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## 50. A Carbon-13 Study of *bis*-Phosphine Platinum Complexes

by P. S. Pregosin and R. Kunz

Laboratorium für anorganische Chemie

Eidgenössische Technische Hochschule, Universitätstrasse 6, 8006 Zürich

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**Summary.** The  $^{13}\text{C}$ -NMR. spectra of a series of complexes of type  $[\text{PtCl}_2(\text{PR}_3)_2]$  and  $[\text{PtCl}_4(\text{PR}_3)_2]$  have been measured. The values  $^2J(\text{Pt}, \text{C})$  are shown to reflect changes in the metal hybridization while the values  $[^3J(\text{P}_A, \text{C}) + ^5J(\text{P}_B, \text{C})]$  are found to vary only slightly. It is suggested that the phosphorus hybridization in these complexes varies only slightly.

**Introduction.** – Although  $^{13}\text{C}$ -NMR. is used increasingly in organometallic chemistry [1] there are as yet no systematic studies of the effects of molecular geometry and metal hybridization state on the  $^{13}\text{C}$ -parameters of complexes of the type  $[\text{PtCl}_2(\text{PR}_3)_2]$  and  $[\text{PtCl}_4(\text{PR}_3)_2]$ . These molecules are of interest in that their  $^{13}\text{C}$ -NMR. spectra offer the opportunity to investigate a) interactions within the ligand *via* observation of the values  $^2J(\text{P}, \text{C})$ , b) changes at the metal center *via*  $^2J(\text{Pt}, \text{C})$  and c) potential long range intra ligand interactions *via* changes in the  $^{13}\text{C}$  chemical shifts,  $\delta^{13}\text{C}$ . The latter parameter is recognized to be sensitive to non-bonded steric interactions [2].

**Experimental.** –  $^{13}\text{C}$ -NMR. spectra were measured as deuteriochloroform solutions in spinning 10 mm tubes using a Bruker HX-90 spectrometer equipped with Fourier Transform (FT) accessories.

The deuteriated solvent served as both internal  $^{13}\text{C}$  reference and stabilization signal ( $^2\text{H}$ ). Chemical shifts are reported relative to tetramethylsilane and are estimated to be correct to  $\pm 0.1$  ppm. Coupling constants are  $\pm 1.5$  Hz.

The spectra were routinely measured in FT mode using pulse lengths of 4–7  $\mu\text{s}$  (90° pulse is approximately 12  $\mu\text{s}$ ). Samples were measured in single coil mode, thus allowing the transmitter coil, normally used in crossed coil mode, to carry a second (usually phosphorus) decoupling frequency provided by a Bruker frequency synthesizer. Spectra were normally run under conditions of complete  $^1\text{H}$ -decoupling. The compounds under consideration are all known previously

and were synthesized using literature methods [3]. Satisfactory fits of calculated with observed  $^{13}\text{C}$ -NMR. spectra were obtained using the program NMRCAL<sup>1)</sup>.

**Results and Discussion.** In order to facilitate interpretation of the spectra of the platinum analogs we have measured the  $^{13}\text{C}$  spectra of some *trans*- $[\text{PdCl}_2(\text{PR}_3)_2]$  complexes. A typical example is that of *trans*- $[\text{PdCl}_2(\text{PPr}_3)_2]$  shown in Fig. 1. The nomenclature for the various coupling constants and chemical shifts for the remainder of this article will be consistent with structure 1. The relative geometry of

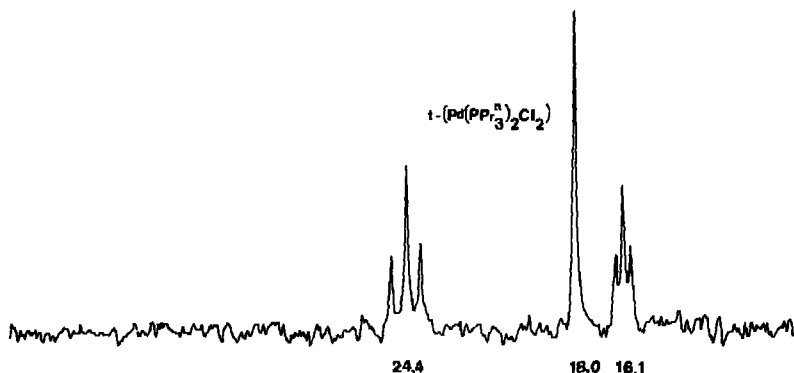
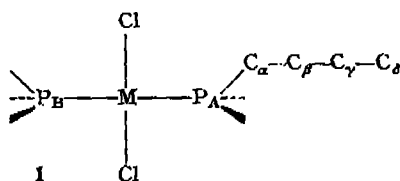


Fig. 1.  $^{13}\text{C}$ -NMR. Spectrum of *trans*- $[\text{PdCl}_2(\text{PPr}_3)_2]$  with  $^1\text{H}$  decoupling

phosphorus atoms A and B will be specified in each instance. Despite the simplification which is produced by proton noise decoupling, each of the carbon resonances in Fig. 1 represents the X portion of the spin system ABX.



The magnetic non equivalence of the phosphorus atoms in these complexes, and thus the decision to consider this ABX and not an AA'X, is a consequence of the carbon isotope effect on phosphorus (when P-atom A is adjacent to  $^{13}\text{C}$  P-atom B is adjacent to  $^{12}\text{C}$ ). The magnitude of this isotope effect is not certain, however we believe it to be relatively small<sup>2)</sup>. The numbers of lines observed for the  $m^{\text{th}}$  carbon atom resonance in a molecule of this type has been recently shown [5] to depend upon the relative values of  $^3J(\text{P}_A, \text{P}_B)$ ,  $J(\text{P}_A, \text{C}_m)$  and  $J(\text{P}_B, \text{C}_m)$  as well as the chemical shift difference between the phosphorus atoms. Thus it is possible to observe from two to six lines for a given carbon atom. The 1:2:1 triplets observed for the  $\alpha$  and  $\gamma$  carbons (lowest and highest field resonances respectively), in Fig. 1 result

<sup>1)</sup> The computer program NMRCAL was provided by Nicolet Instrument Co. Madison, Wisconsin, 1971.

<sup>2)</sup> Our calculations for these and similar spin systems suggest a magnitude of  $\approx 0.5$ – $1.0$  Hz. For related references see [5].

whenever  ${}^3J(P_A, P_B)$  is relatively large [6] and when the value  $[J(P_A, C_m) + J(P_B, C_m)]$ , which represents the separation of the two equally intense lines of the triplet, is observable. The  ${}^{13}\text{C}$ -NMR. spectra were assigned using expected aliphatic substituent effects within a homologous series, off-resonance decoupling techniques and suitable model compounds. In Fig. 2 is shown the  ${}^{13}\text{C}$ -NMR. spectrum of *trans*- $[\text{PtCl}_4(\text{PEt}_3)_2]$ .

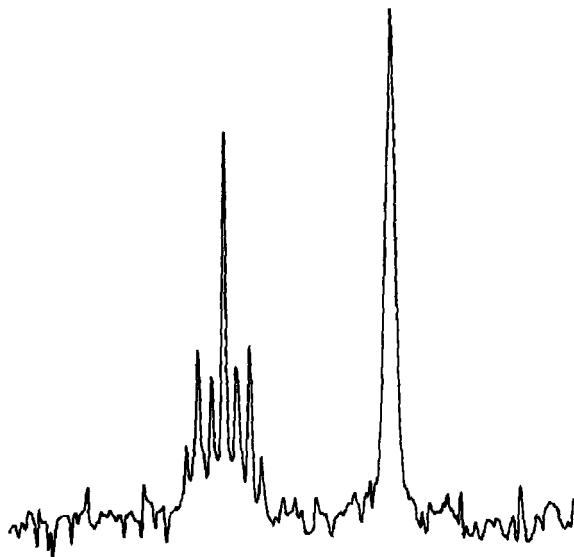


Fig. 2.  ${}^{13}\text{C}$ -NMR. Spectrum of *trans*- $[\text{PtCl}_4(\text{PEt}_3)_2]$  with  ${}^1\text{H}$  decoupling

In addition to the features produced by the presence of the phosphorus atoms the spectrum now contains the  ${}^{195}\text{Pt}$  ( $I = 1/2$ , natural abundance = 33.7%) satellites. In the seven line multiplet representing  $C_\alpha$ , the three most intense lines (lines 2, 4 and 6 from left to right) represent the X portion of the *ABX* with the separation of lines 2 and 6 having the value  $[{}^1J(P_A, C) + {}^2J(P_B, C)]$ . The remaining four lines are the  ${}^{195}\text{Pt}$  satellites. When, as in this case, the value  ${}^2J(\text{Pt}, C)$  is approximately one half of  $[{}^1J(P_A, C)]$  several of the satellite resonances may overlap. Thus the resonance immediately to the left of the center line, line 3, is the result of the overlap of the low field satellite of line 4 with the high field satellite of line 2. Similarly, line 5 is the superimposition of the high field satellite of line 4 with the low field satellite of line 6. The resonance of  $C_\beta$  appears as a broadened single line presumably the result of unresolved small couplings to both metal and phosphorus atoms. It is interesting to note, as is shown by both figures, that there is no observable coupling of phosphorus to  $C_\beta$ . In similar fashion one can extract the various coupling constants from the spectra of the remaining complexes.

In Table 1 are listed the two-bond couplings of platinum to  $C_\alpha$  which may be seen to vary from  $\approx 14$ –41 Hz. The range is similar to those found by Clark *et al.* [7] in their study of platinum alkyl derivatives containing *trans*-dimethylphenylphosphine groupings. However, in addition to observing a decrease in  ${}^2J(\text{Pt}, C)$  on going from Pt(II) to Pt(IV), as have these authors, we observe a dependence of the values  ${}^2J(\text{Pt}, C)$  on molecular geometry. Thus the values  ${}^2J(\text{Pt}, C)$  in the molecules *cis*-

Table 1. Couplings<sup>a)</sup> to the  $\alpha$ -<sup>13</sup>C-atom in the Complexes  $[Pt(PR_3)_2Cl_2]$  and  $[Pt(PR_3)_2Cl_4]$ 

R	<i>cis</i>		<i>trans</i>	
	<sup>2</sup> J(Pt, C)	[ <sup>1</sup> J(P <sub>A</sub> , C) + <sup>3</sup> J(P <sub>B</sub> , C)]	<sup>2</sup> J(Pt, C)	[ <sup>1</sup> J(P <sub>A</sub> , C) + <sup>3</sup> J(P <sub>B</sub> , C)]
	Pt(II)			
Et	41.0	38.8	24.9 <sup>b)</sup>	33.7 <sup>b)</sup>
<i>n</i> -Pr	36.6	38.1	22.7	33.0
<i>n</i> -Bu	36.6	38.0	22.7 <sup>c)</sup>	32.2
	Pt(IV)			
Et	22.0 <sup>b)</sup>	36.6	16.1	32.2
<i>n</i> -Pr	20.5	33.7	16.1	32.2
<i>n</i> -Bu	20.9	34.4	14.6	32.2

a) Coupling constants are estimated to be correct to  $\pm 1.5$  Hz.

b) Measured in CD<sub>2</sub>Cl<sub>2</sub>.

c) This coupling constant has a positive sign.

$[PtCl_2(PR_3)_2]$  (R = Et, *n*-Pr, *n*-Bu) are of the order of 36–41 Hz while the corresponding *trans* derivatives fall in the range 22–25 Hz. The analogous ranges for the Pt(IV) derivatives are 20–22 Hz and 14–16 Hz respectively. Additionally, we find good agreement between the values <sup>2</sup>J(Pt, C) in the *cis* Pt(II) isomers and the Pt(II) bridged species  $[Pt_2Cl_4(PR_3)_2]$ , R = Et, *n*-Pr (Table 2).

Table 2. NMR. Parameters<sup>a)</sup> for the compounds *trans*- $[Pd(PR_3)_2Cl_2]$  and *sym-trans*- $[Pt_2(PR_3)_2Cl_4]$ 

R	<i>trans</i> - $[Pd(PR_3)_2Cl_2]$					
	C <sub>α</sub>		C <sub>β</sub>		C <sub>γ</sub>	
	[ <sup>1</sup> J(P <sub>A</sub> , C) + <sup>3</sup> J(P <sub>B</sub> , C)]	δ	[ <sup>2</sup> J(P <sub>A</sub> , C) + <sup>4</sup> J(P <sub>B</sub> , C)]	δ	[ <sup>3</sup> J(P <sub>A</sub> , C) + <sup>5</sup> J(P <sub>B</sub> , C)]	δ
Et	28.0	14.0	<sup>b)</sup>	8.0		
<i>n</i> -Pr	26.4	24.4	<sup>b)</sup>	18.0	13.2	16.1
<i>n</i> -Bu <sup>c)</sup>	26.4	21.5	<sup>b)</sup>	26.4	13.2	24.5

R	<i>sym-trans</i> - $[Pt_2(PR_3)_2Cl_4]$							
	C <sub>α</sub>			C <sub>β</sub>			C <sub>γ</sub>	
	<sup>2</sup> J(Pt, C)	[ <sup>1</sup> J(P <sub>A</sub> , C) + <sup>3</sup> J(P <sub>B</sub> , C)]	δ	<sup>2</sup> J(Pt, C)	[ <sup>1</sup> J(P <sub>A</sub> , C) + <sup>3</sup> J(P <sub>B</sub> , C)]	δ	[ <sup>3</sup> J(P <sub>A</sub> , C) + <sup>5</sup> J(P <sub>B</sub> , C)]	δ
Et	38.1	40.3	14.9	24.2	<sup>b)</sup>	9.2		
<i>n</i> -Pr	36.3	39.5	24.5	23.4	3	17.5	16.8	15.7
<i>n</i> -Bu		39.6	22.1		<sup>b)</sup>	25.8	14.6	24.1

<sup>a)</sup> Coupling constants are  $\pm 1.5$  Hz. Chemical shifts are relative to the carbon resonance of 1 MDS and are  $\pm 0.1$  ppm.

<sup>b)</sup> Not observed.

The dependence of a platinum-ligand atom coupling constant on both metal oxidation state and molecular geometry has been observed previously. Thus <sup>1</sup>J(Pt-<sup>31</sup>P) [8], <sup>1</sup>J(Pt-<sup>15</sup>N) [9], <sup>3</sup>J(Pt-N-CH) [10] and <sup>3</sup>J(Pt-P-CH) [11] have all

been shown to have such a dependence. Of particular interest is the good correlation (see Table 3) between  $^3J(\text{Pt}, \text{C})$  and  $^1J(\text{Pt}, \text{P})$  with respect to relative sensitivity to changes of either molecular geometry or metal oxidation state. Additionally, there seems also to be a similar dependence of  $^3J(\text{Pt}, \text{C})$  on both metal oxidation state and molecular geometry (see Table 4).

Table 3. *A Comparison of the Effects of Configuration and Oxidation State on the Values  $^1J(^{195}\text{Pt}, ^{31}\text{P})$ ,  $^3J(^{195}\text{Pt}, ^{13}\text{C})$  and  $[^1J(\text{P}_A, \text{C}) + ^3J(\text{P}_B, \text{C})]$  for the Complexes with  $R = n\text{-Butyl}$*

	$^1J(\text{Pt}, \text{P})$	$^3J(\text{Pt}, \text{C})$	$[^1J(\text{P}_A, \text{C}) + ^3J(\text{P}_B, \text{C})]$
<i>cis</i> Pt(II)	1.5	1.6	1.2
<i>trans</i> Pt(II)			
<i>cis</i> Pt(IV)	1.4	1.4	1.1
<i>trans</i> Pt(IV)			
<i>cis</i> Pt(II)	1.7	1.8	1.1
<i>cis</i> Pt(IV)			
<i>trans</i> Pt(II)	1.6	1.6	1.0
<i>trans</i> Pt(IV)			

Table 4. *Coupling constants<sup>a)</sup> to the  $\beta$  and  $\gamma$  carbon atoms in the complexes*

	<i>cis</i>		<i>trans</i>	
	$^3J(\text{Pt}, \text{C})$	$[^3J(\text{P}_A, \text{C}) + ^5J(\text{P}_B, \text{C})]$	$^3J(\text{Pt}, \text{C})$	$[^3J(\text{P}_A, \text{C}) + ^5J(\text{P}_B, \text{C})]$
	Pt(II)			
Et	27.8		16.1	
<i>n</i> -Pr	26.3	15.4	15.4	13.9
<i>n</i> -Bu	25.8	14.6	15.3	13.2
	Pt(IV)			
Et	9.5		b)	
<i>n</i> -Pr	b)	16.1	b)	13.2
<i>n</i> -Bu	11.4	14.6	b)	12.5

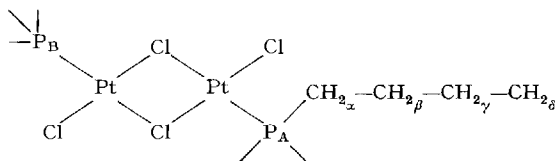
a) Estimated to be correct to  $\pm 1.5$  Hz.

b) Not observed.

The values  $[J(\text{P}_A, \text{C}) + J(\text{P}_B, \text{C})]$  are shown in Tables 1, 2 and 4 and may be seen to vary from 32–40 Hz, for the  $\alpha$ -carbon (Table 1) and from 12–16 Hz for the  $\gamma$ -carbon (Table 4). Couplings of phosphorus atom to the  $\beta$ -carbon atom are always less than 6 Hz and are frequently below the spectral resolution.

Recently Mann [12] has reported the various phosphorus-carbon coupling constants for a number of trialkyl phosphines and noted that the magnitudes of  $^1J(\text{P}, \text{C})$ ,  $^2J(\text{P}, \text{C})$  and  $^3J(\text{P}, \text{C})$  vary only slightly and thus, in those molecules, have a limited diagnostic utility. This apparently is not the case for platinum and palladium complexes since these magnitudes vary considerably. We note that in the bridged species, **2**,  $[\text{Pt}_2\text{Cl}_4(\text{PR}_3)_2]$ ,  $R = \text{Et}, n\text{-Pr}, n\text{-Bu}$ , where  $J(\text{P}_B, \text{C})$  is across 5 bonds, the magnitudes of the phosphorus-carbon couplings closely parallel those of the complexes

(see Table 2), suggesting that, although we may only extract [ $nJ(P_A, C_m) + n+2J(P_B, C_m)$ ] from the 'simple'  $^{13}\text{C}$ -NMR. spectra of the *bis*-phosphine complexes, we may qualitatively take this value to approximate  $nJ(P_A, C_m)$  when  $n > 1$ . This is reasonable since couplings of phosphorus atom to carbon atom through 4 or more bonds in aliphatic systems are usually quite small [12] [13]. The values  $^3J(P, C)$  seem to show a small dependence on molecular geometry but no significant dependence on the metal oxidation state. The values [ $^1J(P_A, C) + ^3J(P_B, C)$ ] vary slightly as a function of these two parameters; however, as is seen from Table 3 not nearly as dramatically as the values  $^2J(\text{Pt}, C)$ .



In considering all the data the good correlation of  $^2J(\text{Pt}, C)$ , and to a lesser extent,  $^3J(\text{Pt}, C)$ , with  $^1J(\text{Pt}, P)$  is interesting in that it suggests a common term in the theoretical expressions for these couplings. In the consideration of the factors affecting the values  $^1J(\text{Pt}, P)$  the dominance of the *Fermi* contact term (equ. 1) is assumed [14]. Since some experimental evidence exists suggesting that the  $\Delta E$  [9] [10] and [ $\psi_{6s}(\text{O})$ ] $^2$   $^3$ ) terms are not

$$^1J(\text{Pt}, P) \propto \gamma_{\text{Pt}} \gamma_{\text{P}} \alpha_{\text{Pt}}^2 \alpha_{\text{P}}^2 [\psi_{6s}(\text{O})]^2 [\psi_{3s}(\text{O})]^2 / \Delta E \quad (1)$$

important several authors [8] [14] have settled on the term  $\alpha_{\text{Pt}}^2$  (a term which is common to both couplings) as the dominant factor. There is, however, little direct evidence that  $\alpha_{\text{P}}^2$  should be discounted. Recently we have shown [16] that, in amine complexes of Pt(II) and Pt(IV) containing  $^{15}\text{N}$  enriched dodecylamine, one observes values of  $^1J(^{15}\text{N}, \text{H})$  (71–73 Hz) which suggest the nitrogen hybridization is  $\text{sp}^3$  and does not change as a function of molecular geometry in these two metal oxidation states [17]. Since conclusions concerning the electronic and structural configuration of phosphine complexes are drawn from the magnitude of  $^1J(\text{Pt}, P)$  it would be useful to know if this constancy was also true for phosphorus.

If one assumes constant carbon hybridization<sup>4)</sup> the values  $nJ(P, C_m)$  should, in some measure, reflect the changes which occur at phosphorus. In our complexes we observe only small changes in the values [ $^3J(P_A, C) + ^5J(P_B, C)$ ], which we approximate as  $^3J(P_A, C)$ , suggesting no major alterations at phosphorus. Additionally the magnitudes of these couplings (12.5–16.1 Hz) are in reasonable agreement with those observed in phosphonium salts<sup>5)</sup> ( $n\text{-Bu}_4\text{P}^+\text{Br}^-$ ; 15.4 Hz,  $n\text{-Bu}_3\text{PH}^+\text{Cl}^-$ ; 14.9 Hz and  $n\text{-Bu}_3\text{MeP}^+\text{I}^-$ ; 15.7 Hz) where the phosphorus hybridization is approximately  $\text{sp}^3$ . The couplings [ $^1J(P_A, C) + ^3J(P_B, C)$ ], which vary from 32–39 Hz, are also re-

<sup>3)</sup> The term  $\psi_{6s}(\text{O})^2$  will be similar for coupling to different phosphorus atoms in the same molecule. Thus in trisubstituted trialkylphosphine complexes of Pt(II) similar *cis/trans* ratios are observed as in the *bis* trialkylphosphine complexes [16].

<sup>4)</sup> Duddell *et al.* [12] comment that in complexes of type  $[\text{PtCl}_2(\text{PMe}_2)_2]$  the values  $^1J(^{13}\text{C}, \text{H})$ , in a series of related complexes, are essentially invariant.

<sup>5)</sup> See [2a], p. 159.

vealing but more difficult to interpret due to lack of information concerning the sign and magnitude of  ${}^3J(\text{P}_B, \text{C})$ .

Several authors [13] [18] have reported on the values  ${}^1J(\text{P}, \text{C})$  and these are recognized to be positive and have magnitudes in the range 40–56 Hz for compounds of the type  $\text{R}_2\text{R}^1\text{P}^+\text{X}^-$ ,  $\text{R} = \text{alkyl}$ ,  $\text{R}^1 = \text{H}$  or  $\text{alkyl}$ ,  $\text{X} = \text{halogen}$ . In the halogen bridged species,  $[\text{Pt}_2\text{Cl}_4(\text{PR}_2)_2]$ , the observed  ${}^1J(\text{P}, \text{C})$  values are  $\sim 40$  Hz. Goodfellow & Goggin [19] have found for  $\text{NR}_4[\text{PtCl}_3(\text{PMe}_2)]$  and  $\text{NR}_4[\text{PtCl}_5(\text{PMe}_2)]$  values of  ${}^1J(\text{P}, \text{C})$  for 43.6 and 46.4 Hz respectively. The  ${}^{13}\text{C}$  resonances of the  $\alpha$ -carbon atoms of the *cis* Pt(II) complexes are not deceptively simple and thus may be analysed using literature methods [5b]. We calculate<sup>6)</sup> for  ${}^1J(\text{P}_A, \text{C})$  values of approximately +39 Hz and for  ${}^3J(\text{P}_B, \text{C})$  values of approximately -1 Hz. Allowing for small changes in  ${}^3J(\text{P}_B, \text{C})$  and a geometric dependence of  ${}^1J(\text{P}_A, \text{C})$  (*cis* > *trans*), which is similar in relative magnitude to  ${}^3J(\text{P}_A, \text{C})$  the observed values of [ ${}^1J(\text{P}_A, \text{C}) + {}^3J(\text{P}_B, \text{C})$ ] now seem understandable. Thus the values in the range 32–36 Hz result from small<sup>7)</sup> decreases in  ${}^1J(\text{P}_A, \text{C})$  in combination with a small negative value for  ${}^3J(\text{P}_B, \text{C})$ .

We therefore conclude that since the relative changes in the coupling constants  ${}^3J(\text{Pt}, \text{C})$  and  ${}^1J(\text{Pt}, \text{P})$  are of the order of magnitude 40–80% they are indeed dominated by the changes which occur at the metal and that the supposition of the dominance of the term  $\alpha_{\text{Pt}}^3$  in the *Fermi* contact term (equ. 1) is most probably correct.

The  ${}^{13}\text{C}$  chemical shifts for the complexes are shown in Table 5. It is worth noting that a) the resonance positions of the  $\alpha$ -carbon atoms of the *cis* isomers are consistently to low field of those of the *trans* isomers by approximately 4–5 ppm and b) the chemical shifts of the carbon atoms further down the chain are rather insensitive to both metal oxidation state and complex geometry and thus do not offer any evidence for *intra* ligand interactions. Several explanations for observation a) are possible:

- 1) the presence of a proximate phosphorus atom bearing a partial positive charge;
- 2) a neighboring group anisotropic effect;
- 3) a subtle rehybridization effect as it manifests itself in small changes in the phosphorus-carbon bond lengths.

We consider the first suggestion unlikely in that quaternization of phosphorus induces a *high field* shift in the  $\alpha$ -carbon atom (*n*- $\text{Bu}_3\text{P}$ :  $\delta = 29.3$  [12], 25.2 [2a]; *n*- $\text{Bu}_4\text{P}^+\text{Br}$ ,  $\delta = 18.9$ ) [17]. If, as shown by X-Ray studies (see [21a] and [21b]) donation from the phosphorus atom to the metal atom in the *cis* isomers results in

<sup>6)</sup> Although the calculated values for  ${}^1J(\text{P}_A, \text{C})$  and  ${}^3J(\text{P}_B, \text{C})$  give a correct fit with the observed spectrum it is likely that this solution is not unique. The overlap of platinum satellites with the lines noted by both Bovey and Nelson [6] as 10, 11, required that we carry out a series of calculations based on linewidths to estimate the separation of these lines. Additionally we do not have exact knowledge of the isotope effect,  $(\nu_A - \nu_B)$ , and have made a second group of calculations based on values of  $(\nu_A - \nu_B)$  of 0.5–2 Hz. Other reasonable solutions gives values of  ${}^1J(\text{P}_A, \text{C})$  up to  $\approx 45$  Hz and  ${}^3J(\text{P}_B, \text{C})$  of  $\sim -6$  Hz. These changes do not invalidate our qualitative conclusions since a 10% change in  ${}^1J(\text{P}_B, \text{C})$  in conjunction with a value of -4 to -8 Hz for  ${}^3J(\text{P}_B, \text{C})$  give the observed [ ${}^1J(\text{P}_A, \text{C}) + {}^3J(\text{P}_B, \text{C})$ ] values. If the coupling  ${}^3J(\text{P}_B, \text{C})$  changes algebraically (the values  ${}^1J(\text{Pt}, \text{P})$  are all positive) and in similar ratio to other couplings modified by the changing term  $\alpha_{\text{Pt}}^3$  then in the Pt(IV) isomers  ${}^3J(\text{P}_B, \text{C})$  may be of the order of -10 Hz and  ${}^1J(\text{P}_A, \text{C})$  will have changed less than 10%.

<sup>7)</sup> We feel, from our data, that a 10–15% change might be possible. Others [20] have suggested values of 1–2%.

Table 5.  $^{13}\text{C}$  Chemical shifts<sup>a)</sup> in Platinum complexes of the type  $[\text{Pt}(\text{PR}_3)_2\text{Cl}_n]$ 

R	n = 2		n = 4	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
<b>Et</b>				
C <sub>α</sub>	17.1	13.0	18.1 <sup>b)</sup>	12.7 <sup>b)</sup>
C <sub>β</sub>	8.7	8.0	9.2	7.9
<b>Pr</b>				
C <sub>α</sub>	27.2	23.3	26.7	22.3
C <sub>β</sub>	18.1	17.5	18.2	17.2
C <sub>γ</sub>	15.6	16.0	15.8	15.9
<b>Bu</b>				
C <sub>α</sub>	24.4	20.6	24.5	20.0
C <sub>β</sub>	26.5	26.1	26.2	25.4
C <sub>γ</sub>	24.1	24.4	24.2	24.3
C <sub>δ</sub>	13.7	13.9	13.7	13.7

<sup>a)</sup>  $^{13}\text{C}$  Chemical shifts are relative to the carbon resonance of TMS and are estimated to be correct to  $\pm 0.1$  ppm.

<sup>b)</sup> Measured in  $\text{CD}_2\text{Cl}_2$ .

shorter bond lengths than in the *trans* isomers one might expect *more* positive charge to be developing on these molecules and thus, as in phosphonium ions, a high field shift. Point 2 seems equally unlikely since there is little change from the C<sub>α</sub> resonance position of the planar complexes after two chlorine atoms are added to the metal atom in *cis* position to phosphorus and *trans* to each other (*trans*- $[\text{PtCl}_2(\text{PBu}_3)_2] = 20.6$ , *trans*- $[\text{PtCl}_4(\text{PBu}_3)_2] = 20.0$ ). The last suggestion seems reasonable, although not definite. We know the C–P–C bond angles in free phosphines are less than  $109^\circ$  (see [22]) presumably due to the greater s-character of the lone pair. As the quaternization of the phosphorus atom proceeds, *via* complexation, more s-character is distributed through the P–C bonds thus making them shorter. The equation for  $\sigma_{\text{P}}$ , the paramagnetic screening term in the overall screening term  $\sigma$ , has an inverse dependence on the *cube* of the bond lengths to carbon [2]. Thus a small difference in the phosphorus-carbon bond lengths in the complexes, associated with the small differences we observe in our phosphorus-carbon couplings, might produce the observed effect<sup>a)</sup>. A shorter P–C<sub>α</sub> bond length in the *cis* isomers increases the relative magnitude of  $\sigma_{\text{P}}$  which in turn results in a higher frequency for the resonance of that carbon.

$$\sigma_{\text{P}} \propto -1/r^3 \quad (2)$$

$$\nu = \gamma H_0 (1 - \sigma). \quad (3)$$

The dependence of the  $^{13}\text{C}$  chemical shift on molecular geometry may prove diagnostically useful and we are currently engaged in studies of phosphine complexes

<sup>a)</sup> X-Ray structures for any complete set of four complexes are, unfortunately, not in the literature.



of different metals in an effort to assess its generality. Similarly we feel that the magnitude of  $^2J(\text{Pt}, \text{X}, \text{C})$ , where X is a donor atom other than phosphorus, may potentially be useful as a diagnostic probe, especially where platinum-proton couplings are not readily observed. Lastly, our conclusions concerning donor atom hybridization should add yet another nail to the lid of the coffin which will bury the  $\pi$ -bonding theory as a major source of the NMR. *trans* influence [23] in phosphine complexes. We have shown, *via*  $^1J(\text{P}, \text{C}_m)$  values, that the phosphorus does not change its nature to any major extent in our complexes and certainly not sufficiently to account for the changes in  $^2J(\text{Pt}, \text{C})$ . Arguments which embrace platinum-phosphorus d-d  $\pi$  bonding and a consequent large synergic increase in the donor ability of the ligand atom seem unfounded.

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