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Isomerization, Ligand Exchange and Solvent Effect in the $\eta^1 \rightleftarrows \eta^3$ Allyl Conversion of $[(\eta^1\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)Cl]$

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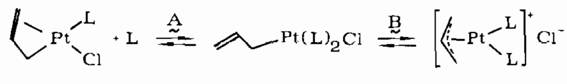
The behaviour of the title compound was studied in toluene and in CH_2Cl_2 solution by ^1H and ^{31}P NMR spectroscopy at various temperatures. In toluene at low temperature only one η^1-allyl species is present, whereas in CH_2Cl_2 five species are present, among which are the possible isomers of $[(\eta^1\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)Cl]$, $[(\eta^3\text{-}C_3H_5)Pt(PPh_3)_2]Cl$ and $[(\eta^1\text{-}C_3H_5)Pt(2,6\text{-}Me_2C_6H_3NC)_2Cl]$. This behaviour has been discussed in terms of ligand exchange and isomerization reactions which take place along with the $\eta^1 \rightleftarrows \eta^3$ allyl conversion.

Introduction

In the context of our studies on allyl complexes of Pt(II) [1, 2] we became interested in the synthesis of η^1-allyl species [3, 4]. Four coordinate Pt(II) η^1-allyl derivatives were prepared by oxidative addition of allyl halides to Pt(0) complexes [5–9]. η^1-allyl species have also been obtained by the reaction of neutral donor ligands with cationic [10] or neutral [3, 4] η^3-allyl platinum(II) complexes. We assumed that in the latter case the asymmetry induced by the two different ancillary ligands on the allyl moiety is the driving force of the reaction [3].

We exploited the ability of neutral entering ligands to displace the "olefinic" end of the formally $\sigma + \pi$ bonded allyl group in $[(\eta^3\text{-allyl})Pt(L)Cl]$:



The formation of the η^1-allyl species, according to equilibrium **A**, requires that L be a strongly coordinating ligand [11, 12]. Once formed, however, the η^1-allyl derivative may undergo $\eta^1 \rightleftarrows \eta^3$ conversion through displacement of chloride ion. Such a conversion appears to be a frequent feature of η^1-allyl Pt(II) derivatives [4, 6, 13].

In other words, a neutral entering ligand may either displace the "olefinic" end of the allyl moiety (yielding η^1-allyl species) or the chloride ion (yielding cationic η^3-allyl derivatives). We have also found that for $[(\eta^1\text{-allyl})Pt(PPh_3)(MeNC)Cl]$ equilibrium **B** is operating in CH_2Cl_2 solution even at low temperature, when equilibrium **A** is driven completely to the right [13].

Equilibrium **B** should in principle be affected by a variety of factors such as the nature of ancillary ligands, possible isomerization reactions [7], formation of five-coordinate adducts or dimers [14] as intermediates, and nature of the solvent [6].

In a effort to detect the specific role of such factors, we have studied by NMR spectroscopy the solution behaviour of the new complex $[(\eta^1\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)Cl]$ (**1**) which, unlike its MeNC analog, is very soluble even in apolar solvents. Apart from this experimental advantage, this compound contains an isocyanide with electronic and steric properties different from MeNC, thereby providing a means to gain additional and hopefully conclusive evidence on the factors affecting equilibrium **B**.

Results and Discussion

Preparation of Complexes and ^1H NMR Measurements

The complex $[(\eta^1\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)Cl]$ (**1**) was synthesized as the corresponding MeNC species. Its IR spectrum (nujol mull) displays the $\nu_{C=C}$ of uncoordinated double bond of the allyl group at 1615 cm^{-1} [15], the $\nu_{C\equiv N}$ of coordinated isocyanide at 2160 cm^{-1}, and ν_{Pt-Cl} at 320 cm^{-1}. The $\nu_{C\equiv N}$ absorption in toluene still appears at 2160 cm^{-1} as one single band, indicating that no free isocyanide is present in solution in equilibrium with Pt(II)-coordinated isocyanide.

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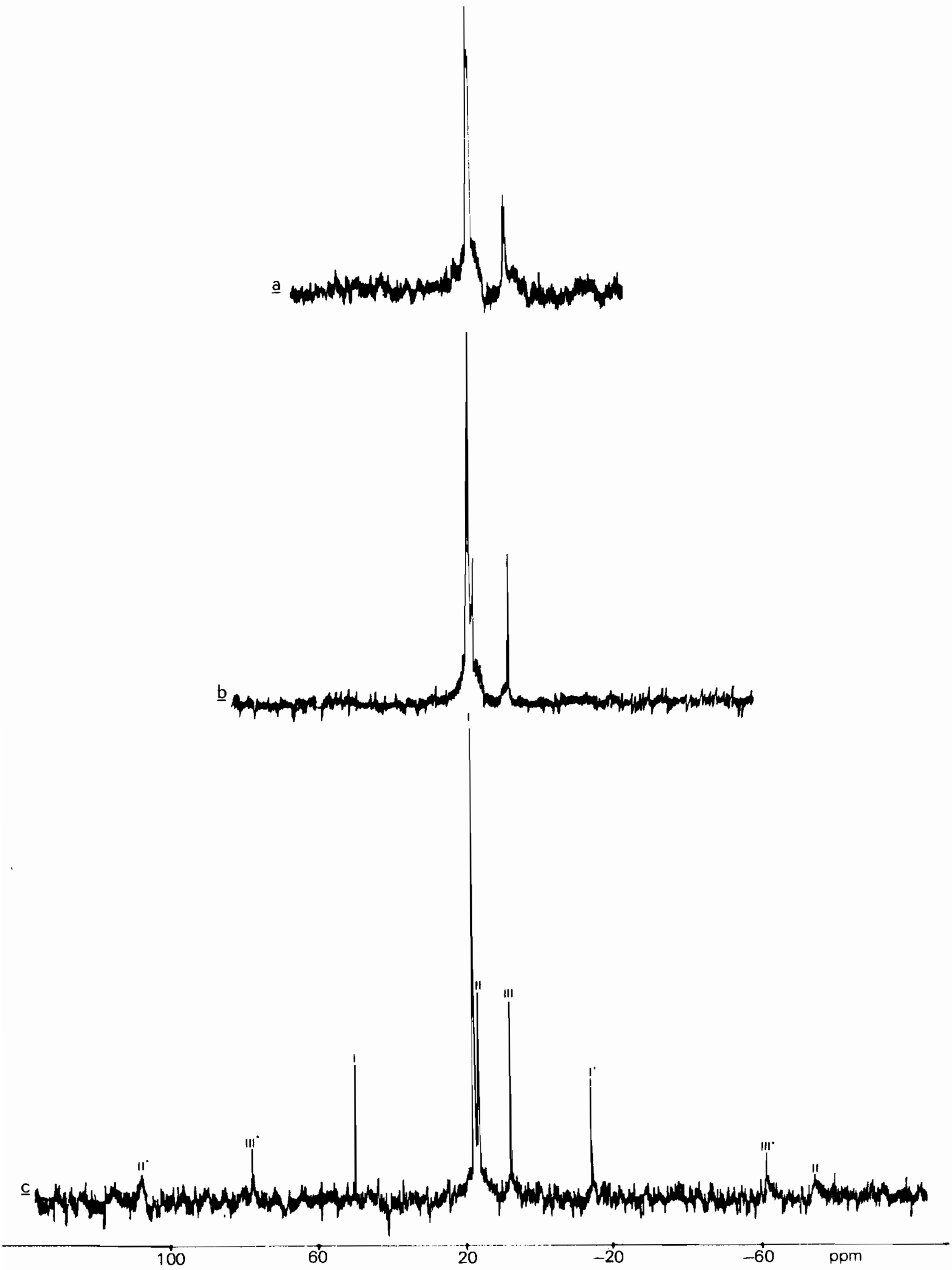


Figure 1. ^{31}P NMR spectra of complex [(η^1-allyl)Pt(PPh_3)(2,6-$Me_2C_6H_3NC$)Cl] (**1**) at 32 (*a*), −10 (*b*) and −45 °C (*c*).

The complex $(C_3H_5)Pt(PPh_3)_2Cl$ (**2**) was prepared by the addition of a stoichiometric amount of PPh_3 to a CH_2Cl_2 solution of $[(\eta^3\text{-allyl})Pt(PPh_3)Cl]$. Its IR spectrum in Nujol mull shows a $\nu_{C=C}$ absorption at 1620 cm^{-1} due to the free olefinic tooth of the allyl group and a band at 265 cm^{-1} due to ν_{Pt-Cl} (indicative of planar *trans*- configuration [16]). Conductivity measurements in CH_2Cl_2 and ^{31}P NMR data (+15,23 ppm and J_{Pt-P} = 3966 Hz) indicate the formulation $[(\eta^3\text{-}C_3H_5)Pt(PPh_3)_2]^+Cl^-$ for this complex in solution [17].

The complex $[(\eta^3\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)]^+ BF_4^-$ was obtained by treatment of (**1**) with $AgBF_4$.

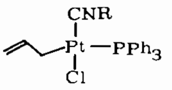
Complex (**1**) is dissociated only to a small extent in CH_2Cl_2, as shown by conductivity measurements, unlike its MeNC analog [13].

^1H NMR spectra of (**1**) in $CD_3C_6D_5$ solution show the phenyl proton resonances of PPh_3 and isocyanide in the range 2.3–2.9 τ and the methyl protons of $Me_2C_6H_3NC$ at 7.5 τ. The allyl protons are almost undetectable. On cooling, the allyl proton resonances show up in the regions 6.8–7.0, 6.2–5.5 and 4.5–3.9 τ but the signals are broad and no fine structure can be observed. These scant data do not allow us to gain further evidence on the behaviour of (**1**) in solution.

^{31}P NMR Measurements

In toluene solution

The ^{31}P NMR spectrum of (**1**) in toluene at room temperature shows a single broad peak centered at +18.10 ppm (no J_{Pt-P} is observed). At −35 °C this peak sharpens and is flanked by ^{195}Pt satellites (J_{Pt-P} = 1538 Hz). This indicates that the only species present at low temperature is the η^1-allyl complex (**1**), with the PPh_3 being in *trans* position to the σ-bonded allyl moiety, as shown by the J_{Pt-P} value [7, 13] (structure **I**).



I

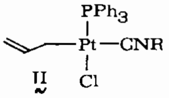
The failure to observe any Pt–P coupling at room temperature can be accounted for simply by the PPh_3 exchange concomitant to $\eta^1 \rightleftarrows \eta^3$ conversion (*cf.* equilibrium A). Thus, unlike for *trans*-$[(\eta^1\text{–}CH_2\text{–}CH{=}CHCH_3)Pt(PPh_3)_2Cl]$ in benzene [6], in our case the ligand being displaced in such conversion is the one *trans* to the η^1-allyl group.

In dichloromethane solution

Figure 1 shows the ^{31}P spectra of (**1**) at various temperatures. At 32 °C this spectrum consists of two broad signals centered at +18.02 and at +8.30 ppm (Figure 1*a*). On cooling (Figure 1*b*) the signals sharpen and the spectrum at −45 °C (Figure 1*c*) indicates the presence of three species being involved in slow equilibria (each signal is now flanked by the corresponding ^{195}Pt patterns). It is clear that the species at +18.55 and +16.89 ppm are generated by the signal at +18.02 ppm of spectrum *a* whereas that at +8.59 ppm arises from the peak at +8.30 ppm.

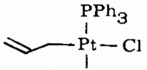
The most prominent species at +18.55 ppm (J_{Pt-P} = 1540 Hz) can be safely identified as the isomer **I**. A compound of this type was found to participate in slow equilibrium with the cationic complex $[(\eta^3\text{-allyl})Pt(PPh_3)(MeNC)]^+Cl^-$ in CH_2Cl_2 at room temperature. This involves Cl^- exchange with the exclusion of PPh_3 or isocyanide displacements [13]. Such an equilibrium is ruled out in the present case since none of the signals of spectrum *c* corresponds to any species $[(\eta^3\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)]^+$ independently prepared (^{31}P resonance at +15.52 ppm, J_{Pt-P} = 3928 Hz).

The resonance at +16.89 ppm (J_{Pt-P} = 4398 Hz) can be assigned to isomer **II** of (**1**), as indicated by the fact that the J_{Pt-P} for the ^{31}P resonance is close to that of an analogous η^1-allyl species, for which the chloride has been shown to be in *trans* position to PPh_3 [7].



II

The remaining signal at 8.59 ppm (J_{Pt-P} = 3350 Hz) can be assigned to isomer **III** of (**1**)



III

As a matter of fact, a low value of J_{Pt-P} is expected for isomer **III** on the basis of the fairly large *trans* influence of isocyanide groups [18].

Upon an almost twofold increase in the concentration of (**1**) the spectrum of Figure 2 is obtained which, compared with spectrum *c* of Figure 1, shows that the ratio of **I** and **II** concentrations has remained constant, whereas the intensity of the peak at +8.59 ppm has decreased along with the appearance of a new signal at +15.23 ppm (J_{Pt-P} = 3966 Hz).

Owing to the ligand exchange occurring in CH_2Cl_2 solution at room temperature and to the complexity of the system, a reaction of type:

$$2[(\eta^1\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)Cl] \longrightarrow$$

$$[(\eta^3\text{-allyl})Pt(PPh_3)_2]^+Cl^- +$$

2

$$[(\eta^1\text{-allyl})Pt(2,6\text{-}Me_2C_6H_3NC)_2Cl]$$

3

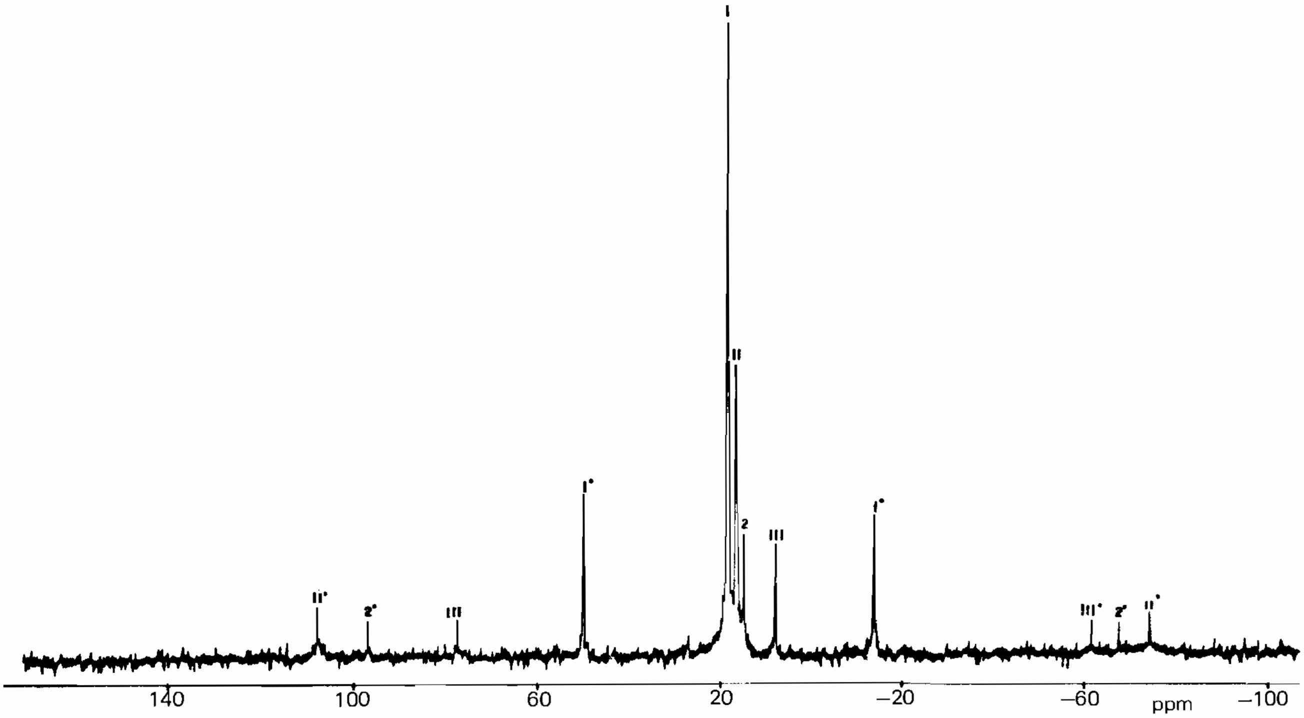
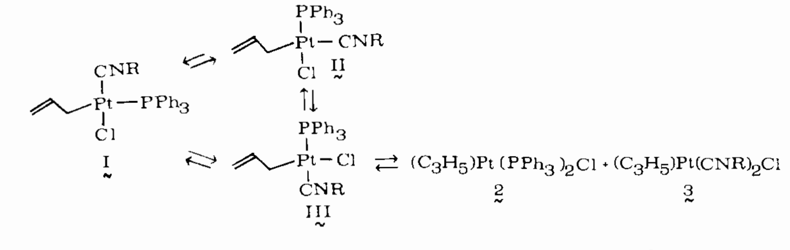


Figure 2. ^{31}P NMR spectrum of complex $[(\eta^1\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)Cl]$ (**1**) at −45 °C with a concentration of (**1**) ~ twice the concentration used for spectrum *c* of Figure 1.

cannot be *a priori* ruled out. The ^{31}P NMR spectrum of (**2**) in CH_2Cl_2 at −45 °C shows a single resonance at +15.23 ppm (J_{Pt-P} = 3966 Hz). These values are identical with the new signal appearing in the spectrum of Figure 2, implying the presence of an equimolar amount of (**3**) in solution.

The species (**2**), (**3**) and isomer **III** of (**1**) (whose signals are generated from the resonance at +8.30 ppm of the room temperature spectrum) are involved in a slow equilibrium at low temperature which depends on the total concentration of (**1**). Therefore, the processes at low temperature can be outlined in the following scheme:



At room temperature all these equilibria are fast, with the exception of **I** ⇄ **III** and **II** ⇄ **III**. This parallels the results pertaining to $[(\eta^1\text{-}CH_2\text{—}CH\text{=}CHCH_3)Pt(PPh_3)_2Cl]$ for which *cis* ⇄ *trans* isomerization was found to require a high activation energy [6].

Since all the above equilibria take place at low temperature without PPh_3 exchange, η^3-allyl cationic species can be assumed as transient intermediates in equilibria **I** ⇄ **II**, **I** ⇄ **III**, and **II** ⇄ **III**, whereas the equilibrium between **III** and (**2**) + (**3**) probably involves a dimeric intermediate.

Conclusions

It is noteworthy that a simple change of the nature of the isocyanide ligand causes a dramatic change in the behaviour of these η^1-allyl Pt(II) complexes in solution. For instance, we failed to detect any cationic η^3-allyl species even at low temperature. This is likely to be related to the fact that $2,6\text{-}Me_2C_6H_3NC$ is a better π acceptor than MeNC. As a consequence, the *d* metal orbitals become less available for the bonding with the allyl moiety in the η^3-allyl species, resulting in a overall destabilization of possible η^3-allyl intermediates.

Experimental

Spectral Measurements

^1H NMR spectra were recorded in $^2H_8$-toluene solution with a Varian NV 14 spectrometer using TMS as internal standard. ^{31}P NMR spectra were obtained in CH_2Cl_2 or toluene solutions containing *ca.* 15% of $^2H_6$-benzene to provide a ^2H field-frequency lock. The spectra were registered 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 IUPAC recommended sign convention that increasing frequency is positive was adopted [19].

IR spectra were recorded with a Perkin–Elmer 457 spectrophotometer. Conductivity experiments were made using a LKB Conductolyzer type 5300B.

Materials

$[Pt(allyl)(PPh_3)Cl]$ [20] and $[Pt(allyl)Cl]_4$ [21] were prepared as previously described. 2,6-$Me_2C_6H_3NC$ was commercially purchased (Fluka).

$[(\eta^1\text{-}C_3H_5)Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)Cl]$

A toluene solution of $[(\eta^3\text{-allyl})Pt(PPh_3)Cl]$ (1068 mg, 2 mmol) was treated with 2,6-$Me_2C_6H_3NC$ (262 mg, 2 mmol) under nitrogen with stirring. The mixture was left aside for 12 hr and then evaporated to a small volume under reduced pressure. On adding petroleum ether precipitation of the pale yellow compound occurs (yield 78%, m.p. 150 °C dec.). The same reaction may be run even in CH_2Cl_2. *Anal.* Found: C 54.30, H 4.42; Cl 5.30; $PtC_{30}H_{29}PNCl$ requires: C 54.17, H 4.39, Cl 5.33%.

$(C_3H_5)Pt(PPh_3)_2Cl$

To a stirred CH_2Cl_2 solution of $[(\eta^3\text{-}C_3H_5)Pt(PPh_3)Cl]$ (535 mg, 1 mmol in 30 cm^3) was added dropwise 1 mmol (263 mg) of PPh_3 in CH_2Cl_2 solution (20 cm^3). The resulting solution was evaporated to a small volume from which the white product crystallizes by addition of n-hexane (yield 83%, m.p. 200 °C). *Anal.* Found: C 59.26, H 4.61. Cl 4.17; $PtC_{39}H_{35}P_2Cl$ requires: C 58.83; H 4.42, Cl 4.45%.

$[(\eta^3\text{-allyl})Pt(PPh_3)(2,6\text{-}Me_2C_6H_3NC)]^+BF_4^-$

To a CH_2Cl_2 solution of complex (**1**) (333 mg, 0.5 mmol) was added $AgBF_4$ (97 mg, 0.5 mmol) with stirring under nitrogen. The precipitated AgCl was filtered off and on adding ethyl ether the white complex was separated from the solution, filtered off and dried under vacuum (yield 74%, m.p. 220 °C dec.). *Anal.* Found: C 49.85. H 3.83, N 1.70; $PtC_{30}H_{29}PNBF_4$ requires: C 50.29, H, 4.07, N 1.95%. IR $\nu_{C\equiv N}$ of isocyanide 2190 cm^{-1}.

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17 It is worth mentioning that the reaction of C_3H_5Cl with $[Pt(PPh_3)_4]$ in $CHCl_3$ yields a complex corresponding to the formulation $[(\eta^3\text{-}C_3H_5)Pt(PPh_3)_2]^+Cl^-$ also in the solid state. In fact, its IR spectrum in nujol mull shows no bands in the regions of C=C and Pt–Cl stretchings [8]. Moreover, the reaction of C_3H_5Cl with $[Pt(PPh_3)_3]$ in ethyl ether yields a complex whose IR spectrum in nujol mull is indicative of a five-coordinate structure of type $[(\eta^3\text{-}C_3H_5)Pt(PPh_3)_2\ Cl]$ [9].
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