$Co(NH_3)_5Cl^{2+} > Co(NH_3)_5F^{2+}$, with that for other inner-sphere reductants. The order is the same as that observed for Cr^{2+} [28] and $Co(CN)_5^{3-}$ [5] as reductants but the reverse of that observed for Eu^{2+} [3] and Fe^{2+} [30] which are also believed to reduce these cobalt(III) complexes by inner-sphere mechanisms and which exhibit the reactivity order, $Co(NH_3)_5F^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5I^{2-}$. Since the inner-sphere mechanism involves transfer of the bridging ligand from the cobalt to the reductant, *i.e.*

$$\text{Co–X} + \text{red} \longrightarrow \text{Co} + \text{X–red}$$

it is to be expected that the reactivity order when X is varied will be influenced by the variation of the strengths of both the bond being broken (Co-X) and the bond being formed (X-red). For the oxidants and reductants in question the trend is almost certainly for both bond strengths to increase in the order I < Br < Cl < F. It might further be expected that for highly reactive reductants the influence of bond making in the transition state is of less importance than bond breaking, and hence that the reactivity order should follow the sequence determined by the strength of the bond being broken, *i.e.*, $Co(NH_3)_5I^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5F^{2+}$. For reductants of low reactivity, on the other hand, stabilization of the transition state by bond making to the reductant is expected to assume greater importance, and the reactivity order should thus be influenced to a greater degree by the strength of the bond being formed, *i.e.*, F > Cl > Br > I. Put in a somewhat different way, this is equivalent to saying that in highly exo-free energetic reactions the transition state tends to resemble the reactants, whereas in endo-free energetic reactions it tends to resemble the product. The observed reactivity orders of the different reductants toward the halopentaammine complexes are consistent with this interpretation when considered in the light of the absolute reactivities of these reductants which follow the order: H (1.6×10^9) > $Co(CN)_5^{3-}$ (2×10^7) > Cr^{2+} (2.6×10^6) > Eu^{2+} (3.9×10^2) > Fe^{2+} (1.4×10^{-3}), the values in parentheses being the rate constants (in M^{-1} sec^{-1} at 25°) for reaction with $Co(NH_3)_5Cl^{2+}$.

Finally some comment is in order on those complexes that contain ligands which are reactive toward H atoms in the uncomplexed state. In these cases the possibility must be considered that the reactivity of the complex toward H atoms is essentially that of the ligand, influenced only to a minor degree by the presence of the reducible cobalt(III) center, and hence that these reactions differ in a rather fundamental way from those of the other cobalt(III) complexes. While the observed comparisons of the reactivities of several of the complexes and the corresponding free ligands (notably fumarate, NO_2^-, and N_3^-) are consistent with this view, they do not rule out some influence of the cobalt(III) center, and further investigations directed at elucidating this important point would appear to be called for.

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[30] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1964); H. Diebler and H. Taube, *ibid.*, **4**, 1029 (1965).

Electronic Character of Metal–Anion Bonds

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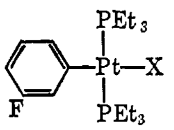
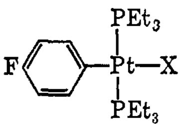
Received September 13, 1965

Abstract: The F^{19} nmr shielding parameters of *m*- and *p*-fluorophenylplatinum(II) complexes provide a criterion of the electronic characteristics of other metal-ligand bonds in the compounds. The σ-donor characteristics measured in this way parallel the basicities of the anions involved. The CN^-, $C_6H_5C{\equiv}C^-$, and $SnCl_3^-$ ions are strong π acceptors, but the halide ions have a net π-donor effect.

The electronic interaction between a metal ion and a coordinated ligand has been studied by many physical techniques.[1] The electronic spectra of ionic complexes[2] and the infrared spectra of octahedral metal carbonyls[3] have been particularly useful in assessing the nature of the metal-ligand bond. In complexes of the type $XMn(CO)_5$, the C=O stretching frequency of the carbonyl *trans* to the anionic ligand X can be related to the σ-donor and π-acceptor character of the Mn-X bond. A recent communication[4] described the use of F^{19} nmr shielding parameters of fluorophenylplatinum complexes (**1** and **2**) to study the Pt-X bond. A fuller description of this technique is reported here.



1



2

The F^{19} shielding parameter of a monosubstituted fluorobenzene is a very sensitive criterion of the electronic effect of the substituent.[5,6] An inductive elec-

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[1] Physical studies of metal-ligand interaction in the phenomenon of the *trans* effect are reviewed by F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[2] C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962.

[3] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references cited therein.

[4] G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 5367 (1964).

[5] L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

[6] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

tron donor such as the methyl group enhances the electron density through the aromatic ring and, as a consequence, shielding of the F^{19} nucleus increases. A substituent which withdraws electrons by an inductive process produces deshielding (negative chemical shift relative to fluorobenzene). In addition to this inductive effect observed in any ring position, substituents which donate or withdraw electrons by resonance mechanisms produce further shielding or deshielding of *o*- or *p*-fluorines.

The fluorophenylplatinum complexes **1** and **2** generally show strongly positive shielding parameters. The implication is that $-PtX(PEt_3)_2$ group, when bound to fluorobenzene, is an electron donor in both the inductive and resonance senses. There is a strong dependence of the shielding parameter on the nature of the *trans* substituent, X. The significance of these parameters will be considered separately for the *m*- and *p*-fluorophenyl compounds and also for the *cis* analogs of **1** and **2**.

Results

***m*-Fluorophenyl Compounds.** The F^{19} nmr shielding parameters for **1** with a variety of *trans* ligands (X) are shown in Table I. These values cover a range of about 4 ppm with the alkyl and aryl ligands producing much larger chemical shifts than the halide and pseudohalide ions. The shielding parameter sequence parallels the basicity[7] sequence of X as measured in a nonpolar solvent, *e.g.*, $CH_3^- > C_6H_5^- > C_6H_5C{\equiv}C^-$, and $CN^- > Cl^- > Br^- > I^-$. This result seems quite reasonable because the inductive enhancement of the F^{19} shielding parameter should be proportional to the electron density injected into the σ-bond system of the complex by the variable ligand X.

Table I. F^{19} Shielding Parameters (Δ_m) of 1

Ligand X	Solvent: Acetone	Solvent: Cyclohexane
CH_3	3.93	4.26
C_6H_5	3.46	3.72
$(C_2H_5)_3P$	3.35[a]	...
p-FC_6H_4	3.30	3.44
$C_6H_5C{\equiv}C$	3.21	3.37
m-FC_6H_4	3.07	...
OCN (or NCO)	2.30	2.48
CN	2.27	2.53
Cl	2.11	2.50
Br	1.97	2.34
SCN (or NCS)	1.75	1.90
I	1.56	2.00
$SnCl_3$	−0.23	...

[a] Average shielding parameter for five *cis* complexes.

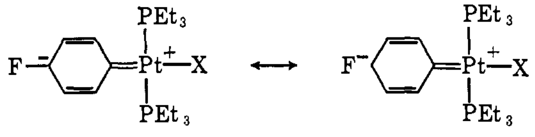
The chemical shift sequences determined in acetone and cyclohexane are mutually consistent except for the position of the halide ions. Although all the *m*-fluorophenyl complexes give smaller shielding parameters in acetone than in cyclohexane, this effect is particularly pronounced for Cl^-, Br^-, and I^-.

***p*-Fluorophenyl Compounds (Table II).** The F^{19} shielding parameters for **2** are much larger than those for the *m*-fluorophenyl compounds even though the *p*-fluorine is more remote from the donor substituent. This difference in magnitude can be explained by the contributions of resonance structures such as **2a** and **2b** which enhance the electron density at the *para* (and *ortho*) position.[8] This resonance effect, as noted earlier by Taft,[6] is superimposed on the inductive effect measured by the *meta* shielding parameter.

Table II. Parameters for Compound 2

Ligand X	F^{19} shielding parameter (Δ_p): In acetone	F^{19} shielding parameter (Δ_p): In cyclohexane	π-acceptor parameter[a]
CH_3	11.70	11.7	0
C_6H_5	10.9	10.9	0.3
p-FC_6H_4	10.8	10.8	0.3
m-FC_6H_4	10.6	10.5	0.3
$C_6H_5C{\equiv}C$	10.4	10.4	0.6
OCN (or NCO)	10.1	10.2	0
Cl	10.1	10.2	−0.2
Br	9.86	10.0	−0.1
I	9.54	9.70	−0.2
CN	9.32	9.11	0.7
SCN (or NCS)	9.29	9.20	0.2
$SnCl_3$	6.96	...	0.6

[a] This parameter is the difference, $(\Delta_p - \Delta_m)_{CH_3} - (\Delta_p - \Delta_m)_X$, using the values obtained in acetone solution.



2a **2b**

The sequence of shielding parameters for **2** is similar to that for **1** except for the positions of the potential π-acceptor ligands, $C_6H_5C{\equiv}C^-$, CN^-, and SCN^-. The somewhat smaller chemical shifts for the complexes containing these ligands are anticipated because a π-acceptor ligand on platinum will compete with the fluorophenyl ring for the electron density in the π orbitals of the complex.

In order to separate the resonance and inductive effects, the shielding parameter of **1** was subtracted from that of **2**. The differences $(\Delta_p - \Delta_m)_X$ for the various ligands were then subtracted from the difference $(\Delta_p - \Delta_m)_{CH_3}$ for the methyl group to give the π-acceptor parameter shown in Table II. The significance of this parameter is that it compares the π-acceptor capacity of a given ligand with that of a ligand with no accessible π orbitals.

Most of the π-acceptor abilities indicated by these parameters are in agreement with those obtained by other methods. The $C_6H_5C{\equiv}C^-$ and CN^- ions are strong acceptors, the aryl and thiocyanate ligands are

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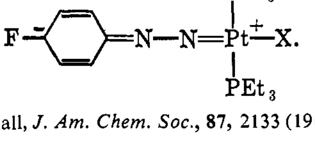
(7) (a) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962), and references cited therein; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

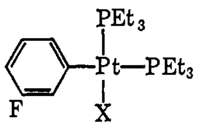
(8) Analogous resonance structures can be drawn for the arylazoplatinum compounds described in a preceding paper.[9] The author is indebted to the readers who pointed out that the resonance structure therein should have been rendered as



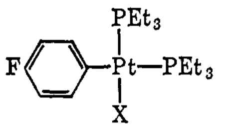
(9) G. W. Parshall, *J. Am. Chem. Soc.*, **87**, 2133 (1965).

modest π acceptors, and the cyanate[10] group has no π-acceptor tendencies. The most interesting results are those for $SnCl_3^-$, a strong π acceptor, and for the halide ions which give negative π-acceptor parameters. These negative values indicate that the halide ions are π donors in these platinum(II) complexes. The donor p_π action is probably stronger than the acceptor d_π action as predicted by Orgel.[11]

cis **Complexes.** The *cis* complexes **3** and **4** were studied in order to compare the electronic properties of triethylphosphine as a *trans* ligand with those of the anionic ligands. If the *cis* ligand (X) in **3** and **4** had properties similar to $(C_2H_5)_3P$, a valid comparison should be possible. Triethylphosphine could then be used as a standard to match sequences of anionic ligands against sequences of neutral ligands.



3



4

The F^{19} shielding parameters of **3** cover a relatively small range for the five ligands shown in Table III. The average of these five values, 3.35 ppm, places triethylphosphine as a σ-donor ligand comparable in strength to an aryl group (Table I). The shielding parameters of **4**, however, are less readily interpreted. The parameters themselves are somewhat larger than for the corresponding *trans* compounds (**2**). The range of values for $(\Delta_p - \Delta_m)$ is so large that a meaningful estimate of the π-acceptor character of $(C_2H_5)_3P$ cannot be made. The only sure conclusion is that the π interactions between *cis* ligands are much larger than the σ interactions.

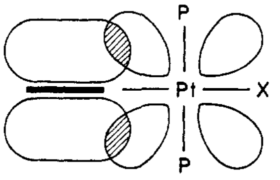
Table III. F^{19} Shielding Parameters of *cis* Compounds[a]

X	Compd 3	Compd 4
C_6H_5	3.55	11.6
p-FC_6H_4	3.55	11.4
m-FC_6H_4	3.44	11.2
CN	2.85	9.48
Cl	3.37	9.75

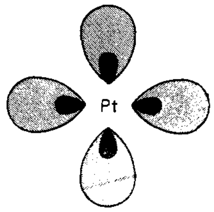
[a] All values measured in 2–5% solutions in acetone.

Discussion

The strongly positive F^{19} shielding parameters for the *p*-fluorophenylplatinum complexes **2** and **4** suggest extensive interaction between the π orbitals of the benzene ring and those of the platinum atom (*i.e.*, a large contribution from resonance stuctures such as **2a** and **2b**).[12] The orbital interactions believed to be responsible for this effect are pictured in structure I. The most favorable orientation of the benzene ring is probably perpendicular to the plane defined by the other three ligands, although free rotation doubtlessly occurs. If the ligands are placed on the *x* and *y* axes, the expansive $5d_{xy}$ orbital will overlap the π orbitals of the aromatic ring. A similar overlap will also take place between the $5d_{xy}$ orbital and any π orbitals on the *trans* ligand X. Thus, if X has filled p orbitals as in the halide ions, electron density is displaced in the direction of the ring and the shielding of the *p*-fluorine nucleus is enhanced. Vacant orbitals such as the π^* orbitals of the cyanide ion withdraw electrons from the aromatic ring and cause deshielding.



I



II

It should be noted that π-donor or -acceptor ligands in the *cis* position to the fluorophenyl ring can interact through the $5d_{xy}$ orbital in the same way. Hence, π-acceptor ligands should affect the detector ligand similarly whether in the *cis* or *trans* positions. The comparable large ranges of F^{19} shielding parameters for **2** and **4** are certainly in accord with this concept.

The small range of shielding parameters for the *cis*-*m*-fluorophenyl compounds (**3**) indicates a very small interaction between orthogonal σ orbitals. This lack of *cis* interaction is also manifest in the fact that P^{31}-P^{31} spin coupling between the phosphine ligands is much smaller in the *cis* than in the *trans* complexes.[13] The contrast between the magnitudes of *cis* and *trans* σ effects is probably due to the differences in effective overlap of *cis* and *trans* σ orbitals in square-planar complexes. As shown in structure II, the "tail" of each directed dsp^2 hybrid bond overlaps the *trans* orbital. There is little overlap between *cis* orbitals, however, and little electronic interaction is expected.

The results discussed here have interesting implications with regard to the mechanism of nucleophilic substitution of transition metal complexes. A dual mechanism has been proposed[14] for the *trans* effect, the phenomenon by which certain ligands labilize the *trans* ligand in a square-planar complex. Strong donor ligands were presumed to weaken the *trans* metal-ligand bond by polarization of the platinum atom, while π-acceptor ligands facilitate substitution by stabilizing the transition state during the reaction.

The polarization aspect of this dual mechanism can now be described more exactly by considering the orbital interactions as shown in structure II. Introduction of a strong σ-donor ligand such as R_3P or $C_6H_5^-$ into a σ orbital will displace electron density into the *trans* orbital and weaken the metal-ligand bond. However, as demonstrated by the F^{19} shielding parameter differences, even a strong donor ligand will have little effect on the *cis* ligands *via* the σ orbitals.

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(10) The infrared evidence for Pt–O *vs.* Pt–N bonding of the cyanate group is inconclusive. The CN and CO stretching vibrations are very similar to those of known metal isocyanates but some of the long wavelength absorption bands are obscured by aryl vibration modes: *cf.* J. Powell and B. L. Shaw, *J. Chem. Soc.*, 3879 (1965).

(11) L. E. Orgel, "An Introduction to Transition Metal Chemistry," Methuen and Co., London, 1960, p 37.

(12) An alternative explanation which cannot be rigorously excluded in this instance has been suggested by a referee. "The marked difference in shielding parameter for *meta*- and *para*-substituted phenyl, respectively, will arise when the substituent (platinum grouping in this case) is less electronegative than hydrogen. The alternating charges of the phenyl carbon atoms result from substitution in benzene whether or not the substituent can bond to the π system of the ring."

(13) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(14) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

The observed acceleration of *trans* substitution by π-acceptor ligands[1] is not predictable from the present results. The similarity in π-bonding effects in the *cis*- and *trans*-fluorophenylplatinum complexes suggests that a π-acceptor ligand should have similar effects on *cis* and *trans* substituents. However, the present measurements do not reflect interaction in the d_{xz} orbital which is believed to be involved in the stabilization of the transition state in *trans* substitution.

Implications for Catalysis. Studies of homogeneous catalysis have shown that the course of catalytic reactions is strongly dependent on the nature of the "nonreactive" ligands present on the catalytic metal atom. Characterization of the metal-ligand bond should aid in explaining this dependence. The present results show that two types of ligands, the $SnCl_3^-$ ion and the halide ion, have peculiar electron characteristics which may bear on their role in catalysis.

Platinum complexes stabilized by the $SnCl_3^-$ ligand have been found to catalyze the hydrogenation of olefins under mild conditions. They also facilitate the carbonylation of olefins to esters in alcoholic media.[15] Studies of the platinum-tin species present in these solutions have shown the existence of two five-coordinate species,[16] $[Pt(SnCl_3)_5]^{-3}$ and $[HPt(SnCl_3)_4]^{-3}$. The stabilization of this unusual coordination state of platinum is probably due to the $SnCl_3$ ligand. It is a very weak σ donor and strong π acceptor, a combination of properties very much like those of carbon monoxide. These characteristics prevent the buildup of negative charge on the central metal atom even when five negative ligands are assembled about it. The π-acceptor property probably also favors the trigonal bipyramidal arrangement of ligands predicted for a d^8 transition metal ion.[17] A similar stabilization of the five-coordinate state has been noted for tertiary stibine complexes of platinum.[18] The stibine and $SnCl_3^-$ ligands share the property of having vacant 5d orbitals of the proper size and symmetry to form π bonds with filled 5d orbitals of platinum.

The π-acceptor character of $SnCl_3^-$ makes it a powerful *trans*-activating ligand.[19] As a result, other ligands bound to the same transition metal atom are labilized. For example, the rate of ethylene exchange in Zeise's salt is greatly enhanced by a trace of $SnCl_2$.[20] The ligand lability is probably a key characteristic of catalytically active complexes.

Halide ions have been found to be desirable or essential in several homogeneously catalyzed reactions. For example, the solution polymerization of butadiene[21] by $RhCl_3$ and the rhodium-catalyzed dimerization of olefins[22] are dependent on the presence of halide. The unique π-donor characteristic of the halide anions found in the present study is probably a significant factor in this effect. The π-donor character added to the σ-donor properties of the ions probably has a powerful influence in labilizing metal-ligand σ bonds. As a result, insertion of an olefin into an alkyl-metal bond, as in coordination polymerization, should be facilitated.

Experimental Section

Spectral Properties. The F^{19} nmr spectra were determined at 56.4 Mc/sec on dilute solutions (2–10%) of the fluorophenylplatinum compounds in cyclohexane or acetone with fluorobenzene (10%) as an internal reference. Temperature and solvent dependence studies were made on *trans-m*-fluorophenyl-*p*-fluorophenylbis(triethylphosphine)platinum in order to determine the effects of these two variables on the chemical shift. The *p*-fluoro shielding parameter of this compound in toluene solution showed no change over the range of −46 to +100°. The *meta* parameter rose from 3.20 to 3.53 ppm over this range. The shielding parameters determined in toluene, CCl_4, CCl_3F, and benzene were very similar to those determined in cyclohexane.

The proton magnetic resonance spectra were determined on a Varian A-60 spectrometer with acetone-d_6 or carbon tetrachloride as the solvent and tetramethylsilane as an internal reference. The numbers of protons of different types were determined by integration and, in all cases, were in agreement with the assigned structures. The configurations of the complexes (*cis vs. trans*) were assigned by the technique of Jenkins and Shaw.[13] The *trans*-bis(triethylphosphine)platinum complexes showed a very characteristic five-line pattern for the methyl group ($J_{CH_2CH_3} = 7.8 \pm 0.5$, $J_{(P+P')H} = 16$ cps). The spectra of the *cis* complexes were much more complex and usually showed seven lines for the methyl resonance. The methylene absorptions were too complex for interpretation, and for the diaryl compounds they often overlapped the methyl peaks.

The infrared spectra were usually determined in CCl_4 solution on a Perkin-Elmer 237 grating spectrometer. When the long wavelength spectrum was desired, Nujol mulls of the complexes were scanned in the 250–4000 cm^{-1} range with a Perkin-Elmer 521 grating spectrometer.

Preparation of Complexes. ***trans*-Di-*m*-fluorophenyl- and -di-*p*-fluorophenylbis(triethylphosphine)platinum** were prepared by Grignard reactions of *trans*-dichlorobis(triethylphosphine)platinum as described previously.[9] The *trans*-chloro compounds (**1** and **2**, X = Cl) were prepared by HCl cleavage of the difluorophenyl compounds.[9] Analyses of these and the new complexes are shown in Table IV.

***cis*-Di-*m*-fluorophenylbis(triethylphosphine)platinum** was prepared by reaction of reaction of 50 ml of 1 *M* *m*-fluorophenylmagnesium bromide solution in ether with 6 g of *cis*-dichlorobis(triethylphosphine)platinum in 100 ml of benzene. The mixture was stirred at room temperature for 1 hr, and 10 ml of dioxane was added to precipitate the magnesium salts. The mixture was filtered, and the filtrate was evaporated to a volume of 20 ml. The long, white needles which form on standing were recrystallized from hexane, mp 159–160° dec.

***cis*-Di-*p*-fluorophenylbis(triethylphosphine)platinum** was prepared similarly as white crystals, mp 160–161°, from hexane.

***cis*-Chloro-*m*-fluorophenylbis(triethylphosphine)platinum** was prepared by treating a solution of 3.5 g of the di-*m*-fluorophenyl complex in toluene with an equimolar quantity of anhydrous hydrogen chloride in 20 ml of toluene. The reaction mixture was evaporated to dryness, and the residue was recrystallized from hexane to give white needles, mp 133–134°.

***cis*-Chloro-*p*-fluorophenylbis(triethylphosphine)platinum,** obtained similarly, was recrystallized from hexane to give white needles, mp 142–144°.

***trans*-*m*-Fluorophenyl-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained by treatment of 0.56 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum in 5 ml of ether with 3.0 ml of 1 *M* *p*-fluorophenylmagnesium bromide. After 1 hr at room temperature, the ether was evaporated, and the solid residue was extracted with hexane. On cooling, the hexane extract gave white crystals, mp 174°.

***cis*-*m*-Fluorophenyl-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained similarly from the *cis*-chloro-*m*-fluorophenyl compound. Crystallization from hexane gave clusters of white needles, mp 161–163° dec.

Phenyl-*m*-fluorophenylbis(triethylphosphine)platinum. A 0.30-ml portion of 2 *M* phenyllithium solution was added to a solution of 0.28 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum in 10 ml of hexane. After 1 hr at 25°, the mixture was filtered, and the filtrate was chromatographed on neutral alumina (activity

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(15) R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

(16) R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

(17) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

(18) A. D. Westland, *ibid.*, 3060 (1965).

(19) R. V. Lindsey, G. W. Parshall, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

(20) R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

(21) R. E. Rinehart, H. P. Smith, H. S. Witt, and H. Romeyn, Jr., *J. Am. Chem. Soc.*, **84**, 4145 (1962).

(22) R. D. Cramer, *ibid.*, **87**, 4717 (1965).

Table IV. Analyses of $FC_6H_4PtX(PEt_3)_2$ Isomers

			Found							
Ligand	Calculated		1		2		3		4	
X	C	H	C	H	C	H	C	H	C	H
m-FC_6H_4	46.36	6.16	46.72	5.97	...	...	46.84	6.26	...	...
p-FC_6H_4	46.36	6.16	47.06	6.31	46.76	6.26	46.62	6.31	46.44	6.22
C_6H_5	47.74	6.51	48.01	6.43	48.46	6.62	...	...	47.36	6.40
CH_3	42.13	6.89	42.18	6.63	41.45	6.56	...	...	...	...
CN	41.29	6.20	41.31	6.20	41.58	5.97	41.70	6.25	41.63	6.24
$C_6H_5C{\equiv}C$	49.75	6.27	50.11	6.42	49.92	6.19	...	...	...	...
CNO	40.13	6.03	39.74	6.31	39.68	6.36	...	...	...	...
CNS	39.03	5.86	38.52	5.94	38.97	5.78	...	...	...	...
Cl	38.46	6.10	38.72	6.06	38.30	6.00	38.52	6.28	38.86	6.27
Br	35.64	5.65	36.20	5.97	37.13	5.60	...	...	...	...
I	33.09	5.24	33.75	5.50	33.28	5.05	...	...	...	...
$SnCl_3$	28.77	4.57	29.08	4.84	28.77	4.43	...	...	...	...

grade 3). The first fraction was the *trans* isomer which formed colorless crystals, mp 187–188°, by recrystallization from hexane. A later fraction proved to be the *cis* isomer, mp 142–144°.

***cis*-Phenyl-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained similarly as white crystals, mp 159–160°, by recrystallization from a benzene–hexane mixture.

***trans*-Phenyl-*p*-fluorophenylbis(triethylphosphine)platinum** was formed by reaction of *p*-fluorophenylmagnesium bromide with *trans*-chlorophenylbis(triethylphosphine)platinum in hexane at room temperature. The *trans*-diaryl compound crystallized from hexane as white plates, mp 171–172°.

***trans*-Methyl-*m*-fluorophenylbis(triethylphosphine)platinum.** A solution of 0.56 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum in 5 ml of ether was stirred at 0° while 0.50 ml of 3 *M* methylmagnesium bromide solution was added dropwise. The mixture was allowed to warm to room temperature, and the solvent was evaporated in a nitrogen stream. The residue was extracted with benzene, and the extract was evaporated almost to dryness. The precipitate which formed was crystallized from hexane to give white crystals, mp 72–72.5°. The Pt-CH_3 peak in the H^1 nmr spectrum appeared at τ 10.67 as a triplet (J_{PH} = 6.0 cps) with Pt^{195} satellites (J_{Pt-H} = 50.0 cps).

***trans*-Methyl-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained as white needles, mp 83–84°, by recrystallization from hexane. The proton nmr spectrum showed the Pt-CH_3 peak at τ 10.08 as a triplet (J_{P-H} = 5.8 cps, J_{PtH} = 49.5 cps).

***trans*-Phenylethynyl-*m*-fluorophenybis (triethylphosphine)platinum** was obtained by treating 0.56 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum with 0.16 g of phenylethynyllithium in ether solution. The mixture was evaporated to dryness, and the residue was extracted with hexane. The clear, colorless filtrate was cooled to −78° to give white crystals of the product. Recrystallization from methanol gave long, white needles, mp 84–85°. The infrared spectrum (CCl_4 solution) contained a C≡C stretching band at 2105 cm^{-1}.

***trans*-Phenylethynyl-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained similarly as white needles, mp 114–115°, from methanol. The C≡C vibration appeared at 2110 cm^{-1}.

***trans*-Cyano-*m*-fluorophenylbis(triethylphosphine)platinum.** A solution of 0.03 g of potassium cyanide in 1.0 ml of 90% methanol was added to a solution of 0.24 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum in 3.0 ml of methanol. The milky mixture was stirred for 1 hr and was filtered. The filtrate was evaporated, and the residue was partitioned between ether and water. On cooling, the ether layer gave white crystals of the cyano complex, mp 97–99°. The infrared spectrum (CCl_4) showed a single sharp C≡N stretching band at 2130 cm^{-1}.

***trans*-Cyano-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained as white needles, mp 134–135°, by crystallization from hexane. The C≡N stretching absorption appeared at 2132 cm^{-1}.

***cis*-Cyano-*m*-fluorophenylbis(triethylphosphine)platinum** was prepared similarly from the *cis*-chloro compound. Recrystallization from benzene gave white needles, mp 129–130°.

***cis*-Cyano-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained as white needles, mp 144–145°, from acetone. The C≡N stretching band appeared at 2125 cm^{-1}.

***trans*-Isothiocyanato-*m*-fluorophenylbis(triethylphosphine)platinum.** A solution of 0.24 g of potassium thiocyanate and 0.24 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum in 3 ml of acetone was boiled for 10 min. The mixture was evaporated, and the residue was extracted with ether. Evaporation of the ether gave a white solid which produced white needles, mp 145–147°, on recrystallization from hexane. The infrared spectrum contained a CN stretching band at 2105 (CCl_4) or 2090 (KBr) cm^{-1} and C=S stretch as a shoulder at 817 cm^{-1}. This latter band seems to indicate that the product has the Pt—N=C=S structure in the solid state because it falls in the range of 780–860 cm^{-1} assigned to isothiocyanates.[23]

***trans*-Isothiocyanato-*p*-fluorophenylbis(triethylphosphine)platinum** was obtained similarly as fine, white needles, mp 109–110°, from hexane. The CN band appeared at 2107 cm^{-1} (CCl_4) and the C=S band at 823 cm^{-1} (KBr).

***trans*-Bromo-*m*-fluorophenylbis(triethylphosphine)platinum.** A solution of 0.24 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum and 1.0 g of lithium bromide in 15 ml of acetone was boiled under reflux for 10 min. Isolation as for the isothiocyanate complex gave white crystals, mp 94°.

***trans*-Bromo-*p*-fluorophenylbis(triethylphosphine)platinum,** prepared similarly, crystallized from hexane as white plates, mp 102–104°.

***trans*-Iodo-*m*-fluorophenylbis(triethylphosphine)platinum.** Metathesis of 0.24 g of *trans*-chloro-*m*-fluorophenylbis(triethylphosphine)platinum with 0.15 g of sodium iodide in 5 ml of acetone and isolation as for the isothiocyanate complex gave short white crystals, mp 122–123°.

***trans*-Iodo-*p*-fluorophenylbis(triethylphosphine)platinum** formed fine white crystals, mp 141–142°, from hexane.

***trans*-Phenyltrichlorotin(II) Bis(triethylphosphine)platinum.** A solution of 1.50 g of *trans*-chlorophenylbis(triethylphosphine)platinum in 23 ml of ethanol was stirred at room temperature with a solution of 0.66 g of $SnCl_2 \cdot 2H_2O$ in 5 ml of methanol. The mixture became yellow, and a white solid precipitated. Recrystallization from a 2:1 hexane–benzene mixture gave colorless crystals, mp 186–188° dec. The infrared spectrum in the 500–4000-cm^{-1} range was very similar to that of the starting chloro complex, but an Sn–Cl stretching absorption appeared as a doublet at 318 and 341 cm^{-1}. *Anal.* Calcd for $C_{18}H_{35}Cl_3P_2PtSn$: C, 29.46; H, 4.81; Cl, 14.50; Pt, 26.60; Sn, 16.18. Found: C, 29.91; H, 4.79; Cl, 14.96; Pt, 26.32; Sn, 15.66.

***trans*-*p*-Fluorophenyltrichlorotin(II) bis(triethylphosphine)platinum** was prepared similarly on a smaller scale. The product crystallized from acetone as clusters of white crystals, mp 169–171° dec. The SnCl stretching bands appeared at 322 and 343 cm^{-1}.

***trans*-*m*-Fluorophenyltrichlorotin(II) bis(triethylphosphine)platinum** was obtained in the same way as white crystals, mp 147–149° dec. The SnCl stretching absorption appeared at 318 and 341 cm^{-1}.

***trans*-Cyanato-*m*-fluorophenylbis(triethylphosphine)platinum** was prepared by boiling a solution of 0.25 g of the corresponding chloro complex and 0.7 g of potassium cyanate in 15 ml of acetone for 40 min. The mixture was evaporated and the residue was extracted with ether. The extract was evaporated and the residue was recrystallized from hexane to give white crystals, mp 86–87°. The infrared spectrum showed CN stretching at 2225 cm^{-1} and C–O stretching at 1325 cm^{-1}.

***trans*-Cyanato-*p*-fluorophenylbis(triethylphosphine)platinum** was prepared similarly as white crystals, mp 90–92°. The CN stretching band was at 2230 cm^{-1} and the C–O band at 1325 cm^{-1}.

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(23) (a) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961); (b) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).