creases the coalescence temperature, while leaving the low-temperature spectrum in the absence of exchange unaffected. Addition of small aliquots of acetone has no effect on the coalescence temperature. This behavior is identical with the effect of these solvents on the exchange of methyl environments in bridged carboxylate complexes of type I. Furthermore the palladium-oxygen bond length in π-allylpalladium acetate dimer is similar to that trans to Me_2PhP in $[Cl(Me_2PhP)Pd(OOCCH_3)]_2$ (2.11 ± 0.02 and 2.13 ± 0.02 Å, respectively).[13] As such it is probable that exchange of the nonidentical allyl groups in the nonsymmetrical conformer of π-allylpalladium acetate also occurs *via* a partially dissociative mechanism and not *via* the previously proposed inversion of the $Pd_2C_2O_4$ ring.

In the complexes $[(\pi\text{-allyl})_2Pd_2[OOC(CH_2)_nCOO]]$ (n = 7, 8), the absence of exchange on the nmr time scale of the nonidentical allyl groups of the nonsymmetrical isomer prior to intermolecular exchange of allyl groups between isomers has been taken by van Leeuwen and Praat[2] to indicate that the apparent "intramolecular exchange process occurring in the nonsymmetrical isomer of allylpalladium acetate does not occur in the corresponding azelate and sebacate complexes." We have found these complexes to be partially polymeric and/or tetrameric in solution (Table II) and to give temperature-dependent nmr spectra which are too complex to interpret mechanistically.

Acknowledgment.—The authors wish gratefully to acknowledge the contribution of crystallographic data by Professor S. C. Nyburg's group and to thank the National Research Council and the Province of Ontario for financial support of this investigation.

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Reactions of Tris(triphenylphosphine)platinum(0). I. The Preparation and Properties of Bis(triphenylphosphine)platinum(0)–Silicon Tetrafluoride[1a]

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Received August 9, 1971

Treatment of tris(triphenylphosphine)platinum(0) with silicon tetrafluoride affords the Lewis salt bis(triphenylphosphine)-platinum(0)–silicon tetrafluoride, $[(C_6H_5)_3P]_2Pt\cdot SiF_4$ (I). The reactions of compound I with I_2, HCl, and NH_3 are discussed. The pyrolysis of I is compared to that of $[(C_6H_5)_3P]_3Pt$ with both complexes affording benzene and a nonvolatile platinum species which exhibits an esr signal, g = 2.014. A new SiF_5^- salt, triphenylmethylphosphonium pentafluorosilicate, has been prepared and the chemistry of SiF_5^- salts is discussed and compared to that of I.

Introduction

The preparation and characterization of the Lewis acid–base adduct, $[(C_6H_5)_3P]_2Pt\cdot SiF_4$, is described herein while adducts with BCl_3 are reported elsewhere.[2] The isolated Lewis acid complexes of platinum may be viewed as model compounds for intermediates probably formed during the general reaction referred to as oxidative addition.

Results and Discussion

Preparation and Purification of $[(C_6H_5)_3P]_2Pt\cdot SiF_4$.—Treatment of $[(C_6H_5)_3P]_3Pt$, dissolved in benzene, with SiF_4 at room temperature affords a finely divided off-white crystalline precipitate, $[(C_6H_5)_3P]_2Pt\cdot SiF_4$ (I). The mole ratio of platinum complex to silicon halide is 1:1 within 3 mol %. After filtration, $P(C_6H_5)_3$ can be isolated from the filtrate in *ca.* 1:1 mole ratio with the starting platinum complex. This chemical transformation is summarized by eq 1. Halpern has demonstrated that $[(C_6H_5)_3P]_3Pt$ dissociates in benzene to the reactive intermediate $\{[(C_6H_5)_3P]_2Pt\}$ and free triphenylphosphine.[3] The "bis" adduct of platinum is probably the reactive species in the reaction with SiF_4; therefore as the reaction proceeds, eq 1, the concentration of free $P(C_6H_5)_3$ increases which results in a decreased concentration of the "bis" adduct thereby decreasing the rate of formation of I. The consistency of this postulate is inferred from the data summarized in Table I.

$$[(C_6H_5)_3P]_3Pt + SiF_4 \longrightarrow [(C_6H_5)_3P]_2Pt\cdot SiF_4 + P(C_6H_5)_3 \quad (1)$$

Infrared Studies.—The infrared spectrum of I, Figure 1 and Table II, has absorptions at 875, 780, 477, and 443 cm^{-1} which are assigned to SiF vibrations. The remaining absorptions can be assigned to coordinated $P(C_6H_5)_3$ ligand vibrations. The infrared spectra of complexed $P(C_6H_5)_3$ ligands are practically invariant from 4000 to 250 cm^{-1}. The region from 4000 to 600 cm^{-1} is characteristic of monosubstituted benzene; the absorptions occurring from 600 to 250 cm^{-1} are associated with P–C modes; however, no specific bands can be assigned to P–C stretching vibrations becase they are often coupled with ring vibrations. There are several bands, called "X"-sensitive vibrations, which change with the nature of the complex. The most important of these vibrations occurs at 1100 ± 20 cm^{-1}. Kross and Fassel[4] observed that this band shifts to higher energy as the electronegativity of the

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[1] (a) Presented at the Second Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 3–5, 1970. (b) In partial fulfillment of the requirements for the Ph.D. degree, 1971.

[2] T. R. Durkin and E. P. Schram, *Inorg. Chem.*, **11**, 1054 (1972).

[3] J. P. Birk, J. Halpern, and A. L. Pickard, *ibid.*, **7**, 2672 (1968).

[4] R. D. Kross and V. A. Fassel, *J. Amer. Chem. Soc.*, **77**, 5858 (1955).

TABLE I

EFFECT OF INITIAL CONCENTRATION OF $[(C_6H_5)_3P]_3Pt$ ON RATE OF FORMATION OF I

Amt of $[(C_6H_5)_3P]_3Pt$, mmol	Amt of C_6H_6, ml	Molarity	Reaction time, hr
0.22	50	4.4×10^{-3}	1.5
1.26	50	2.5×10^{-2}	4.5
1.27	25	5.1×10^{-2}	<36

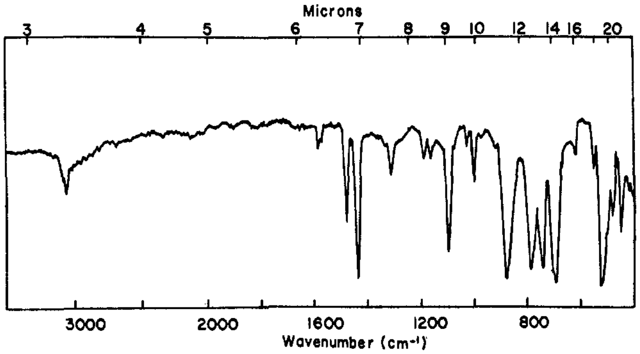


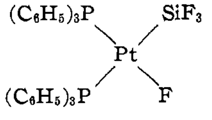
Figure 1.—Infrared spectrum of $[(C_6H_5)_3P]_2Pt \cdot SiF_4$.

TABLE II

INFRARED FREQUENCIES AND TENTATIVE ASSIGNMENTS FOR $[(C_6H_5)_3P]_2Pt \cdot SiF_4$

Freq ($\pm$5), cm^{-1}	Assignment	Freq ($\pm$5), cm^{-1}	Assignment
3050 w	ν(C–H)	915 vw	γ(C–H)
1584 w	ν(C–C)	875 s	ν_{as}(SiF, equatorial)
1570 w	ν(C–C)	780 s	ν_{as}(SiF, axial)
1480 m	ν(C–C)	740 s	γ(C–H)
1437 s	ν(C–C)	702 s, sh	
1308 w		690 vw	ϕ(C–C)
1204 vw		612 vw	
1185 w	β(C–H)	540 m	
1159 w	β(C–H)	520 vs	"X" sensitive
1094 m	"X" sensitive	494 m	"X" sensitive
1070 vw	β(C–H)	477 m	δ(SiF, axial)
1022 vw	β(C–H)	443 m	δ(SiF, equatorial)
995 w	ρ(ring)	420 vw	"X" sensitive ?
970 vw	γ(C–H)		

phosphorus increases. For example, in all triphenylalkylphosphonium salts the absorptions are above 1100 cm^{-1} while the absorption occurs at 1089 cm^{-1} in triphenylphosphine. In I the absorption at 1095 cm^{-1} is assigned to the "X"-sensitive vibration indicating a slight increase in electronegativity of the phosphorus upon complexation. More important is the fact that this absorption is a singlet indicating both $P(C_6H_5)_3$ ligands are equivalent. The absorptions at 875 and 780 cm^{-1} are in the proper region for five-coordinate SiF stretching modes. Four-coordinate SiF stretching modes are in the region of 1050–850 cm^{-1} while six-coordinate SiF stretching modes are lower to 800–700 cm^{-1}, Table III. On the basis of the infrared data, the silicon atom in I is five-coordinate; therefore a simple oxidative addition product can be ruled out as a possible structure type, e.g.



(or trans)

There are four likely geometric isomers for an MX_4Z species, C_{2v}, C_{3v}, C_{4v}, and C_s. The expected stretching vibrations associated with these different geometries are summarized in Table IV. Unfortunately only two infrared-active bands can be definitely assigned to the ν(SiF) in the spectrum of I because of masking by $P(C_6H_5)_3$ ligand vibrations. Attempts to obtain a Raman spectrum on a powdered sample or potassium bromide pellet of I were unsuccessful. The Raman spectrum of $P(C_6H_5)_3$ is also difficult to obtain owing to fluorescence;[5] finely powdered samples often yield very weak Raman spectra.[6] Therefore the geometry about the silicon atom can only be inferred from observations made by other authors on pentacoordinate silicon compounds.

TABLE III

DEPENDENCE OF ν(SiF) ON COORDINATION NUMBER OF THE SILICON

Compd	Coord no.	ν(SiF), cm^{-1} Asym	Sym
SiF_4[a]	4	1030	...
$C_6H_5SiF_3$[b]	4	862	970
SiF_5^-[c]	5	785	874
I	5	780	875
SiF_6^{2-}[d]	6	740	...
$SiF_4 \cdot 2NH_3$[e]	6	725	...

[a] E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielson, *J. Chem. Phys.*, **19**, 243 (1951). [b] H. Kriegsmann and K. H. Schowtha, *Z. Phys. Chem.*, **209**, 261 (1959). [c] H. C. Clark, K. R. Dixon, and J. G. Nicolson, *Inorg. Chem.*, **8**, 450 (1969). [d] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970. [e] R. C. Aggarwal and M. Onyszchuk, *Can. J. Chem.*, **41**, 876 (1968).

TABLE IV

STRETCHING MODES FOR FIVE-COORDINATE SILICON–FLUORINE IN VARIOUS SYMMETRIES

	Symmetry C_{2v}	C_{3v}	C_{4v}	C_s
Si–F_{ax}	$A_1{}^a + B_{1a}{}^a$	$A_1{}^a$	...	A'^a
Si–F_{eq}	$A_1{}^a + B_2{}^a$	$A_1{}^a + E^a$	$A_1{}^a + B_1{}^b + E^a$	$2A'^a + A''^a$

[a] Infrared and Raman active. [b] Raman active only.

The square-pyramidal geometries (C_{4v} and C_s) are less favored, based on the fact that nucleophilic substitutions at an asymmetric silicon atom occur with configurational inversions, which indicate the transition state has trigonal-bipyramid geometry.[7] Pentafluorosilicates and alkyl pentacoordinate silicon fluorides have trigonal-bipyramidal structures as determined by ^{19}F nmr spectra and infrared spectroscopy.[8] Finally, the 1:1 adduct of trimethylamine and silicon tetrafluoride is proposed to be trigonal bipyramidal although the substitution site (axial or equatorial) is not yet established.[9] The preferred geometry for I involves the equatorially substituted adduct, *i.e.*, C_{2v} symmetry, which appears more likely on the bases of the observations of Muetterties, *et al.*, for pentacoordinate d^0 species.[10] These studies indicate that the most electronegative ligands associated with a pentacoordinate species tend to assume the axial positions in trigonal bipyramids. This geometry also results in minimum steric interactions.

Nmr Studies.—The ^1H nmr of I, τ 0–18, consists only of a multiplet centered at τ 2.82; these absorptions

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(5) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 845 (1968).

(6) J. R. Ferraro, *Spectrochim. Acta*, **20**, 901 (1964).

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(8) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **7**, 155 (1968).

(9) I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 155 (1970).

(10) E. L. Muetterties and R. A. Schun, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

are assigned to the aromatic protons on the ligands. The ^{19}F nmr spectrum of I at room temperature in acetone consists of a singlet at ϕ 137.3 ppm with a half-height width of 0.6 cps. At the outset this single absorption is surprising when considering the number of nuclei in the complex which have nuclear spins, *i.e.*, ^{31}P, ^{195}Pt, ^{1}H, ^{29}Si, and ^{19}F. Initially, even when invoking the argument of pseudorotation about the silicon atom, the single ^{19}F absorption appears inconsistent with the preferred C_{2v} Si geometry for I. For example, the ^{19}F spectrum of HPF_4, which has the same geometry suggested for I, indicates magnetic equivalence of the fluorines but there is phosphorus–fluorine and hydrogen–fluorine coupling observed in the spectrum.[11] Therefore by analogy, fluorine–platinum and fluorine–silicon coupling should be observed for I. Muetterties and Klanberg have studied the ^{19}F nmr spectra of some pentacoordinate silicon fluorides.[8] In the case of the monosubstituted anions $RSiF_4^-$, where R = CH_3 or C_6H_5, the room-temperature spectra consisted of singlets. The authors postulated that the absence of coupling between the fluorines and protons was due to a dissociative exchange process for the anions

$$RSiF_4^- \rightleftharpoons RSiF_3 + F^- \qquad (2)$$

Such a process is consistent with the ^{19}F nmr of I, as well as being chemically feasible. Therefore the solution behavior of I is described by

$$[(C_6H_5)_3P]_2Pt\cdot SiF_4 \rightleftharpoons [(C_6H_5)_3P]_2Pt + SiF_4 \qquad (3)$$

Furthermore, when a suspension of I in toluene is refluxed for several hours under a nitrogen atmosphere, a yellow solution develops. A fine red powder can also be isolated from this solution which exhibited an infrared spectrum identical with that of the pyrolysis product of $[(C_6H_5)_3P]_3Pt$ which involves a predissociation of $P(C_6H_5)_3$. Referring to eq 3, this reaction can be interpreted as a shift in the equilibrium to the right in solution, with a yellow solution and red complex formed as a result of the formation of $[(C_6H_5)_3P]_2Pt$ followed by thermal decomposition at 111° (boiling point of toluene).

^{19}F field positions are practically linear with respect to coordination number in silicon fluorides. For example the resonances for the series SiF_4, SiF_5^-, and SiF_6^{2-} occur at 160.3, 136.0, and 128.2 ppm, respectively.[11] Therefore, the observed ^{19}F chemical shift for I, 137.3 ppm, is consistent with five-coordinate silicon.

Chemical Properties of I. Pyrolysis.—The chemical properties of I were investigated and compared to those of SiF_5^- salts in order to establish I as a simple Lewis acid–base adduct and also eliminate the possibility that I contained SiF_5^-. When I is heated to 155° *in vacuo*, silicon tetrafluoride and benzene are evolved in a 1:1 mole ratio according to

$$1.0[(C_6H_5)_3P]_2Pt\cdot SiF_4 \xrightarrow{155^\circ} 0.44SiF_4 + 0.44C_6H_6 + \text{red residue} \qquad (4)$$

The benzene most likely arises as the result of ortho proton exchange because the sample of I used in this experiment was prepared using toluene as the solvent. The infrared spectrum of the nonvolatile red residue exhibits absorptions characteristic of the starting material at 875 and 780 cm^{-1} whose relative intensities were *ca.* 30% of those observed in I; therefore the degradation was not complete. However, new absorptions did appear in the spectrum, most of which could be assigned to complexed $P(C_6H_5)_3$ ligand vibrations. By way of comparison, when $(n\text{-}C_3H_7)_4NSiF_5$ is heated to 230°, *in vacuo*, for 12 hr only a trace of propylene is evolved. The failure to generate SiF_4 indicates that SiF_5^- anions are thermally stable to 230° and the only decomposition which occurs is due to the cation. When $[(C_6H_5)_3P]_3Pt$ is heated to 204° *in vacuo*, $P(C_6H_5)_3$ and benzene are evolved according to

$$1.00[(C_6H_5)_3P]_3Pt \xrightarrow{204^\circ} 0.57C_6H_6 + 1.00P(C_6H_5)_3 + \text{red residue} \qquad (5)$$

The infrared spectrum of this red residue is identical with that of the pyrolysis product of I except that the latter's spectrum exhibited absorption characteristic of the starting material. In addition, the red solid, eq 5, exhibits an esr spectrum in the solid state and benzene solution with $g = 2.014$.

Reaction with Iodine.—Treatment of I with elemental iodine, *in vacuo*, in the absence of a solvent affords SiF_4, 31% of the theoretical yield. When CH_2Cl_2 is added to this mixture, the violet color of the iodine is rapidly discharged and additional SiF_4 is generated, total of 81% of the theoretical yield (0.033 mmol missing). The nonvolatile residue was identified as bis(triphenylphosphine)diiodoplatinum(II); therefore this reaction may be summarized by

$$[(C_6H_5)_3P]_2Pt\cdot SiF_4 + I_2 \xrightarrow{CH_2Cl_2} [(C_6H_5)_3P]_2PtI_2 + SiF_4\uparrow \qquad (6)$$

It should also be noted that no $(C_6H_5)_3PI_2$ was observed in the reaction products as evidenced by X-ray powder pattern data. Such a phosphorane would be expected to be formed if there was any labile phosphine ligands present in the complex.[12] The reaction presented by eq 6 involves oxidation of Pt(0) to Pt(II), and because platinum(II) complexes would not be expected to exhibit Lewis base character, the simple adduct is destroyed with the Lewis acid SiF_4 evolved.

When $(n\text{-}C_3H_7)_4NSiF_5$ is treated with a CH_2Cl_2 solution of iodine, only a trace (1.3%) of SiF_4 is generated after 6 hr. This difference in reactivity toward I_2 certainly indicated that I does not contain SiF_5^-. On the other hand the cation possibly could change the course of the I_2 reaction with the cation accepting a F^- with subsequent SiF_4 evolution. In order to test this hypothesis the reaction of I with I_2 was carried out except that after the SiF_4 was removed the excess I_2 and/or any interhalogen compound which may have been formed was scavenged with mercury. This entire reaction mixture was qualitatively tested for fluoride ion. The tests indicated the absence of fluoride; therefore I_2 quantitatively affords SiF_4 with no fluoride-containing residue as would be expected for SiF_5^-.

Reaction with Deuterium Chloride.—While the reactions of I with halogens were discussed in terms of the oxidation of platinum, they also can be rationalized from the viewpoint of the electron-accepting or acid properties of the halogens compared to those of SiF_4. Although HCl is not an oxidizing agent, it does have a

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[11] R. M. Treichel, R. A. Goodrich, and S. P. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).

[12] A. D. Beveridge, F. Inglis, and G. S. Harris, *J. Chem. Soc. A*, 520 (1966).

high electron affinity and its reaction with I may be considered an acid-exchange reaction with a Lewis adduct. Treatment of I with DCl, in the absence of a solvent, results in the slow evolution of SiF_4. The reaction is slower than the displacements of SiF_4 with I_2 and Br_2 as evidenced by an infrared spectrum of the nonvolatile residue which, after 4 hr, consisted mostly of absorptions assigned to the starting material. This is in agreement with the fact that electron affinity and oxidizing ability of the halogens are much larger than those of HCl (DCl). However, this is only a qualitative observation because the reactions were carried out in different phases which could affect the relative rates. It should also be noted that proton exchange occurred during the reaction because significant quantities of HCl were observed with the SiF_4 and excess DCl over the solid. The only source of protons in the reaction system is the phenyl rings of the $P(C_6H_5)_3$ ligands. An exchange with the ortho protons is quite possible in light of the known reactivity of the ortho protons of $P(C_6H_5)_3$ when the ligand is in a coordinatively unsaturated complex. For example, Parshall has demonstrated the reactivity of ortho protons in $[(C_6H_5)_3P]_3Ru\cdot HCl$ by exchange with deuterium gas.[13]

Reaction with Ammonia.—Just as a strong Lewis acid can be used to displace a weaker acid from a Lewis salt, a stronger base should displace $[(C_6H_5)_3P]_2Pt$ from I. However, treatment of I with ammonia does not afford the expected Lewis salt $SiF_4\cdot 2NH_3$, but rather a 1:1 adduct results, eq 7. The infrared spectrum of the nonvolatile residue exhibited absorptions at 720 and 480 cm^{-1} which are assigned to SiF stretching and bending modes in a trans octahedral geometry.[14]

$$[(C_6H_5)_3P]_2Pt\cdot SiF_4 + NH_3 \longrightarrow [(C_6H_5)_3P]_2Pt\cdot SiF_4\cdot NH_3 \qquad (7)$$

The absorptions assigned to five-coordinate SiF are absent in the spectrum indicating that the ammonia has bonded with the silicon. The ir spectrum also has a weak band at 3300 cm^{-1} which is assigned to an NH stretching mode. Therefore it is concluded the SiF_4 is functioning as a diacid with the bases being 1 molar equiv of NH_3 and 1 molar equiv of $Pt[P(C_6H_5)_3]_2$. In order to demonstrate that the silicon tetrafluoride part of the complex was still intact, the ammonia complex was treated with Br_2 resulting in the rapid elimination of SiF_4.

Nature of the PtSi Bond in I.—The fact that NH_3 does not displace $[(C_6H_5)_3P]_2Pt$ from I is at first glance very surprising because this implies that $[(C_6H_5)_3P]_2Pt$ is a stronger Lewis base toward SiF_4 than NH_3. The stability of I toward NH_3 can be explained when one recalls that SiF_4 often functions as a diacid, *i.e.*, accepts two electron pairs. For example, 1:2 adducts are known with the bases NH_3, $N(CH_3)_3$, and pyridine.[15] The reason of course for its diacidity is the incorporation of the vacant 3d orbitals of the silicon. When 1:2 adducts are formed, the hybridization about the silicon is sp^3d^2 using the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals to form the six-coordinate species. Likewise in 1:1 adducts the hybridization about the silicon is sp^3d and only the $3d_{z^2}$ orbital is used in the hybrid when the geometry is trigonal bipyramidal. For both coordination numbers the $3d_{xz}$ and $3d_{yz}$ orbitals are vacant and are able to accept electron pairs if the donor orbitals have the proper symmetry. The Pt atom associated with I has filled $5d_{xz}$ and $5d_{yz}$ orbitals which may interact with both Si and P vacant d orbitals. Evidence for this Si–Pt π interaction is the fact that SiF_4 displaces $(C_6H_5)_3P$ from $[(C_6H_5)_3P]_3Pt$ (a trans effect) while BCl_3 does not,[2] even though SiF_4 will not complex with $(C_6H_5)_3P$, while BCl_3 will form a 1:1 adduct. Therefore, the stability of I toward cleavage by NH_3 is suggested to be the result of very strong Si–Pt interaction including extensive overlap of the Pt filled orbitals with the vacant d orbitals on silicon. Such π overlap would not be effected when NH_3 is added because the change in hybridization of the silicon orbitals only involves those d orbitals with σ symmetry, *i.e.*, $3d_{z^2}$ and $3d_{x^2-y^2}$. With regard to an indication of the oxidation of Pt in I the ESCA Pt $4f_{7/2}$ binding energies were determined for I (73.6 eV), $[(C_6H_5)_3P]_2PtI_2$ (73.4 eV), and $[(C_6H_5)_3P]_3Pt$ (72.8 eV). These latter data compare favorably with those of similar species investigated by Siegbahn[16] and clearly establish the charge on Pt in I as being greater than that on Pt in $[(C_6H_5)_3P]_2PtI_2$ and similar to that of $[(C_6H_5)_3P]_2PtCl_2$.[16] These data are most consistent with a Pt–Si multiple bond model.

Experimental Section

Equipment.—Manipulations which involved air-sensitive materials were performed in a conventional vacuum line fitted with mercury float valves. Nonvolatile air-sensitive substances were handled in a Kewanee Scientific Corp. drybox. The drybox was continually flushed with Burdett Hi-purity dry nitrogen previously dried by passage through drying tubes containing Linde Molecular Sieve 4A and granular phosphorus pentoxide, P_2O_5. Any residual moisture was removed by placing additional P_2O_5 into the box.

Filtrations and recrystallizations of air-sensitive materials were performed using the vacuum filtration apparatus consisting of a 4-mm Delmar-Urry Teflon stopcock connected to a medium-porosity frit. Two 50-ml flasks were connected to the body of the apparatus by Delmar-Urry O-ring joints fitted with Vitron A O-rings.

Conductivities were measured using the Industrial Instrument Model RC-1613 conductivity bridge. Measurements were made at ambient temperature at frequencies of 1000 and 50 cps with a cell of constant 2.12.

Infrared spectra were obtained using Perkin-Elmer 337 and 457 grating spectrometers. Gas-phase spectra were obtained using a 10-cm gas cell equipped with potassium bromide optics. Liquid samples were measured as thin films between potassium bromide plates. Solid samples were prepared as a combination of Fluorolube (4000–1350 cm^{-1}) and Nujol (350–250 cm^{-1}) mulls between potassium bromide and polyethylene plates. Both Fluorolube and Nujol were dried over Linde Molecular Sieve 4A. Absorption intensities were measured using the method of Durkin, DeHayes, and Glore.[17]

Varian Associates A-60 and HA-100 spectrometers were used in obtaining ^1H and ^{19}F nmr spectra at 60 and 94.1 MHz, respectively. Solutions were hermetically sealed in 5-mm o.d. Pyrex tubes. Various solvents were used as internal ^1H nmr standards but all resonances were reported with respect to TMS, and ^{19}F nmr resonances were reported with respect to CCl_3F.

A Varian Associates E-3 spectrometer was used to obtain esr spectra. Solutions were hermetically sealed in 3-mm i.d. quartz tubes while solid samples were hermetically sealed in 1-mm Pyrex melting point capillary tubes.

Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type N-12045, with copper Kα radiation

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(13) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 4990 (1969).

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(15) I. R. Beattie, *Quart. Rev., Chem. Soc.*, **17**, 382 (1963).

(16) C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, **93**, 1904 (1971).

(17) T. R. Durkin, J. Glore, and L. DeHayes, *J. Chem. Educ.*, **48**, 452 (1971).

and a nickel filter. Samples were sealed in 0.5-mm o.d. glass capillary tubes.

The Pt $4f_{7/2}$ ESCA data were collected on the Berkeley instrument as described in the literature.[18]

Analyses.—Platinum and phosphorus were determined gravimetrically as platinum metal and ammonium phosphomolybdate. The samples (30–100 mg) were heated with 5 ml of concentrated sulfuric acid and 1 ml of 90% nitric acid in a Kjeldahl flask until sulfur trioxide fumes were evolved. Another 1 ml of nitric acid was added and the mixture was reheated. This process was continued until the solution was clear and platinum metal was observed. The solution was carefully diluted with 30 ml of distilled water and filtered through Wattman No. 42 ashless filter paper. The residue was transferred to a crucible and ignited at 900° to constant weight for platinum percentage. The filtrate was treated with the Lorenz ammonium molybdate reagent according to the method described in Pregl in order to determine the phosphorus percentage.[19] Platinum was also determined by igniting the complexes in a crucible at 900° to constant weight. Carbon and hydrogen analyses were obtained from Galbraith Microanalytical Laboratory, Knoxville, Tenn. Carbon and hydrogen analyses were also obtained using a standard combustion train with the absorbants being Drierite and Ascarite for H_2O and CO_2, respectively. Samples of I were pretreated with Br_2 to liberate SiF_4 which interfered with the C and H analyses. Platinum was determined from the ash.

Chemicals. Reagents.—**Benzene** (analytical reagent, ACS grade, J. T. Baker Co.) was distilled from molten potassium and stored over calcium hydride. **Toluene** (analytical reagent, ACS grade, J. T. Baker Co.) was distilled from molten sodium and stored over calcium hydride. **Tetrahydrofuran** (Matheson Coleman and Bell) was dried over calcium hydride or liquid sodium–potassium alloy. **Diethyl ether** (analytical reagent, ACS grade, J. T. Baker Co.) was dried over powdered lithium aluminum hydride or liquid sodium potassium alloy. **Hexane** (analytical reagent, ACS grade, Mallinckrodt Chemical Works) was dried over calcium hydride. **Dichloromethane** (analytical reagent, ACS grade, J. T. Baker Co.) was dried over calcium hydride. **Absolute ethanol** (USP, U. S. Industrial Chemical Co.) was used as received. **Triphenylphosphine** (Matheson Coleman and Bell) was used as received; mp 80° (lit.[20] mp 80°). **Iodine** (reagent grade, Allied Chemical Co.) was used as received. **Bromine** (analytical reagent, ACS grade, J. T. Baker Co.) was dried by decantation from concentrated sulfuric acid. **Silicon tetrafluoride** (The Matheson Co.) was fractionated through a −126° trap into a trap maintained at −196° until the vapor pressure at −112° was 122 Torr (lit.[20] pressure 122 Torr). **Hydrofluoric acid** (analytical reagent, ACS grade, J. T. Baker Co.) was used as received. **Tetrapropylammonium bromide** (Eastman Organic Chemicals) was used as received. **Triphenylmethylphosphonium iodide** was prepared by dissolving methyl iodide in a toluene solution of triphenylphosphine. White crystals precipitated from the solution which were collected by filtration and dried under vacuum. **Ammonia** (The Matheson Co.) was dried over sodium before use. **Triphenylphosphine oxide** was prepared from triphenylphosphine and tris(triphenylphosphine)-platinum(0) as described in the literature.[3] White needles were obtained by recrystallization from ethyl acetate. **Deuterium chloride** was prepared by hydrolyzing excess boron trichloride with deuterium oxide (99.75 atom %, Isotopes, Inc.). **Acetonitrile** (Fisher Scientific Co.) was used as received.

Syntheses. Platinum Complexes.—**Potassium hexachloroplatinate(IV)**, K_2PtCl_6, was prepared from platinum wire as described in the literature.[21] **Potassium tetrachloroplatinate(II)**, K_2PtCl_4, was prepared as described in the literature.[21] **Tetrakis(triphenylphosphine)platinum(0)**, $[(C_6H_5)_3P]_4Pt$, was prepared from K_2PtCl_4 as described in the literature.[22] The pale yellow powder was stored *in vacuo*. The infrared spectrum and assignments were identical with the literature values. X-Ray powder pattern data are as follows (Å): 10.4 (vs), 9.55 (vs), 7.10 (m), 6.25 (w), 5.63 (w), 4.37 (s), 4.04 (w), 3.81 (m).

Tris(triphenylphosphine)platinum(0), $Pt[P(C_6H_5)_3]_3$, was prepared using three methods. (1) A suspension of tetrakis(triphenylphosphine)platinum(0) in absolute ethanol was refluxed resulting in the dissociation of 1 equiv of triphenylphosphine.[23] (2) A suspension of bis(triphenylphosphine)dioxygenplatinum in toluene was treated with triphenylphosphine yielding tris(triphenylphosphine)platinum(0) and triphenylphosphine oxide.[3] (3) Tetrakis(triphenylphosphine)platinum(0) was dissolved in toluene resulting in the dissociation of 1 equiv of triphenylphosphine. The volume of the solution was reduced by evaporation resulting in the precipitation of tris(triphenylphosphine)platinum-(0). The precipitation was completed by the addition of *n*-hexane. The complex was collected by filtration and dried under vacuum. The bright yellow complex was stored under vacuum; mp (under vacuum) 204° (lit.[23] 205°). The infrared spectrum and assignments are in agreement with the literature values.[23] X-Ray powder pattern data follow (Å): 12.7 (m), 10.5 (m), 8.25 (vs), 7.39 (m), 5.52 (m), 4.43 (s), 4.30 (s), 4.00 (w), 3.77 (w), 3.60 (m), 3.19 (w), 3.00 (m), 2.90 (m), 2.74 (w), 2.62 (m), 2.09 (m).

***cis*-Bis(triphenylphosphine)diiodoplatinum(II)**, $[(C_6H_5)_3P]_2PtI_2$, was prepared from tris(triphenylphosphine)platinum(0) and elemental iodine as described in the literature;[24] mp 290° (lit.[24] mp 285°). The X-ray powder pattern data follow (Å): 10.3 (s), 8.53 (s), 7.64 (s), 6.82 (s), 6.20 (m), 5.51 (w), 4.70 (s), 4.42 (w), 4.17 (w), 3.79 (m), 3.66 (w), 3.59 (w), 3.43 (m), 3.05 (w), 2.86 (m).

Attempted Preparation of the Triphenylphosphine–Silicon Tetrafluoride Adduct.—(a) Solid triphenylphosphine was exposed to gaseous silicon tetrafluoride (*ca.* 400 Torr) over the temperature range −96 to +80° without any uptake of SiF_4.

(b) A benzene solution of triphenylphosphine was exposed to silicon tetrafluoride (*ca.* 700 Torr) without any uptake of SiF_4. The solvent was removed *in vacuo* leaving white crystals which were identified by melting point as the starting material.

Pentafluorosilicate Salts.—**Triphenylmethylphosphonium pentafluorosilicate**, $(C_6H_5)_3PCH_3SiF_5$, was prepared by dissolving triphenylmethylphosphonium iodide and silica in a methanol–aqueous hydrogen fluoride solution in a Nalgen beaker. The solution was evaporated, methanol was added, and the solution was reevaporated until no more hydrogen fluoride was evolved. Chloroform was added to the residue, and the mixture was filtered. Ethyl acetate was added to the filtrate, precipitating white needle crystals. The salt was recrystallized from chloroform and ethyl acetate and dried *in vacuo*, mp (in air) 165–168°. The ^1H nmr (in dichloromethane) consisted of a multiplet centered at τ 2.40 (J_{P-C-H} = 13 cps) of relative intensity 4.8 and a doublet at τ 7.15 (J_{P-C-H} = 13 cps) of relative intensity 1.0 attributed to the phenyl and methyl protons, respectively. The following infrared absorptions were recorded: 3060 (vw), 2995 (w), 2920 (w), 1588 (m), 1481 (m), 1439 (vs), 1340 (w), 1319 (w), 1190 (vw), 1165 (vw), 1116 (s), 1060 (w), 1029 (vw), 997 (w), 905 (s), 878 (vs), 787 (vs), 749 (s), 743 (s, sh), 718 (m), 689 (s), 511 (s), 501 (s), 480 (s), and 448 (s) cm^{-1}. *Anal.* Calcd for $C_{19}H_{18}F_5PSi$: C, 57.00; H, 4.50. Found: C, 57.67; H, 4.59.

Tetrapropylammonium pentafluorosilicate, $(n\text{-}C_3H_7)_4NSiF_5$, was prepared by the method previously described by Clark;[25] mp (in air) 205° (lit.[25] mp 207.5–208.5°). The infrared spectrum agreed with the literature values with absorptions characteristic of SiF_5^- at 875 (vs, b), 780 (vs, b), 480 (s), and 447 (s) cm^{-1}.[25]

Reactions of $(n\text{-}C_3H_7)_4NSiF_5$. Pyrolysis.—*n*-Tetrapropylammonium pentafluorosilicate (0.54 g, 1.8 mmol) was heated *in vacuo* for 4 hr at 230°. A trace (*ca.* 0.1 mmol) of highly volatile material was evolved which was identified as propylene by its vapor pressure and infrared spectrum. The nonvolatile residue had an infrared spectrum identical with that of the starting material.

Bromine.—Elemental bromine was condensed onto a dried sample of tetrapropylammonium pentafluorosilicate under vacuum. After 6 hr the reaction mixture was cooled to −78° and a trace of volatile material condensed into an infrared gas cell. The spectrum was identical with that of silicon tetrafluoride. The reaction mixture was warmed to room temperature and the excess bromine was removed. The spectrum of the residue was identical with that of the starting material.

Iodine.—Excess elemental iodine was condensed onto a dried sample of tetrapropylammonium pentafluorosilicate (0.4612 g,

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1.49 mmol) under vacuum. No reaction occurred. Dichloromethane was then condensed onto the mixture forming a purple solution. After 8 hr a trace of silicon tetrafluoride (0.02 mmol, 1.3% yield) was evolved. The excess iodine and solvent were removed by condensation into a trap maintained at −196°. The nonvolatile residue had an infrared spectrum identical with that of the starting material.

The Bis(triphenylphosphine)platinum–Silicon Tetrafluoride Adduct, $[P(C_6H_5)_3]_2Pt\cdot SiF_4$(I). Synthesis.—A freshly prepared sample of tris(triphenylphosphine)platinum(0) (1233.4 mg, 1.257 mmol) was dissolved in *ca.* 50 ml of benzene. The resulting bright yellow solution was exposed to silicon tetrafluoride (1.908 mmol) at a pressure of 218 Torr. After 10 min a finely divided white crystalline material began to precipitate. The precipitation continued for 4.5 hr and the solution turned colorless indicating absence of the starting complex. After an additional 10 hr of exposure to silicon tetrafluoride vapors, the volatile reactants and some solvent were removed by condensation into a trap maintained at −196° while the reaction mixture was held at −78°. The silicon tetrafluoride benzene mixture was separated by repeated fractional condensation through two traps maintained at −126° into a trap at −196°. The fraction which passed through the −126° traps was 0.614 mmol of silicon tetrafluoride identified by its infrared spectrum.[26] The reaction mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The resulting white solid was identified as triphenylphosphine by its infrared spectrum[27] and melting point; mp 80° (lit.[20] mp 80°). The white crystalline residue (I) from the filtration was dried, *in vacuo*, for 2 hr; dec pt (under N_2) 235°. Using the same method, I can be prepared with diethyl ether, toluene, ethyl acetate, or tetrahydrofuran as the solvent instead of benzene.

Purification and Characterization of I.—The infrared spectrum of the crude adduct had a weak absorption at 2175 cm^{-1} which is in the proper region for ν(Pt–H). Triphenylphosphine and tetrahydrofuran were added to the crude product and the suspension was heated to 63° in air until a yellow solution developed (*ca.* 15 min). The mixture was filtered and diethyl ether was added to the filtrate precipitating an off-white crystalline solid. The material was washed twice with *n*-pentane and dried under reduced pressure; dec pt (in air) 235°. The ^{1}H nmr spectrum (in acetonitrile) consisted of a multiplet centered at τ 2.82 which is assigned to the aromatic protons. The ^{19}F nmr spectrum consisted of a singlet at ϕ 137.3 ppm with a half-height width of 0.6 cps when I was dissolved in acetone. When acetonitrile was used as a solvent the absorption was shifted to ϕ 137.1 ppm with a half-height width of 8.0 cps. The molar conductance of I in acetonitrile is Λ = 35 ohm^{-1} cm^2 mol^{-1} for 4.0×10^{-4} and 2.2×10^{-4} *M* solutions indicating a nonelectrolyte.[28] *Anal.* Calcd for $C_{36}H_{30}F_4P_2PtSi$: C, 52.49; H, 3.64; Pt, 23.69. Found: C, 53.1; H, 3.6; Pt, 23.52.

Pyrolysis.—A 204.3-mg (0.248-mmol) sample of I was heated to 155° *in vacuo* at which temperature a measurable pressure was observed. After 1 day at 155°, the volatile products were removed from the resulting red liquid by condensation into a trap maintained at −196°. These products were fractionated through two −126° traps into a trap maintained at −196°. The product stopping at −126° was identified as benzene (0.114 mmol) by its infrared spectrum.[29] The product which condensed into the −196° trap was identified as silicon tetrafluoride (0.107 mmol) by its infrared spectrum. Upon cooling to room temperature the red residue (164.1 mg) solidified. Its infrared data are summarized: 3060 (w), 1970 (vw), 1900 (vw), 1815 (vw), 1582 (w), 1478 (m), 1435 (s), 1306 (w), 1182 (w), 1160 (w), 1117 (m), 1096 (m), 1067 (vw, sh), 1025 (w), 998 (w), 872 (m), 784 (m, sh), 740 (vs), 720 (s, sh), 692 (vs), 533 (s), 510 (m), 490 (s), 480 (s, sh), 445 (w), and 418 (vw) cm^{-1}.

Reaction of I with Iodine.—A sample of I (100.6 mg, 0.122 mmol) was treated with elemental iodine. Upon warming the reaction mixture from −196° to room temperature the sample turned brown and a volatile material was evolved. While maintaining the flask at −78°, the volatile product was collected in a −196° trap. This gas was identified as silicon tetrafluoride (0.038 mmol) by its infrared spectrum. Dichloromethane (*ca.* 1 ml) was next condensed onto the reaction mixture at −196°. Upon warming to room temperature a deep purple solution formed which quickly changed to yellow with bubbling. Again the flask was cooled to −78° and the volatile products were collected. They were fractionated through two −126° traps into a trap maintained at −196°. The fraction passing through the −126° traps was identified as silicon tetrafluoride (0.061 mmol) by its infrared spectrum. The total amount of silicon tetrafluoride generated was 0.099 mmol. Normal hexane was added to the dichloromethane solution precipitating a yellow-orange crystalline solid. The solid was collected by filtration and identified as diiodobis(triphenylphosphine)platinum(II) by comparison of its X-ray powder pattern to that of an authentic sample. The previous reaction was repeated with similar quantities and conditions except that, after removing the silicon tetrafluoride, mercury was added to the reaction mixture. The mercury reacted with the excess iodine and any interhalogen compounds which may have formed. The entire mixture was then fused with sodium and dissolved in water. The aqueous solution was qualitatively tested for fluoride ion with 0.04 *M* thorium nitrate solution[30] and calcium chloride solution:[30] both tests were negative.

Reaction of I with Bromine.—Compound I (118.5 mg, 0.144 mmol) was cooled to −78° and bromine condensed onto it *in vacuo*. Upon warming to room temperature a rapid reaction ensued which generated a highly volatile gas. After 30 min the reaction mixture was cooled to −95° and the volatile product was removed by condensation into a trap maintained at −196°. This gas was identified as silicon tetrafluoride (0.123 mmol) by its infrared spectrum. The excess bromine was removed under reduced pressure yielding a pale yellow crystalline solid.

Reaction of I with Ammonia.—Compound I (176.8 mg, 0.21 mmol) was cooled to −196° and ammonia was condensed onto it. After 12 hr at room temperature the mixture was cooled to −78° and the volatile products were removed by condensation into a trap maintained at −196°. The product was identified as ammonia by its infrared spectrum[29] and vapor pressure, 45 Torr at −78° (lit.[20] pressure 44 Torr). The mixture was then warmed to room temperature with no pressure being observed. Total uptake of ammonia was 0.24 mmol. Infrared data associated with this adduct follow: 3310 (w), 3050 (w), 1583 (vw), 1477 (m), 1432 (s), 1308 (vw), 1180 (w), 1162 (w), 1113 (vw, sh), 1093 (m), 1065 (w, sh), 1024 (w), 996 (s), 970 (vw), 872 (w), 850 (vw, sh), 740 (vs), 720 (s), 692 (vs), 550 (w), 540 (w), 525 (m), 514 (m), 499 (m), 478 (m), 447 (vw) cm^{-1}. Upon addition of bromine to the NH_3 adduct, a rapid reaction ensued with the generation of a gas. The gas was identified as silicon tetrafluoride by its infrared spectrum.

Reaction of I with Deuterium Chloride.—Compound I (91.5 mg, 0.111 mmol) was cooled to −196° and excess deuterium chloride was condensed onto it. After 4 hr at room temperature the volatile products were condensed into an infrared gas cell. The infrared spectrum was consistent with a mixture of hydrogen chloride, deuterium chloride, and silicon tetrafluoride.

Pyrolysis of Tris(triphenylphosphine)platinum(0).—Tris(triphenylphosphine)platinum(0) (297.3 mg, 0.303 mmol) was heated to 204° at which temperature a measurable pressure was observed over solid and white crystals sublimed into the condenser. After 24 hr of heating, the volatile products were removed by condensation into a trap maintained at −196°. The product was identified as benzene (0.166 mmol) by its infrared spectrum. The sublimate was collected and identified as triphenylphosphine (84.6 mg, 0.323 mmol) by its infrared spectrum and melting point (80°). The red nonvolatile residue weighed 191.2 mg and contained infrared bands at 3050 (w), 1960 (vw), 1890 (vw), 1582 (w), 1568 (w, sh), 1476 (m), 1432 (vs), 1306 (w), 1272 (vw), 1181 (w), 1157 (w), 1117 (vw, sh), 1094 (m) ("X" sensitive), 1067 (vw, sh), 1028 (w), 997, (w), 845 (vw), 737 (vs), 724 (m, sh), 693 (vs), 617 (vw), 562 (vw, sh), 534 (s, sh), 517 (s), 480 (m), and 377 (m) cm^{-1}. The esr spectrum of this deep red solid in a benzene solution consisted of a singlet with g = 2.016. An identical signal was obtained when a solid sample was used. The magnetic moment, determined at room temperature using the Faraday technique, was <0.1 BM. *Anal.* Found: C, 57.35; H, 3.89; P, 9.46.

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Acknowledgment.—Support of the work by the National Science Foundation, under Grants GP-9308 and GP-21118, and by the Petroleum Research Fund administered by the American Chemical Society, Grant No. 2803-AC1,3, is most appreciated. We also thank Dr. M. M. Millard for carrying out the ESCA measurements.

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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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Received August 9, 1971

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,

$$[(C_6H_5)_3P]_3Pt + 2BCl_3 \longrightarrow [(C_6H_5)_3P]_3Pt \cdot 2BCl_3 \qquad (1)$$

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 $PtBCl_2$ 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

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(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.

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