting, sealed tube). Anal. Calcd for $C_{38}H_{46}B_{10}OP_2Pt$: C, 51.63; H, 5.26; B, 12.23; O, 1.81; P, 7.00; Pt, 22.07. Found: C, 51.73; H, 5.38; B, 12.47; P, 7.03; Pt, 22.23. Infrared spectrum (cm^{-1}, Nujol mull): 3050 m, 2530 s, 1475 s, 1430 s, 1320 sh, w, 1310 m, 1210 br, m, 1160 m, 1090 s, 1080 sh, m, 1035 m, 1010 s, 980 m, 940 br, w, 855 br, w, 740 s, 725 w, 695 vs. The abbreviations used for ir peaks are s = strong, m = medium, w = weak, br = broad, and sh = shoulder. ^1H NMR data (CH_2Cl_2 solution): τ 2.78 (30),[23] phenyl protons; τ 6.24 (2); ethoxy methylene protons; τ 2.20 (3), ethoxy methyl protons; τ 12.94, B–H–B proton.

The second band eluted contained compound IIa, 0.61 g (23.3% based on Pt), which was also recrystallized from methylene chloride–hexane (mp 243–270° dec without melting, sealed tube). Anal. Found: C, 51.68; H, 5.40; B, 12.50; P, 6.95; Pt, 22.00. Infrared spectrum (cm^{-1}, Nujol mull): 3050 m, 2520 s, 1470 s, 1430 s, 1340 w, 1255 w, 1210 br, vs, 1185 sh, 1160 m, 1150 sh, 1100 s, 1055 sh, w, 1040 sh, w, 1030 m, 1010 s, 985 w, 945 br, w, 925 w, 900 w, 810 br, w, 755 vs, 745 sh, 710 vs. ^1H NMR data (CH_2Cl_2 solution): τ 2.77 (30),[23] phenyl protons; τ 7.04 (2), ethoxy methylene protons; τ 9.06 (3), ethoxy methyl protons; τ 12.73, B–H–B proton.

Reaction of (diphos)$PtCl_2$ with $K_2B_{10}H_{10}$ in Alcoholic Chloroform. The preparation followed that described above, except a 200-ml, three-necked flask was employed. The (diphos)$PtCl_2$ (1.0 g, 1.51 mmol) was dissolved in 100 ml of $CHCl_3$ and the reaction mixture was heated 12 hr at the reflux temperature after the addition of the ethanol (60 ml)–$K_2B_{10}H_{10}$ (1.2 g, 6.07 mmol) slurry.

After isolation from the mother liquor, the crude crystalline product (1.2 g) was dissolved in the minimum amount of CH_2Cl_2, the solution was stripped onto Florisil (ca. 30-ml dry volume), and this was placed atop a column of Florisil packed in *n*-hexane (ca. 250-ml dry volume). Carefully enriching the eluent in dichloromethane developed three bands. The first band contained complex IIa (111 mg, 9.5% based on Pt) which was recrystallized from CH_2Cl_2–*n*-hexane by slow evaporation to yield a pale yellow, microcrystalline solid (mp 265–276° dec, sealed tube). Anal. Calcd for $C_{28}H_{40}B_{10}OP_2Pt$: C, 44.38; H, 5.33; B, 14.26; O, 2.11; P, 8.17; Pt, 25.74. Found: C, 44.09; H, 5.28; B, 14.02; P, 8.29; Pt, 26.02. Infrared spectrum (cm^{-1}, Nujol mull): 3050 m, 2510 s, 1475 m, 1430 s, 1410 w, 1300 w, 1200 br, s, 1170 sh, 1160 m, 1100 m, 1070 w, 1040 w, 1030 w, 1000 w, 980 w, 930 br, w, 890 sh, 880 m, 834 m, 750 s, 720 m, 714 sh, 706 m, 697 s. ^1H NMR data (CH_2Cl_2 solution): τ 2.48 (20),[23] phenyl protons; τ 6.68 (2), ethoxy methylene protons; τ 9.35 (3), ethoxy methyl protons; τ 12.2, B–H–B proton.

The second compound to elute was IIb which was recrystallized from CH_2Cl_2–hexane to yield bright yellow crystals (0.85 g, 74.1% based on Pt; mp 230–260° dec, sealed tube). Anal. Found: C, 43.51; H, 5.30; B, 14.91; P, 8.55; Pt, 25.94. Infrared spectrum (cm^{-1}, Nujol mull): 3050 w, 2520 s, 1475 m, 1430 s, 1400 w, 1370 m, 1360 sh, 1310 w, 1295 sh, 1260 w, 1200 br, m, 1160 m, 1110 s, 1070 w, 1040 br, w, 1010 s, 980 w, 930 br, w, 900 w, 880 m, 825 m, 753 s, 742 sh, 715 s, 705 s, 693 s. ^1H NMR data (CH_2Cl_2 solution): τ 2.50 (20),[23] phenyl protons; τ 6.71 (2), ethoxy methylene protons; τ 9.02 (3), ethoxy methyl protons; τ 10.9, 12.1, B–H–B protons.

The final compound (IIc) to elute was recrystallized from CH_2Cl_2–C_6H_{14} as bright yellow flakes (190 mg, 16.4% based on Pt; mp 230–240° dec, sealed tube). Anal. Found: C, 44.27; H, 6.24; B, 13.20; P, 8.20; Pt, 25.10. Infrared spectrum (cm^{-1}, Nujol mull): 3050 w, 2500 s, 1475 m, 1430 s, 1410 w, 1310 sh, 1295 w, 1220 br, s, 1170 sh, 1160 m, 1110 s, 1090 br, w, 1070 sh, 1010 s, 980 m, 825 m, 750 s, 716 sh, 705 sh, 700 s, 695 s. ^1H NMR data (CH_2Cl_2 solution): τ 2.43 (20),[23] phenyl protons; τ 6.44 (2), ethoxy methylene protons; τ 8.94 (4), diphos methylene protons; τ 9.53, ethoxy methyl protons; τ 10.2, B–H–B proton.

Preparation of III from $B_{10}H_{14}$·$2SEt_2$ and $Pt(PPh_3)_3$. Benzene (20 ml) and $Pt(PPh_3)_3$ (1.0 g, 1.02 mmol) were placed into a 100-ml, three-necked flask equipped with reflux condenser, stirring apparatus, equipment to maintain an N_2 atmosphere in the system, and a 50-ml pressure equalizing funnel after the apparatus had been thoroughly swept with dry N_2. Decaborane, $B_{10}H_{14}$ (0.183 g, 1.5 mmol), and 15 ml of benzene were placed into the addition funnel, and the solution was added dropwise over a 20-min period; gas evolution was noted. The resulting crystalline product was collected via Schlenk techniques, washed with ether, and dried in a N_2 stream to yield $(PPh_3)_2PtB_{10}H_{12}$, III (0.725 g, 85% yield based on Pt), identified by its infrared and ^{11}B NMR spectra.

Preparation of III from $B_{10}H_{12}$·$2S(C_2H_5)_2$ and $Pt(PPh_3)_3$. Into a 100-ml, three-necked flask equipped with a condenser, N_2 bubbler, and stirring apparatus was placed $B_{10}H_{12}$·$2SEt_2$ (0.123 g, 0.51 mmol) and $Pt(PPh_3)_3$ (0.5 g, 0.51 mmol) after the flask was thoroughly flushed with dry N_2. Benzene (10 ml) was added and the solution was briefly heated at the reflux temperature (ca. 2 min). The solution was cooled and filtered. To this solution was added an equal volume of dry, N_2-saturated ether, and after ca. 20 min under N_2, the yellow crystalline needles which formed were collected via Schlenk techniques, washed with ether, and dried in a N_2 stream to yield 0.05 g (<10% based on Pt) of $(PPh_3)_2PtB_{10}H_{12}$, III. The compound was identified by its ir and ^{11}B NMR spectra.

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Registry No. *cis*-$(PPh_3)_2PtCl_2$, 15604-36-1; (diphos)$PtCl_2$, 14647-25-7; $K_2B_{10}H_{10}$, 12447-89-1; $(PPh_3)_2PtB_{10}H_{11}(OC_2H_5)$, 54999-66-5; (diphos)$PtB_{10}H_{11}(OC_2H_5)$, 54999-67-6; $(PPh_3)_2PtB_{10}H_{12}$, 36670-41-4; $Pt(PPh_3)_3$, 13517-35-6; $B_{10}H_{14}$, 17702-41-9.

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(20) The letters in brackets following boron atom numbers are in reference to the basis of boron atom numbering: [a] bicapped-square-antiprism structure (reactant borane); [b] 11-vertex icosahedral fragment structure (product metalloborane).

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