atoms form a closed shell. In this latter compound the copper atoms form a triangle with $\sim D_3$ symmetry.[20]

Assuming that some metal–metal interaction occurs in the trimers, an asymmetric mixing of empty orbitals energetically close to the filled ground orbitals, a second-order Jahn–Teller interaction,[35] may account for the distortions observed. An asymmetric mixing is possible between empty and filled d orbitals of the palladium atoms. If, for example, one assumes that the dominant orbital splitting of palladium d orbitals is caused by a square arrangement of sulfur atoms, the metal $d_{x^2-y^2}$ orbitals are empty but only an electron volt or so removed from the filled d orbitals. In D_3 symmetry these $d_{x^2-y^2}$ orbitals transform as A_2 and E. The highest filled orbital set is likely d_{z^2} which transforms as A_1 and E. The vibrational coordinates which change the metal–metal distances transform as A_1 and E, also. Consequently this model would lead to an asymmetric mixing of the filled d_{z^2} with the empty $d_{x^2-y^2}$ orbitals by means of the e vibrational coordinate. Displacement along this coordinate leads to removal of the trigonal symmetry. While it is impossible at present to determine quantitatively the magnitude of the effect, the features required qualitatively are present in the trimeric palladium complexes.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8566.

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^{13}C Nuclear Magnetic Resonance Studies of Organometallic Compounds. I. *trans*-Methylplatinum(II) Derivatives[1]

M. H. Chisholm, H. C. Clark,*[2] L. E. Manzer, J. B. Stothers, and J. E. H. Ward

Contribution from the Department of Chemistry, The University of Western Ontario, London, Ontario, N6A 3K7, Canada. *Received June 16, 1973*

Abstract: The ^{13}C nmr spectra have been obtained for three series of *trans*-methylplatinum(II) complexes of the type *trans*-$[(CH_3)Pt(As(CH_3)_3)_2L]^+PF_6^-$, *trans*-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$, and *trans*-$(CH_3)Pt(P(CH_3)_2(C_6H_5))_2X$, where L is a neutral ligand and X is an anionic substituent. The ^{13}C shieldings and ^{13}C–^{195}Pt coupling constants are discussed and compared with data derived from ^{1}H nmr spectra of the complexes. Evidence is obtained which supports the rehybridization theory of the nmr trans influence.

In principle, there are certain distinct advantages of using ^{13}C nmr rather than ^{1}H nmr spectroscopy for the investigation of organometallic compounds. ^{13}C nmr parameters have been demonstrated to exhibit considerably greater sensitivity to changes in bonding and molecular structure.[3] The use of off-resonance and noise-modulated proton decoupling enables first-order assignments to be made without the sometimes tedious spectral analysis. Moreover, ^{13}C nmr offers a unique method of directly observing the effects of stereochemical and bonding alterations of coordinated groups such as acetylenes, carbonyls, isocyanides, and olefins, which contain carbon atoms immediately bonded to a transition metal.

Our preliminary ^{13}C nmr investigations[4,5] have attempted to exploit this potential. In those studies, we examined a number of organoplatinum derivatives and were able to show that valuable information could be derived from the coupling of the ^{195}Pt ($I = {}^1/_2$, 34% natural abundance) and ^{13}C nuclei, as well as from the ^{13}C shieldings. Although ^{13}C nmr investigations of organometallic compounds are now relatively common, few reports[6-11] have appeared which involve detailed examination of series of closely related complexes.

We now wish to describe a *systematic* study of three series of σ-bonded platinum(II) complexes, (I) *trans*-$[(CH_3)Pt(As(CH_3)_3)_2L]^+PF_6^-$, (II) *trans*-$[(CH_3)Pt$-

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[1] This work may also be regarded as part 35 of the series ^{13}C Nmr Studies. Part 34: J. B. Stothers and C. T. Tan, *Can. J. Chem.*, in press.

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Table I. Analytical Data for the New Complexes *trans*-$[RPt(L)_2L']^+PF_6^-$

Complex	R	L′	L	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Yield, %	Mp, °C
2	CH_3	*p*-$CH_3OC_6H_4CN$	$As(CH_3)_3$	24.7	3.87	25.0	3.59	85	178–180
3	CH_3	$CH_3C_5H_4N$	$As(CH_3)_3$	22.7	4.10	22.9	3.86	86	151–152
4	CH_3	$(C_6H_5)_3As$	$As(CH_3)_3$	33.3	4.02	33.8	3.88	94	216–217
5	CH_3	CH_3CH_2NC	$As(CH_3)_3$	18.5	4.03	18.5	3.75	79	65–68
6	CH_3	CH_3NC	$As(CH_3)_3$	17.0	3.80	17.2	3.67	87	146–150
7	CH_3	CO[a]	$As(CH_3)_3$	15.4	3.39	15.6	3.13	80	131–132
13	Cl	CO[b]	$As(CH_3)_3$	13.1	2.80	13.0	2.96	62	143–144
21	CH_3	$CH_3C_5H_4N$	$P(CH_3)_2(C_6H_5)$	38.1	4.45	38.0	4.20	94	*c*
23	CH_3	CH_3CH_2NC[d]	$P(CH_3)_2(C_6H_5)$	35.0	4.40	35.2	4.32	95	81–82

[a] ν_{CO} = 2085 (±2) cm^{-1} (CH_2Cl_2). [b] ν_{CO} = 2104 (±2) cm^{-1} (CH_2Cl_2). [c] Compound **21** is an oil. [d] Previously isolated as the SbF_6^- salt: H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **11**, 503 (1972).

$(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$, and (III) *trans*-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2X]$ where X is an anionic substituent such as chloride or cyanide, while L is a neutral ligand such as a nitrile, isocyanide, or carbene. We have specifically chosen L and X so that these substituents encompass a wide range of the nmr trans influence.[12] In addition, we have included three carbene derivatives derived from series I, in which the platinum methyl groups are replaced by chloro substituents.

The ^{13}C and ^1H data derived from these complexes are discussed in the light of the current rehybridization theory of the trans influence. We also comment on some interesting correlations that emerge from these data.

Experimental Section

The following chemicals were obtained commercially and used without further purification: γ-picoline, triphenylarsine, and anisonitrile from Eastman Organic Chemicals, carbon monoxide from Liquid Carbonic Canadian Corporation Ltd., and silver hexafluorophosphate from Alfa Inorganics Inc.

Potassium tetrachloroplatinate was prepared from platinum sponge by a modified method of Keller.[13] *trans*-Methylchlorobis(trimethylarsino)platinum(II)[14] and *trans*-methylchlorobis(dimethylphenylphosphino)platinum(II)[15] were synthesized following the procedures of Ruddick and Shaw, and *cis*-dichlorobis(trimethylarsino)platinum(II)[16] was prepared by a modified procedure of Goggin, *et al.* Methyl and ethyl isocyanide were obtained by the method of Casanova, Schuster, and Werner.[17]

All reactions and recrystallizations were carried out using spectrograde solvents. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer using 0.5-mm potassium bromide cells. Uncorrected melting points were determined on a Thomas Hoover "Uni-melt" 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. The spectra were usually determined with proton noise decoupling, but, in several cases, coupled spectra were obtained by off-setting the decoupling frequency by *ca.* 30 kHz. Using both 5- and 10-mm sample tubes, the spectra were usually taken on chloroform-*d*, methylene-d_2 chloride, or acetone-d_6 solutions and were calibrated with tetramethylsilane as the internal reference. In some cases the solvent resonances were used as secondary calibration standards.[18]

^1H nmr spectra were recorded on a Varian HA-100 spectrometer and the ^1H chemical shifts are reported with tetramethylsilane as the internal standard.

A. Preparation of *trans*-$[(CH_3)Pt(As(CH_3)_3)_2(p\text{-}NCC_6H_4OCH_3)]^+PF_6^-$ **(2).** To a solution of *p*-$NCC_6H_4OCH_3$ (0.227 g, 1.71 mmol) and *trans*-$(CH_3)Pt(As(CH_3)_3)_2Cl$ (0.826 g, 1.71 mmol) in 20 ml of acetone was added $AgPF_6$ (0.431 g, 1.71 mmol). The solution was stirred for 10 min and the precipitated silver chloride was removed by centrifuging the solution. The solvent was removed on a rotary evaporator and the remaining oil was taken up in 5 ml of chloroform. Ether was added dropwise to afford large colorless crystals, which were filtered and washed with ether, yielding **2** (1.06 g, 85%).

B. Preparation of *trans*-$[(CH_3)Pt(As(CH_3)_3)_2(As(C_6H_5)_3)]^+PF_6^-$ **(4).** To a solution of *trans*-$(CH_3)Pt(As(CH_3)_3)_2Cl$ (0.200 g, 0.41 mmol) in 10 ml of acetone was added a solution of $AgPF_6$ (0.104 g, 0.41 mmol) in 2 ml of acetone. After being stirred for 15 min, the reaction mixture was centrifuged and the colorless solution decanted from the residual silver chloride. To this solution was added $(C_6H_5)_3As$ (0.126 g, 0.41 mmol). After the mixture had been stirred for 15 min, the solvent was evaporated yielding a white solid. This was washed thoroughly with ether, the crystals were dissolved in methylene chloride, and the solution was filtered through a small amount of Florisil. Addition of ether to this solution caused crystallization of **4** (0.348 g, 94%), which was washed thoroughly with ether and vacuum dried.

C. Preparation of *trans*-$[(CH_3)Pt(As(CH_3)_3)_2(CNCH_3)]^+PF_6^-$ **(6).** To a solution of *trans*-$(CH_3)Pt(As(CH_3)_3)_2Cl$ (0.540 g, 1.11 mmol) in 20 ml of acetone was added methyl isocyanide (0.057 ml, 1.11 mmol) followed by KPF_6 (0.205 g, 1.11 mmol). The reaction mixture was stirred for 30 min and the solvent was removed by rotary evaporation. The complex was extracted from the residue with dichloromethane, and these washings were filtered. Addition of ether followed by cooling at 0° for 4 hr afforded white needles of **6** (0.611 g, 87%).

D. Preparation of *trans*-$[(CH_3)Pt(As(CH_3)_3)_2(CO)]^+PF_6^-$ **(7).** *trans*-$(CH_3)Pt(As(CH_3)_3)_2Cl$ (0.517 g, 1.07 mmol) was dissolved in 15 ml of acetone, and carbon monoxide was bubbled through the solution. $AgPF_6$ (0.269 g, 1.07 mmol) in 10 ml of acetone was added and the solution was stirred under a carbon monoxide atmosphere for 10 min. The silver chloride was removed by centrifuging the reaction mixture and the volume of the solution was reduced to *ca.* 5 ml and cooled in ice. White crystals slowly precipitated upon the addition of ether, and the solution was then cooled at 0° for 12 hr. After filtering and washing with ether, the solid was dried *in vacuo* yielding **7** (0.535 g, 80%).

The preceding four procedures are typical of those used for the preparation of all the new complexes described here. The compounds *trans*-$[(CH_3)Pt(As(CH_3)_3)_2L]^+PF_6^-$ where L = γ-picoline, **3**, and ethyl isocyanide, **5**, as well as *trans*-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$ where L = γ-picoline, **21**, and ethyl isocyanide, **23**, were prepared by methods similar to that described in B. The chlorocarbonyl derivative *trans*-$[ClPt(As(CH_3)_3)_2(CO)]^+PF_6^-$ was synthesized from $((CH_3)_3As)_2PtCl_2$ by a procedure similar to D. References for the preparations of all the other complexes accompany their nmr data which are presented later.

The analytical data for the new complexes are summarized in Table I.

Results

The ^{13}C nmr shieldings and coupling constants obtained from the spectra of the complexes of series I–III are summarized in Tables II–V. Some of these param-

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Table II. ^{13}C Shieldings[a] and Coupling Constants[b] for *trans*-$[RPt(As(CH_3)_3)_2L]^+PF_6^-$ and Related Complexes, **1–15**

Complex	R	L	Solvent	Platinum methyl δC	Platinum methyl $\lvert ^1J_{PtC}\rvert$	Platinum methyl $\lvert ^1J_{CH}\rvert$	Arsine methyls δC	Arsine methyls $\lvert ^2J_{PtAsC}\rvert$	Other ^{13}C nmr data	Ref[c]
1	CH_3	C_6F_5CN	$(CH_3)_2CO$	−25.5	616 (±2)		8.3	48 (±2)	δC_6F_5,[d] δCN[d]	*g*
2	CH_3	*p*-$CH_3OC_6H_4CN$	$CDCl_3$	−26.9	613 (±2)	127 (±2)	8.1	48 (±2)	δCN 121.2, $^2J_{PtNC}$ = 82 (±2); δC_1 99.5; $\delta C_{2,6}$ 134.4; $\delta C_{3,5}$ 115.3; δC_4 164.2; δOCH_3 55.6	*h*
			CD_2Cl_2	−26.9	612 (±2)		8.3	50 (±2)		
			$(CD_3)_2CO$	−27.4	615 (±2)		7.7	47 (±2)		
3	CH_3	γ-$CH_3C_5H_4N$	$CDCl_3$	−30.8	566 (±2)	127 (±2)	7.3	50 (±2)	δCH_3 20.7; $\delta C_{3,5}$ 127.4; δC_4 150.4; $\delta C_{2,6}$ 150.6	*h*
4	CH_3	$(C_6H_5)_3As$	CD_2Cl_2	−6.8	512 (±2)		9.9	42 (±2)	δC_6H_5 129.1–134.8[e]	*h*
5	CH_3	CH_3CH_2NC	CD_2Cl_2	−14.0	475 (±2)	125 (±2)	9.4	45 (±2)	δCH_3 13.9, δCH_2 39.5, δNC[d]	*h*
6	CH_3	CH_3NC	$CDCl_3$	−14.0	475 (±2)		9.7	47 (±2)	δCH_3 29.5, δNC[d]	*h*
7	CH_3	CO	$(CH_3)_2CO$	−6.8	470 (±2)	128 (±2)	10.0	42 (±2)	δCO 178.7, $^1J_{PtC}$ = 1005 (±3)	*h*
8	CH_3	$:C(CH_3)(N(CH_3)_2)$	CD_2Cl_2	−19.8	385 (±1)		9.2	53 (±1)	$\delta :C$ 245.1, $^1J_{PtC}$ = 694 (±6)[f]	*i*
9	CH_3	$:C(CH_3)(NH(CH_3))$	CD_2Cl_2	−17.6	381 (±1)		9.1	51 (±1)	$\delta :C$ 247.3, $^1J_{PtC}$ = 687 (±3)[f]	*i*
10	CH_3	$:C(CH_3)(NH_2)$	CD_2Cl_2	−18.6	380 (±1)		8.8	53 (±1)	$\delta :C$ 255.6, $^1J_{PtC}$ = 666 (±3)[f]	*i*
11	CH_3	$:C(CH_3)(OCH_3)$	$(CH_3)_2CO$	−15.9	360 (±3)		9.5	50 (±3)	$\delta :C$ 321.0, $^1J_{PtC}$ = 759 (±3); δCH_3 44.2, $^2J_{PtCC}$ = 86 (±3); δOCH_3 70.6, $^3J_{PtCOC}$ = 67 (±3)	*j*
12	CH_3	Cl^-	$(CH_3)_2CO$	−28.4	643 (±2)		7.9	53 (±2)		*k*
13	Cl	CO	CD_2Cl_2				10.0	33 (±2)	δCO 159.2, $^1J_{PtC}$ = 1747 (±3)	*h*
14	Cl	$:C(CH_3)(OCH_3)$	$(CD_3)_2CO$				8.7	48 (±2)	$\delta :C$ 278.3; δCH_3 9.2, $^2J_{PtCC}$ = 78 (±2); δOCH_3 72.1, $^3J_{PtCOC}$ = 95 (±2)	*i*
15	Cl	$:C(CH_3)(N(CH_3)_2)$	$(CD_3)_2CO$				8.6	50 (±3)	$\delta :C$ 210.3, $^1J_{PtC}$ = 1070 (±3)[f]	*i*

[a] In ppm (±0.1) from TMS (downfield positive). [b] In Hz. [c] Reference to synthesis and ^1H nmr data. [d] Resonance(s) not observed. [e] Multiplet. [f] See Table V. [g] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971). [h] This work. [i] M. H. Chisholm and H. C. Clark, to be submitted for publication. [j] M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971). [k] H. C. Clark and R. J. Puddephatt, *ibid.*, **9**, 2670 (1970).

Table III. ^{13}C Shieldings[a] and Coupling Constants[b] for the Complexes *trans*-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$, **16–27**

Complex	L	Solvent	Platinum methyl δC	Platinum methyl $\lvert ^1J_{PtC}\rvert$	Platinum methyl $\lvert ^2J_{PPtC}\rvert$	Phosphine methyls δC	Phosphine methyls $\lvert ^1J_{PC} + {}^3J_{PPtPC}\rvert$	Phosphine methyls $\lvert ^2J_{PtPC}\rvert$	Other ^{13}C nmr data	Ref[c]
16	$(CH_3)_2NCHO$	CD_2Cl_2	−27.8	698 (±2)	5 (±2)	11.0	36 (±2)	36 (±2)	δCH_3 32.0, 38.2; δCO 166.9, δC_6H_5 128.6–131.9[e]	*m*
17	*p*-$CH_3OC_6H_4CN$	$(CD_3)_2CO$	−19.1	652 (±2)	6 (±2)	11.9	38 (±2)	38 (±2)	δCN 121.2, $^2J_{PtNC}$ = 82 (±2); δC_1 100.8, $\delta C_{2,6}$ 135.6, $\delta C_{3,5}$ 115.9, δC_4 165.0, δOCH_3 56.3, δC_6H_5 131.4–135.2[e]	*n*
18	$CH_3C{\equiv}CCH_3$	CD_2Cl_2	−4.2	632 (±4)	6 (±2)	11.4	38 (±2)	38 (±2)	δCH_3 8.1, J_{PtC} = 14 (±2); $\delta C{\equiv}C$ 69.5, J_{PtC} = 18 (±2), δC_6H_5 129.1–131.7[e]	*o*
19	$CH_2{=}CH_2$	CD_2Cl_2	+5.6	615 (±6)	6 (±2)	10.5	40 (±2)	40 (±2)	δCH_2 84.4, J_{PtC} = 50 (±2), δC_6H_5 128.3–132.1[e]	*m*
20	C_5H_5N	$(CD_3)_2CO$	−22.7	598 (±2)	6 (±2)	11.0	38 (±2)	38 (±2)	*d*	*p*
21	γ-$CH_3C_5H_4N$	CD_2Cl_2	−23.0	594 (±2)	6 (±2)	11.0	38 (±2)	37 (±2)	δC_6H_5 132.9; C_5H_4N: $\delta C_{3,5}$ 127.0, δC_4 150.4, $\delta C_{2,6}$ 150.6; δCH_3 20.7	*q*
22	$(C_6H_5)_3As$	CD_2Cl_2	0.0	548 (±2)	6 (±2)	13.3	40 (±2)	40 (±2)	δC_6H_5 128.8–134.2[e]	*q*
23	CH_3CH_2NC	CD_2Cl_2	−7.2	510 (±2)	*g*	13.5	*g*	*g*	δCH_3 13.1, δCH_2 39.3, δC_6H_5 128.7–130.9[e]	*q*
24	CH_3NC[h,i]	CD_2Cl_2	−7.1	510 (±2)	7 (±2)	13.2	38 (±2)	37 (±2)	δCH_3 29.2, δC_6H_5 128.7–133.5[e]	
25	CO	CD_2Cl_2	0.0	509 (±3)	6 (±2)	13.6	40 (±3)	40 (±2)	δCO 177.6, $^1J_{PtC}$ = 986 (±5), $^2J_{PPtC}$ = 10 (±3)	*p*
26	$:\overline{C^1C^2H_2C^3H_2C^4H_2O}$	CD_2Cl_2	−10.1	395 (±2)	9 (±2)	12.1	40 (±2)	40 (±2)	δC^4 87.9, J_{PtC^4} = 50 (±2); δC^3 18.9, J_{PtC^3} = 17 (±2), δC^2 57.2, J_{PtC^2} = 90 (±2), δC^1 299.2, δC_6H_5, 128.6–134.2[e]	*r*
27	$(CH_3)_2(C_6H_5)P$[j]		+0.7	457 (±2)	*g*, *k*	16.6 13.8	40 (±2) 36 (±2)	20 (±2)[l] *g*	δC_6H_5 129.6–132.3	*p*

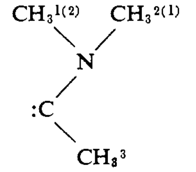
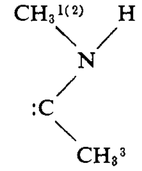
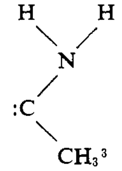
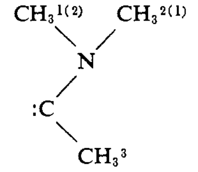
[a–f] See Table II. [g] Coupling constant not resolved. [h] SbF_6^- counterion used. [i] ^1H nmr spectrum obtained at 0°. [j] *trans*-Phosphine ligands are exchanging. [k] $^2J_{PPtC}$(trans) = 75 Hz. [l] $^1J_{PC}$ = 30 Hz. [m] M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **12**, 991 (1973). [n] H. C. Clark and L. E. Manzer, *ibid.*, **10**, 2699 (1971). [o] M. H. Chisholm and H. C. Clark, *ibid.*, **10**, 2557 (1971). [p] H. C. Clark and J. D. Ruddick, *ibid.*, **9**, 1226 (1970). [q] This work. [r] M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971).

Table IV. ^{13}C Shieldings[a] and Coupling Constants[b] for the Complexes *trans*-$(CH_3)Pt(P(CH_3)_2(C_6H_5))_2X$, **28–32**

Complex	X	Solvent	Platinum methyl			Phosphine methyls			Other ^{13}C nmr data	Ref[c]
			δC	$\lvert {}^1J_{PtC} \rvert$	$\lvert {}^2J_{PPtC} \rvert$	δC	$\lvert {}^1J_{PC} + {}^3J_{PPtPC} \rvert$	$\lvert {}^2J_{PtPC} \rvert$		
28	Cl	CD_2Cl_2	−18.7	673 (±3)	7 (±1)	12.0	36 (±1)	36 (±1)	δC_6H_5[d]	15
29	I	$CDCl_3$	−7.3	664 (±2)	6 (±2)	15.2	38 (±2)	38 (±2)	δC_6H_5[d]	15
30	NCS[f]	$CDCl_3$	−22.8	632 (±2)	6 (±2)	12.3	38 (±2)	38 (±2)	δC_6H_5 127.5–133.7,[e] δNCS[d]	*g*
31	NO_2	CD_2Cl_2	−26.1	564 (±2)	6 (±1)	12.3	38 (±2)	38 (±2)	δC_6H_5[d]	*g*
32	CN	CD_2Cl_2	−11.1	495 (±2)	8 (±2)	14.2	40 (±2)	40 (±2)	δCN 138.5, $^2J_{PPtC} = 12\ (\pm 3)$; δC_5H_5 128.1–134.7[e]	*g*

[a–e] As in Table II. [f] Nmr (T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, **11**, 1786 (1972)) and infrared studies (K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1966, p 173) indicate that NCS is N bonded. [g] T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, **11**, 1786 (1972).

Table V. ^{13}C Shieldings[a] and Coupling Constants[b] for the Carbene Complexes *trans*-$[RPt(As(CH_3)_3)_2(carbene)]^+PF_6^-$, **8–10** and **15**

Complex	R	Carbene	δC^1	$\lvert {}^3J_{PtCNC^1} \rvert$	δC^2	$\lvert {}^3J_{PtCNC^2} \rvert$	δC^3	$\lvert {}^2J_{PtCC^3} \rvert$
8	CH_3		50.5	56 (±1)	41.1	20 (±1)	31.9	51 (±1)
9	CH_3		39.6	60 (±1)			36.6	50 (±1)
10	CH_3						37.7	58 (±1)
15	Cl		41.6	94 (±3)	52.0	40 (±3)	33.0	76 (±3)

[a,b] As in Table II.

eters differ slightly from those we recorded in our previous communication.[4] We have not performed relative sign determinations for either the ^{13}C or ^1H coupling constants. Although one- and two-bond coupling constants may be anticipated to have opposite signs,[3a, 19] the use of absolute values of the coupling constants is adequate for our purposes. The ^{13}C nmr spectrum of $[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2CN]$ (**32**) is a typical example which is shown in Figure 1.

In all cases, except **13–15**, the high field resonances in the spectra were assigned to the methylplatinum groups of series I–III. These assignments were made on the basis of the relative intensities of these peaks in comparison with those of the arsine (*ca.* 1:6) or phosphine (*ca.* 1:4) methyl substituents. The central resonances of the platinum methyl groups are flanked by ^{195}Pt satellites (*ca.* one-fourth of the central signal's intensity) whose separation appears to be sensitive to the nature of the trans substituent L or X.

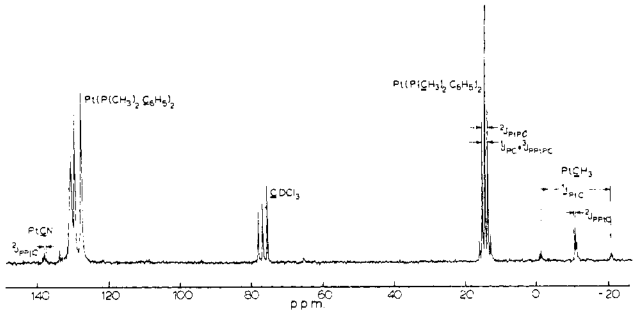


Figure 1. ^{13}C nmr spectrum (25.2 MHz) of $(CH_3)Pt(P(CH_3)_2(C_6H_5))_2CN$ (**32**) in CD_2Cl_2 solution.

In the case of the phosphine derivatives **15–32** each of the three components of the platinum methyl resonances appear as 1:2:1 triplets, due to equal coupling of the methyl carbon with the two phosphorus nuclei. This typical pattern is illustrated in Figure 1.

Similarly, the carbon resonances of the phosphine methyl groups appear as triplets, flanked by ^{195}Pt

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(19) (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).

Table VI. ^{1}H Nmr Chemical Shifts[a] and Coupling Constants[b] for the New Complexes *trans*-$[RPt(L)_2L']^+PF_6^-$

					Platinum methyl			L methyls			
Complex	R	L′	L	Solvent	δCH_3	$\lvert ^2J_{PtCH}\rvert$	$\lvert ^3J_{PPtCH}\rvert$	δCH_3	$\lvert ^3J_{PtPCH}\rvert$	$\lvert(^1J + {}^3J)_{PH}\rvert$	Other ^{1}H nmr data
2	CH_3	*p*-$CH_3OC_6H_4CN$	$As(CH_3)_3$	$CDCl_3$	0.50	79.5[c]		1.57	22.0		δOCH_3 3.90
				CD_2Cl_2	0.51	79.0		1.52	23.0		δOCH_3 3.86
				$(CD_3)_2CO$	0.55	78.0		1.59	23.0		δOCH_3 4.16
3	CH_3	$CH_3C_5H_4N$	$As(CH_3)_3$	CD_2Cl_2	0.41	73.6		1.23	22.9		δCH_3 2.41 δC_5H_4N 7.44, 8.53, $^3J_{HCCH}$ = 7
4	CH_3	$(C_6H_5)_3As$	$As(CH_3)_3$	CD_2Cl_2	0.83	65.2		1.14	21.5		δC_6H_5 7.22–7.81[d]
5	CH_3	CH_3CH_2NC	$As(CH_3)_3$	CD_2Cl_2	0.34	60.6		1.58	24.0		δCH_3 1.43, δCH_2 3.70, $^3J_{HCCH}$ = 7
6	CH_3	CH_3NC	$As(CH_3)_3$	$CDCl_3$	0.36	62.8		1.62	23.6		δCH_3 3.39, $^4J_{PtCNCH}$ = 12.8
7	CH_3	CO	$As(CH_3)_3$	$CHCl_3$	0.65	62.4		1.75	24.8		
13	Cl	CO	$As(CH_3)_3$	$CHCl_3$				1.89	21.7		
21	CH_3	$CH_3C_5H_4N$	$P(CH_3)_2(C_6H_5)$	CD_2Cl_2	0.41	74.0	7.5	1.52	32.0	4.0	δCH_3 2.25, δC_5H_4N 7.12, 8.27, $^3J_{HCCH}$ = 7, δC_6H_5 7.29–7.80[d]
23	CH_3	CH_3CH_2NC	$P(CH_3)_2(C_6H_5)$	CD_2Cl_2	0.23	62.4	7.8	1.91	32.5	4.0	δCH_3 1.12, δCH_2 2.95, $^3J_{HCCH}$ = 7, δC_6H_5 7.37–7.84[d]

[a] In ppm (±0.005) from tetramethylsilane. [b] In Hz (±0.5). [c] This value is used for the correlations. [d] Resonances are a complex multiplet.

satellites. This is consistent with a mutually trans orientation of the two phosphorus nuclei and large $^{31}P-^{31}P$ coupling constants.[20,21] The ^{13}C resonances of the arsenic methyl groups of series I appear simply as 1:4:1 triplets.

In contrast, assignment of the trans ligand ^{13}C resonances was not always so straightforward. It was sometimes useful to compare the ^{13}C spectra of analogous complexes from series I and II since the variations of the carbon shieldings are small on changing a phosphine donor to an arsine substituent. In this manner we were able to assign resonances to the trans ligands. The arguments outlined below describe several special cases.

The signals arising from the anisonitrile ligand in **2** and **17** were readily assigned by their relative intensities and comparison with the values for anisonitrile.[22] The specific assignments for this ligand were made by assuming additivity of the individual substituent effects on the aryl carbon shieldings.[3b] The observed (in $CDCl_3$) and predicted values (in parentheses) are C_1, 103.4 (105.4); $C_{2,6}$, 133.4 (133.1); $C_{3,5}$, 114.4 (114.7); and C_4, 162.4 (163.8) ppm. In the complexes, C_1 is most strongly affected as expected since it is closest to the site of coordination. The nitrile carbon in anisonitrile absorbs at 118.7 ppm and the methoxyl carbon at 55.2 ppm.

The carbon resonances of the heterocyclic rings of the γ-picoline derivatives **3** and **21** were assigned by a similar method.[3b]

The carbene derivatives **8, 9,** and **15** presented certain problems. The *N*-methyl groups may adopt cis or trans orientations with respect to the platinum atom, because of restricted rotation about the C–N bond, as found in related carbene systems.[23] Without further information about the angular dependence of $^3J_{PtCNC}$ values, we must reserve comment on the stereochemical assignments of these substituents.

Assignments of the heterocyclic ring carbons in **26** also require comment. Comparison with the values for tetrahydrofuran ($C_{2,5}$, 68.6 ppm; $C_{3,4}$, 26.7 ppm)[24] led to the assignment of the 18.9 and 87.9 ppm signals to C_3 and C_4, respectively, with the 57.2 ppm resonance ascribed to C_2. The latter may be expected to be substantially deshielded since it is bonded to the carbene carbon.

The ^{1}H nmr data for the new complexes are assembled in Table VI. References for the proton data of the complexes which have been reported previously are given in Tables II–V.

Few difficulties were encountered in assigning the ^{1}H nmr spectra of the new complexes in this work. However, the ^{1}H signals of the arsenic methyl groups were not always 1:4:1 triplets. Frequently we observed significant broadening of the platinum satellites, sometimes by as much as a factor of 2–3 over the central resonance. This phenomenon has been recognized in a series of trimethylarsine mercury derivatives, as well

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(20) B. E. Mann, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc., Chem. Commun.*, 151 (1972).

(21) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).

(22) J. B. Stothers, unpublished results.

(23) (a) E. O. Fisher, M. Leupold, C. G. Kreiter, and J. Muller, *Chem. Ber.*, **105**, 150 (1972); (b) E. O. Fisher, H. J. Beck, C. G. Kreiter, J. Lynch, J. Muller, and E. Winkler, *ibid.*, **105**, 162 (1972), and references therein.

(24) G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965). The carbon shieldings have been adjusted to the TMS scale.[3a]

as in $[(C_6H_5)_4P][Pt(As(CH_3)_3)Cl_3]$,[25] and has been related to the rapid relaxation of the ^{195}Pt spin by scalar coupling with the ^{75}As nucleus. In the complexes of series I, it is possible that exchange of the trans trimethylarsine substituents gives rise to satellite broadening. For example, the addition of ethyl isocyanide to a chloroform solution of **23** results in complete loss of the ^{195}Pt satellites of the phosphorus methyl resonances and in the loss of the ^{31}P coupling with the platinum methyl protons. Similar behavior occurs when trace amounts of ethyl isocyanide are added to solutions of **26**.[26]

Discussion

The Trans Influence. The trans influence is defined as the tendency of a ligand in a metal complex to weaken the bond trans to itself[27,28] and is thought to reflect rehybridization of metal σ-orbitals in response to changes of ligands. In addition, the π-acceptor properties of L and the charge of a complex may have some effect on a ligand's σ-donor ability, and thus on its trans influence.

Numerous nmr studies[12,27,29–31] of organoplatinum complexes have made use of the assumption that the Fermi contact term dominates one-bond platinum–substituent coupling constants. Equations have been proposed which express these J values in terms of (a) the gyromagnetic ratios of the two nuclei, (b) α^2, the s character of the hybrid orbitals used in bonding by each atom, (c) the outermost s-orbital electron densities at each nucleus, and (d) ΔE, an average excitation energy. In series of related organoplatinum complexes, several authors[12,27,32,33] have considered the $\alpha_{Pt}{}^2$ term to be mainly responsible for alterations in one-bond platinum–substituent coupling constants.

Since the rehybridization of platinum and ligand σ orbitals is common to the theories of the trans influence and the one bond coupling interactions, it is possible to deduce a relative trans influence series of ligands *via* nmr. As well, the above arguments have been extended to two- and three-bond coupling constants in methyl,[29,34,35] perfluoromethyl,[35] and vinyl platinum derivatives.[36] Finally, it should be pointed out that trans influence series may be derived by other physical means, such as infrared spectroscopy. We emphasize that care should be taken when comparisons are made between data obtained by different spectroscopic methods, which may be sensitive to dissimilar molecular parameters.

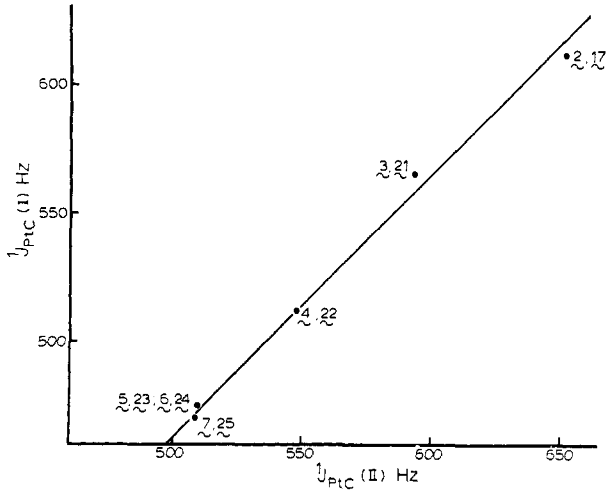

Figure 2. Plot of $^1J_{PtC}$ (series I) *vs.* $^1J_{PtC}$ (series II) for those complexes sharing common ligands trans to the platinum methyl group.

The ^{13}C and ^{1}H Nmr Data. General Information. The nmr data obtained from complexes **1–32** reveal that with variations in the ligands trans to the platinum methyl group, large relative fluctuations in the ^{13}C and ^{1}H nmr parameters may occur. For example, when a methyl(methoxy)carbene substituent in series I is replaced by chloride the value of $^1J_{PtC}$ for the platinum methyl group increases from 360 to 643 Hz, while $^2J_{PtCH}$ increases from *ca.* 48 to 82 Hz. From both the ^{13}C and ^{1}H nmr parameters we may use these coupling constant variations to derive an approximate nmr trans influence series, such as follows, for the ligands used in **1–15**: carbene > CO ≈ isonitrile > arsine > nitrile, and for **28–32**: CN > NO_2 > NCS > I > Cl. These trans influence series are similar to those reported by other workers[12] for related complexes. As the σ-donor ability of the ligand trans to the platinum methyl group increases, the ligand will compete more effectively for Pt(6s) character. The increase in s character in the platinum–ligand bond is obtained partially at the expense of the trans platinum–carbon bond of the methyl group, and lower values of $^1J_{PtC}$ are observed.

On the other hand, the values of the ^{13}C–^{1}H coupling constants of the platinum methyl groups of four members of series I are constant, within the experimental error of measurement. In addition, the ^{13}C and ^{1}H nmr parameters of the two arsine or phosphine substituents do not seem to vary appreciably within their respective series.

^{13}C and ^{1}H Coupling Constants. A. Platinum Methyl Substituents. First, we examined the data of series I and II to determine if there were relationships between $^1J_{PtC}$ (I) and $^1J_{PtC}$ (II). Good linear correlations exist for cationic members of series I and II sharing common ligands. A plot of $^1J_{PtC}$ (I) for *trans*-$[(CH_3)Pt(As(CH_3)_3)_2L]^+PF_6^-$ *vs.* $^1J_{PtC}$ (II) for *trans*-$[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2L]^+PF_6^-$ where L = *p*-$CH_3OC_6H_4CN$, γ-$CH_3C_5H_4N$, $(C_6H_5)_3As$, CH_3CH_2NC, CH_3NC, and CO is shown in Figure 2. The parameters derived from a linear regression analysis of these data are summarized in eq 1 and 2.[37]

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(25) P. L. Goggin, R. J. Goodfellow, S. R. Haddock, and J. G. Eary, *J. Chem. Soc. Dalton Trans.*, 647 (1972).

(26) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 11, 1269 (1972).

(27) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(28) S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 6669 (1968).

(29) F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 2700 (1968).

(30) M. J. Church and M. J. Mays, *ibid.*, 3074 (1968).

(31) P. W. Atkins, J. C. Green, and M. L. H. Green, *ibid.*, 2275 (1968).

(32) M. J. Church and M. J. Mays, *ibid.*, 1938 (1970).

(33) W. G. Schneider and A. D. Buckingham, *Discuss. Faraday Soc.*, 34, 147 (1962).

(34) H. C. Clark and J. D. Ruddick, *ibid.*, **9**, 1226 (1970).

(35) T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *ibid.*, 11, 1786 (1972).

(36) T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Can. J. Chem.*, 51, 2243 (1973).

(37) 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–VI. It is worthwhile noting that these variations represent the maximum error in *precision* and that as such they may be generous estimates.

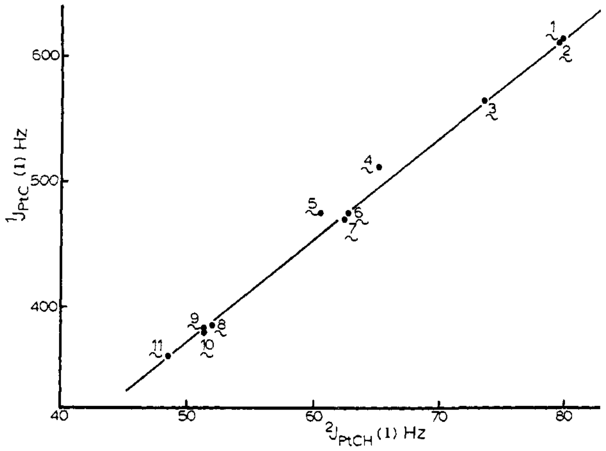

Figure 3. Plot of $^1J_{PtC}$ *vs.* $^2J_{PtCH}$ for complexes of the type *trans*-$[(CH_3)Pt(As(CH_3)_3)_2L]^+PF_6^-$ where L is a ligand used in series I.

$$^1J_{PtC}\text{ (I)} = 1.000\,(\pm 0.001)\,^1J_{PtC}\text{ (II)} - 37.7\,(\pm 0.2);\quad r = 0.998 \quad (1)$$

$$^2J_{PtCH}\text{ (I)} = 1.05\,(\pm 0.13)\,^2J_{PtCH}\text{ (II)} - 4.3\,(\pm 8.6);\quad r = 0.998 \quad (2)$$

These results indicate that the factors governing the nmr trans influence of the ligand trans to the platinum methyl group may be very similar for the trimethylarsine and dimethylphenylphosphine complexes. That is, the cis influences of the arsines and phosphines act in a parallel manner for a given ligand trans to the platinum methyl group. Although the cis influence is not as well understood as its trans counterpart, this result suggests that the cis influences of the phosphine and arsine ligands are similar and small, relative to their trans influences. One might anticipate poorer correlations if the cis influences of the ligands were large or were significantly different.

Next, we sought possible relationships between the $^1J_{PtC}$ and $^2J_{PtCH}$ values within a particular series. This examination revealed some interesting linear correlations which are summarized in eq 3–5. Figure 3

$$^1J_{PtC}\text{ (I)} = 8.2\,(\pm 0.4)\,^2J_{PtCH}\text{ (I)} - 35\,(\pm 28);\quad r = 0.997 \quad (3)$$

$$^1J_{PtC}\text{ (II)} = 8.3\,(\pm 0.5)\,^2J_{PtCH}\text{ (II)} - 14\,(\pm 36);\quad r = 0.994 \quad (4)$$

$$^1J_{PtC}\text{ (III)} = 8.0\,(\pm 0.5)\,^2J_{PtCH}\text{ (III)} + 7\,(\pm 40);\quad r = 0.986 \quad (5)$$

graphically represents the data for the arsine series I.

The three linear relationships may be taken as a demonstration that the factors affecting $^1J_{PtC}$ values parallel, and thus are likely very similar to, those governing $^2J_{PtCH}$ coupling constants within a series (I–III) of closely related compounds. Since all the slopes and intercepts lie almost within the limits of experimental error, it is difficult to place significance on differences between these values. It is particularly interesting to note that the charge of the complex appears to have little bearing on either the slope or intercept. In contrast with our previous claim[4] that a plot of $^1J_{PtC}$ *vs.* $^2J_{PtCH}$ for complexes of the type in series I passes through the origin, it now seems that we cannot expressly validate that statement, due to the rather large experimental uncertainty. If the lines do not pass through the origin, they at least pass relatively close to it and this evidence lends support to the notion that $^2J_{PtCH}$ values are dominated by the Fermi contact mechanism, as has been assumed for the $^1J_{PtC}$ values of the platinum methyl groups.

In comparison, McFarlane[38] has noted that an analogous plot of $^1J_{SnC}$ *vs.* $^2J_{SnCH}$ for a series of methyltin halides does not pass through the origin and it was concluded that terms other than the Fermi contact interaction may make significant contributions. However, the different stereochemistries of the tetrahedral tin derivatives and the square-planar platinum complexes may well render such a comparison invalid.

We should also point out that several other workers[29,34,35] have commented on the parallel relationship between $^2J_{PtCH}$ in complexes of the type *trans*-$(CH_3)Pt$(tertiary phosphine)$_2$X and $^1J_{PtH}$ from the related platinum hydride complexes *trans*-HPt(tertiary phosphine)$_2$X. This constitutes another case in which $^2J_{PtCH}$ for a platinum methyl group may be related to one-bond platinum coupling constants.

In one of these reports,[35] variations in $^2J_{PtCH}$ were specifically related to α_{Pt}^2 the amount of Pt(6s) orbital contribution to the platinum–methyl bond, for a series of similar complexes. Such a supposition bears the implicit assumption that changes in α_C^2 and α_H^2 remain relatively unimportant within the series and that the hydrogen nucleus is mainly sensitive to changes in α_{Pt}^2. We are now able to present evidence which enables us to test these assumptions for the complexes of series I, *trans*-$[(CH_3)Pt[As(CH_3)_3]_2L]^+PF_6^-$.

The ^{13}C nmr spectra of the complexes, where L = *p*-$CH_3OC_6H_4CN$ (**2**), γ-$CH_3C_5H_4N$ (**3**), CO (**7**), and CH_3CH_2NC (**5**), obtained without proton decoupling yielded $^1J_{CH}$ values for the platinum methyl substituents of 127, 127, 128, and 125 Hz, respectively. These coupling constants are the same within the experimental error (±2 Hz). Since the variations in $^1J_{PtC}$ (*ca.* 470–613 Hz) and $^2J_{PtH}$ (*ca.* 62–80 Hz) are large for this series of four complexes, it appears that the assumptions that α_C^2 and α_H^2 do not vary are indeed valid. However, with the data at hand we cannot definitely rule out the possibilities that (a) α_C^2 and/or α_H^2 vary but $^1J_{CH}$ is not particularly sensitive to this, (b) α_C^2 and α_H^2 vary simultaneously to cancel the effect of one another as manifest in $^1J_{CH}$, or (c) other terms change resulting in canceling any apparent variations in α_C^2 and/or α_H^2. Nevertheless, this tentative conclusion, together with the excellent linear correlations between $^1J_{PtC}$ and $^2J_{PtCH}$ for series I–III, adds support to the case for using $^2J_{PtCH}$ values as a reasonable method of determining nmr trans influences within series of similar derivatives.

We have obtained ^{13}C nmr spectra of **2** in chloroform-*d*, methylene-d_2 chloride, and acetone-d_6 solutions to examine briefly the solvent dependence of the ^{13}C nmr parameters. The $^1J_{PtC}$ and $^2J_{PtAsC}$ values are the same (614 and 49 ± 2 Hz) while the shieldings of the platinum and arsenic methyl groups vary by as much as 0.5 ppm. Apparently the use of one-bond ^{13}C–^{195}Pt coupling constants derived from spectra determined in different solvents will not drastically alter the correla-

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[38] W. McFarlane, *J. Chem. Soc. A*, 528 (1967).

tions or conclusions we have presented. In comparison, the $^2J_{PtCH}$ values appear more sensitive to solvent changes, varying over a range of *ca.* 1.5 Hz for the same three solvents.

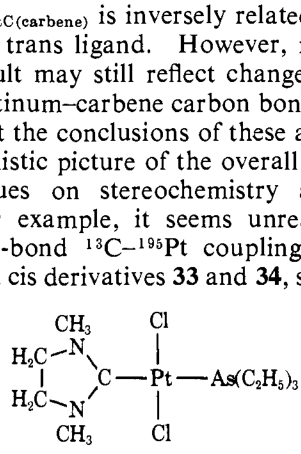
B. Other Substituents. As discussed in previous sections, the magnitude of $^1J_{PtC}$ should be related to $\alpha_C{}^2$, the carbon 2s orbital contribution to the platinum–carbon bond. Numerous examples from the ^{13}C nmr data of ligands trans to the platinum methyl groups illustrate this trend.

First, $^1J_{PtC(sp^3)}$ values for the platinum methyl groups fall in the range 360–698 Hz, while $^1J_{PtC(sp^2)}$ for the carbenes vary from 666 to 1070 Hz, and $^1J_{PtC(sp)}$ for the carbonyl derivatives lie in the range 986–1774 Hz. Hence, it seems that gross changes in $^1J_{PtC}$ indeed may result from rehybridization of the carbon atom directly bonded to the platinum.

Like the $^1J_{PtC(sp^3)}$ values, $^1J_{PtC(sp^2)}$ and $^1J_{PtC(sp)}$ are also dependent on the nature of the ligand trans to the carbon atom, and these changes parallel those found for the sp^3 hybridized carbons. For example, in the complexes *trans*-$[(R)Pt(As(CH_3)_3)_2(CO)]^+PF_6{}^-$ the J_{PtCO} values are 1005 and 1747 Hz for R = $CH_3{}^-$ and Cl^-, respectively. The trans influence of a methyl group is, as we would anticipate,[12] much larger than that of a chloro substituent. This is in accordance with the observations of Allen and Pidcock[29] who examined a series of complexes of the type *cis*-$(CH_3)Pt(P(CH_2CH_3)_3)_2X$, where X is an anionic ligand such as Cl^-, Br^-, $NO_2{}^-$, $CH_3{}^-$, etc. The phosphorus nucleus trans to a methyl group was observed to have a 1856 Hz coupling constant with platinum. When the methyl group was replaced by a chloro substituent, this coupling constant increased to 4179 Hz.

^{13}C nmr spectroscopy affords a unique method for studying the bonding in the carbene complexes *trans*-$[(CH_3)Pt(As(CH_3)_3)_2(:CX(CH_3))]^+PF_6{}^-$, where X is a substituent such as $-OCH_3$, $-NH_2$, or $-N(CH_3)_2$. The $^1J_{PtC}$ values for both the platinum methyl carbon and the carbene carbon atom vary as a function of the heteroatom and its substituents. For the carbene carbon $^1J_{PtC}$ *decreases in* the order X = $OCH_3 > NR_2$ while $^1J_{PtC}$ for the platinum methyl carbon *increases* in the order $OCH_3 < NR_2$. These opposite trends suggest that the platinum–carbene bond, and hence the trans influence of the carbene, is sensitive to the hybridization of the carbene carbon atom. This is a good example supporting the rehybridization concept of the nmr trans influence, since changes in the hybridization at the carbene carbon atom induced by changing a methoxyl to an amino substituent results in *inverse* changes in hybridization of the trans platinum–methyl bond.

Several groups have reported[10,39–41] ^{13}C nmr data derived from their investigations of other organometallic carbene derivatives and one of these studies[40] presented one-bond ^{13}C carbene–^{195}Pt coupling constant information. The complexes **33** and **34** have $^1J_{PtC(carbene)}$ values of 1073.6 and 756.4 Hz, respectively. Based on this evidence and the ^{13}C–^{195}Pt coupling constant of the carbene carbon of one other derivative, the authors noted that their data do not support the idea[4,28] that $^1J_{PtC(carbene)}$ is inversely related to the σ-donor ability of the trans ligand. However, it was conceded that this result may still reflect changes in hybridization of the platinum–carbene carbon bond. We wish to emphasize that the conclusions of these authors may *not* portray a realistic picture of the overall dependence of $J_{PtC(carbene)}$ values on stereochemistry and ligand substituents. For example, it seems unreasonable to compare the one-bond ^{13}C–^{195}Pt coupling constants for the trans and cis derivatives **33** and **34**, since the nature and mode of the nmr cis influence in this sort of complex are not well understood.



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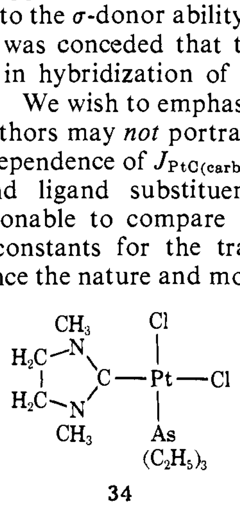

34

We now turn to the two- and three-bond ^{13}C–^{195}Pt coupling constants reported for the platinum(II) methyl(amino)carbene complexes[42] in Table V. The ^{195}Pt coupling to the methylamino carbon atoms apparently differs for cis and trans orientations of the methyl group. For example, $^3J_{PtC}$ values of 56 and 20 Hz are observed for the methylplatinum methyl(dimethylamino)carbene complex **8**, while these values are 94 and 40 Hz for the corresponding chloroplatinum methyl(dimethylamino)carbene derivative **15**. As well as indicating a stereospecificity of the three-bond ^{13}C–^{195}Pt coupling constants, the ^3J values reflect the marked differences in trans influence of the methyl- and chloroplatinum substituents.

Coupling between ^{195}Pt and the nitrile carbon in the cationic derivatives $[(CH_3)Pt(As(CH_3)_3)_2(p\text{-}NCC_6H_4OCH_3)]^+PF_6{}^-$ (**2**) and $[(CH_3)Pt(P(CH_3)_2(C_6H_5))_2(p\text{-}NCC_6H_4OCH_3)]^+PF_6{}^-$ (**17**) has been observed. It is interesting to note that the coupling constants, *ca.* 82 Hz, are seemingly independent of the nature of the cis substituent, $As(CH_3)_3$ or $P(CH_3)_2(C_6H_5)$. On the other hand, our repeated efforts to observe the isocyanide carbon resonances in **5**, **6**, **23**, and **24** were unsuccessful, presumably due to relatively long relaxation times and broadening caused by coupling with the ^{14}N nucleus. Indeed, the methyl and methylene carbons in the ethyl isocyanide derivatives **5** and **23** are significantly broader than the other carbon resonances, again probably due to ^{13}C–^{14}N interaction.

^{13}C Shieldings. A. Platinum Methyl Groups. The platinum methyl carbon shieldings for all complexes in series I–III, except the ethylene **19** and the dimethylphenylphosphine **27** derivatives vary from *ca.* 0 to 28 ppm *upfield* from TMS. In this respect these shieldings are similar to the high field hydride chemical shifts observed for some analogous platinum hydride complexes $HPt(P(CH_3)_2(C_6H_5))_2L$,[43] where L is an anionic or neutral ligand.

The ^{13}C shieldings of the platinum methyl carbons were first scrutinized to determine possible relationships

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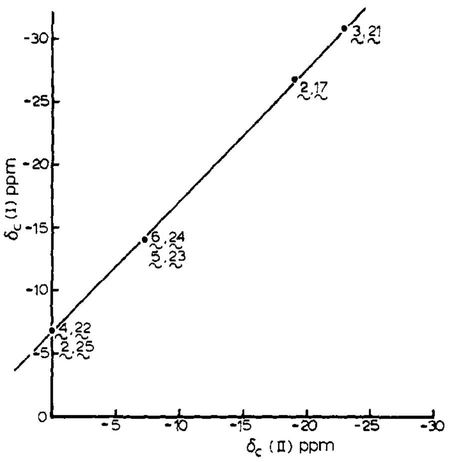


Figure 4. Plot of δC (series I) *vs.* δC (series II) for the platinum methyl groups of those complexes sharing common ligands trans to the platinum methyl group.

between common members of series I and II. Not surprisingly, this examination revealed an excellent linear correlation which is shown in Figure 4. The parameters derived from a least-squares analysis of these data, as well as from the ^{1}H nmr data of the platinum methyl groups, are summarized in eq 6 and 7. It seems that the factors affecting both the ^{13}C and

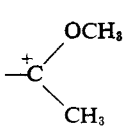
$$\delta_{CH_3}(\text{I}) = 1.04\ (\pm 0.02)\delta_{CH_3}(\text{II}) - 6.70\ (\pm 0.18) \qquad r = 0.998 \quad (6)$$

$$\delta_{CH_3}(\text{I}) = 0.81\ (\pm 0.31)\delta_{CH_3}(\text{II}) + 0.16\ (\pm 0.14) \qquad r = 0.929 \quad (7)$$

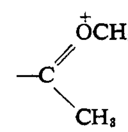
^{1}H chemical shifts are the same for both $As(CH_3)_3$ and $P(CH_3)_2(C_6H_5)$ derivatives and the shielding properties that these ligands confer on the platinum methyl groups are not appreciably altered by changing the ligand trans to the platinum methyl substituent. The significantly poorer correlation for the proton chemical shifts may arise from their greater relative sensitivity to the solvent, compared to those found for carbon shieldings.

We also inspected the ^{13}C and ^{1}H nmr data for possible correlations between shieldings and coupling constants. As one might anticipate, these attempts failed to give good linear fits for the data. These results are interesting in view of the correlation found between $^1J_{PtH}$ and δ_H for complexes of the sort *trans*-$PtHX(P(CH_2CH_3)_3)_2$, where X is an anionic ligand.[31] Evidently the factors governing the shielding of platinum-bonded protons differ from those affecting platinum methyl carbon shieldings.

B. Other Substituents. The ^{13}C shieldings of the carbene complexes **8–11**, **14**, **15**, and **26** warrant comment. The occurrence of the carbene carbon of the methyl(methoxy)carbene ligand at extremely low field (321 ppm) is consistent with considerable positive charge localized at this position as in **35a**. This deshielding is comparable to that found for tertiary alkyl carbonium ions[44] (*ca.* 320–334 ppm), and thus we have described these carbene complexes as metal stabilized carbonium ions. On the other hand, there is considerable evidence, essentially chemical in nature, that coordinated carbenes behave as **35b**.[45] The low field shielding of the carbene carbon atom is consistent with both resonance forms.



35a



35b

Comparison of the ^{13}C shieldings of carbonium ions $RR'C^+R''$ and $RR'C^+OH$ reveals a marked upfield shift of *ca.* 80 ppm for the positively charged carbon upon replacement of an alkyl group by hydroxyl.[44] If hydroxyl and methoxyl groups cause similar shifts one may predict a shielding of *ca.* 400 ppm for a carbene carbon with alkyl substituents. Thus the platinum atom apparently deshields the carbene carbon. This is consistent with the conclusions drawn by other workers.[40]

Substitution of the methoxyl group in $[(CH_3)Pt(As(CH_3)_3)_2(:C(CH_3)(OCH_3))]^+PF_6^-$ (**11**) by NH_2, $NH(CH_3)$, and $N(CH_3)_2$ causes substantial upfield shifts of the carbene resonance. This may result from the increased stabilization achieved by π-donation from nitrogen into the carbon $2p_z$ orbital.[10,41] Alternatively, it has been suggested that this upfield shift can be attributed to the difference in electron release between the methoxyl and amino groups.[10a,39] In one study[40] it was noted that a carbene carbon is deshielded, the greater the trans influence of the ligand trans to the carbene. Our results agree with this observation. For a given carbene ligand, the carbene carbon is shielded by *ca.* 40 ppm on replacing a methyl by a chloro substituent. For example, the shielding of the carbene carbon in the methyl(methoxy) derivative **11** is 321.0 ppm while the substitution of a chloro for the trans methyl group reduces this value to 278.3 ppm, in **14**.

Recently, ^{13}C nmr has been shown to be an informative technique for studying metal carbonyl derivatives.[6–8] With the addition of the "shiftless relaxation reagent" tris(acetylacetonato)chromium(III),[46] we were able to observe the carbonyl carbon and platinum satellites of the carbonyl derivatives **7**, **13**, and **25**. The ^{13}C shieldings of the carbonyl carbon nuclei in **7** and **25**, which are both trans to methyl groups, are alike, 178.7 and 177.6 ppm, respectively, as expected. On the other hand, the carbonyl carbon in the chloro complex **13**, which resonates at 159.3 ppm is much more shielded than its methyl analog **7**. This behavior is directly analogous to the behavior of the carbene carbon shieldings discussed above.

Similar shifts have been observed by Gansow and coworkers.[8] Their studies of a series of neutral iron carbonyl complexes of the type h^5-$C_5H_5Fe(CO)_2Z$, where Z is an anionic ligand, revealed that an upfield shift of the carbonyl carbon resonance occurred as the electron withdrawing ability of Z increased. They found that ^{13}C shieldings are linearly related to ν(CO) and they presented an argument relating the iron d orbital overlap with the carbonyl π^* orbitals to account for these variations. In our case, although the carbonyl

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stretching frequencies are high, indicating that π back-bonding may be minor, a similar argument may be used. On replacing the platinum methyl group trans to the carbonyl by a chloro substituent, ν(CO) increases from 2085 to 2104 cm^{-1} while $\delta_{C(carbonyl)}$ changes from 178.7 to 159.3 ppm. Concomitant with the increased carbon–oxygen bond order is an increased paramagnetic screening of the carbon nucleus.

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Structure of (Tetraphenylporphinato)(carbonyl)(pyridine)ruthenium(II)–1.5-Toluene

Robert G. Little and James A. Ibers*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received June 9, 1973*

Abstract: The crystal structure of Ru(CO)(py)(TPP) has been determined from three-dimensional X-ray diffraction data. The compound crystallizes in the triclinic space group C_i^1-$P\bar{1}$ (a = 11.665 (1), b = 19.667 (2), c = 10.758 (2) Å; α = 92.22 (1), β = 93.32 (1), γ = 96.50 (1)°; Z = 2), with three toluene molecules of crystallization. Least-squares refinement has led to a final value of the conventional R factor (on F) of 0.065 for the 4617 reflections having $F_o^2 > 3\sigma(F_o^2)$. The Ru(II) atom is 0.079 Å out of the porphyrin plane toward the carbonyl carbon atom. The Ru–C–O angle is 178.4 (7)° and the Ru–CO distance is 1.838 (9) Å. The Ru–N(pyridine) distance is 2.193 (4) Å, compared with the average Ru–N(porphyrin) distance of 2.052 (9) Å. The long axial Ru–N(py) bond length is attributed to a trans effect of the carbonyl group. The bond lengths and angles within the porphyrin compare well with those observed previously in Ru(CO)(EtOH)(TPP).

This study of carbonyl complexes of metalloporphyrins is of general importance with respect to the carbonyl complexes of the corresponding Fe hemes. The position of the metal relative to the mean plane of the porphyrin and the effect, if any, of the carbonyl group on the distance of the trans ligand from the metal are of import in developing models for conformational changes that may occur in hemoglobin on carbonylation. Although compounds of the type Fe(CO)(base)(porphyrin) have been prepared,[1,2] no crystal structures of these systems have yet appeared.

Although the chemistry of Ru and Fe porphyrins shows marked differences, both the Ru and Fe complexes of the type M(CO)(base)(porphyrin) are presumably pseudooctahedral low-spin diamagnetic complexes. Accordingly, studies of these systems, when M = Ru, are not totally unrelated to the biological models. Recently the structure of Ru(CO)(EtOH)(TPP)[3] was reported. In that study the linearity of the Ru–C–O linkage was demonstrated, but because of disorder problems the metrical details were necessarily inaccurate. The present study of Ru(CO)(py)(TPP) was undertaken to provide more reliable results on the relation of the metal to the mean porphine plane and on the trans labilizing effect of the CO on the axial base.

Experimental Section

A sample of Ru(CO)(py)(TPP), [$RuC_{49}H_{32}N_5O$], was prepared according to literature methods[3,4] and was kindly supplied by Professor R. H. Holm. Suitable crystals were obtained by dissolving this material in boiling toluene, diluting with ether, and then allowing this solution to evaporate slowly over a period of months. On the basis of the present structural study, the compound thus obtained is Ru(CO)(py)(TPP)·1.5toluene. Preliminary precession photographs taken with Cu Kα radiation showed only the required center of symmetry and hence the space group is either $P1$ or $P\bar{1}$. The crystal selected for data collection was a pseudoparallelepiped with major bounding faces of the forms {110}, {010}, {001}, and minor faces, {100}. The distances between the faces of these forms are 0.116, 0.198, 0.553, and 0.205 mm. The crystal was mounted with the c^* axis approximately along the spindle axis.

The lattice parameters, obtained as previously described[6] by hand centering of 13 reflections with Cu Kα_1 radiation in the range $60 \leq 2\theta \leq 65°$, are a = 11.665 (1) Å, b = 19.667 (2) Å, c = 10.758 (2) Å, α = 92.22 (1)°, β = 93.32 (1)°, and γ = 96.50 (1)°. The calculated density, based on two molecules of porphyrin complex and three of toluene per unit cell, is 1.29 g/cm^3 and agrees well with an observed value of 1.30 (1) g/cm^3, as measured by flotation in aqueous zinc chloride solution.

Data were collected in shells of 2θ by the θ–2θ scan method using Cu Kα radiation prefiltered with Ni foil. The scan range in 2θ was from 0.9° below the Cu Kα_1 peak to 0.9° above the Cu Kα_2 peak. The takeoff angle was 3.0° and the receiving counter was positioned 32 cm from the crystal with an aperture 5.0 mm high and 5.0 mm wide. The pulse height analyzer was set to admit about 90% of the Cu Kα peak. Initially background counts of

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[4] The compound Ru(CO)(py)(OEP) (OEP = octaethylporphyrin) has also been prepared.[5] We have found that it crystallizes in the triclinic space group $P1$ or $P\bar{1}$: a = 9.85, b = 10.82, c = 7.54 Å; α = 97.7, β = 106.9, γ = 93.2°; Z = 1 (precession photographs).

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