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STEREOSELECTIVE COORDINATION OF THE VINYLIC LIGAND IN *cis*-DICHLORO(*p*-TOLUIDINE) (OLEFIN)PLATINUM(II) COMPLEXES

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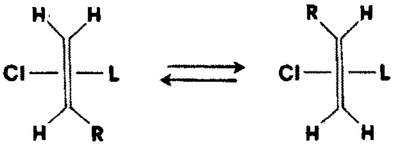
Summary

Variable temperature ^{1}H NMR studies on *cis*-dichloro(*p*-toluidine) (olefin)-platinum(II) complexes have shown that the coordination of the olefin ligand is completely stereoselective, only one stereoisomer being present in solution. Steric repulsive interactions determine the conformational arrangement of the ligands in the complexes containing simple α-olefins, namely 1-butene and 4,4′-dimethyl-1-pentene. Attractive interactions involving the formation of an intramolecular hydrogen bond predominate over the repulsive steric interactions in the case of the complexes containing unsaturated ethers, viz. t-butyl vinyl ether, (*Z*)-1-ethoxy-1-propene and methyl allyl ether.

Introduction

With square-planar platinum(II) complexes of monosubstituted olefins with various neighboring *cis*-ligands, like PtCl (acac) (olefin) (I) [1], (acac = acetylacetonate) and *cis*-$PtCl_2L$(olefin) (II) [2], (L = AsR_3, PR_3, NR_3) complexes, in principle two isomers, differing by a 180° rotation about the metal–olefin bond axis, are possible (Scheme 1). The two rotational isomers of each complex can be detected in solution



I : L = O
II : L = AsR_3, PR_3, NR_3

SCHEME 1.

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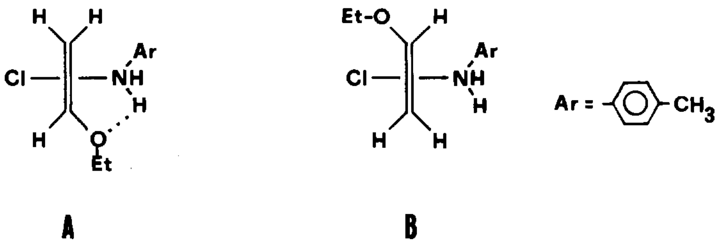


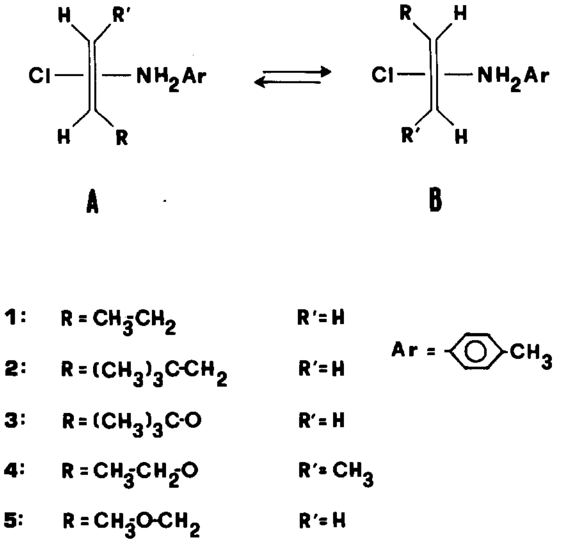
SCHEME 2.

by ^1H NMR studies if the interconversion is slow on the NMR time scale. As shown by Lewis and coworkers, in complexes I and II ($L = AsR_3$, PR_3) the predominance of one conformer over the other is mainly determined by the steric contrasts in the ligands *cis* to the olefin.

Until now no data about the rotational isomerism in complexes in which L is a primary amine have been available. Recently we demonstrated that in *cis*-dichloro(amine) (olefin)platinum(II) complexes, in which the amine is the *p*-toluidine and the olefin is the ethyl vinyl ether, the attractive interaction between the oxygen atom of the unsaturated ether and the amine group resulted in the presence in solution of only rotamer **A** (Scheme 2) [3]. The formation of this rotamer is the opposite of what would be expected on the basis of steric requirements, which should favour the **B** conformer having the OR group directed towards the Cl atom, i.e. the less hindered *cis*-ligand.

The objectives of the present work were:

(i) to determine the influence of the steric interactions on the position of the equilibrium depicted in Scheme 3 for *cis*-dichloro(*p*-toluidine) (olefin)platinum(II)



SCHEME 3.

complexes containing alkyl-monosubstituted ethylene (1-butene, 4,4′-dimethyl-1-pentene) as the olefin ligand.

(ii) to assess the relative contributions of electronic interactions and steric requirements to orientation in solution of the ligands in the *cis*-dichloro(*p*-toluidine) (olefin)platinum(II) complexes containing unsaturated ethers (t-butyl vinyl ether, (*Z*)-1-ethoxy-1-propene, methyl allyl ether) as the olefin ligands.

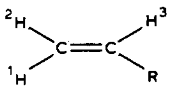
Results

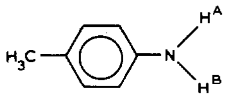
The *cis*-dichloro(*p*-toluidine) (olefin)platinum(II) complexes (1-butene (**1**), 4,4′-dimethyl-1-pentene (**2**), t-butyl vinyl ether (**3**), (*Z*)-1-ethoxy-1-propene (**4**), methyl allyl ether (**5**)) were obtained by displacement of ethylene by the appropriate olefin [4] from *cis*-dichloro(*p*-toluidine) (ethylene)platinum(II) complex [5] in $CHCl_3$ as solvent. The crude products were crystallised from $CHCl_3/Et_2O$ (1/1) (**1**, **2**) and $CHCl_3$/n-hexane (1/1) (**3**, **4**, **5**). Pure samples of **1** (m.p. 140°C), **2** (m.p. 94°C), **3** (m.p. 145°C), **4** (m.p. 72°C) and **5** (m.p. 138°C) were obtained as pale yellow crystals soluble in acetone or chlorinated solvents.

The *trans*-dichloro(*p*-toluidine) (olefin)platinum(II) complexes (1-butene (**6**), 4,4′-dimethyl-1-pentene (**7**), t-butyl vinyl ether (**8**), (*Z*)-1-ethoxy-1-propene (**9**),

TABLE 1

^{1}H CHEMICAL SHIFTS [a] FOR *cis*-DICHLORO(*p*-TOLUIDINE)(ALKYL-MONOSUBSTITUTED ETHYLENE)PLATINUM(II) IN $CDCl_3$





Complex	R	T(°C)	H(1)	H(2)	H(3)	H^A	H^B
1 [b]	CH_3CH_2	+35	4.38(d)	4.22(d)	4.80(m)	5.99(bs)	6.15(bs)
		+25	4.38(d)	4.22(d)	4.80(m)	5.99(bs)	6.15(bs)
		0	4.46(bs)	4.19(bs)	4.75(m)	6.24(bs)	6.24(bs)
		−30	4.49(d)	4.14(d)	4.79(m)	6.25(d)	6.43(d)
		−60	4.47(d)	4.08(d)	4.85(m)	6.26(d)	6.56(d)
2 [c]	Neopentyl	+35	4.38(bs)	4.25(d)	5.00(bm)	6.16(bs)	6.24(bs)
		+25	4.38(bs)	4.20(bs)	5.00(bm)	6.26(bs)	6.44(bs)
		0	4.40(d)	4.12(bs)	5.06(bm)	6.22(bd)	6.83(bd)
		−30	4.36(d)	4.02(d)	5.22(m)	6.10(d)	7.2–7.3 [d]
		−60	4.32(d)	3.94(bs)	5.38(m)	5.88(bd)	7.3–7.6(bd)

[a] In ppm from TMS. Multiplicities given in parentheses; s, singlet; bs, broad singlet; d, doublet; bd, broad doublet; t, triplet; m, multiplet; bm, broad multiplet. [b] Coupling constants (Hz): J(H(1),H(3)) 13; J(H(2),H(3)) 7; $J(H^A,H^B)$ 13. Methylenic protons of 1-butene at +35°C: δ 1.66 ppm (m), δ 2.20 ppm(m). Methylic protons of 1-butene at +35°C: δ 1.16 ppm (t), J_{vic} 7 Hz. Methylic protons of *p*-toluidine: δ 2.32 ppm (s). Aromatic protons of *p*-toluidine at 35°C: δ 7.16 ppm (d), δ 7.34 ppm (d), J 8.4 Hz. [c] Coupling constants (Hz): J(H(1),H(3)) 14; J(H(2),H(3)) 8; $J(H^A,H^B)$ 8. Methylenic protons of olefin at +35°C: δ 1.60 ppm (d), δ 1.71 ppm (t), J_{gem} 12 Hz. Methylic protons of olefin at +35°C: δ 0.92 ppm (s). Methylic protons of *p*-toluidine: δ 2.32 ppm (s). Aromatic protons of amine: δ 7.18 ppm (d), δ 7.38 ppm (d), J 8 Hz. [d] The resonance of the proton H^B is covered by the absorption of the aromatic protons of the *p*-toluidine.

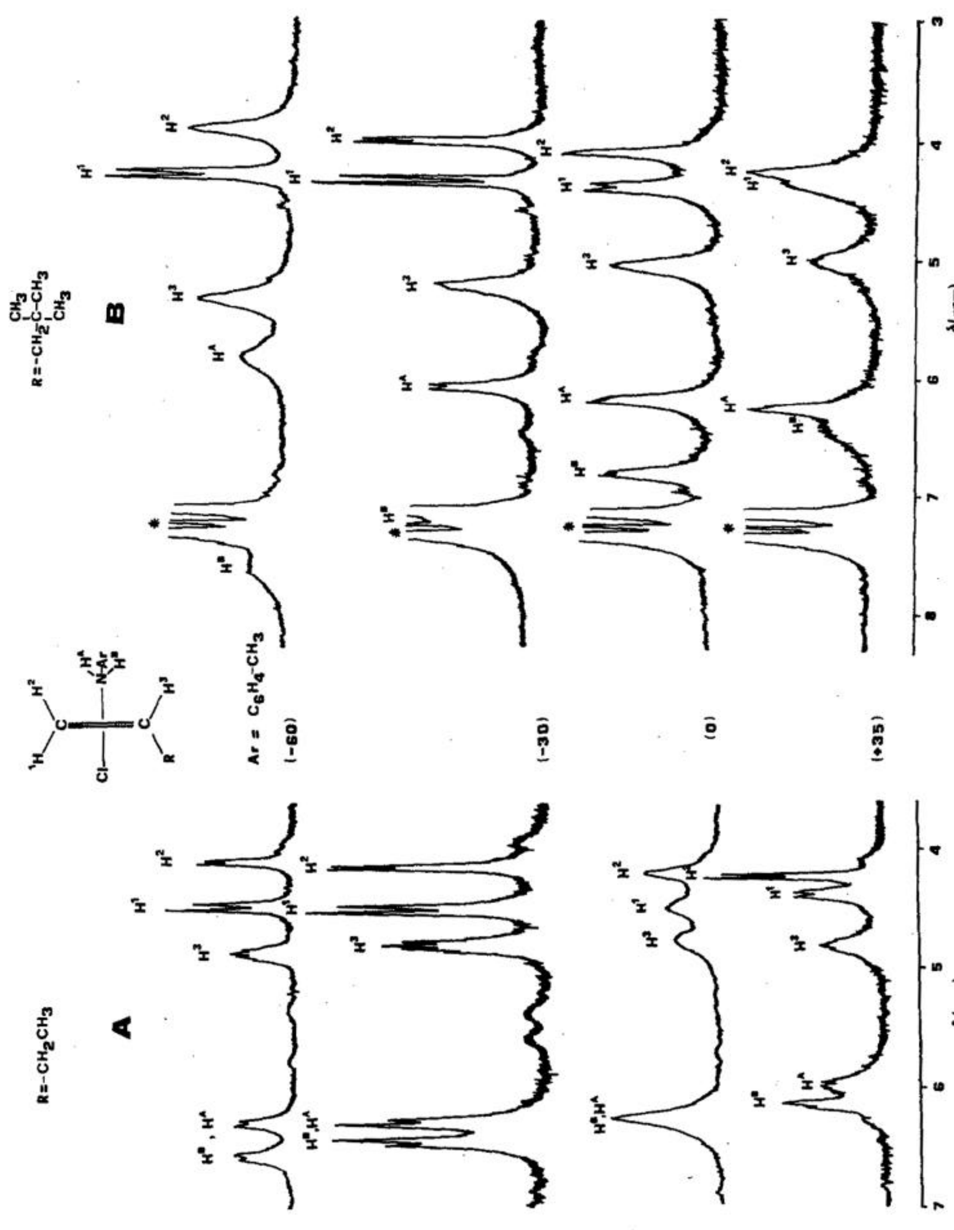


Fig. 1. ^{1}H NMR spectra at 250 MHz of *cis*-dichloro(*p*-toluidine)(1-butene)platinum(II), complex **1** (A), and *cis*-dichloro(*p*-toluidine)(4,4′-dimethyl-1-pentene)platinum(II) complex **2** (B), in $CDCl_3$ at various temperatures. The temperatures (°C) are shown in parentheses, and δ in ppm from TMS. (★ denotes resonances of the aromatic protons of *p*-toluidine)

methyl allyl ether (**10**)) were obtained analogously from *trans*-dichloro(*p*-toluidine)(ethylene)platinum(II) complex. The products were isolated as microcrystalline yellow-orange solids from $CHCl_3$/n-pentane (1/2).

Alkyl-monosubstituted olefin-platinum(II) complexes

The 3.5–7 ppm region of the spectra of the complex **1** in $CDCl_3$ between +35°C and −60°C is shown in Fig. 1, and Table 1 summarizes the relevant parameters.

The resonances of the amine protons are temperature dependent: at +35°C the amine protons give two broad absorptions, centered at 6.15 and 5.99 ppm respectively. At O°C signals converge into a single broad peak centered at 6.24 ppm, whereas at −30°C there are two sharp doublets at 6.25 and 6.43 ppm, with J_{gem} 13 Hz. At −60°C an even larger separation of the signals is observed.

The signals from the vinylic protons do not show coalescence phenomena: the H(1) proton resonance is a doublet centered at 4.38 ppm at +35°C (J(H(1), H(3)) 13 Hz) and this is shifted down-field to 4.47 ppm on going to −60°C. The H(2) proton absorption is a doublet centered at 4.22 ppm at +35°C and is shifted up-field to 4.08 ppm at −60°C (J(H(2), H(3)) 7 Hz). The H(3) proton absorption is a multiplet centered at 4.80 ppm at +35°C and at 4.85 ppm at −60°C. At 0°C there is a broadening of the H(1), H(2), H(3) proton resonances, but at lower temperatures only one well resolved absorption for each proton is again observed. The resonances of the other protons of complex **1** show negligible variations with the temperature.

Between +35°C and −60°C the signals from the amine protons of complex **2** show a temperature variation similar to that observed for complex **1**. As shown in Fig. 1, at +35°C these protons appear as two broad, partially superimposed signals, centered at 6.16 and 6.24 ppm. At 0°C they are two well separated signals at 6.22 and 6.83 ppm. The splitting for geminal coupling is observed at −30°C only for the resonance which falls at 6.10 ppm, the other amine proton resonance being hidden by the signals from the aromatic protons of the *p*-toluidine. On going to −60°C the amine proton indicated by H^A is shifted slightly up-field to 5.88 ppm, while the proton indicated by H^B shows a marked downfield shift to 7.3–7.6 ppm. The decrease in the solubility of complex **2** accounts for the broadening of the H^A and H^B resonances at −60°C.

It is noteworthy that for both complexes **1** and **2** no coupling between the amine protons and 195 Pt is observed in the 250 MHz spectra, but it is clearly observed in 100 MHz spectra up to +70°C. Furthermore, upon adding one equivalent of the amine ligand to complexes **1** and **2**, two well defined signals are observed between +25 and +70°C for both coordinated and free amine.

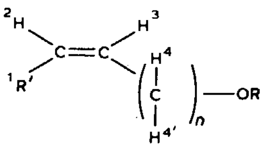
The vinylic protons of complex **2** do not show coalescence phenomena: the H(1) vinylic proton absorption is at 4.38 ppm at +35°C, and stays almost unchanged at this position over the whole temperature range investigated. At +35°C the H(2) resonance is at 4.25 ppm and this is shifted up-field by 0.31 ppm on going to −60°C; the H(3) absorption is at 5.00 ppm at +35°C and at 5.38 ppm at −60°C.

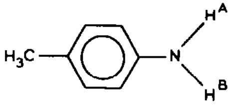
The chemical shifts and the coupling constants for complex **2** are shown in Table 1.

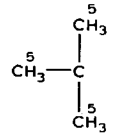
The most significant differences between the NMR behaviour of the *cis*-complexes **1** and **2** and that of the *trans*-complexes **6** and **7** appear in the resonances from the H(2) and H(3) vinylic protons: as shown in Table 3, at +25°C these are

TABLE 2

^{1}H CHEMICAL SHIFTS [a] FOR *cis*-DICHLORO(*p*-TOLUIDINE)(UNSATURATED ETHER)PLATINUM(II) IN $CDCl_3$





Complex	*n*	R	R′	T(°C)	H(1)	H(2)	H(3)	H(4)	H(4′)	H(5)	H(6)	H^A	H^B
3 [b]	0	 $\overset{5}{C}H_3-C(\overset{5}{C}H_3)_2$	H(1)	+35	3.36(dd)	3.80(dd)	6.88(dd)	–	–	1.58(s)	–	4.68(d)	6.42(d)
				−60	3.32(bd)	3.82(bd)	6.90(dd)	–	–	1.62(s)		4.60(d)	6.90(d)
4 [c]	0	$\overset{5}{C}H_3-\overset{6}{C}H_2$	CH_3(1)	+35	1.27(dd)	4.75(dq)	6.62(d)	–	–	1.27(t)	3.98(m)	5.14(d)	6.00(d)
				−60	1.28(dd)	4.81(dq)	6.68(d)			1.22(t)	3.98(m)	5.22(d)	6.32(d)
5 [d]	1	$\overset{5}{C}H_3$	H(1)	+35	4.10(d)	4.20(d)	5.60(dd)	4.60(d)	4.01(d)	3.58(s)	–	5.77(bd)	6.96(bd)
				−60	4.07(d)	4.13(d)	5.60(dd)	4.61(d)	4.02(d)	3.54(s)	–	5.87(bd)	7.27(bd)

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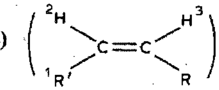
[a] In ppm from TMS. Multiplicities given in parentheses; s, singlet; d, doublet; dd, double doublet; bd, broad doublet; t, triplet; dq, double quartet; m, multiplet. [b] Coupling constants (Hz): *J*(H(1),H(2)) 2.2; *J*(H(1),H(3)) 11; *J*(H(2),H(3)) 4.4; *J*(H(1),Pt) 68; *J*(H(2),Pt)78; *J*(H(3),Pt) 72; *J*(H^A,H^B) 12; *J*(H^A,Pt) 56; *J*(H^B,Pt) 80. Methyl group of *p*-toluidine: δ 2.32 ppm(s). Aromatic protons of *p*-toluidine: δ 7.12 ppm (d), δ 7.32 ppm (d), *J* 8.5 Hz. [c] Coupling constants (Hz): *J*(H(1),H(2)) 6.5; *J*(H(1),H(3)) 2; *J*(H(2),H(3)) 7; *J*(H(1),Pt) 40; *J*(H(2),Pt) 80; *J*(H(3),Pt) 70; *J*(H(5),H(6)) 7; *J*(H^A,H^B) 12. Methyl group of *p*-toluidine; δ 2.31 ppm (s). Aromatic protons of *p*-toluidine: δ 7.10 ppm (d), δ 7.48 ppm (d), *J* 8 Hz. [d] Coupling constants (Hz): *J*(H(1),H(3)) 14; *J*(H(2),H(3)) 9; *J*(H(1),Pt) 70; *J*(H(2),Pt) 60; *J*(H(3),H(4,4′) < 2; *J*(H(4),H(4′)) 16; *J*(H^A,H^B) 8; *J*(H^A,Pt) 70; *J*(H^B,Pt) 75. Methyl group of *p*-toluidine; δ 2.32 ppm (s). Aromatic protons of *p*-toluidine: δ 7.17 ppm (d), δ 7.34 ppm (d), *J* 8.4 Hz.

TABLE 3

^{1}H CHEMICAL SHIFTS[a] OF THE VINYLIC PROTONS IN *cis*- AND *trans*-DICHLORO(*p*-TOLUIDINE)



AT 25°C IN $CDCl_3$

Complex	R	R'	Isomer	H(1)	H(2)	H(3)
1	CH_3CH_2	H	*cis*	4.38	4.22	4.80
6			*trans*	4.37	4.43	5.25
2	Neopentyl	H	*cis*	4.38	4.20	5.00
7			*trans*	4.40	4.58	5.40
3	T-BuO	H	*cis*	3.36	3.82	6.90
8			*trans*	4.14	3.84	7.2–7.3
4	CH_3CH_2O	CH_3	*cis*	1.27	4.75	6.62
9			*trans*	1.54	4.72	6.93
5	CH_3OCH_2	H	*cis*	4.10	4.20	5.61
10			*trans*	4.56	4.18	6.02

[a] In ppm from TMS.

both shifted down-field in the *trans*-complexes relative to the cis-complexes. In contrast, the H(1) resonance is virtually unchanged in position in the *cis*- and *trans*-complexes.

Unsaturated ether-platinum(II) complexes

In the case of complexes **3**, **4** and **5** containing unsaturated ethers, no coalescence behaviour is observed for the vinylic and amine protons between +35 and −60°C.

Table 2 shows the ^{1}H NMR parameters for complex **3** at +35 and −60°C. Figure 2 shows the 3.5–7 ppm region of the spectrum of complex **3** at +35°C: the two amine protons, indicated by H^A and H^B, give two doublets at 4.68 and 6.42 ppm, respectively, with $J(H^A,H^B)$ 12 Hz, $J(H^A,Pt)$ 56 Hz and $J(H^B,Pt)$ 80 Hz. At −60°C the position of the absorption of the H^A proton is almost unchanged, while the H^B resonance is shifted downfield to 6.90 ppm. The resonances of the vinylic protons are not temperature dependent: at +35°C the H(1) signal is a double doublet at 3.36 ppm, with J(H(1),H(2)) 2.2 Hz, J(H(1),H(3)) 11 Hz, J(H(1),Pt) 68 Hz. The H(2) resonance is centered at 3.80 ppm (J(H(2),H(3)) 4.4 Hz, J(H(2),Pt) 78 Hz) and the H(3) signal is a double doublet at 6.88 ppm, with J(H(3),Pt) 72 Hz.

Table 2 shows the NMR parameters for complex **4** at +35 and −60°C. As observed for complex **3**, the resonances of the amine protons of the complex **4** are temperature dependent, while those of the vinylic protons remain unchanged between +35 and −60°C. Fig. 3 shows the 3–7 ppm region of the spectrum of complex **4** at +35°C: the H^A and H^B amine protons appear as two doublets, centered at 5.14 and 6.00 ppm, respectively, $J(H^A,H^B)$ 12 Hz. At −60°C the H^A resonance is nearly unchanged in position, while the H^B one is shifted downfield to 6.32 ppm.

The H(2) and H(3) vinylic proton resonances appear as a doublet of quartets at 4.75 ppm and a doublet at 6.62 ppm, respectively, with J(H(2),H(3)) 7 Hz, J(H(2),Pt) 80 Hz and J(H(3),Pt) 70 Hz. On going to −60°C there is a negligible downfield shift of 0.06 ppm of both the resonances of the H(2) and H(3) protons. The protons of the methyl group bonded to the double bond give a doublet of

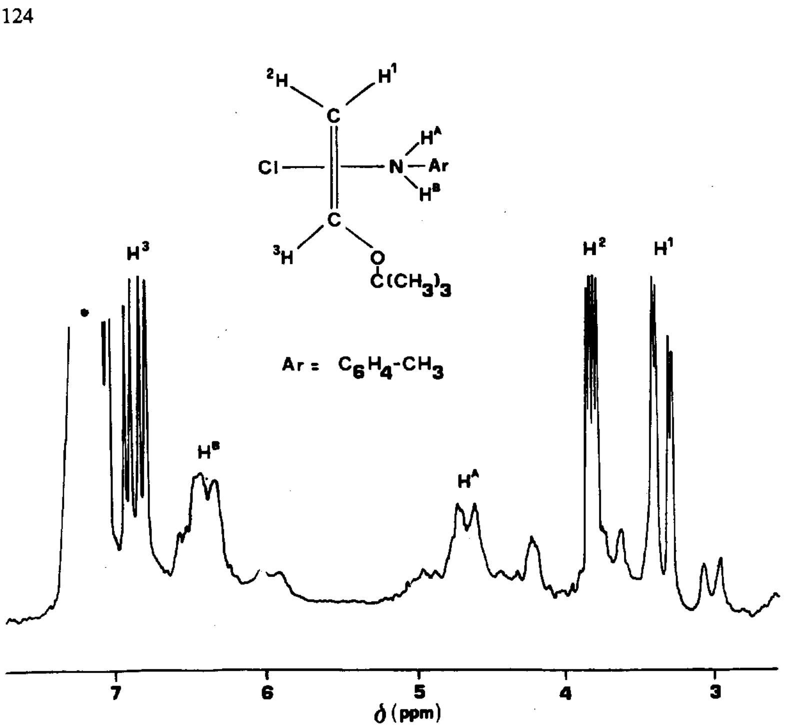


Fig. 2. ^1H NMR spectrum at 100 MHz of *cis*-dichloro(*p*-toluidine)(t-butyl vinyl ether)platinum(II), complex 3, in $CDCl_3$, at +35°C, δ in ppm from TMS. (★ denotes resonances of the aromatic protons of the *p*-toluidine).

doublets centered at 1.27 ppm, with $J(H(2),CH_3)$ 6.5 Hz, $J(CH_3,H(3))$ 2 Hz and $J(CH_3,Pt)$ 40 Hz. At 3.98 ppm the spectrum shows a complicated multiplet which arises from superimposition of the absorptions of the diastereotopic protons of the methylenic group bonded to the oxygen atom.

The ^1H NMR parameters for complex 5 at 35 and −60°C are shown in Table 2. The 3.5–7 ppm region of the spectrum of complex 5 is shown in Fig. 4: the amine protons H^A and H^B give separated resonances over the whole temperature range investigated; these appear as two broad doublets centered at 5.77 and 6.96 ppm, respectively, at +35°C, with $J(H^A,H^B)$ 8 Hz, $J(H^A,Pt)$ 70 Hz, $J(H^B,Pt)$ 75 Hz. At −60°C the H^B proton is shifted downfield to 7.27 ppm, while the H^A proton chemical shift is unchanged. The vinylic protons are unaffected by temperature change: the H(1) proton gives a doublet centered at 4.10 ppm, the H(2) proton is a doublet centered at 4.20 ppm, and the H(3) proton a multiplet centered at 5.60 ppm. The coupling constants are: $J(H(1),H(3))$ 14 Hz, $J(H(2),H(3))$ 9 Hz, $J(H(1),Pt)$ 70 Hz and $J(H(2),Pt)$ 60 Hz. The diastereotopic methylenic protons of the CH_2–O group give rise to two sharp doublets centered at 4.01 and 4.60 ppm, respectively (J_{gem} 16 Hz) and these show fine structure due to the vicinal coupling with the H(3) vinylic proton ($J_{vic} < 2$ Hz).

Discussion

Unsaturated ether-platinum(II) complexes

The observed variations with the temperature of the amine and vinylic proton

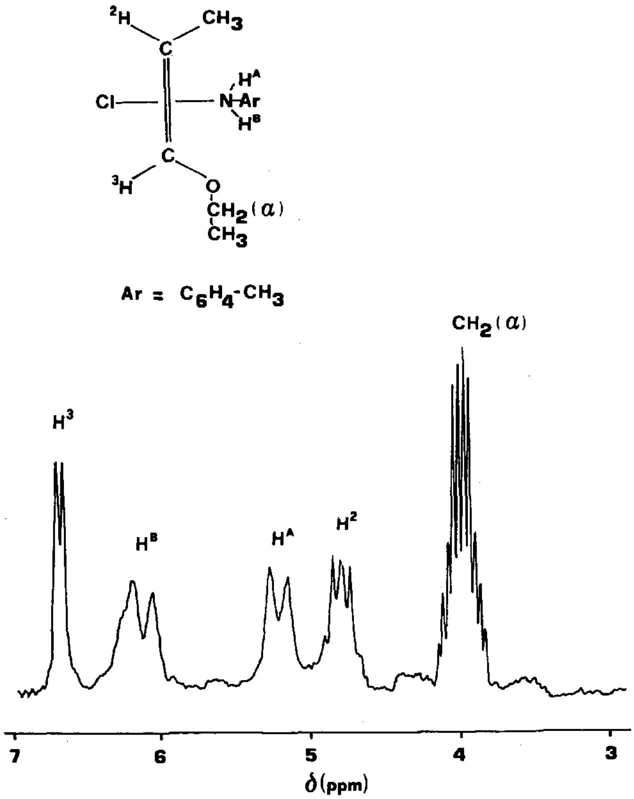


Fig. 3. ^1H NMR spectrum at 100 MHz of *cis*-dichloro(*p*-toludine)((*Z*)-1-ethoxy-1-propene)platinum(II), complex 4, in $CDCl_3$, at +35°C; δ in ppm from TMS.

resonances of the *cis*-complexes containing unsaturated ethers are consistent with the presence in solution of only one conformer over the whole temperature range investigated. No coalescence behaviour of the vinylic proton resonances is observed, and the H^A and H^B amine protons are inequivalent, showing geminal coupling and coupling with ^{195}Pt. Analysis of the data in Table 3 shows that the signals from the H(1) vinylic proton of the *cis*-complexes **3**, **4**, **5** are shifted upfield relative to those for the *trans*-complexes **8**, **9**, **10**, whereas the H(2) proton shows the same chemical shift in the *cis*- and *trans*-complexes.

These results indicate that, of the two possible rotational isomers depicted in Scheme 3, the only one present in solution is A, in which the OR group of the unsaturated ether points towards the amine ligand. In this arrangement the H(2) proton is bent towards the Cl ligand as in the *trans*-complexes, while the H(1) proton points towards the phenyl group of the amine, and is shielded by this group [2].

The conformational preference for the coordinated ligands in the *cis* complexes containing unsaturated ethers is the opposite of that expected on the basis of steric requirements, which should favour the conformer B in which the OR group is directed towards the chlorine atom, i.e. the less bulky *cis*-ligand. The formation of an intramolecular hydrogen bond between the oxygen atom of the ether and a proton of the amine is the reason for this preference.

The resonance of the amine proton H^B is shifted downfield on going to −60°C,

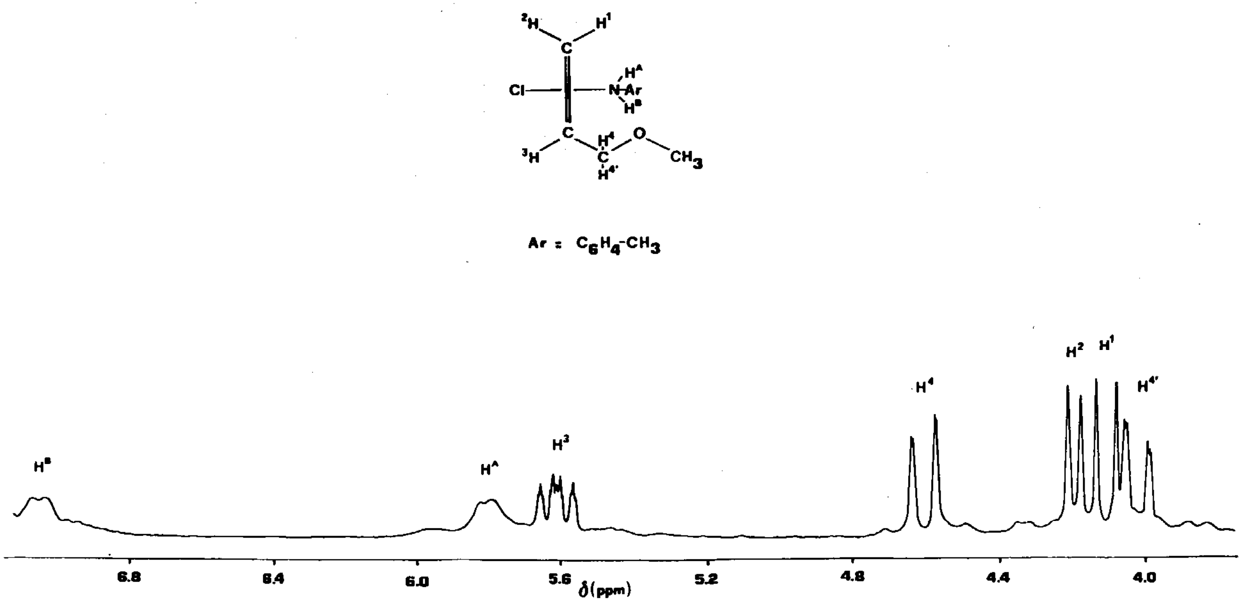


Fig. 4. ^{1}H NMR spectrum at 250 MHz of *cis*-dichloro(*p*-toluidine)(methyl allyl ether)platinum(II), complex 5, in $CDCl_3$, at +35°C, δ in ppm from TMS.

whereas the H^A resonance is nearly unchanged in position, we can identify H^B as the proton engaged in the intramolecular hydrogen bonding.

Alkyl-monosubstituted olefin-platinum(II) complexes

The temperature variation behaviour of complexes **1** and **2** containing alkyl-monosubstituted ethylene ligands strongly suggests that the equilibrium between the two conformers A and B lies almost completely over one of them (Scheme 3). Thus between +35 and −60°C the H(1), H(2), H(3) vinylic protons show no coalescence phenomena.

Comparison between the chemical shifts for these protons at 25°C in the *cis*-complexes **1** and **2** and those for the analogous *trans*-complexes **6** and **7** indicates that the B conformer, in which the R group of the olefin is near to the Cl ligand, is the predominant isomer. Thus the chemical shifts for the H(1) protons are the same in the *cis*- and *trans*-complexes, whereas those for the H(2) and H(3) protons are shifted upfield in the *cis*-complexes relative to those of the *trans* species, in keeping with the proximity of the phenyl group of the amine to the H(2) and H(3) protons in complexes **1** and **2**.

The behaviour of the signals from the amine protons H^A and H^B is striking: there are distinct resonances over all the full range of temperatures investigated, but the shapes of the peaks are strongly dependent on the temperature. The coupling of the amine protons with ^{195}Pt persists up to +70°C, but no geminal coupling is observed above room temperature. Below room temperature the H^A and H^B protons give geminal coupling in addition to the coupling with the ^{195}Pt.

This trend indicates that at low temperatures intramolecular rotation of the amine about the Pt–N bond is restricted. Probably in the most favourite conformation the phenyl group of the amine ligand lies in a plane at right angles to that of the complex, and the amine protons H^A and H^B are bent towards the olefin and chlorine ligands, respectively.

Experimental

cis-Dichloro(p-toluidine)(1-butene)platinum(II) (1). A suspension of 0.4 g (1 mmol) of *cis*-dichloro(*p*-toluidine) (ethylene)platinum(II) in 5 ml of $CHCl_3$ was treated at room temperature with gaseous 1-butene until all the solid dissolved. The solvent was evaporated off under vacuum. Pale yellow crystals of *cis*-dichloro(*p*-toluidine)-(1-butene)platinum(II) were obtained by cristallisation from $CHCl_3/Et_2O$ (1/1). Yield 0.38 g (0.9 mmol), m.p. 140°C.

The ^{1}H NMR parameters of the complex at 25°C in $CDCl_3$ are listed in Table 1. Anal.: $C_{11}H_{17}PtCl_2N$ calcd.: C, 30.78; H, 3.99; N, 3.26%. Found: C, 31.15; H, 4.26; N, 3.12.

cis-Dichloro(p-toluidine)(4,4′-dimethyl-1-pentene)platinum(II) (2). This complex was similarly prepared by reaction of 0.4 g (1 mmol) of *cis*-dichloro(*p*-toluidine)-(ethylene)platinum(II) with 0.19 g (2 mmol) of 4,4′-dimethyl-1-pentene, in $CHCl_3$. The crude product was crystallised from $CHCl_3/Et_2O$ (1/1) and the *cis*-dichloro-(*p*-toluidine)(4,4′-dimethyl-1-pentene)platinum(II) was isolated as pale yellow crystals. Yield 0.4 g (0.85 mmol), m.p. 94°C.

The ^{1}H NMR parameters of the complex at 25°C in $CDCl_3$ are listed in Table 1. Anal.: Found: C, 36.18; H, 4.63; N, 2.64. $C_{14}H_{23}PtCl_2N$ calcd.: C, 35.67; H, 4.92; N, 2.97%.

cis-Dichloro(p-toluidine)(t-butyl vinyl ether)platinum(II) (3). To a suspension of 0.4 g (1 mmol) of the ethylene complex in 5 ml of $CHCl_3$ was added 0.2 g (2 mmol) of t-butyl vinyl ether. After removal of the solvent, the residue was crystallised from $CHCl_3$/n-hexane (1/1) to give yellow crystals. Yield 0.33 g (0.7 mmol), m.p. 145°C.

The ^1H NMR parameters of the complex, measured at +35°C in $CDCl_3$, are listed in Table 2. Anal.: Found: C, 34.27; H, 4.62; N, 2.63. $C_{13}H_{21}PtCl_2NO$ calcd.: C, 33.05; H, 4.48; N, 2.97%.

cis-Dichloro(p-toluidine)((Z)-1-ethoxy-1-propene)platinum(II) (4). The ethylene complex (0.4 g, 1 mmol) in 5 ml of $CHCl_3$ was treated under reflux with 0.34 g (4 mmol) of (*Z*)-1-ethoxy-1-propene. When the solid dissolved the solvent and the excess of ether were evaporated off under vacuum. Yellow-orange crystals of *cis*-dichloro(*p*-toluidine) ((*Z*)-1-ethoxy-1-propene)platinum(II) (0.3 g, 0.65 mmol) were obtained when a solution in $CHCl_3$/n-hexane (1/1) was kept for 2 days at −5°C; m.p. 72°C.

The ^1H NMR parameters of the complex at +35°C in $CDCl_3$ are listed in Table 2. Anal.: Found: C, 30.22; H, 4.38; N, 2.96. $C_{12}H_{19}PtCl_2NO$ calcd.: 31.38; H, 4.17; N, 3.05%.

cis-Dichloro(p-toluidine)(methyl allyl ether)platinum(II) (5). By the above procedure, the complex was prepared from 0.4 g (1 mmol) of *cis*-dichloro(*p*-toludine)(ethylene)platinum(II) and 0.14 g (2 mmol) of methyl allyl ether in 5 ml of $CHCl_3$. After solvent evaporation, the residue was crystallised from $CHCl_3$/n-hexane (1/1) to give *cis*-dichloro(*p*-toluidine)(methyl allyl ether)platinum(II), (0.35 g, 0.8 mmol) as yellow-orange crystals, m.p. 138°C.

The ^1H NMR parameters of the complex, measured at +35°C in $CDCl_3$ are listed in Table 2. Anal.: Found: C, 30.04; N, 3.92; N, 3.05%. $C_{11}H_{17}PtCl_2NO$ calcd.: C, 29.66; H, 3.85; N, 3.14%.

trans-Dichloro(p-toluidine)(1-butene)platinum(II) (6). A mixture of *trans*-dichloro(*p*-toluidine)(ethylene)platinum(II) (0.4 g, 1 mmol) and 5 ml of $CHCl_3$ was treated with 1-butene until the solid dissolved. The product was crystallised from $CHCl_3$/n-pentane (1/2). Yield 0.30 g (0.7 mmol), m.p. 89°C. Anal.: Found: C, 29.32; H, 4.10; N, 3.13. $C_{11}H_{17}PtCl_2N$ calcd.: C, 30.78; H, 3.99; N, 3.26%.

trans-Dichloro(p-toludine)(4,4′-dimethyl-1-pentene)platinum(II) (7). Addition of 0.19 g (2 mmol) of 4,4′-dimethyl-1-pentene to a suspension of 0.4 g (1 mmol) of the ethylene complex in $CHCl_3$ produced a solution, which then was evaporated to dryness under vacuum. The residue was crystallised from $CHCl_3$/n-pentane (1/2) to give *trans*-dichloro(*p*-toluidine)(4,4′-dimethyl-1-pentene)platinum(II) as a yellow-orange mycrocristalline product, which decomposed upon melting. Yield 70%. Anal.: Found: C, 36.08; H, 5.13; N, 2.64. $C_{14}H_{23}PtCl_2N$ calcd.: C, 35.67; H, 4.92; N, 2.97%.

trans-Dichloro(p-toluidine)(t-butyl vinyl ether)platinum(II) (8). By the above procedure complex **8** was obtained as a microcrystalline solid from $CHCl_3$/n-pentane (1/2), m.p. 117°C. Yield 75%. Anal.: Found: C, 32,87; H, 4.54; N, 2.80. $C_{13}H_{21}PtCl_2NO$ calcd.: C, 33.05; H, 4.48; N, 2.97%.

trans-Dichloro(p-toluidine)((Z)-1-ethoxy-1-propene)platinum(II) (9). Complex **9** was obtained similarly. Yield 60%, m.p. 37°C. Anal.: Found: 31.02; H, 4.28; N, 3.18. $C_{12}H_{19}PtCl_2NO$ calcd.: C, 31.38; H, 4.17; N, 3.05%.

Trans-Dichloro(p-toluidine)(methyl allyl ether)platinum(II) (10). Complex **10** was obtained as described for the complexes **1–9**. Yield 72%, m.p. 106°C. Anal.: Found: C, 30.14; H, 3.73; N, 3.09. $C_{11}H_{17}PtCl_2NO$ calcd.: C, 29.66; H, 3.85; N, 3.14%.

References

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