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$\eta^1 \rightleftarrows \eta^3$ Conversion of $[(\eta^1\text{-allyl})Pt(PPh_3)(CH_3NC)Cl]$ in CH_2Cl_2 Solution

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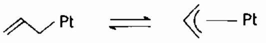
PMR and ^{31}P NMR spectroscopy on dichloromethane solution of the title compound indicates at room temperature extensive $\eta^1 \rightleftarrows \eta^3$ allyl conversion through PPh_3, Cl^- and CH_3NC ligand displacements. At lower temperatures this conversion occurs to a far lower extent and only involves chloride displacement; possible structure isomers of the title compound are also assumed at lower temperatures.

Introduction

The base-promoted $\eta^3 \leftrightarrows \eta^1$ interconversion of the allyl group has been shown to occur via intermediate four-coordinate η^1-allyl species for both Pd(II) and Pt(II) complexes. In the case of cationic Pt(II) derivatives of type $[(2\text{-methylallyl})Pt(L\text{–}L)(PPh_2Me)]^+PF_6^-$ (L–L = bis-diphenylphosphinoethane, bis-diphenylarsinoethane), the η^1-allyl nature of the 2-Me-allyl group could be shown by low temperature NMR spectra [1]. In other neutral Pt(II) allyl systems, such $\eta^3 \leftrightarrows \eta^1$ conversion was invoked to rationalize their NMR behaviour [2, 3].

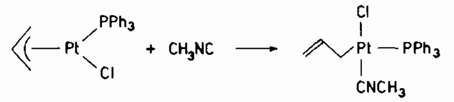
We have recently prepared the η^1-allyl Pt(II) complex $[(\eta^1\text{-allyl})Pt(PPh_3)(CH_3NC)Cl]$ (I), from the reaction of $[(\eta^3\text{-allyl})Pt(PPh_3)Cl]$ with CH_3NC [4]. An X-ray structure investigation of this product has shown unequivocally that in the solid state the σ-allyl group is bonded to platinum in *trans* position to the phosphine ligand, with the Pt–P bond distance being among the longest so far observed (2.359 (4) Å). Unlike *cis*-$[(\eta^1\text{-allyl})Pt(\text{isocyanide})_2Cl]$, which is stable in solution [5], this compound when dissolved in CH_2Cl_2 at room temperature undergoes a series of ligand displacements. This behaviour in solution is related to $\eta^1 \leftrightarrows \eta^3$ allyl conversion processes promoted by chloride and/or neutral ligand displacements in a possibly concerted ring closure by the olefinic double bond. Analogously the η^1-allyl compound *trans*-$[(\eta^1\text{-}CH_2CH{=}CHMe)Pt(PPh_3)_2Cl]$ undergoes $\eta^1 \rightleftarrows \eta^3$ conversion in solution [6, 7]. It appears, therefore, that the ancillary ligands in the η^1-allyl Pt(II) complexes are effective in promoting the ring closure by the allyl carbon–carbon double bond.

In the case of the title compound, the presence of different ancillary ligands was expected to provide a means of detecting all possible chemical species in solution. Thus, we have investigated thoroughly the solution behaviour of (I) and related species with the aim of gaining more insight into the nature of species involved in the $\eta^1 \rightleftarrows \eta^3$ allyl conversion:



Results and Discussion

Treatment of a dichloromethane solution of $[(\eta^3\text{-allyl})Pt(PPh_3)Cl]$ with an equimolar amount of isocyanide in ethyl ether leads to separation of a white solid. The precipitation can be completed by dilution with ether after the solution has been left aside overnight:



III I

Analytical data for complex (I) agree with the formulation $[(C_3H_5)Pt(PPh_3)(CH_3NC)Cl]$. The η^1-allylic nature of the C_3H_5 group is indicated by the presence of uncoordinate double bond stretch at 1615 cm^{-1} in the IR spectrum [5, 8]. Also, $\nu_{C\equiv N}$ of the isocyanide (2210 cm^{-1})** and $\nu_{Pt\text{–}Cl}$ (324 cm^{-1}) are observed. This latter frequency excludes that the chloride ion is in *trans* position to a σ Pt–C bond in the solid state [9].

Dichloromethane solutions of (I) are conducting (Λ = 40 mol^{-1} cm^2 Ω^{-1}), in agreement with partial chloride dissociation. The ^1H NMR spectrum (Figure 1) at room temperature in CD_2Cl_2 solution shows the

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**In reference [4] this value was misprinted as 2260.

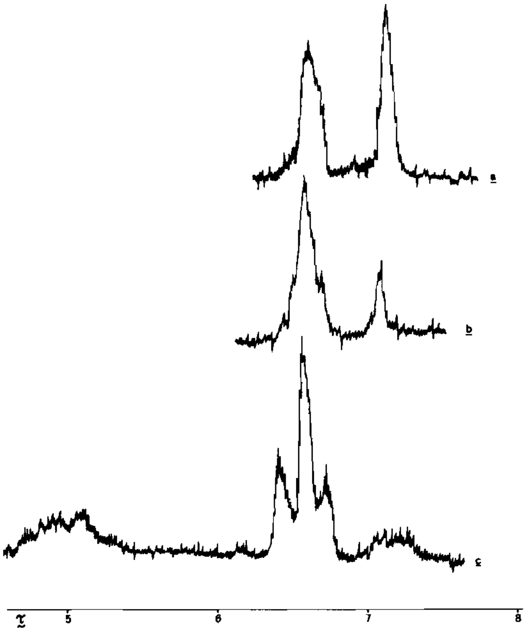


Figure 1. Variable temperature ^1H NMR spectra of $[(\eta^1$-allyl)Pt(CH$_3$NC)(PPh$_3$)Cl] at 38 (*a*), 10 (*b*), and −65 °C (*c*).

resonance of isocyanide methyl protons as two distinct signals (6.5–6.7 and 7.09τ), the latter corresponding to free CH_3CN [10]; the low field peak is in the range of Pt(II) coordinated CH_3NC [11], although the ^{195}Pt–H coupling is lost and the absorption is rather broad. The allyl proton resonances appear as very broad signals, virtually lost in the noise.

The results indicate that the equilibrium between free and coordinated CH_3NC is slow, whereas those among Pt-coordinated isocyanide species might be fast (no ^{195}Pt satellites on the peak at 6.5–6.7τ are observed). Unfortunately, the chemical shift of coordinated CH_3NC is not very sensitive to the nature of the other ligands, so that ^{195}Pt patterns of the isocyanide resonance in Pt–$CNCH_3$ coordinated species might be overlapped.

On cooling, the PMR spectrum shows a decrease of the free CH_3NC peak with concomitant increase of the amount of coordinated isocyanide (Figure 1). At −65 °C the ^{195}Pt patterns become evident, though somewhat broader than usually (J_{Pt-H} = 19 Hz). The resonance for the C_3H_5 group appears at 7.10–7.30, 4.80–5.20, and 3.50–3.90τ, and integrates roughly as 2/2/1. However, the signals are quite broad and the fine structure is lost, therefore they do not provide any conclusive evidence for the η^1-allyl complex (**I**) being the only species in solution.

Complex (**I**) reacts with $AgPF_6$ in CH_2Cl_2 solution to give immediate precipitation of AgCl. From the solution a white compound can be separated which was identified as the cationic compound $[(\eta^3$-allyl)-Pt(PPh$_3$)(CH$_3$NC)]$^+$PF$_6^-$, (**II**), by elemental analysis and spectral data.

The PMR spectrum of (**II**) in CD_2Cl_2 solution at r.t. shows resonances of isocyanide protons at 6.72τ ($^3J_{Pt-H}$ = 19 Hz) and of PPh_3 protons in the range 2.3–2.7τ. The allyl protons appear in the regions 7.5–7.3, 6.0–6.3 and 4.5–5.1τ as broad complex multiplets, in substantial agreement with a η^3-allyl configuration of the type described for numerous asymmetric allyl derivatives with static configuration [12].

Compound (**II**) readily reacts in CH_2Cl_2 solution with the stoichiometric amount of $AsPh_4Cl$ to give $[(\eta^1$-allyl)Pt(CH$_3$NC)(PPh$_3$)Cl], (**I**), in virtually quantitative yield.

These findings demonstrate the presence in solution of the following equilibria:

$$\begin{array}{ll} \underset{\textbf{III}}{[(\eta^3\text{-allyl})\mathrm{Pt(PPh_3)Cl}]} \underset{(-\mathrm{CH_3NC})}{\overset{(+\mathrm{CH_3NC})}{\rightleftarrows}} & \\ & [(\eta^1\text{-allyl})\mathrm{Pt(CH_3NC)(PPh_3)Cl}] \\ & \quad (-\mathrm{Cl^-}) \Big\downarrow\!\Big\uparrow (+\mathrm{Cl^-}) \quad \textbf{I} \\ & [(\eta^3\text{-allyl})\mathrm{Pt(CH_3NC)(PPh_3)}]^+ \\ & \qquad \textbf{II} \end{array}$$

The possibility to obtain quantitatively a single species depends on the experimental conditions. This set of equilibria is similar to other well recognized systems [1, 13, 14], and our results may be taken as a border line case; in fact we were able to isolate in the solid state complexes (**I**), (**II**) and (**III**).

Since the X-ray structure determination of (**I**) has shown a fairly long Pt–P distance [4], participation of PPh_3 to the equilibria reported above cannot be ruled out. Moreover, the ^{31}P NMR spectrum in CH_2Cl_2 of compound (**III**) and (**II**) shows the phosphorus resonance at +22.8 ppm with J_{Pt-P} = 4440 Hz and at +16.9 ppm with J_{Pt-P} = 3933 Hz, respectively. This indicates a static ligand organization, in agreement with their static allyl configuration.

At variance, the ^{31}P NMR spectrum of compound (**I**) at room temperature shows a quite broad signal centered at +17.7 ppm without ^{195}Pt satellites. On cooling, the spectrum *c* of Figure 2 was obtained, in which the most prominent feature is the presence of two peaks at +16.9 and +18.3 ppm. The latter resonance displays the ^{195}Pt patterns (J_{Pt-P} = 1552 Hz) and is attributable to species (**I**). As a matter of fact, both phosphorus chemical shift and the J_{Pt-P} value are in agreement with those reported for Pt(II) complexes having PPh_3 and σ-alkyl groups in *trans* position [15, 16].

The lack of ^{195}Pt patterns for the resonance at +16.9 ppm cannot be immediately rationalized and prompted us to investigate the behaviour of compound (**II**) in CH_2Cl_2 solution in the presence of

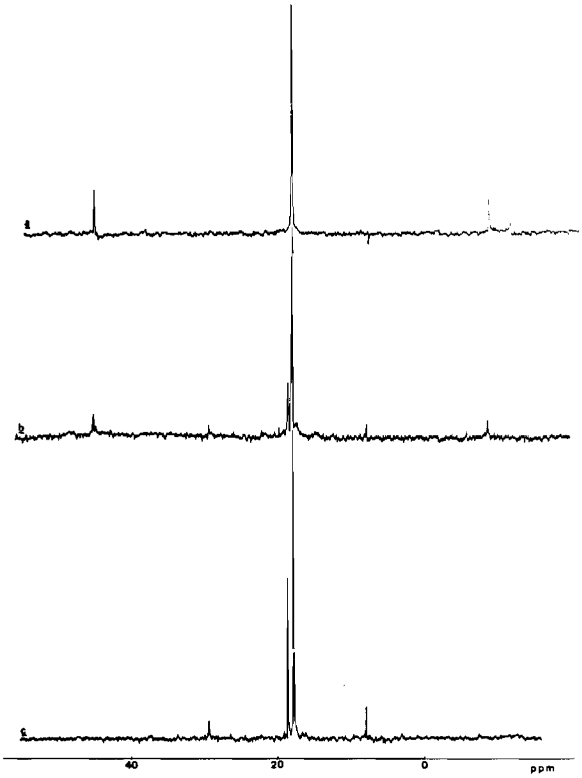
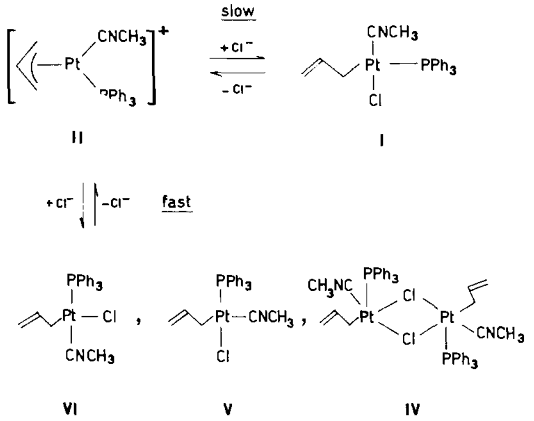


Figure 2. ^{31}P NMR spectra of $[(\eta^3\text{-allyl})Pt(CH_3NC)(PPh_3)]^+$ at –55 °C in the presence of Cl^-: *a*, $Cl^-/Pt = 0.2$; *b*, $Cl^-/Pt = 0.7$; *c*, $Cl^-/Pt = 1.0$.

different amounts of added Cl^-. At room temperature addition of Cl^- to the cationic complex (**II**) caused disappearance of the ^{195}Pt coupling with ^{31}P and the spectra vary appreciably with temperature. Thus addition of 0.2 mol of Cl^- per Pt atom caused disappearance of ^{195}Pt satellites at r.t., but at low temperature these patterns are present (spectrum *a* of Figure 2). Addition of about 0.7 mol of Cl^-/Pt gave, at 55 °C, the resonances of (**I**) and (**II**) flanked by ^{195}Pt satellites (spectrum *b* of Figure 2). Further addition of Cl^- ($Pt/Cl^- = 1$) caused an increase of the signal at 18.3 ppm and the spectrum is the same as that obtained for complex (**I**) at the same temperature (spectrum *c* of Figure 2).

The combined results of conductivity, ^1H and ^{31}P NMR indicate that all the ancillary ligands CH_3NC, PPh_3 and Cl^- at room temperature are interested in the $\eta^1 \rightleftarrows \eta^3$ allyl conversion of compound (**I**).

At low temperature such interconversion does not imply exchange of PPh_3 or CH_3CN. In fact spectrum *c* of Figure 1 and spectrum *b* of Figure 2 show CH_3NC and PPh_3 respectively completely coordinated to the central metal. The lack of ^{195}Pt patterns for the resonance at +16.9 ppm in the ^{31}P NMR spectrum at –55 °C of compound (**I**), cannot be interpreted in terms of formation of intermediates directly interested in the equilibrium between (**I**) and (**II**). Indeed at low temperature this process is slow as shown by spectrum *b* of Figure 2 and this implies that the possible reaction intermediates of this $\eta^1 \rightleftarrows \eta^3$ allyl interconversion are transient species. On the other hand, as the concentration of Cl^- increases, we cannot exclude that species (**II**) is interested in fast equilibria involving Pt(II) complexes different from (**I**). Dimeric 5-coordinate intermediates of type (**IV**) and structural isomers of (**I**), such as (**V**) and (**VI**), may be interested in such equilibria:



It has to be noted that chemical species analogous to (**IV**) were reported by Vrieze *et al.* [17] and the occurrence of structural isomers of type (**V**) and (**VI**) has been very recently established [18] in the case of the η^1-allyl complexes $[(CH_2CHCHPh)Pt(PPh_3)_2Cl]$.

Experimental

^1H NMR spectra were recorded in CD_2Cl_2 solutions with a Varian NV-14 60 MHz spectrometer using TMS as internal standard. ^{31}P NMR spectra were made in CH_2Cl_2 solutions containing *ca.* 15% of $^2H_6$ benzene to provide a ^2H field-frequency lock. The data were collected with a Bruker WP-60 spectrometer operating at 24.28 MHz, in Fourier-transform mode, with ^1H complete decoupling. 85% H_3PO_4 was used as external standard. The sign convention recommended by I.U.P.A.C. was adopted [19]. IR spectra were registered on a Perkin–Elmer 457 Spectrophotometer in Nujol mulls.

Materials

$[Pt(allyl)Cl]_4$ was prepared as previously described [20]. Methylisocyanide was prepared according to the literature methods [10]. $[Pt(allyl)(PPh_3)Cl]$ was obtained following the same procedure described in the literature [12].

Compound (I)

The CH_2Cl_2 solution of $[(\eta^3\text{-allyl})Pt(PPh_3)Cl]$ (535 mg, 1 mmol) was treated under nitrogen with CH_3NC (41 mg, 1 mmol) dissolved in ethyl ether with stirring. The mixture turns yellow with eventual precipitation of a yellow product. On standing overnight the solution turns colourless and dilution with ether gives precipitation of the white compound. Yield 75%. *Anal.* Found: C 47.55; H 4.04; N 2.61; Cl 5.98%; $PtC_{23}H_{23}NPCl$ requires: C 48.06, H. 4.00; N 2.34; Cl 6.16%.

Compound (II)

To a CH_2Cl_2 solution of $[(\eta^1\text{-allyl})Pt(PPh_3)(CH_3NC)Cl]$ (288 mg, 0.5 mmol) was added anhydrous $AgPF_6$ (152 mg, 0.6 mmol) with stirring under nitrogen. Immediate formation of AgCl occurred which was filtered off. On adding ethyl ether to the clear solution the white product was separated. The complex was then filtered and dried under vacuum. Yield = 81%. *Anal.* Found: C 40.40; H 3.46; N 2.00%; $PtC_{23}H_{23}NP_2F_6$ requires: C 40.33; H 3.39; N 2.04%. IR: $\nu_{C\equiv N}$ of isocyanide 2225 cm^{-1}.

Reaction of Compound (II) with $AsPh_4Cl$

To a CH_2Cl_2 solution of $[(\eta^3\text{-allyl})Pt(PPh_3)(CH_3NC)]^+PF_6^-$ (173 mg, 0.3 mmol) was added $AsPh_4Cl \cdot H_2O$ (126 mg, 0.3 mmol). The solution was taken to dryness and the solid was extracted twice with 50 ml of toluene. From this solution after concentration to small volume under reduced pressure and addition of n-hexane, the white compound (**I**) was obtained. It was characterized by comparison of the IR spectra with an authentic sample.

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