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Spectroscopic Studies and Correlation Analysis of Substituent Effects in Arylplatinum(II) Complexes: Cis and Trans Influences of Aryl Ligands

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Spectroscopic data have been measured for arylplatinum(II) complexes of the types *trans*-PtX(C₆H₄Y)(PEt₃)₂ and [Pt(C₆H₄Y)(PEt₃)₃]BF₄, where X is H or Br and Y is one of a wide range of electron-withdrawing or electron-releasing substituents in the meta or para position to platinum. The results have been analyzed by means of Taft's dual substituent parameter (DSP) equation. Good correlations with the DSP equation are obtained for the following parameters: (1) Pt-H stretching frequencies, $\nu(\text{PtH})$, in PtH(C₆H₄-*m*-Y)(PEt₃)₂ and PtH(C₆H₄-*p*-Y)(PEt₃)₂, which increase as Y becomes more electron withdrawing; (2) hydride chemical shifts, $\delta(\text{PtH})$, in PtH(C₆H₄-*m*-Y)(PEt₃)₂, which move to lower frequency as Y becomes more electron withdrawing; (3) platinum-phosphorus coupling constants, $^1J(\text{PtP})$, *trans* to aryl in [Pt(C₆H₄-*m*-Y)(PEt₃)₃]BF₄, which increase as Y becomes more electron withdrawing; (4) platinum-phosphorus coupling constants, $^1J(\text{PtP})$, *cis* to aryl in all three series of compounds for both *m*- and *p*-Y, which decrease as Y becomes more electron withdrawing. In all cases meta substituents give a better fit to the DSP equation than do para substituents. Platinum-hydride coupling constants, $^1J(\text{PtH})$, in *trans*-PtH(C₆H₄Y)(PEt₃)₂ are surprisingly insensitive to the substituent. The existence of correlation 4, and the inverse linear correlation between $^1J(\text{PtP})$ (*cis* to aryl) and $\nu(\text{PtH})$ for *trans*-PtH(C₆H₄Y)(PEt₃)₂, provide evidence for a *cis* influence of aryl groups that is opposite in effect to their *trans* influence. The changes in $^1J(\text{PtP})$ in *trans*-PtX(C₆H₄Y)(PEt₃)₂ (X = Cl, Br; Y = *p*-N(CH₃)₂, *p*-CF₃, *p*-CO₂CH₃, H, *m*-CN, *m*-N(CH₃)₂) do not cause observable changes in the Pt-P bond lengths of the chloro complexes as determined by single-crystal X-ray analysis. In contrast, the Pt-Cl stretching frequencies, $\nu(\text{PtCl})$, measured in the solid state, correlate with the Pt-Cl bond lengths, although they do not vary systematically with the nature of the substituent Y.

Introduction

Spectroscopic studies of platinum(II) complexes containing tertiary phosphines have played an important role in the development of the *trans*-influence series, which gives a relative estimate of the ability of a ligand to weaken the bond *trans* to itself in the ground state of a complex.^{1,2} The wide range of hydrido complexes of general formula *trans*-PtHX(PR₃)₂ (X = various anionic or neutral ligands) has been a particularly rich source of information, and there have been many reports dealing with the dependence of the hydride chemical shift, δ_{H} , the platinum-195 to hydrogen coupling constant, $^1J(\text{PtH})$, and the platinum-hydrogen IR stretching frequency, $\nu(\text{PtH})$, on the ligand X *trans* to H.³⁻⁹ Our recent synthesis^{10,11} of complexes of this type in which X = CH₃ or C₆H₅ prompted us to prepare a series of hydrido complexes containing meta- and para-substituted aryl groups, *trans*-PtH(C₆H₄Y)(PEt₃)₂, in order to study the sensitivity of the spectroscopic parameters mentioned above to changes in the substituents.¹² We chose triethylphosphine as coligand because of its modest bulk and because the complexes are conveniently soluble in a range of solvents. We also wanted to probe possible *cis* effects by studying the variation of $^1J(\text{PtP})$ with Y; whereas the *trans* influence has been examined extensively by ³¹P NMR, the *cis* influence has received relatively little attention and is not well understood. The results obtained in this part of the work led us to study $^1J(\text{PtP})$ in the related series *trans*-PtBr-

(C₆H₄Y)(PEt₃)₂ and *trans*-[Pt(C₆H₄Y)(PEt₃)₃]BF₄.

There have been several attempts to use aryl groups as indicators of the bonding in platinum(II) complexes. The difference in the ¹⁹F NMR chemical shifts of *p*- and *m*-fluorophenyl complexes of the type *trans*-PtX(C₆H₄F)(PEt₃)₂ has been related to the electronic characteristics of the *trans*-ligand X,¹³ and the ¹³C NMR spectra of phenylplatinum(II) complexes have been studied with a similar aim.^{14,15}

Experimental Section

Synthesis. (1) *trans*-PtBr(C₆H₄Y)(PEt₃)₂. These complexes were prepared by oxidative addition of the appropriate *m*- or *p*-substituted bromobenzene (obtained commercially or prepared by standard procedures) to Pt(PEt₃)₄¹⁶ in toluene, following a literature procedure.¹⁷ Yields of pure products based on K₂PtCl₄ were generally 60–85% after one or two recrystallizations from aqueous methanol or dichloromethane/*n*-hexane. Some difficulty was encountered in the preparation of the *m*- and *p*-cyano derivatives owing to competing oxidative addition of the Ar-CN bond.¹⁷ Reaction mixtures containing Pt(PEt₃)₄ and *m*- or *p*-bromonitrobenzene in toluene rapidly turned black after only 5 min of heating near reflux temperature, and the required platinum(II) complexes were obtained in poor yield after chromatography on silica gel in dichloromethane and several recrystallization from either dichloromethane/*n*-hexane or boiling *n*-hexane. Analytical and melting point data are given in Table I (supplementary material).

(2) *trans*-PtH(C₆H₄Y)(PEt₃)₂. These complexes were prepared by NaBH₄ reduction of *trans*-[Pt(C₆H₄Y)(CH₃OH)(PEt₃)₂]BF₄, as described for the phenyl and *p*-bromophenyl complexes.¹¹ The crude products obtained by evaporation of methanol, extraction with *n*-hexane, and evaporation of the *n*-hexane were substantially pure as judged by their IR and NMR (¹H, ³¹P{¹H}) spectra, yields being generally >70%. Analytical samples were obtained as white or pale cream crystals by low-temperature crystallization from *n*-hexane, *n*-pentane, isopentane, or methanol. Some of the complexes melted below room temperature, and these were stored as solids at -78 °C until analyzed.

As in (1), reactions involving the *m*- and *p*-cyano and *m*- and *p*-dimethylamino derivatives behaved somewhat exceptionally. In the former case, the cyanoaryl group of one molecule appeared to be acting as a donor to a second platinum center in the cationic intermediate,

- (1) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422 and references therein.
- (2) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707–1710.
- (3) Powell, J.; Shaw, B. L. *J. Chem. Soc.* **1965**, 3879–3881.
- (4) Atkins, P. W.; Green, J. C.; Green, M. L. H. *J. Chem. Soc. A* **1968**, 2275–2280.
- (5) Church, M. J.; Mays, M. J. *J. Chem. Soc. A* **1968**, 3074–3078.
- (6) Chatt, J.; Duncanson, L. A.; Shaw, B. L.; Venanzi, L. M. *Discuss. Faraday Soc.* **1959**, No. 25, 131–137. Chatt, J. *Proc. Chem. Soc., London* **1962**, 318–326.
- (7) Dean, R. R.; Green, J. C. *J. Chem. Soc. A* **1968**, 3047–3050.
- (8) Keskinen, A. E.; Senoff, C. V. *J. Organomet. Chem.* **1972**, *37*, 201–208.
- (9) Toniolo, L.; Cavinato, G. *Inorg. Chim. Acta* **1978**, *26*, L5–L6.
- (10) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C17–C20.
- (11) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.*, preceding paper in this issue.
- (12) Some of this work has been reported briefly: Arnold, D. P.; Bennett, M. A.; Crisp, G. T.; Jeffery, J. C. *Adv. Chem. Ser.* **1982**, No. 196, 196–212.

- (13) Parshall, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 704–708.
- (14) Clark, H. C.; Ward, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 1741–1748.
- (15) Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111–3119.
- (16) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *21*, 110–111.
- (17) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360–2366.

and reaction with an approximately equimolar quantity of NaBH_4 at ca. -40°C was incomplete. Better yields of the required *trans*- $\text{PtH}(\text{C}_6\text{H}_4\text{CN})(\text{PEt}_3)_2$ complexes were obtained by use of an excess ($>5:1$) of NaBH_4 at room temperature, although the liquid *m*-cyano derivative was not obtained analytically pure. Addition of AgBF_4 to *trans*- $\text{PtBr}(\text{C}_6\text{H}_4\text{-}m\text{-NMe}_2)(\text{PEt}_3)_2$ and *trans*- $\text{PtBr}(\text{C}_6\text{H}_4\text{-}p\text{-NMe}_2)(\text{PEt}_3)_2$ produced red and purple colorations, respectively, which faded almost completely when the AgBr precipitated. Addition of NaBH_4 in the usual way gave good yields of the desired hydrido complexes.

Melting points, recrystallization solvents, and elemental analyses for the new hydrido complexes are given in Table II (supplementary material).

(3) $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_3]\text{BF}_4$. The solvento salts *trans*- $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{acetone})(\text{PEt}_3)_2]\text{BF}_4$ were generated by addition of an equimolar quantity of AgBF_4 to *trans*- $\text{PtBr}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$ in acetone and were isolated as colorless oils after filtration of AgBr and evaporation of acetone. These were dissolved in dichloromethane, an equimolar amount of triethylphosphine was added, and the solutions were filtered into NMR tubes. Dichloromethane was added so that the volume of solution was the same for the whole series, the concentration of $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_3]\text{BF}_4$ being 0.12–0.15 M. The parent compound $[\text{Pt}(\text{C}_6\text{H}_5)(\text{PEt}_3)_3]\text{BF}_4$ was isolated as colorless crystals, mp $210\text{--}213^\circ\text{C}$, by evaporation of dichloromethane, trituration of the residual solid with ether, and drying in vacuo. Anal. Calcd for $\text{C}_{24}\text{H}_{50}\text{BF}_4\text{P}_3\text{Pt}$: C, 40.4; H, 7.1; P, 13.0. Found: C, 40.5; H, 7.0; P, 13.1.

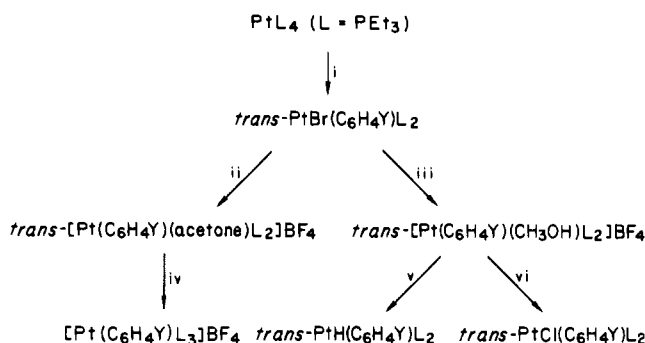
(4) *trans*- $\text{PtCl}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$. These complexes were prepared by addition of a fivefold excess of lithium chloride in methanol to solutions of *trans*- $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{MeOH})(\text{PEt}_3)_2]\text{BF}_4$ generated by abstraction of bromide from *trans*- $\text{PtBr}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$ with AgBF_4 in methanol. The crude products were recrystallized from aqueous methanol to yield colorless crystals in almost quantitative yield. The *p*- NMe_2 and *m*- NMe_2 derivatives produced the same purple and red colorations as mentioned in (2), and even after addition of lithium chloride and several recrystallizations, the complex *trans*- $\text{PtCl}(\text{C}_6\text{H}_4\text{-}p\text{-NMe}_2)(\text{PEt}_3)_2$ was still tinged with purple.

Spectroscopic Measurements. Infrared spectra of the complexes *trans*- $\text{PtH}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$ in the $1900\text{--}2000\text{-cm}^{-1}$ region were run in hexane and acetone solutions (0.06–0.08 M) in 0.2 mm path length cells on a Perkin-Elmer PE225 instrument and were calibrated by use of ^{13}CO . The $\nu(\text{PtH})$ bands are very strong but broad, and reproducibility of ν_{max} was estimated to be not better than $\pm 2\text{ cm}^{-1}$. Infrared spectra in the $\nu(\text{PtCl})$ region for *trans*- $\text{PtCl}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$ were run in CsI disks on a Hitachi FIS-3 grating instrument. Proton NMR spectra were run on a Varian HA-100 spectrometer in benzene- d_6 and acetone- d_6 solutions at 30°C , using Me_4Si as internal lock. Chemical shifts, δ_{H} , and coupling constants, $^1J(\text{PtH})$, were measured by the difference in frequency between the lock signal and the required peak, with use of the frequency counter on the spectrometer console. The peak positions were measured several times and averaged. Reproducibility was ca. ± 0.02 ppm for δ_{H} and ± 4 Hz for $^1J(\text{PtH})$. Phosphorus-31 ($^{31}\text{P}\{\text{H}\}$) NMR spectra were run on a modified Bruker 322S spectrometer operating at 24.3 MHz for ^{31}P . Solvents and temperatures used for the various series of complexes are indicated in the tables. Some series of measurements were made at -40°C because of the marked increase in signal-to-noise ratio on our instrument at this temperature. Chemical shifts are given in ppm to high frequency of external 85% H_3PO_4 . Reproducibility was ca. ± 2 Hz.

Results and Discussion

Synthesis. The complexes *trans*- $\text{PtX}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$ ($\text{X} = \text{H}, \text{Br}, \text{Cl}$) and $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_3]\text{BF}_4$ required for our study were prepared from $\text{Pt}(\text{PEt}_3)_4$ as outlined in Scheme I. The oxidative-addition route provides access to σ -aryl complexes spanning a far wider range of substituents than is usual in organo transition-metal chemistry; this is especially true of aryls containing unsaturated substituents which would be incompatible with Grignard or organolithium reagents. Except for the hydrido complexes, all the new compounds are air-stable, colorless solids. Like the parent compound *trans*- $\text{PtH}(\text{C}_6\text{H}_5)(\text{PEt}_3)_2$,¹¹ several of the hydrides are oils at room temperature and most, especially those of the meta series, are unstable to light and heat, particularly when molten. All the

Scheme I. Preparation of Platinum(II) Complexes from $\text{Pt}(\text{PEt}_3)_4$ ^a



^a Legend: (i) $\text{YCl}_2\text{H}_4\text{Br}$, toluene, 110°C ; (ii) AgBF_4 , acetone; (iii) AgBF_4 , CH_3OH ; (iv) L, CH_2Cl_2 ; (v) NaBH_4 , CH_3OH ; (vi) LiCl , CH_3OH .

hydrides can be stored at -20°C under nitrogen for several weeks without decomposition.

Analysis of Substituent Effects. The effect of substituent Y on the various spectroscopic parameters was analyzed by use of the dual substituent parameter (DSP) approach put forward by Taft et al.¹⁸ (eq 1), where $P(\text{Y})$ and $P(\text{H})$ are the

$$P(\text{Y}) - P(\text{H}) = \rho_1\sigma_1 + \rho_R\sigma_R^0 \quad (1)$$

properties for an aromatic compound with substituent Y and for the unsubstituted compound respectively, σ_1 is a parameter proportional to a polar substituent effect in an aliphatic system, σ_R^0 is a quantitative measure of the ability of a substituent to delocalize electrons into or from an unperturbed benzene ring, and ρ_1 and ρ_R are coefficients of the susceptibility of $P(\text{Y}) - P(\text{H})$ to these two effects. We shall refer to these two terms as "inductive" and "resonance" effects, respectively, in this paper. The values of σ_1 and σ_R^0 for the various substituents are taken from ref 19.

The results of this treatment for the various properties and series of compounds we have studied are collected in Table III, which gives values of ρ_1 , ρ_R , f and λ , together with the estimated error in λ . For ease of reference, each combination of property and complex type has been assigned a code number, which will be used throughout the text. The quantity f represents the "goodness of fit" of the data to eq 1 and is equal to the ratio of the root mean square of the deviations to the root mean square of the $P(\text{Y}) - P(\text{H})$ values. Previous work^{18,20} has indicated that values of $f < 0.1$ indicate an excellent fit and those between 0.1 and 0.2 an acceptable fit. The results can be shown graphically as a plot of $P(\text{Y}) - P(\text{H})$ vs. $\bar{\sigma}$, $\bar{\sigma}$ being defined in terms of the four parameters in eq 1 as

$$\bar{\sigma} = \frac{\sigma_1 + \lambda\sigma_R^0}{1 + |\lambda|} \quad (2)$$

where $\lambda = \rho_R/\rho_1$.

In three of the six series of complexes studied, recommended minimum basis sets of substituents¹⁹ were used, *viz.* $\text{N}(\text{CH}_3)_2$, OCH_3 , F, Br, H, CF_3 , CN, and CO_2CH_3 , plus either or both of COCH_3 and NO_2 in some cases. The only omission in the other three series is Br.

IR Spectra of *trans*- $\text{PtH}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$ (Code Numbers 1, 2, 6, and 7). The $\nu(\text{PtH})$ band in solutions of all the complexes studied appears as a very strong, broad absorption in the $1900\text{--}2000\text{-cm}^{-1}$ region. Values in acetone and *n*-hexane

(18) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80.

(19) Bromilow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766–4770.

(20) Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 1–20.

Table III. Values of Coefficients ρ_I , ρ_R , and λ and Goodness of Fit Parameters f for Arylplatinum(II) Complexes

code no.	complex	property	ρ_I	ρ_R	f	λ	est error in λ
1	<i>trans</i> -PtH(C ₆ H ₄ - <i>p</i> -Y)(PEt ₃) ₂	ν (PtH) (acetone)	28.3	13.4	0.12	0.47	0.06
2		ν (PtH) (hexane)	30.6	11.5	0.14	0.38	0.09
3		δ_H (acetone- <i>d</i> ₆)	0.35	0.37	0.33	1.06	0.35
4		δ_H (benzene- <i>d</i> ₆)	0.64	0.68	0.26	1.06	0.27
5		¹ J(PtP)	-71.4	-34.9	0.18	0.49	0.11
6	<i>trans</i> -PtH(C ₆ H ₄ - <i>m</i> -Y)(PEt ₃) ₂	ν (PtH) (acetone)	35.9	18.4	0.04	0.51	0.03
7		ν (PtH) (hexane)	37.3	18.6	0.10	0.50	0.07
8		δ_H (acetone- <i>d</i> ₆)	0.62	0.20	0.12	0.32	0.08
9		δ_H (benzene- <i>d</i> ₆)	0.81	0.27	0.14	0.33	0.09
10		¹ J(PtP)	-75.4	-41.7	0.08	0.55	0.06
11	<i>trans</i> -PtBr(C ₆ H ₄ - <i>p</i> -Y)(PEt ₃) ₂	¹ J(PtP)	-135	-61.0	0.16	0.45	0.09
12	<i>trans</i> -PtBr(C ₆ H ₄ - <i>m</i> -Y)(PEt ₃) ₂	¹ J(PtP)	-153	-84.8	0.08	0.55	0.06
13	[Pt(C ₆ H ₄ - <i>p</i> -Y)(PEt ₃) ₃]BF ₄	¹ J(PtP, trans to Ar)	64.2	-35.4	0.23	-0.55	0.18
14		¹ J(PtP, cis to Ar)	-123	-56.5	0.15	0.46	0.07
15	[Pt(C ₆ H ₄ - <i>m</i> -Y)(PEt ₃) ₃]BF ₄	¹ J(PtP, trans to Ar)	109	48.0	0.16	0.44	0.10
16		¹ J(PtP, cis to Ar)	-136	-73.6	0.03	0.54	0.02

Table IV. Spectroscopic Data for *trans*-PtH(C₆H₄-*p*-Y)(PEt₃)₂ Complexes^e

Y	δ_H^a	δ_H^b	¹ J(PtH) ^a	¹ J(PtH) ^b	ν (PtH) ^a	ν (PtH) ^c	δ_P^d	¹ J(PtP) ^d
N(CH ₃) ₂	-6.85	-6.35	656	654	1937	1934	17.9	2808
OCH ₃	-6.98	-6.49	654	654	1942	1941	17.7	2800
F	-7.18	-6.78	653	655	1949	1948	17.5	2781
Br	-7.23	-6.85	647	650	1952	1949	17.0	2773
CH ₃	-7.01	-6.54	649	651	1940	1936	17.5	2803
H	-7.09	-6.67	649	648	1941	1937	17.3	2800
CF ₃	-7.29	-7.02	644	645	1955	1951	17.1	2766
CN	-7.33	-7.03	644	645	1958	1956	20.1	2754
CO ₂ CH ₃	-7.13	-6.81	641	643	1948	1945	17.1	2773
COCH ₃	-7.13	-6.77	642	643	1950	1946	17.3	2786
NO ₂	-7.34	-7.30	641	644	1962	1960	17.2	2747

^a In acetone. ^b In C₆D₆. ^c In hexane. ^d In C₆H₆. ^e J values are in Hz and ν values in cm⁻¹.

Table V. Spectroscopic Data for *trans*-PtH(C₆H₄-*m*-Y)(PEt₃)₂ Complexes^e

Y	δ_H^a	δ_H^b	¹ J(PtH) ^a	¹ J(PtH) ^b	ν (PtH) ^a	ν (PtH) ^c	δ_P^d	¹ J(PtP) ^d
N(CH ₃) ₂	-7.01	-6.56	650	648	1934	1931	18.3	2820
OCH ₃	-7.14	-6.74	650	649	1942	1938	17.9	2798
F	-7.36	-7.01	650	650	1953	1948	17.6	2773
CH ₃	-7.02	-6.68	648	648	1937	1934	17.5	2805
H	-7.09	-6.67	649	648	1941	1937	17.3	2800
CF ₃	-7.33	-7.03	652	650	1958	1955	17.3	2761
CN	-7.49	-7.21	656	654	1963	1961	17.0	2756
CO ₂ CH ₃	-7.22	-6.86	650	651	1951	1947	17.6	2778
NO ₂	-7.50	-7.20	657	656	1967	1964	17.1	2747

^a In acetone. ^b In C₆D₆. ^c In hexane. ^d In C₆H₆. ^e J values are in Hz and ν values in cm⁻¹.

are given in Table IV (para-substituted series) and Table V (meta-substituted series). Results of the DSP analysis of these data can be seen in Table III opposite code numbers 1, 2, 6, and 7 and are shown graphically for numbers 1 and 6 (ν (PtH) in acetone) in Figure 1. The values of f indicate good to excellent fits of the data to eq 1, especially for the meta-substituted complexes. The positive ρ values reflect the fact that ν (PtH) increases as the aryl group becomes more electron withdrawing, an effect that is also qualitatively evident in the series *trans*-PtHXL₂ as the anionic ligand becomes more electron withdrawing.^{3,6,11} In the series of *m*- and *p*-substituted benzoato complexes *trans*-PtH(OCOC₆H₄Y)(PEt₃)₂, ν (PtH) correlates well with the pK_a of the corresponding benzoic acid⁴ and in the thiopheno complexes *trans*-PtH(SC₆H₄Y)(PPh₃)₂ there is a reasonable correlation of ν (PtH) with Hammett substituent parameters σ_p .⁸ In such closely related series of complexes, changes in ν (PtH) may reflect changes in the Pt-H bond length.⁴

In our complexes, the fact that ρ_I and ρ_R are higher for the meta series than for the para series implies that ν (PtH) is more sensitive to changes in substituent at the meta position than at the para position. This observation indicates that the aryl ligands transmit their effect to the Pt-H bond by a predominantly inductive mechanism, because there are fewer inter-

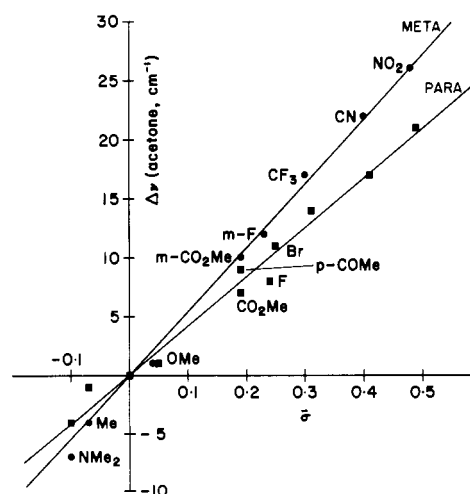


Figure 1. Plot of $\Delta\nu$ (PtH) (cm⁻¹) vs. σ , where $\Delta\nu$ (PtH) = ν (PtH) for *trans*-PtH(C₆H₄Y)(PEt₃)₂ in acetone minus ν (PtH) for *trans*-PtH(C₆H₅)(PEt₃)₂ in acetone.

vening bonds for the meta substituent. The fact that λ ($= \rho_R/\rho_I$) is ≤ 0.5 in all cases also suggests that inductive effects

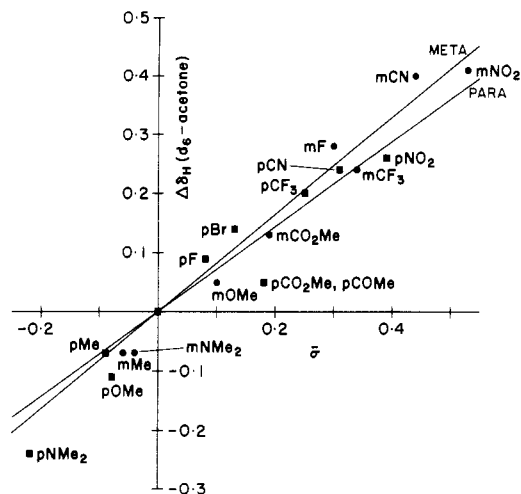


Figure 2. Plot of $\Delta\delta_{\text{H}}$ (ppm) vs. σ , where $\Delta\delta_{\text{H}} = \delta_{\text{H}}$ for *trans*-PtH($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂ in acetone-*d*₆ minus δ_{H} for *trans*-PtH(C_6H_5)(PEt_3)₂ in acetone-*d*₆.

must predominate over resonance effects for both *meta* and *para* series. Although resonance effects appear to be more important in the former than in the latter (i.e. $\lambda_{\text{m}} > \lambda_{\text{p}}$), the difference is not statistically significant since the estimated errors are such that the range of values $\lambda_{\text{m}} \pm \sigma$ and $\lambda_{\text{p}} \pm \sigma$ overlap. "Through-space" field effects are apparently fairly small, since there is no significant difference in the ρ values between the polar solvent acetone and the nonpolar solvent *n*-hexane.

The total extent of the substituent effects, i.e. the range of values from $\text{Y} = p\text{-NO}_2$ to $\text{Y} = p\text{-N}(\text{CH}_3)_2$ (or $p\text{-NH}_2$)⁸, is 25 cm^{-1} for *trans*-PtH($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂, 17 cm^{-1} for *trans*-PtH($\text{SC}_6\text{H}_4\text{Y}$)(PPh_3)₂,⁸ and 13 cm^{-1} for *trans*-PtH(OCOC₆H₄Y)(PEt_3)₂,⁴ which demonstrates the attenuation of electronic effects as the para substituent is respectively five, six, and seven bonds removed from the platinum atom.

¹H NMR Spectra of *trans*-PtH($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂ (Code Numbers 3, 4, 8, and 9). (1) **Hydride Chemical Shifts.** The hydride resonance in these complexes appears as a broad triplet with ¹⁹⁵Pt satellites in the region δ -6 to -7.¹¹ The values of δ_{H} for solutions of the complexes in acetone-*d*₆ and C₆D₆ are given in Tables IV and V for para and meta substituents, respectively. The results of DSP analysis are presented in Table III, and those for code numbers 3 and 8 are plotted in Figure 2.

Qualitatively, the values of δ_{H} are consistent with the high trans influence of aryl groups in comparison with that of electronegative ligands such as chloride, e.g. δ_{H} for *trans*-PtHCl(PEt_3)₂ in C₆H₆ is -16.9.²¹ The total range of δ_{H} is only 0.49 ppm ($p\text{-NO}_2$ to $p\text{-N}(\text{CH}_3)_2$ in acetone-*d*₆). Remarkably, a similar range of values, 0.46 ppm, was found by Atkins et al.⁴ in their study of a series of benzoato complexes *trans*-PtH(OCOC₆H₄Y)(PEt_3)₂, even though the aryl group in this case is two bonds further removed from the hydride ligand than in the hydridoaryl complexes. Despite the small range, δ_{H} for the benzoato complexes correlates linearly with the electronic effect of substituent Y expressed in terms of the pK_{a} of the corresponding benzoic acid. Application of the DSP treatment to the data for the *p*-substituted benzoato complexes gives the results

$$\delta_{\text{H}}^{\text{Y}} - \delta_{\text{H}}^{\text{H}} = 0.38\sigma_{\text{I}} + 0.34\sigma_{\text{R}}^0 \quad f = 0.12$$

$$\lambda = 0.89 \pm 0.13$$

In the case of the *trans*-PtH($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂ complexes, δ_{H} for the para series shows a fairly poor fit to the DSP equation,

with $f = 0.33$ (acetone-*d*₆) and 0.26 (C₆D₆). The values of f for the meta series are much better ($f = 0.12$ and 0.14, respectively). The λ values are consistent between the two solvents (ca. 1 for the para series, ca. 0.3 for the meta series) and, despite the large possible error in λ_{para} , indicate the expected greater dependence on resonance interactions for the para series. The positive value of ρ reflects the fact that electron-withdrawing substituents cause δ_{H} to move to lower frequency, as found in previous studies on platinum(II) hydrides.^{1,4,9}

Atkins et al.⁴ observed a correlation between δ_{H} (τ_{H}) and $\nu(\text{PtH})$ for the benzoato complexes and interpreted it in terms of changes in the Pt-H bond length. We also find a good correlation between δ_{H} and $\nu(\text{PtH})$ (in acetone) for the meta series ($r = -0.980$), but the correlation is only fair for the para series ($r = 0.953$).

(2) **Pt-H Coupling Constants.** The data for ¹J(PtH) are presented in Tables IV and V for the para and meta substituents, respectively. The values lie between 641 Hz ($\text{Y} = p\text{-NO}_2$ in acetone-*d*₆) and 657 Hz ($\text{Y} = m\text{-NO}_2$ in acetone-*d*₆), the range being only 15 Hz for the para series and 9 Hz for the meta series. Since the reproducibility of the measurements is ca. 4 Hz, the variation of ¹J(PtH) with substituent must be regarded as negligible and the data have not been subjected to DSP analysis. In contrast, the ranges of ¹J(PtH) for the thiophenoxy series *trans*-PtH(SC₆H₄Y)(PPh_3)₂⁸ and the benzoato series *trans*-PtH(OCOC₆H₄Y)(PEt_3)₂⁴ are 52 and 48.7 Hz, respectively.

In the series *trans*-PtHXL₂, an increase in the electron-withdrawing ability of X generally causes an increase in the magnitude of ¹J(PtH), and on this basis a fairly consistent NMR trans-influence series has been developed which encompasses a wide range of ligand types, i.e. C donors > P donors > As donors > S donors > N donors > halides > O donors.¹ The trend is well illustrated by comparing our results with those for the hydridobenzoato and hydrido(thiophenoxy) complexes, viz. ¹J(PtH) = 648 Hz for *trans*-PtH(C_6H_5)(PEt_3)₂,¹¹ 969 Hz for *trans*-PtH(SC₆H₅)(PPh_3)₂,⁸ and 1179 Hz for *trans*-PtH(OCOC₆H₅)(PEt_3)₂.⁴ DSP analysis of the published data for para-substituted benzoato⁴ and thiophenoxy⁸ complexes respectively gives the results

$$J(\text{Y}) - J(\text{H}) = 38.2\sigma_{\text{I}} + 37.7\sigma_{\text{R}}^0 \quad f = 0.10$$

$$\lambda = 0.99 \pm 0.11$$

$$J(\text{Y}) - J(\text{H}) = 42.9\sigma_{\text{I}} + 47.2\sigma_{\text{R}}^0 \quad f = 0.14$$

$$\lambda = 1.10 \pm 0.14$$

Comparison of the data for each of these series and between them shows as expected that stronger donors cause ¹J(PtH) to decrease in magnitude. This trend has been explained by arguing that an increase in the σ -donor ability of the ligand X trans to H will make a higher demand on the Pt 6s orbital in the Pt-X bond, thus reducing its availability in the Pt-H bond. This will lower ¹J(PtH), if the usual assumption is made that ¹J(PtH) is determined mainly by the Fermi contact contribution.^{1,2} The insensitivity of ¹J(PtH) in the series *trans*-PtH($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂ suggests that this argument is invalid when two similar strong σ donors (hydride and aryl) are mutually trans.

³¹P{¹H} NMR Spectra of *trans*-PtH($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂ (Code Numbers 5 and 10), for *trans*-PtBr($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂ (Code Numbers 11 and 12), and for [Pt($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₃]BF₄ (Code Numbers 13-16). The ³¹P{¹H} NMR spectra of the bis(triethylphosphine) complexes appear as a singlet with ¹⁹⁵Pt satellites, while those of the tris(triethylphosphine) complexes consist of an AB₂ pattern whose satellites are first-order doublets and triplets. Computer analysis of one of these spectra gave the same ¹J(PtP) values, within instrumental error, as those determined by measurement from the spectrum,

(21) Parshall, G. W. *Inorg. Synth.* 1970, 12, 26-33.

Table VI. ^{31}P NMR Data for $\text{trans-PtBr}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$ Complexes^{a, b}

Y	para		meta	
	δ_{P}	$^1J(\text{PtP})$	δ_{P}	$^1J(\text{PtP})$
$\text{N}(\text{CH}_3)_2$	12.2	2793	11.8	2810
OCH_3	11.9	2771	11.5	2776
F	11.7	2729	11.4	2729
Br	nm	nm	11.1	2717
CH_3	11.7	2783	11.5	2788
H	11.6	2776	11.6	2776
CF_3	11.0	2715	11.2	2705
CN	10.9	2698	11.2	2676
CO_2CH_3	11.0	2729	11.2	2732
COCH_3	12.0	2732	nm	nm
NO_2	nm	nm	12.3	2668

^a Measured on ca. 0.15 M solutions in C_6H_6 at 28 °C. J values are in Hz. ^b Abbreviations: nm, not measured.

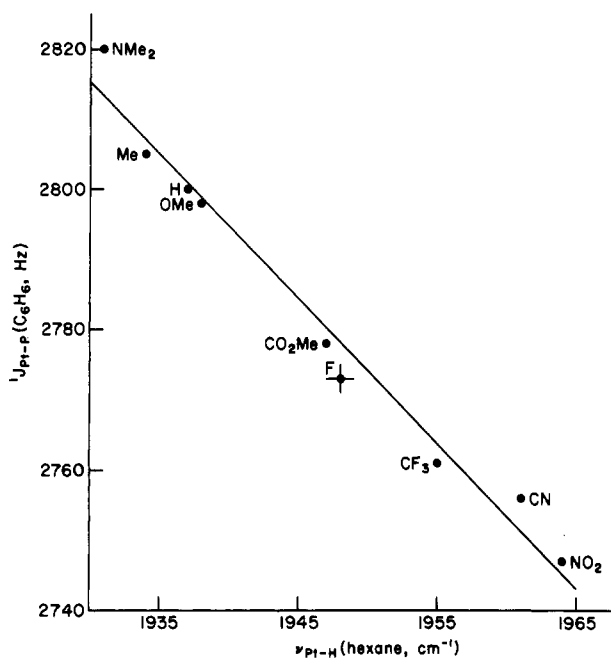


Figure 3. Plot of $^1J(\text{PtP})$ (Hz, C_6H_6) vs. $\nu(\text{PtH})$ (cm^{-1} , n -hexane) for $\text{trans-PtH}(\text{C}_6\text{H}_4\text{-}m\text{-Y})(\text{PEt}_3)_2$.

so values for all compounds have been obtained by the latter method. The values of δ_{P} and $^1J(\text{PtP})$ are given in Table IV for $\text{trans-PtH}(\text{C}_6\text{H}_4\text{-}p\text{-Y})(\text{PEt}_3)_2$, Table V for $\text{trans-PtH}(\text{C}_6\text{H}_4\text{-}m\text{-Y})(\text{PEt}_3)_2$, Table VI for $\text{trans-PtBr}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_2$, and Table VII for $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_3]\text{BF}_4$. Clearly the ^{31}P chemical shifts vary only slightly within each series, the hydrido complexes having δ_{P} ca. 17, the bromo complexes ca. 11, and the tris(triethylphosphine) complexes ca. 1 for P trans to aryl and 6 for P cis to aryl.

The coupling constant data can be conveniently divided into two groups according to whether the PEt_3 ligand is cis to aryl (code numbers 5, 10–12, 14, and 16) or trans to aryl (code numbers 13 and 15). DSP analyses for the first group give good fits for the para series (5, 11, and 14) and excellent fits for the meta series (10, 12, and 16). The negative signs for ρ reflect the fact that electron-withdrawing substituents cause a decrease in $^1J(\text{PtP})$ for all the complexes studied. Figures 3 and 4 show that in the hydridoaryl series $\text{PtH}(\text{C}_6\text{H}_4\text{-}m\text{-Y})(\text{PEt}_3)_2$ and $\text{PtH}(\text{C}_6\text{H}_4\text{-}p\text{-Y})(\text{PEt}_3)_2$ there is an excellent inverse linear correlation between $^1J(\text{PtP})$ and $\nu(\text{PtH})$ ($r = -0.988$ and -0.972 , respectively). These data provide convincing evidence for the operation of a cis influence, which, at least in these complexes, is opposite in effect to the trans influence, i.e. electron-donating substituents in the aryl group weaken the trans bond and strengthen the cis bond. The

Table VII. ^{31}P NMR Data for $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_3]\text{BF}_4$ ^a

Y	$\delta_{\text{P}}(\text{trans to Ar})$	$^1J(\text{PtP})^b$	$\delta_{\text{P}}(\text{cis to Ar})$	$^1J(\text{PtP})^b$
$p\text{-N}(\text{CH}_3)_2$	2.8	1743	8.1	2595
$p\text{-OCH}_3$	2.3	1746	7.6	2568
$p\text{-F}$	1.6	1751	6.9	2539
$p\text{-CH}_3$	2.1	1724	7.1	2588
H	1.6	1714	6.8	2578
$p\text{-CF}_3$	1.0	1741	5.9	2522
$p\text{-CN}$	0.5	1746	5.3	2507
$p\text{-CO}_2\text{CH}_3$	1.0	1729	5.6	2537
$p\text{-COCH}_3$	1.0	1726	5.6	2534
$m\text{-N}(\text{CH}_3)_2$	1.8	1697	7.1	2610
$m\text{-OCH}_3$	1.5	1719	6.7	2573
$m\text{-F}$	0.9	1748	6.4	2534
$m\text{-Br}$	1.0	1763	6.2	2527
$m\text{-CH}_3$	1.8	1711	6.8	2593
$m\text{-CF}_3$	1.1	1768	6.4	2517
$m\text{-CN}$	0.5	1775	5.9	2495
$m\text{-CO}_2\text{CH}_3$	1.2	1746	6.5	2539
$o\text{-CH}_3$	-0.6	1658	3.4	2590

^a Measured on ca. 0.12–0.15 M solutions in CH_2Cl_2 at -40 °C. J values are in Hz. ^b $^2J(\text{PP}) = \text{ca. } 21$ Hz.

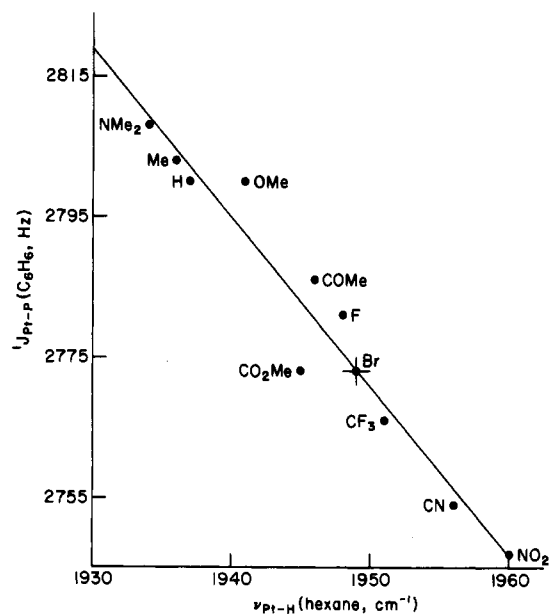


Figure 4. Plot of $^1J(\text{PtP})$ (Hz, C_6H_6) vs. $\nu(\text{PtH})$ (cm^{-1} , n -hexane) for $\text{trans-PtH}(\text{C}_6\text{H}_4\text{-}p\text{-Y})(\text{PEt}_3)_2$.

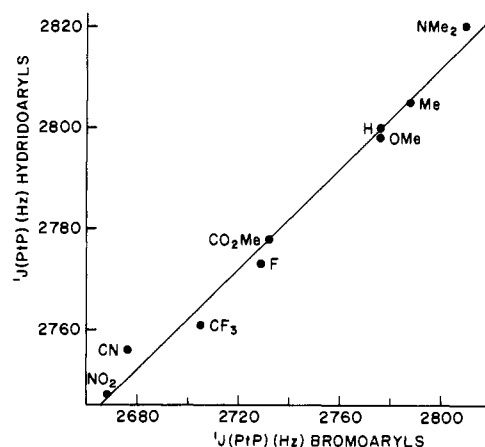


Figure 5. Plot of $^1J(\text{PtP})$ (Hz, cis to aryl) for $\text{trans-PtH}(\text{C}_6\text{H}_4\text{-}m\text{-Y})(\text{PEt}_3)_2$ vs. $^1J(\text{PtP})$ (Hz, cis to aryl) for $\text{trans-PtBr}(\text{C}_6\text{H}_4\text{-}m\text{-Y})(\text{PEt}_3)_2$.

similar value of λ (ca. 0.5) for $\nu(\text{PtH})$ and $^1J(\text{PtH})$ supports this conclusion. Moreover, plotting the values of $^1J(\text{PtP})$ cis to aryl for one type of complex against those for another clearly

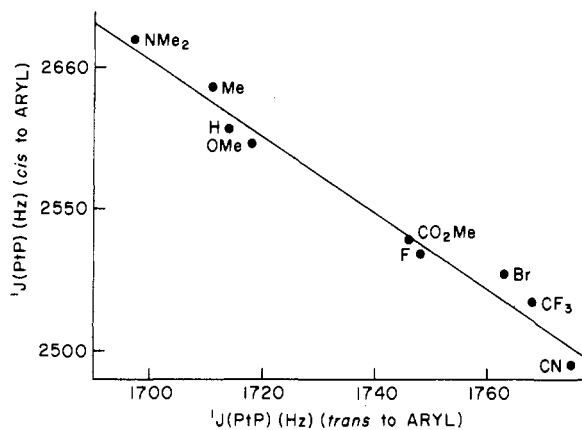


Figure 6. Plot of $^1J(\text{PtP})$ (Hz, cis to aryl) vs. $^1J(\text{PtP})$ (Hz, trans to aryl) for $[\text{Pt}(\text{C}_6\text{H}_4\text{-}m\text{-Y})(\text{PEt}_3)_3]\text{BF}_4$ in CH_2Cl_2 at -40°C .

shows that the substituent effect on $^1J(\text{PtP})$ occurs consistently throughout the series. This is demonstrated in Figure 5, which shows a good linear correlation ($r = 0.992$) between $^1J(\text{PtP})$ cis to aryl for *trans*-PtH($\text{C}_6\text{H}_4\text{-}m\text{-Y}$)(PEt_3)₂ and $^1J(\text{PtP})$ cis to aryl for *trans*-PtBr($\text{C}_6\text{H}_4\text{-}m\text{-Y}$)(PEt_3)₂.

There has been some controversy about the magnitude and direction of cis influences relative to trans influences.¹ The most recent theoretical prediction, based on a perturbation approach to substitution of one ligand by another better σ donor in a $d^8 \text{ML}_4$ complex, is that there will be a trans-bond lengthening, while the effect on the cis bonds will be relatively smaller and in principle can be in either direction, so that steric factors may be decisive.²² Within the series $\text{PtXY}(\text{dppe})$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) no correlation was found between $J(\text{PtP})$ trans to X and $J(\text{PtP})$ cis to X if X is changed and Y is kept constant. However, there are rough inverse correlations in the series $\text{PtX}(\text{CH}_3)(\text{dppe})$ and $[\text{Pt}(\text{CH}_3)\text{L}(\text{dppe})]^+$ between $J(\text{PtP})$ trans to X (or L) and $^2J(\text{PtCH}_3)$, those ligands with the highest $J(\text{PtP})$ values (lowest trans influence) tending to give the lowest $^2J(\text{PtCH}_3)$ values (highest cis influences).²³ From their studies on (trifluoromethyl)thio complexes *cis*- and *trans*-PtX(SCF_3)(PEt_3)₂ and on trifluorovinyl complexes *trans*-PtX(C_2F_3)(PEt_3)₂ and *trans*-[PtL(C_2F_3)(PEt_3)₂]⁺, Dixon et al.^{24,25} have concluded that cis and trans influences are inversely correlated when indirect (greater than one-bond) couplings are considered but that direct coupling constants are sensitive to π -bonding and steric effects (especially for the cis influence), which may mask this correlation over a wide range of ligands. Nevertheless, there is a rough inverse correlation between cis and trans influences based on $^1J(\text{PtP})$ values in the series $[\text{Pt}(\text{ttp})\text{X}]^+$ ($\text{ttp} = \text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$), though the cis influence is considerably smaller than the trans influence.²⁶ In contrast, in the series $[\text{PtR}(\text{PPh}_3)_3]^+$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CF}_3, \text{CH}_2\text{C}_6\text{H}_5, \text{CH}_2\text{CN}, (\text{CH}_2)_2\text{CN}, (\text{CH}_2)_3\text{CN}, o\text{-CH}_2\text{C}_6\text{H}_4\text{CN}, \text{CH}_2\text{NO}_2, \text{CH}_2\text{COCH}_3$), the changes in $^1J(\text{PtP})$ cis to R are almost as large as those in $^1J(\text{PtP})$ trans to R and again, in most cases, there is a reasonable inverse correlation between the two coupling constants.²⁷ A similar inverse correlation also exists in the limited series of complexes $\text{PtCl}(\text{C}_6\text{H}_4\text{Y})(\text{dppe})$ ($\text{Y} = m\text{-Cl}, p\text{-Cl}, p\text{-F}, p\text{-OCH}_3, \text{H}, p\text{-CH}_3$).²⁸ In the series *cis*-Pt($\text{C}_6\text{H}_4\text{Y}$)₂(PPh_3)₂

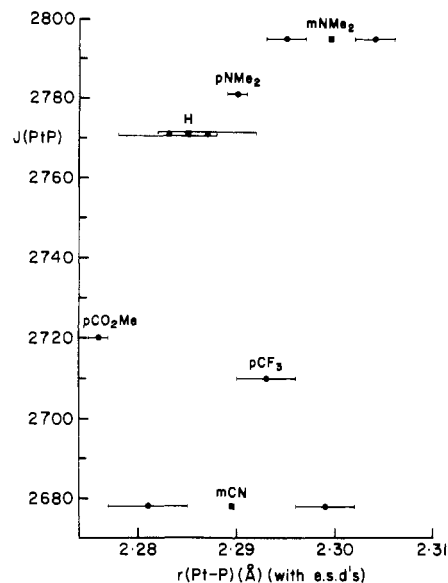


Figure 7. Plot of $^1J(\text{PtP})$ (Hz) vs. Pt-Cl bond length (\AA) for *trans*-PtCl($\text{C}_6\text{H}_4\text{Y}$)(PEt_3)₂.

the $^1J(\text{PtP})$ values were found to correlate well with σ_1 for para substituents, indicating that in this case an electron-withdrawing group causes an increase in $^1J(\text{PtP})$, but this result of course reflects a combination of cis and trans influences. Moreover, the correlation was much worse for meta substituents and for the series $\text{Pt}(\text{C}_6\text{H}_4\text{Y})_2(\text{dppe})$.²⁸

Single-crystal X-ray analysis of the series of complexes *cis*-PtCl₂(PEt_3)L has shown that the ligands L exert a cis influence on the Pt-P bond lengths (ca. 0.06 \AA) which is almost as large as their trans influence on the Pt-Cl(trans to L) bond lengths (ca. 0.07 \AA).²⁹ The cis influence on the Pt-Cl(cis to L) bond length is smaller (ca. 0.03 \AA) but still significant. The order of cis influence of ligands derived from this work is $\text{Cl}^- < \text{C}(\text{NPhCH}_2\text{CH}_2)_2 \approx \text{CNPh} \approx \text{C}(\text{OEt})(\text{NHPH}) < \text{PEt}_3 \approx \text{CO} \approx \text{P}(\text{OPh})_3 \approx \text{PF}_3$. On this basis it has been suggested^{29,30} that high cis influence is related to strong π -acceptor ability, not to ligand size. On the other hand, X-ray structural analyses of the series $[\text{PtX}(\text{PEt}_3)_3]\text{Y}$ ($\text{X} = \text{H}, \text{Y} = \text{PF}_6$; $\text{X} = \text{F}, \text{Cl}, \text{Y} = \text{BF}_4$) show the Pt-P distances cis to X to increase in the order $\text{X} = \text{H}^- < \text{F}^- < \text{Cl}^-$, and it was proposed that this is due to steric interaction of the anionic ligand with the triethylphosphine ligands.³¹

Considering the three parent complexes of our series, viz. *trans*-PtX(C_6H_5)(PEt_3)₂ ($\text{X} = \text{H}, \text{Br}$) and $[\text{Pt}(\text{C}_6\text{H}_5)(\text{PEt}_3)_3]\text{BF}_4$, the order of $^1J(\text{PtP})$ is $\text{H}^- > \text{Br}^- \gg \text{PEt}_3$, corresponding to an ordering in terms of cis influence of $\text{PEt}_3 \gg \text{Br}^- > \text{H}^-$. This is consistent with the order derived from the X-ray studies discussed above, if Br^- is substituted for Cl^- , but it does not fit in with the order of decreasing electron-withdrawing ability implied by the ordering of substituted aryl groups; it is also not the opposite of the expected trans-influence order ($\text{H}^- > \text{PEt}_3 > \text{Br}^-$). However, the magnitudes of the effects of substituents within each series, as measured by the ρ values, show the consistent order $\text{Br}^- > \text{PEt}_3 > \text{H}^-$.

The series $[\text{Pt}(\text{C}_6\text{H}_4\text{Y})(\text{PEt}_3)_3]^+$ (code numbers 13-16) provides an opportunity to assess cis and trans influences of aryl groups by studying changes in the same parameter, $^1J(\text{PtP})$. For the meta series there is a good inverse correlation ($r = -0.988$) between the two coupling constants, as is evident

(22) Shustorovich, E. *Inorg. Chem.* **1979**, *18*, 1030-1039.
 (23) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738-747.
 (24) Dixon, K. R.; Moss, K. C.; Smith, M. A. R. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 373-376; *J. Chem. Soc., Dalton Trans.* **1975**, 990-998.
 (25) Cairns, M. A.; Dixon, K. R.; Rivett, G. A. *J. Organomet. Chem.* **1979**, *171*, 373-385.
 (26) Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 3574-3580.
 (27) Pregosin, P. S.; Favez, R.; Roulet, R.; Boschi, T.; Michelin, R. A.; Ros, R. *Inorg. Chim. Acta* **1980**, *45*, L7-L9.
 (28) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 357-368.

(29) Manojlović-Muir, L.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1977**, *142*, 265-280.
 (30) Russell, D. R.; Tucker, P. A.; Wilson, B. *J. Organomet. Chem.* **1976**, *104*, 387-392.
 (31) Russell, D. R.; Mazid, M. A.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1737-1742.

Table VIII. Metal-Ligand Bond Lengths (Å) in *trans*-PtCl(C₆H₄Y)(PEt₃)₂ Complexes^a

Y	r(Pt-Cl)	r(Pt-P)	r(Pt-C)
<i>p</i> -CO ₂ CH ₃	2.370 (2)	2.276 (1)	1.986 (5)
<i>p</i> -CF ₃	2.416 (6)	2.293 (3)	2.000 (12)
<i>p</i> -N(CH ₃) ₂	2.453 (2)	2.290 (1)	1.999 (6)
H ^b	2.406 (5)	2.283 (5), 2.287 (5)	2.019 (15)
<i>m</i> -CN	2.382 (4)	2.281 (4), 2.299 (3)	2.001 (9)
<i>m</i> -N(CH ₃) ₂	2.409 (4)	2.295 (2), 2.304 (2)	2.021 (12)

^a Data from ref 34. ^b Data calculated from coordinates supplied by: Randaccio, L., personal communication.

from Figure 7, and interestingly, the *trans* influence of the substituents is slightly smaller than the *cis* influence ($\rho_I = 109$ vs. -136 ; $\rho_R = 48.0$ vs. -73.6). In contrast, there is no correlation between ¹J(PtP) *cis* and ¹J(PtP) *trans* to para-substituted aryl groups and the negative value of λ for code number 13 suggests that para substituents exert some specific effect on the *trans*-phosphorus atom. The anomaly can also be seen in the ranges of ¹J(PtP) for the various code numbers, i.e.: 13, 32 Hz; 14, 85 Hz; 15, 78 Hz; 16, 115 Hz. The possibilities that these effects arise from interaction with the dichloromethane solvent used for the measurements or from the fact that the measurements were carried out at -40 °C can be discounted. The spectra of four selected complexes in the series [Pt(C₆H₄-*p*-Y)(PEt₃)₃]BF₄ (Y = N(CH₃)₂, H, COCH₃, CN), measured at room temperature in dichloromethane and acetone, gave different absolute values of ¹J(PtP) for each complex, but a similar scatter of points was evident in the plot of ¹J(PtP) *cis* to aryl vs. ¹J(PtP) *trans* to aryl.

The negative ρ_R value for ¹J(PtP) *trans* to aryl in *trans*-[Pt(C₆H₄-*p*-Y)(PEt₃)₃]⁺ implies that electron withdrawal by a resonance mechanism causes a decrease in ¹J(PtP), while the positive ρ_I value indicates that electron withdrawal by an inductive mechanism causes an increase in ¹J(PtP). The specific ability of para substituents to modify the electronic properties of the carbon atom attached to platinum via the π system appears to strongly perturb the *trans*-Pt-P bond, or at least those factors involved in determining ¹J(PtP, *trans*), while not anomalously affecting ¹J(PtP, *cis*). The situation is very similar to that described above for ¹J(PtH) in the *trans*-PtH(C₆H₄-*p*-Y)(PEt₃)₂ complexes, and it is worth noting that extensive *trans*-influence series based on ¹J(PtP) values have been developed which, in general, agree well with those based on ¹J(PtH).^{1,23} In the present case, there is a possible additional complication of a positive charge on platinum, which may cause unusual electron demand at the directly bound carbon atom and may be partly responsible for the unusual behavior of para substituents.

Comparison of Bond Lengths and Spectroscopic Parameters for *trans*-PtCl(C₆H₄Y)(PEt₃)₂ Complexes. Platinum-chlorine bond lengths and the associated stretching frequency ν (PtCl) in complexes of the type *trans*-PtClXL₂ are one of the most frequently used measures of the *trans* influence of a ligand X. Ligands of high *trans* influence give low values of ν (PtCl), and it has been pointed out that the greatest changes in ν (PtCl) occur at the high end of the *trans*-influence series.¹ A correlation has also been claimed to exist between ¹J(PtP) and Pt-P bond lengths for a range of trialkylphosphine complexes of planar platinum(II) and octahedral platinum(IV),³² although the correlation is poor for the *cis*-PtCl₂(PEt₃)₂ complexes discussed above²⁹ and it breaks down altogether for sterically crowded complexes such as *trans*-PtI₂[P(C₆H₁₁)₃]₂.³³ It therefore seemed worthwhile to obtain accurate bond length

Table IX. ³¹P NMR^a and IR (ν (PtCl))^b Data for *trans*-PtCl(C₆H₄Y)(PEt₃)₂

Y	δ_P	¹ J(PtP), Hz	ν (PtCl), cm ⁻¹
<i>p</i> -CO ₂ CH ₃	14.7	2720	288
<i>p</i> -CF ₃	14.8	2710	271
<i>p</i> -N(CH ₃) ₂	15.1	2781	261
H	15.0	2771	275
<i>m</i> -CN	15.6	2678	289
<i>m</i> -N(CH ₃) ₂	14.3	2795	276

^a For ca. 0.12 M solutions in CH₂Cl₂ at -40 °C. ^b CsI disk.

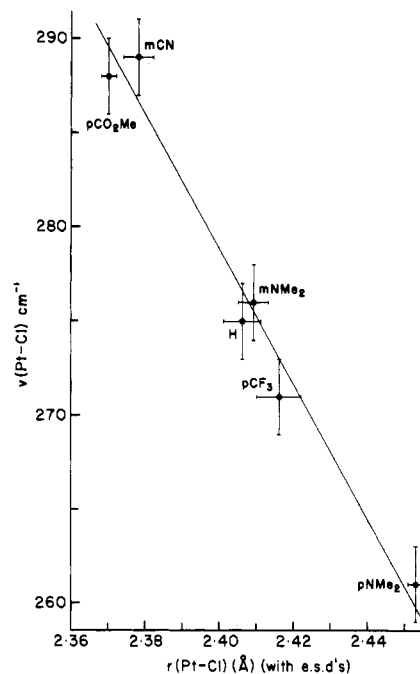


Figure 8. Plot of ν (PtCl) (cm⁻¹) vs. Pt-Cl bond length (Å) for *trans*-PtCl(C₆H₄Y)(PEt₃)₂.

data on selected members of the series *trans*-PtCl(C₆H₄Y)(PEt₃)₂ to see if these showed any regular trends that could be correlated with the nature of Y. The data for the complexes where Y = *p*-N(CH₃)₂, *p*-CF₃, *p*-CO₂CH₃, H, *m*-CN, and *m*-N(CH₃)₂,³⁴ are summarized in Table VIII. The IR (ν (PtCl)) and ³¹P{¹H} NMR data for these complexes are given in Table IX.

Owing to the limited number of substituents these data have not been subjected to DSP analysis, but as Figure 7 shows, there is no correlation between ¹J(PtP) and the Pt-P bond lengths at the level of precision afforded by the X-ray data. The fact that ¹J(PtP) for the chloro complexes correlates very well with ¹J(PtP) for the corresponding bromo complexes ($r = 0.998$) shows that there are no unusual substituent effects peculiar to the chloro complexes. Clearly the changes in ¹J(PtP) *cis* to aryl, which can be accounted for in terms of the electronic effects of the substituents, are not large enough to be reflected in the Pt-P bond lengths and the relationship, if it exists, could be masked by solid-state effects. In contrast, despite the similarity of the aryl ligands, a wide range of Pt-Cl stretching frequencies is observed (261–289 cm⁻¹) and a plot of ν (PtCl) (measured in the solid state) against the Pt-Cl bond length (Figure 8) reveals a consistent trend within this limited series ($r = 0.977$). Although the Pt-Cl bond length for Y = *p*-CO₂CH₃ is, as expected, significantly shorter than that for Y = *p*-N(CH₃)₂, overall the values do not seem to be related in any simple way to the nature of the substituent. In par-

(32) Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* 1973, 2095–2099.

(33) Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* 1977, 2038–2042.

(34) Bilton, M. S.; Robertson, G. B., unpublished work.

ticular, the values of $\nu(\text{Pt}-\text{Cl})$ and $\nu(\text{PtCl})$ for $\text{Y} = p\text{-CF}_3$ are respectively larger and smaller than would have been predicted for this electron-withdrawing substituent. Also, there is no correlation between $\nu(\text{PtH})$ in *trans*-PtH(C₆H₄-*p*-Y)(PEt₃)₂ (measured in solution) and $\nu(\text{PtCl})$ in *trans*-PtCl(C₆H₄-*p*-Y)(PEt₃)₂ (measured in the solid state). In the silyl-platinum(II) complexes *trans*-PtCl[Si(C₆H₄Y)₃](EMe₂Ph)₂ (E = P, As), $\nu(\text{PtCl})$ increases as Y becomes more electron withdrawing, but the value of $\nu(\text{PtCl})$ for Y = H is anomalously low, possibly as a result of a solid-state effect.³⁵

Conclusions. Variation of meta and para substituents in the aryl groups of arylplatinum(II) complexes causes small changes in the spectroscopic parameters characterizing the metal-ligand bonds in both *cis* and *trans* positions. Many of these changes fit the DSP equation reasonably well, the correlation being uniformly better for meta than for para substituents, i.e. $f(\text{para}) > f(\text{meta})$ in Table III. Concepts such as the inductive and resonance transmission of electronic effects are therefore transferable from aromatic organic compounds to arylplatinum(II) complexes, in agreement with earlier work.¹³⁻¹⁵ Anomalous features are the insensitivity of $^1J(\text{PtH})$ to the nature of a para-substituted aryl group and the poor correlation with the DSP equation of $^1J(\text{PtP})$ *trans* to a para-substituted aryl group, for which we have no satisfactory explanation.

The most unexpected regularity is the increase (decrease) of $^1J(\text{PtP})$ *cis* to an aryl group caused by electron-donating (-withdrawing) meta and para substituents. In a recent structural comparison of *trans*-PtCl(CH₃)(PMePh₂)₂ and *trans*-PtCl(C₂F₅)(PMePh₂)₂, we found that the Pt-P bonds in the fluoroalkyl complex are about 0.04 Å longer than those in the methyl complex and suggested that this might be a steric

lengthening caused by the considerably shorter Pt-C and Pt-Cl bonds in the fluoroalkyl complex.³⁶ The longer Pt-P distance in the fluoroalkyl complex is also associated with a smaller value of $^1J(\text{PtP})$. The trend in the arylplatinum(II) complexes is understandably smaller in magnitude, but it operates in the same sense, and it seems more likely to be electronic in origin. An explanation based on π -back-bonding competition between aryl or fluoroalkyl groups and the phosphine ligands similar to that used to account for the trends in *cis*-PtCl₂(PEt₃)L (see above)²⁹ seems to us unconvincing.

Perhaps the most reasonable explanation of the *cis* influence in our complexes is provided by Shustorovich's perturbation approach.²² When one ligand in a planar ML₄ complex is replaced by a better σ donor, the s and d contributions to the change in overlap population in the *trans* position are always negative and larger than the p contribution, which is always positive. In contrast, the s and d contributions to the change in overlap contribution in the *cis* bonds are always of opposite sign, the s being positive and the d negative. Thus, in principle, the *cis* influence may be of either sign and, in the present case, we must assume that the s contribution outweighs the d contribution. This assumption is not unreasonable, since trialkylphosphines have a fairly high *trans* influence¹ and presumably make a high demand on Pt 6s electron density.

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Supplementary Material Available: Listings of analytical data and melting points for *trans*-PtBr(C₆H₄Y)(PEt₃)₂ complexes (Table I) and analytical data, melting points, and recrystallization solvents for *trans*-PtH(C₆H₄Y)(PEt₃)₂ complexes (Table II) (3 pages). Ordering information is given on any current masthead page.

(35) Chatt, J.; Eaborn, C.; Ibekwe, S.; Kapoor, P. N. *J. Chem. Soc. A* 1970, 1343-1351.

(36) Bennett, M. A.; Chee, Ho-Kin; Robertson, G. B. *Inorg. Chem.* 1979, 18, 1061-1070.

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Fluorosulfates of the Noble Metals. 5. Fluorosulfato Derivatives of Platinum(IV) and the HSO₃F-Pt(SO₃F)₄ Superacid System

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A simple synthetic route to pure Pt(SO₃F)₄ is described. This compound is found to be an excellent fluorosulfate ion acceptor, forming either [Pt(SO₃F)₆]⁻ or an oligomeric anion of the composition [Pt(SO₃F)₅]⁻. A number of complexes with the counterions Cs⁺, ClO₂⁺, Ba²⁺, and Br₃⁺ are synthesized and characterized by vibrational spectroscopy. In a solution of HSO₃F the novel dibasic acid H₂[Pt(SO₃F)₆] is formed, which undergoes the following dissociation equilibria: H₂[Pt(SO₃F)₆] + HSO₃F ⇌ H[Pt(SO₃F)₆]⁻ + H₂SO₃F⁺ and H[Pt(SO₃F)₆]⁻ + HSO₃F ⇌ [Pt(SO₃F)₆]²⁻ + H₂SO₃F⁺. The system is investigated by electrical conductance measurements and ¹⁹F NMR, Raman, IR, and UV-visible spectroscopy.

Introduction

The first fluorosulfate of platinum, Pt(SO₃F)₄, was reported in 1972.¹ The synthesis was accomplished by the oxidation of platinum metal using a large excess of bromine(I) fluorosulfate. To achieve complete conversion, a temperature of 95 °C and a reaction time of 3 weeks were required. In addition, reaction intermediates, formulated as Pt(SO₃F)₄·nBrSO₃F, with *n* initially 3.5, required pyrolysis in vacuo over several days, with temperatures ranging up to 110 °C. While this

route seemed rather tedious and time consuming, it had suggested to us the possibility of using Pt(SO₃F)₄ as a fluorosulfate ion acceptor, and two salts containing [Pt(SO₃F)₆]²⁻ were subsequently synthesized: Ag^{II}[Pt(SO₃F)₆]² and Pd^{II}[Pt(SO₃F)₆].³

The main objective in the previous studies had been the characterization of the cations Ag²⁺ and Pd²⁺, rather than of the anion. The present study is undertaken with three ob-

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(1) Johnson, W. M.; Dev. R.; Cady, G. H. *Inorg. Chem.* 1972, 11, 2260.

(2) Leung, P. C.; Aubke, F. *Inorg. Chem.* 1978, 17, 1765.

(3) Lee, K. C.; Aubke, F. *Can. J. Chem.* 1979, 57, 2058.