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NUCLEAR MAGNETIC RESONANCE STUDIES OF *trans*-DICHLORO-(PYRIDINE) (OLEFIN)PLATINUM(II) COMPLEXES

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SUMMARY

The NMR spectra of *trans*-dichloro(pyridine)(olefin)platinum(II) complexes olefin = CH_2=CHR with R = CH_3, $CH(CH_3)_2$, $C(CH_3)_3$) have been recorded and analyzed to give informations about the positions of the ethylenic and aliphatic protons with respect to the platinum.

INTRODUCTION

NMR has been widely used with platinum(II)–olefin complexes to give information about the nature of metal–olefin bond and about stereochemistry[1]. In particular, for asymmetrically substituted ethylene complexes both the chemical shifts and protons coupling constants have been correlated with the distance of the ethylenic protons from the platinum[2-4]. Such analysis has been carried out only for a few α-olefins, however[3,5], and, furthermore, the correlations mentioned above have been criticized[5]. With the aim of making a detailed examination of the relation between NMR parameters and steric disposition of the ethylenic ligand, we have analyzed the NMR spectra of a series of *trans*-dichloro(pyridine)(olefin)platinum(II) complexes (olefin = CH_2=CHR with R = CH_3, $CH(CH_3)_2$, $C(CH_3)_3$), the data for which are listed in Table 1 as (I), (II) and (III), respectively.

EXPERIMENTAL

The complexes (I), (II) and (III) were prepared by treating *trans*-dichloro(pyridine) (ethylene)platinum(II) with the appropriate olefins. All gave satisfactory analyses; the melting points were 79–81° for (I), 114–118° for (II) and 102–106° for III).

The NMR spectra were obtained with a JEOL C-60 HL spectrometer operating at 60 MHz using $CDCl_3$ as solvent with TMS as internal reference. To clarify the aliphatic protons part of the spectrum, the complex (II) was also examinated with a

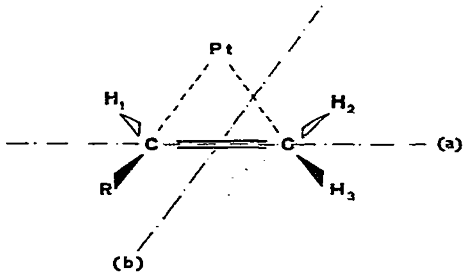


Fig. 1.

Varian 220 MHz spectrometer. The ethylenic protons show spectra of $ABCX_n$ type, with ^{195}Pt satellites, [where n is in our case 3 for (I), 1 for (II) and zero for (III)]. Analysis of the spectra was carried out using a 7090 IBM computer, the protons being numbered as in Fig. 1.

The NMR parameters obtained in the analysis are listed in Table 1, and the observed spectrum of the ethylenic protons of (III) together with the calculated spectrum, is shown as an example in Fig. 2. The accuracy of the analysis, given by the root mean square error (RMSE) in Table 1, is lowered by line broadening due to kinetic phenomena already suggested for this kind of complexes[2,6]. It is apparent from Table 1 that the accuracy increases with the molecular weight of the ethylenic ligand.

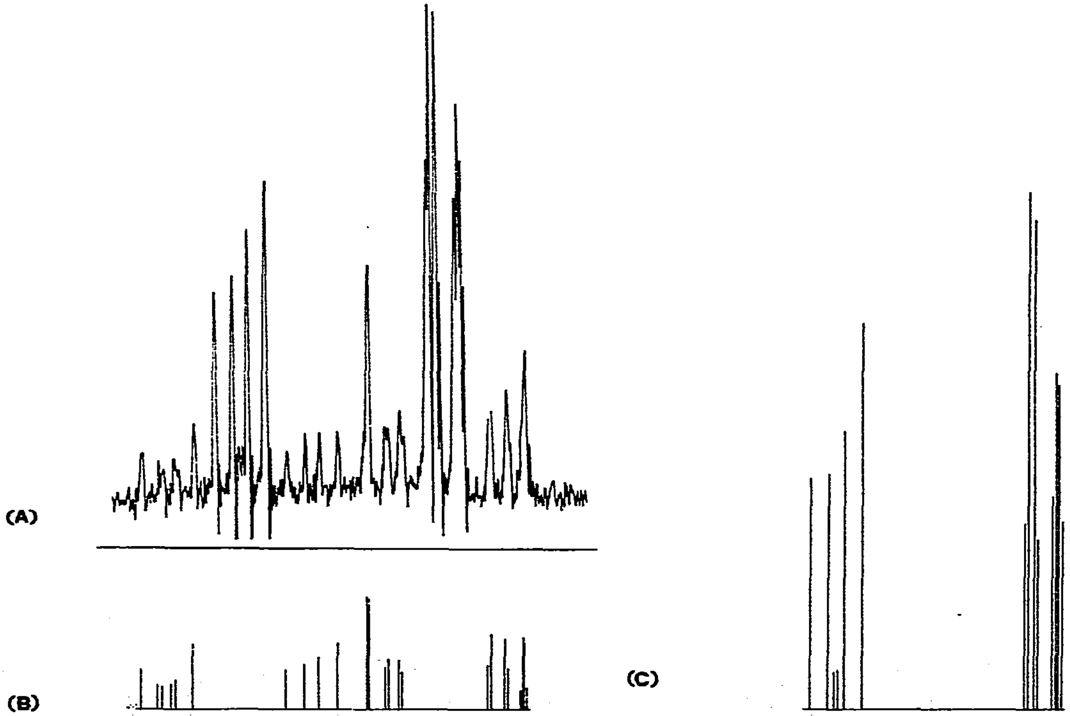
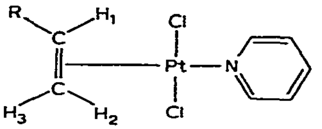
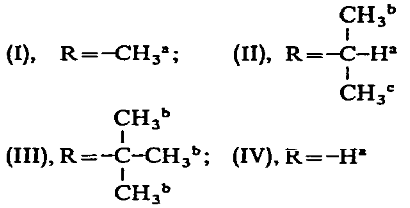


Fig. 2. (A) Ethylenic protons resonance in 60 MHz NMR spectrum of (III). (B) Computer simulated spectrum of complexes with ^{195}Pt. (C) Computer simulated spectrum of complexes with Pt without spin.

TABLE 1a

PROTON CHEMICAL SHIFTS OF OLEFIN PLATINUM COMPLEXES AND OF THE CORRESPONDING FREE OLEFINS




(I), $R=-CH_3^a$; (II), $R=-\overset{CH_3^b}{\underset{CH_3^c}{C}}-H^a$

(III), $R=-\overset{CH_3^b}{\underset{CH_3^b}{C}}-CH_3^b$; (IV), $R=-H^a$

Complex or olefin	RMSE[a] (Hz)	Chemical shifts (Hz)[b]						$\Delta\nu_i$[c] (Hz)		
		H_1	H_2	H_3	H_a	H_b	H_c	H_1	H_2	H_3
(I)	0.3	347.9	287.2	284.8	116.4			−4.1	5.7	13.4
Olefin		343.8	292.8	298.2	103.2					
(II)	0.3	334.3	286.2	281.0	150	70.8	94.8	5.8	3.9	9.9
Olefin		340.2	286.2	291.0	136	60.6	60.6			
(III)	0.1	372.7	280.0	281.1		84.0		−23.6	9	14.5
Olefin		349.1	289.8	295.7		60.0				
(IV)		288	288	288	288			30	30	30
Olefin		318	318	318	318					

[a] Root mean square error. [b] Downfield from TMS internal at 60 MHz. [c] $\Delta\nu_i=\nu H_i$ (olefin)−νH_i (complex).

TABLE 1b

H–H AND Pt–H COUPLING CONSTANTS IN OLEFIN–PLATINUM COMPLEXES AND IN THE CORRESPONDING FREE OLEFINS

Complex or olefin	Coupling constants (Hz)							
	$J(H_1\text{-}H_2)$	$J(H_1\text{-}H_3)$	$J(H_2\text{-}H_3)$	$J(H_1\text{-}H_a)$	$J(Pt\text{-}H_1)$	$J(Pt\text{-}H_2)$	$J(Pt\text{-}H_3)$	$J(Pt\text{-}H_a)$
(I)	7.6	14.2	6.0	1.3	66.0[a]	66.7[a]	58.4[a]	36.5[a]
Olefin	10.2	16.8	6.4	2.0				
(II)[b]	8.2	13.9	9.7	1.6	64.6[a]	63.6[a]	58.3[a]	
Olefin	10.4	17.3	6.5	1.6				
(III)	8.5	14.8		1.3	65.5[c]	62.1[c]	55.1[c]	
Olefin	10.9	16.6		1.2				
(IV)					60	60	60	60

[a] RMSE (root mean square error) 0.4 Hz. [b] $J(Pt\text{-}H_b)$ 6.2 Hz. [c] RMSE 0.3 Hz.

Obviously a lower accuracy is obtained for the platinum satellites.

The relative signs of the coupling constants between ethylenic protons were unambiguously obtained by an intensity comparison between observed and calculated spectra. Furthermore, by the spin tickling technique we have found that the relative sign of $J(H_1\text{-}H_a)$, not obtainable by intensity comparison, is the same as that of the ethylenic protons.

In Table 1 are listed also the NMR parameters for the free olefins, together with the differences $\Delta\nu_i$ between the chemical shifts of the ethylenic protons in the free olefin and in the complex.

DISCUSSION

(*a*). *Chemical shifts*

With complexes of the type examined it has generally been found that the ethylenic protons show an upfield shift with respect to the free olefin. This behaviour was observed in our case also, with two remarkable exceptions, indicated in Table 1. The upfield shifts have been interpreted by some authors[7] as a consequence of some rehybridization of the ethylenic carbon atoms from sp^2 towards sp^3 and a concomitant increased shielding of the ethylenic protons on complexing. In the case of Zeise's salt-homologues the differences $\Delta\nu_i$ were correlated, with the proton–platinum distance[3]. In particular, in the case of non symmetrical α-olefins, it was inferred that the CH_2 groups are positioned closer to the platinum atom than CHR, with a rotation of the ligand about the "*b*" axis of Fig. 1. Moreover, since $\Delta\nu_2$ is greater than $\Delta\nu_3$ it was suggested that the olefin is rotated about the "*a*" axis of Fig. 1 in such a way as to keep R away from the bulk of the complex[3]. Our data seem quite different however. First, the upfield shift is smaller in our case, and varies in no regular way with the ligand size, and even if $\Delta\nu_1$ is smaller than $\Delta\nu_2$ and $\Delta\nu_3$, $\Delta\nu_3$ is always greater than $\Delta\nu_2$. It is probable that if the ligand is rotated to reach a minimum value in sterical interaction then proton 2 will become closer to platinum than proton 3, and so it is quite difficult in our case to accept a simple relation between $\Delta\nu_i$ and the distance from platinum.

Moreover, comparison of our data with those of Fritz and coworkers[3] seems to indicate a strong dependence of $\Delta\nu_i$ on the nature of the ligand in *trans* position to the olefin.

(*b*). *Coupling constants*

The difficulty of correlating NMR parameters with the distance from platinum in such complexes has been well discussed[5]. In our case, however, it seems that coupling constants are more useful for deducing stereochemistry; several authors[3,4,8] have observed in many kinds of platinum α-olefin complexes that the magnitude of J(Pt–H) increases with decreasing Pt–H distance.

From Table 1 we can see that $J(\text{Pt–H}_3)$ is always smaller than $J(\text{Pt–H}_2)$ by about the same amount: however it is noteworthy that for (I) $J(\text{Pt–H}_1)$ is close to, and for (II) and (III) greater, than $J(\text{Pt–H}_2)$. Thus, while our data seem to indicate the rotation of the olefinic moieties about "*a*" axis of Fig. 1, they do not confirm the existence of the other type of rotation about "*b*" axis. This leads us either to reject a simple distance–coupling relation or to admit the possibility of another sterical position of the ethylenic ligand. We merely observe that a different rotation of the CH_2 and CHR groups about the "*a*" axis (see Fig. 3) is possible to some extent, so that R moves away from the bulk of the complex with a concurrent approach of H_1 to the platinum. Such distortion would be consistent not only with the coupling data in Table 1 but also with some proton–platinum couplings for the Zeise's salt homologues [for instance $J(\text{Pt–H}_1)$ in the styrene complexes of ref. 5]; moreover it is noteworthy (Table 1), that $J(\text{Pt–H}_1)$ increases regularly with the size of R. Also in agreement with the assumed correlation, we note that the mean value of the three ethylenic proton platinum couplings for each complex decreases when R becomes larger, for it is likely that the whole ligand will move more and more away from the bulk of the complex

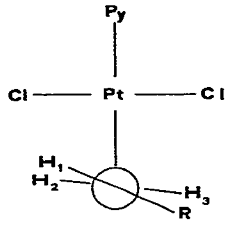


Fig. 3.

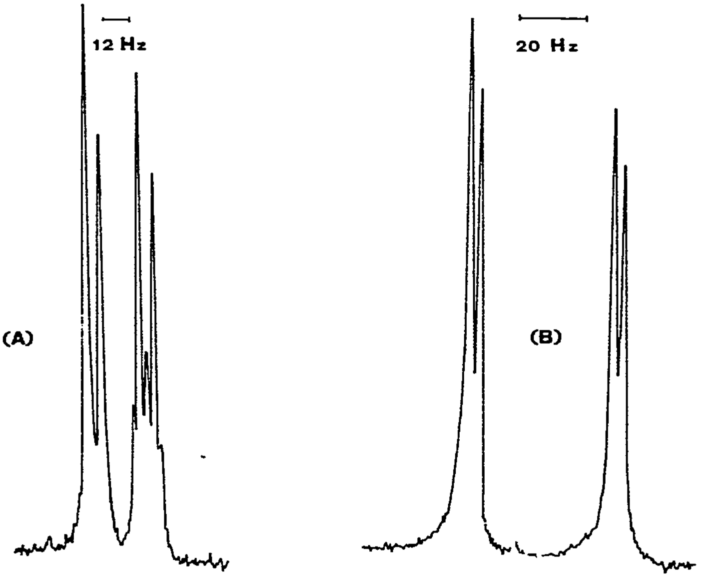


Fig. 4. Methyl resonance in 60 MHz (A) and 220 MHz (B) NMR spectrum of (III).

with increasing size of R.

Mention should be made of the proton–proton ethylenic couplings: the *cis* and *trans* coupling constants $J(H_1{-}H_2)$ and $J(H_1{-}H_3)$ show a decrease with respect to the free olefin, as is usual in such platinum complexes, and in agreement with the proposed electronic structure for the olefinic ligand in the complex[7]. Although the variations in $J(H_2{-}H_3)$ appear very interesting, the few available data do not permit detailed interpretations. The high value of $J(H_1{-}H_a)$ in (II) is noteworthy and indicates that H_4 is in a special sterical position in (II) namely, almost *anti* with respect to H_1.

(*c*) *The spectra of the non-ethylenic protons*

The protons attached to saturated carbon atoms behave in the opposite way to the ethylenic protons, showing on complexing a downfield shift, which cannot be easily explained. This region of spectrum is especially interesting for (II), since it shows a peak doubling for the two methyl groups (CH_3^b and CH_3^c, in consistence with the fact that they become non-equivalent in the coordinated olefin[9]). Moreover, the upfield methyl protons appear to be coupled to the platinum, as shown in Fig. 4. The existence of a coupling to the platinum is clearly supported by the 220 MHz spectrum.

If one accepts that the coupling of platinum with such methyl protons increases with increasing distance[8], the highfield methyl protons would have to be the farther from the platinum. On such a hypothesis, the methyl near the platinum would be the less shielded. This non-equivalence of the saturated groups of protons of α-olefins in platinum complexes and its structural implications will be discussed in a subsequent paper.

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