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Reactions of Tris(triphenylphosphine)platinum(0). II. Preparation and Properties of Boron Trichloride and Aluminum Trimethyl Adducts of Platinum(0)[1a]

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Treatment of $[(C_6H_5)_3P]_3Pt$ with BCl_3 affords $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ whereas $[(C_6H_5)_3P]_4Pt$ affords $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ and $(C_6H_5)_3P \cdot BCl_3$. Reaction of $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ with pyridine (py) yields py $\cdot BCl_3$ while pyrolysis of the adduct affords benzene. Treatment of $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ with BCl_3 yields $[(C_6H_5)_3P]_2Pt \cdot BCl_3$ whereas reaction with $[Al(CH_3)_3]_2$ affords a paramagnetic Pt species and mixed fluoromethylsilanes. Reaction of $[(C_6H_5)_3P]_3Pt$ with $[Al(CH_3)_3]_2$ results in the formation of $[(C_6H_5)_3P]_2Pt \cdot 2Al(CH_3)_3$ which readily decomposes in solution to yield two weakly paramagnetic species. One radical is associated with Pt and the other with Al.

Introduction

During the course of investigating the reaction between $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ and BCl_3 (Lewis acid exchange), it became necessary to prepare phosphine-platinum(0) complexes of BCl_3 directly. The preparation and characterization of these species are herein described. Concerning the mode of bonding between Pt and the Lewis acids, with the relatively weak Lewis acid SiF_4, one may invoke σ and π bonding between Pt and Si whereas the strong Lewis acid BCl_3 can only interact with Pt *via* σ bonds.[2] Treatment of $[(C_6H_5)_3P]_3Pt$ with $Al(CH_3)_3$ was carried out as a logical extension of the reported Lewis acid–base chemistry because $[Al(CH_3)_3]_2$ is a strong Lewis acid which should be able to function as both a σ and π acid.

Results and Discussion

Preparation and Characterization of $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$.—Treatment of $[(C_6H_5)_3P]_3Pt$ with gaseous BCl_3 affords a pale yellow powder, $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ (I), eq 1. From the infrared spectrum of I,
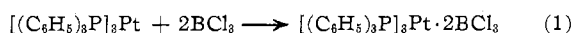
$$[(C_6H_5)_3P]_3Pt + 2BCl_3 \longrightarrow [(C_6H_5)_3P]_3Pt \cdot 2BCl_3 \quad (1)$$

Figure 1 and Table I, some important conclusions can be drawn. The absence of absorptions from 400 to 250 cm^{-1} indicates that no Pt–Cl bonds are present in I.[3] This fact coupled with the absence of bands which could be assigned to three-coordinate B–Cl stretching modes (between 1000 and 800 cm^{-1})[4] rules out the possibility that the structure of I incorporates PtCl and PtBCl₂ bonds which would be expected as a consequence of oxidative addition. From the infrared data one cannot rule out the possibility that I contains salts

of four-coordinate boron, *e.g.*, BCl_4^-, because four-coordinate B–Cl stretching frequencies generally occur in the region between 800 and 650 cm^{-1}. The asymmetric B–Cl stretching vibration in BCl_4^- occurs at 692 cm^{-1} [5] while the asymmetric stretch for $(CH_3)_3N \cdot BCl_3$ occurs at 783 and 755 cm^{-1} for ^{10}B and ^{11}B isotopes.[6] Unfortunately this region of the spectrum of I is masked by phosphine ligand vibrations. However, this region is more complex than normally observed for only ligand vibrations indicating that some of these bands may be due to four-coordinate B–Cl stretching modes. Finally comparison of the infrared spectrum of I with an authentic sample of $(C_6H_5)_3P \cdot BCl_3$ indicates that none of the latter is present. Triphenylphosphine–boron trichloride adduct has its "X"-sensitive vibration[7] at 1100 cm^{-1} while I has the corresponding vibration occurring at slightly lower energy, 1092 cm^{-1}.

Solution Properties.—Attempts to dissolve I in common organic solvents result in decomposition as evidenced by an immediate color change and the odor of hydrogen chloride could often be detected when the mixtures were detached from the vacuum line. This instability toward dissolution severely limits spectral characterization; therefore the characterization of I relies largely on its chemical properties.

Pyrolysis of I.—When I was heated to 190°, *in vacuo*, for 2 days, BCl_3 and benzene were evolved and $(C_6H_5)_3P \cdot BCl_3$ was sublimed away from the hot zone. The BCl_3–benzene mixture was identified by its gas-phase infrared spectrum while $(C_6H_5)_3P \cdot BCl_3$ was identified by comparison of its infrared spectrum and melting point to those of an authentic sample. The degradation was monitored carefully by increasing the pyrolysis temperature gradually. At 68° a gas was evolved although it was not isolated or identified. Considering the two possibilities BCl_3 and benzene, it seems likely that this gas was BCl_3 because benzene arises from the degradation of complexed $P(C_6H_5)_3$ and has been

(1) (a) Presented at the Second Central Regional Meeting of the American Chemical Society, June 4–6, 1970, Columbus, Ohio 43210. (b) Partial fulfillment for the requirements of the Doctor of Philosophy Degree, The Ohio State University, 1971.

(2) T. R. Durkin and E. P. Schram, *Inorg. Chem.*, **11**, 1048 (1972).

(3) D. M. Adams, "Metal-Ligand and Related Vibrations: A Critical Survey of the Infrared and Raman Spectra of Metallic and Organometallic Compounds," St. Martin's Press, New York, N. Y., 1968.

(4) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 1, Methuen, London, 1967, p 293.

(5) T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 2339 (1960).

(6) R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964).

(7) R. D. Kross and V. A. Fassel, *J. Amer. Chem. Soc.*, **77**, 5858 (1955).
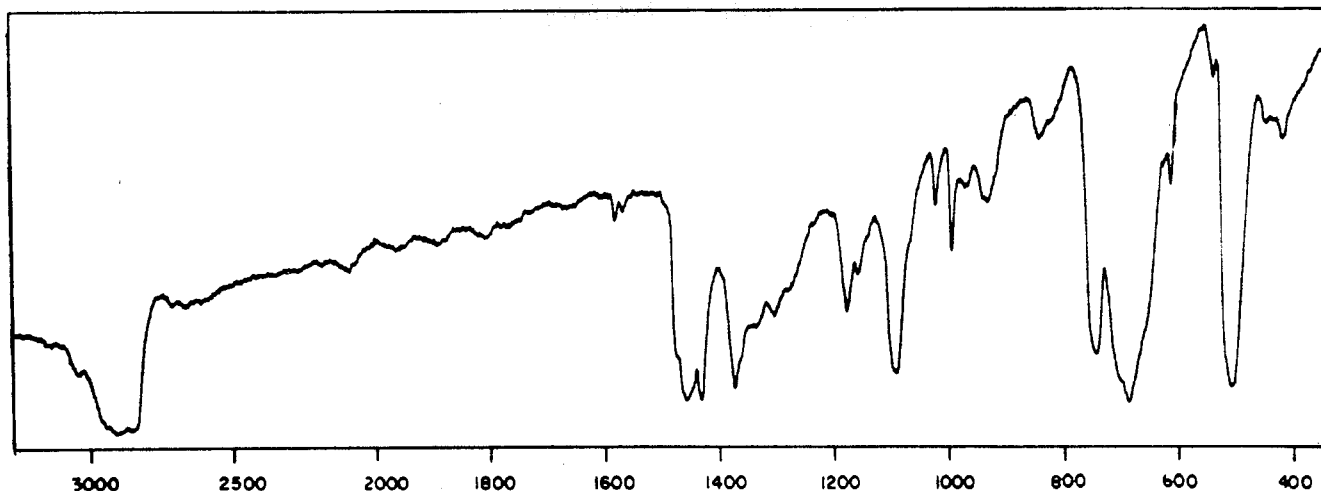
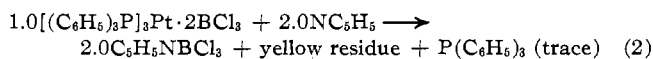Figure 1.—Infrared spectrum of $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ (Nujol mull).

TABLE I

INFRARED FREQUENCIES (± 5 CM^{-1}) FOR $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$

3050 vw	1178 m	935 w	614 w
1582 w	1156 m, sh	840 w	539 vw
1570 vw	1092 s	750 s, sh	508 vs
	("X" sensitive)	740 s	450 vw
1474 m	1024 w	704 s, sh	420 vw
1430 m	997 w	687 vs, b	
1304 vw	970 vw		

demonstrated to occur at temperatures above 155°. When the temperature of I was increased to 113°, white crystals of $(C_6H_5)_3PBCl_3$ began to sublime. This is the same temperature at which an authentic sample of $(C_6H_5)_3P \cdot BCl_3$ sublimes, therefore the adduct probably was formed at a lower temperature and then sublimed when the temperature was increased to 113°. Finally, after the temperature was raised to 190° additional volatile material was evolved and a red residue formed. This is probably caused by the degradation of $P(C_6H_5)_3$ ligands to form benzene similar to that observed in the pyrolysis of $[(C_6H_5)_3P]_3Pt$.[2]

Comparison of the pyrolyses of $[(C_6H_5)_3P]_3Pt$ and I reveals some similarities.[2] In both cases $P(C_6H_5)_3$ is liberated although it is in the form of the boron trihalide adduct in the latter case. More important, however, is the fact that both reactions generate benzene indicating degradation of $P(C_6H_5)_3$. The temperature at which this occurs for I is lower than for $[(C_6H_5)_3P]_3Pt$ which can be interpreted as the result of the formation of some $[(C_6H_5)_3P]_2Pt$ at a lower temperature.

Reaction of I with Pyridine.—Treatment of I with excess pyridine, *in vacuo*, afforded $C_5H_5N \cdot BCl_3$. The amount of pyridine used was determined quantitatively by pumping off the excess pyridine. These results are summarized by eq 2. Investigation of the yellow

$$1.0[(C_6H_5)_3P]_3Pt \cdot 2BCl_3 + 2.0NC_5H_5 \longrightarrow$$
$$2.0C_5H_5NBCl_3 + \text{yellow residue} + P(C_6H_5)_3 \text{ (trace)} \quad (2)$$

residue by X-ray powder pattern data revealed that this material was not pure $[(C_6H_5)_3P]_3Pt$ which would be expected to result from a simple exchange reaction. The infrared spectrum of the residue had peaks which could not be assigned to $[(C_6H_5)_3P]_3Pt$, the most significant of which occurred as 2200 cm^{-1} which may be assigned to ν(Pt–H). A likely source of the Pt–H moiety is ortho proton exchange.[2] Because pyridine

is expected to be a stronger Lewis base than the zero-valent platinum complex, it should displace the metal to form $py \cdot BCl_3$ indicating I is a Lewis salt. Comparison of the difference of the present base exchange to the reaction of $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ with NH_3[2] can readily be explained if one recalls a fundamental difference between SiF_4 and BCl_3. While SiF_4 is diacidic using its empty d orbitals, BCl_3 can accept only one electron pair with its vacant p orbital. Therefore the interaction of BCl_3 with $[(C_6H_5)_3P]_3Pt$ is only through σ bonds and the interaction of SiF_4 can have substantial π bonding. The exchange of BCl_3 between $[(C_6H_5)_3P]_3$-Pt and py affords a more realistic picture of the relative σ base strength of $[(C_6H_5)_3P]_3Pt$ compared to nitrogen bases. The mole ratio for the uptake of pyridine to I is 2.01:1.00. If it is assumed that all of the pyridine initially reacts with BCl_3, the proposed stoichiometry for I is confirmed. Also the fact that the boron-containing species were recovered as $C_5H_5N \cdot BCl_3$ indicates that all of the BCl_3 remains essentially intact throughout the reaction; *i.e.*, BCl_3 does not oxidatively add to Pt affording a Pt–BCl_2 species.

Reaction of Tetrakis(triphenylphosphine)platinum(0) with Boron Trichloride.—When $[(C_6H_5)_3P]_4Pt$ was exposed to BCl_3 vapor for 40 hr, the ratio of BCl_3 absorbed to Pt complex present was 3:1. The pale yellow material which was formed was found to be a mixture of I and $(C_6H_5)_3P \cdot BCl_3$ by its infrared spectrum. Figure 2 shows the region of the spectrum in which the "X"-sensitive bands occur. The shoulder at 1100 cm^{-1} is assigned to $(C_6H_5)_3PBCl_3$ while the peak at 1095 cm^{-1} is assigned to I; therefore this acid–base
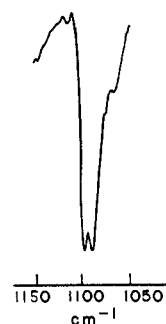
Figure 2.—Infrared spectrum in the "X"-sensitive region of $[(C_6H_5)_3P]_2Pt \cdot 2BCl_3$–$(C_6H_5)_3P \cdot BCl_3$.

reaction can be described by eq 3. Formation of $(C_6$-$H_5)_3P \cdot BCl_3$ indicates that one of the $P(C_6H_5)_3$ ligands is

$$[(C_6H_5)_3P]_4Pt + 3BCl_3 \longrightarrow$$
$$(C_6H_5)_3P \cdot BCl_3 + [(C_6H_5)_3P]_3Pt \cdot 2BCl_3 \quad (3)$$

labile even in the solid state. This parallels the observed behavior of $[(C_6H_5)_3P]_4Pt$ in benzene solution.[8] The solid-state dissociation probably is a consequence of the relative Lewis base strength of $[(C_6H_5)_3P]_4Pt$ and $[(C_6H_5)_3P]_3Pt$.

Tensimetric Titration of $[(C_6H_5)_3P]_3Pt$ with BCl_3 in Benzene.—The instability of I in solution prompted further investigation of the interaction of $[(C_6H_5)_3P]_3Pt$ with BCl_3 in a solvent system. At a 1:1 mole ratio of platinum complex to the boron halide there was still some $[(C_6H_5)_3P]_3Pt$ in solution as evidenced by its bright yellow color. When the mole ratio reached 1:2, all of the starting complex had reacted because the solution was colorless and a light tan precipitate had formed. It can be concluded that the products at this stage of the titration resulted from 1 mol of platinum complex reacting with 2 mol of BCl_3. There are three most probable ways in which adduct formation may occur: formation of $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$; $(C_6H_5)_3P \cdot BCl_3$ and $[(C_6H_5)_3P]_2Pt \cdot BCl_3$; or 2 $(C_6H_5)_3P \cdot BCl_3$ and "$(C_6H_5)_3$-PPt." In an independent experiment in which exactly 2 mol of BCl_3 was added per mole of $[(C_6H_5)_3P]_3Pt$, $(C_6H_5)_3P \cdot BCl_3$ could be detected in the reaction mixture by infrared analysis; thus the formation of $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ is ruled out. Of the two remaining reaction schemes, the one in which only 1 mol of $(C_6H_5)_3P \cdot BCl_3$ is formed is more likely because a complex characterized as $\{[(C_6H_5)_3P]Pt\}_x$ has been reported to be tetrameric and highly colored[9] while this reaction solution was colorless. As more BCl_3 was added, the solution became deep red until a 1:3 mole ratio was reached at which point the absorption of the acid ceased. The final reaction mixture consisted of a deep red solution and a light tan precipitate. The precipitate is probably $(C_6H_5)_3P \cdot BCl_3$ based on the comparison of its slight solubility in benzene to that of an authentic sample.

Based on the conclusions about the nature of the 1:2 reaction stoichiometry, the 1:3 reaction ratio is interpreted to indicate formation of $(C_6H_5)_3PPt \cdot BCl_3$ and 2 $(C_6H_5)_3P \cdot BCl_3$. The possibility of formation of 2 mol of $(C_6H_5)_3P \cdot BCl_3$ and Pt metal is ruled out on the basis of lack of formation of Pt. The last possibility, formation of $[(C_6H_5)_3P]_2Pt \cdot 2BCl_3$, is considered unlikely because the reaction solution was dark red as are "bis" adducts of Pt, *i.e.*, $[(C_6H_5)_3P]_2Pt$.
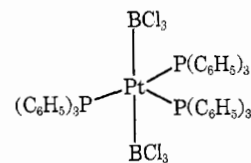
Possible Geometry for I.—All of the chemical evidence collected on I indicates it is a BCl_3 Lewis adduct. There are only two possible Lewis base species, platinum and phosphorus. Either type of bond, B–Pt or B–P, would be cleaved by the reaction with the strong Lewis base pyridine. Evidence from infrared spectra favors platinum as the base site; however, evidence derived from the fingerprint region can, at times, be very shaky. The present situation is somewhat different because careful comparisons can be made between the spectrum of $(C_6H_5)_3P \cdot BCl_3$, the I–$(C_6H_5)_3P \cdot BCl_3$ mixture, and I alone. The fact that

a known mixture (from $[(C_6H_5)_3P]_4Pt$ and 3 BCl_3) has an infrared spectrum which clearly indicates both I and $(C_6H_5)_3P \cdot BCl_3$ being present adds to the integrity of the conclusion that $(C_6H_5)_3P \cdot BCl_3$ is not present in I when formed from $[(C_6H_5)_3P]_3Pt$.

Concerning the geometry of I, the 1:2 stoichiometry can be interpreted in several ways. First, the second molecule of BCl_3 can merely reside in the crystal lattice analogous to a solvated complex. Other Lewis salts with transition metals functioning as the base have been shown to exhibit such behavior, for example, $HgCl_2$ adducts of $Fe(CO)_5$ in a 2:1 mole ratio.[10] The second mole of the mercuric halide is in the crystal lattice as shown by careful examination of the Hg–X stretching vibrations. Pyrolysis of I yields some BCl_3 at a rather low temperature while some of the acid is tenaciously held even when heated to 190°. The apparent nonequivalence of the boron halide could be interpreted as arising from one BCl_3 residing in the lattice; however, two different BCl_3 molecules in the complex can just as easily be due to the thermal stability of a 1:1 adduct compared to that of a 1:2 complex. If there were BCl_3 in the crystal lattice, the infrared spectrum of I should have absorptions near 955 and 994 cm^{-1} which are characteristic of ^{11}B–Cl and ^{10}B–Cl stretching vibrations. These bands should not be appreciably shifted in energy because of the weak interaction involved in solvation. Careful examination of the infrared spectrum of I, Figure 1, reveals that no such absorptions are present in the forementioned regions which could not be assigned to $P(C_6H_5)_3$. Therefore the possibility of one molecule of BCl_3 in the crystal lattice is considered unlikely.

Another possible mode of attachment for the second mole of BCl_3 could be *via* chloride bridges. Such a halogen-bridge structure has been suggested to explain the 1:2 stoichiometry of the BF_3 adduct $[(C_6H_5)_3P]_2Ir(CO)Cl$;[11] however, there are no known examples of chloride bridging two borons.

There is one other mode of attachment of the acids in I which does not involve the cleavage of any B–Cl bonds. Both molecules of boron trichloride are simply attached to the platinum using electron pairs donated from the metal. The X-ray structure of $[(C_6H_5)_3P]_3Pt$ has been shown that the phosphorus atoms and the platinum atom are coplanar in a trigonal-planar geometry.[12] The hybridization of the platinum orbitals in the complex has been postulated to be sp^2; therefore both the p_z and d_{z^2} metal orbitals are not involved in bonding to the ligands. Using a valence bond approach these orbitals could be hybridized to form pd hybrids which are projected above and below the plane described by the phosphorus and platinum atoms. These directionalized orbitals would have electron pairs and could easily be donated to acid sites forming the complex

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(9) R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *Chem. Commun.*, 869 (1966).

(10) D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *J. Chem. Soc. A*, 1067 (1968).

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(12) V. Albano, P. L. Bellon, and W. Scatturin, *Chem. Commun.*, 507 (1966).

This structure is consistent with the chemical data which have been obtained on I; *e.g.*, both molecules of BCl_3 would readily be displaced quantitatively with pyridine. Also the results of the pyrolysis of I are consistent with a diadduct. Assuming that the metal electrons are polarizable, there is much more electron density in the B–Pt bond after the first molecule of BCl_3 has been dissociated, affording a more stable 1:1 adduct.

Reaction of $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ (II) with Boron Trichloride.—Treatment of II[2] with excess gaseous BCl_3 at room temperature results in the generation of SiF_4. Interpretation of the infrared spectrum of the white nonvolatile residue indicates the absence of SiF bonds. In addition, this material does not contain absorptions characteristic of $(C_6H_5)_3P \cdot BCl_3$, but there are a series of absorptions from 800 to 650 cm^{-1}, some of which may be assigned to four-coordinate B–Cl.[5] The acid-displacement reaction is summarized by

$$[(C_6H_5)_3P]_2Pt \cdot SiF_4 + BCl_3 \longrightarrow$$
$$[(C_6H_5)_3P]_2Pt \cdot BCl_3 + SiF_4 \quad (4)$$
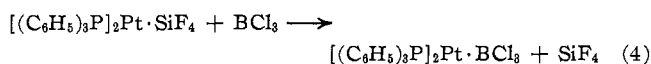
In order to demonstrate that this new Pt–BCl_3 complex (eq 4) was in fact a Lewis adduct, it was treated with pyridine. After the excess pyridine was removed, $C_5H_5N \cdot BCl_3$ was sublimed from the reaction mixture at 80° *in vacuo*, eq 5. This is analogous to the behavior of I with pyridine; therefore $[(C_6H_5)_3P]_2Pt \cdot$
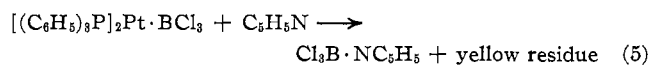
$$[(C_6H_5)_3P]_2Pt \cdot BCl_3 + C_5H_5N \longrightarrow$$
$$Cl_3B \cdot NC_5H_5 + \text{yellow residue} \quad (5)$$

BCl_3 is established as a Lewis salt. In addition it can be concluded that the exchange reaction of II with BCl_3 verifies BCl_3 is a stronger Lewis acid toward Pt than SiF_4.

Preparation and Characterization of $[(C_6H_5)_3P]_2Pt \cdot 2$-$Al(CH_3)_3$ (III).—When $[(C_6H_5)_3P]_3Pt$ is exposed to excess aluminum trimethyl, $[Al(CH_3)_3]_2$, the color of the platinum complex slowly changes from bright yellow to pale orange. The excess $[Al(CH_3)_3]_2$ was removed under reduced pressure and the mole ratio of platinum complex to $Al(CH_3)_3$ was determined to be 1.00:3.05. The pale orange material, III, is unstable to hydrolysis and/or oxidation as evidenced by its fuming upon exposure to air; it is also thermally unstable as evidenced by the fact that heating to 60°, *in vacuo*, affords a deep red solid. A similar red color also develops when the solid is stored at 25° for several days. Purification of III was attempted by fractional sublimation and mixed-solvent recrystallizations (benzene–alkane mixtures). However, due to its instability, these attempts failed as evidenced by a color change to deep red.

Infrared Data.—The infrared spectrum of III indicates the presence of $(C_6H_5)_3P \cdot Al(CH_3)_3$, as determined by the comparison of the ir spectrum of III to that of $(C_6H_5)_3P \cdot Al(CH_3)_3$, *i.e.*, peaks at 1096, 695, and 510 cm^{-1}. Other information which may be extracted from interpretation of these ir spectral data are very sparse; *e.g.*, Pt–C stretching vibrations (which would occur *via* oxidative addition) occur at *ca.* 500 cm^{-1};[13] this region is masked by $P(C_6H_5)_3$ vibrations. The coordination number about the aluminum atom cannot be determined by observing the Al–C stretch-

ing modes as is the case in the BCl_3 and SiF_4 adducts.[2] The assignment of these absorptions is further complicated by the presence of a four-coordinate aluminum species in the reaction mixture, $(C_6H_5)_3P \cdot Al(CH_3)_3$. Also, the region in which Al–C stretches occur, 775–550 cm^{-1}, is again masked by phosphine vibrations.

Stoichiometry.—Because covalent aluminum species may afford both 1:1 and 1:2 adducts with a Lewis base,[14] the stoichiometry of the simple adduct with triphenylphosphine was determined. Aluminum trimethyl was allowed to react with $P(C_6H_5)_3$ in the absence of a solvent and in a benzene solution. The stoichiometry was 1:1 regardless of the method of preparation as determined by measuring the mass increase of the nonvolatile adduct after exposure to excess $[Al(CH_3)_3]_2$. The stoichiometry was also verified by the simple adduct's ^1H nmr spectrum which consisted of a multiplet centered at τ 2.62 and a singlet at τ 10.64 with relative intensities of 15 to 9. These peaks are assigned to the aromatic and methyl protons, respectively.

With the stoichiometry of $(C_6H_5)_3P \cdot Al(CH_3)_3$ established, the reaction $[(C_6H_5)_3P]_3Pt$ with $[Al(CH_3)_3]_2$ may be interpreted in terms of formation of either $(C_6H_5)_3P \cdot Al(CH_3)_3$ and $[(C_6H_5)_3P]_2Pt \cdot 2Al(CH_3)_3$ or 2 $(C_6H_5)_3P \cdot Al(CH_3)_3$ and $(C_6H_5)_3PPt \cdot Al(CH_3)_3$ or finally 3 $(C_6H_5)_3P \cdot Al(CH_3)_3$ and Pt. Because Pt metal was not observed in the reaction mixture, the last possibility is unlikely. Of the other two possibilities, formation of $[(C_6H_5)_3P]_2Pt \cdot 2Al(CH_3)_3$ is favored because treatment of the product with benzene affords a pale yellow solution in contrast to bis adducts of Pt which afford *deep* red solutions.[9] Concerning the reaction between $[(C_6H_5)_3P]_3Pt$ and $[Al(CH_3)_3]_2$, when the product solution is heated for 6 hr at 100°, it develops a deep red color and exhibits an esr signal, $g = 1.996$ ($W_{1/2} = 15$ G). Prolonged heating of the red solution results in a second esr signal, $g = 2.014$ ($W_{1/2} = 15$ G). This latter signal is at the same field position as that observed for the pyrolysis product of $[(C_6H_5)_3P]_3Pt$. When a benzene solution containing both radicals is treated with methanol, the radical ($g = 1.996$) is discharged while the other is not affected. On the bases of these different chemical properties and the fact that one g value is greater than the spin-only value, the radical with $g = 1.996$ is considered associated with an aluminum species while the signal, $g = 2.014$, is assigned to a Pt species. In both cases the radical concentration is low; Faraday measurements indicated diamagnetic materials. When the reaction of $[(C_6H_5)_3$-$P]_3Pt$ and $[Al(CH_3)_3]_2$ is carried out in solution at 60° for 1 hr, two esr signals are observed, $g = 1.996$ and $g = 2.014$. When the solvent is removed, dark red oils result. Thus far, fractional crystallization and column chromatographic separation of these oils have failed.

Reaction of $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ (II) with Aluminum Trimethyl.—Treatment of II with excess $[Al(CH_3)_3]_2$, in the absence of a solvent at 57°, results in the formation of a dark red oil. Highly volatile materials are also generated during the reaction which were identified as mixtures of methylfluorosilanes by their infrared spectra.[15] An infrared spectrum of the nonvolatile red oil indicates the disappearance of the absorptions

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(14) J. K. Ruff and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **82**, 2141 (1960).

(15) R. L. Collins and J. R. Nielsen, *J. Chem. Phys.*, **23**, 351 (1955).

which have been assigned to SiF modes.[2] This spectrum also gives no indication of the formation of $(C_6H_5)_3P \cdot Al(CH_3)_3$. An esr spectrum of a benzene solution of the red oil consists of a singlet with $g = 1.998$. This is the same field position as that of the red solution which is formed when III is heated to 100° in benzene. Indications are therefore that these materials are identical.

Displacement of SiF_4 by $[Al(CH_3)_3]_2$ verifies the accepted order of Lewis acidity; however, in the present case heating was required in order to initiate the reaction. Unfortunately if a simple adduct of $Al(CH_3)_3$ is formed (analogous to the behavior of $[(C_6H_5)_3P]_3Pt$ with $[Al(CH_3)_3]_2$) by a simple exchange, it is thermally unstable at the reaction temperature and decomposes to afford the dark red oil.

Thermal Stability.—The thermal stabilities of $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$ (I), $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ (II), and $[(C_6H_5)_3P]_2Pt \cdot 2Al(CH_3)_3$ (III) vary greatly when the complexes are heated under vacuum; decomposition occurs at 68, 156, and 60°, respectively. On the basis of bond strengths between platinum and the acid sites, this is an unexpected order. The $Al(CH_3)_3$ adduct is expected to be more stable than the BCl_3 adduct. This conclusion is reached on the grounds of relative acid strengths along with the fact that $Al(CH_3)_3$ also can π bond to the platinum through its vacant d orbitals. Therefore some other property or properties of the adducts must be playing an important role in their thermal stabilities.

When one compares adduct formation to oxidative additions, it may be rationalized that adduct formation can be classified as "partial" oxidative addition. Therefore the stronger the acid in the adduct, the more the electrons are drawn from the base; *i.e.*, the platinum is "more oxidized." If the internal bonds in the acids (Si–F, B–Cl, and Al–C) are strong, they would not easily be cleaved to undergo an oxidative addition. On the other hand if these bonds are relatively weak, it would not take much energy to undergo oxidative addition *via* bond cleavage. The bond energies of SiF, B–Cl, and Al–C bonds are 165, 128, and 85 kcal/mol, respectively.[16,17] This is the opposite order which is observed for acid strengths. The instability of III is therefore attributed to its decomposition involving an oxidative addition type reaction instead of a simple dissociation of an adduct into its components. The decomposition of I and II occurs through dissociation as evidenced by the recovery of the acids upon heating while the decomposition of III does not afford free $[Al(CH_3)_3]_2$.

Experimental Section

Equipment and techniques have been previously discussed[2] except ^{11}B nmr spectra were recorded at 32.1 Hz while a Varian Associates E-3 spectrometer was used to obtain esr spectra with samples hermetically sealed in 3-mm i.d. quartz tubes. Reagents were obtained and purified as previously indicated.[2] In addition, boron trichloride (CP) was obtained from the Matheson Co. and fractionated into a −126° trap until the vapor pressure at 0° was 477 Torr (lit.[18] pressure 476 Torr). Pyridine (analytical reagent, ACS grade), from J. T. Baker Co., was dried over calcium hydride or barium oxide. Aluminum trimethyl, from the Ethyl Corp., was used as received.

(16) A. G. MacDiarmid, *Advan. Inorg. Chem. Radiochem.*, **3**, 207 (1961).
(17) C. T. Montimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p 117.
(18) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 282.

Tris(triphenylphosphine)platinum(0)–Bis(boron trichloride) (I). —A freshly prepared sample of $[(C_6H_5)_3P]_3Pt$ (805.2 mg, 0.821 mmol) was heated to 100° *in vacuo* for 2 hr to free the complex of any solvent or excess $P(C_6H_5)_3$. After cooling to room temperature, the complex was exposed to BCl_3 (2.481 mmol) at a pressure of *ca.* 200 Torr. The absorption of BCl_3 was monitored using a Hg manometer. After 26 hr the pressure stabilized and the excess BCl_3 was removed by condensation into a trap maintained at −196°. The mole ratio of the platinum complex to BCl_3 was 1.000:1.999. The infrared spectrum of the pale yellow solid is shown in Figure 1 and summarized in Table I. Attempted solution in benzene, toluene, acetone, tetrahydrofuran, diethyl ether, dichloromethane, *o*-dichlorobenzene, and methanol resulted in decomposition of the complex. *Anal.* Calcd for $[(C_6H_5)_3P]_3$-$Pt \cdot 2BCl_3$: C, 53.29; H, 3.70. Found: C, 53.99; H, 3.76.

Properties of I. Pyrolysis.—A sample of I (286.6 mg, 0.236 mmol) was heated *in vacuo* to 68°, at which temperature a measurable pressure was observed over the solid. At 113° a white solid sublimed away from the hot zone leaving a yellow residue. Finally after 2 days at 190° the volatile products were removed by condensation into a −196° trap from the deep red liquid. The sublimate, 47.2 mg, was identified as the $(C_6H_5)_3P \cdot BCl_3$ adduct by comparison of its infrared spectrum to that of an authentic sample. The volatile products (0.314 mmol) were identified as BCl_3 and benzene by an infrared spectrum of the mixture.[19] No attempt was made to separate the mixture. The deep red residue solidified upon cooling to room temperature. The sample weighed 146.6 mg and was amorphorus to X-rays. Upon addition of methanol to this material, the odor of hydrogen chloride could be detected.

Reaction of I with Pyridine.—Compound I (378.7 mg, 0.311 mmol) was cooled to −78° and excess pyridine (py) was condensed onto it. After 2 hr at room temperature the excess py was removed from the bright yellow solid by condensation into a −196° trap. All traces of py were removed by pumping on the yellow solid until constant weight was attained (24 hr). The weight of py absorbed was 47.3 mg (0.624 mmol). The yellow solid was heated with pumping to 80°, at which temperature white crystals sublimed. After 20 hr of heating 124.5 mg of the sublimate had been collected which was identified as the py $\cdot BCl_3$ adduct (0.633 mmol) and a trace of $(C_6H_5)_3P$ by comparison of its infrared spectrum[20] to those of authentic samples, mp (under N_2) 113° (lit.[20] mp 115°). The yellow residue, 295.5 mg, was neither pure $[(C_6H_5)_3P]_3Pt$ nor $[(C_6H_5)_3P]_4Pt$ by comparison of their X-ray powder patterns.[2] An infrared spectrum of the residue showed a weak Pt–H stretching mode at 2200 cm^{-1} and absorptions characteristic of triphenylphosphine ligands.

Synthesis of I from Tetrakis(triphenylphosphine)platinum(0). —Tetrakis(triphenylphosphine)platinum(0), 529.2 mg (0.425 mmol), was exposed to BCl_3 (2.869 mmol) at a pressure of *ca.* 170 Torr. The absorption of BCl_3 continued for 18 hr. After the absorption ceased, the excess BCl_3 (1.563 mmol) was removed by condensation into a trap maintained at −196°. The mole ratio of the platinum complex to boron trichloride was 1.00:3.073. The infrared spectrum of the pale yellow solid has absorptions characteristic of I along with those of the triphenylphosphine–boron trichloride adduct.

Tensimetric Titration of Tris(triphenylphosphine)platinum(0) with Boron Trichloride in Benzene.—A sample of $[(C_6H_5)_3P]_3Pt$ (480.7 mg, 0.490 mmol) was cooled to −78° and benzene was condensed onto it. After the solution warmed to room temperature, it was treated with increments (*ca.* 0.150 mmol) of BCl_3. As BCl_3 was added, a tan precipitate formed and the solution became a less intense yellow with no increase in the pressure above the solvent (*ca.* 30 Torr). At a Pt complex:BCl_3 mole ratio of 1.00:1.97, the solution was colorless with a tan precipitate. In proceeding from 1:2 to 1:3 reaction ratios, the solution became a very deep red with no increase in pressure while the amount of precipitate remained unchanged. Finally the first addition of BCl_3 after 1:3 caused a pressure increase with no noticeable change in the reaction mixture. The products were not further characterized because all attempts at isolation and purification resulted in decomposition with the evolution of HCl. No free Pt was observed when the deep red solution was filtered. Very finely divided Pt often cannot be observed visually; however,

(19) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970.
(20) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).

when a solution which contains Pt⁰ is filtered through a medium-porosity frit, the metal is retained on the surface of the frit.

Triphenylphosphine–Boron Trichloride Adduct.—$(C_6H_5)_3P \cdot BCl_3$ was prepared by condensing excess BCl_3 onto a toluene solution of $P(C_6H_5)_3$. The white crystalline adduct immediately precipitated. After the excess BCl_3 was removed under reduced pressure, n-hexane was added to complete the precipitation. The solid was collected by filtration, *in vacuo*, and washed with n-hexane; mp (under N_2) 220°. The adduct sublimed under high vacuum at 112°. The [11]B nmr spectrum (in CH_2Cl_3) consisted of a doublet centered at -3.8 ppm with $J_{B-P} = 131$ cps. The infrared data follow: 3025 (w), 1960 (vw), 1912 (vw), 1894 (vw), 1815 (vw), 1770 (vw), 1584 (w), 1570 (vw, sh), 1480 (m), 1434 (s), 1334 (w), 1310 (vw), 1186 (w), 1178 (vw, sh), 1160 (w), 1100 (m), 1070 (w), 1025 (w), 998 (m), 970 (vw), 850 (vw), 758 (vs), 726 (s, sh), 713 (vs), 710 (s, sh), 690 (vs), 680 (s, sh), 615 (vw), 508 (vs), 450 (w), 420 (w) cm⁻¹.

The **pyridine–boron trichloride adduct**, $C_5H_5N \cdot BCl_3$, was prepared by exposing BCl_3 to excess py as described in the literature.[20] The white solid, mp (under N_2) 115° (lit.[20] mp 115°), sublimed under high vacuum at 80°. The infrared data agree with the literature.[20]

Reaction of $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ (II) with Boron Trichloride.—A sample of II (16.0 mg, 0.056 mmol) contained in a 50-ml flask was exposed to excess BCl_3 (0.530 mmol) for 1.5 hr at 25°. Removal of the materials volatile at 25° afforded a pale yellow residue which had the following ir absorptions: 3070 (w), 1570 (vs), 1478 (m), 1432 (vs), 1310 (vw), 1179 (w), 1139 (vw), 1115 (vs, sh), 1092 (m), 1022 (w), 994 (w), 970 (vw), 935 (vw), 915 (vs), 849 (w), 839 (w, sh), 740 (s), 702 (s, sh), 694 (vs), 664 (s, sh), 611 (vw), 544 (vw), 519 (vs), 511 (s, sh), 493 (m), and 479 (vw, sh) cm⁻¹. This pale yellow solid was treated with excess pyridine (py). Removal of the excess py followed by sublimation at 80° afforded $BCl_3 \cdot py$ (*ca.* 0.06 mmol), which was characterized by ir, and a nonvolatile yellow residue. The initial volatile reaction products (from the BCl_3 reaction), which passed through a $-126°$ trap and condensed at $-196°$, proved (by ir) to consist of SiF_4, BF_3, BF_2Cl, and HCl (0.135 mmol total). Treatment of this mixture with excess $(C_6H_5)_3P$ for 18 hr at 25° afforded 0.061 mmol of a mixture of SiF_4 and HCl. Treatment of SiF_4 with BCl_3 (1:1 mole ratio) at 25° and a total pressure of 500 Torr did not result in halogen exchange.

Reaction of Tris(triphenylphosphine)platinum(0) with Aluminum Trimethyl.—Tris(triphenylphosphine)platinum(0) (751.8 mg, 0.765 mmol) was exposed to $[Al(CH_3)_3]_2$ vapors at room temperature with stirring for 6 days; during this interval the yellow crystalline solid became pale orange and a trace of noncondensable gas (<0.1 mmol) was observed. Red areas had also developed where the stirring bar had been rotating. The mixture was cooled to $-78°$ and excess $[Al(CH_3)_3]_2$ (*ca.* 0.6 ml) was added to the reaction mixture. After 6 days at room temperature the excess $[Al(CH_3)_3]_2$ was removed from the reaction mixture by condensation into a trap maintained at $-196°$. All traces of the volatile products were removed by pumping on the orange solid for 2 days. The amount of monomeric $Al(CH_3)_3$ absorbed was 0.22 ml (2.332 mmol). Infrared data follow: 3060 (w), 2320 (vw), 1960 (vw), 1890 (w), 1815 (vw), 1770 (vw), 1665 (vw), 1588 (w), 1574 (w, sh), 1560 (w, sh), 1475 (m), 1434 (s), 1331 (vw), 1310 (w), 1275 (vw), 1183 (m), 1161 (w, sh), 1145

(w, sh), 1122 (vw), 1096 (m) ("X" sensitive), 1090 (m, sh), 1075 (w, sh), 1028 (w), 1000 (w), 880 (w), 850 (vw, sh), 800 (w, sh), 744 (s, sh), 694 (vs, b), 670 (s, sh), 620 (m, sh), 510 (s, b), and 415 (w) cm⁻¹.

Reaction of $[(C_6H_5)_3P]_2Pt \cdot SiF_4$ (II) with Aluminum Trimethyl.—Compound II (195.5 mg, 0.238 mmole) was cooled to $-78°$ and treated with excess $[Al(CH_3)_3]_2$. The mixture was heated to 57°, at which temperature a red oil began to form. After 36 hr of heating, the excess $[Al(CH_3)_3]_2$ and other volatile products were removed by condensation into a trap maintained at $-196°$. A trace of noncondensable gas was observed. The volatile products were fractionated through two $-78°$ traps into a $-196°$ trap. The products passing through the $-78°$ traps were identified as a mixture of SiF_4 and methyl-substituted fluorosilanes by their infrared spectra.[15] All traces of volatile products were removed by pumping on the red oil for 18 hr. The infrared data for the residue are as follows: 3095 (w), 3080 (m, sh), 3060 (m), 3040 (m), 2930 (m), 2900 (m, sh), 2860 (w, sh), 2825 (vw, sh), 2120 (w), 1960 (w), 1890 (vw), 1820 (w), 1589 (w), 1573 (vs), 1480 (m), 1437 (m), 1340 (w), 1411 (w), 1200 (m), 1163 (vw, sh), 1098 (s) ("X sensitive"), 1070 (vw), 1037 (w, sh), 1029 (w), 1001 (m), 847 (w, sh), 747 (vs, sh), 690 (vs, b), 640 (vw), 583 (w), 538 (w, sh), 524 (s), 516 (s, sh), 506 (m, sh), and 495 (m, sh) cm⁻¹. The esr spectrum of this red oil in benzene at room temperature consists of a singlet with $g = 1.979$. The ^{1}H nmr spectrum in benzene-d_6 consists of a multiplet at τ 2.93 and a singlet at τ 10.23 with a relative intensity of 2.3:1.0, assigned to the aromatic and methyl protons, respectively.

The **triphenylphosphine–aluminum trimethyl adduct**, $(C_6H_5)_3P \cdot Al(CH_3)_3$, was prepared by two methods.

(1) Excess $[Al(CH_3)_3]_2$ was condensed at $-78°$ onto $P(C_6H_5)_3$ (1485.4 mg, 5.66 mmol). After 4 hr at room temperature the excess $[Al(CH_3)_3]_2$ was removed by condensation into a trap maintained at $-196°$. Traces of $[Al(CH_3)_3]_2$ were removed by pumping on the white solid for 18 hr. The mass had increased 409.9 mg (5.69 mmol of $Al(CH_3)_3$). The ^{1}H nmr (in CH_2Cl_2) consisted of a multiplet centered at τ 2.62 and a singlet at τ 10.64 assigned to the aromatic and methyl protons, respectively, with relative areas of 15.0:8.2 (calcd 15.0:9.0). The infrared data follow: 3060 (m), 1960 (vw), 1875 (vw), 1810 (vw), 1760 (vw), 1587 (w), 1478 (m), 1437 (s), 1310 (vw), 1205 (w, sh), 1183 (m), 1155 (vw, sh), 1120 (vw), 1098 (m), 1070 (w), 1028 (w), 998 (w), 919 (vw), 895 (vw), 744 (s, sh), 695 (vs, b), 670 (m, sh), 619 (vw, sh), 540 (vw), 510 (m, sh), 499 (m), 430 (vw) cm⁻¹.

(2) Benzene (*ca.* 7 ml) was condensed at $-78°$, *in vacuo*, onto $P(C_6H_5)_3$ (1099.4 mg, 4.196 mmol). Upon warming to room temperature a colorless solution formed. The solution was cooled to $-78°$, excess $[Al(CH_3)_3]_2$ was condensed onto it, and after 1 hr at room temperature the excess $[Al(CH_3)_3]_2$ and solvent were removed by condensation into a trap maintained at $-196°$. Traces of volatile products were removed by pumping on the white solid for 3 hr. The mass increase of the nonvolatile reaction mixture was 309.5 mg (4.28 mmol of $Al(CH_3)_3$). The white solid was identical with the product prepared by method 1.