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Carbon-13 Nuclear Magnetic Resonance Studies of Organometallic Compounds. VII. 1,5-Cyclooctadieneplatinum(II) Derivatives¹

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Abstract: The ¹³C nmr spectra have been obtained for three series of π-bonded 1,5-cyclooctadieneplatinum(II) derivatives of the type [CODPt(CH₃)R], [CODPt(CH₃)L]⁺PF₆⁻, and [CODPtRR'], where R and R' are anionic substituents and L is a neutral donor. The ¹³C shieldings and ¹³C–¹⁹⁵Pt coupling constants are discussed and compared with ¹³C nmr parameters derived from related platinum(II) complexes containing σ-bonded carbons. The ¹³C shielding and coupling constant trends of the π-bonded carbons are generally found to parallel those trends for the σ-bonded carbons.

¹³C nuclear magnetic resonance investigations^{3–20} of π-bonded olefin transition metal complexes are now commonplace. However, there have been only a few reports^{3,4,6,16,17} which involve a detailed examination of series of closely related compounds for which both the olefinic carbon shieldings and metal–olefinic carbon coupling constants have been recorded.

We now wish to report a *systematic* study of three series of π-bonded 1,5-cyclooctadiene²¹ complexes of platinum(II) (¹⁹⁵Pt, 34% natural abundance, *I* = 1/2): [CODPt(CH₃)R] (I), [CODPt(CH₃)L]⁺PF₆⁻ (II), and [CODPtRR'] (III), where R and R' are anionic substituents and L is a neutral donor ligand. For these derivatives, both the olefinic carbon shieldings and ¹³C–¹⁹⁵Pt coupling constants of the COD ligand provide useful information about the mode of olefin–metal bonding.

We have specifically selected the chelating ligand COD to eliminate the possibility of rotation about the metal–olefin bond axis, a feature which has been ignored in the majority of previous studies. The cationic complexes, II, were prepared to enable direct comparisons with the ¹³C nmr parameters derived from analogous σ-bonded platinum(II) complexes of the sort [DIARSpt(CH₃)L]⁺PF₆⁻^{22,23} (A), where L is a neutral ligand. For both series II and A, we

have intentionally chosen a variety of L donors whose nmr trans influences^{24–26} span a wide range.

Experimental Section

All complexes were prepared as previously described.^{27,28} The ¹³C nmr spectra were measured on a Varian XL-100-15 spectrometer operating in the Fourier transform mode at 25.2 MHz. All spectra were determined with noise-modulated proton decoupling. To identify carbon types, off-resonance decoupled spectra were obtained by offsetting the decoupling single frequency using an offset of 1 kHz. By offsetting the noise-modulated frequency by ca. 30 kHz from the optimum value, normal ¹J_{CH} values were obtained from the resulting coupled spectra. The spectra were taken on chloroform-*d*, methylene chloride-*d*₂, and acetone-*d*₆ solutions in 5-mm sample tubes and were calibrated using the solvent resonances as secondary standards.²⁹

Results

The shieldings and coupling constants obtained from the ¹³C nmr spectra of the complexes of series I–III are assembled in Tables I–III. The ¹H nmr parameters for **1–13** have already been reported.^{27,28} No relative sign determinations for the coupling constants were made.

For complexes **1–7**, the high field resonances of their ¹³C nmr spectra were assigned on the basis of their relative in-

Table I. ^{13}C Shieldings^a for the Complexes CODPt(CH₃)R 1–2 and [CODPt(CH₃)L]+PF₆⁻ 3–7

| Complex | R or L | Solvent | Platinum methyl δ_{C} | COD | | | | Other |
|---------|---|------------------------------------|-------------------------------------|--------------------------|--------------------------|------------------------|------------------------|---|
| | | | | $\delta_{\text{CH}_2}^b$ | $\delta_{\text{CH}_2}^c$ | δ_{CH}^b | δ_{CH}^c | |
| 1 | CH ₃ ⁻ | CD ₂ Cl ₂ | +4.8 | 30.3 | | 99.0 | | |
| | | CDCl ₃ | +4.7 | 29.9 | | 98.8 | | |
| | | (CD ₃) ₂ CO | +4.4 | 29.9 | | 98.8 | | |
| 2 | Cl ⁻ | CD ₂ Cl ₂ | +4.5 | 28.1 | 31.9 | 84.1 | 113.2 | |
| 3 | γ -CH ₃ C ₆ H ₄ N | CDCl ₃ | +5.7 | 27.8 | 30.3 | 92.5 | 113.0 | δ_{CH_3} 20.8, $\delta_{\text{C}_{3,6}}$ 127.6, $\delta_{\text{C}_{2,6}}$ 148.3, δ_{C_4} 152.1 |
| 4 | (C ₆ H ₅) ₃ P | CD ₂ Cl ₂ | +5.5 | 29.4 | 29.9 | 116.2 | 108.6 | $\delta_{\text{C}_{6\text{H}_6}}$ 124.5–135.0 |
| 5 | <i>p</i> -CH ₃ OC ₆ H ₄ CN | CDCl ₃ | +1.8 | 27.6 | 30.8 | 91.8 | 113.8 | $\delta_{\text{CH}_3\text{O}}$ 55.6, δ_{C_1} 97.3, $\delta_{\text{C}_{2,6}}$ 135.8, $\delta_{\text{C}_{3,6}}$ 115.0, δ_{C_4} 165.0, δ_{C_N} 123.3 |
| 6 | (C ₆ H ₅) ₃ As | CD ₂ Cl ₂ | +2.4 | 29.7 | 30.4 | 111.5 | 107.9 | $\delta_{\text{C}_{6\text{H}_5}}$ 128.4–133.4 |
| 7 | CH ₃ CH ₂ NC | CDCl ₃ | -2.7 | 28.8 | 29.9 | 110.0 | 110.2 | CH ₃ 13.4, CH ₂ 39.8, NC ^d |

^a In ppm (± 0.1) (downfield positive) from TMS. ^b Trans to R or L. ^c Cis to R or L. ^d Not observed.

Table II. ^{13}C - ^{195}Pt Coupling Constants^{a,b} for CODPt(CH₃)R 1–2 and [CODPt(CH₃)L]+PF₆⁻ 3–7

| Complex | R or L | Solvent | Platinum methyl $ ^1J_{\text{PtC}} $ | COD CH ₂ | | COD CH | |
|---------|---|------------------------------------|--------------------------------------|----------------------------|-----------------------------|-----------------------------|-----------------------------|
| | | | | $ ^2J_{\text{PtCC}} ^c$ | $ ^2J_{\text{PtCC}} ^d$ | $ ^1J_{\text{PtC}} ^e$ | $ ^1J_{\text{PtC}} ^d$ |
| 1 | CH ₃ ⁻ | CD ₂ Cl ₂ | 777 (± 2) | 0 (± 2) | | 55 (± 2) | |
| | | CDCl ₃ | 773 (± 2) | 0 (± 2) | | 55 (± 2) | |
| | | (CD ₃) ₂ CO | 783 (± 2) | 0 (± 2) | | 58 (± 2) | |
| 2 | Cl ⁻ | CD ₂ Cl ₂ | 620 (± 2) | 24 (± 2) | 24 (± 2) | 214 (± 2) | 30 (± 2) |
| 3 | γ -CH ₃ C ₆ H ₄ N | CDCl ₃ | 640 (± 2) | 18 (± 2) | 22 (± 1) | 178 (± 2) | 36 (± 2) |
| 4 | (C ₆ H ₅) ₃ P | CD ₂ Cl ₂ | 592 (± 2) ^e | 0 (± 1) ^f | 12 (± 3) ^g | 75 (± 2) ^h | 46 (± 2) ⁱ |
| 5 | <i>p</i> -CH ₃ OC ₆ H ₄ CN | CDCl ₃ | 575 (± 2) | 25 (± 2) | 28 (± 2) | 215 (± 2) | 35 (± 2) |
| 6 | (C ₆ H ₅) ₃ As | CD ₂ Cl ₂ | 560 (± 2) | 11 (± 2) | 17 (± 2) | 104 (± 2) | 44 (± 2) |
| 7 | CH ₃ CH ₂ NC | CDCl ₃ | 538 (± 2) | 10 (± 2) | 18 (± 2) | 120 (± 2) | 35 (± 2) |

^a In Hz. ^b The ^{13}C - ^{195}Pt coupling constants were not observed for any ligand (R or L) carbons. ^c Trans to R or L. ^d Cis to R or L. ^e $^2J_{\text{PtCC}} = 5$ (± 2) Hz. ^f $^3J_{\text{PtCC}} = 3$ (± 2) Hz. ^g $^3J_{\text{PtCC}} = 2$ (± 1) Hz. ^h $^2J_{\text{PtC}} = 12$ (± 2) Hz. ⁱ $^2J_{\text{PtC}} = 0$ (± 2) Hz.

Table III. ^{13}C Shieldings^a and ^{13}C - ^{195}Pt Coupling Constants^b for the Complexes CODPtRR'

| Complex | R | R' | Solvent | COD | | $ ^1J_{\text{PtC}} $ | Other | |
|---------|--|--|--|------------------------|-----------------------------|----------------------|------------------------------|--|
| | | | | δ_{CH_2} | $ ^2J_{\text{PtCC}} $ | | | |
| 8 | CF ₃ ⁻ | CF ₃ ⁻ | CD ₂ Cl ₂ | 29.3 | 0 (± 2) | 110.8 | 56 (± 2) | |
| 9 | I ⁻ | I ⁻ | CH ₂ Cl ₂ ^c | 31.8 | 0 (± 2) | 103.2 | 124 (± 4) | |
| 10 | CH ₃ CH ₂ ⁻ | CH ₃ CH ₂ ⁻ | CDCl ₃ | 29.6 | 0 (± 2) | 99.0 | 47 (± 2) | |
| 11 | C ₆ H ₅ CH ₂ ⁻ | C ₆ H ₅ CH ₂ ⁻ | CDCl ₃ | 29.5 | 0 (± 2) | 100.1 | 65 (± 2) | δ_{CH_3} 15.7, $^2J_{\text{PtCC}}$ 32 (± 2); δ_{CH_2} 19.4, $^1J_{\text{PtC}}$ 843 (± 2) |
| 12 | C ₆ H ₅ CH ₂ ⁻ | Cl ⁻ | CDCl ₃ | 27.9 ^e | 25 (± 2) ^e | 86.2 ^e | 230 (± 2) ^e | δ_{CH_2} 33.3, $^1J_{\text{PtC}}$ 740; δ_{C_1} 149.1; ^d $\delta_{\text{C}_{2,6}}$ 128.1, $^3J_{\text{PtCC}}$ 34 (± 4); $\delta_{\text{C}_{3,6}}$ 127.5, $^4J_{\text{PtCCCC}}$ 15 (± 2); δ_{C_4} 122.7, $^5J_{\text{PtCCCC}}$ 20 (± 2) |
| | | | | 31.7 ^f | 23 (± 2) ^f | 113.3 ^f | 30 (± 2) ^f | δ_{CH_2} 28.7, $^1J_{\text{PtC}}$ 577 (2); δ_{C_1} 144.8; ^d $\delta_{\text{C}_{2,6}}$ 128.7, $^3J_{\text{PtCC}}$ 20 (± 2); $\delta_{\text{C}_{3,6}}$ 127.8, $^4J_{\text{PtCCCC}}$ 10 (± 2); δ_{C_4} 124.1, $^5J_{\text{PtCCCC}}$ 10 (± 2) |
| 13 | C ₆ H ₅ ⁻ | Cl ⁻ | CDCl ₃ | 27.5 ^e | 24 (± 2) ^e | 87.1 ^e | 208 (± 2) | δ_{C_1} 143.4; ^d $\delta_{\text{C}_{2,6}}$ 133.4, $^2J_{\text{PtCC}}$ 12 (± 2); $\delta_{\text{C}_{3,6}}$ 127.8, $^3J_{\text{PtCC}}$ 50 (± 2); δ_{C_4} 123.7, $^4J_{\text{PtCCCC}}$ 8 (± 2) |
| | | | | 31.7 ^f | 26 (± 2) ^f | 115.2 ^f | 28 (± 2) | |

^a In ppm (± 0.1). ^b In Hz. ^c External D₂O lock, internal TMS. ^d Coupling not observed. ^e Trans to R'(R). ^f Cis to R'(R).

tensities and multiplicities in off-resonance decoupled spectra to the carbons of the platinum methyl groups. The central signals are flanked by widely spaced ^{195}Pt satellites of ca. one-fourth intensity, whose separation appears to be sensitive to the nature of R or L.

The resonances arising from the R and R' substituents of 8–13 were assigned by similar arguments. The signals arising from the phenyl group of 13 were assigned by comparisons with the ^{13}C shieldings and ^{13}C - ^{195}Pt coupling constants of a series of complexes of the sort *trans*-[(C₆H₅)Pt(As(CH₃)₃)₂L]+PF₆⁻ 30 (B). The signals of the aromatic carbons of the benzyl derivatives 11 and 12 were assigned on the basis of the magnitudes of their ^{13}C - ^{195}Pt coupling constants,³⁰ their relative intensities, and the similarity of their shieldings with those for series of monosubstituted benzenes.³¹

The signals arising from the COD olefinic carbons were easily differentiated from those arising from the COD methylene carbons by off-resonance decoupling experiments and by the characteristic shielding differences between π -bonded olefinic carbons and saturated hydrocarbon carbons.^{3,32} The assignments of the olefinic and methylene carbon cis-trans isomeric pairs in 2–7, 12, and 13 require specific comment. Based on the relative magnitudes and ranges of the ^{13}C - ^{195}Pt coupling constants, the signals arising from the olefinic carbons fall into two classes: (1) 75–230 Hz and (2) 28–46 Hz. With our observations on the relative sensitivities of cis and trans substituents to ligand variations,^{23,30,32,33} we have assigned the olefinic carbons trans to L in 3–7 and trans to Cl⁻ in 2, 12, and 13, to class 1.

In contrast, the methylene carbon signals of the COD lig-

Table IV. Linear Regression Analysis Parameters for the Relationships $\delta_{C_i} = A\delta_{C_{ii}}$ (or $\delta_{H_{ii}} \pm B$)

| Eq | δ_{C_i} | A | $\delta_{C_{ii}}$ or $\delta_{H_{ii}}$ | B (ppm) | Correlation coefficient r |
|----|---|---------------------|--|----------------------|---------------------------|
| 1 | δ_C (CH ₃ , series A) | 1.13 (± 0.05) | δ_C (CH ₃ , 3-7) | -12.2 (± 0.1) | 0.908 |
| 2 | δ_C (CH ₃ , series A) | 1.19 (± 0.06) | δ_C (CH ₃ , 2-7) | -12.1 (± 0.2) | 0.908 |
| 3 | δ_C (CH ₃ , series A and C) | 1.02 (± 0.01) | δ_C (CH, 3-7) | -123.1 (± 1.3) | 0.933 |
| 4 | δ_C (CH ₃ , series A and C) | 0.87 (± 0.01) | δ_C (CH, 2-7) | -106.2 (± 1.1) | 0.930 |
| 5 | δ_C (CH trans to L, 3-7) | 29.2 (± 1.0) | δ_H (CH trans to L, 3-7) | -58.0 (± 5.6) | 0.967 |
| 6 | δ_C (CH trans to L or R, 2-7, 12, 13) | 19.5 (± 0.4) | δ_H (CH trans to L or R, 2-7, 12, 13) | -3.0 (± 2.0) | 0.948 |

ands do not appear to be susceptible to such a classification, and thus they have been arbitrarily assigned.

The signals arising from the ligands L were specifically assigned by comparing their ¹³C nmr parameters with those derived from their *trans*-methylplatinum(II) derivatives.³²

Discussion

Numerous factors have been proposed to account for the shieldings and shielding variations of carbon nuclei of olefins π -bonded to transition metals. For example, it has been suggested that the upfield shift of olefinic carbons upon coordination can be associated with σ ,^{3-5,8,16,20} π ,^{3,20} neighbor anisotropy,⁵ and excitation energy^{9,20} effects. In contrast, there have been several reports,^{5,27} which indicate that metal-olefin π -bonding has little effect on the coupling of a metal nucleus with olefinic carbons or protons.

The shieldings of carbons σ -bonded to a transition metal, in comparison, may be mainly governed by σ -bonding and neighbor anisotropy effects,³⁰ while ¹³C-¹⁹⁵Pt coupling constants of these carbons appear to be governed by the σ -hybridization at carbon and platinum and the rehybridization of the platinum σ -bonding orbitals,³² arising from variations in the other ligands.

To test the importance of these factors, we have examined a variety of empirical correlations of the ¹³C nmr parameters of 1-13 and series of related complexes which bear carbons attached to platinum *via* σ -bonds.

¹³C Nmr Data. General Information. The ¹³C nmr data obtained from complexes 1-13 reveal that with variations in ligands, substantial variations in the ¹³C shieldings and ¹³C-¹⁹⁵Pt coupling constants may occur. For example, when γ -picoline in 3 is replaced by ethyl isocyanide (7), the shielding of the platinum methyl carbons increases from +5.7 to -2.7 ppm and the shieldings of the COD olefinic carbon trans to L decrease from 92.5 to 110.0 ppm, while the shieldings for the COD olefinic carbons cis to L increase from 113.0 to 110.2 ppm. In contrast, the ¹³C shieldings of the COD methylene carbons both cis and trans to L remain virtually constant, varying by only *ca.* 1.0 ppm.

Concomitantly, the ¹J_{PtC} value of the platinum methyl carbon decreases from 640 to 538 Hz, and the ¹J_{PtC} value of the COD olefinic carbons trans to L decreases from 178 to 120 Hz, while the ¹J_{PtC} values of the COD olefinic carbons cis to L remain constant at *ca.* 35 (± 2) Hz. Finally, the ²J_{PtCC} value of two of the COD methylene groups decreases from 18 to 10 Hz, while the ²J_{PtCC} values of the other two COD methylene groups remain almost constant at *ca.* 20 (± 2) Hz.

These coupling constant changes exemplify the alterations we have observed for model platinum(II) derivatives,^{23,32,33} for which we showed that the nmr trans influence of a ligand consistently outweighs its nmr cis influence. From the decreasing order of the ¹J_{PtC} values of the platinum methyl groups of 3-7, we may formulate an nmr cis influence series: CH₃CH₂NC > (C₆H₅)₃As > *p*-CH₃OC₆H₄CN > (C₆H₅)₃P > γ -CH₃C₅H₄N. This qualitative series is identical with that observed²³ for a series of

cis complexes of the type [DIARSPt(CH₃)L]⁺PF₆⁻ (A), where L is a neutral ligand. In addition, we may formulate an nmr trans influence series from the ¹J_{PtC} values of the COD olefinic carbons trans to L: (C₆H₅)₃P(phosphine) > (C₆H₅)₃As > CH₃CH₂NC > γ -CH₃C₅H₄N > *p*-CH₃OC₆H₄CN.

With the exception of the interchanged positions of triphenylarsine and ethyl isocyanide, this is the same nmr trans-influence series we have observed for complexes of the type *trans*-[(CH₃)Pt(As(CH₃)₃)₂L]⁺PF₆⁻ (C).^{23,32} Thus, there are at least reasonable *qualitative* relationships between the nmr cis and trans influence series of the COD complexes 3-7 and those observed for model platinum(II) analogs.

The symmetrically substituted neutral platinum(II) complexes 1,³³ and 8-11 fall into a different category from the unsymmetrically substituted derivatives 2-7, 12, and 13. We will consider these two classes separately.

The three chloro derivatives 2, 12, and 13 differ in charge from the cationic complexes 3-7. We have previously shown that^{23,30,32} a variety of empirical correlations may or may not depend on the charge of a complex. In the majority of the correlations considered later the charge of the complex does not appear to be an important factor, and we will not elaborate further on this except where required.

¹³C Shieldings. Platinum Methyl Groups. A plot of the shieldings of the platinum methyl carbons of the model DIARS derivatives [DIARSPt(CH₃)L]⁺PF₆⁻ (A) vs. those of the platinum methyl carbons of the COD complexes 3-7 reveals the linear relationship³⁴ which is summarized in eq 1, given in Table IV. When the data point for the neutral chloro derivative 2 is included in this plot, linear regression analysis affords eq 2 (Table IV). While the platinum methyl carbon shieldings of series A and 3-7 appear to share common factors which affect their shieldings, eq 1 and 2 do not pass through the origin. This suggests that there is some relatively constant term which characterizes the differences between the *absolute* values of the shieldings of those carbons in the two series. For example, the different cis influences of the DIARS and COD ligands could give rise to the nonzero intercepts. We should also note that the correlation coefficients (0.908) are distinctly poorer than the value of 0.998³² observed in the relationship of the platinum methyl carbon shieldings of the series *trans*-[(CH₃)Pt(As(CH₃)₃)₂L]⁺PF₆⁻ (C) and *trans*-[(CH₃)Pt(P(CH₃)₂(C₆H₅)₂)₂L]⁺PF₆⁻ (D). Thus, in addition to those changes arising from a relatively constant term, less regular changes are also occurring. The bonding changes in the donor atoms trans to L or R may give rise to nonparallel changes in the nmr cis influences of those trans atoms, thus affecting the platinum methyl groups (cis to L or R) in a nonparallel fashion.

COD Olefinic Carbons. To compare the shielding trends of the π -bonded olefinic carbons of 3-7 with σ -bonded carbons in similar stereochemical situations (with respect to various ligands), we plotted δ_{CH_3} (*trans*-[(CH₃)Pt(As(CH₃)₃)₂L]⁺PF₆⁻ (C))³² vs. δ_{CH} (3-7, *trans*

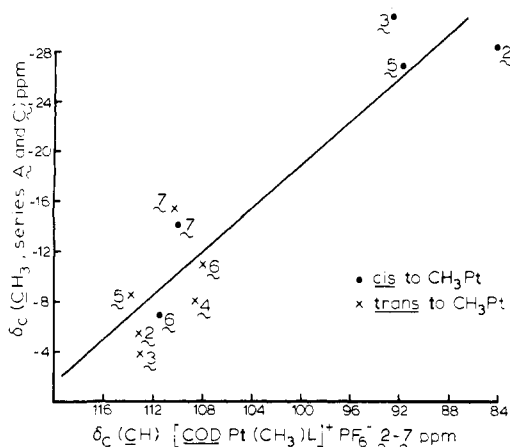


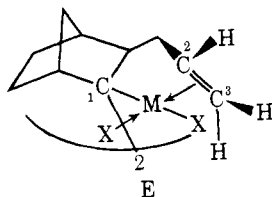
Figure 1. Plot of δ_C (CH_3Pt , series A and C) vs. δ_C (COD CH, 2–7) for complexes sharing common ligands L or R.

to L) and δ_{CH_3} ($[\text{DIARSPt}(\text{CH}_3)\text{L}]^+\text{PF}_6^-$ (A))²³ vs. δ_{CH} (3–7, cis to L), for complexes bearing the same neutral ligands L. Linear regression analysis of the data yielded eq 3, shown in Table IV.

From eq 3, it is evident that there is a linear relationship between the shieldings of the π -bonded olefinic and σ -bonded methyl carbons in like orientations with respect to varied ligands. That the slope of the line is almost unity indicates the very similar sensitivities of both types of carbon to alterations in ligands *cis* or *trans* to themselves.

Thus, it would appear that at least two of the factors giving rise to these parallel shielding variations are σ -bonding and neighbor anisotropy (including the nonbonding shielding parameter⁵ associated with partially filled metal d orbitals) components.³⁰ We would not anticipate that a π -bonding component would be a common factor, since the platinum methyl groups in series A and C are not likely to undergo π -bonding with platinum. It follows that any π -bonding component reflected in the olefinic shieldings of 3–7 either remains fairly constant or changes parallel to the alterations in σ -inductive and neighbor anisotropy effects. The latter choice is unlikely, however, in view of the unit slope of eq 3, although it is possible that the slope is fortuitously unity by a partial canceling of σ and neighbor anisotropic effects with π effects.

These conclusions are in general agreement with those of Cooper, *et al.*⁵ From their observations of parallel trends in the shieldings of the σ -bonded carbons, C₁, and π -bonded carbons, C₂ and C₃, in complexes of the type E, they con-



cluded that their linear correlations would be understandable if the major parameter in all these metal–carbon bonds was a σ -bonding component. The changes in the ¹³C shieldings of series E could be accounted for in terms of nonbonding paramagnetic (neighbor anisotropy) effects.

However, while these linear relationships provide information concerning the parameters varying within closely related series, they do not reveal information about the factors giving rise to the absolute magnitudes of the shieldings of the σ - and π -bonded carbon atoms.

We have previously noted³² that the shieldings (*ca.* 0 to –28 ppm) of the platinum methyl carbons in series C and D

are reminiscent of the high-field hydride chemical shifts observed for some analogous platinum hydride complexes of the sort $[\text{HPt}((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{X}]$ (F), where X is an anionic ligand, and $[\text{HPt}((\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{P})_2\text{L}]^+\text{PF}_6^-$ (G), where L is a neutral ligand.³⁵ Since the high-field hydride shifts are thought to be associated with the paramagnetic shielding (neighbor anisotropy) of the platinum 5d electrons,³⁶ it would appear that a similar factor may be invoked to account for the high field shieldings of the carbons of the platinum methyl groups of C and D. By similar reasoning, we conclude that a major factor causing the olefinic carbon nuclei of the COD ligands in 1–13 to shift upfield upon coordination may also be the neighbor anisotropy of the platinum atom. This feature, then, would appear to be important in determining the absolute *and* relative values of the olefinic carbon shieldings in 1–13.

Further information can be gained by examining the effect of changing the charge of the complexes. When the data points for 2 are included in eq 3, linear regression analysis affords eq 4 (Table IV). The appropriate data are plotted in Figure 1.

A comparison of eq 3 and 4 reveals that the slopes (1.02 and 0.87, respectively) and intercepts (–123.1 and –106.2 ppm, respectively) are markedly different; thus, the charge of the complex appears to be an important factor governing the changes and absolute magnitudes of the olefinic carbon shieldings.

In previous work,³² we showed that an excellent linear correlation exists between the shieldings of platinum methyl carbons for series C and D, for complexes sharing common *neutral* ligands. When the point for the neutral complexes (for a chloro substituent) is included in this plot, a comparison of the slopes and intercepts of these two plots reveals that they are the same, within experimental error.³⁷ Thus, the shieldings of the σ -bonded platinum methyl carbons appear to follow very similar trends, irrespective of the charges of the complexes. From this, we infer that the changes in σ -bonding and neighbor anisotropy terms follow similar trends, irrespective of charge, for series C and D.

If this conclusion can be applied to the COD complexes considered here, it would appear that the large differences between the slopes and intercepts of eq 3 and 4 may not arise from gross deviations in trends followed by the σ -bonding and neighbor anisotropy components. This leaves π -bonding and ΔE effects which may be invoked to account for these differences. For example, the expansion of the platinum d orbitals on going from the cationic to neutral derivatives could give rise to a substantially greater degree of platinum–olefin π -bonding in the latter complexes. As a consequence, the total electron density at the olefinic carbons would increase, and the carbon–carbon π -bond order would decrease.^{3,20} Both factors are expected to cause an increase in the shieldings of the olefinic carbons of the neutral with respect to the cationic complexes. If the shieldings of the olefinic carbons of 2–7 were to exhibit little charge sensitivity in the comparative trends with the σ -bonded carbons, we would anticipate that eq 3 would be applicable to both the cationic (3–7) and neutral 2 complexes. Using that equation and the shieldings (–28.4 and –5.4 ppm, respectively) of the platinum methyl carbons of *trans*- $[(\text{CH}_3)\text{Pt}(\text{As}(\text{CH}_3)_3)_2\text{C}1]$ and $[\text{DIARSPt}(\text{CH}_3)\text{C}1]$, we predict that the olefinic COD carbons of 2 *trans* to Cl^- would have a δ_C value of 92.8 ppm (84.1 ppm observed) while the carbons in 2 *cis* to Cl^- would have a δ_C value of 115.4 ppm (113.2 ppm observed). Thus, both sets of olefinic carbons are found to be more shielded than would be expected if the charge of the complex were not a major factor. This observation is consistent with our proposal that the olefinic carbons will be shielded in the neutral complexes with

Table V. Linear Regression Analysis Parameters for the Relationships ${}^nJ_{\text{PtC}} = A {}^mJ_{\text{PtC(or PtH)}} \pm B$

| Eq | ${}^nJ_{\text{PtC}}$ | A | ${}^mJ_{\text{PtC(or PtH)}}$ | B (Hz) | Correlation coefficient <i>r</i> |
|----|---|--------------|--|-------------|----------------------------------|
| 7 | ${}^1J_{\text{PtC}}$ (CH ₃ , series A) | 0.76 (±0.08) | ${}^1J_{\text{PtC}}$ (CH ₃ , 3-7) | 88 (±46) | 0.992 |
| 8 | ${}^1J_{\text{PtC}}$ (CH ₃ , series A) | 0.75 (±0.09) | ${}^1J_{\text{PtC}}$ (CH ₃ , 2-7) | 94 (±51) | 0.993 |
| 9 | ${}^1J_{\text{PtC}}$ (CH ₃ , series C) | 1.14 (±0.07) | ${}^1J_{\text{PtC}}$ (CH trans to L, 3-7) | 365 (±10) | 0.956 |
| 10 | ${}^1J_{\text{PtC}}$ (CH ₃ , series C) | 1.26 (±0.08) | ${}^1J_{\text{PtC}}$ (CH trans to L or R, 2-7) | 352 (±12) | 0.962 |
| 11 | ${}^2J_{\text{PtAsC}}$ (As(CH ₃) ₂ , series A) | 0.37 (±0.04) | ${}^1J_{\text{PtC}}$ (COD CH, 2-7) | 2.3 (±4.2) | 0.965 |
| 12 | ${}^2J_{\text{PtAsC}}$ (As(CH ₃) ₂ , series A) | 0.26 (±0.03) | ${}^1J_{\text{PtC}}$ (COD CH, 2-7) | 23.1 (±2.0) | 0.993 |
| 13 | ${}^1J_{\text{PtC}}$ (COD CH, 3-7) | 3.3 (±0.3) | ${}^2J_{\text{PtCH}}$ (COD CH, 3-7) | -84 (±15) | 0.956 |
| 14 | ${}^1J_{\text{PtC}}$ (COD CH, 2-7, 12, 13) | 3.9 (±0.3) | ${}^2J_{\text{PtCH}}$ (COD CH, 2-7, 12, 13) | -106 (±16) | 0.960 |
| 15 | ${}^1J_{\text{PtC}}$ (COD CH, 3-7) | 5.4 (±0.3) | ${}^2J_{\text{PtCH}}$ (COD CH, 3-7) | -231 (±13) | 0.994 |
| 16 | ${}^1J_{\text{PtC}}$ (COD CH, 2-7, 12, 13) | 5.7 (±0.3) | ${}^2J_{\text{PtCH}}$ (COD CH, 2-7, 12, 13) | -236 (±13) | 0.987 |
| 17 | ${}^1J_{\text{PtC}}$ (COD CH, 1, 8, 10, 11) | 3.1 (±1.2) | ${}^2J_{\text{PtCH}}$ (COD CH, 1, 8, 10, 11) | -69 (±44) | 0.722 |

respect to the cationic complexes, if all other factors bear an equal significance. If this notion is correct, it would appear that the platinum d orbital expansion on going from the cationic to neutral complexes is either anisotropic or unequally reflected by the olefinic carbon shieldings of **2**. This follows from the unequal variations (*ca.* 9 vs. 2 ppm) of the actual and predicted shieldings for the carbons trans and cis to Cl⁻ in **2**.

In summary, it appears that the degrees of σ - and π -bonding and the neighbor anisotropy contribution of the platinum atom may well have considerable importance in determining the shieldings of the π -bonded olefinic carbons of **2-7**. At this time, however, it would be difficult to assess the importance of the excitation energy term, without recourse to additional data.

Salomon and Kochi²⁰ have noted a curved relationship between the ¹³C and ¹H coordination shifts of olefinic carbons and protons in a series of copper(I) olefin complexes. Thus, we have examined our nmr data to determine whether any relationships existed between the ¹³C shieldings and ¹H chemical shifts of the olefinic segments of **2-7**. Linear regression analysis of the data for the olefinic carbons and methine protons trans to L yielded eq 5, which is given in Table IV. The reasonably good linear relationship indicates that similar factors may be giving rise to the changes in the ¹³C and ¹H shieldings of **3-7**. When the points for the neutral chloro derivatives **2**, **12**, and **13** are included, linear regression analysis of the data yields eq 6, given in Table IV. The distinctly different slopes and intercepts of eq 5 and 6 would appear to arise from the different charges of **2**, **12**, and **13**. We have noted a similar charge sensitivity in eq 3 and 4, where it was suggested that some change in the degree of olefin-platinum π -bonding on going from cationic to neutral complexes may be important. Similarly, the differing sensitivities of the olefinic carbons and protons trans to L may be reflected in the different slopes and intercepts of eq 5 and 6.

When the ¹³C and ¹H shieldings of the olefinic segments of **2-7**, **12**, and **13** cis to L or R are considered, a lack of any correlation was observed (*r* = 0.367). In addition, a combined plot for the olefinic segments cis and trans to L or R also yields a very poor linear correlation (*r* = 0.689). Thus, the parallel trends of those shieldings in eq 5 and 6 are not characteristic of the overall behavior of those parameters for the complete COD ligand in **2-7**, **12**, and **13**.

The shieldings (86-110 ppm) of the olefinic carbons of the neutral complexes **8-13** are comparable to those (84-113 ppm) observed for the same carbons of **2-7**. Hence, we conclude that similar factors give rise to the olefinic carbon shieldings of both series of complexes.

Other ¹³C Shieldings. The shieldings of the COD methylene carbons (27-32 ppm) of **2-13** are very similar to those (28.2 ppm)³⁸ of uncomplexed COD, so it appears that those

carbons are fairly insensitive to the coordination of the COD olefinic carbons to platinum. Likewise, the shieldings of the carbons of the ligands R, R', and L, are very similar to those observed for a host of related platinum(II) derivatives.^{23,30,32} For example, the aromatic carbon shieldings of the phenyl substituent in **13** fall close to the ranges (in parentheses) observed for a series of complexes of the sort *trans*-[(C₆H₅)Pt(As(CH₃)₃)₂L]+PF₆⁻³⁰ (B): δ_{C_1} 143.4 (118.2-146.2), $\delta_{\text{C}_{2,6}}$ 133.4 (135.6-138.4), $\delta_{\text{C}_{3,5}}$ 127.8 (127.3-129.1), δ_{C_4} 123.7 ppm (121.8-125.4 ppm). As was concluded for the *trans* phenyl-platinum complexes, it seems that σ rather than π interactions are dominant in the phenyl-platinum bond.

¹³C-¹⁹⁵Pt Coupling Constants. Platinum-Methyl Groups. The ${}^1J_{\text{PtC}}$ values of the platinum-methyl carbons of the cationic complexes **3-7** were first examined to determine whether their values parallel those in the analogous DIARS complexes of series A. This revealed the linear relationship summarized in eq 7 (Table V). An almost identical line results when the point for the neutral chloro derivatives is included. This relationship is given by eq 8 in Table V.

In view of these results, we conclude that the factors giving rise to the *changes* in ${}^1J_{\text{PtC}}$ values in both series of complexes are similar. The nonzero intercept, which is indicative of the differences in *absolute* values of those coupling constants, probably arises from the differences in the nmr cis influences of the DIARS and COD ligands. In contrast with the plots of δ_{C} (Pt(CH₃), DIARS) vs. δ_{C} (Pt(CH₃), COD) given by eq 1 and 2, better linear relationships are indicated by the correlation coefficients (~ 0.99 vs. ~ 0.91) for the one bond ¹³C-¹⁹⁵Pt coupling constant plots of eq 7 and 8. Thus, it would seem that the lower correlation coefficients in eq 1 and 2 are not arising from irregular changes in a σ -bonding factor but perhaps from irregular alterations in the π -bonding or ΔE parameters.

We should point out that the close relationships described by eq 7 and 8 indicate that the nmr cis influences of the ligands L or R in **2-7** are the same as those in series A. Thus, the ordering of the nmr cis influence series does not appear to depend on the type of complex used. We have reached a similar conclusion in a comparison of the nmr cis influences of ligands in platinum(IV) and platinum(II) complexes.³⁹

COD Olefinic Carbon Coupling Constants. Next, we considered the possible relationships of the ${}^1J_{\text{PtC}}$ values of the COD olefinic carbons of **3-7** with the ¹³C-¹⁹⁵Pt coupling constants of analogous platinum(II) derivatives. Linear regression analysis of a plot of the ${}^1J_{\text{PtC}}$ values from the platinum methyl groups of series C⁴⁰ vs. the ${}^1J_{\text{PtC}}$ values for the COD olefinic carbons trans to L in **3-7** yielded eq 9, given in Table V. When the point for the neutral chloro derivatives was included, linear regression analysis gave eq 10.

First, the correlation coefficients for eq 9 and 10 indicate

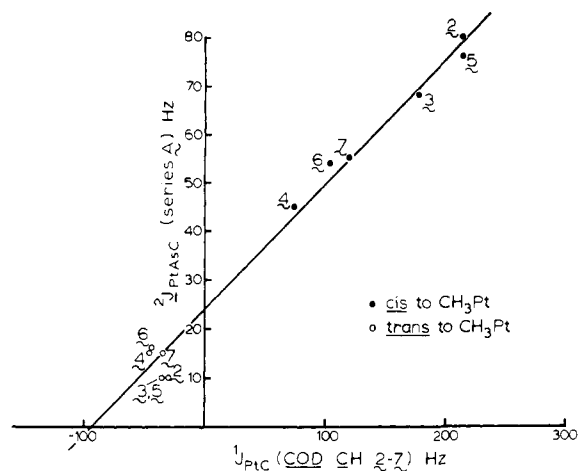


Figure 2. Plot of ${}^2J_{\text{PtAsC}}$ (As(CH₃)₂, series A) vs. ${}^1J_{\text{PtC}}$ (COD CH, 2-7) for complexes sharing common ligands.

that there is a similarity in the factors affecting the changes in both types of ${}^{13}\text{C}$ - ${}^{195}\text{Pt}$ coupling constants. Thus, it would seem that if π -donation from the platinum d orbitals into the empty π^* olefin orbitals were to influence the magnitudes of the ${}^1J_{\text{PtC}}$ (olefin) values, such a factor remains either relatively constant or changes parallel to the changes in the hybridization at platinum. However, the latter alternative would seem unlikely, since the slopes of eq 9 and 10 are close to unity. These conclusions are entirely consistent with those we deduced earlier from comparisons of the shieldings of σ -bonded platinum-methyl carbons of series A and C and the COD olefinic carbons of 2-7 (eq 3 and 4). In addition, the idea that the changes in ${}^1J_{\text{PtC}}$ values of the COD olefinic carbons are independent of any π -bonding with platinum is supported by our observations^{28,30} and those⁴¹ of other workers.

We have also compared the ${}^1J_{\text{PtC}}$ values of both the cis and trans olefinic carbons of 2-7 to the ${}^2J_{\text{PtAsC}}$ values of the analogous cis methyl complexes [DIARS-Pt(CH₃)L]⁺PF₆⁻, series A.²³ Linear regression analysis of these data afforded eq 11, given in Table V. However, we noticed that if the signs of the ${}^1J_{\text{PtC}}$ values for the olefinic carbons of 2-7 cis to L or R were opposite to those of the olefinic carbons trans to L or R, all the data points fell on a straight line. Linear regression analysis of those data yielded eq 12. The data for eq 12 are plotted in Figure 2.

Since the data used in eq 12 provided a significantly better linear fit than that used in eq 11, it may be that the signs of the ${}^1J_{\text{PtC}}$ values for the olefinic carbons cis to L or R are opposite to their trans counterparts. Unfortunately, attempts to determine the relative signs of these coupling constants were thwarted by the broadening of the signals from the olefinic carbons cis to L or R arising from coupling with the COD methylene protons in the ${}^{13}\text{C}$ nmr spectra obtained without proton irradiation. Nevertheless, both eq 11 and 12 provide reasonable linear fits for the ${}^{13}\text{C}$ - ${}^{195}\text{Pt}$ coupling constants suggesting that the factors affecting alterations in both types of J values are very similar.

We have previously observed a variety of linear relationships among one-, two-, and three-bond ${}^{13}\text{C}$ - ${}^{195}\text{Pt}$ and ${}^1\text{H}$ - ${}^{195}\text{Pt}$ coupling constants in a wide variety of organoplatinum derivatives.^{30,32,33,39} These results suggest that we might observe some relationship between the ${}^1J_{\text{PtC}}$ values and the ${}^2J_{\text{PtCH}}$ values of the COD olefinic carbons and protons. Linear regression analysis of the ${}^{13}\text{C}$ and ${}^1\text{H}$ nmr data for the cationic complexes 3-7 for the olefinic segments both cis and trans to the platinum-methyl group yielded eq 13,⁴² shown in Table V. When the data points for the three neutral chloro derivatives were included, eq 14 resulted, and

it is also given in Table V.

However, as previously noted for eq 11 and 12, it is possible that the ${}^1J_{\text{PtC}}$ values for the olefinic carbons cis to the platinum-methyl group may well possess opposite signs to their trans counterparts. Equations 15 and 16 in Table V take this feature into account. These data reveal generally good linear relationships between all the ${}^1J_{\text{PtC}}$ and ${}^2J_{\text{PtCH}}$ values for the olefinic carbons of 2-7, 12, and 13. We have already provided substantial evidence that the major factor giving rise to such changes is the rehybridization of the platinum σ -orbitals in the platinum-carbon bonds.³² As was noted in our comparisons of eq 11 and 12, the improved linear fit for the data when the ${}^1J_{\text{PtC}}$ values of the cis olefinic carbons are assumed to have opposite signs to their trans counterparts lends support to the notion that those two types of coupling constants actually do have opposite signs. Finally, we should note that while the tight clusters of points for the coupling constants of the olefinic carbons cis to L or R fall on lines described by eq 11-16, there do not appear to be any consistent trends for those particular sub-series. This result is also in accord with our observations for a variety of platinum(II) and platinum(IV) derivatives.^{23,33,39} There does not appear to be a simple relationship between the nmr cis and trans influence of a given neutral ligand.²³

An analogous plot for four of the five symmetrical derivatives, 1, 8, 10, and 11, yields a much poorer linear correlation given in eq 17, Table V. For this series of neutral complexes, ligands both cis and trans to a given olefinic segment are varied. The distinctly poorer correlation coefficient ($r = 0.722$) for 1, 8, 10, and 11 compared with those (*ca.* 0.99) derived from data obtained from series³² in which only a trans ligand is varied probably reflects the superimposition of the nonlinearly related nmr cis influence components. We have noted an analogous behavior of the ${}^{13}\text{C}$ nmr data derived from a series of neutral *cis*-dimethylplatinum(II) complexes of the sort *cis*-[(CH₃)₂PtL₂] and [(CH₃)₂Pt(L-L)], where L and L-L are neutral monodentate and bidentate ligands, respectively.³³ The ${}^{13}\text{C}$ nmr data for those complexes revealed that a ligand's nmr trans influence dominates its nmr cis influence.

We have previously noted³ that the nmr trans influences of CH₃⁻ and CF₃⁻ groups are the same, since the absolute values of the ${}^1J_{\text{PtC}}$ values (55 (±2) and 56 (±2) Hz, respectively) and ${}^2J_{\text{PtCH}}$ values (40 and 42 Hz, respectively) for the COD ligands of 1 and 8 are almost the same. This conclusion, however, seems tenuous, since it would imply that the hybridizations of the carbon σ -orbitals in the platinum-methyl and platinum-trifluoromethyl bonds are the same. We could not anticipate this on the basis of the well-known relationship between orbital hybridization and electronegativities of substituents. Thus, it is possible that the signs of ${}^1J_{\text{PtC}}$ (and ${}^2J_{\text{PtCH}}$) for the olefinic carbons of 1 and 8 are opposite. Unfortunately, since we cannot derive the absolute or relative signs of the ${}^1J_{\text{PtC}}$ and ${}^2J_{\text{PtCH}}$ values for 1 and 8, we cannot directly corroborate this new interpretation. However, recent ${}^{129}\text{I}$ Mössbauer results⁴³ have indicated that the trans influences of CH₃⁻ and CF₃⁻ ligands are markedly different. From studies of platinum(II) complexes of the sort *trans*-[Pt(P(CH₃)₂(C₆H₅)₂)₂X], where X = CH₃⁻, CF₃⁻, and I⁻, it was found that the quadrupole splittings for the ${}^{129}\text{I}$ are -774.0, -905.0, and -1172 MHz, respectively. Thus, CH₃⁻ would appear to have a higher trans influence than CF₃⁻ and I⁻, suggesting that the signs of the ${}^1J_{\text{PtC}}$ values of the COD olefinic carbons in 1 are opposite to those values in 8 and 9. Since the nmr trans influence of a ligand dominates its nmr cis influence, it would appear that the signs of all the ${}^1J_{\text{PtC}}$ values of the COD olefinic carbons trans to CH₃⁻ in 1-13 are opposite to

those values for the COD olefinic carbons cis to CH_3^- . This provides added support to our conclusions for eq 12, 15, and 16, where the signs of those coupling constants were assumed to be opposite. In any event, it is obvious that both CH_3^- and CF_3^- have very high nmr trans influences.

Next, we examined the ^{13}C shieldings and ^{13}C - ^{195}Pt coupling constants of the olefinic carbons of 3-7 to determine if there was a relationship between those parameters. To our surprise, a plot of those data for the olefinic segments trans to L revealed an excellent linear relationship, which is given in eq 18.

$$\delta_{\text{C}} (\text{COD CH trans to L, 3-7}) = -0.195 (\pm 0.005) - {}^1J_{\text{PtC}} (\text{COD CH trans to L, 3-7}) + 131.4 (\pm 0.6) \quad (18)$$

$$r = 0.973$$

This is an interesting result because analogous plots for the platinum methyl carbon ^{13}C nmr parameters of series of *trans*-methylplatinum(II) complexes³² do not afford such a linear relationship. It would appear that eq 18 provides a fortuitously good linear correlation.

Other ^{13}C - ^{195}Pt Coupling Constants. A less marked trend appears to occur for a plot of the ${}^1J_{\text{PtC}}$ vs. the ${}^2J_{\text{PtCC}}$ values of the COD olefinic and methylene carbon coupling constants. Due to the uncertainty in assigning the stereochemical dispositions of the COD methylene carbons and to their generally smaller coupling constants (and hence larger relative uncertainties), we have not carried out detailed analyses of those data.

The ^{13}C - ^{195}Pt coupling constants of the phenyl carbons in 13 are similar to those we have observed for a series of *trans*-phenylplatinum derivatives B.³⁰ Those observed values (ranges for series B in parentheses) are ${}^2J_{\text{PtC}_{2,6}} = 12(\pm 2)$ (16-31), ${}^3J_{\text{PtC}_{3,5}} = 50(\pm 2)$ (34-68), and ${}^4J_{\text{PtC}_4} = 8(\pm 2)$ Hz (8-12 Hz). ^{195}Pt coupling to the *quaternary* phenyl carbon was not observed, presumably due to the low intensities of the platinum satellites due to the lack of nuclear Overhauser enhancement of that carbon.

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