(7) R. L. Keiter, Ph.D. Thesis, University of Maryland, 1967.
(8) S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, **4**, 56 (1970).
(9) R. G. Goodfellow, J. G. Evans, P. L. Goggins, and D. A. Duddell, *J. Chem. Soc. A*, 1604 (1968).
(10) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
(11) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. 1, Academic Press, New York, N.Y., 1971, p 42.
(12) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).
(13) G. Booth in "Organophosphorus Compounds", Vol. 1., G. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 433–545.
(14) F. R. Hartley, "The Chemistry of Platinum and Palladium", Halsted Press, New York, N.Y., 1973, pp 27–47, 230–247.
(15) J. H. Nelson and A. W. Verstuyft, unpublished results.
(16) D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).
(17) L. L. Martin and R. A. Jacobsen, *Inorg. Chem.*, **10**, 1795 (1971).
(18) D. A. Redfield, J. H. Nelson, and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **10**, 727 (1974).
(19) A. W. Verstuyft, L. W. Cary, and J. H. Nelson, preceding paper.
(20) E. A. Allen and W. Wilkinson, *J. Inorg. Nucl. Chem.*, **36**, 1663 (1974).
(21) G. B. Ansell, *J. Chem. Soc., Dalton Trans.*, 371 (1973).
(22) D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **14**, 50 (1975).
(23) D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Am. Chem. Soc.*, **96**, 6298 (1974).
(24) D. A. Redfield and J. H. Nelson, *Inorg. Nucl. Chem. Lett.*, **10**, 931 (1974).
(25) W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963).
(26) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 1158 (1963).
(27) A. K. R. Unni, L. Elias, and H. F. Schiff, *J. Chem. Phys.*, **67**, 1216 (1963).
(28) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(29) B. E. Mann, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc., Chem. Commun.*, 151 (1972).
(30) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969).
(31) F. B. Ogilivie, J. M. Jenkins, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 1916 (1970).
(32) D. K. Maples and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **90**, 6045 (1968).
(33) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(34) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 1407 (1966).
(35) B. L. Shaw and J. D. Ruddick, *J. Chem. Soc. A*, 2801 (1969).
(36) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1491 (1969).
(37) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1557 (1970).
(38) P. R. Brookes and B. L. Shaw, *J. Chem. Soc. A*, 1071 (1967).
(39) J. M. Jenkins, B. L. Shaw, and M. S. Lupin, *J. Chem. Soc. A*, 7710 (1966).
(40) J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc. A*, 2796 (1969).
(41) J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 595 (1970).
(42) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 334 (1970).
(43) J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 1793 (1966).
(44) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A*, 605 (1967).
(45) R. G. Hayter and L. F. Williams, *Inorg. Chem.*, **3**, 717 (1964).
(46) J. P. Fackler, J. A. Fetchin, and W. D. Seidel, *J. Am. Chem. Soc.*, **91**, 1217 (1969).
(47) M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969).
(48) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).
(49) R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1965).
(50) W. McFarlane, *Chem. Commun.*, 772 (1967); *J. Chem. Soc. A*, 1922 (1967).
(51) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961).
(52) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1968, p 424.
(53) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
(54) V. Gutmann in "New Pathways in Inorganic Chemistry", E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968.
(55) U. Mayer and V. Gutmann, *Struct. Bonding (Berlin)*, **12**, 113 (1972).
(56) V. Gutmann, *Chem. Br.*, **7**, 102 (1971).
(57) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 70 (1953).
(58) L. M. Venanzi, *Chem. Br.*, **4**, 162 (1968).
(59) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966); C. A. McAuliffe, Ed., "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", Halsted Press, New York, N.Y., 1973.
(60) R. S. Drago, G. C. Vogel, and T. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).
(61) R. S. Drago, *Inorg. Chem.*, **12**, 2211 (1973).
(62) D. G. Cooper and J. Powell, *J. Am. Chem. Soc.*, **95**, 1102 (1973).
(63) D. G. Cooper and J. Powell, *Can. J. Chem.*, **51**, 1634 (1973).
(64) P. Haake and R. M. Pfeiffer, *J. Am. Chem. Soc.*, **92**, 4996, 5243 (1970).
(65) D. A. Redfield and J. H. Nelson, *J. Am. Chem. Soc.*, **96**, 6219 (1974).

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Lewis Base Properties of Platinum(0) Complexes. III. Adducts between Platinum and Titanium Tetrachloride[1a]

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Treatment of tris- and tetrakis(triphenylphosphine)platinum(0) complexes with titanium tetrachloride affords bis(titanium tetrachloride)tris(titanium tetrachloride–triphenylphosphine)platinum(0) (I). Thermolysis of I results in the formation of tris(titanium tetrachloride–triphenylphosphine)platinum(0) (II). Reaction of I with triphenylphosphine or methyldiphenylphosphine also affords II. Treatment of I with boron trichloride affords titanium tetrachloride. Subsequent thermolysis of the reaction residue results in the evolution of additional titanium tetrachloride, boron trichloride–triphenylphosphine adduct, and bis(titanium tetrachloride–triphenylphosphine)platinum(0).

Introduction

The nucleophilic character of triphenylphosphineplatinum(0) complexes has been demonstrated with the isolation of adducts with boron trichloride, silicon tetrafluoride, and aluminum trimethyl.[2,3] Silicon tetrafluoride reacts with $[(C_6H_5)_3P]_3Pt$ to afford a 1:1 adduct, with elimination of one $(C_6H_5)_3P$ ligand, whereas boron trichloride forms an adduct but without ligand displacement. These facts may be rationalized on the basis of silicon exhibiting a trans effect via overlap of vacant 3d orbitals with platinum 5d orbitals thereby decreasing the phosphorus–platinum π-bond strength. When complexed, boron trichloride has no suitable low-lying vacant orbitals; hence trans-ligand labilization is not expected. In an effort to investigate further the nucleophilic character of platinum(0) complexes with strong Lewis acids capable of π bonding, the system $[(C_6H_5)_3P]_3Pt$–$TiCl_4$ was investigated.

Results and Discussion

Treatment of tris(triphenylphosphine)platinum(0), $[(C_6H_5)_3P]_3Pt$, with titanium tetrachloride, $TiCl_4$, results in formation of an emerald green crystalline complex of composition $(TiCl_4)_2Pt[TiCl_4 \cdot P(C_6H_5)_3]_3$. A variety of reaction conditions have been employed in studying this system and a summary of the pertinent data from six reactions is presented in Table I. The measured weight gain of the contents of the reaction apparatus can be directly related to the amount of $TiCl_4$ that has been coordinated to the starting platinum compound because (1) only $TiCl_4$ is added to $[(C_6H_5)_3P]_3Pt$, (2) unreacted $TiCl_4$ is the only volatile material detected at the conclusion of the reaction, (3) $P(C_6H_5)_3$ is not permanently displaced, (4) neither $TiCl_4 \cdot P(C_6H_5)_3$ nor $TiCl_4 \cdot 2P(C_6H_5)_3$ is a reaction by-product, and (5) I represents a single material based on its microcrystalline homogeneous appearance. Based

Table I. Reaction Data for the $[(C_6H_5)_3P]_3Pt-TiCl_4$ System

Reagents			Conditions		Results		
Amt of $[(C_6H_5)_3P]_3Pt$		Amt of $TiCl_4$,[a]	Reaction		Amt of $TiCl_4$[c]		Stoichiometry,
g	mmol	mmol	time, hr	Method[b]	g	mmol	mmol of Ti/mmol of Pt
0.487	0.497	Ca. 18	23	A	0.464	2.44	4.91
0.366	0.373	Ca. 18	22	A	0.362	1.90	5.10
0.575	0.586	Ca. 13	20	A	0.584	3.07	5.24
0.404	0.413	Ca. 9	>50	A	0.394	2.08	5.03
0.425	0.433	Ca. 18	24	A	0.406	2.14	4.94
0.486	0.495	Ca. 9	24	B	0.460	2.42	4.89

[a] Initial $TiCl_4$ employed; determined by estimation of the volume of $TiCl_4$ present. [b] Refer to Experimental Section for a description of the specific method utilized. [c] Calculated from the measured weight gain of the contents of the reaction apparatus.

on the data in Table I, this reaction is

$$[(C_6H_5)_3P]_3Pt + 5TiCl_4 \rightarrow (TiCl_4)_2Pt[TiCl_4 \cdot P(C_6H_5)_3]_3 \qquad (1)$$

Conductance Properties of I. The equivalent conductance at zero concentration of I in *o*-dichlorobenzene is 13.1 ± 1.5 $cm^2/(ohm\ mol)$ as determined by an Onsager plot. Accascina et al. carried out a study of the equivalent conductance of 1:1 electrolytes in *o*-dichlorobenzene and from an Onsager plot arrived at the ideal equivalent conductance for each salt at zero concentration ranging from 35 to 47 $cm^2/(ohm\ mol)$. The indication is that I is not an electrolyte. The conductance of $TiCl_4 \cdot 2P(C_6H_5)_3$ (ca. 4 $cm^2/(ohm\ mol)$) and of I can possibly be attributed to solvation of $TiCl_4$ with subsequent ionization of the solvate. The basis for this suggestion is found in the solvation of $TiCl_4$ by acetyl chloride, CH_3COCl.[5]

Solution Behavior of I. Evidence has been obtained for the dissociation of $TiCl_4$ from I when dissolved in *o*-dichlorobenzene, eq 2. The fact that this equilibrium favors I at room temperature was verified by the observation that when a solution of I was maintained, in vacuo, for 14 hr at 25°, it remained dark green and very opaque. Furthermore, the infrared spectrum of the volatiles, in equilibrium above the solution, indicated only the solvent and no gaseous $TiCl_4$. However, this equilibrium may be disturbed by removing the solvent, and likewise $TiCl_4$, under reduced pressure. The solution becomes less opaque and appears brown to transmitted light as soon as it is exposed to a dynamic vacuum. This color change is accompanied by isolation of gaseous $TiCl_4$, which is detectable in the infrared spectrum of the volatile material removed from the solution.

$$(TiCl_4)_2Pt[TiCl_4 \cdot P(C_6H_5)_3]_3 \rightleftarrows (TiCl_4)_{2-x}Pt[TiCl_4 \cdot P(C_6H_5)_3]_3 + xTiCl_4 \qquad (2)$$

All of the labile $TiCl_4$ is removed during the early stages of pumping and the solution is completely brown and quite transparent. Continued pumping removes only the remainder of the solvent and leaves behind a brown solid somewhat wetted with the solvent. It is difficult completely to pump away the *o*-dichlorobenzene because it has a low volatility at room temperature.

The weight loss of I, eq 2, indicates a value for x of 1.34. From thermal dissociation studies, discussed below, the expected value for x is 2. The low value can be attributed to the fact that not all the solvent has been removed, as confirmed by the wet nature of the brown solid and the presence of some absorptions in the infrared spectrum of the solid residue which can be attributed to *o*-dichlorobenzene. Qualitatively, the weight loss is consistent with the fact that at least one and probably no more than two $TiCl_4$ groups have been dissociated. The presence of at least two distinct platinum species in solution is further verified by recovery of a brown solid from dark green solutions of I using the technique of mixed-solvent separation as indicated in the Experimental Section. Because concentrated solutions of I are still dark green when this brown material is recovered, only a small amount of it is recoverable; therefore it is apparent that the equilibrium, eq 2, lies to the left at room temperature.

Thermolysis of I. The thermally induced dissociation of I to afford $Pt[TiCl_4 \cdot P(C_6H_5)_3]_3$, II, is summarized by eq 3.

$$(TiCl_4)_2Pt[TiCl_4 \cdot P(C_6H_5)_3]_3 \xrightarrow[150°]{\text{in vacuo}} Pt[TiCl_4 \cdot P(C_6H_5)_3]_3 + 2TiCl_4 \qquad (3)$$

Experimental results indicate a $TiCl_4$:I mole ratio of 2.14 and 2.08 for duplicate thermolyses. Compound II is quite air sensitive due to the presence of hydrolyzable Ti–Cl bonds and is soluble in *o*-dichlorobenzene to an upper limit of ca. 10^{-1} *M*. A conductivity study afforded a value of around 8 $cm^2/(ohm\ mol)$ indicating a nonelectrolyte. Compound II decomposes above 170°, *in vacuo*, with evolution of $TiCl_4$, HCl, and benzene. The benzene arises from the thermal decomposition of the $P(C_6H_5)_3$ ligand, as has been previously noted for the pyrolysis of $Pt[P(C_6H_5)_3]_3$ at 204°, in vacuo.[2]

I may be regenerated by treatment of II with excess $TiCl_4$ (reverse of eq 3). Duplicate results indicate a $TiCl_4$:II mole reaction ratio of 2.10 and 2.08.

Reactions of I with Phosphine Derivatives. Treatment of a solution of I with either $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$ results in the formation of $TiCl_4$·phosphine and II (identified by ir). Both of these reactions represent a chemical method of shifting the position of equilibrium toward II, eq 2.

Reaction of I with BCl_3. Treatment of I with BCl_3 results in the chemical transformation which may be represented by either eq 4a or 4b.

$$(TiCl_4)_2Pt[TiCl_4 \cdot P(C_6H_5)_3]_3 + BCl_3 \rightarrow$$

$$TiCl_4Pt[TiCl_4 \cdot P(C_6H_5)_3]_2 + Cl_3B \cdot P(C_6H_5)_3 + 2TiCl_4 \qquad (4a)$$

$$Cl_3BPt[TiCl_4 \cdot P(C_6H_5)_3]_3 + 2TiCl_4 \qquad (4b)$$

Unfortunately, overlapping bands in the ir spectrum of the nonvolatile reaction mixture do not allow identification of $Cl_3B \cdot P(C_6H_5)_3$; however, subsequent thermolysis of this mixture results in the sublimation of $Cl_3B \cdot P(C_6H_5)_3$ accompanied by evolution of one $TiCl_4$ per Pt. The reaction represented by eq 4a indicates direct electrophilic displacement of $P(C_6H_5)_3$ by BCl_3 to afford $Cl_3B \cdot P(C_6H_5)_3$, whereas eq 4b involves electrophilic displacement of $TiCl_4$ by BCl_3. Subsequent thermolysis of the nonvolatile product(s), eq 4a or 4b, is considered to result in either dissociation of $TiCl_4$ and sublimation of $Cl_3B \cdot P(C_6H_5)_3$ (eq 4a) or rearrangement of the platinum complex (eq 4b) to afford $Cl_3B \cdot P(C_6H_5)_3$ and $TiCl_4$. In either case the final product is suggested to be $Pt[TiCl_4 \cdot P(C_6H_5)_3]_2$.

Infrared Spectroscopy—General Discussion. The detailed discussion concerning interpretation of the infrared spectra of I and II deals with three major features: (1) the X-sensitive absorptions around 1100 and 700 cm^{-1} that reflect the electronegativity of substituents that are bonded to a phenyl ring,[6] (2) absorptions that have shifted from their position in the infrared spectrum of the starting platinum complex, $[(C_6H_5)_3P]_3Pt$, and (3) absorptions that correspond to the

Table II. Infrared Data for (1) $P(C_6H_5)_3$, (2) $TiCl_4 \cdot P(C_6H_5)_3$, (3) $TiCl_4 \cdot 2P(C_6H_5)_3$, and (4) $[(C_6H_5)_3P]_3Pt$[d]

1: 3055 w (ν(C–H)), 1909 vw (ν(C–H comb.)), 1887 vw (ν(C–H comb.)), 1812 vw (ν(C–H comb.)), 1583 w (ν(C–C)), 1568 vw (ν(C–C)), 1475 s (ν(C–C)), 1436 s (ν(C–C)), 1431 s (ν(C–C)), 1323 vw (δ(C–H)), 1308 w (δ(C–H)), 1280 vw (δ(C–H)), 1270 vw, sh (δ(C–H)), 1178 w (δ(C–H)), 1155 w (δ(C–H)), 1106 vw, 1089 m (X-sens[a]), 1070 w (δ(C–H)), 1025 m (γ(C–H)), 995 w (ρ ring), 968 vw, 916 vw (γ(C–H)), 908 vw, 851 w (γ(C–H)), 753 m, sh (γ(C–H)), 742 vs (γ(C–H)), 694 vs (φ ring), 616 vw (X-sens[b]), 540 vw (X-sens), 512 m (X-sens), 497 s (X-sens), 491 s (X-sens), 427 w (X-sens), 417 w (X-sens)

2: 1585 vw,[c] 1571 vw, 1479 m, 1434 s, 1332 w, 1310 w, 1188 w (δ(C–H)), 1161 w (δ(C–H)), 1112 w, 1093 m (X-sens), 1070 vw, 1027 w, 998 w, 972 vw, 921 vw, 882 vw, br, 848 vw, 748 s, 706 m (X-sens), 692 s, 519 m, 505 m, 499 m, 467 s (ν_{as}(Ti–Cl) or ν(Ti–P)), 452 s (ν_{as}(Ti–Cl) or ν(Ti–P)), 436 w (ν(Ti–Cl)), 427 w (ν(Ti–Cl)), 372 vs (ν(Ti–Cl))

3: 1586 vw,[c] 1570 vw, 1480 m, 1432 s, 1334 vw, br, 1312 vw, 1189 w (δ(C–H)), 1160 vw (δ(C–H)), 1117 vw, 1088 m (X-sens), 1070 vw, 1027 w, 997 w, 974 vw, 845 vw, 745 s, 701 m, sh (X-sens), 692 vs, 520 s, 498 m, 488 m, sh, 445 w (ν(Ti–P)), 434 w (ν(Ti–P)), 384 vs (ν_{as}(Ti–Cl))

4: 3050 w,[c] 1955 vw, br, 1885 vw, br, 1812 vw, br, 1584 w, 1568 vw, 1475 s, 1431 vs, 1323 vw, 1304 w, 1265 w, 1178 w (δ(C–H)), 1155 vw (δ(C–H)), 1088 m (X-sens), 1066 w, 1027 w, 997 w, 970 vw, 809 vw, 849 vw, 748 m, 742 m, 693 vs, 687 m, sh, 617 vw, 517 vs, 508 vs, 446 w, sh, 438 w, sh, 422 m (ν(Pt–P))

[a] Reference 7. [b] G. B. Deacon, R. A. Jones, and P. E. Rogasch, *Aust. J. Chem.*, **16**, 360 (1963). [c] Absorptions not specifically assigned are due to $P(C_6H_5)_3$. [d] Key: comb., combination; vw, very weak; w, weak; m, medium; s, strong; vs, very strong; X-sens, X-sensitive; sh, shoulder; br, broad; ν, stretch; δ, in-plane deformation; γ, out-of-plane deformation; ρ, ring breathing; φ, out-of-plane ring deformation; s, symmetric; as, asymmetric.

presence of coordinated $TiCl_4$. The specific infrared spectral data that are necessary for these comparative studies are summarized in Table II: (1) $P(C_6H_5)_3$, (2) $TiCl_4 \cdot P(C_6H_5)_3$, (3) $TiCl_4 \cdot 2P(C_6H_5)_3$, (4) $[(C_6H_5)_3P]_3Pt$.

The most diagnostic X-sensitive bands for the $P(C_6H_5)_3$ ligand are a medium–strong absorption around 1090 cm^{-1} and a strong–very strong absorption around 700 cm^{-1}. Kross and Fassel found that there is an absorption characteristic of monosubstituted benzene in the region 1045–1185 cm^{-1} whose frequency is dependent upon the nature of the substituent that is bonded to the benzene ring.[7] In particular, they were able to arrive at an excellent linear correlation between the frequency of this absorption and the partial ionic character of the carbon–substituent bond, when the substituent was a monoatomic species. The trend they discovered is that as the partial ionic character of the bond between the carbon atom and the substituent increases, due to the increasing electronegativity of the substituent atom, the frequency of this X-sensitive vibration increases. Table III presents X-sensitive frequencies for various monosubstituted benzene derivatives and for complexes of $P(C_6H_5)_3$ that are important to the discussion of the infrared spectrum of platinum–titanium complexes.[3,7]

While Kross and Fassel discovered that the substituent atom has a direct effect on the frequency of the X-sensitive vibration, it can be seen from the data associated with the seven $P(C_6H_5)_3$ complexes, Table III, that when an atom or molecule is coordinated to the P atom, the X-sensitive vibration can shift, with the electronegativity or electropositivity of the coordinated species determining the direction of the shift. For the monoadducts of $P(C_6H_5)_3$ with $TiCl_4$, $Al(CH_3)_3$, and BCl_3, the Lewis acidity of these species causes the electronegativity of the P atom to increase and, consequently, the X-sensitive vibration shifts from 1089 to 1093, 1098, and 1100 cm^{-1}, respectively. Qualitatively, $TiCl_4$ is not as acidic as the other two species, possibly due to π back-bonding from the filled p orbitals on Cl to the vacant d orbitals on Ti. This type of π donation is not possible with complexed BCl_3 (B has no vacant, low-lying d orbitals) or with $Al(CH_3)_3$ (the CH_3 group has no lone electron pairs in p orbitals). This proposed decrease in Lewis acidity of $TiCl_4$ is further substantiated by comparisons of ^1H NMR chemical shifts for the species $(CH_3)_{4-x}MCl_x$ where $x = 1$–3 and M = C, Si, Sn, Ti. With regard to the Si and Ti species, abnormally high shielding of CH_3 derivatives was observed.[8] This property of $TiCl_4$ is especially apparent in $TiCl_4 \cdot 2P(C_6H_5)_3$, whose X-sensitive vibration is at 1088 cm^{-1}, the same frequency as for $P(C_6H_5)_3$ itself, Table III. For this compound it is suggested that $TiCl_4$ is able to balance its electron acceptance and donation by nonbonding chlorine p electrons so that there is no change in the effective electronegativity of the P atom of $P(C_6H_5)_3$. This decreased Lewis acid character of $TiCl_4$ with respect to BCl_3, as determined by the X-sensitive ir absorption frequencies, is further substantiated by the fact that BCl_3 completely displaces $P(C_6H_5)_3$ from $TiCl_4 \cdot 2P(C_6H_5)_3$.

Table III. X-Sensitive Frequencies for Various Monosubstituted Benzene Derivatives and $P(C_6H_5)_3$ Complexes

Compd	Freq, cm^{-1}	Ref
C_6H_5F	1159	*a*
C_6H_5Cl	1082	*a*
C_6H_5Br	1070	*a*
C_6H_5I	1066	*a*
$(C_6H_5)_3N$	1182	*a*
$(C_6H_5)_3P$	1088 (1089[b])	*a*
$(C_6H_5)_3As$	1075	*a*
$(C_6H_5)_3Sb$	1065	*a*
$TiCl_4 \cdot P(C_6H_5)_3$	1093	*b*
$TiCl_4 \cdot 2P(C_6H_5)_3$	1088	*b*
$BCl_3 \cdot P(C_6H_5)_3$	1100	*c*
$Al(CH_3)_3 \cdot P(C_6H_5)_3$	1098	*c*
$[(C_6H_5)_3P]_3Pt$	1088	*b*
$[(C_6H_5)_3P]_4Pt$	1082	*b*
$(TiCl_4)_2Pt[TiCl_4 \cdot P(C_6H_5)_3]_3$	1096	*b*

[a] Reference 7. [b] Observed. [c] Reference 3.

The X-sensitive vibration can also reflect decreases in the electronegativity of the P atom as with $[(C_6H_5)_3P]_4Pt$ where the X-sensitive vibration has shifted from 1089 cm^{-1}, in $P(C_6H_5)_3$, to 1082 cm^{-1} for this complex. This shift is due to the ability of $P(C_6H_5)_3$, and other phosphine and arsine ligands in general, to serve as medium-strength π acceptors in addition to their normal role as σ donors. Several authors have mentioned this dual role of phosphines, and also arsines, in explaining their function as a ligand.[9-11] In this particular instance the acceptance of electron density over the π framework is sufficient to decrease the electronegativity of the P atom and hence lower the X-sensitive vibration of $P(C_6H_5)_3$ to 1082 cm^{-1}. For $[(C_6H_5)_3P]_3Pt$, the X-sensitive vibration is at 1088 cm^{-1}, indicating that the phosphines have equalized their electron withdrawal and electron donation to the extent that the net change in the electronegativity of the P atom is negligible.

Another X-sensitive vibration that is useful to study, but not nearly as diagnostic as the q mode vibration at 1089 cm^{-1}, is the r mode at 698 cm^{-1}. This r mode is unfortunately obscured by the strong phenyl out-of-plane deformation at 694 cm^{-1} in the parent phosphine, $P(C_6H_5)_3$.[12] The primary utility of this r mode is to confirm the shift of the q mode, e.g., in $TiCl_4 \cdot P(C_6H_5)_3$ where the q mode is at 1093 cm^{-1}, the r mode is at 706 cm^{-1}; in $BCl_3 \cdot P(C_6H_5)_3$ where the q mode is at 1100 cm^{-1}, the r mode is at 710 cm^{-1}. Sometimes the r mode will become apparent if the phenyl out-of-plane deformation shifts to a lower frequency; e.g., in $TiCl_4 \cdot 2P(C_6H_5)_3$ (where the deformation is at 692 cm^{-1}) there is a shoulder at ca. 700 cm^{-1}. This shoulder corresponds to the r mode and this mode is unchanged from its position in the parent $P(C_6H_5)_3$ just as

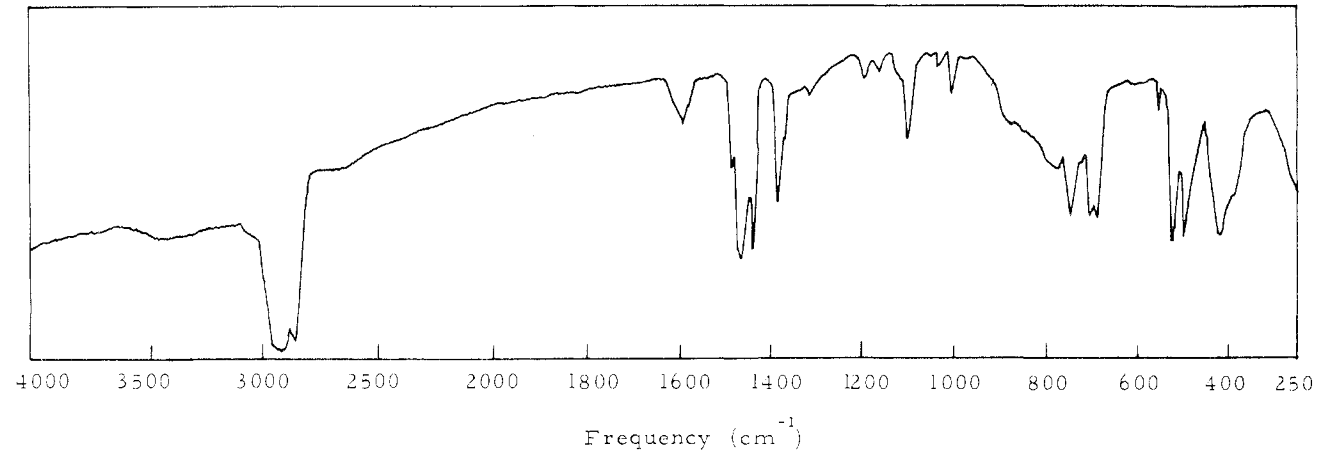

Figure 1. Infrared spectrum of $(TiCl_4)_2Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$.

Table IV. Infrared Frequencies and Tentative Assignments for $(TiCl_4)_2Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$

Freq (±2), cm^{-1}	Assignment[a]	Freq (±2), cm^{-1}	Assignment
1586 vw		970 vw	
1573 vw		845 m, br	
1480 m		796 m, br	
1438 vs		742 s	
1312 w		701 s	X-sensitive
1189 w	δ(C–H)	692 s	
1161 w	δ(C–H)	548 w	
1096 m	X-sensitive	522 vs	
1070 vw, sh		496 s	
1025 w		420 s	ν_{as}(Ti–Cl)
998 w		385 m, sh	ν_{as}(Ti–Cl)

[a] Absorptions not specifically assigned are due to $P(C_6H_5)_3$, Table II.

Table V. Frequencies of Two C–H In-Plane Deformations for Various $P(C_6H_5)_3$ Compounds

Compd	Freq, cm^{-1}	Reference
$P(C_6H_5)_3$	1178, 1154	*a*
$[(C_6H_5)_3P]_3Pt$	1178, 1155	*a*
$[(C_6H_5)_3P]_4Pt$	1180, 1155	*a*
$TiCl_4{\cdot}P(C_6H_5)_3$	1188, 1161	*a*
$TiCl_4{\cdot}2P(C_6H_5)_3$	1189, 1160	*a*
$(TiCl_4)_2Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$	1189, 1161	*a*
$BCl_3{\cdot}P(C_6H_5)_3$	1186 (1188[a]), 1160 (1163[a])	*b*
$[(C_6H_5)_3P]_3Pt(BCl_3)_2$	1178, 1156	*b*

[a] Observed. [b] Reference 3.

the q mode at 1088 cm^{-1} is virtually unchanged from its position at 1089 cm^{-1} in the parent $P(C_6H_5)_3$.

Infrared Spectrum of $(TiCl_4)_2Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$, I. The infrared spectrum of I is reproduced in Figure 1 and summarized in Table IV. The X-sensitive vibrations are at 1096 and 701 cm^{-1}, the latter appearing as a shoulder on the stronger peak at 693 cm^{-1}. The frequency for the q mode reflects the coordination of $TiCl_4$ to $P(C_6H_5)_3$, increasing the electronegativity of the P atom. The fact that this absorption is a single peak is important in that it indicates all the phosphines are equivalent in the complex; i.e., they are all coordinated to the same type of site with the result being that the effective electronegativities of all the P atoms are similar. It is possible to relate the number of distinct absorptions in the X-sensitive region to the number of chemically different $P(C_6H_5)_3$ groups. A reaction mixture was recovered from the reaction of excess $TiCl_4$ with $[(C_6H_5)_3P]_3Pt$ that was terminated when incomplete. The stoichiometry was quite low, 2.12 mmol of $TiCl_4$/mmol of platinum complex. Although the solid residue was dark green as in I, the infrared spectrum clearly showed the presence of unreacted $[(C_6H_5)_3P]_3Pt$ and I by the X-sensitive absorptions at 1089 and 1093 cm^{-1}, respectively. Absorptions at 708 and 701 cm^{-1} further verify these same conclusions, i.e., the presence of $[(C_6H_5)_3P]Pt$ and I, respectively.

Concerning I, the coordination of $P(C_6H_5)_3$ to $TiCl_4$, rather than to Pt, can be shown even more clearly by considering two C–H in-plane deformations, δ(C–H) at ca. 1180 and ca. 1160 cm^{-1}. Aside from the two X-sensitive vibrations, these two vibrations are the only other absorptions in the infrared pattern of $P(C_6H_5)_3$ that shift from their positions in $[(C_6H_5)_3P]_3Pt$ to new positions in I. Table V presents a summary of the frequencies of these two absorptions for various $P(C_6H_5)_3$ compounds. When $P(C_6H_5)_3$ is either uncoordinated or coordinated to Pt, the two vibrations occur at ca. 1180 and 1155 cm^{-1}, while when it is coordinated to an electrophile, e.g., $TiCl_4$ or BCl_3, the two vibrations occur at somewhat higher frequencies, ca. 1189 and 1161 cm^{-1}. While these shifts are not as dramatic as the shift of the X-sensitive q mode, they are nonetheless very consistent and therefore valuable in distinguishing between $P(C_6H_5)_3$ coordinated to Pt or to an electrophile.

In the case of $[(C_6H_5)_3P]_3Pt(BCl_3)_2$ the X-sensitive vibrations occur at 1092 and 704 cm^{-1}, reflecting the presence of the electrophilic BCl_3, but the δ(C–H) vibrations occur at 1178 and 1156 cm^{-1}, indicating that the $P(C_6H_5)_3$ ligands are still coordinated to the Pt. This agrees with other experimental evidence that BCl_3 is directly bound to Pt in $[(C_6H_5)_3P]_3Pt$.[3] For I the frequencies of these vibrations are at 1189 and 1161 cm^{-1}, very close to the values observed for $TiCl_4{\cdot}2P(C_6H_5)_3$ and $TiCl_4{\cdot}P(C_6H_5)_3$, indicating that the phosphines have been displaced from the Pt atom and are now coordinated to the $TiCl_4$ moiety.

The final diagnostic feature of the infrared spectrum of I involves the new absorptions that are directly a result of the presence of $TiCl_4$, i.e., the very strong absorptions at 420 cm^{-1} and the shoulder on this absorption at 385 cm^{-1}. The frequency of a ν(M–X) vibration, where M is Ti, V, Fe, Co, Zr, Hf, and most other transition and nontransition metals and X is a specific halogen, has been found to be dependent upon three basic factors: (1) the oxidation number of M, (2) the coordination number of M, and (3) the mass of M.[13] For the purpose of studying the $TiCl_4$ coordination in I, the second factor is the only one of importance. Table VI presents a tabulation of the frequency of the ν_{as}(Ti–Cl) vibration, derived from the ν_3 mode of $TiCl_4$, for a series of Ti(IV) complexes with varying coordination numbers.[13-18] The relationship clearly evident is that as the coordination number of Ti(IV) increases, the frequency of the ν_{as}(Ti–Cl) vibration decreases. In the case of the infrared spectrum of I, the ν_{as}(Ti–Cl) vibrations are at 420 and 385 cm^{-1}, the latter being at the

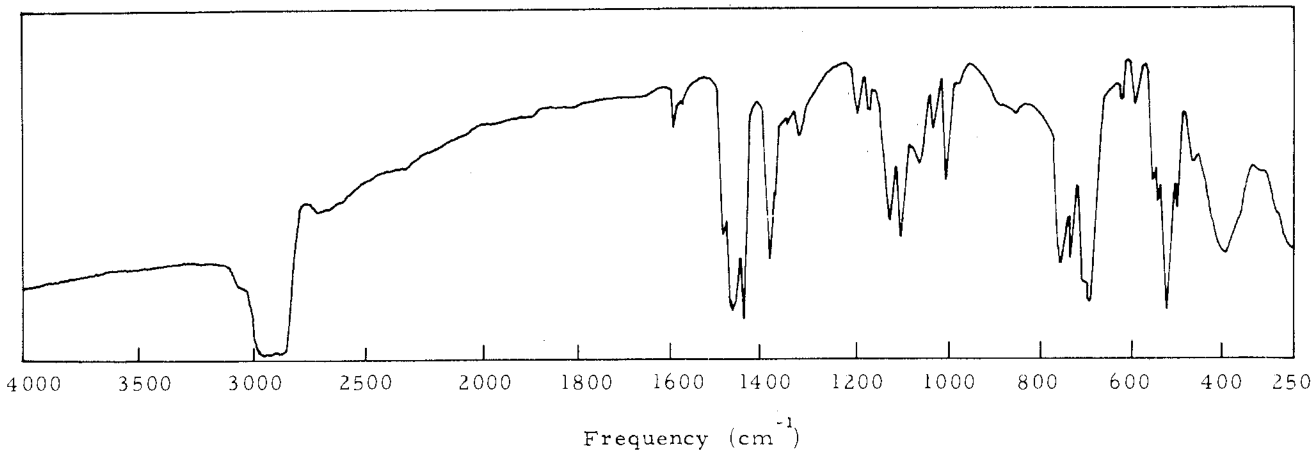

Figure 2. Infrared spectrum of $Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$.

Table VI. Frequency of ν_{as}(Ti–Cl) as a Function of the Ti(IV) Coordination Number

Compd[a]	Coordn no.	Freq,[b] cm^{-1}	Ref
$TiCl_4$	4	498 (499)	*c*
$TiCl_4{\cdot}N(CH_3)_3$	5	456 (461)	*d*
$TiCl_4{\cdot}PH_3$[e]	5	481	*d*
$TiCl_4{\cdot}P(CH_3)_3$[f]	5	448	*d*
$TiCl_4{\cdot}P(C_6H_5)_3$	5	463 (467) 452 (452)	*g*
$TiCl_4{\cdot}2CH_3CN$	6	387	*h*
$TiCl_4{\cdot}2C_6H_5N$	6	368	*h*
$TiCl_4{\cdot}2P(CH_3)_3$	6	336	*g*
$TiCl_4{\cdot}2P(CH_3)_2(C_6H_5)$	6	340	*g*
$TiCl_4{\cdot}2P(CH_3)(C_6H_5)_2$	6	374	*i*
$TiCl_4{\cdot}2P(C_6H_5)_3$	6	381 (384)	*j*
$TiCl{\cdot}3S_2CNR_2$ ($R = C_2H_5, CH_3$, *i*-C_3H_7, *i*-C_4H_9)	7	360–370	*k*
$TiCl_4{\cdot}2D$	8	317	*l*

[a] All spectra are recorded as Nujol mulls unless otherwise noted. [b] Observed frequencies are in parentheses. [c] Reference 14. [d] Reference 15. [e] Spectrum recorded neat at −196°. [f] Spectrum recorded in benzene solution. [g] Reference 16. The exact assignment of ν_{as}(Ti–Cl) is not made but it is one of these two frequencies. [h] Reference 13. [i] Observed. [j] Reference 17. [k] Reference 18, ν_{as}(Ti–Cl) is obscured by ν(Ti–S) in all complexes. [l] Reference 13; D = *o*-phenylenebis(dimethylarsine).

Table VII. Infrared Frequencies and Tentative Assignments for $Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$

Freq (±2), cm^{-1}		Freq (±2), cm^{-1}	Assignment
1584 w		888 w, br	
1570 w		845 w, br	
1479 m		744 s	
1437 vs		701 s, sh	X-sensitive
1336 vw		691 vs	
1312 w		617 w	
1188 w	δ(C–H)	586 w	
1161 w	δ(C–H)	548 m	
1118 s		537 m	
1094 s	X-sensitive	521 vs	
1095 m, br		498 m	
998 m		460 m	ν(Ti–P)
972 vw		395 s, br	ν_{as}(Ti–Cl)

[a] Absorptions not specifically assigned are due to $P(C_6H_5)_3$, Table II.

frequency for six-coordinate Ti(IV) and the former being attributable to five-coordinate Ti(IV).

Infrared Spectrum of $Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$, II. The infrared spectrum of II is reproduced in Figure 2 and summarized in Table VII. The presence of electrophilic $TiCl_4$ groups is indicated by the fact that the X-sensitive vibrations for II are at 1094 and 701 cm^{-1}, virtually unchanged from their positions in the infrared spectrum of I. The loss of two $TiCl_4$ ligands has not resulted in a decrease in these X-sensitive frequencies; these results are interpreted to indicate the dissociated $TiCl_4$ moieties were not complexed to P in I.

The δ(C–H) vibrations for II are at 1188 and 1161 cm^{-1}, essentially unchanged from their frequencies in I. This is consistent with the conclusion that the $P(C_6H_5)_3$ groups associated with II are still coordinated to the electrophilic $TiCl_4$; i.e., no drastic rearrangement of the Pt–Ti–P framework has taken place. If the $P(C_6H_5)_3$ groups had shifted from the Ti atoms to the Pt atom, the two δ(C–H) vibrations would reflect this by their shift to lower frequency ca. 1180 and 1155 cm^{-1}, respectively.

A very important feature of the infrared spectrum of II is the disappearance of the strong absorption at 420 cm^{-1}, in the region of five-coordinate Ti(IV), with the loss of two $TiCl_4$ groups from I. The infrared spectrum of II shows only a strong, broad absorption at 395 cm^{-1}, in the region of six-coordinate Ti(IV). The frequency of this ν_{as}(Ti–Cl) absorption is nearly the same as the frequency of the shoulder on the very strong absorption at 420 cm^{-1} in the infrared spectrum of I. The evolution of 2 equiv of $TiCl_4$ is accompanied by the disappearance of the absorption at 420 cm^{-1}. This is consistent with the assignment of this absorption to a ν_{as}(Ti–Cl) vibration for the five-coordinate Ti(IV) atoms in I. Compound II does not show an absorption at 420 cm^{-1}; hence it is considered not to contain five-coordinate Ti(IV). Both I and II exhibit an absorption near 390 cm^{-1} indicating the presence of six-coordinate Ti(IV).

A feature of the infrared spectrum of II that is directly related to the absence of the very strong absorption at 420 cm^{-1} is the appearance of a new absorption at 460 cm^{-1}. This absorption may be tentatively assigned to a ν(Ti–P) vibration by comparing its frequency to that of known ν(Ti–P) vibrations.[19] For $TiCl_4{\cdot}2P(C_6H_5)_3$ the two ν(Ti–P) vibrations, arising from the cis geometry of the adduct, are at 445 and 434 cm^{-1}. For $TiCl_4{\cdot}P(C_6H_5)_3$, the ν(Ti–P) vibration is either at 467 or 454 cm^{-1}, the exact assignment not being known. Although the infrared spectrum of I would be expected to show a ν(Ti–P) vibration at ca. 460 cm^{-1}, because I contains Ti–P bonds just as II, it is evident that the very strong absorptions at 496 and 420 cm^{-1} obscure this weak absorption.

Proposed Structures for Platinum–Titanium Complexes. Based on the reported chemistry and interpretation of the infrared spectral features of I, the suggested geometry is considered to involve five-coordinate platinum. The axial positions are considered to be occupied by two five-coordinate $TiCl_4$ moieties with the fifth coordination site platinum. The equatorial positions are considered to be occupied by the $TiCl_4{\cdot}P(C_6H_5)_3$ species with the sixth coordination position of titanium being platinum. Thermolysis of I affords II with loss of $TiCl_4$ from the two axial positions on platinum.

Treatment of I with BCl_3, eq 4, followed by thermolysis is suggested to afford $Pt[TiCl_4 \cdot P(C_6H_5)_3]_2$. The infrared spectrum of this latter species, in particular the C–H in-plane deformation frequencies, is interpreted to indicate $P(C_6H_5)_3$ coordinated to Ti rather than Pt.

Experimental Section

Equipment and techniques employed were similar to those previously described.[2] Manipulations involving nonvolatile materials were carried out in a Kewaunee Scientific Equipment drybox which was modified with a circulation system to remove oxygen and water more efficiently from the atmosphere, which was provided by Burdett prepurified argon. This gas was constantly circulated through a column containing BASF catalyst R3-11 heated to 110° and through Linde 4A molecular sieves. When the drybox was operating at optimum conditions, it could support a 25-W light bulb with its filament exposed to the atmosphere in the box for 8 hr, indicating the presence of 10–15 ppm of oxygen and water.

Conductivities were measured on an Industrial Instruments Model RC-16B conductivity bridge using a frequency of 60 Hz for nonelectrolytes and 1000 Hz for electrolytes. Measurements on air-sensitive compounds were handled in a Vacuum Atmospheres Corp. Dri-Lab, which was coupled to a VAC Dri-Train and equipped with electrode connections to the outside of the box. The cell constant was 1.96 and all measurements were made at ambient temperature.

Spectroscopy. All infrared and ^1H NMR spectra were recorded as previously described.[2,3]

Reagents. Benzene, analytical reagent, J. T. Baker Co., was distilled from potassium and stored over calcium hydride. **Dichloromethane,** analytical reagent, Mallinckrodt Chemical Works, was stored over lithium aluminum hydride. **Pentane,** reagent, Mallinckrodt Chemical Works, was used as received. **Absolute ethanol,** Commercial Solvents Corp., was used as received. **1,2-Dichlorobenzene (*o*-dichlorobenzene),** analytical reagent, J. T. Baker Co., was stored over lithium aluminum hydride and distilled from the hydride before use on a Nester-Faust spinning-band column at 59.5°, 10.0 Torr, (lit.[20] 59.1°, 10 Torr). **Triphenylphosphine,** $P(C_6H_5)_3$, Matheson Coleman and Bell, was used as received, mp 80° (lit.[21] 80°). **Methyldiphenylphosphine,** $P(CH_3)(C_6H_5)_2$, Strem Chemicals Inc., was used as received and stored in the drybox. **Titanium tetrachloride,** $TiCl_4$, 99.9%, Alfa Products, was purified immediately before each use by fractionating it into a −15° trap, while all the more volatile impurities passed through into a −196° trap. The −15° fraction was repeatedly fractionated into a −15° trap until its infrared spectrum showed no signs of any impurities.[22] Usually hydrogen chloride, HCl, was the only major impurity and its removal by fractionation was taken as good indication that the $TiCl_4$ was pure. When purified in this manner the $TiCl_4$ was a clear, colorless liquid. **Boron trichloride,** BCl_3, CP, The Matheson Co., was purified by fractionating it into a −126° trap until the vapor pressure did not change significantly; vapor pressure (0°) 474 Torr (lit.[23] 476 Torr).

Platinum Complexes. Potassium hexachloroplatinate(IV), K_2PtCl_6 was prepared as described in the literature.[24] **Potassium tetrachloroplatinate(II),** K_2PtCl_4, was prepared as described in the literature.[25] **Tetrakis(triphenylphosphine)platinum(0),** $[(C_6H_5)_3P]_4Pt$, was prepared as described in the literature[26] and was stored, in vacuo; mp (vacuum) 160–163°, with decomposition to an orange liquid (lit.[26] 159–160°). **Tris(triphenylphosphine)platinum(0),** $[(C_6H_5)_3P]_3Pt$, was prepared from $[(C_6H_5)_3P]_4Pt$ as described in the literature[27] and was stored, in vacuo; mp (vacuum) 202–204°, with decomposition to a red liquid (lit.[27] 205–206°, with decomposition to a red liquid).

Titanium Tetrachloride Adducts. Titanium tetrachloride–bis(triphenylphosphine), $TiCl_4 \cdot 2P(C_6H_5)_3$, was prepared following a modification of the literature method.[28] The solid was dried and stored in vacuo in the drybox; mp = 150–151° (lit.[19] 149–151°). Conductance data associated with $TiCl_4 \cdot 2P(C_6H_5)_3$ are shown in Table VIII.

Titanium tetrachloride–triphenylphosphine, $TiCl_4 \cdot P(C_6H_5)_3$, was prepared following modified literature methods.[16,19] The stoichiometry from weight gain is $0.900TiCl_4 \cdot 0.870P(C_6H_5)_3$. The solid was stored, in vacuo, in the drybox; mp 151–154° (lit.[16] 147.5–149°).

A sample of $TiCl_4 \cdot P(C_6H_5)_3$ (0.399 g, 0.885 mmol) was heated with constant pumping on the solid to study the sublimation behavior. As the temperature reached ca. 70° a condensable gas was detected above the solid. The condensable gas was evolved during a 1-hr period in which the temperature rose to 165°. As the gas evolution ceased, dark red crystals started to sublime into the neck of the sublimation bulb. The heating was continued at ca. 165° for 30 min and then terminated. The contents of the sublimation apparatus were dried, in vacuo, to a constant weight. The measured weight loss was 0.745 g, corresponding to 0.392 mmol of $TiCl_4$, the only species identified as being present in the infrared spectrum of the volatiles evolved during the sublimation. An infrared spectrum of the dark red crystals that sublimed at 165° matched exactly the infrared spectrum of $TiCl_4 \cdot 2P(C_6H_5)_3$.

Table VIII

Concn × 10^3, M	λ_{eq}, cm^2/(ohm mol)	Concn$^{1/2}$ × 10^2, $M^{1/2}$
4.65	3.53 ± 0.30	6.82
2.49	5.19 ± 0.31	4.99
2.32	5.00 ± 0.30	4.82
0.580	4.48 ± 0.50	2.41

Reaction of $TiCl_4 \cdot 2P(C_6H_5)_3$ with BCl_3. An excess of BCl_3 (5.85 mmol) was condensed onto a sample of $TiCl_4 \cdot 2P(C_6H_5)_3$ (0.115 g, 0.161 mmol) maintained at −196°. The contents of the reaction bulb were warmed to 0° and kept at this temperature for the remainder of the reaction time. Two minutes after the contents of the bulb reached 0°, a light colored solid was noted along with the red-purple $TiCl_4 \cdot 2P(C_6H_5)_3$, and as the reaction continued over a 30-min period, the red-purple solid disappeared and was replaced by this light pink solid. The reaction was terminated at this stage by removing the unreacted BCl_3 and all other volatiles and drying the reaction product, in vacuo, to a constant weight. The measured weight gain of the reaction apparatus was 0.0118 g. The infrared spectrum of the volatiles recovered from the reaction system showed BCl_3[29] and $TiCl_4$.[14] An infrared spectrum of the light pink solid matched exactly the infrared spectrum of $BCl_3 \cdot P(C_6H_5)_3$, a white, crystalline solid prepared by condensing excess BCl_3 onto a toluene solution of $P(C_6H_5)_3$.[3] When a sample of the light pink solid was heated under dynamic vacuum it sublimed at ca. 110° as light pink crystals, whose infrared spectrum matched the infrared spectrum of $BCl_3 \cdot P(C_6H_5)_3$, which sublimes, in vacuo, at 112°.[3]

Bis(titanium tetrachloride)tris(titanium tetrachloride–triphenylphosphine)platinum(0), $(TiCl_4)_2Pt[TiCl_4 \cdot P(C_6H_5)_3]_3$. Synthesis from $[(C_6H_5)_3P]_3Pt$. Method A. A typical reaction consists of treating a sample of $[(C_6H_5)_3P]_3Pt$ (0.487 g, 0.497 mmol) with small aliquots, 0.1–0.2 ml, of $TiCl_4$, which were condensed onto the sample over a 30–60-min period to allow the reaction to proceed slowly. The first contact between liquid $TiCl_4$ and the bright yellow solid produced a dark green color within 2–5 sec but only in the area where the liquid–solid contact was made. Each successive condensation would produce more areas of green solid or make those areas already present darker and wetter looking. Occasionally a trace of red color could be detected in those areas of solid where the green color was most intense, but usually no color other than dark green could be detected.

After the successive small aliquots of $TiCl_4$ had succeeded in visibly changing all the yellow solid to dark green, a large excess of $TiCl_4$ (ca. 2 ml, ca. 18 mmol) was condensed into the reaction bulb and the reaction mixture was stirred slowly or shaken gently during the remainder of the reaction time. Because the dark green solid was insoluble in the liquid $TiCl_4$, it was important not to agitate the flask violently, as the green solid would be thrown out of contact with the liquid onto the walls of the bulb.

The reaction was allowed to continue for ca. 22 hr, after which it was terminated by removing the unreacted $TiCl_4$ under reduced pressure. An infrared spectrum of the volatiles above the liquid showed no trace of hydrogen chloride, HCl, or any other gaseous species except $TiCl_4$. Anytime a small amount of HCl would be detected in the volatiles, the possibility of an air leak during the course of the reaction would have to be considered, and likewise, the absence of HCl indicated that the reaction system had remained intact during the course of the reaction. The contents of the reaction bulb were dried, in vacuo, to a constant weight and the measured weight gain of the bulb was 0.464 g, which corresponds to 2.44 mmol of $TiCl_4$.

Method B. Typically this method involved condensing a large amount of $TiCl_4$ (ca. 1 ml, ca. 9 mmol) onto the sample of $[(C_6H_5)_3P]_3Pt$ (0.486 g, 0.495 mmol) maintained at −196° and observing the reaction as the contents of this flask were warmed to room temperature. As the $TiCl_4$ melted, at ca. −25°, the yellow solid turned dark gold. As the flask warmed to slightly below room temperature, traces of green solid appeared where the liquid was in most direct contact with the solid. At no time during which the color change from dark gold to dark green takes place was any trace of red color noted. The reaction was allowed to continue with slow stirring for 24 hr, and then the unreacted $TiCl_4$ was removed and the dark green, crystalline solid was dried, in vacuo, to a constant weight. The measured weight gain was 0.640 g, which corresponds to 2.42 mmol of $TiCl_4$.

Failure to extract $P(C_6H_5)_3$ with benzene from the reaction product, I, for both preparative methods A and B, indicates the absence of displaced $P(C_6H_5)_3$. Furthermore, failure to extract $TiCl_4{\cdot}2P(C_6H_5)_3$ with $TiCl_4$ indicates the absence of both $TiCl_4{\cdot}P(C_6H_5)_3$ and $TiCl_4{\cdot}2P(C_6H_5)_3$ as reaction by-products.

Synthesis from $[(C_6H_5)_3P]_4Pt$. Method A. Typically a sample of $[(C_6H_5)_3P]_4Pt$ (0.398 g, 0.321 mmol) was treated with small aliquots, 0.1–0.2 ml, of $TiCl_4$ which were condensed onto the sample over a 30–60-min period to allow the reaction to proceed slowly. The first contact between the liquid $TiCl_4$ and the pale yellow solid produced a green color. Approximately 10 min after the first condensation, in those areas where the green color had developed to the greatest extent, definite traces of red color could be detected. Once this red color appeared in a particular area of dark green solid, it remained throughout the course of the reaction, unless it was washed away in some liquid $TiCl_4$. As the reaction continued in the early stages, the development of the dark green color became more complete and the small areas of red color also grew in extent. To complete this reaction an additional aliquot of $TiCl_4$ was condensed into the flask to make the total amount of this reagent equal to ca. 2 ml (ca. 18 mmol) and the contents of the bulb were stirred slowly or shaken gently for an additional 20 hr. The major product was a dark green solid, which was insoluble in the $TiCl_4$, just as in the $[(C_6H_5)_3P]_3Pt$ system, and the minor product was the red solid, which was soluble in the $TiCl_4$. The reaction was terminated by removing the unreacted $TiCl_4$ under reduced pressure. An infrared spectrum of the volatiles from the reaction showed only $TiCl_4$. The green and red solids were dried, in vacuo, to a constant weight, and the measured weight gain was 0.365 g, which corresponds to 1.92 mmol of $TiCl_4$.

Method B. Typically this procedure involved condensing a large excess of $TiCl_4$ (ca. 1 ml, ca. 9 mmol) onto the pale yellow solid, $[(C_6H_5)_3P]_4Pt$ (0.781 g, 0.630 mmol) at −15° and observing the course of the reaction as the contents of the bulb warmed to room temperature. The cold, liquid $TiCl_4$ changed the platinum complex to a dark gold solid, which started to turn green 5 min after the warming started. During the next 3 min the green color spread to all of the solid and became darker as well. The flask was still slightly below room temperature at this stage, and during the next minute the red color appeared for the first time and rapidly spread throughout the flask. The reaction was complete by all appearances within 7–9 min of the first appearance of any green color and, as with the previous method, the red color did not appear until all the solid had become dark green. The total amount of $TiCl_4$ was increased to ca. 3 ml (ca. 27 mmol) and the reaction was allowed to continue for 5 hr, with slow stirring of the reaction mixture. The unreacted $TiCl_4$ was removed under reduced pressure and the green and red solids were dried, in vacuo, to a constant weight. The measured weight gain was 0.725 g, which corresponds to 3.81 mmol of $TiCl_4$.

Isolation and Identification of the Products from the $[(C_6H_5)_3P]_4Pt$ System. The major product from each of the reactions involving $[(C_6H_5)_3P]_4Pt$ and $TiCl_4$ was the dark green solid which could be purified by extracting the red solid from it with the same $TiCl_4$ that was used for the reaction. The infrared spectra of I prepared from $[(C_6H_5)_3P]_3Pt$ and $[(C_6H_5)_3P]_4Pt$ matched exactly. The infrared spectrum of the dark red, crystalline solid matched exactly the infrared spectrum of $TiCl_4{\cdot}P(C_6H_5)_3$.[16]

Physical Properties of I. I is a dark green, crystalline solid which is quite air sensitive. When first exposed to air, the odor of hydrogen chloride can be detected above the solid, and over a period of several hours the solid decomposes to a pale yellow solid. This compound can be stored, in vacuo, in the drybox indefinitely without any detectable decomposition; mp 105–130° (with decomposition to a brown solid).

I is insoluble in $TiCl_4$ and benzene; the latter turns the crystalline solid into an oil and affects the infrared spectrum with regard to certain relative peak intensities. Dichloromethane dissolves I to form a golden brown solution and the golden brown oil recovered after removal of the solvent shows an infrared spectrum drastically different than that of I, indicating dichloromethane is also unsuitable as a solvent.

Table IX

Soln	Concn, M	λ_{eq}, cm^2/(ohm mol)	Concn$^{1/2}$, $M^{1/2}$
1	2.27×10^{-3}	8.20 ± 0.6	0.0477
2	1.33×10^{-3}	9.72 ± 1.0	0.0364
3	1.14×10^{-3}	10.7 ± 1.0	0.0337
4	6.63×10^{-4}	11.3 ± 1.1	0.0258
5	5.68×10^{-4}	10.3 ± 0.6	0.0238
6	2.84×10^{-4}	11.9 ± 1.0	0.0168
7	1.66×10^{-4}	16.0 ± 1.7	0.0129
8	1.42×10^{-4}	11.5 ± 1.7	0.0119
9	8.27×10^{-5}	<9.7	0.0091
10	7.10×10^{-5}	<11.2	0.0084

Table X

Concn, M	λ_{eq}, cm^2/(ohm mol)	Concn$^{1/2}$ × 10^2, $M^{1/2}$
4.07×10^{-3}	8.00 ± 0.05	6.38
2.03×10^{-3}	8.53 ± 0.07	4.56
5.09×10^{-4}	8.15 ± 0.12	2.26
2.55×10^{-4}	6.90 ± 0.60	1.60

o-Dichlorobenzene dissolves I to afford a dark green solution with an upper concentration limit of ca. 10^{-2} M. Using this solvent, it was possible to perform a conductivity study. (See Table IX.) For the Onsager plot, solutions 9 and 10 were not considered because they gave resistance readings beyond the upper limit (2.500×10^6 ohms) of the instrument, and solution 7 was not considered because it did not correlate with the other seven solutions. The least-squares line that fit the seven selected solutions gave a value for the equivalent conductance at zero concentration of $\lambda^0_{eq} = 13.1 \pm 1.5$ cm^2/(ohm mol).

A sample of I (0.138 g, 0.0713 mmol) was hydrolyzed with 25% aqueous sodium hydroxide previously degassed in vacuo. The green solid became golden brown after the first 40 min of the hydrolysis and remained insoluble in the solution. Continued reaction at 25° for 67 hr and at 75° for 43 hr produced no changes in the hydrolysis mixture and no noncondensable gas.

Thermal Properties of I. Synthesis of Tris(titanium tetrachloride–triphenylphosphine)platinum(0), $Pt[TiCl_4{\cdot}P(C_6H_5)_3]_3$, II. Typically a sample of I (0.159 g, 0.0821 mmol) was heated slowly while the pyrolysis bulb was constantly pumped on through a −196° trap. As the temperature reached 75°, a condensable gas was detected above the sample and the evolution of this gas continued as the temperature rose to 140° during a 1-hr period. At ca. 90° the mass of green solid began to develop bubbles as gas was evolved, and from 90 to 110° the color of the bubbly mass changed to dark brown. Heating was continued at 140° for 1 additional hr after which time no further evolution of condensable gas was detected. When the pyrolysis vessel, containing the dark brown solid (II), was weighed, a weight loss of 0.0335 g was recorded. The infrared spectrum of the condensable gas evolved during the controlled pyrolysis was identical with that of authentic $TiCl_4$.

When the pyrolysis was continued beyond 150°, the dark brown solid, II, melted at ca. 180° and condensable gas could be detected above the dark brown liquid. After heating the liquid at 205° for 10 hr the pyrolysis was stopped and this time the infrared spectrum of the condensable gas showed it to be a mixture of benzene, $TiCl_4$, and HCl.

Physical and Spectral Properties of II. The dark brown, crystalline solid, II, resulting from the controlled pyrolysis of I, to a temperature of 150°, is air sensitive, as indicated by the odor of HCl, but can be stored indefinitely, in vacuo. II is insoluble in benzene, becoming an oil when treated with it. It is also insoluble in $TiCl_4$ and will react when kept in prolonged contact with it, as is reported below. It is soluble in *o*-dichlorobenzene affording a yellow-brown solution up to the upper concentration limit of ca. 10^{-1} M. A conductivity study of II in *o*-dichlorobenzene afforded the data of Table X.

Reaction of II with $TiCl_4$. A sample of II (0.269 g, 0.173 mmol) was placed in contact with excess $TiCl_4$ (ca. 1 ml, ca. 9 mmol) by condensing the $TiCl_4$ onto the solid at −196° and then warming the mixture to ambient temperature. The dark brown solid was insoluble in the $TiCl_4$, but after 1 hr of slow stirring with the liquid, the dark brown solid had started to become dark green. The reaction was continued for ca. 20 hr by which time all the solid had become dark green. This solid was completely insoluble in $TiCl_4$ and could be recovered as a dark green, crystalline solid by removing the unreacted $TiCl_4$ under reduced pressure. The infrared spectrum of the volatiles above the reaction mixture showed only $TiCl_4$. When the contents of the reaction bulb were dried to a constant weight, in vacuo, the measured weight gain was 0.0689 g, corresponding to 0.362 mmol of $TiCl_4$. The infrared spectrum of this dark green solid matched exactly the infrared spectrum of I.

Dissociation of I. A sample of I (0.305 g, 0.158 mmol) was dissolved in a minimum amount of *o*-dichlorobenzene (ca. 15 ml) affording a dark green solution, ca. 0.01 *M*. This solution was degassed, in vacuo, and after it remained under reduced pressure for 14 hr, an infrared spectrum of the volatiles above the liquid showed only *o*-dichlorobenzene. Approximately 6 ml of solvent was removed under reduced pressure and the solution became less opaque and appeared brown with transmitted light. An infrared spectrum of the volatiles removed showed $TiCl_4$ in addition to *o*-dichlorobenzene. Removal of the remainder of the solvent under reduced pressure produced a brown solution in the later stages of pumping, and an infrared spectrum of the volatiles above the final 10 ml of solvent removed again showed only *o*-dichlorobenzene. The brown solid remaining after removal of the bulk of the solvent was dried, in vacuo, to a constant weight and the measured weight loss was 0.0403 g, which corresponds to 0.212 mmol of $TiCl_4$.

When benzene was added to a dark green solution of I in *o*-dichlorobenzene, the solution became cloudy with a precipitate and a brown oil was removed by filtration. This oil became dry and powdery when ground. Infrared analysis indicated this brown solid was II.

Reaction of I with $P(C_6H_5)_3$. A solution of I, ca. 5×10^{-3} *M*, in *o*-dichlorobenzene, was prepared and a small amount of $P(C_6H_5)_3$ added. Within 5 sec the solution became red and remained free of any insoluble materials. The solution was transferred to a fritted funnel and benzene was added to the solution to separate out a brown oil, which could be recovered by filtration. The filtrate remained red during this mixed-solvent separation. This material became dry and powdery when ground and its infrared spectrum matched that of II.

Reaction of I with $P(CH_3)(C_6H_5)_2$. A solution (ca. 8×10^{-3} *M*) of I, in *o*-dichlorobenzene, was prepared and a small amount of $P(CH_3)(C_6H_5)_2$ was added with a syringe. Within 3 sec the solution became red and remained free of any insoluble materials. The solvent was removed under reduced pressure and the dark red residue was washed with *o*-dichlorobenzene. The filtrate was red and a dark solid remained on the frit. It was difficult to dry this brown solid completely due to residual amounts of the nonvolatile liquid, $P(CH_3)(C_6H_3)_2$. Infrared data indicated this material to be ca. 90% II and $P(CH_3)(C_6H_5)_2$.

When a sample of I was treated with excess $P(CH_3)(C_6H_5)_2$, neat, the dark green solid did not dissolve in the $P(CH_3)(C_6H_5)_2$, nor did any red color develop during 1 min of gentle shaking. However, when *o*-dichlorobenzene was added, the characteristic red color of the previous reaction appeared within 5 sec.

Reaction of I with BCl_3. An excess of BCl_3 (8.78 mmol) was condensed into a sample of I (0.160 g, 0.0827 mmol) maintained at −196°. The contents of the reaction bulb were then warmed gradually to 0° and held at this temperature for the duration of the 24-hr reaction. I was insoluble in the liquid BCl_3 and the mixture was slowly stirred throughout the reaction. An the conclusion of the reaction, there were no visible changes in either the green solid or the BCl_3.

The reaction was terminated by removing the unreacted BCl_3, leaving a pale green solid in the reaction bulb. The volatiles were fractionated through a −78° trap into a −196° trap. The −78° fraction was identified as $TiCl_4$ by its infrared spectrum. The −196° fraction was identified as BCl_3 by its infrared spectrum. The amount of BCl_3 recovered was 8.70 mmol. The green solid was dried, in vacuo, to a constant weight and the measured weight loss was 0.0206 g. The infrared spectrum of the green reaction mixture contained absorptions at 1584 (w), 1571 (w), 1477 (m, sh), 1437 (vs), 1310 (w), 1273 (w, br), 1185 (w), 1159 (w), 1095 (s), 1072 (w), 1026 (w), 999 (m), 971 (vw), 888 (vw), 844 (vw), 742 (s), 702 (s, sh), 691 (s), 617 (vw), 547 (m), 522 (vs), 499 (s), 465 (w), 423 (vs, br), and 390 (s) cm^{-1}.

A sample of this green solid was heated gradually at 145° over a 1-hr period. At 70° a condensable gas was detected above the solid and the evolution of this gas continued as the temperature rose. At 105° the green solid could be noted changing color to a brown solid, and at 130°, a trace of a pink, crystalline sublimate was noted in the upper neck of the pyrolysis bulb. After heating at 145° for 1 hr, the evolution of condensable gas had ceased, all the solid in the bulb had become brown, and the pink sublimate remained in the upper neck of the bulb. The heating was terminated at this time and the condensable gas was identified as $TiCl_4$ by its infrared spectrum. The measured weight loss of the pyrolysis apparatus was 0.0187 g, which corresponds to 0.0985 mmol of $TiCl_4$. The pink sublimate was identified as $BCl_3 \cdot P(C_6H_5)_3$ by its infrared spectrum.[3] The infrared spectrum of the brown pyrolysis residue contained absorptions at 1587 (w), 1572 (w), 1478 (s), 1436 (vs), 1302 (w), 1267 (w, br), 1186 (w), 1160 (w), 1093 (s), 1026 (w), 999 (m), 971 (w), 920 (vw, br), 890 (vw, br), 844 (w), 743 (s), 703 (vs, sh), 692 (vs), 618 (w), 547 (m), 522 (vs), 499 (s), 465 (w), 400 (s), 372 (s), 321 (w), and 285 (w) cm^{-1}.

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Registry No. I, 54822-95-6; II, 54822-94-5; $TiCl_4$, 7550-45-0; $[(C_6H_5)_3P]_3Pt$, 13517-35-6; $[(C_6H_5)_3P]_4Pt$, 14221-02-4; $P(C_6H_5)_3$, 603-35-0; $P(CH_3)(C_6H_5)_2$, 1486-28-8; BCl_3, 10294-34-5; $TiCl_4 \cdot P(C_6H_5)_3$, 14318-97-9; $TiCl_4 \cdot 2P(C_6H_5)_3$, 33678-19-2; $TiCl_4 \cdot 2P(CH_3)(C_6H_5)_2$, 54751-62-1; $BCl_3 \cdot P(C_6H_5)_3$, 3230-03-3.

References and Notes

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

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

(4) F. Accascina, E. L. Swarts, P. L. Mercier, and C. A. Kraus, *Proc. Natl. Acad. Sci. U.S.*, **39**, 917 (1953).

(5) R. C. Paul, D. Singh, and S. S. Sandhu, *J. Chem. Soc. A*, 315 (1959).

(6) D. H. Whiffen, *J. Chem. Soc. A*, 1350 (1956).

(7) R. D. Kross and V. A. Fassel, *J. Am. Chem. Soc.*, **77**, 5858 (1955).

(8) M. P. Brown and D. E. Webster, *J. Phys. Chem.*, **64**, 698 (1960).

(9) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

(10) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(11) R. Mason, *Chem. Soc. Rev.*, **1**, 431 (1972).

(12) G. B. Deacon and J. H. S. Green, *Chem. Ind.* (*London*), 1031 (1965).

(13) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

(14) R. J. H. Clark, B. K. Hunter, and D. M. Rippon, *Inorg. Chem.*, **11**, 56 (1972).

(15) I. R. Beattie and R. Collis, *J. Chem. Soc. A*, 2960 (1969).

(16) F. Calderazzo, S. A. Losi, and B. P. Susz, *Helv. Chim. Acta*, **54**, 1156 (1971).

(17) G. W. A. Fowles and R. A. Walton, *J. Chem. Soc. A*, 4330 (1964).

(18) E. C. Alyea and B. S. Ramaswamy, *Inorg. Nucl. Chem. Lett.*, **9**, 399 (1973).

(19) A. D. Westland and L. Westland, *Can. J. Chem.*, **43**, 426 (1965).

(20) D. R. Stull, *Ind. Eng. Chem.*, **39**, 523 (1947).

(21) R. C. Weast, "Handbook of Chemistry and Physics", 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p C-473.

(22) R. B. Johannesen, C. L. Gordon, J. E. Stewart, and R. Gilchrist, *J. Res. Natl. Bur. Stand.*, **53**, 197 (1954).

(23) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969, p 279.

(24) R. N. Keller, *Inorg. Synth.*, **2**, 247 (1946).

(25) J. Kleinberg, *Inorg. Synth.*, **7**, 240 (1963).

(26) R. Ugo, F. Cariati, and G. LaMonica, *Inorg. Synth.*, **11**, 105 (1968).

(27) R. Ugo, F. Cariati, and G. LaMonica, *Inorg. Synth.*, **11**, 107 (1968).

(28) J. Chatt and R. G. Hayter, *J. Chem. Soc. A*, 1343 (1963).

(29) R. E. Scruby, J. R. Lachter, and J. D. Park, *J. Chem. Phys.*, **19**, 386 (1951).