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Correlation Analysis of ^{13}C and ^{19}F NMR Substituent Effects in Arylplatinum Complexes

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Abstract: ^{13}C NMR spectra have been obtained for a series of complexes of the type *trans*-$(PEt_3)_2Pt(C_6H_5)X$ (I). Correlations of the associated chemical shifts and coupling constants with sets of both Taft and modified Swain–Lupton substituent constants were examined. Similarly, correlations involving previously determined ^{19}F chemical shifts associated with the complexes *trans*-$(PEt_3)_2Pt(C_6H_4F)X$ (II) were also examined. The observed correlations provide evidence that substituent parameters obtained from organic systems may be used, within limits, to accurately describe the effects of substituents bonded to platinum. An anomalous behavior of the substituents I and Br in these correlations was also noted. Finally, evidence is presented supporting the presence of significant π interactions between platinum and an aryl ligand.

The study of the nature of the aryl–metal bond has been the subject of numerous investigations.[1] Most of these studies have dealt with questions concerning the importance of π bonding in such bonds. However, in spite of the substantial effort devoted to this problem, controversy still surrounds the interpretation of the available physical data. Nevertheless, the problem remains important since an increased understanding of the nature of the aryl–metal bond could have far-reaching implications in the interpretations of such reactivity phenomena as the trans effect[2] and metal catalysis.

A significant portion of the work concerned with this problem has involved the study of arylplatinum complexes. Starting with Parshall's study[3] of substituent effects on the ^{19}F NMR chemical shifts of fluoroarylplatinum complexes, most of this work has employed NMR spectroscopy as a structure probe. However, possible shortcomings to using this technique have recently been documented.[1,32] In this connection, it is also important to note that chemical shifts associated with the aryl group of a series of substituted aryl–metal complexes can, at best, be an approximate measure of the *sensitivity* of the π and σ components of the aryl–metal bond to the effects of substituents. They cannot, without auxiliary information, represent a measure of the *magnitudes* of the π or σ bond orders of these bonds. On the other hand the *existence* of an aryl–metal π interaction may be implied by the observation of a sensitivity to substituent effects characteristic of such interactions.

Recent studies[1,4] have emphasized the use of ^{13}C NMR spectroscopy to measure substituent effects on aryl carbons. In an important investigation, Clark and Ward[1] examined the ^{13}C chemical shifts, δ^C, and coupling constants, $^nJ_{PtC}$, associated with a series of arylplatinum complexes. On the basis of the chemical shift data they concluded that "σ rather than π interactions are dominant in the phenyl–platinum bond."

To gain further insight into the nature of aryl–platinum bonds, we have examined correlations of both ^{13}C and ^{19}F NMR substituent effects observed in arylplatinum complexes with substituent parameters derived from organic systems. Furthermore, we have examined these substituent effects as contributions from field/inductive and resonance effects using both a modified Swain–Lupton[5] model and the Taft[6] model for determining the separation of such effects. Arylplatinum metal systems were studied since previous studies[1,3] had demonstrated both their ease of preparation and the additional and valuable information gained through observing spin–spin couplings of ^{195}Pt ($I = \frac{1}{2}$, 34% natural abundance) with both ^{13}C and ^{19}F.

Results

Preparation of Phenylplatinum Complexes. The phenylplatinum complexes, I, were prepared by conventional metathesis reactions with the exception of I ($X = F_2H$) which was

Table II. ^{13}C NMR Chemical Shifts[a] of C_6H_5X and Phenylplatinum Complexes (I)

	C_6H_5X			*trans*-$(PCH_2CH_3)_2Pt(C_6H_5)X$					
X	Ortho	Meta	Para	Ortho	Meta	Para	P–C	PCH_2–C	Other
H	128.50	128.50	128.50						
CH_3	129.19	128.39	125.47	139.90	126.90	120.36	13.94	8.00	
C_2H_5	127.90	128.38	125.63	140.03	126.81	120.56	13.38	8.04	$\delta_{PtCH_2} = 4.26$
$CH{=}CH_2$	126.33	128.60	127.90	140.18	126.80	120.69	14.17	7.86	δ_{CH}(vinyl) = 140.18 δ_{CH_2}(vinyl) = 121.86
C_6H_5	127.36	128.87	127.36	140.00	126.87	120.83	13.81	7.82	
b				136.40	126.80	120.60	15.64	8.15	
F_2H				136.48	127.74	121.96	12.79	7.50	
F	115.46	130.11	124.01	137.20	127.32	121.33	12.89	7.46	
Cl	128.76	129.84	126.55	137.35	127.85	121.75	13.54	7.77	δ_{C_1} (aryl) = 139.88
b				136.20	127.20	122.40	16.94 15.04	8.07 8.31	$\delta_{C_1'}$ (aryl) = 157.90
Br	131.73	130.17	126.98	137.18	127.90	121.85	14.14	7.77	
I	137.56	130.27	127.52	136.91	128.01	122.07	15.33	7.83	δ_{C_1}(aryl) = 144.0
NCO	124.82	129.62	125.79	~137.8	127.84	121.75	14.02	7.71	
N_3	119.11	129.85	124.94	137.24	127.85	122.03	13.81	7.77	
OCH_3	113.99	129.53	120.73	138.16	127.21	120.89	12.68	7.71	
SC_2H_5	(129.20)[c]	(128.88)[c]	125.86	138.05	127.58	121.33	13.48	7.98	
CN	132.32	129.25	132.86	138.05	127.91	122.30	15.49	8.00	$\delta_{CN} = 35.81$ δ_{C_1} (aryl) = 151.44
NO_2	123.58	129.41	134.70	137.72	127.68	122.66	13.60	7.61	
$SnCl_3$	134.10	133.24	130.49	135.95	128.93	124.02	16.73	8.27	

[a] In ppm from internal tetramethylsilane (downfield positive). [b] Cis isomer. [c] Assignment not known because of inability to distinguish ortho from meta using Scott's method.[9]

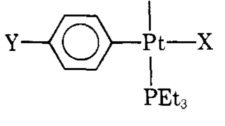
prepared unexpectedly during attempts to prepare I (X = F).

$$trans\text{-}(PEt_3)_2Pt(C_6H_5)_2 \xrightarrow{HF} [trans\text{-}(PEt_3)_2Pt(C_6H_5)F]$$

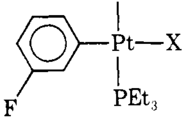
$$\xrightarrow{HF} trans\text{-}(PEt_3)_2Pt(C_6H_5)F_2H$$

In addition to elemental analysis and the ^{13}C NMR spectrum, important evidence for the structure of this unusual bifluoride complex came from an examination of the ^1H NMR. Along with the resonances expected for the aryl and ethyl groups a broad resonance at δ 10.7 (0.9 proton) was found and assigned to the acidic bifluoride proton.

The modes of bonding of the substituents X = NCO and X = NO_2 in I were assigned on the basis of the structures reported for closely related complexes.[7]



I, Y = H
IIa, Y = F



IIb

X = F_2H, F, Cl, Br, I, CH_3, CH_2CH_3, C_6H_5, $CH{=}CH_2$, OCH_3, SCH_2CH_3, N_3, NO_2, CN, NCO, $SnCl_3$

Table I documents the melting points and elemental analyses of the complexes prepared. (See paragraph at end of article regarding supplementary material.)

^{13}C NMR Chemical Shift and Coupling Constant Assignments. The ^{13}C NMR chemical shifts, δ^C, and coupling constants, $^nJ_{PtC}$, $^nJ_{PC}$, appropriate to the complexes I were determined and are summarized in Tables II and III. In addition, the ^{13}C NMR chemical shifts of the parent aromatic compounds, C_6H_5X, corresponding to each of the complexes were determined and are included in Table II.

In the arylplatinum complexes, the high-field resonances were assigned to the ethyl groups present in the phosphorus ligands. In most cases a rather simple pattern emerged. The methylene carbons appeared as a pseudoquintet as a result of coupling to two equivalent phosphoruses and to platinum. The methyl carbons appeared as a pseudotriplet as a result of coupling to platinum. This overall pattern is consistent with the assignment[8] of a trans configuration to the complexes. The ortho and meta resonances of the aromatic carbons were differentiated using the method described by Scott[9] where the assignments were unknown. The para and quaternary aromatic carbon resonances were distinguished from one another and from the ortho and meta resonances by their relative intensities. In fact, in only a few cases were the quaternary carbon resonances actually observed. Spin–spin couplings of carbon to platinum were observed for all the carbons except the quaternary carbons whose signal intensities were too low to observe. Also, couplings to phosphorus were observed for the carbons of the ethyl groups and, in a few cases, for the quaternary carbons. Both the chemical shifts and coupling constants, $^nJ_{PtC}$, are consistent with those reported by Clark and Ward[1] for analogous systems.

Table III. Aryl Carbon–Platinum Coupling Constants[a,b] for Phenylplatinum Complexes, I

X	$^2J_{PtC}$	$^3J_{PtC}$	X	$^2J_{PtC}$	$^3J_{PtC}$
CH_3	20	44	Br	38	75
C_2H_5	20	44	I[c]	39	76
$CH{=}CH_2$	20	41	NCO	Complex	73
$CH{=}C(CH_3)_2$	21	41	N_3	34	72
C_6H_5	22	40	OCH_3	30	60
cis-C_6H_5	32	68	SC_2H_5	30	60
F_2H	36	76	CN	24	50
F	28	71	NO_2	28	59
Cl[c]	35	74	$SnCl_3$	40	73
cis-Cl	19	45			

[a] Values in Hertz (Hz). [b] The coupling constants for the phosphine ligand carbons displayed mostly small variations: $^2J_{PtC} = 34 \pm 2$ Hz, $^3J_{PtC} = 25 \pm 2$ Hz, and $|^1J_{PC} + {}^3J_{PC}| = 17 \pm 1$ Hz for the trans isomers. The values of $^4J_{PtC}$ were generally less than 10 Hz and were not usually sufficiently well-resolved to permit a definite assignment. [c] $^2J_{PC}$(aryl) = 8 Hz.

Substituent Effect Models. Previous analyses[4,5,10] of aromatic NMR spectral data using substituent constants have mostly involved attempts to relate a given spectral parameter to a *single* substituent parameter. Recent studies[4a,d,5] have

Table IV. Modified Swain–Lupton Substituent Constants

Substituent	σ_I^{a}	R^n	Substituent	σ_I^{a}	R^n
$N(CH_3)_3^+$	1.00^{b}	$0^{h,i}$	SC_2H_5	0.23	-0.15^{n}
F	0.50	$-0.42^{h,j}$	N_3	0.44^{d}	-0.29^{o}
Cl	0.46	$-0.28^{h,j}$	NCO	0.36^{e}	-0.18^{e}
Br	0.44	-0.24^{h}	SCN	0.61^{f}	-0.15^{n}
I	0.39	-0.16^{h}	CN	$0.56\ (0.48)^{g}$	$0.05^{i}\ (0.13)^{g}$
CH_3	-0.04	$-0.06^{h,j}$	NO_2	$0.65\ (0.56)^{g}$	$0.03^{i}\ (0.11)^{g}$
C_2H_5	-0.04	-0.06^{h}	NH_2	0.12	-0.38^{i}
C_6H_5	0.10	-0.07^{k}	$N(CH_3)_2$	0.06	-0.31^{i}
$C{\equiv}CC_6H_5$	0.14	-0.01^{m}	$COCH_3$	0.28	0.18^{i}
$CH{=}CH_2$	0.05^{c}	-0.04^{l}	CO_2CH_3	0.30	0.09^{i}
OCH_3	0.27	$-0.40^{h,j}$			

[a] The σ_I values were taken from S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, Jr., *Prog. Phys. Org. Chem.*, 10, 1 (1973), unless otherwise noted. [b] C. F. Wilcox and C. Leung *J. Am. Chem. Soc.*, **90**, 336 (1968). [c] R. W. Taft et al., *ibid.*, **85**, 709 (1963). [d] R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5343 (1959). [e] F. S. Fawcett and W. A. Sheppard, *ibid.*, 87, 434 (1965). [f] A. Fredga, *Z. Phys. Chem.*, **[2]** 123, 129 (1929). [g] These values are derived from ^{19}F chemical shifts of $C_6H_4F(X)$ in cyclohexane using Taft's relationships (see ref 23). [h] J. F. J. Dippy, *Chem. Rev.*, **25**, 151, 175 (1939). [i] A. J. Hoefnagel and B. M. Wepster, *J. Am. Chem. Soc.*, **95**, 5357 (1973). [j] A. Fischer, B. R. Mann, and J. Vaughan, *J. Chem. Soc.*, 1093 (1961); these values are averaged with those taken from footnote *h*. [k] Y. Yukawa, Y. Tsuno, and M. Sawacla, *Bull. Chem. Soc. Jpn.*, 39, 2274 (1966). [l] R. W. Taft et al., *J. Am. Chem. Soc.*, **85**, 3146 (1963). [m] J. K. Kochi and G. S. Hammond, *ibid.*, 75, 3452 (1953). [n] W. A. Sheppard and R. W. Taft, *ibid.*, 94, 1919 (1972). [o] The corresponding σ_p value (0.15) taken from O. Exner and J. Lakomy, *Collect. Czech. Chem. Commun.*, **35**, 1371 (1970); using Swain and Lupton's correlations the corresponding $\sigma_p{}^n$ value (0.22) was derived.

tended to expand these analyses by devising correlations involving two or three substituent parameters. Topsom and Brownlee[11] have recently given cogent arguments favoring the use of these multiparameter treatments of spectral data. They assume that at least two independent mechanisms of electronic transmission affect NMR spectral parameters. The two most basic mechanisms are the well-known field/inductive and the resonance interactions which operate principally through σ-bond (or through space) and π-bond networks, respectively. Since the dependence of field/inductive effects on molecular geometry is known[11,12] to differ from that shown by resonance effects, there may not be a constant relationship between the transmission of these two effects as molecular structures change. This observation is particularly pertinent to comparisons of aryl-metal structures with conventional aromatic structures since their relative geometries are usually quite different.

The choice of appropriate substituent parameters which independently reflect field/inductive and resonance effects remains controversial. Perhaps the two most widely applied models claiming the separation of these effects are those advanced by Swain and Lupton[5] and by Taft.[6] Both of these models assume that experimental substituent constants are related to these effects through simple additive relationships. However, they differ in their assumptions[13] regarding both the relative and absolute magnitudes of the field/inductive effects operating at positions meta and para to a substituent. Furthermore, since the Swain–Lupton model is based on data obtained from substituted benzoic acids, the so-called "direct resonance"[14] effects of the R substituents are significant in this model. Since these effects are in large part determined by the nature of the probe group (i.e., CO_2H in this case), they are not reliable indicators of charges induced in an aromatic ring by the substituent alone. For this reason we felt that a modification of the Swain–Lupton model which would eliminate or at least minimize these "direct resonance" effects would be desirable. To accomplish this we first simply shifted the resonance effect data base from the substituted benzoic acids to the corresponding phenylacetic acids. This also allows for a better comparison of the two substituent effect models since the Taft model, too, is based on substituted phenylacetic acids. Also, a more rigorous comparison of the two models would be obtained if the data bases for the field/inductive effects were identical. Because of its easy availability for most substituents, the σ_I substituent parameter was chosen to represent the field/inductive parameter in this modified Swain–Lupton model, replacing σ' in the original model. The resulting relationships are given in eq 1 and 2 [The Swain–Lupton substituent constants R^n and F used in this paper are designated as script $\mathcal{R}^n$ and $\mathcal{F}$ in the current literature.]

$$\sigma_p{}^n = \alpha\sigma_I + R^n \qquad (1)$$

$$\sigma_m{}^n = \alpha'\sigma_I + \beta R^n \qquad (2)$$

The coefficients α and α' are determined by assuming that R^n, the resonance parameter, is equal to zero for the trimethylammonium substituent. This assumption was also used by Swain and Lupton in their original model. Using an appropriate $\sigma_p{}^n$ value[14] for Me_3N^+ ($\sigma_p{}^n = 1.16$)[15] and its corresponding σ_I value ($\sigma_I = 1.00$)[17] the value of α was calculated to be 1.16 from eq 1. R^n values for any substituent may then be calculated from this equation using the value of α given here and appropriate $\sigma_p{}^n$ and σ_I values. Table IV lists σ_I and R^n values for various substituents. The relative independence of these parameters was also shown by the absence of any significant correlation between them ($r \geq -0.20$, depending upon the substituents examined, for $n \geq 14$). Assuming the equivalence of σ^n and σ^0 values, the relationship of this modified Swain–Lupton model to the Taft model is given by eq 3.

$$\sigma^0{}_R = R^n + 0.16\sigma_I \qquad (3)$$

In both models, of course, the field/inductive effects of a substituent are defined by the σ_I parameter.

Correlations of NMR Data with Substituent Constants. Theoretical models[12,17] for correlating NMR chemical shifts or coupling constants with substituent constants have not yet progressed to the stage where *quantitative* correlations are possible. Thus, an empirical approach is necessary to establish such correlations. In such treatments simple linear models are usually assumed and their significance is tested statistically. This is essentially the approach taken by Swain and Lupton[5] in their study of substituent effect correlations and is adopted here.

If it is assumed that NMR substituent effects are linearly dependent upon the individual field/inductive and resonance effects of the substituents, then one of the following relationships *may* hold true depending upon the accuracy of the model employed.

$$Z_i = a_i\sigma_I + b_iR^n + c_i \qquad (4)$$

(Modified Swain-Lupton model)

$$Z_i = a_i'\sigma_I + b_i'\sigma^0{}_R + c_i' \qquad (5)$$

(Taft model)

Table V. Correlation Analysis of ^{13}C Chemical Shift Data for C_6H_5X[a]

			$Z = a\sigma_I + bR^n + c$				
Z	n[b]	a[c]	b[c]	c[c]	E_z[d]	r[e]	$\% R^n$[f]
δC_{meta}	13	1.93 ± 0.35	−2.06 ± 0.54	128.45 ± 0.13	0.288	0.90	39.1 ± 5.7
δC_{para}	14	9.19 ± 0.87	21.33 ± 1.34	127.63 ± 0.33	0.713	0.978	58.8 ± 4.3

[a] The data set (n = 14) was taken from the compounds where X = H, F, Cl, Br, I, CH_3, C_2H_5, CH=CH_2, C_6H_5, OCH_3, SC_2H_5, N_3, NO_2, and CN. Data for X = SC_2H_5 were omitted from the correlation involving δ_{meta} because of an ambiguity in the chemical shift assignments. [b] The number of observations is denoted by n. [c] The errors noted following the regression coefficients are equal to one standard deviation. [d] E_z is the standard deviation between the observed and calculated values of Z. [e] r is the population-corrected correlation coefficient. [f] $\% R^n$ is defined, according to ref 5, as the percent resonance contribution to Z.

Table VI. Correlation Analysis[a] of ^{13}C NMR Data for Phenylplatinum Complexes (I)

			$Z = a\sigma_I + bR^n + c$				
Z	n[b]	a	b	c	E_z	r	$\% R^n$
δC_{meta}	13	1.70 ± 0.36	−0.01 ± 0.54	126.91 ± 0.15	0.284	0.797	
	11	1.58 ± 0.33	0.045 ± 0.49	126.90 ± 0.13	0.253	0.827	1.8 ± 19.6
δC_{para}	13	3.10 ± 0.29	1.26 ± 0.44	120.68 ± 0.12	0.229	0.950	
	11	3.01 ± 0.27	1.28 ± 0.40	120.67 ± 0.11	0.206	0.963	21.8 ± 5.5
	11	2.85 ± 0.38	0 (def)	120.52 ± 0.14	0.294	0.922	0
δC_{P-CH_2}	13	1.05 ± 0.89	3.27 ± 1.32	14.07 ± 0.36	0.688	0.528	
	11	0.73 ± 0.70	3.33 ± 1.04	14.01 ± 0.29	0.541	0.676	
$^3J_{PtC}$[c]	13	34.54 ± 9.65	−48.34 ± 14.45	40.50 ± 3.97	7.56	0.838	
	11	30.50 ± 7.29	−46.74 ± 10.81	39.91 ± 2.96	5.61	0.900	50.1 ± 8.3

[a] For an explanation of terms used in this table see footnotes in Table V. [b] The substituents given in Table V were used omitting X = H when n = 13 and omitting X = H, Br, I when n = 11. [c] $^3J_{PtC}$ refers to coupling observed with the meta aryl carbons.

In these relationships, the ith NMR parameter is designated by Z_i. These relationships were tested by applying them to the NMR data of Tables II, III, and VII using σ_I and R^n values taken from Table IV. Through linear least-squares multiple correlation analyses, the regression coefficients and associated statistics were determined. A general purpose computer program similar to that used by Swain and Lupton[5] was used to carry out calculations. Tables V, VI, VIII, and IX summarize the results. Several of the more important correlations are also shown in Figures 1-5. The regression coefficients given in these tables are appropriate to the correlations based on the modified Swain-Lupton model (eq 4). The coefficients appropriate to the Taft model correlations are easily determined by using eq 3 to transform eq 4 into eq 5. These tables also include a "percent resonance" parameter, $\%R^n$, defined to be analogous to the parameter, $\%R$, used by Swain and Lupton[5] to describe the resonance contribution to a given parameter. The correlation coefficients, r, used here are also population corrected to account for changes in n, the number of observations.

Correlations with ^{13}C Chemical Shifts of C_6H_5X. Correlations involving the parent aromatic compounds, C_6H_5X, were examined first since it was felt that they would most likely yield the basepoints for the maximum expected correlations for the phenylplatinum complexes. As seen from Table V and Figure 1, a very good correlation is obtained for the para ^{13}C chemical shifts, δC_{para}, with σ_I and R^n. Similar correlations of δC_{para} with σ_+ ($n = 13$, $r = 0.98$; $n = 14$, $r = 0.992$,),[4a,f] σ_I, and σ^0_R (standard deviation = 0.52)[11] and with F and R ($n = 9$, $r = 0.992$)[4d,5] have already been reported. Unfortunately, comparison of these correlations is difficult because of the use of quite different substituents and solvent systems in each case. In all cases, however, the dominance of resonance effects in determining these shifts is evident.

The correlation obtained with the meta chemical shifts, δC_{meta}, is less satisfactory (see Table V and Figure 1). However, this represents the best correlation of δC_{meta} with substituent constants obtained to date.[4] Nevertheless, other unknown factors significantly affect these chemical shifts since only about 80% of their variation is accounted for by this correlation. Interestingly, if the substituents Br and I are omitted from the correlation there is a significant improvement ($n = 11$, $r = 0.98$), suggesting that a factor peculiar to these substituents is perturbing δC_{meta}.[33] Field/inductive and resonance effects appear equally important in determining δC_{meta}. However, since only a fair correlation was obtained, it is dangerous to ascribe much significance to these regression coefficients.

The Halogen Anomaly. Correlations involving the arylplatinum complexes, I and II, were calculated from data sets in which data related to complexes where X = Br and I were both included and omitted. The reason for doing this is related to the probable anomalous behavior of both Br and I when they are bonded to platinum instead of sp^2 carbon. The earliest evidence for this apparent "halogen anomaly" was reported by Chatt and Shaw[19] when, in the course of measuring dipole moments of compounds of the type *trans*-$L_2Pt(R)X$, they found the moments of the complexes, where X = Cl, Br, and I, to *increase* in the same order. This was unexpected since the electronegativities (and the σ_I's) of these X's predict an increase in the reverse order. As one possible explanation, they postulated the existence of strong dπ-dπ back-bonding contributions from Pt to X increasing along the series X = Cl, Br, I and causing a buildup of negative charge on X in excess of and overriding that expected on the basis of electronegativity considerations alone. They also suggested that this effect could be due to geometrical distortions caused by an increase in steric bulk of the halogen substituents in the same order.

In our work, we have found the chemical shift of the aromatic quaternary carbon in I to increase on going from X = Cl to X = I (see Table II). Since these chemical shifts have been shown to correlate well with σ_I values[18] (or electronegativities[21]) of substituents attached to the quaternary carbon, this order is consistent with a buildup of positive charge on platinum going from Cl to I.[34]

Since significant dπ-dπ back-bonding or geometrical distortions would not be expected between halogen and a directly bonded aromatic ring, an additional substituent effect could arise when halogen (especially Br and I) is bonded to Pt instead of aromatic carbon. It also seems reasonable to expect that this new effect might manifest itself in a trans-bonded phenyl ligand as an anomalously high field/inductive and/or low res-

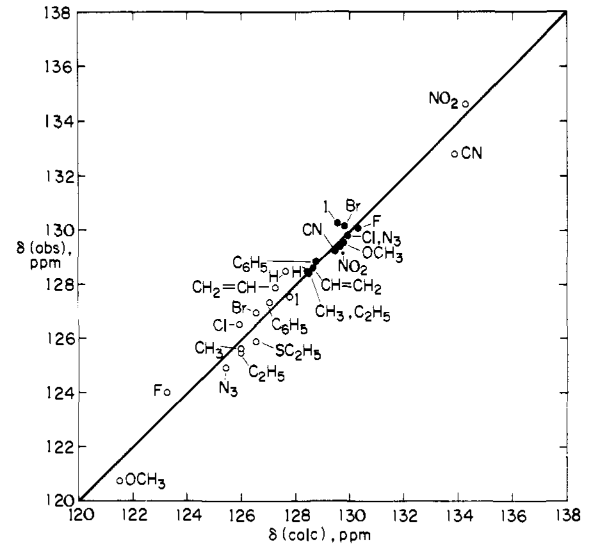


Figure 1. Observed (obsd) vs. calculated (calcd) ^{13}C chemical shifts (δ) of C_6H_5X: (●) meta carbons, (○) para carbon. Tables II and V give the numerical values.

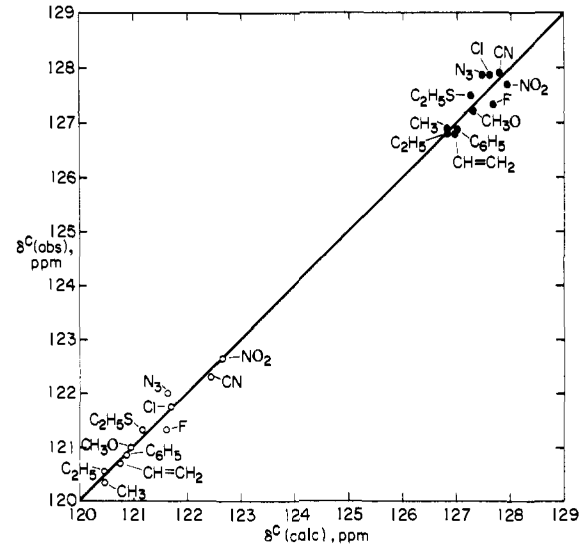


Figure 2. Observed (obsd) vs. calculated (calcd) ^{13}C chemical shifts (δ^C) of *trans*-$(PEt_3)Pt(C_6H_5)X$ (I) (●) meta carbons, (○) para carbon. Tables II and VI give the numerical values.

onance effect, since the electron density on Pt is apparently considerably diminished as a result of this effect. If the $d\pi$–$d\pi$ back-bonding explanation is correct then the trend exhibited by this effect also suggests that the effect should be considerably less significant for other substituents whose bonding atoms (to Pt) are elements of the first three rows of the Periodic table, since their d-orbital energies are higher than those of Br, I, and Pt.

The correlations obtained with the arylplatinum complexes, I and II, support the existence of this halogen anomaly since significantly improved correlations were obtained in every case where Br and I substituents were omitted from the data set (see Tables VI, IX). Furthermore, the deviations shown by Br and I were in the direction expected for substituents exhibiting abnormally high σ_I values and/or low R^n values.

Correlations with ^{13}C Chemical Shifts of I. Very good correlations were found between $\delta^C{}_{para}$ of the phenylplatinum complexes, I, and σ_I and R^n (see Table VI and Figure 2). The small difference between the correlation coefficients obtained for C_6H_5X and I (omitting Br and I) can probably be mostly accounted for by the increased importance of errors in the chemical shifts of I because of the smaller shift range relative to that of C_6H_5X (2.3 ppm vs. 14.0 ppm). The high correlation found here is strong evidence that the major factors perturbing this chemical shift are essentially the same whether the substituent is directly bonded to the aromatic ring or is attached through platinum. The regression coefficients for this correlation also show that inductive effects are clearly dominant in determining $\delta^C{}_{para}$. However, a significant resonance contribution apparently does exist (22% R^n). The statistical significance of this apparent resonance contribution was tested by examining a two-parameter model where only field/inductive effects influenced the chemical shift. As seen from Table VI, this restricted model yielded a significantly lower correlation with the chemical shifts. Significantly, the largest deviations in this correlation were associated with the substituents F and OCH_3. These substituents are also expected to exhibit the largest resonance effects (see Table IV) of the substituents examined. Comparing the two models using the F-ratio test[20] revealed a preference for the three-parameter model at the 2% level of significance. Thus, assuming a normal distribution of errors, the results imply that there is only a 2% risk of erroneously rejecting a valid two-parameter model.

The meta ^{13}C chemical shifts, $\delta^C{}_{meta}$, show a poor correlation with σ_I and R^n (see Table VI and Figure 2). This is not unexpected since the parent system, C_6H_5X, also gave a low, though somewhat better, correlation at the meta positions. Again, experimental errors may well be primarily responsible for the difference between these two correlations. Unlike the correlation noted previously for the para position, however, the probable resonance contribution to the meta chemical shift correlation is virtually insignificant (1.8% R^n).

Clark and Ward[1] in their recent ^{13}C NMR study of arylplatinum complexes relied heavily upon the difference between the meta and para chemical shifts, $\delta^C{}_{para} - \delta^C{}_{meta}$, as representing a measure of a pure resonance interaction of the substituents with the aryl ring. Using the relationships described in Table VI, this supposed resonance parameter may be expressed in one of two forms depending on which substituent effect model is preferred ($n = 11$).

$$\delta^C{}_{para} - \delta^C{}_{meta} = 1.44\sigma_I + 1.23R^n - 6.24 \qquad (6)$$

(Modified Swain-Lupton model)

$$\delta^C{}_{para} - \delta^C{}_{meta} = 1.24\sigma_I + 1.23\sigma_R{}^0 - 6.24 \qquad (7)$$

(Taft model)

As seen from this analysis, this difference parameter apparently contains substantial field/inductive character by either the modified Swain-Lupton or Taft model. Probably more important, however, is the relatively poor correlation calculated for this relationship ($r = 0.899$) reflecting the uncertain regression coefficient values. In any case, it appears that this difference parameter is not an accurate measure of the resonance interaction of substituents with an aryl ring in arylplatinum complexes. A similar analysis of this difference parameter for the parent system (C_6H_5X) revealed a parameter containing a greater resonance contribution but still a significant field/inductive parameter.

Correlations with ^{195}Pt–^{13}C Coupling Constants. The largest ^{195}Pt–^{13}C coupling constants observed were those associated with the meta carbons of the phenyl ring (see Table III). As anticipated from Clark's study, these coupling constants, $^3J_{PtC}$, were also found to be highly correlated with those of the ortho carbons ($n = 11$, $r = 0.944$). The coupling constants associated with the para carbons, $^4J_{PtC}$, however, were generally $\leq$10 Hz and were often insufficiently resolved for accurate measurements.

A fair correlation of $^3J_{PtC}$ with σ_I and R^n was also found (see Table VI and Figure 3). The resonance and field/inductive

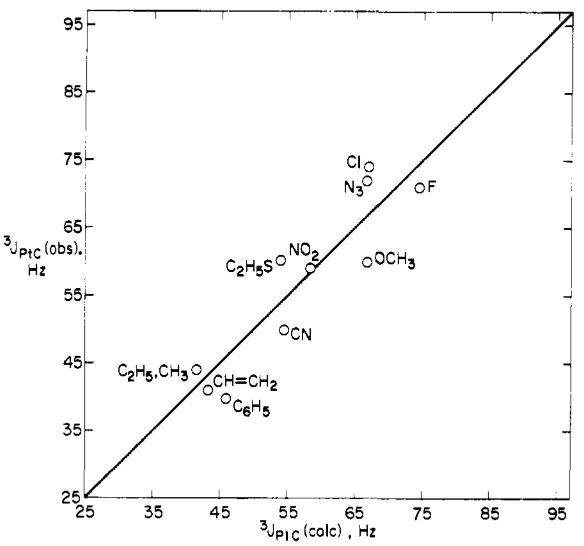


Figure 3. Observed (obsd) vs. calculated (calcd) coupling constants $^3J_{PtC}$ of *m*-aryl carbons with platinum in *trans*-$(PEt_3)_2Pt(C_6H_5)X$, I. Tables III and VI give the numerical values.

contributions appear to be of approximately equal significance here, though opposite in sign.

Other Correlations. Correlations between $\delta^C{}_{P\text{-}CH_2}$ and σ_I and R^n were found to be quite poor (see Table VI) suggesting additional unknown factors determining these chemical shifts. However, an unexpectedly high correlation was noted between $^3J_{PtC}$ and $\delta^C{}_{ortho}$ for the aryl carbons ($r = -0.945$, $n = 13$).

Correlations with ^{19}F Chemical Shifts. As noted earlier the correlations of the *m*-aryl ^{13}C chemical shifts, $\delta^C{}_{meta}$, with substituent constants were fair at best. However, Taft has shown that ^{19}F chemical shifts of both meta and para fluorine, $\delta^F{}_{meta}$ and $\delta^F{}_{para}$, exhibit high correlations with σ_I and $\sigma^0{}_R$ of directly bonded substituents. Since there appeared to be a close correspondence between the correlation of δ^C with substituent constants in both C_6H_5X and I, it seemed reasonable to expect the same correspondence to occur with the δ^F values and substituent constants. Good correlations involving $\delta^F{}_{para}$ were especially likely since there exists ample precedent for linear correlations of $\delta^C{}_{para}$ with $\delta^F{}_{para}$ in aromatic systems.[10] The ^{19}F NMR data needed to establish these correlations were, fortunately, already available from Parshall's studies[3,24,31] (see Table VII).

An excellent correlation of $\delta^C{}_{para}$ with $\delta^F{}_{para}$ was found for the arylplatinum complexes I and IIa (see Table VIII and Figure 4). Using this correlation and the ones found earlier between $\delta^C{}_{para}$ and σ_I and R^n, relationships between $\delta^F{}_{para}$ and these correlation parameters were easily derived (see Table IX and Figure 5).

A surprisingly good correlation of $\delta^C{}_{meta}$ with $\delta^F{}_{meta}$ was found for the arylplatinum complexes I and IIb (see Table VIII and Figure 4). As seen from Figure 4, the data from I and II where X = $SnCl_3$ are significant determinants of this high correlation coefficient. A relationship between $\delta^F{}_{meta}$ and the substituent parameters σ_I and R^n could be most easily derived using this correlation and the one found earlier between $\delta^C{}_{meta}$ and these same parameters. However, the latter correlation was of such poor quality as to recommend against using such a procedure. In spite of the availability of fewer observations, a better procedure involves the direct correlation of $\delta^F{}_{meta}$ with the substituent constants. The results of such an analysis are given in Table IX and Figure 5. As expected, the correlation obtained is quite good.

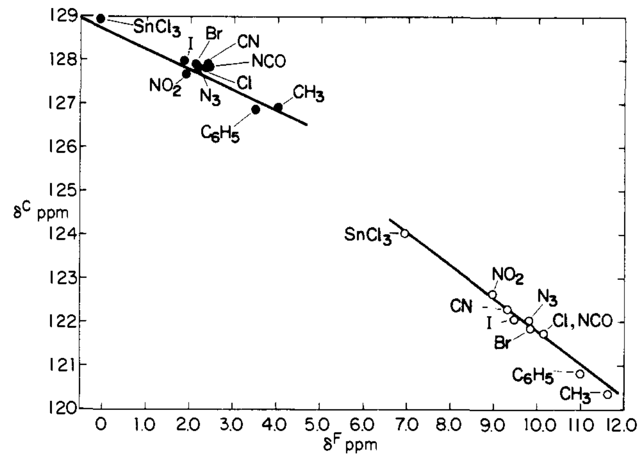


Figure 4. ^{13}C chemical shifts (δ^C) vs. ^{19}F chemical shifts (δ^F) of *trans*-$(PEt_3)_2Pt(C_6H_5)X$, I, and *trans*-$(PEt_3)Pt(C_6H_4F)X$, IIa and IIb, respectively: (●) meta positions, (○) para positions relative to platinum substituent. Tables VII and VIII give the numerical values.

Table VII. ^{19}F Chemical Shift Data[a] for Fluoroarylplatinum Complexes (IIa and IIb)

	Chemical shift, ppm[b]			
	In acetone		In cyclohexane	
Ligand (X)	Meta	Para	Meta	Para
CH_3	4.05	11.63	4.20	11.68
C_6H_5	3.54	10.99	3.71	10.96
$C_6H_5C{\equiv}C$	3.39[c]	10.40	3.37	10.4
Cl	2.37	10.15	2.52	10.23
Br	2.14	9.82	2.28	9.96
I	1.88	9.48	2.03	9.61
N_3	2.18	9.81	2.32	9.88
NCO	2.48[c]	10.15	2.48	10.2
NO_2	1.92	8.98	2.07	9.04
CN	2.43	9.31	2.49	9.29
SCN	1.88	9.21	1.99	9.22
$SnCl_3$	−0.05[c]	6.96		

[a] The data for this table were compiled from G. W. Parshall, *J. Am. Chem. Soc.*, **88**, 704 (1966); 96, 2360 (1974). G. W. Parshall has also kindly supplied additional unpublished data. [b] All spectra were measured at 2–10% substrate concentrations relative to fluorobenzene (10%) as an internal standard; positive shifts are upfield. [c] Published values were empirically adjusted to correct for solvent effects noted at high concentrations in acetone.

Table VIII. Correlation Analysis[a] of ^{19}F and ^{13}C Chemical Shift Data for Arylplatinum Complexes (I and II)

$Z = aX + b$						
Z	X	n[b]	a	b	E_z	r
$\delta^F{}_{meta}$	$\delta^C{}_{meta}$	10	−0.52 ± 0.05	128.96 ± 0.13	0.17	−0.961
$\delta^F{}_{para}$	$\delta^C{}_{para}$	10	−0.79 ± 0.03	129.62 ± 0.31	0.12	−0.994

[a] See Table V for an explanation of the terms used in this table. [b] The data for complexes I and II with X = CH_3, C_6H_5, Cl, Br, I, N_3, NCO, CN, NO_2, and $SnCl_3$ were used here (see Tables II and VII).

In these correlations, a significantly greater resonance contribution is observed in the para than in the meta positions. Interestingly, the difference between the shift parameters for these positions represents a resonance-dominated parameter (r = ca. 0.96) by either the modified Swain–Lupton (78% R^n) or Taft model.

$$\delta^F{}_{para} - \delta^F{}_{meta} = -0.80\sigma_I - 2.21\sigma^0{}_R + 7.44 \tag{8}$$

$$\delta^F{}_{para} - \delta^F{}_{meta} = -0.45\sigma_I - 2.21R^n + 7.44 \tag{9}$$

This difference parameter is probably more accurate than the one found previously with the δ^C's in view of the higher correlation coefficient obtained.

Table IX. Correlation Analysis[a] of ^{19}F Chemical Shift Data for Fluoroarylplatinum Complexes (IIa and IIb)

$Z = a\sigma_I + bR^n + c$							
Z	n	a	b	c	E_z	r	$\% R^n$
δF_{meta}	11[b]	-3.43 ± 0.38	0.79 ± 0.54	3.99 ± 0.16	0.25	0.944	15
	9[b]	-3.37 ± 0.26	0.59 ± 0.39	4.01 ± 0.11	0.17	0.977	11
δF_{para}	13[c]	-3.94 ± 0.40	-1.60 ± 0.56	11.44 ± 0.21	0.29	0.95	23
	11[c]	-3.82 ± 0.38	-1.62 ± 0.51	11.45 ± 0.20	0.26	0.96	26

[a] See Table V for an explanation of the statistical terms used in this table. [b] The data were taken from complexes IIa and IIb measured in cyclohexane with X = CH_3, C_6H_5, $C_6H_5C{\equiv}C$, Cl, Br, I, NCO, N_3, SCN, CN, and NO_2 when $n = 11$ and omitting X = Br, I when $n = 9$. [c] The data set given in Table VII applies here. The E_z and r values are approximate since it was assumed that $r = 1.00$ (vs. $r = 0.963$, actual) for the correlation coefficient of δC_{para} with δF_{para} in the calculation.

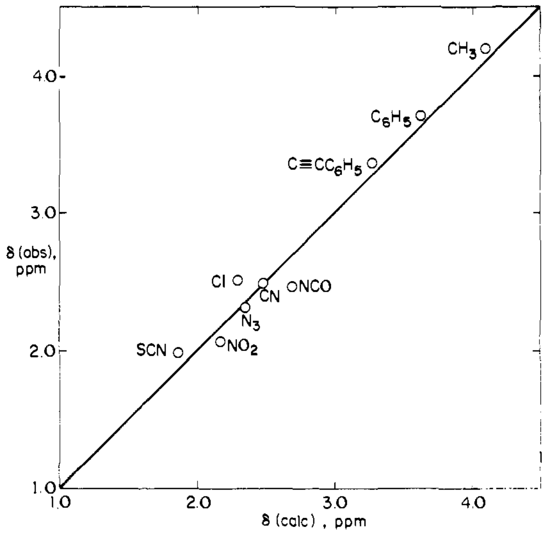


Figure 5. Observed (obsd) vs. calculated (calcd) ^{19}F chemical shifts of *trans*-$(PEt_3)_2Pt(m\text{-}C_6H_4F)X$, IIb. Tables VII and IX give the numerical values.

As found with all of our previous correlations involving arylplatinum complexes, the omission of the substituents Br and I improved the correlation of $\delta^F{}_{meta}$ with σ_I and R^n. Interestingly, this "halogen anomaly" persisted when similar correlations of $\delta^F{}_{meta}$ with these substituent parameters were examined for related Ni and Pd complexes.[24] Thus, the evidence indicates that the higher halogens (i.e., Br, I) are anomalous in their behavior as substituents attached to either Ni, Pd, or Pt with respect to correlations involving organic substituent constants.

Other Factors Affecting Correlations. The experimental errors in measuring both the NMR data and the substituent constants are important determinants of the degree of correlation obtained between them. However, the estimation of errors was hampered by a lack of data, especially that associated with substituent constants. Nevertheless, rough estimates of the probable errors are shown in Table X (see paragraph at end of article with regard to supplementary materials).

Neglect of solvent effects could significantly affect the quality of the correlations. Since most of the substituent constants were calculated from data obtained using aqueous or alcoholic solutions, correlations with data using other solvents could lead to difficulties if the substituent constants are influenced by the surrounding solvent. This has been reported to be the case for several substituents in comparisons[23] of σ_I and $\sigma^0{}_R$ values obtained by ^{19}F NMR methods with those from reactivity data. We have, in fact, found it necessary to employ adjusted σ_I and R^n values for the substituents NO_2 and CN when examining ^{19}F correlations in cyclohexane solutions (see Table IV). However, the correlations observed in chloroform and acetone solution were not sufficiently in error to justify the use of solvent adjusted substituent constants in these systems. Also, solvent effects resulting from changes in reagent concentration are negligible within the range of concentrations examined (0.2-0.5 M). Duplicate chemical shifts measured at the extremes of this range for I(X = Cl) and C_6H_5F were found to be within the experimental errors noted for duplicates measured at identical concentrations.

Finally, the application of a nonweighted linear least-squares treatment to the data is not strictly correct since there are indications that certain data are more reliable than others. It is felt, however, that the application of a weighting procedure would not significantly improve the results.

Discussion

The good correlations observed between certain substituent effects in the arylplatinum complexes, I and II, and σ_I and R^n values are good evidence for the physical dependence of these effects on the same properties which determine the σ_I and R^n values of these substituents. It may seem that such a relationship would allow for an interpretation of the σ–π donor/acceptor properties of such substituents *toward platinum* in terms of these substituent parameters. However, as pointed out by Church and Mays,[25] this need not necessarily follow since the substituent effects are generally measured at a ligand atom (e.g., aryl carbon or fluorine) and not at platinum. Thus, a substituent effect at platinum could be significantly altered following transmission to a ligand atom. However, independent evidence[28] exists suggesting that substituent effects measured by changes in $^nJ_{PtC}$ are largely determined by electronic changes at platinum. If this is true, then correlations between $^nJ_{PtC}$ and σ_I and R^n values may be interpreted as evidence supporting a correspondence between σ–π donor/acceptor properties of a substituent at platinum and these substituent constants. In fact, this correspondence does appear to be somewhat warranted, based on the qualities of the correlations observed with $^3J_{PtC}$ (see Table VI). However, our observation of a possible anomalous behavior of the substituents I and Br is a warning that if such a correspondence does exist it is probably limited to substituents which cannot engage in appreciable dπ–dπ back-bonding with platinum and/or cannot cause severe geometrical distortions. For example, the anomalous position of $P(Et)_3$ relative to $P(OR)_3$ in a "π-acceptor" series found by Church and Mays[25] in their examination of ^{19}F chemical shifts in complexes of type II can probably be understood in such terms.

In view of the physical significance of the correlation found between $^3J_{PtC}$ and σ_I and R^n, it appears justified to attempt to explain its origin. Assuming a dominant influence by the Fermi contact term, $^3J_{PtC}$ is probably determined primarily by the Pt(6s) character of the σ-bonding orbitals between the respective atoms.[1] An increase in the σ-donor capacity of the atom bonded to Pt (trans to the phenyl group) should decrease the Pt (6s) character of the bonding MO connecting the appropriate aromatic carbon to platinum.[1] This change should then be reflected as a decreased coupling constant, $^3J_{PtC}$. Now σ_I may be viewed as a measure of σ-donor/acceptor capacity;

e.g., σ_I values are known to roughly correlate with group electronegativities.[21] Thus, the σ-donor capacity of a substituent should increase as σ_I decreases and a positive correlation of σ_I with $^3J_{PtC}$ would be expected. Increases in the π-donor capacity of the substituent atom should lower the Pt (6s) character of the Pt-*substituent* bond. This should arise from the contraction of the bonding σ orbitals due to the increased positive charge on the substituent atom. The observed change should be an increase in $^3J_{PtC}$. R^n values, by definition, show a negative correlation to the π-donor capacity of substituents bonded to an aryl ring. The R^n values might then be expected to negatively correlate with the $^3J_{PtC}$ values as is, in fact, observed.

It should be noted, however, that this explanation breaks down in rationalizing the increase in $^3J_{PtC}$ in the series F < Cl < Br < I. Possibly the factors responsible for the "halogen anomaly" may also contribute to disrupting this correlation by causing changes in other factors influencing the coupling constants. For example, the 6s electron density at the Pt nucleus, $|\Psi_{Pt(6s)}(0)|^2$, could be increased by an increase in dπ–dπ back-bonding from platinum. This would be expected to cause an increase in $^3J_{PtC}$ in the order observed for halogen substituents.[22]

It is tempting to conclude that the probable existence of significant resonance contributions to δ^C_{para} and δ^F_{para} of I and IIa implies an arylplatinum π bond. Though necessary, this finding is insufficient evidence for such a conclusion. This may be seen by first assuming the arylplatinum bond in complexes such as I to exist as a pure sigma bond and then deducing the expected substituent effects on δ_{para} and δ_{meta}. In such a system π effects arising from a platinum–substituent (X) π bond could conceivably be transmitted to the aryl ring through field and/or σ-π inductive mechanisms. Changes in the chemical shifts, δ_{para} and δ_{meta}, could then be interpreted in terms of *σ and π* effects of the substituents. However, if this were the correct explanation for the observed π effects, then one would expect the relative contributions of the σ and π effects of the substituent to be the same at both the meta and para positions, since the models considered here permit only one mechanism or a set of dependent mechanisms) for the transmission of these effects through σ bonds or through space. Thus, according to either the Swain–Lupton or Taft model, the ratios of the field/inductive and resonance coefficients of the correlations involving δ_{para} and δ_{meta} should be identical if the arylplatinum bond were a pure σ bond. This, of course, is not the case as seen from comparisons of these coefficients taken from Tables VI and IX. The best test of this hypothesis is found among the ^{19}F correlations (see Table IX). Here a significant difference is found between the ratios of these coefficients ($(a/b)_{para} = 2.34$; $(a/b)_{meta} = -5.71$). The reliability of these coefficients, especially when compared to those found for δ^C, emphasizes the significance of this difference. Thus, assuming the validity of the modified Swain–Lupton or Taft model for the separation of field/inductive and resonance effects in aromatic systems, the correlations support the existence of a significant π interaction between platinum and an aryl ligand. Such a π interaction may, of course, be either bonding or antibonding in nature. However, our results do not permit a distinction between these possibilities. While these correlations shed no light on the relative magnitude of this interaction, other considerations[26] suggest that it is small and probably dependent upon the nature of the trans substituent.

A relationship between the NMR data presented here and the so-called trans influence[27] is not directly accessible because of a lack of information concerning the relative arylplatinum bond strengths of the complexes studied. Generally, it is assumed that an indirect assessment of the bond strengths of trans bonded ligands may be obtained from measurements of certain ground-state properties associated with these ligands. NMR chemical shifts and coupling constants are usually included among these properties.[2,28] We were unable, however, to define a unique trans-influence series from the NMR data (cf. Tables II and III). Series based on chemical shifts compared especially poorly with those based on coupling constants. Such poor comparisons were, of course, not unexpected since these two NMR parameters were already shown (vide supra) to depend on quite different factors associated with the trans-bonded ligands. While such contradictions have apparently been recognized in the past,[27] it does appear worth emphasizing the lack of even qualitative agreement between various NMR trans-influence series.

Experimental Section

The ^{13}C NMR spectra were measured on either a Bruker WH-90 or HFX-90 spectrometer both operated in the Fourier transform mode at 22.63 MHz. Noise-modulated proton decoupling was employed in most measurements. The spectra were measured on chloroform-*d* solutions of the compounds (0.2–0.5 M) in 10-mm sample tubes. Chemical shifts are reported in parts per million relative to tetramethylsilane (TMS) as an internal standard (ca. 5 wt %). Positive shifts are downfield in accord with the ^{13}C TMS convention (benzene = 128.50 ppm).

All of the parent aromatic compounds were commercially available and were purified by distillation, where necessary, prior to analysis.

The platinum complexes were prepared as follows. Table I documents the elemental analyses and melting points obtained for each of the complexes prepared (see paragraph at end of article regarding supplementary material).

Preparation of *trans*-Fluorophenylbis(triethylphosphine)platinum(II), I (X = F). A solution of AgF (1.41 g, ca. 10 mmol) was prepared by vigorously stirring the AgF with 100 cm^3 of dry methanol. This solution was then immediately added to a solution of *trans*-$(PEt_3)_2Pt(C_6H_5)Cl$ (5.44 g, 10 mmol) in 150 cm^3 of dry methanol. Filtration of the AgCl followed by evaporation of the filtrate gave an oil containing a black precipitate. This material was stirred with 20 cm^3 of hexane and filtered, and the filtrate was evaporated of volatiles giving a pale tan oil. The oil was placed under a high vacuum (5 μ pressure) for 96 h at room temperature to remove the last traces of methanol. The resulting oil was twice recrystallized (from 18 and then 12 cm^3 of hexane at −40 °C) giving 1.1 g (21% yield) of colorless crystals.

Preparation of *trans*-Bifluoridophenylbis(triethylphosphine)platinum(II), I (X = F_2H). A solution of *trans*-diphenylbis(triethylphosphine)platinum(II) (4.0 g, 6.83 mmol) in 40 cm^3 of dry benzene was placed in a polypropylene bottle under nitrogen. Hydrogen fluoride gas was added through a Kel-F greased polypropylene syringe (66 cm^3, 6.83 mmol) over 10 min. The mixture was stirred overnight and was then evaporated of volatiles. The residue was taken up in 45 ml of hexane and allowed to stand at −35 °C overnight. The resulting crystals were filtered off and dried (3.35 g, mp 74–130 °C). Two further recrystallizations were required to give 0.61 g of colorless crystals of the required purity.

Preparation of *trans*-Ethanethiolatophenylbis(triethylphosphine)platinum(II), I (X = SEt). A solution of sodium thioethylate was prepared by adding NaH (0.027 g, 1.10 mmol) to ethanethiol (0.068 g, 1.10 mmol) in 5 cm^3 of dry methanol. This solution was then added to *trans*-$(PEt_3)_2Pt(C_6H_5)Cl$ (0.544 g, 1.0 mmol) in 10 ml of dry methanol. The solution was allowed to stir for ca. 16 h. Evaporation of volatiles gave a white solid. This solid was stirred briefly with 8 ml of benzene and then filtered. The filtrate gave a white solid on evaporation of volatiles. This solid was recrystallized from 8 cm^3 of hexane at −50 °C, giving colorless needles (0.235 g, 58% yield).

Preparation of *trans*-Methoxyphenylbis(triethylphosphine)platinum(II), I (X = OCH_3). To a solution of *trans*-$(PEt_3)_2Pt(C_6H_5)Cl$ (1.09 g, 2.0 mmol) in 10 cm^3 of dry acetone was added, with stirring, a solution of $AgBF_4$ (0.41 g, 2.1 mmol) in 5 cm^3 of dry acetone over ca. 5 min. The precipitate of AgCl was removed by filtration and washed with acetone. The filtrate was evaporated on a rotary evaporator giving a white solid. This solid was dissolved in 10 cm^3 of dry methanol and a solution of $NaOCH_3$ (0.135 g, 2.5 mmol) in 1.25 cm^3 of methanol and added with stirring. The resulting solution was evaporated as before giving a white solid which was dissolved in ca. 15 ml of pentane and filtered, and the filtrate was again evaporated of volatiles giving a white solid. This latter procedure was repeated using 4 cm^3 of pentane. The resulting solid was placed under high vacuum (5 μ pressure) for 4 h at 75–80 °C to remove the last traces of methanol. The resulting pale yellow solid was twice recrystallized from 4 cm^3 of pentane by cooling to −40 °C giving 0.52 g of colorless crystals.

Structure verification came from an examination of the ^{1}H NMR (C_6D_6): δ (ppm) 8.05–6.82 (m, 5 H), 4.05 ($^3J_{PtH}$ = 27 Hz, 3 H), 1.1–2.0 (m, 12 H), 1.00 (quintuplet, $|^3J_{PH} + {}^5J_{PH}| + {}^3J_{HH}$ = 16 Hz, 18 H).

Preparation of *trans*-(Cyanato-*O*)phenylbis(triethylphosphine)platinum(II), I (X = NCO). The title complex was prepared according to a procedure described previously for the preparation of the *m*-fluorophenyl analog.[3] A colorless crystalline solid (75% yield) was obtained. Infrared analysis revealed a strong broad absorption at 2225 cm^{-1} (C≡N stretch).

Preparation of *trans*-Azidophenylbis(triethylphosphine)platinum(II), I (X = N_3). To a solution of *trans*-chlorophenylbis(triethylphosphine)platinum(II) (0.544 g, 1.0 mmol) in 13 ml of methanol was added a methanolic solution of sodium azide (0.065 g, 1.10 mmol). The resulting solution was stirred for 24 h and then evaporated of volatiles under vacuum. The residue was extracted with 2 × 7 ml of ether. The combined ether phases on evaporation of the ether gave a white solid which on crystallization from cold hexane (5 ml) gave 0.495 g (90% yield) of colorless crystals. Infrared analysis revealed a strong absorption at 2030 cm^{-1} (N_3^-, asymmetric stretch).

Preparation of *trans*-Nitrophenylbis(triethylphosphine)platinum(II), I (X = NO_2). A solution of sodium nitrite (0.49 g, 7.0 mmol) in methanol (20 cm^3) was prepared. To this solution was added a second solution containing *trans*-chlorophenylbis(triethylphosphine)platinum(II) (2.00 g, 3.68 mmol) in methanol (35 cm^3). The mixture was allowed to stir for 45 h. The resulting mixture was evaporated to dryness and the residue extracted with 4 × 15 cm^3 of ether and 10 cm^3 of water. The ether layers were combined and evaporated leaving a solid which was recrystallized from 25 cm^3 of 5:1 hexane–acetone giving 1.10 g of faint yellow crystals. An additional amount was obtained from the mother liquor. When recrystallized an additional 0.310 g was obtained.

Preparation of *trans*-Methylphenylbis(triethylphosphine)platinum (II), I (X = CH_3). To a solution of *trans*-chlorophenylbis(triethylphosphine)platinum(II) (0.75 g, 1.38 mmol) in 8 ml of ether was added an ethereal solution of methylmagnesium bromide (1.0 ml, 2.2 mmol). The mixture was stirred for 15 min and evaporated to dryness after quenching the reaction with 0.5 cm^3 of methanol. The resulting semisolid was mixed with 5 cm^3 of water and extracted with 3 × 5 ml of ether. The ether layers were combined and evaporated to dryness. This residue was then recrystallized from ca. 8 ml of hexane giving 0.64 g of colorless crystals.

Preparation of *trans*-Ethylphenylbis(triethylphosphine)platinum(II), I (X = C_2H_5). To a solution of *trans*-ethylphenylbis(triethylphosphine)platinum(II) (0.544 g, 1.0 mmol) in 5 ml of tetrahydrofuran was added a solution of ethyl magnesium bromide (1.5 mmol) in the same solvent. The solution was stirred for 1.5 h, evaporated of volatiles, and extracted with 2 × 5 ml of hexane. The hexane phase was concentrated to ca. 3 ml and cooled to −30 °C. Colorless crystals (0.38 g) were separated which on recrystallization gave 0.29 g (54% yield) of the title complex.

Preparation of *trans*-Ethenylphenylbis(triethylphosphine)platinum(II) I (X = CH=CH_2). Following the procedure described for the ethyl analogue and employing vinyl magnesium bromide as the Grignard reagent gave 0.44 g (41% yield) of the title complex.

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Supplementary Material Available: Table I containing analytical and melting point data for *trans*-$(PEt_3)_2(C_6H_5)PtX$ and Table X containing estimated standard errors and standard deviations contained in NMR and substituent constant data (2 pages). Ordering information is given on any current masthead page.

References and Notes

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