

to 20-hr exposure to ~25-mW helium-neon laser radiation. In this respect, the permethylaurates are more stable than the parent compounds $\text{CH}_3\text{AuP}(\text{C}_6\text{H}_5)_3$ and $(\text{CH}_3)_3\text{AuP}(\text{C}_6\text{H}_5)_3$, which slowly deposit gold at room temperature both in solutions and in the solid state. The increase in intrinsic stability upon replacement of phosphine by the methyl group is accompanied by an increase in reactivity, however, due to the increased electron density at the gold center. This is shown by comparisons of oxidative addition to $\text{CH}_3\text{AuP}(\text{C}_6\text{H}_5)_3$ and $(\text{CH}_3)_2\text{Au}^-$,^{2,3} and by the deposition of metallic gold when the permethylaurates are exposed to air or protic solvents.

Recent discussions of transition metal alkyls⁵⁻⁷ have pointed out that stabilization by phosphines has little to do with π -acceptor characteristics of the ligand but is primarily due to coordinative saturation of the metal. Mechanistic studies have indicated that $\text{CH}_3\text{AuP}(\text{C}_6\text{H}_5)_3$ and $(\text{CH}_3)_3\text{AuP}(\text{C}_6\text{H}_5)_3$ have as the first step in their decompositions the dissociation of phosphine.^{8,9} The increased thermal stability upon replacement of the phosphine with an additional methyl group would appear to be due to the less ready dissociation of a methyl group from a permethylaurate than that of phosphine from a neutral complex. This also would explain the instability of $\text{Li}[(\text{CH}_3)_2\text{Au}]$ and $\text{Li}[(\text{CH}_3)_4\text{Au}]$ in the solid state; the bare lithium cation should interact strongly with the methyls, promoting their dissociation from gold, whereas the interaction of etherated lithium in solution or PMDT-chelated lithium in the solid state should be weak. It appears that Li^+ is more effectively chelated, as expected, by one pentamethyldiethylenetriamine ligand than by the analogous oxygen ligand diethylene glycol dimethyl ether.

The permethylaurates may be compared to trimethylphosphonium-methylide compounds recently reported by Schmidbaur and coworkers,¹⁰⁻¹² of which the closest analogues to the aurates are $\text{CH}_3\text{AuCH}_2\text{P}(\text{CH}_3)_3$ ¹¹ and $(\text{CH}_3)_3\text{AuC-H}_2\text{P}(\text{CH}_3)_3$.¹² As the aurates, these are thermally stable to above 100°, and the stability was attributed to the stabilizing effect of the onium center on the gold-carbon bonds.¹² In view of the comparable thermal stability of the permethylaurates, however, it would appear that while the positive center may well reduce the susceptibility of the compounds to electrophilic attack by decreasing the electron density on the gold atom, their thermal stability is the result of introducing an additional gold-carbon bond to the CH_3Au^I and $(\text{CH}_3)_3\text{Au}^{III}$ units. It is becoming apparent that stabilization of the gold methyls is not dependent upon special ligands such as phosphines but upon coordinative saturation of the gold center by any ligand which is strongly bound; methyl groups appear to be quite good as "stabilizing ligands".

The isolation of compounds containing the tetramethylaurate(III) would appear to complete the series of $\text{R}_n\text{Au}^{III}$ compounds that began with the preparation of $(\text{C}_2\text{H}_5)_2\text{AuBr}$ in 1907¹³ and continued with the synthesis of unstable¹⁴ and stable¹⁵ $(\text{CH}_3)_3\text{Au}^{III}$ compounds in 1943 and 1963, respectively.

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Registry No. $\text{CH}_3\text{AuP}(\text{C}_6\text{H}_5)_3$, 23108-72-7; $(\text{CH}_3)_3\text{AuP}(\text{C}_6\text{H}_5)_3$, 33635-47-1; $[\text{Li}(\text{PMDT})][(\text{CH}_3)_2\text{Au}]$, 57444-57-2; $[\text{Li}(\text{PMDT})][(\text{CH}_3)_4\text{Au}]$, 57444-55-0; $[\text{Li}(\text{PMDT})][\text{I}]$, 52451-34-0.

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Reaction of Some Boron Halide Compounds with Platinum(0) and Platinum(II) Species

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The ability of many transition metal compounds to act as Lewis bases toward boron halides and related compounds is well established, and compounds of the types $(\text{C}_6\text{H}_5)_2\text{W-H}_2\text{-BF}_3$ ¹, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Rh}(\text{CO})\text{Cl}\cdot\text{BX}_3$ ($\text{X} = \text{Cl}$ or Br)², and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ir}(\text{CO})\text{Cl}\cdot x\text{BF}_3$ ($x = 1$ or 2)^{3,4} have been reported. More recently the type of compound resulting from the action of BCl_3 on phosphineplatinum(0) derivatives has been shown to be very dependent upon the choice of starting materials and conditions.⁵ Thus when $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Pt}$ is treated with BCl_3 vapor, $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Pt}\cdot 2\text{BCl}_3$ is formed, but in benzene 3 mol of the trichloride is consumed and the proposed products are $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot\text{BCl}_3$ (1 mol) and $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BCl}_3$ (2 mol). The exposure of solid $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pt}$ to the trichloride vapor also results in the formation of $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Pt}\cdot 2\text{BCl}_3$ in addition to 1 mol of $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BCl}_3$. The only reported route to the bis(phosphine) adduct, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot\text{BCl}_3$, is the displacement of silicon tetrafluoride from $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot\text{SiF}_4$ by BCl_3 .⁵ We now report the results of our experiments involving the action of a variety of boron halide compounds on similar phosphineplatinum(0) derivatives.

Results and Discussion

The nature of the reaction between boron halides and phosphineplatinum(0) compounds is dependent upon both the halogen atom present and the type of boron halide compound used. It is convenient, therefore, to discuss the results separately, dealing first with the boron trihalides BX_3 ($\text{X} = \text{F}$, Cl) and then with the alkyl or aryl derivatives R_2BX ($\text{R} = \text{C}_6\text{H}_5$, CH_3 ; $\text{X} = \text{Cl}$, Br). In general two stoichiometries were found for the products, 1:1 and 1:2, and the results are summarized in Table I. The solid adducts are hydrolyzed in air with the exception of the adduct $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot 2\text{BF}_3$.

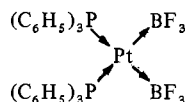
A tensimetric titration shows that when tetrakis(tri-phenylphosphine)platinum is treated with boron trifluoride (in toluene), 4 mol of the latter is consumed per mole of platinum compound. However, the white precipitate is a mixture which we were unable to separate into its constituent compounds. We consider it unlikely that all the phosphine ligands are removed from the metal to form 4 mol of $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BF}_3$ since there is no evidence for the existence of metallic platinum in the precipitate. A much simpler reaction occurs when $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}(\text{C}_2\text{H}_4)$ is treated with boron trifluoride; the ethylene is liberated quantitatively and 2 mol of boron trifluoride is consumed as shown tensimetrically. This adduct appears to be a four-coordinate Pt(0) species (I) rather than

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Table I. Compounds Obtained from Reaction of Phosphineplatinum(0) with Some Boron Halides

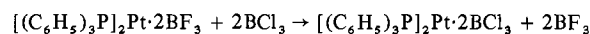
Reactants	Solvent	Molar ratio Pt compd: B compd	Product
$[(C_6H_5)_3P]_2Pt + BF_3$	$C_6H_5CH_3$	1:4	$[(C_6H_5)_3P]_2Pt \cdot 2BF_3 + 2(C_6H_5)_3P \cdot BF_3$
$[(C_6H_5)_3P]_2Pt \cdot (C_2H_4) + BF_3$	$C_6H_5CH_3$	1:2	$[(C_6H_5)_3P]_2Pt \cdot 2BF_3 + C_2H_4$
$[(C_6H_5)_3P]_2Pt \cdot 2BF_3 + BCl_3$		1:2	$[(C_6H_5)_3P]_2Pt \cdot 2BCl_3^a + 2BF_3$
$[(C_6H_5)_3P]_2Pt \cdot (C_2H_4) + BCl_3$		No reaction; reactants recovered unchanged ^b	
$[(C_6H_5)_3P]_4Pt + (C_6H_5)_2BBR$	C_6H_{12}	1:1	$[(C_6H_5)_3P]_2Pt \cdot [B(C_6H_5)_2]BR$
$[(C_6H_5)_3P]_4Pt + (C_6H_5)_2BCl$	C_6H_{12}	1:1	$[(C_6H_5)_3P]_2Pt \cdot [B(C_6H_5)_2]Cl$
$[(C_6H_5)_3P]_4Pt + (CH_3)_2BBR$	C_6H_{12}	1:2	$[(C_6H_5)_3P]_2Pt \cdot [B(CH_3)_2]_2(Br)_2^c$
$[(C_2H_5)_2(C_6H_5)P]_2Pt + (C_6H_5)_2BCl$	C_6H_{12}	1:1	$\{[(C_2H_5)_2(C_6H_5)P]_2Pt \cdot [B(C_6H_5)_2]\}^+Cl^-$

^a Product is air reactive and not fully characterized by analysis. ^b No reaction apparent also in toluene solution (see text). ^c Probably structural formulation, containing a six-coordinate platinum(IV) atom.



a mixture of $[(C_6H_5)_3P]Pt \cdot BF_3 + (C_6H_5)_3P \cdot BF_3$ or $[(C_6H_5)_3P]Pt(F)(BF_2) + (C_6H_5)_3P \cdot BF_3$ both from its mode of preparation and its properties. Thus it is monomeric in CH_2Cl_2 solution; its ir spectrum shows strong absorptions from the coordinated $(C_6H_5)_3P$ ligands near 3000, 1480, 700, and 500 cm^{-1} and other bands at 1100–1000 cm^{-1} which are typical of B–F vibrations in coordinated BF_3 ,^{6,7} rather than bands at 1450–1200 cm^{-1} due to a Pt– BF_2 group.⁸ The product does, however, lack the profile of strong broad absorptions between 1100 and 1000 cm^{-1} which characterize $(C_6H_5)_3P \cdot BF_3$.⁹ The ¹⁹F NMR spectrum (in CH_2Cl_2) consists of a quartet, from coupling to the ¹¹B nucleus ($I = 3/2$), at δ 14.3 ppm to high field of $CFCl_3$ (δ 0) which is similar to shifts for other BF_3 adducts [e.g., $(C_6H_5)_3P \cdot BF_3$ at 14.0 ppm]. Unfortunately no satisfactory ¹¹B NMR spectrum could be obtained due to the limited solubility of the compound. On heating to 170–200° under vacuum $[(C_6H_5)_3P]_2Pt \cdot 2BF_3$ decomposes, yielding platinum metal and $(C_6H_5)_3P \cdot BF_3$. A similar decomposition product, $(C_6H_5)_3P \cdot BCl_3$, arises when $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ is heated between 68 and 190°, but in this reaction benzene was also formed in contrast to the above reaction where no volatile hydrocarbons were detected.

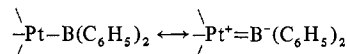
The relative Lewis acidities of the boron halides, namely, $BCl_3 > BF_3$, are demonstrated by the quantitative displacement of the boron trifluoride when the adduct is treated with 2 mol of boron trichloride



The colorless reaction product rapidly evolves HCl in the air; it is unstable in CH_2Cl_2 solution, but the ir spectrum of the solid does not clarify whether it is the adduct formulated as above or a mixture of $[(C_6H_5)_3P]Pt \cdot BCl_3$ and $(C_6H_5)_3P \cdot BCl_3$. Previous workers have also experienced difficulties in characterizing $[(C_6H_5)_3P]Pt \cdot BCl_3$.⁵ Only trace quantities of $(C_6H_5)_3P \cdot BCl_3$ sublime when the product is heated up to 200° which argues against large amounts of $(C_6H_5)_3P \cdot BCl_3$ being present initially. We were not successful in attempts to prepare

$[(C_6H_5)_3P]_2Pt \cdot 2BCl_3$ from $[(C_6H_5)_3P]_2Pt(C_2H_4)$ by the action of BCl_3 with or without a solvent (benzene or toluene).

With the aryl and alkyl boron halides the nature of the products (Table I) varied according to the reagents. In the reactions with $(C_6H_5)_2BX$ ($X = Cl, Br$) oxidative addition of the B–X bond occurs at the Pt(0) center and the 1:1 products are best formulated as four-coordinate derivatives of Pt(II) as either $[(C_6H_5)_3P]_2Pt[B(C_6H_5)_2](X)$ ($X = Cl, Br$) or $\{[(C_6H_5)_3P]_2Pt[B(C_6H_5)_2]\}^+Cl^-$. Thus both types of compounds show bands in their ir spectra associated with Pt–P vibrations (470–420 cm^{-1}), but only with the neutral compounds can Pt–halogen bands be detected (see Experimental Section), and no derivative shows any absorptions from B–halogen bonds. Limited solubility of the adducts with triphenylphosphine prevented any NMR spectra from being obtained, but with the more soluble $\{[(C_6H_5)_3P]_2Pt[B(C_6H_5)_2]\}^+Cl^-$ the ¹H NMR (in CH_2Cl_2) showed signals from the aromatic and aliphatic protons in the ratio 22:30 (cf. 25:30 expected). The ¹¹B NMR spectrum shows a broad signal centered at -44.5 ± 1 ppm ($BF_3 \cdot Et_2O = 0$) which is shifted 23.5 ppm to high field of $(C_6H_5)_2BCl$ (δ –68.0 ppm) and is consistent with the presence of a three-coordinate boron atom. The $B(C_6H_5)_2$ group in the cation may be regarded as a pseudocarbene

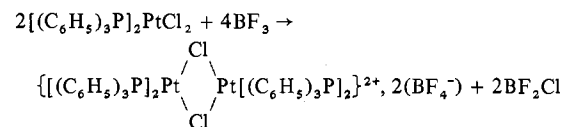


and it is noteworthy that similar high-field shifts of 15–25 ppm have been observed in compounds such as $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Co(BX_2)_2$ derived from the boron trihalides.¹⁰

The reaction between $[(C_6H_5)_3P]_4Pt$ and $(CH_3)_2BBR$ follows a slightly different path and a 1:2 stoichiometry is observed, but the extreme air sensitivity of the product prevented reliable spectra from being obtained. Based upon the above formulations a six-coordinate Pt(IV) derivative $[(C_6H_5)_3P]_2Pt[B(CH_3)_2]_2(Br)_2$ is the probable product.

An interesting reaction occurs when the above compounds are dissolved in benzene in that a turbidity develops on standing and the appearance of an absorption at 2020 cm^{-1} from a Pt–H bond (shown from the reaction using deuteriobenzene) in the hydride compound $[(C_6H_5)_3P]_2Pt(H)(X)$ ($X = Cl$ or Br) is observed. The same product, $X = Br$, is obtained when $[(C_6H_5)_3P]_2Pt[B(CH_3)_2]_2(Br)_2$ is treated with bromine in cyclohexane. We assume that HBr is first generated, and this subsequently attacks a further molecule of the adduct, liberating $(CH_3)_2BBR$ and forming the hydride. The action of a Br_2-CCl_4 mixture upon $[(C_6H_5)_3P]_2Pt[B(C_6H_5)_2](Cl)$ liberates $(C_6H_5)_2BCl$, which may be detected from its ¹¹B NMR spectrum (δ –68.0 ppm), and the resulting solid is a 1:1 mixture of $[(C_6H_5)_3P]_2PtBr_2$ and $[(C_6H_5)_3P]_2PtBr_4$.

We have also investigated briefly the action of $(CH_3)_2BBR$ on some platinum(II) species in view of other reports that boron trihalides react to yield ionic products,^{11,12} e.g.



When $[(C_6H_5)_3P]_2PtCl_2$ is treated with $(CH_3)_2BBR$ in benzene, an orange 1:1 adduct, which is best formulated as $[(C_6H_5)_3P]_2Pt[B(CH_3)_2](Br)_3$, is precipitated. The ir spectrum does not contain any bands near 800 cm^{-1} from the B–Br group but does contain absorptions near 1120 and 1190 cm^{-1} arising from $B(CH_3)_2$ groups, and the ¹¹B NMR spectrum shows a broad signal centered at δ –60 \pm 1 ppm, a shift typical of a three-coordinate boron atom. In this case we therefore prefer to formulate the product as a six-coordinate

Pt(IV) derivative rather than a type of four-coordinate Pt(II) species containing a $(\text{CH}_3)_2\text{BBr}$ molecule coordinated to the metal atom as, e.g., $2\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}[(\text{CH}_3)_2\text{BBr}](\text{Br})^+\}_2(\text{Br}^-)$.

Experimental Section

The NMR spectra were taken using Varian HA 100 and Varian A-60 instruments, and the ir spectra were run on a Perkin-Elmer 457 or 325 spectrophotometer. All solvents were dried, usually with LiAlH_4 , except the halogenated hydrocarbons, and distilled under nitrogen before use. Microanalyses were carried out by the microanalytical section in the University of Sheffield or the University of Marburg (Lahn). The highly hydrolytic compounds $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot 2(\text{CH}_3)_2\text{BBr}$ and $[(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2\text{P}]_3\text{Pt}\cdot(\text{C}_6\text{H}_5)_2\text{BCl}$ gave persistently high values for C and H probably due to handling in normal atmosphere, while samples for B and halogen are satisfactory as a result of working under dry N_2 . The compounds $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pt}$,¹³ $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot\text{C}_2\text{H}_4$,¹⁴ $[(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\text{P}]_4\text{Pt}$,¹⁵ $(\text{C}_6\text{H}_5)_2\text{BCl}$,¹⁶ $(\text{C}_6\text{H}_5)_2\text{BBr}$,¹⁶ and $(\text{CH}_3)_2\text{BBr}$ ¹⁶ were all prepared by established methods. Boron trifluoride (99.5%) was obtained from Matheson, purified as described elsewhere,¹⁷ and characterized from its ir spectrum.¹⁸ Chemical shift values in the NMR data are quoted relative to TMS (^1H) and $\text{BF}_3\cdot(\text{C}_2\text{H}_5)_2\text{O}$ (^{11}B) as standards.

Reaction of Tetrakis(triphenylphosphine)platinum(0) with Boron Trifluoride. Tetrakis(triphenylphosphine)platinum(0) (2.317 g, 1.86 mmol) was dissolved in toluene (50 ml) in a 100-ml flask which contained a magnetic follower. After attachment of the flask to the vacuum line and cooling of the system to -196° , boron trifluoride (0.126 g, 1.86 mmol) was distilled into the flask which was then allowed to warm to 0° with stirring. After 45 min the vapor pressure in the flask was measured, and, following six further additions in the same way, the plot of the vapor pressure against the number of moles of gas added showed a sharp rise after the addition of 4 mol, indicating that reaction had ceased when a ratio of $(\text{C}_6\text{H}_5)_3\text{P}_4\text{Pt}:\text{BF}_3 = 1:4$ had been attained. A white solid was precipitated from solution on each addition up to 4 mol, and after filtering and drying of the compound, the ir spectrum (Nujol mull) showed bands at $1100\text{--}1000\text{ cm}^{-1}$ (coordinated BF_3) and $750\text{--}690$ and $550\text{--}500\text{ cm}^{-1}$ (platinum-phosphine group). The analysis is consistent with the view that the solid is a mixture of 1 mol of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot 2\text{BF}_3$ and 2 mol of $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BF}_3$. Anal. Calcd for the mixture, $\text{C}_{72}\text{H}_{60}\text{B}_4\text{F}_{12}\text{P}_4\text{Pt}$: C, 57.06; H, 3.96. Found: C, 58.4; H, 4.29. Attempts to separate the two solids by fractional crystallization using benzene or toluene proved unsuccessful.

Reaction of Bis(triphenylphosphine)platinum(0)-Ethylene with Boron Trifluoride. The reaction was carried out in a similar manner to that described above. The boron trifluoride (0.0536 g, 0.79 mmol) was added stepwise to the bis(triphenylphosphine)platinum(0)-ethylene (0.5904 g, 0.79 mmol), and the tensimetric titration showed the uptake of 2.0 mol of the former. The ethylene liberated (18.2 ml, 0.81 mmol) was separated from the toluene by distillation in vacuo. After removal of all the solvent, the residual yellow solid was analyzed. Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{B}_2\text{F}_6\text{P}_2\text{Pt}$: C, 50.55; H, 3.54. Found: C, 50.88; H, 3.64. The molecular weight was determined in dichloromethane by osmometry as 871 (calcd 857). Infrared spectrum (Nujol mull, cm^{-1}): 1480 (m), 1325 (w), 1096 (m), 1065 (s), 1030 (sh), 1010 (sh), 995 (w), 845 (sh), 840 (m), 835 (sh), 750 (sh), 730 (m), 720 (sh), 700 (m), 555 (m), 515 (m), 495 (m).

Reaction of Bis(triphenylphosphine)platinum-Bis(boron trifluoride) with Boron Trichloride. The complex $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot 2\text{BF}_3$ (0.2468 g, 0.29 mmol) was placed in a flask which was attached to the vacuum line. Boron trichloride (0.0678 g, 0.58 mmol) was distilled onto the solid and the mixture was left at room temperature for 1 hr. After this time the volatile material was removed from the flask and identified as boron trifluoride (0.0384 g, 0.57 mmol) from its infrared spectrum. The pale yellow solid remaining in the flask fumed vigorously in the air, liberating hydrogen chloride. Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{B}_2\text{Cl}_6\text{P}_2\text{Pt}$: C, 45.3; H, 3.17. Found: C, 44.6; H, 3.29. The chlorine analysis on this material gave persistently low results, presumably due to partial hydrolysis in handling.

Reaction of Tetrakis(triphenylphosphine)platinum(0) with Diphenylboron Halides. Tetrakis(triphenylphosphine)platinum(0) (1.25 g, 1 mmol) was dissolved in 60 ml of cyclohexane at 70°C and $(\text{C}_6\text{H}_5)_2\text{BCl}$ (0.2 ml, 1.1 mmol) was added to the solution. No visible reaction occurred, but after 2 days at ambient temperature a fluffy

cream-colored product (780–800 mg) was collected, washed with cyclohexane, and dried in vacuo (1 Torr); mp 244°C (turning brown at 156°C). Anal. Calcd for $\text{C}_{48}\text{H}_{40}\text{BClP}_2\text{Pt}$: C, 62.65; H, 4.38; B, 1.17; Cl, 3.85; P, 6.73. Found: C, 61.02; H, 4.36; B, 0.9; Cl, 3.52; P, 6.73. Selected ir bands: $\nu(\text{Pt-P})$ 458, 432 cm^{-1} ; $\nu(\text{Pt-Cl})$ 326 cm^{-1} .

Reaction of Tetrakis(triphenylphosphine)platinum(0) with Dimethylboron Bromide. A suspension of tetrakis(triphenylphosphine)platinum(0) (1.8 g, 1.5 mmol) in 20 ml of pentane was treated with $(\text{CH}_3)_2\text{BBr}$ (1.8 g, 15 mmol) with strong agitation in the absence of light. The color of the reaction mixture turned to a fluffy white. Excess $(\text{CH}_3)_2\text{BBr}$ and solvent were removed after several hours in vacuo, and the solid was extracted with 50 ml of benzene. The highly hygroscopic product was precipitated by the addition of pentane (yield 500 mg, 29%; mp $\sim 160^\circ\text{C}$ dec). Anal. Calcd for $\text{C}_{40}\text{H}_{42}\text{B}_2\text{Br}_2\text{P}_2\text{Pt}$: C, 49.98; H, 4.40; B, 2.25; Br, 16.63. Found: C, 54.4; H, 4.46; B, 2.0; Br, 18.5.

Reaction of Tetrakis(phenyldiethylphosphine)platinum(0) with Diphenylboron Chloride. $[(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2\text{P}]_4\text{Pt}$ (0.7 g, 0.8 mmol) was dissolved in 95 ml of pentane. A solution of 0.15 ml of $(\text{C}_6\text{H}_5)_2\text{BCl}$ in 5 ml of pentane was added with stirring. A colorless solution of $(\text{C}_6\text{H}_5)_2\text{BCl}$ was formed from which an oily precipitate separated rapidly. All volatile components were removed in vacuo during several hours leaving a waxy product, which at -40°C turned crystalline and became soft again at ambient temperature. Anal. Calcd for $\text{C}_{42}\text{H}_{55}\text{BClP}_4\text{Pt}$: C, 56.42; H, 6.20; B, 1.21; Cl, 3.96. Found: C, 61.5; H, 6.33; B, 0.9; Cl, 3.88. The NMR spectra show the following: $\delta(^{11}\text{B})$, -44.5 ± 0.5 ppm in benzene; $\delta(^1\text{H})$, multiplets centered at -7.4 , -1.8 , and 1.0 ppm in CH_2Cl_2 solution; ratio $\text{H}_{\text{arom}}:\text{H}_{\text{aliph}}$, calcd 25:30, found 22:30.

Reaction of cis-Bis(triphenylphosphine)platinum(II) Chloride with Dimethylboron Bromide. A 700-mg (0.9-mmol) sample of the platinum compound, 30 ml of benzene, and 2 ml of $(\text{CH}_3)_2\text{BBr}$ were kept under reflux for 20 min. The solid turned orange. After filtration the product was precipitated from the solution with some pentane yielding an orange microcrystalline material of mp $225\text{--}230^\circ\text{C}$; yield 250 mg ($\sim 28\%$). Anal. Calcd for $\text{C}_{38}\text{H}_{36}\text{BBBr}_2\text{P}_2\text{Pt}$: C, 45.63; H, 3.63; B, 1.08; Br, 23.96. Found: C, 44.76; H, 3.41; B, 1.0; Br, 23.9. NMR: $\delta(^{11}\text{B})$, -60.0 ppm (broad). Selected ir bands: 3100, 2980, 2920, 1260, 1190, 1120, 722 cm^{-1} .

Reaction of Bis(triphenylphosphine)diphenylboronplatinum Chloride with Bromine. A suspension of 230 mg (0.25 mmol) of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}[\text{B}(\text{C}_6\text{H}_5)_2]$ was treated dropwise with a dilute CCl_4 solution of bromine with stirring until no more Br_2 was consumed, and the solution turned reddish brown. The solid formed decomposed at $\sim 150^\circ\text{C}$ and the solution exhibited a ^{11}B NMR signal at -68 ppm $[(\text{C}_6\text{H}_5)_2\text{BCl}]$. Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{Br}_3\text{P}_2\text{Pt}$: Br, 25.2. Found: Br, 24.4.

Registry No. $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot 2\text{BF}_3$, 57473-94-6; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}\cdot 2\text{BCl}_3$, 57473-95-7; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}[\text{B}(\text{C}_6\text{H}_5)_2]\text{Br}$, 18024-77-6; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}[\text{B}(\text{C}_6\text{H}_5)_2]\text{Cl}$, 18024-76-5; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}[\text{B}(\text{C}_6\text{H}_5)_2]_2(\text{Br})_2$, 57474-00-7; $[(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\text{P}]_3\text{Pt}[\text{B}(\text{C}_6\text{H}_5)_2]^+\text{Cl}^-$, 57473-96-8; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}[\text{B}(\text{CH}_3)_2](\text{Br})_3$, 57474-01-8; $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pt}$, 14221-02-4; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}(\text{C}_2\text{H}_4)$, 12120-15-9; $[(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\text{P}]_4\text{Pt}$, 57474-02-9; *cis*- $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}_2$, 15604-36-1; BF_3 , 7637-07-2; BCl_3 , 10294-34-5; $(\text{C}_6\text{H}_5)_2\text{BBr}$, 5123-17-1; $(\text{C}_6\text{H}_5)_2\text{BCl}$, 3677-81-4; $(\text{CH}_3)_2\text{BBr}$, 5158-50-9.

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