

246. A ^{13}C - and ^{195}Pt -NMR. Study of the Complexes *trans*-PtCl₂(amine)(CH₂=CH₂)

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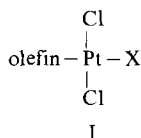
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Summary

^{13}C - and ^{195}Pt -NMR. spectra for the complexes *trans*-PtCl₂(amine)(CH₂=CH₂) have been measured. For amine=(*S*)-*N*-methyl-*a*-methylbenzylamine the two diastereomers present may be distinguished from the values $^3J(\text{Pt}, \text{C})$. The ^{195}Pt -chemical shift is shown to be sensitive to subtle differences stemming from intramolecular non-bonded interactions.

1. Introduction. - The assumption that metal olefin complexes are likely intermediates in the hydrogenation of alkenes has led to numerous studies concerned with the interaction of double bonds with metals [1]. In particular a number of ^1H - and ^{13}C -NMR. studies (*cf.* [2] and [3], resp.) concerned with platinum complexes of type I, in which the olefin is frequently ethylene and X a pyridine derivative, have

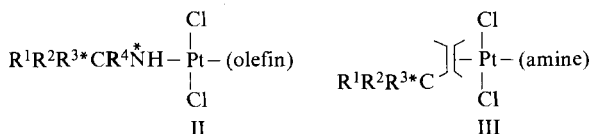


recently appeared. Both $\delta^{13}\text{C}(\text{CH}_2=\text{CH}_2)$ and $^1J(\text{Pt}, \text{C})$ have been found to provide useful estimates of the *trans*-influence of X and in all cases the sequence $\text{N} > \text{Cl} > \text{O}$ was observed [3]. For the situation in which the olefin is a *para*-substituted styrene both ^{13}C -NMR. and X-ray studies have shown that the group in the *para* position significantly influences the way in which the double bond coordinates to the metal [4].

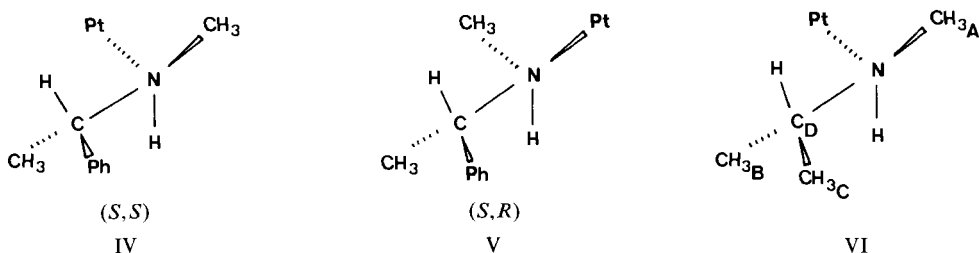
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For X = a *para*-substituted pyridine evidence has been presented suggesting that the ring substituent produces only small fluctuations in the σ -donor component of the platinum carbon bond [3a], but a significant change in the σ and π contributions to the Pt,N-bond [5]. Recently, a report concerned with the solid state structure of the complexes *trans*-PtCl₂(CH₂=CH₂)(pyr), pyr = 4-methyl- and 4-cyano-pyridine, has shown that neither the platinum-ethylene- nor platinum-nitrogen-bond lengths are significantly affected by the *para*-substituent [6]. Calculations concerned with the extent to which π -bonding contributes to metal-ethylene bond have suggested that the σ -component dominates [3a].

The compounds II and III, formed when either a chiral secondary amine or a chiral α -olefin coordinate to a metal are interesting in that diastereomeric complexes are produced. It has been shown [7] that ¹H-NMR. techniques are useful for



the distinction and identification of these optically active products. It is thought that the ¹H-chemical shifts, in complexes of type III, may be related to proximity to the metal [7]. The X-ray structural analysis of *trans*-dichloro-[(*S*)-*N*-methyl- α -methylbenzylamine] (ethylene)platinum (II) has shown that this molecule exists as the (*S,S*)-diastereomer IV in the solid state [8a]; however, ¹H-NMR. studies have shown [8b] that the molecule isomerizes to an 85:15 (*S,S*:*R,S*)-mixture in CDCl₃ solution.



We have previously found the multinuclear NMR. approach to questions of structure and bonding in molecules of this type to be most useful [9]. Thus, in order to shed further light on whether bonding and/or non-bonding effects are responsible for the population difference observed for these diastereomers and to further develop methods by which these types of molecules may be distinguished we have measured ¹³C- and ¹⁹⁵Pt-NMR. spectra for these and related complexes. Molecules such as these, in which a single ligand is easily changed, allow us to extend our studies concerned with the factors affecting ¹⁹⁵Pt-chemical shifts [10] since there are still relatively few data available for this nucleus.

2. Experimental Part. - The complexes were prepared as previously described [11]. Typically, a solution of the amine in 0.1N HCl was added to an equimolar solution of Zeises salt in water. The

resulting solution was then neutralized with 0.1N KOH to pH 6 and the yellow precipitate which separates collected *via* filtration. The complexes were recrystallized from CH₂Cl₂/pentane 1:2 and gave satisfactory elemental analyses. ¹³C- and ¹⁹⁵Pt-NMR. spectra were measured at 22.63 and 19.34 MHz respectively, as CDCl₃ solutions in 10 mm tubes using a Bruker HX-90 spectrometer operating in FT mode. The ¹³C-NMR. spectra were recorded at 31-32° since, unlike the compounds I (X = pyridine) [2c], the aliphatic amines exchange slowly at these temperatures. The ¹⁹⁵Pt-NMR. spectra were measured between -35° and -40° at which temperature the broadening of the metal resonance due to unresolved coupling with ¹⁴N (I = 1) is minimal. This 'thermal decoupling' of a quadrupolar nucleus from a nucleus of spin I = 1/2 probably stems from the change in the viscosity of the solution and has been observed previously [12]. For the *N*-methyl- and *N*-ethyl-amine derivatives the ¹⁴N/¹⁹⁵Pt coupling was clearly visible in the metal spectrum at 50° [¹J(¹⁹⁵Pt, ¹⁴N) ≈ 200 Hz ± 10 in both cases]. ¹⁹⁵Pt-chemical shifts are reported relative to Na₂PtCl₆ (a low field reference) with a negative sign indicating a shift to higher field (lower frequency).

3. Results and Discussion. - Since there was relatively little known concerning either the ¹³C- or ¹⁹⁵Pt-NMR. characteristics of a system such as I (X = aliphatic amine) we have prepared and studied a series of these derivatives with both primary and secondary amines. The ligands chosen cover an acidity range of approximately 2 pK_a units and differ considerably in size.

In *Tables 1* and *2* are tabulated the appropriate ¹³C- and ¹⁹⁵Pt-NMR. data respectively.

3.1. ¹³C-NMR. parameters for the coordinated ethylene. Previous ¹³C-NMR. studies [3] for related molecules have shown that δ¹³C₂H₄ and ¹J(Pt, C) values for ethylene complexes such as I vary from approximately 60-80 ppm and 220 to 150 Hz respectively, with smaller δ values and larger ¹J(Pt, C) values corresponding to ligands such as pyridine-*N*-oxide and Cl⁻. Typical values for 4-substituted pyridine derivatives are in the range 75-77 ppm and 160-166 Hz, respectively [3]. The ¹³C-signals (main band plus ¹⁹⁵Pt satellites) in our complexes fall between 73 and 75 ppm with ¹J(Pt, C) values of approximately 153 to 163 Hz. There seem to be only small differences between primary and secondary amines with the former showing δ 73.9-75.3 ppm, ¹J(Pt, C) 160-163 Hz and the latter δ 73.1-74.8 ppm, ¹J(Pt, C) 157-162 Hz. If one assumes that ¹J(Pt, C) is proportional to the s-character in the Pt, C-bond [13], and that the *trans*-influence of a group *trans* to the ethylene is reflected qualitatively by changes in the strength of the σ-component of the Pt, C-bond [14], then the secondary amines Me₂NH, EtMeNH and piperidine would seem to have a slightly larger *trans*-influence than the primary amines. The 7 Hz difference in ¹J(Pt, C) between the piperidine and 2,6-dimethyl-piperidine complexes is significant and we shall return to this subject when we consider the question of ¹⁹⁵Pt chemical shifts.

3.2. ¹³C-NMR. parameters of the coordinated amines. Coupling constants. In order to appreciate the observed ⁿJ(Pt, C) values in the diastereomers we consider first the various two and three bond couplings in the simple primary and secondary amines and employ the nomenclature shown in VI, such that C_D is always the substituted carbon atom attached to the nitrogen atom. Striking is the large difference between ³J(Pt, C) (at least a factor of five) in the secondary amine complexes. Of particular interest in this connection are the values of ³J(Pt, C) for *N*-methylisopropylamine, the (*S,S*)- and (*S,R*)-diastereomers of (*S*)-*N*-methyl-*α*-methylbenzylamine and the piperidine and 2,6-dimethylpiperidine complexes

(entries 7, 9a, 9b, 10 and 11 in Table 1). The ^{13}C -spectrum of the amine section of the *N*-methylisopropylamine complex shows four resonances, each of relative unit intensity. Thus the two isopropyl methyl groups are non-equivalent and show a marked difference in their coupling to platinum (see Table). This is readily explained if one assumes hindered rotation about the $\text{C}_D\text{-N}$ -bond and that the *N*-methylisopropylamine complex exists mostly in a conformation such as VI, in which CH_3B is *cis* to platinum and CH_3C *trans* to platinum. Given that there are numerous examples of the conformational dependence of a vicinal coupling (e.g. Karplus type relationships have been suggested for $^3J(\text{H}, \text{H})$ [15], $^3J(\text{P}, \text{C})$ [16] and $J(\text{Pt}, \text{C})$ [17]) it is not surprising that $^3J(\text{Pt}, \text{CH}_3\text{C}) > ^3J(\text{Pt}, \text{CH}_3\text{B})$.

If one assumes that the N,Pt-bond occupies an equatorial position²⁾ in the complex I (X = piperidine), then it is reasonable to expect large $^3J(\text{Pt}, \text{C})$ values for both X = piperidine and X = 2,6-dimethyl-piperidine since we have CH_2 within the ring *trans* to platinum. Although the piperidine value is larger (35.4 vs. 27.5 Hz) this is clearly the case. Returning briefly to the $\text{CH}_2=\text{CH}_2$ ^{13}C -data we find that $^1J(\text{Pt}, \text{C})$ has a value of 153.8 Hz for the piperidine complex suggesting that this amine may be more strongly bound than the other secondary amines and thus is not directly comparable with the acyclic systems. This difference for piperidine probably stems from its cyclic nature. The bulkier 2,6-dimethylpiperidine complex (whose

Table 1. ^{13}C -NMR. Parameters^{a)} for the complexes

$$\begin{array}{c} \text{Cl} \\ | \\ \text{ethylene}-\text{Pt}-\text{X} \\ | \\ \text{Cl} \end{array}$$

		$^1J(\text{Pt}, \text{C})$	$\text{CH}_2=\text{CH}_2$	δNC		$^2J(\text{Pt}, \text{NC})$		δNCC	$^3J(\text{Pt}, \text{NCC})$
				C_D	C_A	C_D	C_A		
1)	MeNH ₂	160.3	73.9	32.1		16.2			
2)	EtNH ₂	160.3	75.3	40.8		14.0		16.5	30.9
3)	<i>i</i> -PrNH ₂	160.3	75.1	48.3		8.8		24.2	23.5
4)	PhCH ₂ NH ₂	163.3	75.2	49.8		12.2			
5)	Me ₂ NH	156.7	74.8		41.7		14.7		
6)	EtMeNH	156.6	74.7	50.0	40.4	12.6	16.9	14.3	~10 ^{b)}
7)	<i>i</i> -PrMeNH	158.0	73.9	54.4	37.0	12.5	19.1	23.7 20.3	7.4 26.5
8)	PhCH ₂ MeNH	159.6	74.2	58.3	39.0	12.5	14.7		
9)	<i>a</i> -Phenethyl-MeNH								
	a) <i>S,S</i>	160.0	74.0	63.0	37.8	8.9	19.1	23.8	< 5 ^{c)}
	b) <i>S,R</i>	162.0	73.1	61.7	36.3	13.2	15.5	18.5	25.7
10)	Piperidine	153.8	74.4	51.1		14.7		27.1	35.4
11)	2,6-Me ₂ -Piperidine	160.8	73.3	57.6		14.6		34.7-CH ₂ 23.3-CH ₃	27.5 < 5 ^{d)}

^{a)} CDCl₃ solns; δ in ppm from TMS; J in Hz.

^{b)} Shoulders due to ^{195}Pt satellites observable but signals not resolved.

^{c)} Estimated based on the line width.

^{d)} Use of a positive exponential on the FID reveals $^3J(\text{Pt}, \text{C}) \sim 4$ Hz.

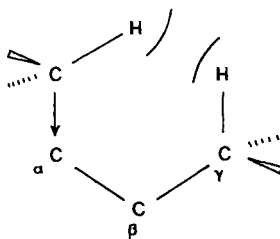
²⁾ This is the case for the nitrogen carbon bond in *N*-methylpiperidine (see [18]).

one bond coupling to the ethylene carbon atoms = 160.8 Hz) seems more in keeping with our other measurements. The latter compound is interesting as well since it also clearly demonstrates the suggested dependence of $^3J(\text{Pt}, \text{C})$ with $^3J(\text{Pt}, \text{CH}_3)$ for the *gauche* methyl group much smaller than $^3J(\text{Pt}, \text{CH}_2)$ for the *trans* methylene.

Given the existence of a dependence of $^3J(\text{Pt}, \text{C})$ on dihedral angle and the X-ray structure determination for the (*S,S*)-diastereomer IV, our ^{13}C -coupling constant data for the diastereomers IV and V are readily understood. In the (*S,S*)-isomer the CH_3 group on the carbon is *cis* (*gauche*) to platinum and therefore shows a small value for $^3J(\text{Pt}, \text{C})$ (<5 Hz). In the (*S,R*)-isomers this CH_3 is *trans* to platinum and therefore shows a larger vicinal coupling (25.7 Hz). There are relatively few values of $^3J(\text{PtNCC})$ in the literature; however, we and others [3] have found $^3J(\text{Pt}, \text{C})$ in pyridine complexes to be ~ 34 – 37 Hz. Values of the order of 20–50 Hz have also been found [17] in some ethylene diamine complexes. Thus it would seem that the observed values of $^3J(\text{Pt}, \text{C})$ are within the expected boundaries for this coupling.

From the data in Table 1 it may be seen that the two-bond coupling to C_D , $^2J(\text{Pt}, \text{C}_D)$, varies from 8.8 to 16.2 Hz. Interesting here is that this coupling seems to decrease somewhat with increasing substitution of C_D ; however, within the *N*-methyl derivatives the variation for $^2J(\text{Pt}, \text{CH}_3_A)$ is smaller (14.7–19.1 Hz). We note the significant difference in $^2J(\text{Pt}, \text{C}_D)$ between the diastereomers 9a and 9b but have no explanation for this change at this time.

3.3. ^{13}C -NMR. *parameters of the coordinated amines. Chemical shifts.* A structure such as VI implies the presence of a marked ^{13}C - γ -methylsubstituent effect [19] between CH_3_A and CH_3_C . The γ -effect (the effect at C_γ of substituting a methyl group at C_α) which is thought to be steric in origin [20], produces an upfield shift of



(VII)

between ≈ 2.5 – 5.0 ppm when the two carbon atoms are *cis* or *gauche* to each other (see VII). That this is the case for the *N*-methylisopropylamine complex is shown by the upfield shift of 3.4 ppm of CH_3_A , relative to the HNMeEt analog, and the 3,4 ppm difference between CH_3_B and CH_3_C with the latter at higher field. If indeed the lower frequency methyl resonance in this complex is CH_3_C this resonance should show the larger coupling to platinum (see VI), and this is in fact observed. If this type of chemical shift correlation is valid we should expect to find both methyl groups in the (*S,R*)-diastereomer V at higher field than their counterparts in the (*S,S*)-diastereomer and this is the case [$\delta \text{NCH}_3(\text{S,S}) - \delta \text{NCH}_3(\text{S,R})$]

= 1.5 ppm; $\delta\text{CH}_3(S,S) - \delta\text{CH}_3(S,R) = 5.3$ ppm]. It would seem that the ^{13}C -chemical shift information nicely complements the coupling constant data.

In discussing the chemical shifts of nuclei within a coordinated ligand it is customary to consider the coordination chemical shift, $\Delta\delta$, ($\delta\text{complex} - \delta\text{free ligand}$). For the carbon atoms directly attached to the nitrogen atom the $\Delta\delta$ values in our complexes range from +2.3 to 5.9 ppm. We find no correlation of these values with any of our other NMR. data, due perhaps to the varying degree of interaction of the free ligands with CDCl_3 .

4. ^{195}Pt Chemical Shifts. - The ^{195}Pt -chemical shifts, shown in *Table 2*, may be seen to fall 2953 to 3087 ppm upfield from Na_2PtCl_6 . These values are in the same region as that reported previously for some *cis*- and *trans*-2-butene complexes of platinum [9]. Although the literature [21] pertaining to ^{195}Pt -NMR. has grown since the first reports [21a, b] for this nucleus there is still no definitive theory governing the interpretation of platinum chemical shifts. All authors agree that σ_p , the paramagnetic screening contribution to the total screening, σ_t , is dominant for this nucleus. Attempts [21a] have been made to correlate the ΔE term in σ_p to band shifts observed in the VIS./UV. spectra of some arsine and phosphine derivatives with some success. There seems also to be some correlation of $\delta^{195}\text{Pt}$ with the ligand field strength of the donor but no inviolate rules are obvious here either. A general tendency for a shift to higher field (lower frequency) has been observed [22] in the complexes *trans*- $\text{PtCl}_2(\text{NH}_2(\text{CH}_2)_5\text{CH}_3)\text{X}$ where $\text{X} = \text{Cl}^-$, amine, olefin, arsine, phosphine ($\text{P} > \text{As} > \text{olefin} > \text{N}$) when X is replaced by a stronger donor.

A similar effect has been reported for a series of *cis*- and *trans*- PtX_2L_2 complexes [21g]. It is clear, however, that substitution of ligand A for ligand B often produces a change of hundreds if not thousands of ppm in $\delta^{195}\text{Pt}$. Solvent and temperature effects may also amount to tens of ppm [10]. Thus our observed changes in $\delta^{195}\text{Pt}$ are, at best, moderate in size.

A comparison of the primary and secondary amine complexes shows that $\delta^{195}\text{Pt}$ for the latter are shifted upfield relative to the former by some 17-41 ppm (compare MeNH_2 (-3040 ppm) with Me_2NH (-3074 ppm) and EtNH_2 (-3020 ppm) with EtMeNH (-3049 ppm)). Most notable is the resonance position (-3087 ppm) of the piperidine derivative. Its relatively high field position is in keeping with our suggestion, based on the ^{13}C -NMR. data, that this amine is not directly comparable with the other secondary amines in this study. Of interest is that both the ^{13}C - and

Table 2. ^{195}Pt -Chemical Shifts for the Complexes *trans*- $\text{PtCl}_2(\text{CH}_2=\text{CH}_2)(\text{amine})$

Amine	$\delta^{195}\text{Pt}^a$ (ppm)	Amine	$\delta^{195}\text{Pt}^a$ (ppm)	Amine	$\delta^{195}\text{Pt}^a$ (ppm)
MeNH_2	-3040	$\text{PhCH}(t\text{-bu})\text{NH}_2$	-2990	(<i>S</i>)- $\text{PhCH}(\text{CH}_3)\text{MeNH}$	
EtNH_2	-3020	Me_2NH	-3074	<i>S, S</i>	-3045
<i>i</i> - PrNH_2	-3008	EtMeNH	-3049	<i>S, R</i>	-2996
PhCH_2NH_2	-3030	<i>i</i> - PrMeNH	-3030	Piperidine	-3087
$\text{PhCH}(\text{CH}_3)\text{NH}_2$	-3016	PhCH_2MeNH	-3047	2,6-Me ₂ -Piperidine	-2953

^a) To high field of Na_2PtCl_6 ; see experimental part for further details.

^{195}Pt -NMR. data point to a stronger Pt,N-interaction for piperidine than for the other amines.

We are not certain as to the exact source of the change in $\delta^{195}\text{Pt}$ when the amine is varied; however it seems to us that non-bonded interactions can result in a low field shift of the ^{195}Pt resonance based on the following observations: a) in the series Me, Et, *i*-Pr, $\delta^{195}\text{Pt}$ shifts progressively to lower field for both classes of amine; b) when the aliphatic carbon atom of benzylamine is substituted, shifts to lower field are found ($\text{PhCH}_2\text{NH}_2 = -3030$, $\text{PhCH}(\text{CH}_3)\text{NH}_2 = -3016$, $\text{PhCH}(t\text{-Bu})\text{NH}_2 = -2990$ ppm respectively); c) methyl substitution at the 2- and 6-positions of piperidine results in a 134 ppm downfield shift of $\delta^{195}\text{Pt}$ relative to the unsubstituted complex.

Given that, within a set of primary or secondary amine derivatives, steric effects may result in downfield shifts of the ^{195}Pt -resonance of >40 ppm ($\text{Me}_2\text{NH} = -3074$ ppm, *i*-PrMeNH = -3030 ppm) then the observed difference in the ^{195}Pt -resonance positions for the (*S,S*)- and (*R,S*)-diastereomers IV and V of 51 ppm can be rationalized.

We know from previous X-ray work [8] and confirm through our ^{13}C -NMR. data, that the (*S,S*)-isomer exists as IV. In this conformation the phenyl group and platinum are *trans* to one another and we see that the (*S,S*)-diastereomer has a $\delta^{195}\text{Pt}$ value similar to that for the *N*-methyl-benzylamine and *N*-methylisopropylamine analogs. In the (*S,R*)-situation the two 'groups' are *cis*³⁾ thus bringing the larger phenyl group closer to the metal and its remaining ligands with a resulting deshielding effect on the platinum shift. We cannot say, at this time, whether these repulsive interactions occur between the substituent on the amine and the halogen atoms, or between the amine substituents and electron density located above or below the plane defined by the two halides, metal and nitrogen atoms; however, the difference in $\delta^{195}\text{Pt}$ between the diastereomers is sufficiently large to make us think that there is a significant perturbation in the electron density around the metal in the (*S,R*)-isomer relative to the (*S,S*)-complex.

We conclude that both ^{13}C - and ^{195}Pt -NMR. can provide useful information concerned with the solution structure of molecules such as I and that, in particular, subtle conformational and bonding differences for the diastereomers of *trans*-dichloro[(*S*)-*N*-methyl-*a*-methylbenzylamine] (ethylene)platinum (II) are measurable using a combination of these NMR. methods.

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³⁾ The conformation shown as V is likely to be the most populated; however, the remaining conformers may well contribute to a lesser extent.

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