13C Nuclear Magnetic Resonance Studies of Organometallic Compounds. II. trans-Phenylplatinum(II) Derivatives[1,2]

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Abstract: The 13C nmr spectra have been obtained for a new series of σ-bonded phenylplatinum(II) derivatives of the type trans-[(C$_6$H$_5$)Pt(As(CH$_3$)$_3$)$_2$L]$^+$PF$_6^-$, where L is a neutral ligand. The 13C shieldings and 13C–195Pt coupling constants are discussed and compared with 13C nmr data from related trans-methylplatinum(II) complexes. Strong evidence is obtained which indicates that the overall electron density in the phenyl ring remains relatively constant. The evidence is consistent with a bonding model in which σ rather than π interactions are dominant in the phenyl–platinum bond.

For nearly 2 decades, substantial efforts have been directed toward the determination of the nature of the aryl–metal bond. In contrast with the alkyl–metal bond, which is usually viewed as a purely σ linkage, it is possible that (i) σ-inductive, (ii) π-inductive, and (iii) σ–π conjugative effects may be important in aryl–metal bonds. Support for the occurrence of π bonding has been derived from thermochemical, reactivity, X-ray crystallographic, esr, and nmr investigations; a number of these studies have been cited in a recent report by Stewart and Treichel.[3]

Nmr spectroscopy has been used frequently for this type of investigation. While 1H nmr has been employed in only a few instances,[4] 19F nmr has been used extensively in the examination of fluorinated aryl metal complexes. This activity has undoubtedly been stimulated by the original research of Taft and his coworkers.[5]

Aryl–metal bonding in fluorinated σ-aromatic derivatives of the group IV elements has been studied by a number of nmr methods. Using 19F substituent chemical shifts, Adcock, Kitching, and their coworkers[6] have indicated that σ–π conjugative effects are operative in these systems. In addition, their studies have revealed that 19F chemical shifts in aryl fluoride derivatives are subject to the effects of geometrical distortion.[6a] Eaborn[7] and coworkers have shown that the method of Taft provides an inconclusive means of assessing the relative importance of the inductive and conjugative effects in a series of fluorinated aryl silicon compounds. They suggest that their anomalous results may arise via steric compression or by through-space interactions of the aryl groups with the remaining silicon substituents.

Bonding in aryl transition metal derivatives has also been extensively examined via nmr spectroscopy. Studies of platinum,[3,8–10] iron,[3,11,12] manganese,[3,11–13] and a number of other transition metal systems have been inconclusive in showing that π aryl–metal interactions may be operative within a given series of compounds. For example, the 19F chemical shifts obtained by Parshall[8] for a series of meta- and para-fluorinated aryl platinum complexes, trans-(m- and p-C$_6$H$_4$F)Pt(P(CH$_2$CH$_3$)$_3$)$_2$X, where X is an anionic ligand, were originally interpreted in terms of a σ and π aryl–metal bonding model. In contrast, a subsequent reinvestigation[3] of these data via Taft's method indicated that variations in the inductive parameter were appreciable, while the resonance parameter was essentially invariant. Hence it was concluded that inductive effects are dominant in the transition metal–aryl bond.

Thus, it appears that the 19F nmr method of studying the bonding in transition metal aryl derivatives is beset by problems and that the interpretation of 19F chemical shift changes is uncertain. In particular, the discovery that geometrical[6a] and steric alterations,[7] as well as electronic factors, may be important in determining the chemical shifts of fluorine nuclei bound to aryl groups in metal derivatives places the conclusions derived in many of these studies on an even more tenuous footing.

Fortunately, 13C nmr spectroscopy potentially provides a technique of examining metal–aryl bonding which is not so severely hampered by such uncertainties. The measurement of *shieldings* of carbon atoms of aryl rings affords a mode of *directly observing electronic alterations* within series of σ-bonded aromatic derivatives. Thus, this method avoids the necessity of using an indirect nmr probe, such as a fluorine substituent. Moreover, since the nucleus being observed is an integral part of the aromatic ring, the additional perturbations due to *steric and geometrical interactions* of the aryl group with other substituents bonded to the metal *will be minimized*. Another advantage is that electronic interactions may be observed in terms of the

(1) Presented in part at the 56th Canadian Chemical Conference, Montreal, Canada, June 1973.

(2) For part I of this series see M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, **95**, 8574, (1973).

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(13) A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **9**, 2578 (1970).

coupling of the ^{13}C nuclei of all the aryl carbons with an appropriate metal. This particular technique has apparently been exploited in only a few studies of the nature of the aryl–metal bond.

The tin–aryl system has been examined most thoroughly by ^{13}C nmr spectroscopy, and very similar investigations[14,15] have appeared recently which presented ^{13}C shielding and coupling constant data for series of meta- and para-substituted phenyltrimethylstannanes. Roberts and his coworkers[16] have reported coupling constants between phenyl carbons and ring-bonded atoms in mercury, phosphorus, boron, and fluorine derivatives, but few ^{13}C shieldings accompanied these data. As well, there have been reports of ^{13}C nmr data obtained from several other metal phenyl derivatives[17] and most of these have been summarized by Stothers[17a] and Levy and Nelson.[17b]

In view of the above situation, it would appear that an intensive examination of a series of closely related σ-aromatic transition metal derivatives could provide significant new information about the nature of the aryl–metal bond. Accordingly, we have synthesized and obtained the ^{13}C nmr spectra of a series of complexes of the type trans-$[(C_6H_5)Pt(As(CH_3)_3)_2L]^+PF_6^-$, where L is a neutral ligand. We have specifically chosen L so that the ligands encompass a wide range of the trans influence.[18] Platinum was selected as the metal since valuable information can be obtained from coupling of ^{195}Pt ($I = \frac{1}{2}$, 34% natural abundance) with the carbons of the phenyl ring as well as from their ^{13}C shieldings. A comparison of the ^{13}C nmr data for the aryl platinum complexes with those for a series of trans-methylplatinum complexes[2] reveals that we can reach certain conclusions about the mode of metal–aryl bonding interactions in this particular series of derivatives.

Experimental Section

The following chemicals were obtained commercially and used without further purification: γ-picoline, triphenylarsine, anisonitrile, dimethylformamide, pyridine, acetyl chloride, carbon monoxide, and 3-butyne-1-ol. Phenyllithium (2.15 M in 70:30 benzene–ether) and silver hexafluorophosphate were purchased from Alfa Inorganics, Inc.

Potassium tetrachloroplatinate was prepared from platinum sponge by a modified method of Keller,[19] while trimethylarsine was smoothly prepared by the convenient new method described by Fournier and Riess.[20] cis-Dichlorobis(trimethylarsino)platinum(II) was synthesized following a modified procedure of Goodfellow, et al.[21a] Ethyl isocyanide was obtained by the method of Casanova, et al.[21b]

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(16) (a) F. J. Weigert and J. D. Roberts, J. Amer. Chem. Soc., 91, 4940 (1969); (b) F. J. Weigert and J. D. Roberts, Inorg. Chem., 12, 313 (1973).

(17) (a) J. B. Stothers, "Carbon-13 N.M.R. Spectroscopy," Academic Press, New York, N. Y., 1972; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972; (c) J. Schraml, N.-D. Chuy, V. Chvalousky, M. Magi, and E. Lippma, J. Organometal. Chem., 51, C5 (1973).

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(21) (a) R. J. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, J. Chem. Soc. A, 1604 (1968); (b) J. Casanova, Jr., R. E. Schuster, and N. D. Werner, J. Chem. Soc., 4280 (1963).

All reactions and recrystallizations were carried out using spectroscopic grade solvents. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. The infrared spectrum was recorded on a Perkin-Elmer 621 spectrometer using 0.5-mm potassium bromide cells. Uncorrected melting points were determined on a Thomas Hoover "unimelt" capillary melting point apparatus.

The ^{13}C nmr spectra were measured on a Varian XL-100-15 spectrometer operating in the Fourier transform mode at 25.2 MHz. Most spectra were determined with noise-modulated proton decoupling. In several cases, proton-coupled spectra were obtained by off-setting the decoupling frequency by ca. 30 kHz. The spectra were taken on chloroform-d and/or methylene-d_2 chloride solutions in 5-mm sample tubes and were calibrated using the solvent resonances as secondary calibration standards.[22]

A. Preparation of $((CH_3)_3As)_2Pt(C_6H_5)_2$ (1). Under a nitrogen atmosphere, 2.15 M C_6H_5Li (20 ml, 43 mmol) in 70:30 benzene-ether was added to an ice-cold suspension of $((CH_3)_3As)_2PtCl_2$ (3.0 g, 5.9 mmol) in 150 ml of diethyl ether. While the solution was stirred for 16 hr, the reaction mixture was allowed to come slowly to room temperature. Following hydrolysis with a saturated aqueous ammonium chloride solution, the ether layer was washed with water, and the combined aqueous phases were extracted with ether. The ether layers were combined (ca. 200 ml) and dried with anhydrous magnesium sulfate. Next, hexane (150 ml) was added to the ether solution, and white crystals were deposited as the solution was reduced to ca. 20 ml by rotary evaporation. After decanting the remaining liquid, the crystals were washed with two 20-ml portions of hexane, and the complex was dried under high vacuum. Evaporation of the hexane wash solutions yielded an additional amount of 1[23] (total yield 3.0 g, 86%).

B. Preparation of trans-$(C_6H_5)Pt(As(CH_3)_3)_2Cl$ (2). To a solution of $((CH_3)_3As)_2Pt(C_6H_5)_2$ (1) (0.542 g, 0.92 mmol) in 40 ml of 1:1 methylene chloride–methanol was added acetyl chloride (65.3 μl, 0.92 mmol). After the reaction mixture had been stirred for 16 hr, the solvent was evaporated under vacuum and the residue was dissolved in methylene chloride. The solution was mixed with a small quantity of activated charcoal and the mixture was filtered through a short Florisil column yielding a pale yellow solution. To this was added an equal volume of hexane, and the solvents were slowly removed on the rotary evaporator. The white crystals which deposited were washed with hexane and vacuum dried. The combined washings afforded a second crop of crystals of 2 (total yield 0.439 g, 87%).

C. Preparation of trans-$[(C_6H_5)Pt(As(CH_3)_3)_2CO]^+PF_6^-$ (9). To a solution of trans-$(C_6H_5)Pt(As(CH_3)_3)_2Cl$ (2) (0.200 g, 0.365 mmol) in 15 ml of acetone was added a solution of $AgPF_6$ (0.0925 g, 0.365 mmol) in 3 ml of acetone. Silver chloride precipitated immediately and was removed by centrifuging the reaction mixture. After bubbling carbon monoxide through this solution for 0.5 hr, the solvent was distilled on the rotary evaporator and the residue dissolved in a small amount of methylene chloride. The solution was passed through a short Florisil column and the solvent was evaporated to ca. 3 ml. The addition of ether resulted in the formation of white crystals which were washed with ether and vacuum dried, yielding 9 (0.160 g, 64%).

D. Preparation of trans-$[(C_6H_5)Pt(As(CH_3)_3)_2(:COCH_2CH_2CH_2)]^+PF_6^-$ (10). To a solution of trans-$(C_6H_5)Pt(As(CH_3)_3)_2Cl$ (2) (0.150 g, 0.275 mmol) in 20 ml of methanol was added $AgPF_6$ (0.070 g, 0.276 mmol) in 3 ml of methanol. Silver chloride immediately precipitated and was removed by centrifuging the solution; next, $HC\equiv CCH_2CH_2OH$ (21 μl, 0.275 mmol) was added, and the solution was stirred for 5 min. During this period the reaction mixture turned yellow. After removing the solvent on a rotary evaporator, the residual oil was dissolved in methylene chloride and this solution was mixed with a small quantity of activated charcoal and passed through a short Florisil column. White crystals precipitated from the solution on the addition of ether and these were washed with ether and then vacuum dried, yielding 10 (0.133 g, 67%).

The latter two procedures are typical of those used for the preparation of all the cationic complexes described here. The analytical data for the new complexes 1–10 are summarized in Table I.

(22) G. C. Levy and J. D. Cargioli, J. Magn. Resonance, 6, 143 (1972).

(23) 1 appears to be a mixture of cis and trans isomers since we observed two separate signals for the trimethylarsino ligands in the ^{13}C nmr spectrum of this material.

Table I. Analytical Data for the New Phenylplatinum Complexes $(C_6H_5)Pt(As(CH_3)_3)_2R$ **(1, 2)** and trans-$[(C_6H_5)Pt(As(CH_3)_3)_2L]$ $^+PF_6^-$ **(3–10)**

Complex	L (or R)	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Yield, %	Mp, °C
1	$C_6H_5^-$	36.7	4.79	36.8	4.89	86	160–170[b]
2	Cl^-	26.3	4.23	26.3	3.93	87	202–204
3	$(CH_3)_2NCHO$[a]	24.7	4.14	24.6	3.88	72	165–166[b]
4	$p\text{-}CH_3OC_6H_4CN$	30.4	3.83	30.6	3.64	64	164–165
5	C_5H_5N	27.7	3.83	27.8	3.67	78	218–224
6	$\gamma\text{-}CH_3C_5H_4N$	28.8	4.03	28.9	3.80	73	172–173
7	$(C_6H_5)_3As$	37.4	3.98	37.6	3.95	82	254–255
8	CH_3CH_2NC	25.3	3.96	25.5	3.67	80	163–164
9	CO[c]	22.8	3.38	22.8	32.7	64	195–215[b]
10	$:COCH_2CH_2CH_2$	26.4	4.02	26.3	3.80	67	153–154[b]

[a] $(CH_3)_2NCHO$ is probably O bonded; see M. H. Chisholm and H. C. Clark, Inorg. Chem., **12**, 991 (1973). [b] Complex melts with decomposition. [c] $\nu_{CO} = 2096(\pm2)\,cm^{-1}\,(CH_2Cl_2)$.

Table II. ^{13}C Shieldings[a] for trans-$(C_6H_5)Pt(As(CH_3)_3)_2Cl$ **(2)** and trans-$[(C_6H_5)Pt(As(CH_3)_3)_2L]$ $^+PF_6^-$ **(3–10)**

Complex	L	Solvent	δ_{C_1}	$\delta_{C_{2,6}}$	$\delta_{C_{3,5}}$	δ_{C_4}	$[\delta_{C_4} - \delta_{C_{3,5}}]$	δ_{AsC}	Other
2		CDCl₃	131.9	136.7	127.3	121.8	−5.5	7.9	
3	$(CH_3)_2NCHO$	CDCl₃	118.4	135.8	127.4	122.6	−4.8	7.5	δ_{CH_3} 32.3, 38.0; δ_{CHO} 168.2
		CD₂Cl₂	118.9	136.3	127.8	123.0	−4.8	7.7	δ_{CH_3} 32.5, 38.1; δ_{CHO} 168.2
4	$p\text{-}CH_3OC_6H_4CN$	CDCl₃	126.8	135.9	128.0	123.3	−4.7	8.1	δ_{CH_3O} 55.7, δ_{C_1} 99.3 $\delta_{C_{2,6}}$ 134.8, $\delta_{C_{3,5}}$ 115.4, δ_{C_4} 164.5, δ_{NC} 123.5
5	C_5H_4N	CDCl₃	126.4	136.6	127.4	122.9	−4.5	7.3	$\delta_{C_{3,5}}$ 126.7, $\delta_{C_{2,6}}$ 151.8, δ_{C_4} 138.5
		CD₂Cl₂	127.1	136.9	127.8	123.1	−4.7	7.4	$\delta_{C_{3,5}}$ 127.1, $\delta_{C_{2,6}}$ 152.1, δ_{C_4} 137.4
6	$\gamma\text{-}CH_3C_5H_3N$	CDCl₃	126.9	136.6	127.5	122.7	−4.8	7.3	δ_{CH_3} 20.8, $\delta_{C_{3,5}}$ 127.5, $\delta_{C_{2,6}}$ 151.0, δ_{C_4} 150.8
7	$(C_6H_5)_3As$	CD₂Cl₂	142.7	136.7	128.0	124.6	−3.4	10.0	$\delta_{C_6H_5}$ 129.0–134.2
8	CH_3CH_2NC	CDCl₃	142.0	136.4	128.0	123.5	−4.5	9.2	δ_{CH_3} 13.8, δ_{CH_2} 39.4
9	CO	CD₂Cl₂	141.7	135.6	129.1	125.4	−3.7	10.0	δ_{CO} 177.6
10	$:C^1C^2H_2C^3H_2C^4H_2O$	CDCl₃	146.2	138.4	127.6	123.5	−4.1	9.3	δ_{C_1} 275.6, δ_{C_2} 58.9, δ_{C_3} 19.5, δ_{C_4} 87.9

[a] In ppm (±0.1) from TMS (downfield positive).

Table III. $^{13}C\text{-}^{195}Pt$ Coupling Constants[a] for trans-$(C_6H_5)Pt(As(CH_3)_3)_2Cl$ **(2)** and trans-$[(C_6H_5)Pt(As(CH_3)_3)_2L]$ $^+PF_6^-$ **(3–10)**

Complex	L	Solvent	$\mid^1J_{PtC_1}\mid$	$\mid^2J_{PtC_{2,6}}\mid$	$\mid^3J_{PtC_{3,5}}\mid$	$\mid^4J_{PtC_4}\mid$	$\mid^2J_{PtAsC}\mid$	Other
2		CDCl₃	858 ($\pm$1)	28 ($\pm$1)	64 ($\pm$1)	12 ($\pm$1)	55 ($\pm$2)	
3	$(CH_3)_2NCHO$	CDCl₃	b	31 ($\pm$1)	66 ($\pm$1)	12 ($\pm$2)	53 ($\pm$2)	
		CD₂Cl₂	b	28 ($\pm$2)	68 ($\pm$2)	b	53 ($\pm$2)	
4	$p\text{-}CH_3OC_6H_4CN$	CDCl₃	818 ($\pm$1)	26 ($\pm$1)	59 ($\pm$1)	8 ($\pm$2)	50 ($\pm$2)	
5	C_5H_4N	CDCl₃	754 ($\pm$1)	25 ($\pm$2)	56 ($\pm$1)	10 ($\pm$2)	50 ($\pm$2)	$^3J_{PtC_{3,5}}$ 22 ($\pm$2)
		CD₂Cl₂	758 ($\pm$2)	25 ($\pm$1)	56 ($\pm$1)	10 ($\pm$2)	52 ($\pm$2)	$^3J_{PtC_{3,5}}$ 21 ($\pm$1)
6	$\gamma\text{-}CH_3C_5H_3N$	CDCl₃	752 ($\pm$1)	24 ($\pm$1)	55 ($\pm$1)	8 ($\pm$2)	50 ($\pm$2)	$^3J_{PtC_{3,5}}$ 27 ($\pm$2)
7	$(C_6H_5)_3As$	CD₂Cl₂	692 ($\pm$2)	26 ($\pm$1)	52 ($\pm$2)	10 ($\pm$2)	45 ($\pm$2)	
8	CH_3CH_2NC	CDCl₃	646 ($\pm$1)	21 ($\pm$1)	45 ($\pm$1)	8 ($\pm$1)	48 ($\pm$2)	
9	CO	CD₂Cl₂	642 ($\pm$2)	23 ($\pm$1)	46 ($\pm$1)	8 ($\pm$1)	43 ($\pm$2)	$^1J_{PtCO}$ 884 ($\pm$1)
10	$:C^1C^2H_2C^3H_2C^4H_2O$	CDCl₃	502 ($\pm$1)	16 ($\pm$1)	34 ($\pm$1)	b	50 ($\pm$2)	$^1J_{PtC_1}$ 764 ($\pm$4), J_{PtC_2} 97 ($\pm$2), J_{PtC_4} 48 ($\pm$2)

[a] In Hz. [b] Platinum satellites not observed.

Results

The ^{13}C nmr shieldings and coupling constants obtained from the spectra of complexes **2–10** are summarized in Tables II and III, respectively. We have not determined the relative signs of the $^{13}C\text{-}^{195}Pt$ coupling constants; thus the absolute values of these parameters are presented in Table III. Although the signs of $^1H\text{-}^{13}C$, $^{19}F\text{-}^{13}C$, and $^{31}P\text{-}^{13}C$ coupling constants in benzene,[16] fluorobenzene,[16] and triphenylphosphine[24] are well known, there do not appear to be any sign

(24) S. Sørensen, R. S. Hansen, and H. J. Jakobsen, J. Amer. Chem. Soc., **94**, 5900 (1972).

determinations for monosubstituted benzenes with main group or transition metal substituents. Needless to say, the use of absolute values of coupling constants is adequate for the arguments we will present later. The ^{13}C nmr spectrum of the aromatic region of trans-$(C_6H_5)Pt(As(CH_3)_3)_2Cl$ **(2)** is a typical example which is shown in Figure 1.

In all cases, the high field resonances in the spectra were assigned to the arsenic methyl groups. The intense central signals are flanked by ^{195}Pt satellites of ca. one-fourth intensity. The shieldings of these signals, ca. 7–10 ppm, and the $^2J_{PtAsC}$ values, ca. 43–55 Hz are
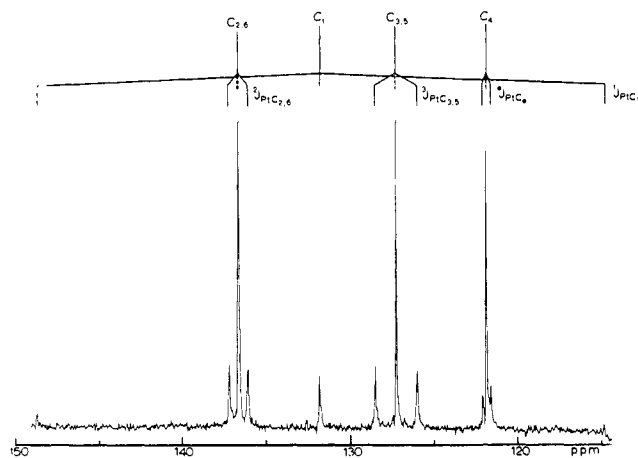
Figure 1. ^{13}C nmr spectrum (25.2 MHz) of the aromatic region of trans-$(C_6H_5)Pt(As(CH_3)_3)_2Cl$ (2) in $CDCl_3$ solution.

reminiscent of the values we obtained for the series of complexes of the type trans-$[(CH_3)Pt(As(CH_3)_3)_2L]^+$-$PF_6^{-2}$, which were ca. 7–10 ppm and 42–53 Hz, respectively. Thus the trimethylarsino ligands appear to occupy mutually trans orientations as we have found for the arsino substituents of the trans-methylplatinum series. Furthermore, if the arsino donors adopted a cis orientation, we would anticipate separate arsine methyl carbon resonances due to their inherent nonequivalence.

The assignments of the carbon resonances of the phenyl substituents warrant special consideration. The para and quaternary carbon signals could be distinguished from one another and from the ortho and meta carbons on the basis of their relative intensities. The ortho and meta carbons of 2 and 3 were differentiated by the method described by Scott.[25] In their proton coupled ^{13}C nmr spectra, the ortho carbon resonances exhibited two $^3J_{CH}$ values (ca. 7 Hz) while the meta carbon signals showed only one $^3J_{CH}$ value. Both ^{13}C shieldings and coupling constants for all the complexes 2–10 are consistent with the assignments[17a,b] proposed for related organometallic phenyl derivatives.

The signals arising from the ligands trans to the phenyl substituent were specifically assigned by comparing their ^{13}C nmr parameters with those derived from the analogous trans-methylplatinum complexes.[2]

Discussion

Theory. The qualitative origins of ^{13}C shieldings in monosubstituted benzenes have received considerable attention;[17a,b,26] both quaternary and ortho carbons appear to be susceptible to inductive, resonance, and anisotropic effects of the substituent. On the other hand, substituent effects contribute minimally to meta carbon shieldings which span a relatively small range for a wide variety of compounds. It is possible that meta carbon shieldings are related to the inductive properties of the substituent, but apparently this has not been conclusively established. For example, there is no obvious relationship in a plot of the Taft σ_I parameters vs. meta carbon shieldings for an extensive series of monosubstituted benzenes.[26] Conversely, a large body of evidence exists which supports the view that para

carbon shieldings are governed by substituent σ and π inductive effects. The shieldings of these carbons span a range of ca. 20 ppm for a large selection of monosubstituted benzenes, where a good linear relationship is observed for a plot of the Taft σ_R values vs. the para carbon shieldings.[26] Moreover, an improvement in the linear relationship results when the para carbon shieldings are "corrected" by plotting $[\delta_{C(para)} - \delta_{C(meta)}]$ vs. σ_R. This "corrected" parameter presumably reflects pure resonance interactions of a substituent within the phenyl ring.

Assuming that the Fermi contact mechanism is dominant, one-bond ^{13}C–^{195}Pt coupling constants are anticipated to be sensitive mainly to the hybridization of the σ-bonding orbitals between these atoms.[18] For a series of trans-methylplatinum derivatives, we recently showed that substitution of the ligand trans to the methyl group resulted in large changes in $^1J_{PtC}$, while $^1J_{CH}$ for the methyl group was essentially invariant.[2] This evidence supports the theory that α_{Pt}^2, the s character of the hybrid platinum σ-bonding orbital, is mainly responsible for alterations in $^1J_{PtC}$ and $^2J_{PtCH}$. In addition, similar arguments have been extended to two- and three-bond coupling constants in methyl,[27–29] perfluoromethyl,[28] and vinyl[30] platinum derivatives. Thus, we may expect that the one- to four-bond ^{13}C–^{195}Pt coupling constants of the phenyl carbon atoms of the complexes we have examined here will also exhibit a similar dependence on hybridization at the ^{195}Pt and ^{13}C nuclei.

The trans influence,[31] which is defined as the tendency of a ligand to weaken a bond trans to itself, is also believed to reflect the rehybridization of metal σ orbitals, in response to ligand changes. Thus, relative trans influence series may be deduced via nmr spectroscopy. The π-acceptor properties of a trans ligand L and the charge of a complex also may have some effect on the σ-donor ability of a ligand and hence on its nmr trans influence. However, for series of platinum derivatives, it has not yet been demonstrated that the nmr trans influence is sensitive to these phenomena.

To summarize, we expect that the ^{13}C shieldings of the aryl carbons in a series of phenylplatinum derivatives will reflect anisotropic, σ-inductive, π-inductive, and σ–π interactions within the aryl–metal bond. In comparison, ^{13}C–^{195}Pt coupling constants may exhibit variations due to changes in σ bonding in the platinum–ligand, platinum–phenyl, and possibly the ring carbon–carbon bonds by σ-inductive, σ-rehybridization, and/or σ–π conjugative interactions.

^{13}**C Nmr Data. General Information.** The nmr data obtained from the new phenylplatinum derivatives 2–10 reveal that, with variations in the ligands trans to the phenyl group, large relative fluctuations in the ^{13}C nmr parameters may occur. The shieldings of the quaternary aromatic carbons change from the extremes of ca. 118–146 ppm when dimethylformamide is replaced by the cyclic carbene :$\overline{CCH_2CH_2CH_2O}$. In distinct con-

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trast, the shieldings of the ortho, meta, and para carbons change within much smaller ranges.

As anticipated, the $^{13}C-^{195}Pt$ coupling constants in the phenyl group also exhibit a dependence on the trans ligand. $^1J_{PtC_1}$, $^2J_{PtC_{2,6}}$, and $^3J_{PtC_{3,5}}$ span the ranges 502–858, 16–31, and 34–68 Hz, respectively, while $^4J_{PtC_4}$ appears to remain almost constant, being ca. 10 (± 2) Hz. From either the $^1J_{PtC_1}$, $^2J_{PtC_{2,6}}$ or $^3J_{PtC_{3,5}}$ values we can derive approximate nmr trans-influence series, such as that shown below for some of the ligands used in 3–10.

<div align="center">carbene > CO ≈ isocyanide > arsine > nitrile</div>
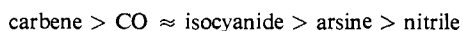
This nmr trans-influence series generally holds irrespective of which type of coupling constant is used. Moreover, it is identical with that series which we observed for the related trans-methylplatinum derivatives.[2] As the σ-donor ability of the ligand trans to the phenyl group increases, the ligand will compete more effectively for Pt(6s) character. This is obtained partially at the expense of the platinum–carbon bond of the phenyl group, and lower values of J_{PtC_1} are observed.

In comparison, the ^{13}C shieldings and $^{13}C-^{195}Pt$ coupling constants of the trimethylarsino donors, like those of their related methylplatinum complexes, do not vary so appreciably.

^{13}C **Shieldings.** Earlier, we briefly noted that the ^{13}C shieldings of the quaternary carbons of the platinum phenyl groups vary from 118.4 to 146.2 ppm, a span of ca. 28 ppm. In contrast, the shieldings of the ortho, meta, and para carbons fall in the ranges 135.6–138.4, 127.3–129.1, and 121.8–125.4 ppm, respectively, spanning 3, 2, and 4 ppm in that order. These results immediately indicate that only minor changes in σ-inductive, π-inductive, or σ–π conjugative effects occur between the platinum and phenyl ring. If these effects are operative, and the ortho, meta, and para carbon shieldings are as sensitive as the quaternary carbon shieldings, we might anticipate much larger alterations in the ortho and para carbon shieldings. Additional support for this idea comes from the observation that the ortho and para carbons span ranges similar to that of the meta carbons which, if anything, will only weakly reflect σ-inductive alterations.

The similarity of the shieldings of the meta carbons (127.3–129.1 ppm) with those of benzene (128.7 ppm)[17a] is consistent with the general observation that meta carbon shieldings are relatively insensitive to substituent variations. On the other hand, the ortho and para carbon shieldings differ significantly from 128.7 ppm; indeed, it is apparent that aryl–platinum interactions are occurring and that the ortho and para carbon shieldings are sensitive to these effects.

A curious feature of these ^{13}C shielding data is the relative insensitivity of the ortho carbons to changes in the ligand trans to the phenyl group. For changes in group directly bonded to a monosubstituted benzene, fluctuations for ortho carbons of ca. one-third the changes in the shieldings of the quaternary carbons occur.[26] Quite possibly, the phenomenon we observe is related to the fact that the point of substitution of the ligand is one bond removed from the phenyl ring.

It is also interesting to note that the ortho carbons in 2–10 are deshielded relative to benzene, while the para carbons are shielded. Presumably the neighborhood anisotropy of platinum outweighs any σ-inductive, π-inductive, or σ–π conjugative changes reflected at the

ortho position. It appears that the anisotropy effect may be a deshielding factor, while the through bond electronic effects seem to shield the aromatic carbons. This scheme would account for the opposite deviations of the ortho and para carbons from 128.7 ppm.

In any event, it appears that neither changes in σ-inductive, π-inductive, or σ–π conjugative effects result in gross bonding modifications through the phenyl ring. It is possible, however, that the shieldings of the ortho, meta, and para carbons are not particularly sensitive to these types of modification, even if they are appreciable. On the other hand, there definitely seems to be some significant interaction of platinum with the phenyl carbons over and above that revealed by the shielding variations induced by ligand variations.

As we mentioned earlier, an informative treatment of $^{19}F^5$ and $^{13}C^{26,32}$ nmr data involves subtracting the shielding of a nucleus at the meta position from that at the para position, the result being used to provide a measure of pure resonance interactions of a substituent within the phenyl ring. We have carried out these subtractions and the differences [$\delta_{C_4} - \delta_{C_{3,5}}$] are given in Table II, together with the other ^{13}C shielding data. For derivatives 3–6 and 8 this value (ca. −4.7 ppm) is virtually constant, indicating again that changes in π interactions are small in these complexes. On the other hand slight variations occur for the complexes with triphenylarsine (−3.4 ppm), carbon monoxide (−3.7 ppm), and the cyclic carbene (−4.1 ppm). These donors are the most likely of all the ligands used here to undergo π bonding with platinum, and it is possible that these differences arise from some changes in this type of interaction. The differences do not seem to result from solvent effects, since the parameter [$\delta_{C_4} - \delta_{C_{3,5}}$] is constant within the experimental error for 3 (ca. −4.8 ppm) and 5 (ca. −4.6 ppm), which were examined in both chloroform-d and methylene-d_2 chloride solutions. The slight difference in the shielding of the para carbon of the chloro derivative 2 may similarly result from minor modifications in phenyl–metal π interaction, possible as a reflection of the different charge of the complex.

Next, we reviewed the ^{13}C shielding data to determine if there was a relationship between δ_{C_1} (phenyl) and δ_C (methyl) of the related trans-[(CH$_3$)Pt(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$-L]$^+$PF$_6^-$ complexes.[2,33] To our gratification, this ex-

(32) A referee has suggested that we "might find it enlightening" to convert our ^{13}C nmr parameters to Taft σ_R^0 and σ_I values as was done by Stewart and Treichel[3] for their ^{19}F nmr parameters. In view of the lack of correlation between the Taft σ_I parameters and meta carbon shieldings for a large series of monosubstituted benzenes,[26] a strictly analogous derivation is not possible. Moreover, we have already considered several of the pitfalls inherent in such ^{19}F nmr methods in the introduction. Nevertheless, the observed linear correlation between [$\delta_{C_4} - \delta_{C_{3,5}}$] for monosubstituted benzenes allows us to calculate σ_R^0 values for the "[Pt(As(CH$_3$)$_3$)$_2$L]$^+$PF$_6^-$" portions of the phenylplatinum complexes. As was observed previously for fluorinated phenyl platinum derivatives,[3] the calculated σ_R^0 parameters vary in a relatively small range (0.06 units), again indicating that the changes in π-inductive interactions in the phenyl rings are relatively small, assuming that such a derivation is valid.

(33) We have previously demonstrated[2] that excellent linear relationships exist between both $^1J_{PtC}$(CH$_3$) values and the methyl carbon shieldings of two series trans-[(CH$_3$)Pt(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$L]$^+$PF$_6^-$ (A) and trans-[(CH$_3$)Pt(As(CH$_3$)$_3$)$_2$L]$^+$PF$_6^-$ (B) for complexes having common ligands. While it would be most appropriate to compare the phenyl derivatives with the complexes of series B, the availability of more complexes of series A with all the same ligands used in the phenyl derivatives makes series A a more useful choice for comparative purposes. Due to the excellent linear relationships, we have already noted between series A and B, the use of series B in this study would not alter our conclusions in any significant manner.
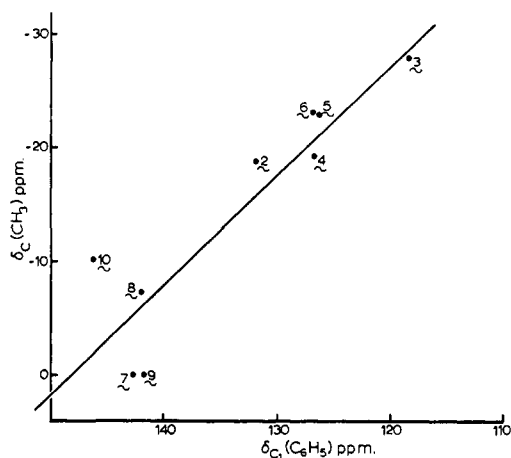
Figure 2. Plot of $\delta_C(CH_3)$ vs. $\delta_{C_i}(C_6H_5)$ for complexes of the type trans-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$ and 2–10.

amination revealed a reasonably good linear correlation which is summarized in the following equation[34]

$$\delta_C(CH_3) = 0.96(\pm 0.02)\delta_{C_i}(C_6H_5) - 142.3(\pm 2.5);$$

$$r = 0.903 \quad (1)$$

The relationship is shown in Figure 2.

This result suggest that the σ-inductive and neighborhood anisotropy effects of the analogous methyl- and phenylplatinum series parallel one another and that the π-inductive and σ–π conjugative effects of the latter series either remain fairly constant or change parallel to the alterations in σ-inductive and neighborhood anisotropy effects. The latter choice is unlikely, however, in view of the restricted range we have noted for the para carbon shieldings in 2–10.

Since the trans ligands used in 2–10 are capable of a range of π-inductive effects, it is useful to consider separately the complexes which bear ligands not expected to undergo major π interactions with platinum. The omission of the data points for the triphenylarsine 7, carbonyl 8, and cyclic carbene 10 complexes yields the linear relationship[34]

$$\delta_C(CH_3) = 0.87(\pm 0.02)\delta_{C_i}(C_6H_5) - 131.3(\pm 2.1);$$

$$r = 0.971 \quad (2)$$

For these derivatives the substantially improved linear fit adds support to our inference that the amount of π-inductive interaction between platinum and the phenyl ring is almost constant. Additionally, it does appear that the points for 7, 9, and 10, which lie significantly away from the line described by eq 2, deviate because of changes in π interactions with the phenyl ring.

Nevertheless, these conclusions do not provide information about the actual magnitude of platinum–phenyl π interactions for the complete series 2–10. If the amount of π bonding were large, we might anticipate large changes in the shieldings of the phenyl ring carbons upon the introduction of carbon monoxide, an excellent π-bonding ligand. For 9, the shielding of C_4 is ca. 2.5 ppm upfield from the average C_4 shielding (ca.

(34) The average deviations of the slopes and intercepts for all the linear equations presented here are calculated on the basis of the maximum possible error due to the inherent uncertainty of the experimental measurements. These errors have already been cited in Tables II and III. It is worthwhile noting that these variations represent the maximum error in *precision* and that as such they may be generous estimates.

123.0 ppm) for the non-π-bonding ligands 2–6 and 8. This relatively small change is consistent with a model in which the absolute magnitude of phenyl–platinum π-bonding is small; a similar conclusion has been reached by Stewart and Treichel for their fluorinated phenylplatinum complexes.[3] They claim "that minor changes in σ_R^0 reflect the relative unimportance of π bonding to the ring relative to other ligands." While this sort of evidence is not unequivocal in favor of a model in which the absolute magnitude of phenyl–platinum π-bonding is relatively small, it certainly is consistent with such an interpretation.

It is also interesting to note that the points for the same ligands (triphenylarsine, carbon monoxide, and the cyclic carbene), which produced deviations from the usual $[\delta_{C_4} - \delta_{C_{3,5}}]$ values of 3–6 and 8, lie significantly away from the line described by eq 2. This information may provide corroborative grounds for the use of the $[\delta_{C_4} - \delta_{C_{3,5}}]$ values to indicate changes in resonance interactions within the platinum–quaternary carbon bond. However, since both positive and negative deviations of the points for 7, 9, and 10 occur, it is not clear that such a use of $[\delta_{C_4} - \delta_{C_{3,5}}]$ is definitive.

$^{13}C–^{195}Pt$ Coupling Constants. First, the $^{13}C–^{195}Pt$ coupling constants of the phenylplatinum groups were examined in order to determine if any quantitative interrelationships existed between the $^{1-4}J_{PtC}$ values. The parameters derived from a linear regression analysis of these data are summarized in Table IV.[34]

Table IV. Linear Regression Analysis Parameters[a] for $^{13}C–^{195}Pt$ Coupling Constants of the Phenylplatinum Groups for the Relationships $^nJ_{C_x} = A^mJ_{C_y} \pm B$

$^nJ_{C_x}$	A	$^mJ_{C_y}$	B, Hz	r
$^1J_{PtC_1}$	$+27.9 (\pm 2.0)$	$^2J_{PtC_{2,6}}$	$+48 (\pm 48)$	0.924
$^1J_{PtC_1}$	$+11.9 (\pm 1.1)$	$^3J_{PtC_{3,5}}$	$+97 (\pm 55)$	0.993
$^1J_{PtC_1}$	$+28.4$	$^4J_{PtC_4}$	$+476$	0.544
$^2J_{PtC_{2,6}}$	$+0.41 (\pm 0.13)$	$^3J_{PtC_{3,5}}$	$+2.9 (\pm 6.7)$	0.959
$^2J_{PtC_{2,6}}$	$+1.5$	$^4J_{PtC_4}$	$+11.7$	0.840
$^3J_{PtC_{3,5}}$	$+3.3$	$^4J_{PtC_4}$	$+24.5$	0.755

[a] Error limits are not provided for the relationships involving $^4J_{PtC_4}$ whose values have an extremely high *relative* error.

Plots of $^1J_{PtC_1}$ vs. $^2J_{PtC_{2,6}}$ and $^3J_{PtC_{3,5}}$ for the derivatives 2–10 are shown in Figure 3. In our previous work,[2] we showed that the differences in the relationships of $^1J_{PtC}$ vs. $^2J_{PtCH}$, for series of the type trans-$(CH_3)Pt(P(CH_3)_2(C_6H_5))_2X$ and trans-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$, where X and L are anionic and neutral ligands, respectively, did not appear to depend appreciably on the charge of the complex. Thus we have included the neutral chloride derivative 2, in our calculations of the linear regression parameters.[35]

It is immediately evident that good linear relationships exist involving $^1J_{PtC_1}$, $^2J_{PtC_{2,6}}$, and $^3J_{PtC_{3,5}}$, and not $^4J_{PtC_4}$. To a first approximation, it seems that the factors governing $^1J_{PtC_1}$ parallel and thus may be very similar to those affecting $^2J_{PtC_{2,6}}$ and $^3J_{PtC_{3,5}}$. This

(35) It is noteworthy that the correlation coefficients generally decrease with the increasing relative errors of the coupling constants. For example, the equation for $^1J_{PtC_1}$ vs. $^3J_{PtC_{3,5}}$ yields $r = 0.993$, while $^1J_{PtC_1}$ vs. $^2J_{PtC_{2,6}}$ gives $r = 0.924$, probably reflecting the larger relative errors in $^2J_{PtC_{2,6}}$ compared with $^3J_{PtC_{3,5}}$. Thus, any comments on the significance of these differences in correlation coefficients must take into account the inherent differences due to variations in the relative errors of the J values.
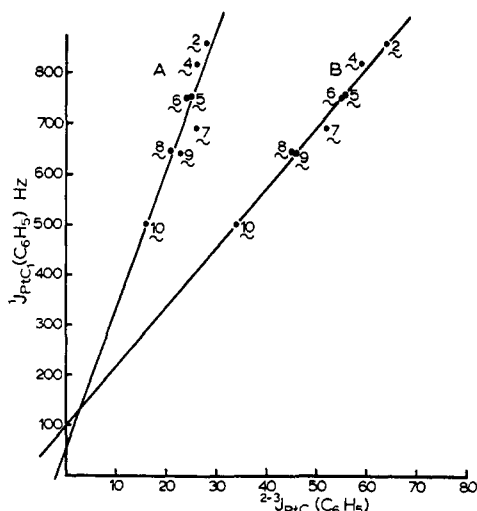
Figure 3. Plots of $^1J_{PtC_1}$ vs. $^2J_{PtC_{2,6}}$ (A) and $^3J_{PtC_{3,5}}$ (B) for 2 and 4-10.

Figure 4. Plots of $^1J_{PtC}(CH_3)$ vs. $^1J_{PtC_1}$ (A), $^2J_{PtC_{2,6}}$ (B), and $^3J_{PtC_{3,5}}(C_6H_5)$ (C) for complexes of the type trans-[(CH₃)Pt(P-(CH₃)₂(C₆H₅))₂L]⁺PF₆⁻ and 2-10.

may also be the case for $^4J_{PtC_4}$; however, the large relative errors in this parameter probably mask any such correlation. That $^4J_{PtC_4}$ is very small and seemingly invariant with $^{1-3}J_{PtC}$ indicates that changes in σ-orbital hybridization at the platinum atom are reflected very poorly at the para carbon. The differences in the intercepts of the plots of $^1J_{PtC}$ vs. $^2J_{PtC_{2,6}}$ and $^1J_{PtC}$ vs. $^3J_{PtC_{3,5}}$ from themselves and the origin, while possibly not significant, may result from small contributions to one or both of the J values by terms other than the Fermi contact interaction. Possibly σ-inductive and/or σ-π conjugative effects or some other aryl-platinum interaction give rise to these nonzero intercepts. Nevertheless, this evidence is consistent with the idea that the values of $^1J_{PtC}$, $^2J_{PtC_{2,6}}$, and $^3J_{PtC_{3,5}}$ are dominated by the Fermi contact mechanism.

Next, we compared the one-bond $^{13}C-^{195}Pt$ coupling constants for the methyl group of an analogous series of complexes trans-[(CH₃)Pt(P(CH₃)₂(C₆H₅))₂L]⁺PF₆⁻ [2,33] with the $^{1-4}J_{PtC}$ values of the phenyl groups of 2-10. This examination revealed even more informative linear correlations which are summarized in Table V, and three of these are shown graphically in Figure 4.

Table V. Linear Regression Analysis Parameters[a] for the Relationships $^1J_{PtC}((CH_3)Pt)$ vs. $^nJ_{PtC}((C_6H_5)Pt)$: $^1J_{PtC}(CH_3) = A^nJ_{PtC}(C_6H_5) \pm B$

A	$^nJ_{PtC}$	B	r
0.79 (±0.03)	$^1J_{PtC_1}$	−1 (±18)	0.999
21.0 (±2.1)	$^2J_{PtC_{2,6}}$	61 (±50)	0.940
9.4 (±1.0)	$^3J_{PtC_{3,5}}$	75 (±51)	0.994
27.4	$^4J_{PtC_4}$	337	0.670

[a] Error limits are not provided for the relationships involving $^4J_{PtC_4}$ whose values have an extremely high relative error.

First and most importantly, we point out the excellent linear relationship between the two one-bond coupling constants which passes through the origin. Hence, it appears that (a) the one-bond $^{13}C-^{195}Pt$ coupling constants of the two series are strongly related, almost certainly through σ-inductive and σ-rehybridization effects and (b) $^1J_{PtC}$ for the quaternary phenyl carbons does not seem to reflect the influences of any π-

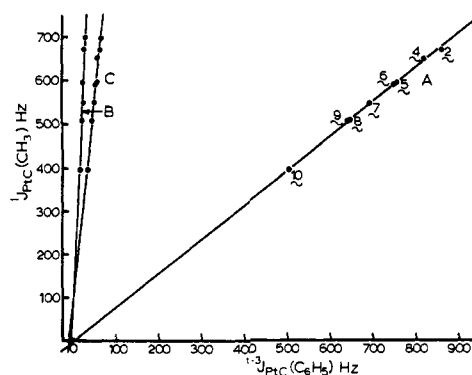inductive or σ-π conjugative effects. Furthermore, from the linear relationship of $^1J_{PtC}(CH_3)$ with $^2J_{PtC_{2,6}}$ and $^3J_{PtC_{3,5}}$, which have very similar intercepts, we can deduce that the effects of rehybridization of the platinum σ-orbitals reflected at the ortho and meta carbons parallel those governing one-bond platinum-carbon coupling constants of a platinum methyl group and one another. This supports our conclusion that the differences observed in the plots of $^1J_{PtC_1}(C_6H_5)$ vs. $^2J_{PtC_{2,6}}$ and $^3J_{PtC_{3,5}}$ are probably not very significant. Finally, the rather poorer correlation we derived for $^1J_{PtC}(CH_3)$ vs. $^4J_{PtC_4}$ is also in accord with the notion that $^4J_{PtC_4}$ is insensitive to rehybridization changes in the phenyl-platinum bond, or such a relationship is at least masked by the large relative errors in this four-bond coupling constant.

We now turn from the linear relationships to a discussion of some other interesting features which examination of the $^{13}C-^{195}Pt$ coupling constants reveals. The $^1J_{PtC_1}$ values for 2-10, which span the range 502-858 Hz, are reminiscent of the values of the one-bond $^{13}C-^{195}Pt$ coupling constants (666-1080 Hz) we determined for the sp² hybridized carbons of carbene ligands in some trans-methylplatinum complexes.[2] $^1J_{PtC(carbene)}$ (764 Hz) of the cyclic carbene complex 10 also falls in this range. In addition, $^1J_{PtC(carbonyl)}$ of the carbonyl complex 9 is 884 Hz, approximately in line with those values (986-1774 Hz) we determined for the sp hybridized carbons of other carbonyl derivatives.[2] These observations add support to the idea that gross changes in $^1J_{PtC}$ result from rehybridization of the carbon atom directly bonded to platinum. A comparison of the $^1J_{PtC(carbonyl)}$ value for 9 with that value (1005 Hz) which we observed for the methylplatinum analog trans-[(CH₃)Pt(As(CH₃)₃)₂CO]⁺PF₆⁻ indicates that the nmr trans influence of a C₆H₅⁻ group is significantly higher than that of a CH₃⁻ ligand. To date, we are not aware of any corroborative evidence for this observation, although we would anticipate this result on the basis of the hybridizations of the quaternary phenyl and methyl carbons.

Finally, we briefly consider the effects of solvent variations on the ^{13}C nmr parameters. As for trans-methylplatinum derivatives,[2] the effects of changing the solvent from chloroform-d to methylene-d₂ chloride do not induce significant variations in any of the coupling constants, although the ^{13}C shieldings do appear to behave more sensitively.

Conclusion

From our systematic examination of the ^{13}C nmr parameters of the phenylplatinum derivatives 2–10, we have deduced the following bonding information: (1) σ-inductive, π-inductive, and σ–π conjugative effects remain relatively constant in the phenyl rings of this series of compounds, (2) the absolute magnitude of the phenyl–platinum π interaction may be small while the absolute magnitude of the σ interaction appears to be appreciable, (3) σ–π conjugative interactions do not appear to occur.

There are several other important conclusions concerning the ^{13}C shieldings and ^{13}C–^{195}Pt coupling constants which arise from this work: (1) modifications in one- to three-bond ^{13}C–^{195}Pt coupling constants in the phenyl rings are probably dominated by platinum σ-orbital rehybridization, (2) one-bond ^{13}C–^{195}Pt coupling constants do not seem to reflect π-inductive or σ–π conjugative effects.

Idealized Polytopal Forms. Description of Real Molecules Referenced to Idealized Polygons or Polyhedra in Geometric Reaction Path Form

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Abstract: Molecules or ions in the cluster and coordination compound classes can be systematically ordered and rationalized for all x-atom families in terms of idealized geometric (polytopal) forms. With the exception of forms with cubic symmetry, explicit descriptions of polyhedra require information on symmetry *and* shape parameters. It is sometimes difficult to distinguish between reference idealized models for a real molecule in the condensed physical states. Most precise data are derived from X-ray studies of the crystalline state where the molecule departs to varying degrees from idealized models. A comprehensive and quantitative measure of shape in such aggregates can be readily obtained from the dihedral angles formed by the normals to adjacent polytopal faces. This measure is presented in terms of reaction paths that interrelate probable idealized geometries. It is recommended that these dihedral angle data be reported in structure investigations not only for a guide to pictorialization of the molecular geometry but also for the generation of extensive data that may bear on intramolecular rearrangements of the molecules (or ions) in the liquid, solution, or gaseous state.

An irksome phrase, encumbered with imprecise English and often[2] encountered in structural papers, is "the molecule is a distorted trigonal bipyramid" or octahedron, square plane, etc. Certain atoms in a molecule may describe *precisely* the vertices of a *regular* tetrahedron or *may nearly* describe the vertices of some idealized polygon or polyhedron. Such descriptions, properly phrased and soundly based, are of great value to the follower of structural chemistry. A more objective and quantitative assessment of shape referenced to common or readily visualized geometric forms would further assist the casual and the serious reader in a substantive fashion. There are many examples in present-day crystallographic papers where a sensible measure of shape cannot be gained from the impressive tabulations of data and structural parameters short of construction of a model from the table of positional parameters or from the distance–angle parameters for the molecule. We propose a procedure, which is an extension and generalization of a specific application made by Porai-Koshits and Aslanov,[3] that leads to a quantitative measure of polytopal shape referenced to idealized geometries and that imposes little additional burden on the crystallographer. This measure of shape, couched in terms of geometric reaction paths, should be of general value to those scientists interested in or studying intramolecular rearrangements[4–14] in molecular systems.

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(2) We both admit to having used such phraseology.