

C–C coupling of aryl groups and allyl derivatives on Pt(II)-phenanthroline fragments: crystal and molecular structure of the *tbp* $[(\eta^1, \eta^2\text{-2-allyl, 5-methyl-phenyl})\text{i}odo(1, 10\text{-phenanthroline})\text{platinum(II)}]$ complex containing the N–N ligand in axial-equatorial coordination mode

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Abstract

The reactions between allyl compounds $\text{CH}_2=\text{CHCH}_2\text{Fn}$ bearing electron-withdrawing functional (Fn) groups and cationic $\{\text{Pt}(\text{aryl})(1,10\text{-phenanthroline})\}^+$ fragments generated in situ are described. The aryl and platinum addition to the terminal and, respectively, internal unsaturated carbon is generally observed. The subsequent $\text{H}-\text{C}_{\text{aryl}}$ bond activation, followed by HFn elimination, affords the *ortho* organic fragment (*Pt*)– $\text{aryl}-\text{CH}_2\text{CH}=\text{CH}_2$ η^1, η^2 -chelate to the platinum. This process does not occur when the regiochemistry is of Markownikov type and the $\text{Pt}-\text{CH}_2\text{CH}(\text{aryl})\text{CH}_2\text{Fn}$ fragment is formed. The described results are compared with those concerning the behaviour of unsubstituted α -olefins. The X-ray crystal structure of the title five-coordinate complex shows a distorted *tbp* arrangement of the ligands with the iodide in the equatorial plane and the unusual axial-equatorial coordination mode of the 1,10-phenanthroline.

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1. Introduction

The insertion of a C=C bond in a nearby metal-carbon σ -bond on a metal centre is a pivotal step of most important catalytic cycles prompted by transition elements [1]. In the olefin polymerisation catalysis the σ -bound group is of alkylic type and the insertion

replicates extensively to afford the polymeric chain. When the insertion is followed by hydrogen shift and reductive elimination, an olefin moiety higher than the starting one is the final product. The last reaction pathway is typically observed, mainly in late transition ions chemistry, when aryl–metal bonds are involved. The Heck processes are the most outstanding examples of this behaviour [2].

In this paper attention is focused on the insertion involving aryl groups and allyl derivatives. As for

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previous studies in this field from this laboratory [3] we recall that investigation of the links between the electronic and steric features of the two interacting moieties and the regiochemistry and stereochemistry of the reaction has been grounded on stoichiometric processes, more suited to the characterisation of possible intermediates. Thus, the choice of the metal and of the ancillary ligands was tailored to obtain moderate reactivity of the two interacting organic moieties while avoiding inertness. In this work we have attempted to examine the insertion behaviour in $\{\text{Pt}(\text{aryl})(\text{N}-\text{N})\}^+$ cations ($\text{N}-\text{N}$ = chelating nitrogen ligand) analogous to species previously used to assess the reactivity of α -olefins. For this type of complex substrate clean insertion of $\text{R}-\text{CH}=\text{CH}_2$ ($\text{R} = \text{H}$, hydrocarbyl) in $\text{Pt}-\text{aryl}$ bond to give the sequence $\text{Pt}-\text{CH}_2-\text{CHR}-\text{aryl}$ was previously [3c] observed, while if an alkyl group was present in place of the aryl no insertion ensued [4] (Scheme 1).

The choice of 1,10-phenanthroline (phen), a rigid chelate, as ancillary ligand was dictated by the need of favouring the contemporary presence in adjacent sites of the two organic moieties. Phenanthroline, with low trans ability donors, is in particular expected to favour the bonding of poorly coordinating allyl derivatives. As for the choice of dealing with allylic substrates it is to note: (i) the presence of the oxygenated substituents should reasonably affect the regiochemistry and the stereochemistry of the insertion and the observed influence should add information on the reaction features; (ii) the attainment of functionalized products is in principle more worth of attention if the results on our system can add ground for catalytic processes.

2. Experimental

$^1\text{H}[^{13}\text{C}]$ NMR spectra were recorded on Varian XL-200 or Varian Gemini-300 spectrometers. $^1\text{H}[^{13}\text{C}]$ chemical shifts are reported in δ (ppm) relative to the solvent (CHCl_3 , $\delta = 7.26$ [77.0, $^{13}\text{CDCl}_3$]; CHD_2NO_2 , $\delta = 4.33$). The neutral platinum(II) complexes $[\text{Pt}(4-\text{R}'-\text{C}_6\text{H}_4)\text{I}(\text{phen})]$ (**1a–d**) used as precursors were obtained according to described procedures [3c] and their characterization data are reported as [supplementary material](#).

Solvents and reagents were of AnalaR grade and used without further purification.

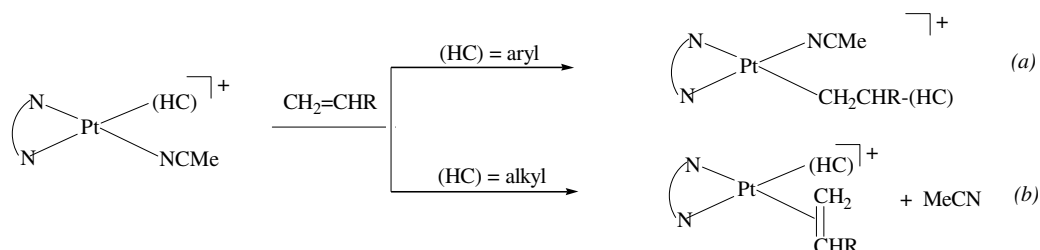
2.1. General reaction procedures

To a stirred suspension of 0.2 mmol of the neutral $[\text{Pt}(4-\text{R}'-\text{C}_6\text{H}_4)\text{I}(\text{phen})]$ (**1a–d**) complex in 1.5 mL of CD_3NO_2 , an equimolar amount of AgBF_4 dissolved in 0.5 mL of the same solvent was added at room temperature. Dissolution of the platinum complex immediately ensued, while slowly precipitating silver iodide. An equimolar amount of the allyl derivative dissolved in 0.5 mL of CD_3NO_2 was then added and, after 5 min stirring, the mixture was quickly filtered through a thin layer of Celite to remove silver iodide. Alternatively, AgBF_4 was added as CD_3NO_2 (0.5 mL)/THF (0.2 mL) solution to the platinum complex suspension. Silver iodide immediately precipitated and, after filtration on Celite, the allyl substrate was added as above. The reaction mixture was then monitored by ^1H NMR until signals of the reacting allyl substrate disappeared. After filtration on Celite, the final solution was divided in two portions (i) and (ii).

(i) The solution was evaporated until an oily residue was obtained, that was dissolved in 0.5 mL of CDCl_3 . Gaseous dry HCl was added and the mixture was stirred for 2 h at room temperature. An orange microcrystalline solid separated, that was identified as the $[\text{PtCl}_2(\text{phen})]$ complex. After filtration on Florisil, the resulting clear solution was examined by ^1H NMR. Identification of the organic compounds was achieved by comparison of the recorded spectra with those of authentic samples and/or literature data.

(ii) An excess of solid NaI was added to the solution, which was stirred for 1 h at room temperature. A yellow solid formed, that was separated and re-crystallized from $\text{CH}_2\text{Cl}_2/n$ -hexane to give the type **3''** complex. The mother liquor was concentrated to a small volume and diethyl ether carefully added to crystallize the type **3'** complex as orange crystals. It is to note that, according the used allyl substrate (see Section 3) both complexes can be obtained or only one of them (**3'** or **3''**).

Experimental details and analytical data are reported as [supplementary material](#). Relevant $^1\text{H}[^{13}\text{C}]$ NMR data for the **3'** and **3''** complexes are listed in [Tables 1 and 2](#).



Scheme 1. Olefin addition to cationic Pt(II)-hydrocarbyl complexes.

Table 1
Selected $^1\text{H}[^{13}\text{C}]$ NMR data for $3'$ complexes^a $[\text{Pt}\{\text{CH}_2\text{CH}(\text{CH}_2\text{OH})\text{C}_6\text{H}_4\text{-4-R}'\}\text{I}(\text{phen})]$

Complex	$4\text{-R}'\text{-C}_6\text{H}_4$			$\text{Pt-C}^3\text{H}_2\text{-}$	$\text{-C}^2\text{H}(\text{C}^1\text{H}_2\text{OH})\text{-}$		$\text{H}_2, \text{H}_9(\text{phen})^b$
	β, β'	γ, γ'	R'		CH	CH_2	
3'a	7.0–7.4 (m) ^c			2.75 (t, ^d); 2.15 (dd,85) 3.20 (t,72);	2.95 (m)	3.80 (m)	9.88 (d,20); 9.15 (d,54) 10.18 (d,20); 9.18 (d,54)
3'b	7.30 (d)	7.10 (d)	2.35 (s) [21.1]	2.18 (dd,96) [3.4] 3.25 (t,61);	3.00 (m) [51.3]	3.90 (m) [68.6]	10.25 (d, 22); [153.4, 148.8]
3'c	7.38 (d)	6.85 (d)	3.80 (s) [55.1]	2.25 (dd,80) [5.2]	3.00 (m) [51.5]	3.90 (m) [68.8]	9.20 (d, 61) [153.5,148.7]

^a Spectra recorded in CDCl_3 (reference δ 7.26, CHCl_3 [77.0, $^{13}\text{CDCl}_3$]). The coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s (singlet), d (doublet), dd (double doublet), t (triplet), m (multiplet).

^b The resonance with the higher value of the ^{195}Pt coupling constant refers to the proton on the carbon adjacent to the nitrogen *trans* to the iodide.

^c Phenyl protons.

^d Coupling constant with ^{195}Pt not evaluable.

Table 2
Selected $^1\text{H}[^{13}\text{C}]$ NMR data for $3''$ complexes^a $[\text{Pt}(\eta^1, \eta^2\text{-R}'\text{-C}_6\text{H}_3\text{CHYCH}=\text{CH}_2)\text{I}(\text{phen})]$ (Y = H, Me, CH_2OH)

Complex	$\text{R}'\text{-C}_6\text{H}_3\text{-}$			$\text{Ar-C}^3\text{HH-}$ or $\text{ArC}^3\text{H}(\text{Me}, \text{CH}_2\text{OH})$	$\text{-C}^2\text{H}=\text{C}^1\text{H}_2$		$\text{H}_2, \text{H}_9(\text{phen})^b$
	β', γ'	γ	R'		$\text{-C}^2\text{H}=\text{}$	$=\text{C}^1\text{H}_2$	
3''a	7.00 (m) ^c	8.20 (d, ^d)		3.30 (dd), 2.55 (d)	3.62 (m,93)	3.18 (d, ^d) 3.00 (d,53) 3.21 (d, ^d)	9.10 (d,22) 8.95 (d, ^d) 9.18 (d,26)
3''b	6.95 (d) 6.85 (d)	8.25 (s,26)	2.43 (s) [21.2]	3.36 (dd), 2.56 (d) [40.1]	3.65 (m, 92) [74]	3.07 (d,69) [60.5] 3.18 (d, ^d)	8.98 (d, ^d) [149.4,147.7] 9.15 (d,29)
3''c	6.90 (d) 6.58 (d)	– ^e	3.85 (s) [55.1]	3.30 (dd), 2.50 (d) [42.3]	3.62 (m, ^d) [74]	3.00 (d,70) [62.3]	8.92 (d,15) [150.0,148.5]
3''d	7.22 (d) 7.10 (d)	8.65 (s,17)		3.30 (dd), 2.58 (d)	3.61 (m, 91)	3.20 (d, ^d) 2.98 (d,67) 3.18 (d, ^d)	8.95 (br) 9.10 (d,28)
3''b(Me)^f	6.85(m)	8.20 (s,32)	2.38 (s)	3.30 (m); 1.00 (Me,d)	3.65 (m, ^d)	2.90 (d, ^d)	8.90 (d, ^d)
3''b(CH₂OH)	6.98 (d) 6.85 (d)	– ^e	2.38 (s)	2.80(m); 4.20,3.70 (CH ₂ OH,m)	– ^e	3.50 (d, ^d) 3.20 (d, ^d)	9.18 (d,32) 8.85 (d, ^d)

^a Spectra recorded in CDCl_3 (reference δ 7.26, CHCl_3 [77.0, $^{13}\text{CDCl}_3$]). The coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s (singlet), d (doublet), dd (double doublet), m (multiplet), br (broad).

^b The resonance with the higher value of the ^{195}Pt coupling constant refers to the proton on the carbon adjacent to the equatorial nitrogen.

^c β' , γ' and δ phenyl protons.

^d Coupling constant with ^{195}Pt not evaluable.

^e Obscured by other signals.

^f Figures refer to the more abundant diastereoisomer.

2.2. Structure determination

Single crystals of $[\text{Pt}(\eta^1, \eta^2\text{-2-allyl,5-methyl-phenyl})\text{I}(\text{phen})]$ (**3b''**), suitable for X-ray analysis were obtained by slow crystallization from CHCl_3 solution at low temperature (277 K).

Accurate cell parameters were obtained through a least-squares fit to the θ angles of 24 strong reflections in the range $9.88^\circ \leq \theta \leq 10.79^\circ$ on an Enraf–Nonius MACH 3 diffractometer, using graphite monochromatised Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Data collection was performed on the same apparatus in the ω scan mode at 293 K. Crystals of complex **3b''**, $\text{C}_{22}\text{H}_{19}\text{N}_2\text{PtI}$, are orthorhombic, $Pbca$ space group, $a = 8.924(4) \text{ \AA}$, $b = 32.92(5) \text{ \AA}$, $c = 14.303(5) \text{ \AA}$, $V = 4202(7) \text{ \AA}^3$, $M = 633.40$, $Z = 8$, $D_c = 2.002 \text{ g/cm}^3$, $\mu = 8.155 \text{ mm}^{-1}$.

The yellow crystal selected was prismatic, $0.03 \times 0.15 \times 0.18 \text{ mm}^3$. 5498 reflections were collected, 5067 independent ($R_{\text{int}} = 0.0907$, $\theta_{\text{max}} = 28.02^\circ$). Empirical absorption correction was applied using DIFABS program [5]. The structure was solved by direct methods (SHELXS program of SHELX 97 package [6]), completed by difference Fourier methods and refined by the full matrix least squares method (SHELXL program of the same package). Refinement was on F^2 against all independent measured reflections. All non-H atoms were anisotropic. H atoms were placed in calculated positions except for olefinic H atoms that were found from a difference Fourier map. All H atoms were refined by the riding model. 235 Parameters were refined. Final results: $R_1 = 0.056$, $wR_2 = 0.1177$ on F (based on 2384 reflections with $I > 2\sigma(I)$); $R_1 = 0.1612$, $wR_2 = 0.1524$ on F^2 (all data).

Largest peak and hole in the last Fourier difference were 1.150 and -0.967 ($e \text{ \AA}^{-3}$), near heavy atoms.

3. Results and discussion

3.1. Synthesis

The allyl derivatives and the Pt(II) complexes used as precursors of the reactive species are reported in Scheme 2.

In the reaction with allyl alcohol all the four **1a–d** complexes were employed. The attainment of the cationic species actually involved in the insertion reaction can be effected in situ by treatment in nitromethane solution with silver ions in presence of the olefin. However, no isolation and thorough characterization of the reactive cation could be effected in this case. On the other hand, the uptake of the poorly coordinating $\text{CH}_2=\text{CHCH}_2\text{OH}$ by analogous methyl-Pt(II) compounds under these conditions is well established [4] and affords the corresponding $[\text{PtMe}(\text{CH}_2=\text{CHCH}_2\text{OH})(\text{N-N})]^+$ cationic complexes, which do not undergo insertion.

Alternatively the iodide could be previously exchanged with a “labile” ligand such as acetonitrile to form a cation. This cationic complex can be isolated, characterized, and used in exact stoichiometric amount for reaction with the olefin. However, olefins bearing electron-withdrawing groups are not able to substitute even the “labile” acetonitrile ligand, owing to the draining of electron density from the C=C bond.

The in situ procedure involves a problem. In fact, removal of a iodide with Ag^+ from a Pt(II) iodide complex is not an immediate and simple reaction in absence of donors apt to avoid the further coordinative unsaturation of the d^8 ion [7]. Precipitation of silver iodide is fairly slow, thus conflicting with the requirement of

homogeneity of the system and influencing its composition. For this reason, in case the reaction mixture had to be NMR monitored as the deuterated solvent was used nitromethane containing a 10% by volume of tetrahydrofuran, which speeds up AgI precipitation without hindering appreciably the coordination of the allyl substrates.

3.2. Reactions involving $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$

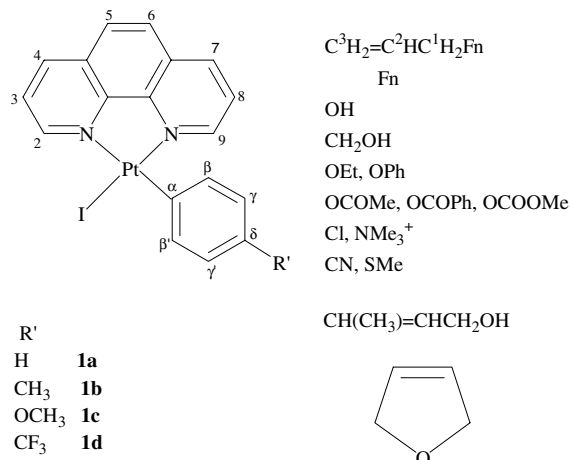
The four complexes **1a–d** were reacted with allyl alcohol (equimolar amount) in nitromethane in presence of AgBF_4 . In all cases the comprehensive reaction path could be depicted by Scheme 3, but for the lack of the type **3'd** final product. The reactions of **1a–c** were complete in ca. 2 h at room temperature, while completion in case of **1d** required ca. 12 h.

[Notations for compounds recall species **1** as for the letter. The apex denotes the type of proposed cationic intermediate and the derived final product. In case of type **2''** (and **3''**) complexes a subscript (in parentheses) identifies the groups on C^3 , if different from hydrogen].

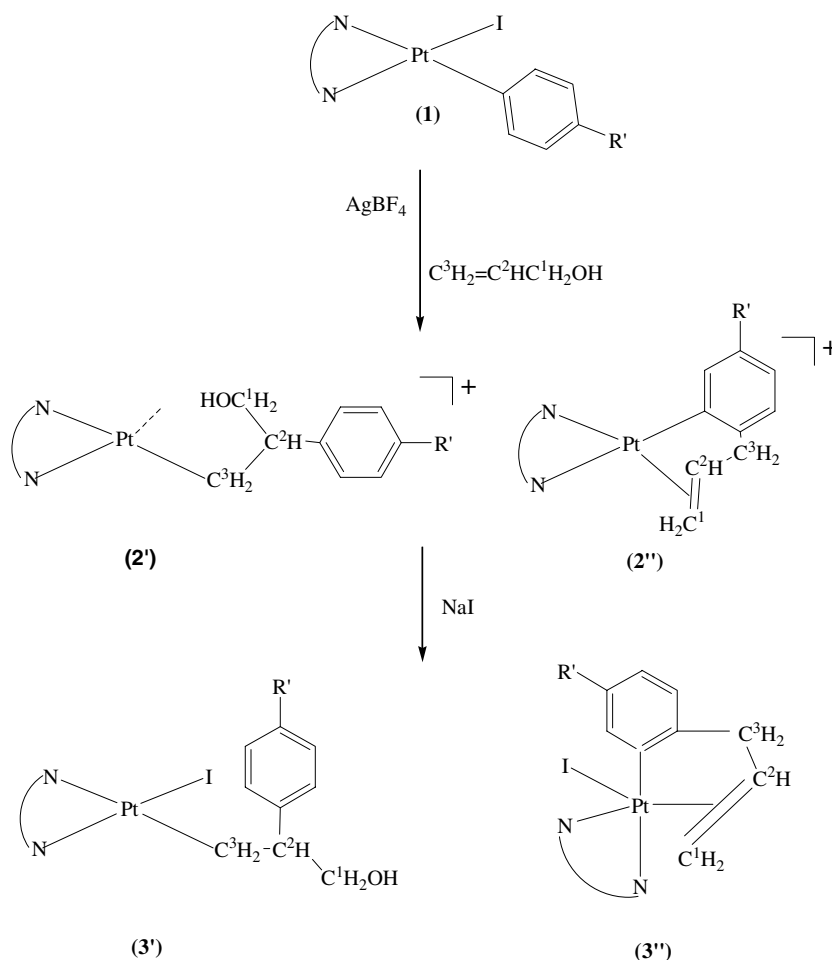
Monitoring the reaction course by ^1H NMR, the formation of two platinum complexes containing a different organic moiety bound to the metal was observed (**2'** and **2''**). Cations **2'** and **2''** were not isolated but their presence could be reasonably inferred on the ground of the ^1H NMR spectra of the reaction mixture. For instance, **2'b**: 4.0 (m, CH_2OH), 3.0 (m, CHAr), 2.70 (app t, $\text{Pt}-\text{CHH}$, $^2J_{\text{PtH}}$ not evaluable) and 2.50 δ (dd, $\text{Pt}-\text{CHH}$, $^2J_{\text{PtH}}$ not evaluable); **2''b**: 6.0 δ (m, $=\text{CH}$, $^2J_{\text{PtH}} = 78$ Hz), 4.62 δ (d, $=\text{CHH}$, $^2J_{\text{PtH}} = 60$ Hz), 4.45 (d, $=\text{CHH}$, $^2J_{\text{PtH}}$ not evaluable), 4.08 (dd, $\text{Ar}-\text{CHH}$) and 3.20 δ (d, $\text{Ar}-\text{CHH}$). Furthermore, the HCl treatment of the reaction mixture allowed the recovery of the alcohols $4\text{-R}'\text{-C}_6\text{H}_4\text{-CHMeCH}_2\text{OH}$ (from **2'a–c**) and the olefins $4\text{-R}'\text{-C}_6\text{H}_4\text{-CH}_2\text{CH}=\text{CH}_2$ (from **2''a–d**).

Type **2'** compounds reasonably derive from an insertion step involving the terminal carbon C^3 of the allylic system. We guess that they are moderately stabilized by $\text{Pt}\cdots\text{OH}$ interaction and by the attainment of a five-member ring. Formation of a type **2''** product should be attributed to an initial insertion step involving bonding of the central carbon of the allylic system to the metal, followed by a rearrangement based on the $\text{H}-\text{C}_{\text{aryl}}$ activation and its oxidative addition to Pt. A similar process has been previously observed [3] in similar systems for propene insertion, which however is completed by the reductive elimination involving the $\text{Pt}-\text{C}_{\text{aryl}}$ bond, while the final step to give the organic moiety in **2''** is water elimination to afford a coordinate unsaturated bond. This reaction sequence is shown in Scheme 4.

After treatment of the reaction mixture with sodium iodide, the corresponding neutral complexes **3'** and **3''** were obtained, separated as crystalline solids and fully characterized by usual procedures.



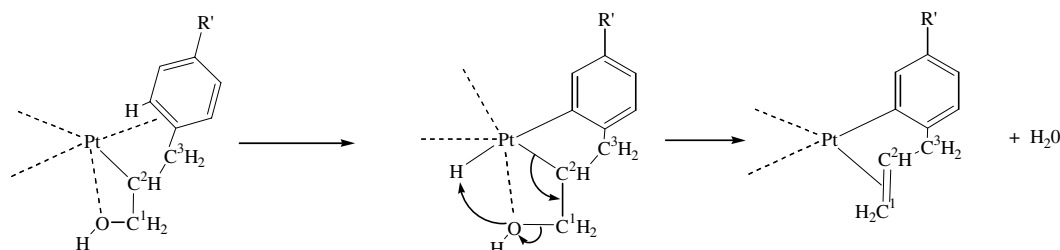
Scheme 2. Platinum(II) complexes and allyl substrates.

Scheme 3. Reactions between **1a–d** complexes and allyl alcohol.

Noteworthy features of **3''** are the coordination geometry and saturation. While the reaction mixture spectra (example above) point to a square planar **2''** species, both the spectral evidence and one crystallographic analysis prove that the corresponding neutral compounds are five-coordinate. As for ^1H NMR spectra we can compare with the above reported signals the corresponding ones observed in the **3''b** spectrum: 3.65 δ (m, =CH, $^2J_{\text{PtH}} = 92$ Hz), 3.20 δ (d, =CHH, $^2J_{\text{PtH}}$ not evaluable) and 3.03 δ (d, =CHH, $^2J_{\text{PtH}} = 69$ Hz). The dramatic high-field shift clearly points to a five-coordi-

nate structure [8], which was confirmed by X-ray analysis.

The spectral patterns of the type **3''** compounds with different substituents R' also disclose structural features in agreement with the pathways in Scheme 4. Making reference to **3''b**, it is clearly seen a signal pertaining to the H_γ (or $\text{H}_{\gamma'}$) of the aryl bound to Pt as singlet at 8.25 δ , $^3J_{\text{PtH}} = 26$ Hz. Signals due to $\text{H}_{\beta'}$ and $\text{H}_{\gamma'}$ (or H_β and H_γ) are two coupled ($^3J_{\text{HH}} = 6$ Hz) doublets centred at 6.85 and 6.95 δ . Thus, the R' group on the phenyl, which is initially *para* to the metal, is *para* to the C_3

Scheme 4. Pathway to **2''** reaction products.

organic fragment in the product. This is true in all cases. Furthermore, according to the proposed oxidative addition step the signal of the β (or β') aryl hydrogen is disappeared and the H_γ (or $H_{\gamma'}$) is coupled to Pt.

The structure of $3''\mathbf{a-d}$ complexes deserves a few comments. As these five-coordinate *tbp* compounds present two stereogenic centres (the coordinated prochiral double bond and the metal atom), four stereoisomers (actually two enantiomeric pairs) can be in principle expected. In all cases only one enantiomeric couple was observed in solution, thus indicating that the absolute configurations of the two chiral centres must be strictly correlated. A simple molecular model, built on the basis of the actual configuration correlation of the two centres, disclosed by the X-ray structure of $3''\mathbf{b}$ (see Section 3.6), has in fact shown that too short contacts arise between the platinum-bound aryl and the phenanthroline heteroaromatic ring occupying the equatorial site, on changing the absolute configuration of only one centre. As for the 1,10-phenanthroline coordination mode, we note that a large number of five-coordinate $[\text{Pt}(\text{N-N})(\text{olefin})\text{ZZ}']$ complexes ($Z, Z' =$ halogen and/or hydrocarbyl ligands) are known, which are all characterized by the presence of an N–N ligand with an in-plane sterical hindrance (e.g., 2,9-dimethyl-1,10-phenanthroline) prompting to disfavour the usual square-planar four-coordination. They generally adopt a typical *tbp* geometry with the nitrogen chelate lying in the equatorial plane [8]. A few cases of axial-equatorial coordination mode have been reported, although tendency to isomerise to the typical cited structure via a Berry pseudo-rotation mechanism was exhibited by those complexes in solution [9]. On the other hand, the obtained species $3''$ do not display the typical ligand arrangement above described and isomerization was not observed in solution. By inspection of the $3''\mathbf{b}$ molecular model, we note that the observed stereochemistry corresponds to that of the possible intermediate in the associative ligand exchange in which the *entering* iodide is substituting a *leaving* group belonging to a chelate ligand (one phenanthroline nitrogen or the double bond). Conceivably, this process is energetically disfavoured. In addition, the cited isomerization via a Berry pseudo-rotation should involve a transient different *tbp* environment with a phenanthroline nitrogen and the double bond in axial position. As the absolute configuration of the coordinate double bond is fixed, there are sterical restraints to the isomerization. Therefore, once the iodide has coordinated, the attained ligand arrangement is reasonably the most favoured and thus it stands stable.

3.3. Reactions involving $\text{MeCH}=\text{CH}-\text{CH}_2\text{OH}$ and $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{OH}$

Results concerning the two title alcohols added further information on the insertion regiochemistry. Reac-

tion of crotyl alcohol with $1\mathbf{b}$ required 12 h at room temperature for completion and the reaction mixture (only the type $2''$ ionic compound being observed) afforded by iodide addition the type $3''$ derivative as the final product. Treatment of the reaction mixture with HCl gave $4\text{-Me-C}_6\text{H}_4\text{-CHMeCH}=\text{CH}_2$, as expected. Thus, the position of the CHMe group gives further evidence that the regiochemistry of the insertion step is such that the terminal C^3 of the allylic system binds to the aryl, while the internal C^2 is linked to the metal. On the other hand, the terminal final position of the $\text{C}=\text{C}$ bond is in keeping with a rearrangement of the type depicted in Scheme 4. It is to note that two diastereoisomeric compounds, of which one is quite prevailing (over 90%), are observed in the crude reaction product. They must differ for the absolute configuration at the stereogenic centre C^3 (compare with the previous discussion). On the other hand, as the C^2 and C^3 carbon atoms of the crotyl alcohol interact with the platinum and the aryl group via a concerted *cis*-addition mechanism, their absolute configurations cannot independently vary. Therefore, the observed diastereoisomeric ratio in the crude $2''\mathbf{b}_{(\text{Me})}$ (and $3''\mathbf{b}_{(\text{Me})}$) product is related to the *trans-cis* composition of the commercial crotyl alcohol.

Reaction of 3-buten-1-ol with $1\mathbf{b}$ yielded a mixture of two type $2'$ species which on treatment with HCl afforded both the alcohols $4\text{-Me-C}_6\text{H}_4\text{-CHMeCH}_2\text{CH}_2\text{OH}$ and $4\text{-Me-C}_6\text{H}_4\text{-(CH}_2)_3\text{OH}$ in ca. 2:1 ratio.

Results on these substrates converge to sustain the attribution of the structure and of the role of cations in Scheme 3. The CH_2OH group has to be considered an electron withdrawing substituent in this context, in contrast with the methyl in propene. However, the observed loss of regiospecificity in the insertion of allyl alcohol (aryl addition on both the unsaturated carbon is represented) respect to that observed with propene (sequence $\text{Pt-CH}_2\text{CHMe-aryl}$ only) fits well with the moderate inductive effect of CH_2OH . Moreover, it is easily understood that by balancing the electronic effect of the hydroxymethyl by introducing a methyl group (crotyl alcohol) or by reducing that effect by distancing the group (3-buten-1-ol) the regiospecificity is recovered. Also, the effect of the ability of the OH group to interact with the metal finds a rationale on the ground of the proposed H-C_{aryl} activation. In fact, the Pt–OH interaction can afford “pushing” of the phenyl ring far from the metal, thus contrasting the activation of the H-C_{aryl} bond. Therefore, if the length of the Pt-bound hydrocarbon chain allows that the OH group can be involved in a fairly stable five- or six-member ring, the reaction stops with attainment of a type $2'$ product. No pushing away of the phenyl is expected to be involved in shorter Pt-bound hydrocarbon chains, which can evolve after rearrangement to the $2''$ type product.

3.4. Reactions involving allyl-ethers and esters

Reaction of **1b** with two allyl-ethers and three allyl-esters (see Scheme 2) was relatively fast (1.5–2 h) at room temperature and afforded in quantitative yield the same type **2''b** cation and thereafter type **3''b** neutral five-coordinate complex as obtained in the reaction of **1b** with allyl alcohol (Scheme 3). In analogy to that case, water elimination is substituted by alcohol (from allyl-ethers) or acid (from allyl-esters) release. Using the reacting substrate allyl-methyl carbonate, methanol (deriving from HOCOOME decomposition) is detected in solution.

The reaction of **1b** and the cyclic allyl ether 2,5-dihydrofuran presents a similar pathway and involves rupture of the ether ring (Scheme 5).

On comparing the product with that formed from crotyl alcohol it can be observed that the only difference is the presence of methyl instead of CH₂OH in that compound. It is to note that in contrast with the crotyl derivative, only one diastereoisomer is observed for the dihydrofuran product. This is consistent with the unique *cis* configuration of the double bond in the starting unsaturated cyclic ether and the *cis* addition mechanism (see discussion in Section 3.3).

3.5. Reactions involving other allyl substrates

Complex **1b** has been reacted with two allyl compounds CH₂=CH–CH₂F_n where F_n is again an electron-withdrawing but not an oxygenated group, i.e., F_n = Cl or NMe₃⁺. No variation is observed in the reaction, **3b''** compound being finally isolated.

It is on the other hand that if the group F_n contains a good soft donor, the allylic substrates coordinates to the metal through F_n and no activation of the double bond is obtained. This is in fact the behaviour of CH₂=CHCH₂CN and of CH₂=CHCH₂SMe.

3.6. X-Ray structure of complex **3''b**

Molecular structure is reported in Fig. 1, relevant bond lengths and bond angles are reported in Table 3.

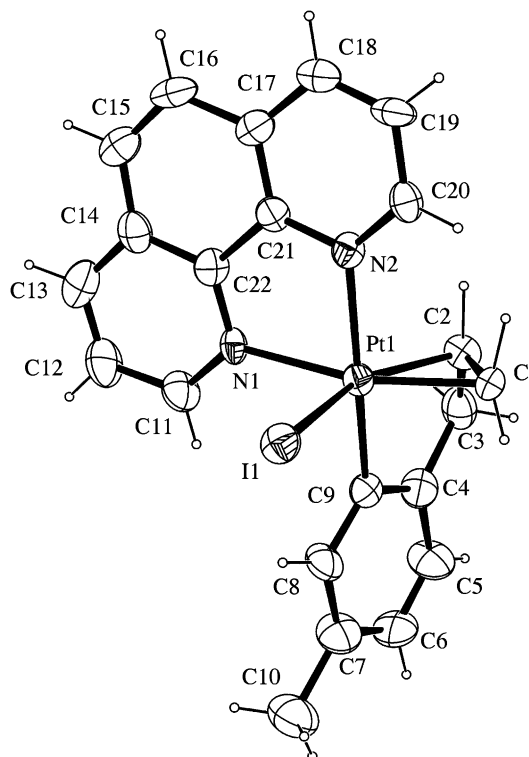
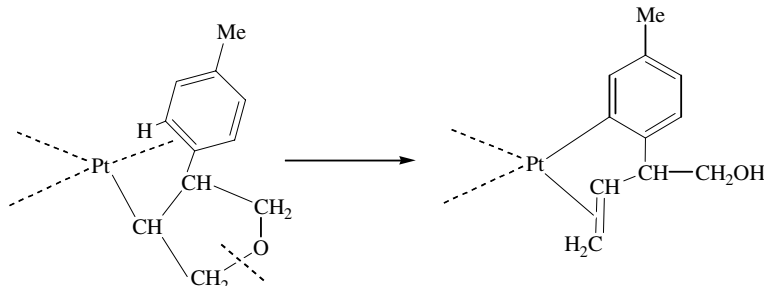


Fig. 1. Molecular structure of the complex [(η¹,η²-2-allyl,5-methylphenyl)iido(1,10-phenanthroline)platinum(II)] (**3''b**).

Pt adopts a distorted bipyramidal trigonal coordination, with phen ligand occupying one axial and one equatorial position, in an unusual and only one time found position [7]. Moreover two of the other coordination positions (C9 and the double bond C1=C2) belong to the same ligand and, as a consequence, some peculiar distortions are expected. The axial positions are occupied by N2 of phenanthroline and C9 of phenyl ligand. The angle N2–Pt–C9 = 172.5(4)° shows a deformation that could be ascribed to the steric hindrance of phenyl moiety with phenanthroline ligand and to the axial-equatorial coordination of the phenyl moiety, this way of coordination being dictated by the need of forming a C9–Pt–(C1=C2) angle near to 90°. The equatorial plane is defined by I, N1 atom of phenanthroline and the double bond C1=C2. The major deformation in this plane



Scheme 5. Pathway to **2''b**_(CH₂OH) (and **3''b**_(CH₂OH)) reaction product for 2,5-dihydrofuran.

Table 3
Selected bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Pt–I	2.840(1)	N(1)–Pt–N(2)	77.9(4)
Pt–N(1)	2.14(1)	C(1)–Pt–C(9)	84.3(5)
Pt–N(2)	2.14(1)	C(2)–Pt–C(9)	82.5(5)
Pt–C(9)	2.01(1)	N(2)–Pt–C(1)	96.3(5)
Pt–C(1)	2.07(1)	N(2)–Pt–C(2)	93.5(4)
Pt–C(2)	2.10(1)	I–Pt–N(1)	86.3(3)
C(1)–C(2)	1.40(2)	C(9)–Pt–N(2)	172.5(4)
C(2)–C(3)	1.50(2)		

involves N1 atom as a consequence of the axial-equatorial coordination of phen (N1–Pt–N2 = 77.9(4)°).

The phenanthroline ligand is planar within 0.07 Å and its mean plane is coincident with the plane defined by N1, Pt, N2 within 0.08 Å, while a tilting is observed with the mean plane of phenyl moiety (C8–C9–Pt–N1 = –69(1)°), thus avoiding steric interactions between them. The same steric interactions, mainly due to the intramolecular contact between C8 and C11, prevent the formation of the possible diastereoisomer resulting from the coordination of the other enantioface of the olefin.

Pt–N axial and equatorial distances (Pt–N1 = 2.14(1) Å, Pt–N2 = 2.14(1) Å) show no effect due to the different nature of their position. Pt–C9, Pt–I and C1=C2 bond lengths (2.01(1), 2.840(1) and 1.40(2) Å, respectively) are in the normal range for analogous coordinatively saturated Pt(II) compounds [8].

4. Conclusions

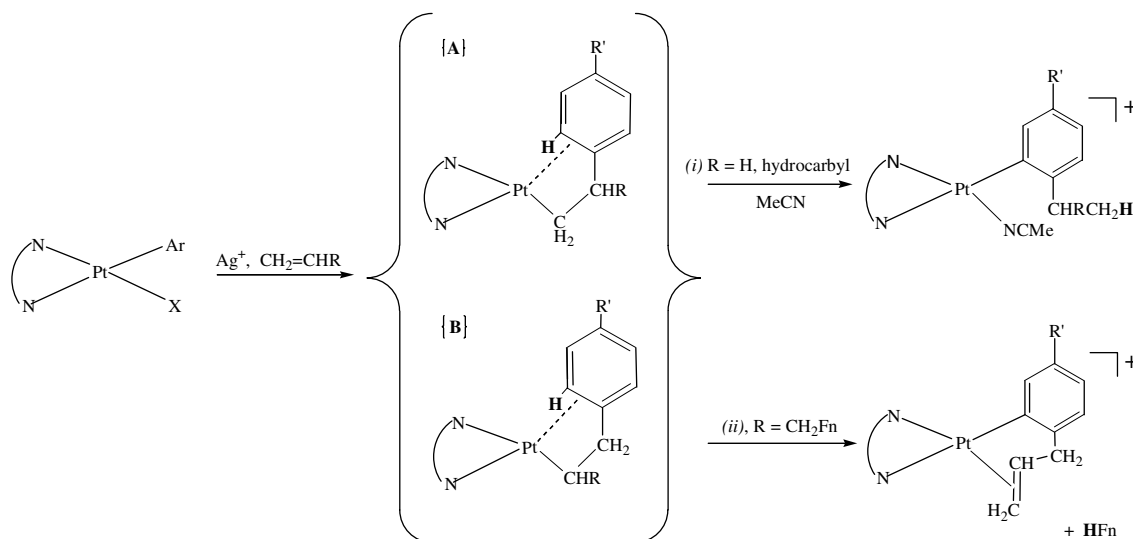
The above described results, when compared with those reported in case of unsubstituted alkenes, allow enlightening some unequivocal features concerning the M-hydrocarbyl/olefin insertion migratory process, at least in Pt(II) chemistry. The required C=C bond activation via coordination to the metal can be easily attained through a ligand substitution reaction only in the case of simple alkenes. The presence of a vicinal electron-withdrawing substituent reduces the C=C bond σ -donor properties at such an extent to disfavour the ligand exchange. Nevertheless, coordination can be achieved if a fragment {Pt-hydrocarbyl(N–N)}⁺ is generated in absence of valuable coordinating species different from the alkene itself. Moreover, the presence of an ancillary bidentate ligand ensures the proper *cis* stereochemistry to the subsequent insertion step. The facile reactivity observed in case of hydrocarbyl = aryl can find a rationale taking into account a possible overlap between a filled π orbital of the aromatic ring with the empty π^* orbital of the double bond, that can occur when the alkene assumes the “in plane” stereochemistry in the transition state. This interaction should lower the activation energy for the insertion process with the respect to the in-

ert Pt(alkyl)(olefin) complexes in which a more energetically demanding electron transfer is instead reasonably required.

As far as the regiochemistry of the insertion is concerned, we note that, in contrast with α -olefins insertion, for the alkenes in this work the electronic and steric features play opposite roles. It appears that the observed regiochemistry is mainly dictated by the electronic properties of the substituent on the double bond favouring bonding of Pt to the internal carbon. This is in good agreement with an intramolecular nucleophilic addition of an aryl carbanion on the coordinated double bond. The only case of regioselectivity loss is related to the presence of a substituent group of moderate inductive effect as CH₂OH. Actually, both the unsaturated carbons of the allyl alcohol were involved in the aryl migration at nearly equal amounts. The spacing out of this group, i.e., the use of 3-butenol, restores, however not completely, the regiochemistry corresponding to an unsubstituted alkene.

A significant aspect of our studies concerns the elucidation of the fate of the metal σ -bound primary insertion product. No organic compound, free or metal-coordinated, deriving from a β -elimination process, which is usual in the Pd(II) chemistry, was ever observed. On the other hand, we recall that, when unsubstituted alkenes were used in the reaction with [Pt(aryl)(N–N)(MeCN)]⁺ compounds [3c], the expected σ aryl-alkyl-Pt(II) cationic product was obtained and its fully characterisation was achieved after conversion to a neutral halo-complex (see Scheme 1(a)). A comparable compound was observed in this work only in peculiar conditions (see below). Allowing that in the present study the reactions must be performed by generating in situ the active {Pt-aryl(phen)}⁺ species, the comparison has to be made with the previously obtained results in the same experimental conditions. In all cases, the lack of a fast pushing away of the aromatic ring far from the platinum favours H–C_{aryl} bond activation. Its oxidative addition to the metal centre is then followed by a reductive elimination according two different paths depending on the electronic properties of the starting alkene and depicted for clarity in Scheme 6.

It is to note that while in the transient intermediate {A} the fission of the Pt–CH₂ bond is the only possible, the cleavage of the CH₂–heteroatom bond is quite preferred in {B}. The formation of an organic moiety η^1, η^2 -chelate to the metal atom could be the driving force for this latter process. It is to strongly emphasize that the above depicted pathways can only occur in absence of whatsoever species able to fill the coordinative unsaturation at the metal atom resulting from the insertion reaction. In fact, the primary fragment {Pt–CH₂–CHAr–CH₂OH(phen)}⁺, deriving from the insertion of the allyl alcohol with a regiochemistry different from that expected by inductive effect, finds its stabilisation



Scheme 6. Olefin depending reaction paths.

through the formation of a five-member ring with a Pt...OH interaction. The same is true in the case of 3-butenol, for which the two variations of the regiochemistry of the insertion afford respectively a five or a six-member ring.

As final remark we wish observe that the above reaction sequence could be of synthetic usefulness allowing a selective and easy removal of the C₃ fragment from allyl ethers or -esters. As matter of fact, in an exploratory test α -phenylethylalcohol was quantitatively released by reaction of the corresponding allylether with the active {Pt-C₆H₅(phen)}⁺ species [10].

Acknowledgements

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Appendix A. Supplementary data

Experimental details and characterization data. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 249352 for the compound **3b''**. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge

CB2 1EZ [Fax +44(1223)336-033] or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.12.010.

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