

CONFORMATION OF THE OLEFINIC LIGAND IN *trans*-DICHLORO-(AMINE)(OLEFIN)PLATINUM(II) COMPLEXES

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SUMMARY

The NMR parameters for the alkyl protons of some aliphatic α -olefins are compared with those for the corresponding *trans*-dichloro(amine)(olefin)platinum(II) complexes. In general a downfield shift of the resonances of the alkyl protons bound to the saturated carbon atoms is observed on going from the free α -olefin to the complex. The extent of the downfield shifts can be related to the distance between the alkyl protons and the platinum atom. These effects can be interpreted by assuming that some of the allowed conformations of the complexed olefin greatly predominate because of steric interactions between an alkyl group and a platinum atom.

INTRODUCTION

Although a large number of *cis*- and *trans*-dichloro(amine)(α -olefin)platinum(II) complexes have been prepared^{1,2}, very little is known about the conformational equilibria of the saturated hydrocarbon chain of the complexed α -olefin. The only relevant data are the results of X-ray analysis of some complexes^{3,4} and some preliminary NMR results on *trans*-dichloro(benzylamine)[(*S*)-3-methyl-1-pentene]-platinum(II)^{5,6}. In the course of our investigation of asymmetric induction in square planar Pt^{II} complexes^{4,5}, we prepared a number of complexes containing aliphatic α -olefins having 4 to 7 carbon atoms (see Table 1) and we discuss below some aspects of the conformational analysis of the olefinic ligands in *trans*-dichloro(amine)(olefin)-platinum(II) complexes which may be relevant to the understanding of the stereochemistry of such complexes.

EXPERIMENTAL

Olefins

Propene and 1-butene (Matheson Co.; 99% pure) were used without further purification. 3-Methyl-1-butene, 4-methyl-1-pentene, 3,3-dimethyl-1-butene and 4,4-dimethyl-1-pentene, (Fluka A.G.; 99% pure) were used after distillation over metallic

sodium. (+)(*S*)-3-methyl-1-pentene ($[\alpha]_D^{25} + 35.2^\circ$; optical purity 94%) was prepared by pyrolysis of the (+)(*S*)-3-methylpentyl acetate⁷, and purified by fractionation from metallic sodium.

trans-Dichloro(pyridine)(olefin)platinum(II) complexes

The ethylene complex, (I), was prepared from Zeise's salt², and used for the preparation of the complexes listed in Table 1 by replacement of the ethylene by the appropriate olefin in CHCl_3 ¹. In the case of (III), the solution was refluxed for 2 days in order to complete displacement of the ethylene.

The complexes were obtained by removal of the solvent *in vacuo* as microcrystalline solids or as oils which crystallized on standing. All were purified by crystallization. Crystallization solvents, melting points, and elementary analyses are shown in Table 1.

TABLE 1

PROPERTIES OF THE *trans*-DICHLORO(PYRIDINE)(OLEFIN)PLATINUM(II) COMPLEXES

Complex	Olefin	Solvent used for crystallization	M.p. (°C)	Element analysis found (calcd.) (%)	
				C	H
(II)	$\text{CH}_2=\text{CH}-\text{CH}_3$	Benzene/pentane (1/1)	79-81	25.08 (24.81)	2.83 (2.86)
(III)	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$	Benzene/pentane (1/1)	108-111	26.98 (26.93)	3.20 (3.26)
(VI)	$\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)_2$	CH_2Cl_2 /pentane (1/2)	116-119	29.03 (28.91)	3.59 (3.64)
(VII)	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}(\text{CH}_3)_2$	CH_2Cl_2 /pentane (1/2)	62-65	31.08 (30.77)	3.98 (3.99)
(IV)	$\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)_3$	Benzene/pentane (1/1)	103-106	30.99 (30.77)	3.93 (3.99)
(V)	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}(\text{CH}_3)_3$	Benzene/pentane (1/1)	123-126	32.42 (32.48)	4.22 (4.20)
(VIII)	$\text{CH}_2=\text{CH}-\overset{\text{(S)}}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2-\text{CH}_3$	Benzene/pentane (1/2)	111-113	30.86 (30.77)	4.04 (3.99)

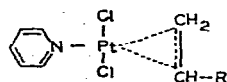
The crystallized complex (VIII) had $[\alpha]_D^{25} - 200^\circ$ (*c* 0.2 g/100 ml; acetone) a few minutes after dissolution, but the optical activity decreased with time, reaching a constant value $[\alpha]_D^{25} - 57^\circ$ in one day.

NMR spectra

NMR spectra were recorded at 20° in CDCl_3 , with TMS as internal standard, on a Jeol C-60 HL or a 220 MHz Varian spectrometer.

In Table 2 NMR data are reported for the protons bound to the saturated carbon atoms of the olefin in the complexes (II) to (VII). Table 3 shows NMR data for the diastereoisomers of the *trans*-dichloro(amine)[(*S*)-3-methyl-1-pentene]-

TABLE 2

CHEMICAL SHIFTS^{a,b} OF THE PROTONS OF THE ALKYL GROUP OF THE OLEFIN NON COMPLEXED AND COMPLEXED TO THE Pt^{II} IN trans-DICHLORO(PYRIDINE)(OLEFIN)PLATINUM(II) COMPLEXES

Complex	Olefin used	Chemical shift (ppm) of the protons of the non complexed olefin δ	Chemical shift of the protons of the complexed olefin δ'	$\delta' - \delta$	$\delta'_2 - \delta'_1$
Methyl					
(II)	CH ₂ =CH-CH ₃	1.72	1.94	0.22	
(III)	CH ₂ =CH-CH ₂ -CH ₃	1.00	1.35	0.35	
(IV)	CH ₂ =CH-C(CH ₃) ₃	1.00	1.40	0.40	
(V)	CH ₂ =CH-CH ₂ -C(CH ₃) ₃	0.90	1.02	0.12	
(VI)	CH ₂ =CH-CH- CH ₃ (1) CH ₃ (2)	1.01	1.18	0.17	0.40
(VII)	CH ₂ =CH-CH ₂ -CH- CH ₃ (1) CH ₃ (2)	0.91	1.04	0.13	0.04
(VIII)	CH ₂ =CH-CH ₂ -CH ₃	1.00	1.02	0.02	
Methylene					
(III)	CH ₂ =CH- H(3) C-CH ₃	1.97	1.95 2.37	-0.02 0.40	0.42
(VII)	CH ₂ =CH- H(3') H(3) C-CH(CH ₃) ₂	1.97	2.03 2.43	0.06 0.46	0.40
(V) ^c	CH ₂ =CH- H(3') H(3) C-C(CH ₃) ₃ (2) H(3')	1.94	2.02 2.52	0.08 0.58	0.50
Methyldiyne					
(VI) ^d	CH ₂ =CH-CH(CH ₃) ₂	2.30	2.50	0.20	
(VII)	CH ₂ =CH-CH ₂ -CH(CH ₃) ₂	1.50	1.76	0.26	

^a In CDCl₃ at 20°; standard TMS. ^b Chemical shift and coupling constants of the methynic and methylenic protons from the spectra at 220 MHz. ^c $J_{2-3} = 4$; $J_{2-3} = 11$; $J_{3-3} = 14$ Hz. ^d $J_{2-3} = 9.7$ Hz (see ref. 11).

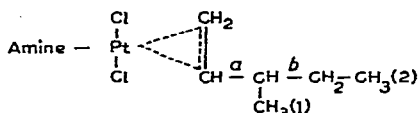
platinum(II) complexes in which the amine is pyridine [(VIIIa) and (VIIIb)] or benzylamine⁵ [(IXa) and (IXb)].

RESULTS AND DISCUSSION

Only a few NMR results have been previously reported for the methyl protons of the propene, 2-butenes and 3,3-dimethyl-1-buteneplatinum complexes; downfield or upfield displacements have been observed depending on the nature of the non-olefinic ligands bound to the platinum atom^{1,10,11}. In the *trans*-dichloro(amine)(olefin)-

TABLE 3

CHEMICAL SHIFTS^a OF THE METHYL PROTONS OF THE (*S*)-3-METHYL-1-PENTENE NON COMPLEXED AND COMPLEXED TO Pt^{II} IN THE (2*R*,3*S*) AND (2*S*,3*S*) DIASTEREOMERS



Chemical shifts δ (ppm) of the methyl protons of the non complexed olefin		Amine used	Complex	Diastereo- isomer	Chemical shifts δ' (ppm) of the methyl protons of the complexed olefin	
CH ₃ (1)	CH ₃ (2)				CH ₃ (1)	CH ₃ (2)
0.98	0.86	C ₅ H ₅ N	(VIII A)	(2 <i>R</i> ,3 <i>S</i>)	1.58	0.92
			(VIII B)	(2 <i>S</i> ,3 <i>S</i>)	1.16	1.12
0.98	0.86	C ₆ H ₅ CH ₂ NH ₂	(IX A)	(2 <i>R</i> ,3 <i>S</i>)	1.46	0.87
			(IX B)	(2 <i>S</i> ,3 <i>S</i>)	1.05	1.07
$\delta'_1 - \delta_1$	$\delta'_2 - \delta_2$	$\delta'_{1R,S} - \delta'_{1S,S}$	$\delta'_{2S,S} - \delta'_{2R,S}$			
0.60	0.06	0.42	0.20			
0.18	0.26					
0.48	0.01	0.41	0.20			
0.07	0.21					

^a All spectra were measured in CDCl₃ (20°) at 220 MHz; the internal reference is TMS.

platinum(II) complexes in which the amine is pyridine or benzylamine, we have observed a downfield shift of the signals of all the alkyl protons with respect to the corresponding signals in the non-complexed α -olefin (Tables 2 and 3).

In the case of the 2*R*,3*S* diastereoisomer of *trans*-dichloro(benzylamine)[(*S*)-3-methyl-1-pentene]platinum(II) complex (IXa), the conformation of the olefin in the crystalline state has been determined by X-ray analysis⁴ [Fig. 1A; (I)-(II)]. The NMR data for the pure 2*R*,3*S* diastereoisomer (Fig. 2A, Table 3) show that the CH₃(1) resonance (a doublet) is shifted much further downfield with respect to the free olefin than is the CH₃(2) (a triplet).

If the internal rotation angle around the bond " " in solution is assumed to be similar to that observed in the crystal, CH₃(1) is closer to the platinum atom than is CH₃(2) in the two allowed conformations⁸ (II) and (III) (Fig. 1A); thus the downfield shift of the CH₃ signals may be correlated with the relative distances of these CH₃ groups from the platinum atom.

It is not easy to decide whether (II) or (III) (Fig. 1A) is more favoured in solution. Because of the rather strong interaction between CH₃(1) and CH₃(2) in (III) compared to that between CH₃(2) and CH(2) in (II), the latter is probably preferred in solution, as in the solid. This is confirmed by the NMR data for the 2*S*,3*S* diastereo-

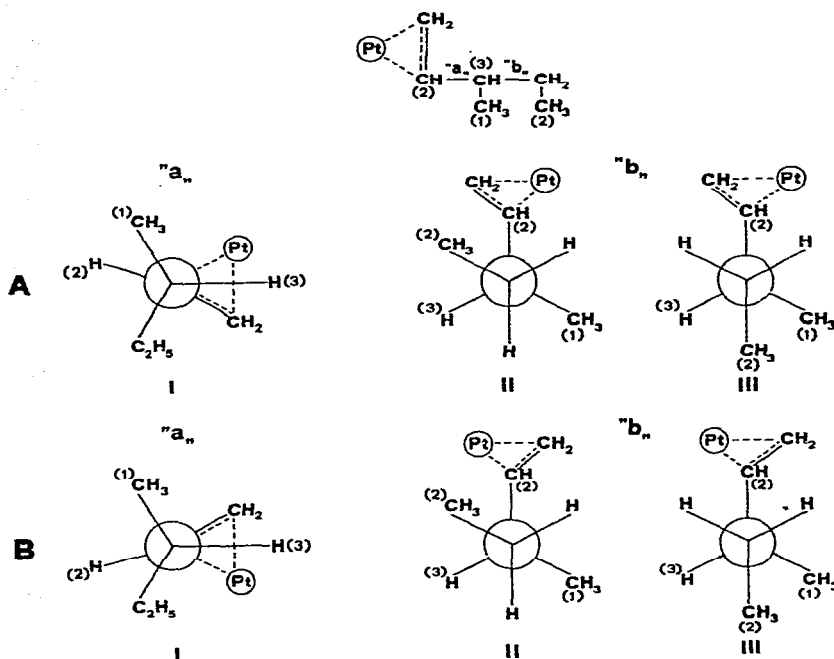


Fig. 1. Conformational analysis of the olefinic ligand: A, in the *trans*-dichloro(benzylamine)[(2*R*,3*S*)-3-methyl-1-pentene]platinum(II) complex (IX_A); B, in the *trans*-dichloro(benzylamine)[2*S*,3*S*]-3-methyl-1-pentene]platinum(II) complex (IX_B).

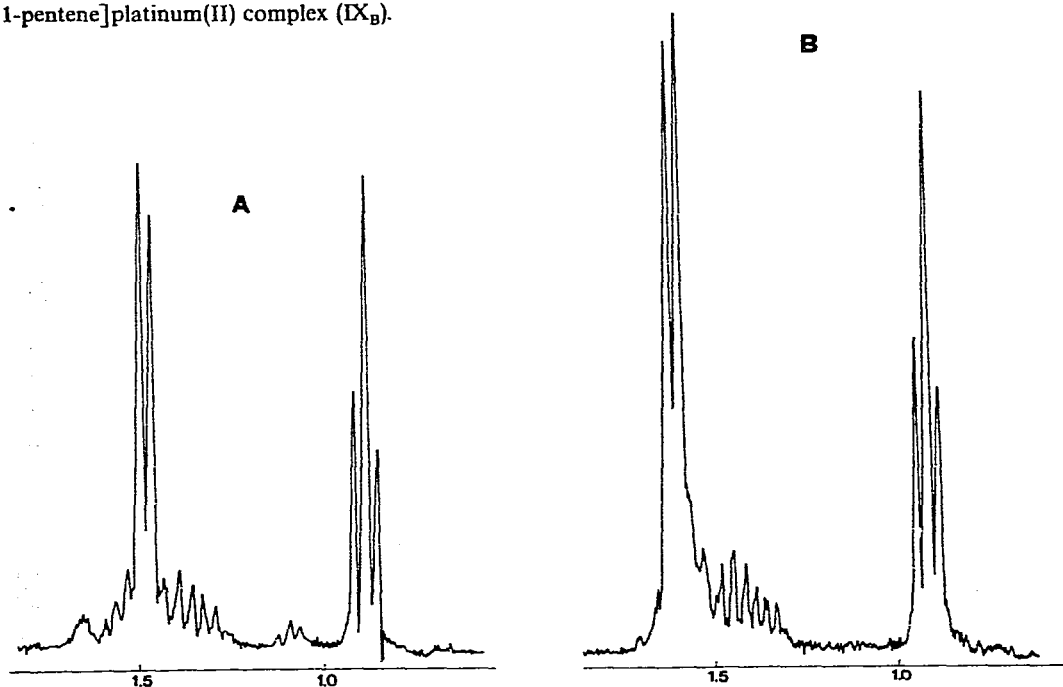


Fig. 2. Methyl resonance in the 220 MHz NMR spectra of the: A, *trans*-dichloro(benzylamine)[2*R*,3*S*]-3-methyl-1-pentene]platinum(II) (IX_A); B, *trans*-dichloro(pyridine)[(2*R*,3*S*)-3-methyl-1-pentene]platinum(II) (VIII_A).

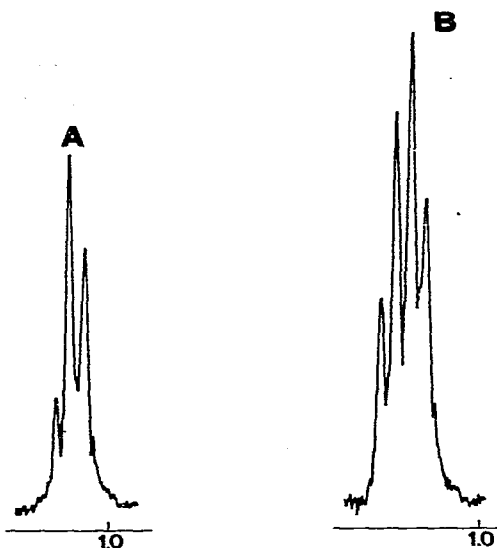


Fig. 3. Methyl resonance in the 220 MHz NMR spectra of the: A, *trans*-dichloro(benzylamine)[(2*S*,3*S*)-3-methyl-1-pentene]platinum(II) (IX_B); B, *trans*-dichloro(pyridine)[(2*S*,3*S*)-3-methyl-1-pentene]platinum(II) (VIII_B).

isomer (Fig. 3A, Table 3); in this case the downfield shift with respect to the free olefin is larger for CH₃(2) than for CH₃(1). In agreement, the conformational analysis shows that if H(2) and H(3) are in a "quasi" *anti*-position, as in the case of the 2*R*,3*S* diastereoisomer, then, at least in (II) (Fig. 1B) the CH₃(2) is closer than CH₃(1) to the Pt atom.

The NMR data show that the situation is closely similar for CH₃(1) and CH₃(2) in the corresponding pyridine complex, there being only a slight change in the $\Delta\delta$ with respect to the free olefin (Table 3, Fig. 2B, and 3B). Therefore, it is reasonable to assume that similar conformational equilibria for the olefinic ligand exist in the benzylamine and pyridine complexes.

The large difference between the chemical shift of the two diastereotopic methyl groups in the 3-methyl-1-butene racemic complex (VI) (Table 2) is very similar to that found between the two CH₃(1) groups in the diastereoisomeric complexes (VIIIa) and (VIIIb), and (IXa) and (IXb) (Table 3). This seems to indicate that the conformational situation around the bond "a" (Fig. 4) is similar in the 3-methyl-1¹ butene and in the 3-methyl-1-pentene complexes. In the former compound the relative positions of the two diastereoisotopic methyl groups with respect to the Pt atom appear to be very different (Fig. 4), and thus the chemical shift difference can be interpreted as for the (*S*)-3-methyl-1-pentene complexes.

A large preference for the conformations (I)_(*S*) and (I)_(*R*) of the two enantiomers (Fig. 4) is indicated also by the fact that the coupling constant between H(2) and H(3) is about 9.7 Hz, not far from the maximum value predicted for an *anti* position of the two protons in aliphatic compounds¹². The corresponding coupling constant in the free olefin is 6.5 Hz, indicating a much larger contribution of the conformations in which the two corresponding protons are in a *syn*-position. As expected from the above assumptions CH₃(1), being the farther from the Pt in (I)_(*S*), shows the lower

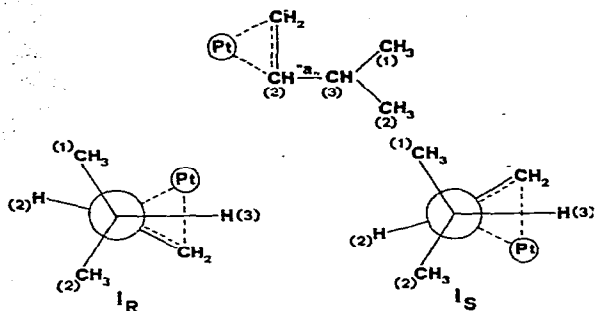


Fig. 4. Preferred conformation of the *trans*-dichloro(pyridine)(3-methyl-1-butene)platinum(II) complex (VI) for the *R* and *S* antipodes.

$\Delta\delta$ and is coupled to ^{195}Pt , as is usual in the case of diastereotopic groups¹¹. On the other hand $\text{CH}_3(2)$, which is nearer to Pt in $(\text{I})_{\text{S}}$, shows the higher $\Delta\delta$ and is apparently not coupled to ^{195}Pt .

The analysis of the NMR spectra of the two methylene hydrogens in the α -position with respect to the double bond in the complexes of 1-butene, 4-methyl-1-pentene and 4,4-dimethyl-1-pentene (Table 2) shows that the chemical shift of the two diastereotopic hydrogens is remarkably different ($\Delta\delta$ 0.40–0.50). In the simplest case [the 4,4-dimethyl-1-pentene complex (V)], the coupling constants between H(2) and the two H(3) atoms are very different; the hydrogen having the lowest $\Delta\delta$ with respect to the non-complexed olefin shows the highest coupling constant (Table 2). As the correlation between the $\Delta\delta$ value for H(3) and H(3') and their relative positions with respect to the Pt atom is still not established in this case, we can only confirm that one of the two conformations in which H(2) and H(3) or H(3') are in an *anti*-position is largely preferred in accordance with the high coupling constant (12.6 Hz)¹³, (II) probably being more stable than (I) in the *R*-antipode for steric reasons (Fig. 5). No significant conformational rigidity seems to exist for the isopropyl group of the 4-methyl-1-pentene (VII), in which, however, a small downfield shift, with respect to free olefin is observed for the two diastereotopic methyl groups, despite the large distance between the methyl groups and the Pt atom.

Even if the interaction between a Pt atom and a paraffinic proton, which causes the observed downfield shifts, is far from being well understood, one can derive inter-

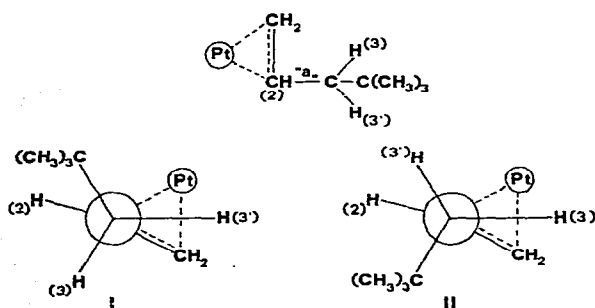


Fig. 5. Conformational analysis of the *trans*-dichloro(pyridine)[(2*R*)-4,4-dimethyl-1-pentene]platinum(II) complex (V).

esting information for conformational analysis of complexed α -olefins; for CH_2 or $\text{CH}(\text{CH}_3)_2$ groups in an α -position to the double bond, the preference for one of the allowed conformations is much greater in the complexes than in the corresponding non complexed α -olefins.

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