The present discussion has intentionally neglected a series of questions which I consider to be most important and not as yet answered satisfactorily.[24] For example, is there any evidence that the TBP, even somewhat distorted, is the stable structure for all phosphoranes, is there any evidence that all intramolecular rearrangements in phosphoranes go *via* the same mechanism or even the same mode, and is there even any compelling evidence that the intramolecular rearrangement observed in noncyclic phosphoranes is a unimolecular process, or could it actually take place *via* a dimer- or solvent-mediated mechanism?

If there is a lesson to be learned from this discussion it is that the chemistry of the nonmetals, essentially that of the hypervalent molecules, can be significantly more complex than organic chemistry due to the different types and greater number of ligands; and it is precisely this complexity which provides the interest in these molecules and should make one proceed with caution before drawing conclusions based on limited experimental evidence.

Acknowledgments. I am grateful to Professor D. Hellwinkel for helpful discussions, the North Atlantic Treaty Organization and the Office of Naval Research for partial support of this research, the latter through Contract N 00014-68-0302-0005, and the National Science Foundation, Grant GP-24789.

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(23) The dynamics of this problem have been almost invariably considered in terms of normal mode analyses (see, *e.g.*, B. J. Dalton, *J. Chem. Phys.*, **54**, 4745 (1971)). This type of analysis, however, unduly favors the motions involved in small deviations from equilibrium and does not consider the much greater freedom usually permitted in organic reaction mechanisms. In this sense, the Ugi-Ramirez turnstile mechanism has provided a thought-provoking alternative to the generally accepted BPR mechanism. Many such alternatives ought to be considered if for no other reason than that it seems unreasonable to assume *a priori* that molecules as unlike as $(C_6H_5)_5P$, VF_5, and $Fe(CO)_5$ will all undergo intramolecular rearrangements *via* the same mechanism.

(24) J. I. Musher, "Conformational Analysis," G. Chiurdoglu, Ed., Academic Press, New York, New York, 1971, p 177.

Metalloboranes. VII.[1] Synthesis and Chemistry of π-Borallyl Complexes and the Crystal Structure of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$

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Abstract: A unique series of complexes containing the π-$B_3H_7^{2-}$ ligand was prepared with nickel, palladium, and platinum. The general reactivity of these complexes decreases in the series Ni > Pd > Pt. Through the facile displacement of the π-borallyl ligand by trialkylphosphines, the first successful synthesis of tetrakis(trialkylphosphine)platinum(0) complexes was demonstrated. Nmr studies showed the π-borallyl complexes to be more stereochemically rigid than the σ-$B_3H_8^-$ metalloboranes. The crystal and molecular structure of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ was determined from three-dimensional X-ray counter data. The crystal structure consists of the packing of discrete molecules with two phosphine ligands and a π-bonded $B_3H_7^{2-}$ ligand coordinated to an essentially square-planar platinum atom. The dihedral angle between the B_3 plane and the platinum-phosphorus plane is 116.8 (24°). The Pt-P distances are 2.301 (4) and 2.311 (4) Å. There is an orientational disorder in the $B_3H_7^{2-}$ ligand which is asymmetrically bonded to platinum. The Pt-B distances are 2.38 (4) Å to a boron atom in the PPtP plane and 2.18 (4) and 2.13 (3) Å to the boron atoms whose midpoint is in this plane. The B-B distances are 1.86 (5) and 1.92 (4) Å; the hydrogen atoms in the $B_3H_7^{2-}$ ligand were not located, but their positions are inferred. The $B_3H_7^{2-}$ ligand is isoelectronic with the $C_3H_5^-$ π-allyl ligand; the Pt-B_3H_7 geometry is compared with the similar geometries found in transition metal π-allyl complexes. Crystals of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ are monoclinic, space group $C2/c$, with eight molecules per cell of dimensions a = 18.155 (9), b = 13.665 (7), c = 17.504 (9) Å, and β = 107.25 (6)°. The structure was refined by least squares to a conventional R of 0.054.

Transition metal complexes were prepared recently[1] of the $B_3H_7^{2-}$ ion which is the formal electronic analog of the familiar π-allyl ion. Complexes prepared were of the type $(R_3P)_2PtB_3H_7$ where the phosphines are triethylphosphine, triphenylphosphine, ethyldiphenylphosphine, dimethylphenylphosphine, or tri-*p*-tolylphosphine. We have now extended this chemistry to include complexes of palladium and nickel. The chemical and spectral evidence[1] for $(R_3P)_2PtB_3H_7$ complexes was suggestive of a different bonding from that found in the $B_3H_8^-$ metal complexes.[2-4] The BH proton nmr (220 MHz) resonances occur with a large spread in an apparent 2:1:2:2 distribution. The ESCA Pt $4f_{7/2}$ binding energy[1] is typical of Pt(II) complexes.[5] The $B_3H_7^{2-}$ ligand also has a greater stereochemical rigidity than the $B_3H_8^-$ ligand.[1]

We also report here the crystal and molecular structure of bis(dimethylphenylphosphine)platinum heptahydridotriborate(2−), $[(CH_3)_2PC_6H_5]_2PtB_3H_7$. The question of possible structural correspondence with the isoelectronic π-allyl metal complexes was paramount in this structure investigation. Borane ligands that are electronically similar to organic ligands might be expected to have similar structural features, a notable example of this being the electronic and structural sim-

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(1) Paper VI: A. R. Kane and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 1041 (1971).

(2) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, 7, 2272 (1968).

(3) L. J. Guggenberger, *ibid.*, **9**, 367 (1970).

(4) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969).

(5) W. M. Riggs, submitted for publication.

ilarities found in π-$C_5H_5^-$ and π-$B_9C_2H_{11}^{2-}$ transition metal complexes.[6,7] The molecular structure of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ is compared with π-allyl structures where all transition metal complexes have the same general feature of a π sandwich-bonded allyl ligand, but with significant differences in the symmetry of the allyl–metal geometry.

Experimental Section

Reagents and Procedure. Solvents were of reagent grade purity. All polar solvents were stored over molecular sieves prior to use. The platinum and palladium halide–phosphine complexes were prepared by standard procedures. The preparation and handling of the π-borallyl complexes were effected in a dry nitrogen atmosphere (Vacuum/Atmospheres Corp. Dri-Train). Melting points (sealed capillaries, nitrogen atmosphere) are uncorrected. Proton nmr spectra were run over a temperature range of −50 to +80° using a Varian HR-220 spectrometer. Temperatures were measured by observing the chemical shift separation in methanol or ethylene glycol samples run before and after each trace. ^{31}P spectra were obtained with a Varian HA-100 spectrometer.

$[(C_2H_5)_3P]_2PtB_3H_7$. To an acetonitrile–triethylamine solution (600 ml, 5:1) of cesium octahydrotriborate (10.41 g, 0.06 mol) was added *cis*-$[(C_2H_5)_3P]_2PtCl_2$ (30.12 g, 0.06 mol). Cesium chloride immediately precipitated from the solution. After 30 min the reaction was filtered and the filtrate was evaporated to dryness *in vacuo*. The residual solids were washed with cold ethanol to remove triethylammonium chloride. This residue was recrystallized from petroleum ether: yield 18.5 g, 65%; mp 93°; nmr data ^1H (60 and 220 MHz, CD_2Cl_2) equivalent phosphines τ 8.0 ($-CH_2CH_3$), 8.94 ($-CH_2CH_3$), ^{11}B (19.2 MHz C_6H_6, CH_2Cl_2), broad hump (+17.5 ppm from external $B(OMe)_3$), ^{31}P (40.5 MHz) equivalent phosphorus atoms (+94 ppm from external P_4O_6 with $J_{^{195}Pt-P}$ of 2620 Hz); ultraviolet spectrum $\lambda_{max}^{CH_3CN}$ 2900 Å (ϵ 3000).

Anal. Calcd for $C_{12}H_{37}P_2PtB_3$: C, 30.6; H, 7.92; B, 6.89; P, 13.2; Pt, 41.4. Found: C, 30.9; H, 8.06; B, 7.13; P, 12.9; Pt, 41.1.

The trimethylphosphine analog was prepared in a similar fashion but the product was obtained only in low yields and rapidly turned brown on isolation even though protected from the atmosphere.

$[(C_6H_5)_2C_2H_5P]_2PtB_3H_7$. A reaction solution (1,2-dimethoxyethane, 100 ml) of cesium octahydrotriborate (1.7 g, 0.01 mol) and *trans*-$[(C_6H_5)_2C_2H_5P]_2PtHCl$ (6.59 g, 0.01 mol) was stirred for 1.5 hr. Hydrogen was evolved during this period. The reaction mixture was filtered and the filtrate was evaporated to yield an oil. Addition of petroleum ether resulted in crystallization to give 5.8 g of crude product which was recrystallized from acetonitrile to give a white crystalline product, yield 3.42 g, 53%.

Anal. Calcd for $C_{28}H_{37}B_3P_2Pt$: C, 50.7; H, 5.62; B, 4.89; P, 9.34; Pt, 29.4. Found: C, 50.8; H, 5.74; B, 5.11; P, 9.48; Pt, 29.4.

This compound was hydrolyzed under acidic conditions and the evolved hydrogen was determined by standard vacuum system–volumetric procedure: theory 270.4 cc/g; found 271.2 cc/g. Mass spectroscopic analysis of this compound supported the formulation; the molecular ion was observed.

$[(C_6H_5)_3P]_2PtB_3H_7$. Cesium octahydrotriborate (0.87 g, 0.005 mol) was dissolved in 50 ml of acetonitrile. To the solution was added 12.5 ml of triethylamine and then a slurry of bis(triphenylphosphine)platinum dichloride (3.95 g, 0.005 mol) in 100 ml of acetonitrile. The reaction mixture was stirred for 1.5 hr and then filtered. The filtrate was evaporated *in vacuo* at room temperature. The residue was washed three times with 50 ml of methanol. The remaining solids were dissolved in hot acetonitrile (~500 ml). After filtration the solution was cooled to −50°. White needles which separated from the cooled solution were collected and then vacuum dried for 1 day at 25°: yield 1.2 g, 32%; mp turned light brown at 185°, melted at 196–197° with decomposition.

Anal. Calcd for $C_{36}H_{37}P_2PtB_3$: C, 57.0; H, 4.91; P, 8.16. Found: C, 56.6; H, 4.92; P, 7.74.

An nmr spectrum of the recrystallized material indicated that there was a slight impurity (carbon–hydrogen compound) present.

$[(CH_3)_2P(C_6H_5)]_2PtB_3H_7$. The procedure described for the triphenylphosphine complex was followed with a modification of the purification procedure. The crude product was washed with 50 ml of petroleum ether and then the solids were extracted with 500 ml of warm petroleum ether (bp 38–52°). The petroleum ether solution was reduced to 10% of the initial volume by evaporation *in vacuo* and then cooled to −50° to give white colorless crystals, mp 112–113°.

Anal. Calcd for $C_{16}H_{29}P_2PtB_3$: C, 37.5; H, 5.90; P, 12.1. Found: C, 38.2; H, 5.76; P, 12.1.

The proton nmr of this complex in deuteriodichloromethane showed that the methyl groups attached to each boron were inequivalent. The chemical shift separation between the two methyl hydrogen environments was 0.2 ppm and the phosphorus–hydrogen coupling constant was 8 Hz.

$[(p\text{-}CH_3C_6H_4)_3P]_2PtB_3H_7$. The procedure described for the preparation of the analogous triphenylphosphine complex was followed except that the reaction mixture was allowed to stir for 16 hr before filtration. The product work-up and recrystallization procedure was that described for the triphenylphosphine complex: yield 0.35 g, 8.3%; mp 180° turned light brown, melted with decomposition at 202–203°.

Anal. Calcd for $C_{42}H_{49}P_2PtB_3$: C, 59.8; H, 5.86. Found: C, 59.4; H, 5.88.

$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]PdB_3H_7$. $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]PdCl_2$ (0.002 mol) was dissolved in acetonitrile (200 ml), tetrahydrofuran (100 ml), and toluene (50 ml). To this solution was successively added triethylamine (5 ml) and cesium octahydrotriborate (0.002 mol). The reaction mixture was stirred for 30 min as white solids slowly deposited. These solids were separated by filtration and the filtrate was evaporated to dryness. The residue from the filtrate was thoroughly washed with methanol (200 ml). The remaining solid was then recrystallized from acetonitrile containing a small amount of activated carbon. The recrystallization procedure consisted of dissolving the solids in a minimum of acetonitrile warmed to 60°. The activated carbon was added, and the mixture was stirred and then filtered while still hot. The filtrate was then slowly cooled to 15° to yield off-white crystals (0.16 g, 15%). The recrystallization procedure was repeated and the crystals were then vacuum dried for 20 hr: mp 173° dec, 176–177° melt with decomposition.

Anal. Calcd for $C_{26}H_{31}B_3P_2Pd$: C, 57.37; H, 5.74; B, 5.95; P, 11.38; Pd, 19.54. Found: C, 56.48; H, 5.31; B, 6.37; P, 11.58; Pd, 19.50.

Reaction of π-Borallylplatinum Complexes with Phosphines. Synthesis of Zerovalent Trialkylphosphineplatinum Complexes. A solution of $[(C_2H_5)_3P]_2PtB_3H_7$ (13.1 g, 0.0278 mol) in $(C_2H_5)_3P$ (25 ml) was heated at 125° for 10 min and then filtered. The resultant dark orange-red solution was cooled to −40° and a white crystalline product was recovered. This was washed with cold triethylphosphine and then cold acetonitrile (16.4 g, 88%). A portion of this was recrystallized twice from petroleum ether containing a little excess phosphine. In both cases slightly off-white crystalline products were obtained by cooling the filtrates to −40° and then washing with cold solvents. The final product was carefully vacuum dried before analysis.

Anal. Calcd for $C_{24}H_{60}P_4Pt$: C, 43.2; H, 9.06; P, 18.5; Pt, 29.2. Found: C, 43.3; H, 9.28; P, 18.5; Pt, 29.3.

Spectral data: mass spectroscopy supports the above composition with the $(P-L)^+$, $(P-2L)^+$, and $(L)^+$ ions being observed; ^1H nmr (60 and 220 MHz) broad and featureless even at low temperature; ^{31}P nmr (40.5 MHz, petroleum ether solutions, ^1H noise decoupling) spectra were temperature dependent with little or no absorption observed at room temperature. At −55°, a sharp line (−15.2 ppm from external tri-*n*-butylphosphine) with $^{195}Pt-P$ satellites ($J = 3740$) was observed.

A sample of $[(C_3H_5)_3P]_4Pt$ (12.5 g, 0.0187 mol) was heated at 50–60° for 1 hr under vacuum. The triethylphosphine which distilled out of the sample was collected and amounted to 2.19 g (theory for 0.0187 mol, 2.21 g). The residue was an orange-red oil.

Anal. Calcd for $C_{18}H_{45}P_3Pt$: C, 39.3; H, 8.25; P, 16.9; Pt, 35.5. Found: C, 39.3; H, 8.28; P, 16.8; Pt, 35.5.

Spectral data: ^1H nmr (60 and 220 MHz) broad and relatively featureless even at low temperatures; ^{31}P nmr (40.5 MHz) a sharp singlet at room temperature (toluene solution, ^1H noise decoupling, −73.9 ppm from external n-Bu_3P) with ^{195}Pt satellites (J = 4220

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(6) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, 90, 879 (1968).

(7) M. F. Hawthorne in "The Chemistry of Boron and its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 311.

Hz). Upon heating a mesitylene solution of $[(C_2H_5)_3P]_3Pt$ to 120° the signal gradually broadened (reversibly). The addition of small amounts of triethylphosphine to room temperature solutions of this complex immediately broadened the phosphorus resonance beyond observance. At low temperatures (−55°) these solutions displayed separate resonances for $[(C_2H_5)_3P]_3Pt$ and $[(C_2H_5)_3P]_4Pt$. With excess phosphine added, the free ligand resonance was also found.

Crystal Data and Structure Determination. The $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ complex was chosen for this structure investigation since the crystals were of better quality than those of the other complexes examined. Crystals are monoclinic with cell dimensions of a = 18.155 (9), b = 13.665 (7), c = 17.504 (9) Å, and β = 107.25 (6)°. These parameters resulted from the least-squares refinement of the angular positions measured for 13 carefully centered reflections on the diffractometer. The systematic intensity observations of hkl, $h + k = 2n$, and $h0l$, $l = 2n$, are characteristic of the space groups $C2/c$ and Cc.[8] The correct space group is $C2/c$ as confirmed by the refinement. The observed and calculated densities for eight molecules per cell are 1.63 and 1.64 g/cm^3, respectively. There is no space group imposed molecular symmetry.

A prismatic crystal with average edge dimensions 0.19 × 0.20 × 0.19 mm was used in the data collection. The crystal was mounted on a Picker four-circle automatic diffractometer with the c^* axis coincident with the diffractometer ϕ axis. The data were measured using Mo radiation (λ 0.7107 Å) diffracted off the 002 planes of a highly oriented graphite (HOG) crystal in the Picker incident beam monochromator.[9] A total of 2950 reflections were measured out to 2θ of 45° using the θ–2θ scan technique with a scan speed of 1°/min and a scan range of 2.80° plus the $K\alpha_1 - K\alpha_2$ angular separation. Individual backgrounds of 20 sec were recorded before and after each scan. Check reflections were recorded every 50 reflections and attenuation was used for counting rates greater than 10,000 cps.

The check reflections were found to decrease slowly and uniformly during the data collection and the data were corrected accordingly. The maximum observed decomposition was 6% in F_{obsd}. At the end of the data collection 50 reflections were remeasured throughout the data collection time range as a check on the decomposition correction. The data were corrected for absorption using the program ACACA[10] with the crystal defined by six plane faces. The linear absorption coefficient for Mo Kα radiation is 72.6 cm^{-1}. The minimum and maximum calculated transmission factors were 0.23 and 0.34, respectively. The errors in the structure factors were estimated as previously described.[11] Structure factors which were less than their estimated standard deviations were considered "unobserved."

The platinum, phosphorus, and carbon atom positions were found by the usual heavy-atom techniques (Patterson and Fourier). The R value $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.072 after several cycles of refinement where the model had isotropic thermal parameters for the carbon atoms and anisotropic thermal parameters for the platinum and phosphorus atoms. It was clear from an electron density difference map at this point that the boron atom positions were not completely ordered. The boron atom peaks were spread out in very specific directions over more than 1 Å. The R was 0.065 after putting the three boron atoms in the model with isotropic thermal parameters. After two cycles of refinement with anisotropic thermal parameters for all atoms, the R was 0.058 and wR, $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, was 0.064.

The benzene and methyl hydrogen atom contributions were added before trying to unravel the nature of the disorder in the $B_3H_7^{2-}$ ligand. The benzene hydrogen atoms were placed in their calculated positions. The electron density difference map was examined for the methyl hydrogen atoms; three hydrogen atoms were placed around each of the methyl carbon atoms at the highest peak positions generally consistent with tetrahedral symmetry. We cannot exclude the possibility of the methyl hydrogen atom positions being disordered between several conformations. The methyl hydrogen atom positions found were refined in an effort to assess their validity. These atoms converged to reasonable positions with an average C–H distance of 1.03 Å (0.76–1.30 Å). These atoms were kept in their refined positions but they were not varied in further refinements because of the possibility of other hydrogen atom conformations. All hydrogen atoms were assigned isotropic thermal parameters of 8.0 Å^2.

Although there is no imposed molecular symmetry, the platinum–phosphine geometry has idealized $C_2(2)$ symmetry. From the boron atom peaks in the electron density difference map it appeared that the boron atoms were split equally between two sets. The twofold field of the platinum–phosphine geometry may lead to a twofold orientational disorder about the idealized $C_2(2)$ molecular symmetry axis. Three separate types of refinements were done in order to characterize the B_3H_7 geometry. In the first refinement the three boron atoms were divided into two sets of three, and the resulting six half atoms were refined individually. This refinement converged, but the added variables did not seem warranted over the third type of refinement. The second refinement treated the two B_3 groups as rigid bodies but this approach was not pursued very far because assumptions had to be made about the geometry of the rigid B_3 group, information we wished to obtain from the refinement. In the third refinement three of the half boron atoms were refined and the other three half boron atoms were mathematically included in the other orientation maintaining the idealized $C_2(2)$ axis. This refinement appears to adequately describe the disorder. The first and third refinements gave the same R and wR, giving also a slight statistical preference for the third refinement.[12] The stereochemical implications are the same for both refinements. Structural parameters here will be presented only for the third type of refinement. We could not locate the hydrogen atom positions in the $B_3H_7^{2-}$ ligand because of the nature of the disorder.

Careful consideration was given to the possibility that the space group is Cc with two independent molecules which might have the $B_3H_7^{2-}$ ligands ordered. This possibility is unlikely in view of the excellent refinement obtained for the rest of the molecule. The data crystal was remounted and all equivalent forms were measured for 42 reflections which gave the largest differences between $F(hkl)$ and $F(\overline{hkl})$ for an ordered structure in space group Cc with the boron atoms in the orientations found in space group $C2/c$. There were no discernible differences in the Friedel pairs; in fact, an average of all members of the form seemed to make more sense than averaging according to the point symmetry. Reflections

Table I. Positional Parameters for $[(CH_3)_2PC_6H_5]_2PtB_3H_7$[a]

Atom	x	y	z
Pt	0.12570 (2)	0.14887 (4)	0.03931 (3)
P(1)	0.10026 (17)	0.30202 (23)	0.08000 (19)
P(2)	0.14835 (16)	0.07428 (22)	0.16265 (21)
C(1)	0.1668 (8)	0.3447 (8)	0.1754 (8)
C(2)	0.1036 (9)	0.4096 (13)	0.0166 (9)
C(3)	0.0059 (8)	0.3159 (9)	0.0946 (7)
C(4)	−0.0501 (7)	0.2449 (9)	0.0637 (7)
C(5)	−0.1233 (7)	0.2532 (9)	0.0728 (9)
C(6)	−0.1427 (10)	0.3289 (14)	0.1085 (11)
C(7)	−0.0903 (13)	0.4021 (13)	0.1364 (10)
C(8)	−0.0138 (11)	0.3970 (11)	0.1312 (9)
C(9)	0.0747 (7)	0.1000 (12)	0.2123 (9)
C(10)	0.1521 (8)	−0.0589 (10)	0.1687 (11)
C(11)	0.2382 (6)	0.1076 (8)	0.2351 (7)
C(12)	0.2478 (10)	0.1096 (10)	0.3163 (10)
C(13)	0.3192 (13)	0.1357 (11)	0.3706 (10)
C(14)	0.3761 (10)	0.1616 (11)	0.3420 (12)
C(15)	0.3694 (8)	0.1606 (11)	0.2624 (11)
C(16)	0.3008 (7)	0.1327 (9)	0.2084 (8)
B(1)	0.0677 (21)	0.2161 (29)	−0.0902 (23)
B(2)	0.1544 (20)	0.1373 (23)	−0.0728 (22)
B(3)	0.1468 (17)	0.0182 (23)	−0.0173 (19)
B(1)′[b]	0.1864	0.0053	0.0095
B(2)′	0.1007	0.0560	−0.0666
B(3)′	0.1076	0.1947	−0.0813

[a] The standard deviations of the least significant digits are given in parentheses. [b] The primed boron atom positions are related to the unprimed ones by the idealized molecular $C_2(2)$ axis.

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(8) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 101.

(9) T. C. Furnas, Jr., *Trans. Amer. Crystallogr. Ass.*, **1**, 67 (1965).

(10) Computer programs used in addition to various local programs were Prewitt's absorption correction program ACACA and least-squares program SFLS5, the Busing–Levy error function program ORFFE, the Johnson plotting program ORTEP, and the Fourier program FOUR, a modification of a program written by C. J. Fritchie, Jr.

(11) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).

(12) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

Table II. Hydrogen Atom Positions for $[(CH_3)_2PC_6H_5]_2PtB_3H_7$[a]

	x	*y*	*z*
H(1)C(1)	0.2199	0.3337	0.1680
H(2)C(1)	0.1733	0.2953	0.2430
H(3)C(1)	0.1472	0.4196	0.1904
H(4)C(2)	0.0545	0.3962	−0.0220
H(5)C(2)	0.1519	0.3924	0.0081
H(6)C(2)	0.1064	0.4361	0.0555
H(7)C(9)	0.0206	0.0826	0.1808
H(8)C(9)	0.0721	0.1672	0.2199
H(9)C(9)	0.0893	0.0563	0.2563
H(10)C(10)	0.1402	−0.0937	0.1990
H(11)C(10)	0.2221	−0.0873	0.1770
H(12)C(10)	0.1074	−0.0959	0.1111
H(13)C(4)	−0.0369	0.1804	0.0293
H(14)C(5)	−0.1665	0.1949	0.0502
H(15)C(6)	−0.2021	0.3357	0.1154
H(16)(C(7)	−0.1086	0.4664	0.1651
H(17)C(8)	0.0286	0.4586	0.1559
H(18)C(12)	0.1983	0.0893	0.3394
H(19)C(13)	0.3252	0.1347	0.4363
H(20)C(14)	0.4313	0.1826	0.3875
H(21)C(15)	0.4183	0.1805	0.2421
H(22)C(16)	0.2943	0.1324	0.1438

[a] The hydrogen atoms are identified also by the carbon atom to which they are attached. The methyl hydrogen atom positions [H(1)–H(12)] were refined but the benzene hydrogen atom positions are calculated positions. The hydrogen atoms of the $B_3H_7^{2-}$ ligand were not included in the model.

Table III. Thermal Parameters for $[(CH_3)_2PC_6H_5]_2PtB_3H_7$[a]

Atom	β_{11} or *B*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	28.8 (2)	94.6 (4)	41.3 (2)	−4.8 (2)	14.4 (1)	−18.2 (2)
P(1)	47.0 (12)	63.4 (19)	39.8 (14)	−10.9 (13)	11.1 (11)	3.6 (14)
P(2)	34.4 (11)	61.1 (20)	68.8 (18)	1.2 (11)	22.5 (12)	5.2 (15)
C(1)	69 (6)	69 (8)	58 (7)	−3 (6)	−1 (5)	−22 (6)
C(2)	89 (8)	143 (14)	59 (8)	−19 (9)	17 (6)	31 (9)
C(3)	59 (6)	73 (8)	36 (6)	17 (6)	19 (5)	12 (6)
C(4)	45 (5)	84 (10)	51 (7)	5 (6)	20 (5)	14 (7)
C(5)	63 (7)	76 (10)	73 (8)	27 (6)	35 (6)	−4 (7)
C(6)	78 (10)	130 (18)	74 (10)	20 (10)	39 (8)	37 (11)
C(7)	114 (12)	105 (13)	55 (9)	62 (11)	37 (9)	20 (9)
C(8)	97 (10)	89 (10)	49 (8)	27 (9)	27 (7)	−2 (8)
C(9)	46 (5)	178 (14)	93 (9)	38 (7)	42 (6)	80 (10)
C(10)	61 (7)	82 (10)	151 (14)	−8 (7)	15 (8)	26 (10)
C(11)	45 (5)	69 (8)	44 (7)	5 (5)	14 (5)	3 (6)
C(12)	72 (8)	85 (10)	60 (8)	8 (7)	31 (7)	3 (7)
C(13)	104 (11)	84 (12)	44 (7)	16 (9)	6 (8)	−2 (7)
C(14)	61 (8)	92 (12)	77 (11)	−6 (7)	2 (8)	15 (9)
C(15)	52 (6)	111 (13)	67 (9)	−8 (7)	14 (6)	3 (9)
C(16)	37 (5)	104 (11)	54 (7)	−10 (6)	16 (5)	5 (7)
B(1)	9.0 (9)					
B(2)	7.3 (8)					
B(3)	6.7 (8)					

[a] The anisotropic temperature factors are $\times 10^4$ and of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

with differences greater than 1 σ were remeasured with longer counting times; all members were then equivalent at the 1-σ level. This supports *C*2/*c* as the correct space group. Also an additional refinement was done in the space group *Cc* with the $B_3H_7^{2-}$ ligands ordered in the two independent molecules. The *R* and *wR* did not improve, the boron atom temperature factors were very anisotropic as before (rms amplitudes vary from 0.02 to 0.52 Å), and the Pt–phosphine geometries were essentially the same as found previously. Correlations in the vicinity of 0.9 were found for refined parameters equivalent in *C*2/*c*. These data also support *C*2/*c* as the space group. Lastly we looked for second harmonic generation upon laser irradiation; we found none, again supporting the centric space group. We have found this test to be far more sensitive than the usual piezoelectric test. All of the evidence indicates that *C*2/*c* is the correct space group.

The atomic positions were refined in two sections: (a) platinum, boron, phosphorus, and methyl carbon atoms, and (b) the benzene carbon atoms. The final parameter shifts were less than 0.5 of the estimated standard deviations. The final *R* values for the 2369 observed reflections were 0.054 for *R* and 0.057 for *wR*. The *R* and *wR* values for all the data were 0.071 and 0.058, respectively. The standard deviation of an observation of unit weight was 1.33. A final check of $w\Delta^2$ *vs.* F_{obsd} and $\sin \theta/\lambda$ indicated that the weak reflections were possibly overweighted but no weighting scheme changes were applied in view of the observed disorder.

Scattering factors for the neutral atoms were used.[13] The platinum atom was corrected for the real and imaginary parts of the anomalous scattering effect[14] in the calculated structure factors. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares program SFLS5.[10]

The final positional parameters are given in Table I. The hydrogen atom positions which were included in the model but not refined are given in Table II. The final thermal parameters are given in Table III. The root-mean-square amplitudes of vibration for the atoms varied anisotropically are given in Table IV. They are in the usual range for the types of atoms involved, the largest motion being for the terminal methyl carbon atoms. A list of observed and calculated structure factors is available.[15]

Discussion

Synthesis and Chemistry. The platinum complexes, $(R_3P)_2PtB_3H_7$, were obtained by the simple procedure of mixing acetonitrile–triethylamine solutions of CsB_3H_8 and *cis*-bis(trialkylphosphine)platinum(II) halide (reaction 1). An analogous reaction was effective with palladium, although this was primarily limited to complexes with bidentate phosphine ligands because of the cis-stereochemical requirement in the halide reagent.

$$\textit{cis}\text{-}(R_3P)_2PtCl_2 + CsB_3H_8 + (C_2H_5)_3N \longrightarrow (R_3P)_2PtB_3H_7 + CsCl + (C_2H_5)_3NHCl \quad (1)$$

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(13) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(14) D. H. Templeton, "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 216.

(15) A list of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5665. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Inter	Max
Pt	0.1957 (7)	0.2223 (7)	0.3164 (7)
P(1)	0.221 (4)	0.240 (4)	0.288 (4)
P(2)	0.212 (4)	0.239 (4)	0.314 (4)
C(1)	0.212 (17)	0.294 (16)	0.375 (17)
C(2)	0.248 (19)	0.344 (17)	0.424 (20)
C(3)	0.206 (18)	0.246 (17)	0.321 (16)
C(4)	0.237 (17)	0.257 (15)	0.305 (17)
C(5)	0.189 (19)	0.312 (19)	0.351 (18)
C(6)	0.253 (21)	0.313 (21)	0.410 (24)
C(7)	0.230 (20)	0.259 (22)	0.469 (22)
C(8)	0.237 (21)	0.280 (19)	0.403 (20)
C(9)	0.203 (17)	0.242 (17)	0.499 (19)
C(10)	0.260 (17)	0.309 (17)	0.487 (21)
C(11)	0.243 (17)	0.250 (17)	0.270 (15)
C(12)	0.262 (19)	0.280 (18)	0.342 (19)
C(13)	0.249 (20)	0.274 (19)	0.424 (22)
C(14)	0.276 (21)	0.287 (19)	0.385 (23)
C(15)	0.275 (17)	0.307 (20)	0.335 (19)
C(16)	0.222 (17)	0.274 (17)	0.323 (17)

A nickel derivative with the $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ ligand was obtained but proved too unstable for complete purification and analysis.

The general reactivity of the π-borallyl complexes to oxygen, water, and heat decreases in the series Ni > Pd > Pt. On exposure to air, the crystalline platinum derivatives slowly discolor; oxidation proceeds much more rapidly for solutions of the complexes. Resistance of the platinum derivatives to hydrolysis was quite marked. A moderate rate of hydrogen evolution required strongly acidic conditions (tetrahydrofuran-concentrated hydrochloric acid). This is in sharp contrast to the behavior of the $B_3H_8^-$ ion and the metalloborane $[(p\text{-}CH_3C_6H_4)_3P]_2CuB_3H_8$, both of which hydrolyze rapidly in slightly acidic media. It should be noted that $(CH_3)_3NB_3H_7$ undergoes only slow hydrolysis under strongly acidic conditions. The platinum derivatives do not decompose *in vacuo* or an inert atmosphere at a visually (discoloration) or tensimetrically (hydrogen evolution) evident rate much below their melting points or below ~150°, whichever is lower. The nickel complex seemed to undergo autoreduction at 25°.

The $B_3H_7^{2-}$ metal derivatives react with excess phosphine to yield tetrakis(phosphine)metal(0). This reaction has provided the first synthesis of tetrakis- and tris(trialkylphosphine)platinum(0) complexes which have an exceptional chemistry of their own.[16]

Spectral Properties of the π-Borallyl Complexes. The infrared spectra of these $B_3H_7^{2-}$ derivatives are distinctive (Figure 1). There is complex BH stretching absorption for $[(C_2H_5)_3P]_2PtB_3H_7$ at ~2493–2288 cm^{-1}, at 1897 and 1642 cm^{-1}, and a relatively sharp absorption at 1557 cm^{-1}. The last is absent in $B_3H_8^-$ salts, $R_3NB_3H_7$, and metalloboranes based on the $B_3H_8^-$ ion.

Representation of the platinum derivatives as platinum(II) complexes is consistent with X-ray photoelectron spectral data. We found the Pt 4f$_{7/2}$ binding energy in $[(C_2H_5)_3P]_2B_3H_7$ to be 72.9 eV. This is very similar to the binding energy found for most platinum(II) compounds, *e.g.*, 73.3 eV for $[(C_2H_5)_3P]_2PtCl_2$ and 72.9 eV for $[(C_2H_5)_3P]_2PtB_8H_{12}$.[17] This range of binding energies for a selected sample of platinum(II) complexes is substantially higher than that found for platinum(0) complexes: 71.6 eV for $[(C_6H_5)_3P]_3Pt$ and $[(C_6H_5)_3P]_4Pt$.

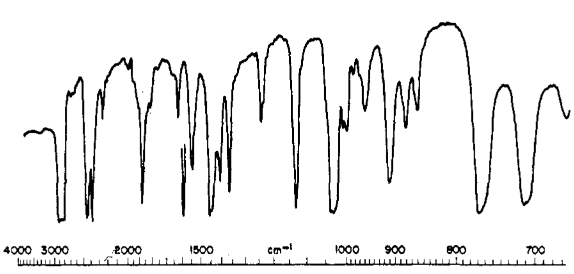

Figure 1. Infrared spectrum of $[(C_2H_5)_3P]_2PtB_3H_7$.

Although the ^{11}B nmr spectra of the π-borallyl complexes were uninstructive (broad and structureless),[18] the ^1H spectra were sharp and rich in stereochemical information. In the proton nmr spectrum, there are three major BH resonances of relative intensities 3:2:2 at 25°. The two relatively broad low-field resonances sharpen significantly on temperature decrease and the peak of intensity 3 shows evidence of asymmetry, suggesting the possibility of a 2:1:2:2 proton distribution which would be consistent with π-allyl formulation. At −26°, the resonances are at approximately −1.1, −0.9 (?), −0.11, and +4.9 ppm (tetramethylsilane reference) of relative intensities of 2:1:2:2 for $[(C_6H_5)_2PC_2H_5)]_2PtB_3H_7$. The resonance at 4.9 ppm is at unusually high field even for B–H–B bridge hydrogen atoms.[19] We suggest that this high-field shift for the bridge hydrogen atoms may reflect a departure of the bridge hydrogen atoms from the B_3 plane *toward* the metal atom. There is no such high-field resonance in $B_3H_8^-$, $R_3NB_3H_7$, $(R_3P)_2CuB_3H_8$, or $(OC)_4Mo(B_3H_8)^-$.

No distinctive ^1H nmr spectral changes for the $B_3H_7^{2-}$ derivatives were observed over the temperature range of −50 to +40° other than line width decrease with temperature decrease ostensibly due to more effective quadrupole induced ^{10}B and ^{11}B spin relaxation. Above +40°, the two low-field peaks broaden and overlap. It is not known whether this reflects further broadening due to quadrupole relaxation effects or the onset of a rearrangement of the π–σ type often encountered in π-allyl metal complexes. In any case, these $B_3H_7^{2-}$ derivatives are relatively rigid in a stereochemical sense. This contrasts sharply with the behavior established for the highly fluxional $B_3H_8^-$ ion and for $(R_3P)_2CuB_3H_8$. Only in the latter case has the hydrogen atom rearrangement rate been lowered sufficiently to detect hydrogen atom inequivalence and this required temperatures of ~−110°.[20]

In the $[(C_6H_5)P(CH_3)_2]PtB_3H_7$ derivative, the methyl groups in each phosphine ligand cannot be environmentally equivalent in a π-borallyl structure, and, in fact, the expected two resonances were observed (0.2-ppm separation).

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(16) D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971).

(17) A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *ibid.*, **92**, 2571 (1970).

(18) This has been typical of phosphinometalloboranes.[1,17]

(19) Most bridge hydrogen resonances are around 0 to +2 ppm from tetramethylsilane. The "unique" hydrogen in B_5H_{11} is +2 ppm from tetramethylsilane: *cf.* T. Onak and J. B. Leach, *J. Amer. Chem. Soc.*, **92**, 3513 (1970), and R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *ibid.*, **92**, 3514 (1970).

(20) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *ibid.*, **92**, 3484 (1970).

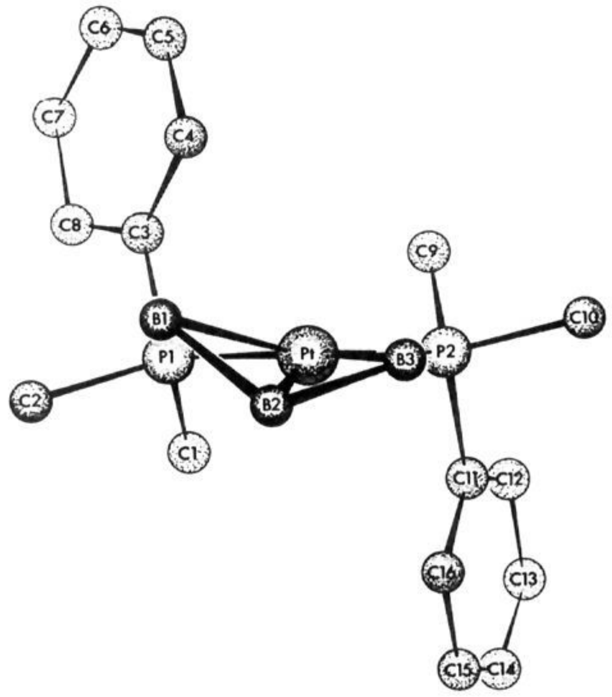

Figure 2. The molecular configuration of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$. All hydrogen atoms have been omitted.

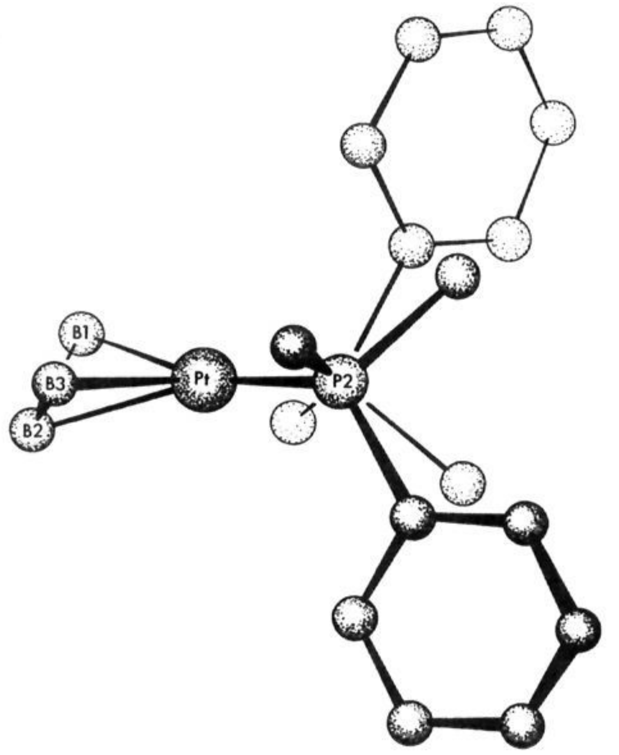

Figure 3. A side view of the $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ molecule illustrating the angle between the borallyl plane and the P(1)PtP(2) plane (P(1) and P(2) overlap in this view).

Structure Description of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$. The crystal structure consists of the packing of discrete molecules of bis(dimethylphenylphosphine)platinum heptahydridotriborate(2−) separated by normal van der Waals contracts. The molecular configuration illustrating the numbering system used here is shown in Figure 2. This view illustrates clearly the idealized $C_2(2)$ axis in the platinum–phosphine geometry. The C_2 axis passes through the Pt atom and the P(1)–P(2) midpoint. The P(1)PtP(2) plane contains the B(3) atom and the midpoint of B(1)–B(2). Figure 3 shows a side view of the molecule emphasizing the relationship with metal–π-allyl complexes (*vide infra*). The dihedral angle between the B(1)B(2)B(3) plane and the P(1)PtP(2) plane is 116.8 (24)°.

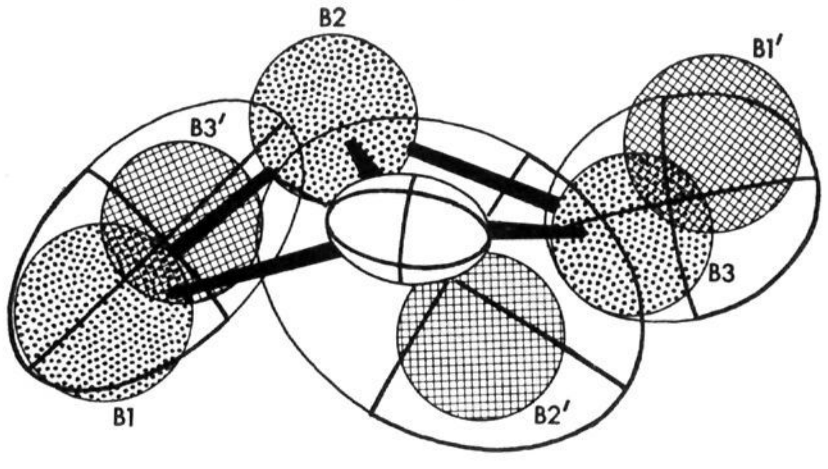

Figure 4. The Pt–B_3H_7 disordered geometry viewed in the direction of the Pt–phosphine idealized $C_2(2)$ axis. The primed and unprimed sets of boron atoms were assumed to occur equally and randomly in the crystal. The boron ellipsoids show the result of averaging the boron electron density in an ordered boron model with individual anisotropic thermal parameters.

The nature of the B_3H_7 disorder is shown in Figure 4 where the Pt–B_3H_7 geometry is viewed in the direction of the molecular $C_2(2)$ axis. The two disordered B_3 groups are shaded differently and superimposed upon these are the thermal ellipsoids obtained from an individual anisotropic refinement assuming an ordered B_3 group. Figure 4 shows how the anisotropic thermal ellipsoids try to accommodate the diffuse electron density resulting from the disorder; the fit is especially bad in the case of B(2) where the B(2)–B(2)′ separation is 1.50 Å. The assumption made here in the refinement of the disordered model is that this is a random disorder with both energy equivalent conformations occurring equally throughout the crystal. Any given molecule has a fixed conformation but the diffraction experiment averages over all the molecules in the crystal giving a superposition of the two conformations. This results in very broad electron density peaks, especially in the B(1)B(3)′B(2) and B(1)′B(3)B(2)′ directions.

A set of interatomic distances is given in Table V and a set of interatomic angles in Table VI. A comparison of the Pt–P distances of 2.301 (4) and 2.311 (4) Å found here with representative observed distances is given in Table VII. The spread in observed Pt–P distances is large indeed and differences from expected "single bonds" are usually ascribed to differences in dπ–pπ bonding. Generally the Pt–P bonding appears to be correlated with the π-acceptor abilities of the remaining ligands, but σ effects may also be influential.[21] In any case the Pt–P bonding competes and tends to compensate for the remaining Pt–ligand bonding. The Pt–P distances observed here are in the upper end of the observed range suggesting fairly strong Pt–B_3H_7 bonding. The P(1)–Pt–P(2) angle of 96.2 (1)° is only slightly larger than the square-planar value of 90°, presumably reflecting intramolecular steric effects.

The Pt–B distances of 2.13 (3), 2.18 (4), and 2.38 (4) Å are indicative of asymmetrical Pt–B_3H_7 bonding. Other observed Pt–B distances are 2.20–2.25 (2) Å found in $[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$.[17] The differences in B–B distances [1.85 (5) Å for B(1)–B(2) and 1.92 (4) Å for B(2)–B(3)] are not statistically significant in view of the errors involved. The large estimated errors in the B–B distances result from the disorder in the $B_3H_7{}^{2-}$ ligand. These distances compare with the hydrogen-bridged B–B distances of 1.82 (1) Å in $[(CH_3)_4N][(CO)_4CrB_3H_8]$[3] and $[(C_6H_5)_3P]_2CuB_3H_8$[4] although they do not by themselves establish the presence of bridg-

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[21] R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, **47**, 20 (1969).

Table V. Selected Interatomic Distances for $[(CH_3)_2PC_6H_5]_2PtB_3H_7$[a]

Bonding contacts		Nonbonding contacts	
Pt–P(1)	2.301 (4)	B(1)–B(3)	3.15 (5)
Pt–P(2)	2.311 (4)	P(1)–P(2)	3.43 (1)
Pt–B(1)	2.38 (4)	P(1)–B(1)	3.09 (4)
Pt–B(2)	2.18 (4)	P(2)–B(3)	3.23 (3)
Pt–B(3)	2.13 (3)	B(1)–C(2)	3.19 (4)
		B(3)–C(10)	3.40 (4)
B(1)–B(2)	1.86 (5)	C(1)–C(2)	2.82 (2)
B(2)–B(3)	1.92 (4)	C(1)–C(3)	2.87 (1)
		C(2)–C(3)	2.84 (1)
P(1)–C(1)	1.84 (1)	C(9)–C(10)	2.81 (2)
P(1)–C(2)	1.85 (2)	C(9)–C(11)	2.88 (1)
P(2)–C(9)	1.83 (1)	C(10)–C(11)	2.81 (2)
P(2)–C(10)	1.82 (1)		
	1.84 (1)	B_3H_7 contacts	
P(1)–C(3)	1.81 (1)	B(1)–B(2)′	2.27
P(2)–C(11)	1.80 (1)	B(1)–B(3)′	0.75
		B(2)–B(2)′	1.50
C(3)–C(4)	1.39 (2)	B(2)–B(3)′	1.13
C(4)–C(5)	1.39 (2)	B(3)–B(1)′	0.75
C(5)–C(6)	1.31 (3)	B(3)–B(2)′	1.13
C(6)–C(7)	1.37 (3)		
C(7)–C(8)	1.42 (3)		
C(8)–C(3)	1.38 (2)		
	1.38 (2)		
C(11)–C(12)	1.38 (2)		
C(12)–C(13)	1.41 (2)		
C(13)–C(14)	1.32 (2)		
C(14)–C(15)	1.36 (2)		
C(15)–C(16)	1.38 (2)		
C(16)–C(11)	1.39 (1)		
	1.37 (1)		

[a] Averages taken were meaningful and the errors of the mean estimated according to $[\Sigma^n(d_i - \bar{d})^2/n(n - 1)]^{1/2}$ where d_i and $\bar{d}$ are the distances and mean distance, respectively. The primed atoms refer to the second set of positions in the $B_3H_7^{2-}$ ligand in the disordered model.

Table VI. Selected Interatomic Angles (degrees) for $[(CH_3)_2PC_6H_5]_2PtB_3H_7$[a]

P(1)–Pt–P(2)	96.2 (1)	B(1)–Pt–B(2)	47.8 (12)
P(1)–Pt–B(1)	82.6 (9)	B(1)–Pt–B(3)	88.3 (13)
P(1)–Pt–B(2)	117.9 (8)	B(2)–Pt–B(3)	52.9 (12)
P(1)–Pt–B(3)	170.4 (9)		
P(2)–Pt–B(1)	164.8 (9)	B(1)–B(2)–B(3)	112.9 (23)
P(2)–Pt–B(2)	141.7 (9)		
P(2)–Pt–B(3)	93.3 (9)	Pt–P(2)–C(9)	113.9 (4)
		Pt–P(2)–C(10)	119.2 (6)
Pt–P(1)–C(1)	115.5 (4)	Pt–P(2)–C(11)	114.7 (4)
Pt–P(1)–C(2)	119.4 (6)	C(9)–P(2)–C(10)	100.6 (8)
Pt–P(1)–C(3)	115.0 (4)	C(9)–P(2)–C(11)	104.7 (5)
C(1)–P(1)–C(2)	99.3 (6)	C(10)–P(2)–C(11)	101.6 (6)
C(1)–P(1)–C(3)	103.4 (5)		
C(2)–P(1)–C(3)	101.6 (5)	P(2)–C(11)–C(12)	122.7 (9)
		P(2)–C(11)–C(16)	119.0 (8)
P(1)–C(3)–C(4)	118.9 (8)		
P(1)–C(3)–C(8)	122.3 (10)	C(12)–C(11)–C(16)	118.3 (12)
		C(11)–C(12)–C(13)	120.7 (13)
C(4)–C(3)–C(8)	118.7 (11)	C(12)–C(13)–C(14)	118.6 (15)
C(3)–C(4)–C(5)	120.8 (11)	C(13)–C(14)–C(15)	122.8 (15)
C(4)–C(5)–C(6)	121.4 (14)	C(14)–C(15)–C(16)	119.5 (14)
C(5)–C(6)–C(7)	119.4 (15)	C(15)–C(16)–C(11)	120.1 (13)
C(6)–C(7)–C(8)	122.1 (15)		
C(7)–C(8)–C(3)	117.5 (15)		120.0 (7)
	120.0 (7)		

[a] Footnote to Table V applies here.

Table VII. Selected Observed Pt–P Bond Distances

Complex	Pt–P (Å)	Ref
trans-$[(C_3H_7)_3P]_2Pt_2Cl_4$	2.230 (9)	*a*
$(PF_3)_4Pt$	2.240 (10)	*b*
$[(C_6H_5)_3P]_2PtCO_3$	2.24	*c*
$[(C_6H_5)_3P]_2PtCS_2$ (trans to S)	2.240 (15)	*d*
$[(C_6H_5)_3P]_2PtCS_2$ (trans to C)	2.346 (10)	*d*
$[(C_2H_5)_3P]PtCl_2[(C_6H_5)NC(OC_2H_5)]$	2.240 (8)	*e*
α-$[(C_3H_7)_3P]_2Pt_2Cl_2(SCN)_2$	2.244 (4)	22
$[(C_6H_5)_3P]_3Pt_2S(CO)$ (ordered groups)	2.226 (9)	*f*
	2.267 (9)	
cis-$[(CH_3)_3P]_2PtCl_2$	2.247 (7)	*g*
$[(C_6H_5)_3P]_3Pt$	2.25–2.28	*h*
$[(C_2H_5)_3P]_2PtHBr$	2.26 (7)	*i*
β-$[(C_3H_7)_3P]_2Pt_2Cl_2(SCN)_2$	2.262 (4)	22
$[(C_6H_5)_3P]_2Pt(O_2)\cdot 1.5C_6H_6$	2.253 (12)	*j*
	2.282 (11)	*j*
$[(C_6H_5)_2PC_2H_5]_2PtHCl$	2.268 (8)	*k*
$[(C_6H_5)_3P]_2Pt[C_2(C_6H_5)_2]$	2.27	*l*
$[(C_6H_5)_3P]_2PtC_2(CN)_4$	2.289 (8)	*m*
$[(C_6H_5)_3P]_2Pt(CF_3CN)$	2.29	*n*
trans-$[(C_2H_5)_3P]_2PtCl_2$	2.298 (18)	*o*
$[(CH_3)_2PC_6H_5]_2PtB_3H_7$	2.301 (4) 2.311 (4)	This work
trans-$[(C_2H_5)_3P]_2PtBr_2$	2.315 (4)	*o*
trans-$[(C_4H_9)_3P]_2Pt(SC_6F_5)_2$	2.329 (8)	*p*
$[(C_6H_5)_3P]_3PtCO$ monoclinic	2.333–2.352 (8)	*q*
$[(C_6H_5)_3P]_3PtCO$ trigonal	2.353–2.369 (10)	*r*
trans-$[(C_2H_5)_3P]_2PtCl(CO)^+$	2.34	*s*
$[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$	2.36	17
	2.39	17
Sum of radii	2.41–2.43	

[a] M. Black, R. H. B. Mais, and P. G. Owston, *Acta Crystallogr., Sect. B*, **25**, 1760 (1969). [b] J. C. Marriott, J. A. Salthouse, M. J. Ware, and J. M. Freeman, *Chem. Commun.*, 595 (1970). [c] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *ibid.*, 408 (1967). [d] R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 1767 (1970). [e] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Commun.*, 1322 (1969). [f] A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. A*, 2772 (1969). [g] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967). [h] V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966). [i] P. G. Owston, J. M. Partridge, and J. M. Brown, *Acta Crystallogr.*, **13**, 246 (1960). [j] T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Chem. Commun.*, 743 (1969). [k] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). [l] J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, **7**, P9 (1967). [m] G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani, and G. Bandoli, *J. Chem. Soc. A*, 1313 (1970). [n] W. J. Bland, R. D. W. Kemmitt, I. W. Nowell, and D. R. Russell, *Chem. Commun.*, 1065 (1968). [o] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966). [p] R. H. Fenn and G. R. Segrott, *J. Chem. Soc. A*, 2781 (1970). [q] V. G. Albano, G. M. B. Ricci, and P. L. Bellon, *Inorg. Chem.*, **8**, 2109 (1969). [r] V. G. Albano, P. L. Bellon, and M. Sansoni, *Chem. Commun.*, 899 (1969). [s] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, **89**, 3360 (1967).

ing hydrogen atoms. The B(1)–B(3) distance of 3.15 (5) Å clearly differentiates the coordinated B_3H_7 geometry from that of B_3H_8 complexes where these atoms are bonded (1.78 (1) Å).[3]

The P–C distances, 1.84 (1) Å for P–C(CH_3) and 1.81 (1) Å for P–C(C_6H_5), and the Pt–P–C and C–P–C angles are quite normal for Pt–phosphine coordination. In particular, it is common to have Pt–P–C angles larger than 109.5° and C–P–C angles less than 109.5°.[22] The benzene distances and angles are also normal. All the C–C distances are equal within experimental errors. The C(5)–C(6) distance is short, but it is correlated in the refinement with the treatment of the disordered $B_3H_7^{2-}$ ligand. This distance in particular

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varied significantly in the different refinements of the $B_3H_7^{2-}$ ligand.

The least-squares planes were examined for the benzene rings and the molecular plane (Pt, P(1), P(2), B(3), B(1)–B(2) midpoint). These results are given in Table VIII. The benzene rings are quite planar.

Table VIII. Least-Squares Planes for $[(CH_3)_2PC_6H_5]_2PtB_3H_7$[a]

Plane 1. $0.0432X - 0.4744Y + 0.8792Z + 0.6878 = 0$
Plane 2. $-0.2938X + 0.9532Y - 0.0707Z - 0.2069 = 0$
Plane 3. $0.9466X + 0.2368Y + 0.2187Z - 0.2593 = 0$

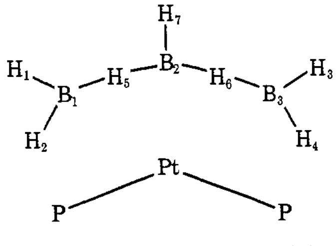
Atoms	Plane 1	Plane 2	Plane 3
Pt			−0.000
P(1)			0.007
P(2)			−0.007
B(3)			0.010
B(1)–B(2) midpoint			−0.010
C(3)	0.01		
C(4)	−0.02		
C(5)	0.00		
C(6)	0.01		
C(7)	−0.02		
C(8)	0.00		
C(11)		0.01	
C(12)		0.01	
C(13)		−0.01	
C(14)		0.01	
C(15)		0.00	
C(16)		−0.01	

[a] The planes are in Cartesian coordinates relative to (*a*, *b*, *c**). The distances from the planes are given for all atoms included in the plane calculation.

The excellent planarity of the molecular plane is consistent with the valence bond description using a four-coordinate square-planar dsp^2 hybridized Pt atom (*vide infra*).

All the intermolecular contacts were calculated. There are no nonhydrogen atom contacts less than 3.5 Å. The shortest contact was 2.44 Å for H(2)–H(15) on adjacent molecules.

We have not explicitly located the hydrogen atoms in the $B_3H_7^{2-}$ ligand because of the disorder, but we can comment on their positions. We believe the hydrogen atom distribution is analogous to $B_3H_8^-$ and other boranes (B_1 and B_3 are bonded in $B_3H_8^-$). We cannot absolutely exclude here the possibility of a Pt–H–B type bond involving terminal hydrogen atoms, as in $(R_3P)_2CuB_3H_8$, but we discount it because of the chemical and spectral evidence[1] and the close structural similarities between Pt–B_3H_7 and metal–π-allyl complexes (*vide infra*) which have no metal–hydrogen bridge bonds. The nmr pattern at −50° of $[(CH_3)_2PC_6H_5]_2PtB_3H_7$ was in an apparent 2:1:2:2 distribution. This would be consistent with a symmetrically π-bonded borallyl, *i.e.*, containing a local mirror plane normal to the P(1)PtP(2) plane. The solid state structure does not possess such a mirror plane suggesting a lower symmetry boron–hydrogen framework. However, this does not necessarily suggest different solid state and solution structures since dynamic effects might be expected in solutions.



Comparison with π-Allyl Geometries. The general structural features of the π-bonded $B_3H_7^{2-}$ borallyl ligand are the same as those found in $C_3H_5^-$ π-allyl-metal complexes. See ref 23–31 for recent structural work on π-allyl-metal complexes; ref 26 and 31 include references to the earlier work. The only Pt-π-allyl structure determined is that of $Pt_2(C_3H_5)_2(acaca)_2$[28] (acaca is acetylacetonate) where the allyl groups are bridging two platinum atoms with one allyl carbon atom σ bonded to Pt(1) and the other two allyl carbon atoms π bonded to Pt(2). The dihedral angles between the allyl plane and the metal–ligand plane in the unsubstituted and monosubstituted π-allyl complexes are in the 111–127° range, entirely consistent with the 116.8 (24)° angle found here for the π-borallyl ligand. Most π-allyl complexes have a symmetrically coordinated allyl ligand judging from the C–C and M–C distances. In general the metal–allyl geometry in the symmetrically coordinated π-allyls is characterized by a localized mirror plane with two equivalent outer M–C distances and a central M–C distance which is the same or usually slightly less than the outer distance. Asymmetrical metal–allyl geometries were found in $[(C_3H_5)_2RhCl]_2$,[32] $[(C_5H_9)PdCl]_2$,[33] and $(C_4H_7)Pd[P(C_6H_5)_3]Cl$.[34]

The allyl asymmetry found in the $[(C_3H_5)_2RhCl]_2$[32] and $(C_4H_7)Pd[P(C_6H_5)_3]Cl$[34] structures was of the same type as found here; namely a short M–C bond in the M–ligand plane associated with a long C–C bond and two longer M–C distances associated with a shorter C–C bond. The midpoint of the shorter bond in $(C_4H_7)Pd[Pd(C_6H_5)_3]Cl$ was in the metal–ligand plane as found here for the B(1)B(2) midpoint; this was not the case in $[(C_3H_5)_2RhCl]_2$, perhaps for steric reasons. The asymmetries in both of these structures seemed to be correlated with trans effects; in both cases the shortest M–C bond was trans to a Cl atom. The asymmetry in the $[(C_5H_9)PdCl]_2$ structure is not as great as in the other two π-allyl structures and the precise nature of the asymmetry is not clear from the note, but the fact that there is some asymmetry is significant since the trans ligands are the same in this structure. The asymmetry was described in terms of crystal packing forces. We cannot rule out packing forces as a cause for asymmetry in $[(CH_3)_2PC_6H_5]_2PtB_3H_7$, but it is certainly possible that maximum ligand–metal overlap is attained

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(33) G. R. Davies, R. H. B. Mais, S. O'Brien, and P. G. Owston, *ibid.*, 1151 (1967).
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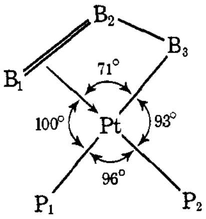
with the B_3H_7 asymmetrically bonded to Pt without invoking crystal packing forces. Of possible importance here is the fact that the B(1)–B(3) distance of 3.15 (5) Å is significantly longer than the terminal C–C distance of 2.42 Å (C–C = 1.40 Å, C–C–C = 120°) found in metal–π-allyl complexes. Thus the steric requirements of the $B_3H_7^{2-}$ borallyl ligand are slightly different from those of the $C_3H_5^-$ allyl ligand in a way which could affect metal–ligand orbital overlap.

Bonding. We can view the bonding here as coordination to a square-planar dsp^2 hybridized Pt atom in valence bond terms. The angles and the strict planarity of the molecular plane (plane 3, Table VIII) support this interpretation. The hybridized Pt orbitals would be directed at B(3) and the midpoint of B(1) and B(2) as indicated by the resonance form



The distance from the Pt atom to the B(1)–B(2) midpoint is 2.09 (4) Å. There is a small, but possibly statistically significant, ground-state trans influence as indicated by the Pt–P(2) distance being 0.010 Å longer than Pt–P(1). This is consistent with the resonance form shown with the trans effect being transmitted through π effects. The distances and angles are not inconsistent with the σ–π formalism; however, we believe it should be considered as an essentially π-bonded B_3H_7 group more appropriately described in terms of molecular orbitals. Others[32,34] have used the σ–π formalism in describing metal–π-allyl complexes, but it has been discouraged[35] especially in view of the nmr results for π-allyl complexes.

The bonding in molecular orbital terms will be outlined briefly analogous to the description given for π-allyl bonding.[36] In the first approximation we separate out the essentially in-plane boron–hydrogen bonding and use perpendicular boron p orbitals for bonding to Pt. The three boron p orbitals in the isolated $B_3H_7^{2-}$ ligand of C_{2v} symmetry combine in the LCAO approach to give two ligand molecular orbitals of b_1 symmetry and one of a_2 symmetry. The lowest energy b_1 ligand orbital is symmetrically distributed over the three boron atoms. The second bonding molecular orbital, of a_2 symmetry, is localized on the two end boron atoms (nodal plane through B(2)). The b_1 ligand orbital, which was estimated to play the major role in Pd–allyl bonding, in particular might be quite insensitive to B_3H_7 rotations in the B_3 plane. The Pt and Pd atomic orbital energies are about the same,[37] but the ionization potential of $B_3H_7^{2-}$ is not known so we have no numbers for the ligand orbital energies to compare with the $C_3H_5^-$ energies. In any case it appears that small perturbations in the molecular orbitals which may not affect the metal–ligand overlap much could easily alter the rotation of the borallyl group in the B_3 plane.

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