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# RESTRICTED ROTATION OF THE OLEFIN AND AMINE LIGANDS IN *cis*-DICHLORO(*p*-TOLUIDINE)(ETHYL VINYL ETHER)PLATINUM(II)

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## Summary

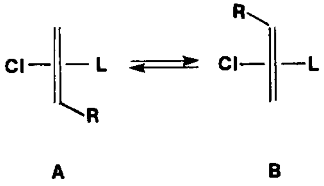
*cis*-Dichloro(*p*-toluidine)(olefin)platinum(II) complexes, in which the olefin is either ethyl vinyl ether or ethylene, have been investigated by $^1$H NMR spectroscopy over a range of temperatures (+50 to −60 °C) in order to study the rotation of the olefin ligand.

The results give no evidence of rotation of the amine or vinyl ether ligands even at the highest temperature investigated, +50 °C; only one of the two possible rotational isomers is present, and this is attributed to the presence of intramolecular hydrogen bonding between the oxygen atom of the vinyl ether and the –NH– group of the amine.

In contrast, the amine and vinyl ligands in the ethylene complex rotate freely at room temperature, coalescence being observed above −25 °C for the ethylene protons.

## Introduction

Olefins coordinated in square-planar platinum(II) complexes are not fixed, but rotate about the platinum–olefin bond. An energy barrier to rotation, in the range 10–15 kcal mol$^{-1}$, has been calculated for the complexes PtCl(acac)(olefin) (acac = acetylacetonate) and *cis*-$PtCl_2L$(olefin) (L = $AsR_3$, $PR_3$) [1,2]. As the barrier to



SCHEME 1

0022-328X/84/$03.00

rotation is so small the pair of rotational isomers (Scheme 1), arising from the coordination of a monosubstituted ethylene ($CH_2$=CH–R) to platinum(II) in *cis*-complexes, interconvert freely at room temperature. The spectra for the individual isomers A and B can be detected in the NMR measurements at temperatures of 0 to −30 °C. The prevalence of one conformer over the other at temperatures below the coalescence temperature is connected mainly with the different steric hindrance of the ligands in the position *cis* to the olefin.

In this connection, platinum complexes like *cis*-dichloro($RNH_2$)($CH_2$=CH–OR)platinum(II) containing a primary amine and a vinyl ether in the *cis*-position are of interest. As shown in the Scheme 2, the –OR group of the vinyl ether may point either at the amine group (rotamer A) or at the chlorine atom (rotamer B). The repulsive interaction between the oxygen and the chlorine atoms in B, and the attractive interaction via an intramolecular hydrogen bond between the oxygen atom and the amine group in A, suggest that the rotamer A will be more stable than B.

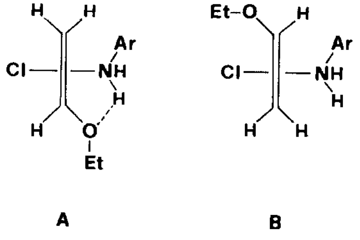
Since no studies have been reported on complexes of this type we have synthesized and investigated by $^1H$ NMR at various temperatures the *cis*- and *trans*-dichloro(*p*-toluidine)(ethyl vinyl ether)platinum(II) complexes. The simple structure of the organic ligands used makes these complexes very suitable for a NMR investigation [3].

## Results

Vinyl ether-platinum(II) complexes can be obtained by the displacement of ethylene from the corresponding ethylene complexes [4] according to the general procedure adopted for simple olefins [5]. *cis*-Dichloro(amine)(ethylene)platinum(II) complexes are white or pale yellow solids which are sparingly soluble in the common organic solvents [6,7]. Of these complexes *cis*-dichloro(*p*-toluidine)(ethylene) platinum(II), complex 1, was chosen for our studies because it is moderately soluble in acetone and presents a very simple $^1H$ NMR spectrum.

The complex 1 (m.p. 158 °C) was prepared from potassium tetrachloroplatinate as described by Cramer [6], while its isomer, *trans*-dichloro(*p*-toluidine)(ethylene)-platinum(II) (2) (m.p. 128 °C), was obtained from Zeise's salt and *p*-toluidine.

*cis*-Dichloro(*p*-toluidine)(ethyl vinyl ether)platinum(II) (3) (m.p. 127 °C) and *trans*-dichloro(*p*-toluidine)(ethyl vinyl ether)platinum(II) (4) (amorphous solid, m.p. 56–58 °C), were prepared from the complexes 1 and 2, respectively; both are well soluble in the common organic solvents.



SCHEME 2

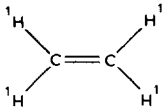
The $^1H$ NMR spectra were obtained in the temperature range +50 to −70 °C, using $CD_2Cl_2$ and $(CD_3)_2CO$ as the solvents for 1 and $CDCl_3$ for the other complexes. The $^1H$ NMR parameters at 25 °C are reported in Table 1 for the complexes 1 and 2 and in Table 2 for the complexes 3 and 4.

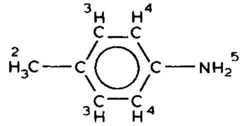
The resonances of the amine and olefin protons of 1 in $CD_2Cl_2$ and in $(CD_3)_2CO$ between +25 and −70 °C are shown in Fig. 1. In $CD_2Cl_2$ above 0 °C the amine protons show a single broad peak centered at 5.9 ppm, while below −10 °C this peak is accompanied by the satellites which result from the coupling with $^{195}Pt$ ($J$(Pt,H) 70 Hz). This resonance is shifted down-field by about 0.3 ppm on going to low temperature (−70 °C).

The ethylene protons behave as a simple $A_4$ system above 0 °C, showing a single

TABLE 1

$^1H$ CHEMICAL SHIFTS[a] FOR *cis* AND *trans*-DICHLORO(*p*-TOLUIDINE)(ETHYLENE)$Pt^{II}$ AT 25 °C



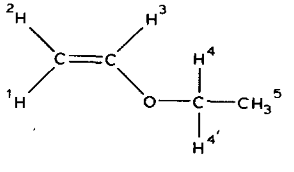


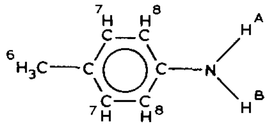
| Isomer | $H^1$ | $H^2$ | $H^3$ | $H^4$ | $H^5$ |
|---|---|---|---|---|---|
| *cis*[b] | 4.22 | 2.36 | 7.21 | 7.21 | 5.7 |
| | (s) | (s) | (s) | (s) | (bs) |
| *trans*[c] | 4.66 | 2.33 | 7.17 | 7.32 | 6.2 |
| | (s) | (s) | (d) | (d) | (bs) |

[a] In ppm from TMS. Multiplicities given in parentheses; s = singlet, bs = broad singlet, d = doublet.
[b] Measured in $CD_2Cl_2$. Coupling constants (Hz): $J(H_1, Pt)$ 65. [c] Measured in $CDCl_3$. Coupling constants (Hz): $J(H_1, Pt)$ 63; $J(H_3, H_4)$ 8.6.

TABLE 2

$^1H$ CHEMICAL SHIFTS[a] FOR *cis*- AND *trans*-DICHLORO(*p*-TOLUIDINE)(ETHYL VINYL ETHER)$Pt^{II}$ IN $CDCl_3$ AT 25 °C





| Isomer | $H^1$ | $H^2$ | $H^3$ | $H^4$ | $H^{4'}$ | $H^5$ | $H^6$ | $H^7$ | $H^8$ | $H^A$ | $H^B$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *cis*[b] | 3.43 | 3.98 | 6.68 | 4.13 | 4.34 | 1.45 | 2.35 | 7.15 | 7.29 | 4.73 | 6.32 |
| | (dd) | (dd) | (dd) | (dq) | (dq) | (t) | (s) | (d) | (d) | (bd) | (bd) |
| *trans*[c] | 4.17 | 3.96 | 7.08 | 4.3-4.0 | 4.3-4.0 | 1.33 | 2.31 | 7.11 | 7.31 | 5.98 | 5.98 |
| | (d) | (d) | (dd) | (m) | (m) | (t) | (s) | (d) | (d) | (bs) | (bs) |

[a] In ppm from TMS. Multiplicities given in parentheses; s = singlet, d = doublet, dd = double doublet, bs = broad singlet, bd = broad doublet, t = triplet, dq = double quartet, m = multiplet. [b] Coupling constants (Hz): $J(H_1, H_2)$ 2.4; $J(H_1, H_3)$ 10.8; $J(H_2, H_3)$ 4.4; $J(H_1, Pt)$ 57; $J(H_2, Pt)$ 73; $J(H_3, Pt)$ 70; $J(H_4, H_{4'})$ 10.2; $J(H_{4,4'}, H_5)$ 7.1; $J(H_A, H_B)$ 10; $J(H_A, Pt)$ 55; $J(H_B, Pt)$ 70; $J(H_7, H^8)$ 8.4. [c] Coupling constants (Hz): $J(H_1, H_3)$ 14; $J(H_2, H_3)$ 4.2; $J(H_{4,4'}, H_5)$ 7; $J(H_7, H_8)$ 8.3; $J(H_{A,B}, Pt)$ 60.

peak at 4.2 ppm coupled with $^{195}$Pt ($J$(Pt,H) 65 Hz). This signal shows an increased broadening at lower temperatures; at −50 °C it appears as a symmetrical multiplet, corresponding to an AA′BB′ system, in which the most intense lines are separated by 33 Hz. No variations with temperature are observed for the other protons of the *p*-toluidine.

The behaviour in $(CD_3)_2CO$ of the ethylene protons is nearly the same as in $CD_2Cl_2$, with −25 °C as the coalescence temperature; however the most intense lines in the AA′BB′ system at −40 °C are separated by 5 Hz. In the same solvent, the amine protons show a coupling with $^{195}$Pt below −20 °C.

In the $^1$H NMR spectra of 2, the amine protons show a behaviour very similar to that observed for 1. As expected, no coalescence phenomena for the olefin protons of 2 are observed on lowering the temperature.

By contrast to what was observed for the complex 1, the $^1$H NMR spectrum of 3 in $CDCl_3$ does not show coalescence phenomena for either the amine or the olefin protons at temperatures between +50 and −60 °C. The resonances for the amine and olefin protons, as well as those of methylene protons, of the complex 3 at +50 °C, are shown in Fig. 2. The absorption of the amine protons, indicated as $H_A$ and $H_B$, are two doublets centered at $\delta$ 4.69 and $\delta$ 6.22 ppm, respectively, with a geminal coupling constant of 10 Hz, and $^{195}$Pt-coupling constants of 70 Hz for $H_B$ and of 55 Hz for $H_A$ [8]. The $H_B$ proton shows a remarkable down-field shift from $\delta$

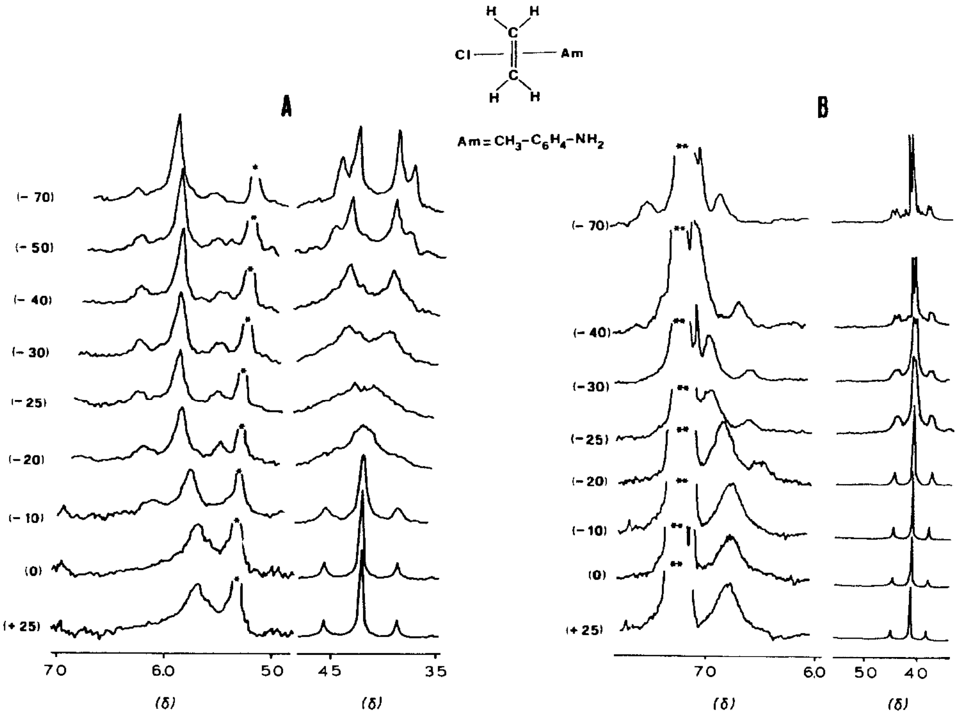


Fig. 1. $^1$H NMR spectra at 100 MHz for *cis*-dichloro(*p*-toluidine)(ethylene)platinum(II), complex 1, in $CD_2Cl_2$ (A) and in $(CD_3)_2CO$ (B) at various temperatures. The temperatures (°C) are indicated in parentheses, and $\delta$ in ppm from TMS. (★, signal of the solvent; ★★, resonances of the aromatic protons of the *p*-toluidine)

6.22 ppm at +50 °C to $\delta$ 6.66 ppm at −60 °C, while only a slight effect of the change of temperature is observed for the $H_A$ proton.

The vinyl $H_1$ proton resonance is a double doublet centered at $\delta$ 3.42 ppm, with $J(H_1, H_2)$ 2.4 Hz, $J(H_1, H_3)$ 10.8 Hz, $J(H_1$ Pt) 57 Hz, and it moves to $\delta$ 3.33 ppm at −60 °C. The spectrum shows the absorption of the vinyl $H_2$ proton as a doublet at $\delta$ 3.98 ppm with $J(H_2, H_3)$ 4.4 Hz, $J(H_2$, Pt) 73 Hz for geminal coupling; its chemical shift is unchanged between +50 and −60 °C.

The double doublet at 6.66 ppm is the absorption of the $H_3$ proton ($J(H_3$, Pt) 70 Hz) and this too is not temperature-dependent.

The diastereotopic protons of the $-CH_2-O-$ methylene group give two well-separated sets of signals, centered at $\delta$ 4.36 and 4.16 ppm, $J_{gem}$ 10 Hz and $J(H, CH_3)$ 7 Hz. On going to lower temperatures the first multiplet is nearly unchanged in position, while the second shows an up-field shift to 3.83 ppm at −60 °C.

The amine protons of the complex 4 are not coupled with $^{195}Pt$ at room temperature; they show coupling below 0 °C and are shifted to low field by 0.3 ppm when the temperature is reduced to −70 °C. The absorption of the vinyl protons of the complex 4 are moderately affected by change in temperature; their chemical shifts at +25 °C are reported in Table 2 together with the corresponding parameters for *cis*-isomer, 3.

## Discussion

The temperature-variation profile shown in Fig. 1 for *cis*-dichloro(*p*-toluidine)(ethylene)platinum(II), complex 1, reflects the olefin ligand rotation. This rotation is slow on the NMR time scale below −25 °C. The energy barrier to rotation, calculated as $\Delta G^{\ddagger} = -RT\ln(\Delta\nu\pi h/2^{1/2}KT_c)$ [9], where $\Delta\nu$ is the relative chemical shift of the peaks at slow exchange and $T_c$ is the coalescence temperature, is $12.3 \pm 0.3$ kcal $mol^{-1}$ in $CD_2Cl_2$ and $13.2 \pm 0.3$ kcal $mol^{-1}$ in $(CD_3)_2CO$.

The absence of $^{195}Pt$-coupling with the amine protons above 0 °C in $CD_2Cl_2$ and above −10 °C in $(CD_3)_2CO$ indicates that the amine ligand undergoes a fast exchange reaction with the solvent above 0 °C or −10 °C, while this reaction is slow on the NMR time scale below these temperatures. An analogous behaviour of the amine protons is also observed for the complexes 2 and 4.

It is worth noting that the non-equivalence of the ethylene protons in the complex 1 was predicted but no confirmed by Cramer [6] many years ago: the use of a 60 MHz instrument and of acetone as solvent can account for the failure to observe the coalescence phenomena for the ethylene protons.

The invariance of the spectrum of 3 with the temperature and the non-equivalence of the $H_A$ and $H_B$ amine protons prove that the rotation of amine and vinyl ether ligands is restricted even at high temperatures. The remarkable difference in the chemical shifts of the amine protons at low temperatures ($\delta_{H_B} - \delta_{H_A}$ 1.95 ppm at −60 °C) as well as at high temperatures ($\delta_{H_B} - \delta_{H_A}$ 1.53 ppm at +50 °C) indicates their very different chemical environments and strongly supports the presence of an intramolecular hydrogen bond between the oxygen atom of the vinyl ether and one proton of the amine group, namely the $H_B$ proton which shows the resonance at lower field. Indeed a low-field shift of the $H_B$ proton resonance is observed on going to lower temperature, which is in keeping with an increase in the hydrogen bond strength.

These results lead to the conclusion that in the complex 3 only A, of the two

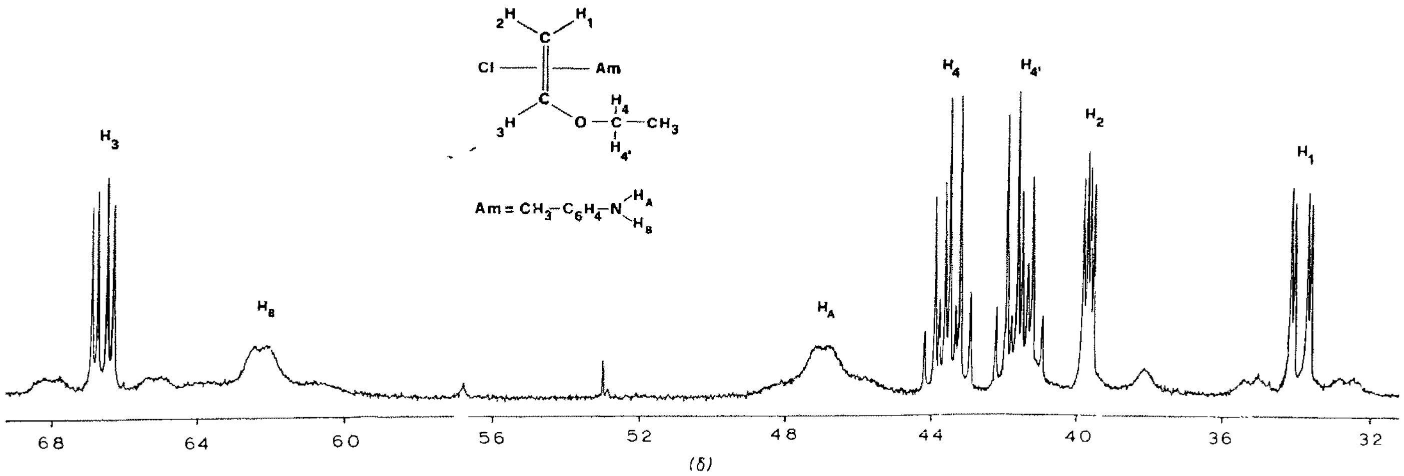


Fig. 2. $^1$H NMR spectrum at 250 MHz for *cis*-dichloro(*p*-toluidine)(ethyl vinyl ether)platinum(II), complex 3, in $CDCl_3$ at +50 °C, δ in ppm from TMS.

possible rotational isomers A and B (Scheme 2), is present in solution over the whole range of temperatures investigated. It has the amine and alkoxyl groups in a *cis*-position, i.e. in the arrangement which allows the formation of the hydrogen bond which limits the conformational freedom of the coordinated vinyl ether and amine. As shown in Fig. 3, the phenyl and the methylene groups lie on the same side of the coordination plane. While the proton $H_1$ points to the phenyl group, the proton $H_2$ is near to the chlorine atom. This is confirmed by comparing the vinyl proton resonances in complex 3 and in the analogous *trans*-complex, 4: the $H_1$ resonance is shifted upfield in the *cis*-complex relative to that in the *trans* complex, as expected on the basis of the shielding effect of the phenyl group of the amine [2], while the $H_2$ resonance is practically the same in the *cis* and *trans* isomers (Table 2).

In conclusion, it is clear that electronic effects are more important than steric ones in determining the conformation of the ligands in complexes in which a vinyl ether and a primary amine occupy *cis* positions. Indeed, owing to the formation of an O ··· H–N intramolecular hydrogen bond, the more hindered R–amine interaction is preferred to the less hindered R–Cl one.

## Experimental

*cis-Dichloro(p-toluidine)(ethylene)platinum(II), 1.* A solution of 5 g (12 mmol) of $K_2PtCl_4$ in 70 ml of water was treated with 1.3 g (12 mmol) of $p$-$CH_3C_6H_4NH_2$. After 24 h a second 1.3 g portion of of *p*-toluidine was added. The mixture was allowed to stand for 4 days at 5 °C and the precipitate was collected by filtration. This yellow powder was treated with 75 ml of 1 *M* aqueous HCl and refluxed for 4 h with vigorous stirring. The resulting yellow solution was separated by filtration from the black residue and shaken with ethylene at 25 °C and 40 p.s.i. pressure for 16 h. A pale yellow solid separated, which yielded 1.4 g (3.5 mmol) of the *cis*-dichloro(*p*-toluidine)(ethylene)platinum(II) complex, m.p. 158 °C, after recrystallisation from acetone/$Et_2O$ (1 : 1).

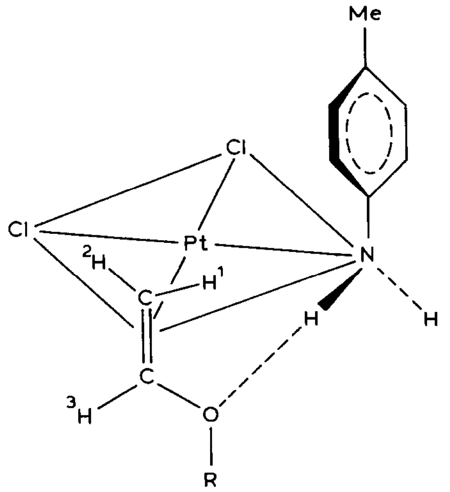


Fig. 3. Arrangement of the ligands in *cis*-dichloro(*p*-toluidine)(ethyl vinyl ether)platinum(II), complex 3. The *R* enantiomer of the complex is shown.

The $^1H$ NMR parameters of the complex in $CD_2Cl_2$ at 25 °C are listed in Table 1. Anal.: Found: C, 27.18; H, 3.42; Cl, 17.35. $C_9H_{13}NCl_2Pt$ calcd.: C, 26.94; H, 3.27; Cl, 17.68%.

*trans-Dichloro(p-toluidine)(ethylene)platinum(II), 2.* A solution of 0.7 g (6.5 mmol) of *p*-toluidine in 5 ml of 3% aqueos HCl was added to a solution of 2.4 g (6.5 mmol) of Zeise's salt in water. Addition of a 3% solution of KOH until pH = 6, gave a pale yellow precipitate. After crystallisation from $CH_2Cl_2/Et_2O$ (1 : 1), 2 g (4.9 mmol) of the complex were obtained as yellow crystals, m.p. 128 °C.

The $^1H$ NMR parameters at 25 °C in $CDCl_3$ are listed in Table 1. Anal.: Found: C, 26.34; H, 3.18; Cl, 17.15. $C_9H_{13}NCl_2Pt$ calcd.: C, 26.94; H, 3.27; Cl, 17.68%.

*cis-Dichloro(p-toluidine)(ethyl vinyl ether)platinum(II), 3.* *cis*-Dichloro(*p*-toluidine)(ethylene)platinum(II) (0.44 g, 1 mmol) was suspended in 5 ml of $CH_2Cl_2$ and 0.14 g (2 mmol) of ethyl vinyl ether were added. Ethylene was vigorously evolved and a complete solubilization of the solid was observed. After removal of the solvent at 25 °C (20 mmHg), the residue was crystallised from acetone/$Et_2O$ (1 : 2). *cis*-Dichloro(*p*-toluidine)(ethyl vinyl ether)platinum(II), (0.35 g, 0.8 mmol), was obtained as pale yellow crystals, m.p. 127 °C.

The $^1H$ NMR parameters of the complex, measured at 25 °C are listed in Table 2. Anal.: Found: C, 30.04; H, 3.92; N, 2.89. $C_{11}H_{17}PtCl_2NO$ calcd.: C, 29.67; H, 3.85; N, 3.14%.

*trans-Dichloro(p-toluidine)(ethyl vinyl ether)platinum(II), 4.* Using the above procedure, this complex was obtained from 0.44 g (1 mmol) of *trans*-dichloro(*p*-toluidine)(ethylene)platinum(II) in 5 ml of $CH_2Cl_2$ and 0.14 g (2 mmol) of ethyl vinyl ether. After solvent evaporation, an oil was obtained, which gave a yellow-brown amorphous solid from $CH_2Cl_2$/n-pentane (1 : 2). Yield 0.27 g (0.6 mmol), m.p. 56–58 °C.

The $^1H$ NMR parameters of the complex at 25 °C are listed in Table 2. Anal.: Found: C, 28.97; H, 3.73; N, 2.98. $C_{11}H_{17}PtCl_2NO$ calcd.: C, 29.67; H, 3.85; N, 3.14%.

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