



A NMR, X-ray, and DFT combined study on the regio-chemistry of nucleophilic addition to platinum(II) coordinated terminal olefins

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ABSTRACT

The series of platinum complexes $[\text{PtCl}(\eta^2\text{-CH}_2=\text{CH-C}_6\text{H}_4\text{-X})(\text{tmeda})](\text{ClO}_4)$ ($\text{X} = \text{H}$, **1b**; 4-OMe, **1c**; 3-OMe, **1d**; 4-CF₃, **1e**; 3-CF₃, **1f**; 3-NO₂, **1g**; tmeda = *N,N,N',N'*-tetramethyl-1,2-ethanediamine) has been considered. In the styrene complex (**1b**) both solution (NMR) and solid state (X-ray) data indicate a significant difference in the Pt–C bond lengths (the longer bond being that involving the olefin carbon atom carrying the phenyl ring). Such a difference increases when X is an electron donor group (EDG, **1c**) and decreases when X is an electron withdrawing group (EWG, **1d–g**). The attack of a nucleophile (MeO[−]) to the substituted carbon (Markovnikov type, M) is by far the most favoured in the case of unsubstituted (**1b**) or EDG-substituted (**1c**) styrenes. The presence of an EWG (compounds **1d–g**) levels off the probability of M and *anti*-M type of attack. DFT calculations on **1b,c** and **1e** were also performed. The NLMO analysis reveals the crucial role of the interaction between the filled π orbital of the olefin and the empty d orbital of platinum; the carbon with greater electron density becoming less susceptible of nucleophilic attack.

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1. Introduction

The metal–olefin linkage plays a relevant role in organometallic chemistry, being present in key steps of many useful processes of polymerization and functionalization of organic molecules [1].

The metal–olefin bond is already well understood on the basis of the model proposed by Duncanson, Chatt and Dewar [2]. It can be described as a continuum between two limiting situations: σ donation of π electrons of the olefin into a vacant $d\sigma$ orbital of the metal and π back-donation from a filled $d\pi$ orbital of the metal into a vacant orbital essentially based on the π^* orbital of the olefin.

A key feature of the coordinated olefin is its activation towards nucleophiles which has been investigated in detail theoretically by Hoffmann and Eisenstein in the early 1980s [3]. The authors found that an ethylene symmetrically bound to a metal centre should undergo nucleophilic attack less easily than in the free state, since in the complex the LUMO is higher in energy than the π^* orbital of the free olefin and less centred on it. In contrast, activation occurs if the metal fragment slips along the C=C axis while the nucleophile is approaching. This geometrical change induces a lowering of the LUMO and favours its interaction with the filled orbital of the donor (the lower in energy is the LUMO of the coordinated olefin,

the higher will be the activation of the unsaturated ligand towards nucleophiles). Therefore the energy of the LUMO appears to be a much better indicator of the olefin reactivity than other parameters such as the overall charge of the complex. On this basis Hoffmann and Eisenstein could rationalize the striking different behaviour of two isolobal complexes: $[\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)]^+$ [4], which is very reactive towards nucleophiles, and $[\text{Fe}(\text{CO})_5(\text{C}_2\text{H}_4)]^{2+}$ [3], which is un-reactive.

The properties and reactivity of terminal olefins bring in an additional issue: the site of attack of the nucleophile which can be either the substituted or the unsubstituted olefinic carbon (Markovnikov or *anti*-Markovnikov type of attack, respectively). The work of Rosenblum on $[\text{CpFe}(\text{CO})_2(\text{CH}_2=\text{CHOMe})]^+$, where the coordinated olefin bears an electron donor substituent, did show the complete regio-specificity of the nucleophilic addition and the unique formation of the Markovnikov product [5]. The X-ray structure of $[\text{CpFe}(\text{CO})_2(\text{CH}_2=\text{CHOMe})]^+$ did show a longer Fe–C_{olefin} bond distance for the substituted carbon, indicative of a certain degree of olefin “slippage” already in the ground state of the complex molecule. The slippage was a consequence of the greater localization of the π orbital on the unsubstituted carbon. The difference between the two Fe–C_{olefin} distances becomes even more pronounced when the substituent is an amino group but, in spite of this, the reactivity of $[\text{CpFe}(\text{CO})_2(\text{CH}_2=\text{CHNMe}_2)]^+$ towards nucleophiles drops considerably. The explanation was found in an

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increased contribution of the limiting structure $[\text{CpFe}(\text{CO})_2(\text{CH}_2\text{-CH}=\text{NMe}_2)]^+$ which reduces the bond order between the two carbon atoms [5]. Recent structural and computational studies performed on this iron complex have come to the same conclusion [6]. This interpretation has gained further support in a recent work by Matchett [7].

Since the seminal paper of Hoffmann, correlations between coordinated olefin parameters and observed reactivity have been tracked over the years. Beyond X-ray structural data, a particular attention has been paid to NMR parameters, olefinic proton and carbon resonances being shifted upfield and the extent of the shift being related to the amount of π back-donation [8,9]. Although absolute values may depend also from the overall charge of the complex and the nature of ancillary ligands, a high upfield shift generally corresponds to a reduced electrophilicity of the coordinated olefin. Furthermore, also the coupling between the metal (when it has nuclear spin) and the olefinic carbons ($^1J_{\text{M-C}}$) can give useful information on the geometry of the unsaturated ligand and its propensity to undergo regiospecific nucleophilic addition.

Over the years some of us have investigated several olefin complexes of platinum having formula $[\text{PtCl}(\eta^2\text{-olefin})(\text{tmeda})](\text{ClO}_4)$, **1**, (tmeda = *N,N,N',N'*-tetramethyl-1,2-ethanediamine) which proved to be highly electrophilic [10]. The nucleophilic addition of methoxide anion to a series of closely related styrene complexes has now been investigated by combining experimental and computational methods.

2. Results and discussion

2.1. The complexes

The prototype compound $[\text{PtCl}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{tmeda})](\text{ClO}_4)$ (**1a**) can be directly prepared from Zeise's salt [10a,b]; $[\text{PtCl}(\eta^2\text{-CH}_2=\text{CHMe})(\text{tmeda})](\text{ClO}_4)$ (**1a'**) can be obtained in quantitative yield by substitution of propene for ethene in **1a** [10c]; **1a'**, in turn, can be used as substrate for further olefin substitution (complexes $[\text{PtCl}(\eta^2\text{-CH}_2=\text{CH-C}_6\text{H}_4\text{-X})(\text{tmeda})](\text{ClO}_4)$ where X = H (**1b**), 4-OMe (**1c**), or 3-OMe (**1d**) were obtained in this way [10g]). However, when the entering olefin is a styrene bearing a strong electron withdrawing group on the phenyl ring (ligands 4-CF₃-styrene (**e**), 3-CF₃-styrene (**f**), and 3-NO₂-styrene (**g**)), its coordinating ability is lowered and the substitution of styrene for propene can be totally impaired. Even in the latter unfavourable circumstances, the metathetic reaction can still be performed by exploiting the different solubilities of the compounds in CH₂Cl₂. In particular, the solubility of $[\text{PtCl}(\eta^2\text{-3-NO}_2\text{-styrene})(\text{tmeda})](\text{ClO}_4)$ (**1g**) is so poor in CH₂Cl₂ that it precipitates quantitatively from the reaction medium when **1a'** is reacted with excess 3-NO₂-styrene. In turn, a suspension of **1g** in dichloromethane, treated with an excess of

4-CF₃-styrene (**e**) or 3-CF₃-styrene (**f**), leads to a solution of $[\text{PtCl}(\eta^2\text{-4-CF}_3\text{-styrene})(\text{tmeda})](\text{ClO}_4)$ (**1e**) or $[\text{PtCl}(\eta^2\text{-3-CF}_3\text{-styrene})(\text{tmeda})](\text{ClO}_4)$ (**1f**), while un-reacted **1g** remains as precipitate and can be removed by filtration.

The new cationic compounds have been characterized via elemental analysis, ¹H and ¹³C NMR (1D and 2D) in solution, and ESI mass spectrometry. We ought to mention that the use of methanol (a classical solvent for ESI-MS experiments) leads to inconclusive data, while much better results are obtained using acetonitrile [11]. Although the latter solvent possesses good coordinating ability and reacts with complexes of type **1** by displacing the olefin, the substitution reaction is rather slow at room temperature and goes to completion in no less than 2 h. Therefore, it is sufficient to perform the ESI-MS determination experiment soon after dissolution for observing a base peak corresponding to the molecular formula of **1**.

The presence on the styrene phenyl ring of an electron withdrawing substituent lowers the stability of the complexes, and their tendency to release the olefin increases; a rough estimate of the stability order is **1f** (3-CF₃-styrene) > **1g** (3-NO₂-styrene) > **1e** (4-CF₃-styrene).

Relevant NMR parameters (¹³C, acetone-*d*₆) for compounds **1** and for the corresponding free olefins are reported in Table 1. The olefinic carbons undergo, upon coordination, an upfield shift which is always more pronounced for the unsubstituted carbon atom. As a consequence, in all considered cases the $\Delta\delta$ between the two olefinic carbon atoms is greater in the complex than in the free olefin. The increase in $\Delta\delta$ upon coordination is also modulated by the nature of the substituent on the phenyl ring (X), it is close to 40% for the styrene derivative (**1b**), increases to >50% for the 4-OMe-styrene (**1c**) and decreases to 35% for the styrenes bearing electron withdrawing substituents (**1e-g**). Both the upfield shift of the olefinic carbons and the increase of the $\Delta\delta$ upon coordination have been related to the amount of charge transfer from the metal to the olefin (back-donation) [9]. Coordinated olefins exhibiting a $\Delta\delta$ increase lower than 10% are considered to have a very poor electrophilic character. Hahn has compared complexes of formula $[\text{M}(\text{PNP})(\text{CH}_2=\text{CHPh})]^{n+}$ (M = Rh(I), *n* = 1; Pd(II) and Pt(II), *n* = 2. PNP = 2,6-bis(diphenylphosphanylmethyl)pyridine)) differing for the electrophilicity of the olefin (very low in the case of rhodium and high in the case of palladium and platinum) [12–14]. The different behaviour has been explained on the basis of a greater metal-to-olefin π back-donation in the case of rhodium (overall complex charge +1) than in the case of palladium and platinum (total charge +2) [8]. The different situation is well described by the ¹³C resonances of the olefin moiety. In the case of rhodium, upon complexation, the shielding of the olefinic carbons increases considerably but $\Delta\delta$ increases only by 10%; in contrast, in the case of palladium and platinum there is a smaller increase in shielding of the olefinic carbons but the increase of $\Delta\delta$ is nearly twice as

Table 1
Selected ¹³C NMR data for complexes $[\text{PtCl}(\eta^2\text{-olefin})(\text{tmeda})](\text{ClO}_4)$, **1**, in acetone-*d*₆ at 21 °C

Olefin	=CH ₂		=CHR		$\Delta\delta^d$		$\Delta(^1J_{\text{Pt-C}})^e$
	Free ^a	Coord ^{b,c}	Free ^a	Coord ^{b,c}	Free ^a	Coord ^b	
Styrene (1b)	113.4	68.5 (174)	137.0	103.2 (81)	23.6	34.7	93
4-OMe-styrene (1c)	110.9	65.0 (187)	136.6	104.5 (66)	25.7	39.5	121
4-CF ₃ -styrene (1e)	117.0	71.0 (n. d.)	136.0	96.5 (n. d.)	19	25.5	n. d.
3-CF ₃ -styrene (1f)	115.5	70.0 (164)	135.5	97.2 (137)	20	27.2	27
3-NO ₂ -styrene (1g)	116.0	70.5 (124)	135.0	96.0 (139)	19	25.5	-15

^a free = free olefin.

^b coord = coordinated olefin.

^c ¹J_{Pt-C} (Hz) in parentheses.

^d $\Delta\delta = \delta_{\text{=CHR}} - \delta_{\text{=CH}_2}$.

^e $\Delta(^1J_{\text{Pt-C}}) = (^1J_{\text{Pt-CH}_2}) - (^1J_{\text{Pt-CHR}})$ (Hz).

much. Therefore it can be concluded that the greater electrophilicity of the olefin in the palladium and platinum complexes stems from a smaller metal-to-olefin π back-donation accompanied by a greater asymmetry in olefin coordination.

In the case of platinum the asymmetry in olefin coordination can also be sized by differences in $^1J_{\text{Pt-C}}$ between the ^{195}Pt nucleus and the olefinic carbons, a greater value of $^1J_{\text{Pt-C}}$ being indicative of a carbon closer to the metal centre [8]. From inspection of Table 1, it can be noted how $\Delta(^1J_{\text{Pt-C}})$ is 93 Hz in the styrene complex (**1b**), increases in the presence of an electron donor substituent (121 Hz in **1c**), while decreases in the presence of electron withdrawing substituents (values in the range 20 Hz for **1e–g**).

From the previous observations it is possible to conclude that the ground state of complexes **1b** and **1c** has a certain degree of olefin slippage (contribution of the η^1 -limiting structure which places a positive charge on the olefinic carbon farther from the metal and a formal negative charge on the carbon attached to the metal atom). A shift from the η^2 - to the η^1 -coordination mode generally occurs when an approaching nucleophile donates a lone pair of electrons to the olefinic carbon which is moving away from the metal. However, in the case of coordinated styrenes (particularly those bearing an electron-donating substituent), a contribution of the η^1 -limiting structure to the ground state can be fostered by delocalization over the phenyl ring of the positive charge accumulating on the distal olefin carbon.

2.2. Regiochemistry of nucleophilic attack

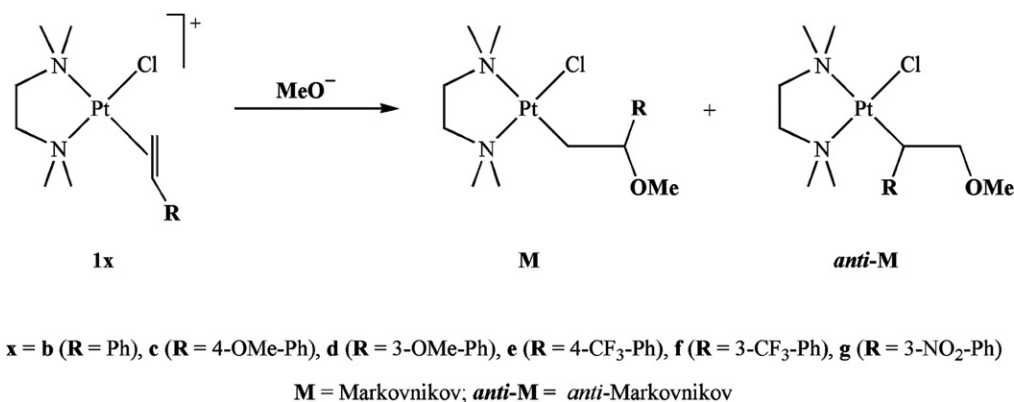
In previous work we have examined the reactivity of **1a'** and **1b** towards several nucleophiles (OH^- , MeO^- , acetylacetonate, etc.) and found a large preference for the Markovnikov type of attack [10c]. More recently the investigation has been extended to secondary amines and it has been found that there is always a kinetic preference for the Markovnikov addition product with an isomeric ratio close to 4:1. In chlorinated solvents the addition products were found to undergo isomerization with a rate which is strongly dependent upon the temperature. The equilibrium composition was shifted even more in favour of the Markovnikov isomer (Markovnikov/*anti*-Markovnikov ratio > 9:1) in the case of **1a'**, while in the case of **1b** and **1c** the shift was strongly in favour of the *anti*-Markovnikov isomer (Markovnikov/*anti*-Markovnikov ratio \sim 1:9 when the amine was NHET_2). Thus the thermodynamically determined composition appeared to be strongly dependent upon the nature of the olefin substituent. A methyl group favours the Markovnikov isomer, whereas a phenyl group favours the *anti*-Markovnikov form. Such a behaviour could be rationalized on the basis of a phenyl stabilization and a methyl destabilization of the high electron charge which accumulates on the carbon bound to the metal atom [10h].

With the present work we were interested in unravelling the kinetic preference for the site of attack (Markovnikov or *anti*-Markovnikov) in compounds **1b–g**. As a nucleophile we chose the methoxide ion for two main reasons: its small size and the stability of the kinetically determined addition product in basic medium (Scheme 1) [10g]. Moreover, since the kinetic of addition reaction can be influenced by steric effects, we selected a group of cationic complexes having very similar steric requirements (**1b–g**).

The methoxide addition reactions were performed by treating a suspension of the olefinic complexes in chlorinated solvents (generally CH_2Cl_2) with a slight excess (+10%) of methanolic KOH. The reaction products (**2b–g**) were obtained in practically quantitative yields. The heterogeneous conditions (incomplete dissolution of the starting substrate) are likely to influence the overall rate of the reaction but not the relative rate of formation of the Markovnikov and *anti*-Markovnikov isomers. The isomeric ratio was evaluated by integration of well separated ^1H NMR signals pertaining to the $\text{Pt-C}_\alpha\text{H}_2\text{C}_\beta\text{H}(\text{OMe})(\text{C}_6\text{H}_4\text{-X})$ and $\text{Pt-C}_\alpha\text{H}(\text{C}_6\text{H}_4\text{-X})\text{C}_\beta\text{H}_2(\text{OMe})$ moieties for the Markovnikov and *anti*-Markovnikov isomers, respectively (Fig. 1).

Apart from performing the reaction on a preparative scale so to isolate and fully characterize the addition products, the addition reactions were also carried out in a NMR tube to directly evaluate the isomeric ratio of the formed reaction products. Moreover, two solvents were used: CDCl_3 and acetone- d_6 ; the results obtained are listed in Table 2. While using CDCl_3 the formation of the addition reaction products was quantitative, in contrast, in the case of acetone, the addition was accompanied by a side reaction with releasing of free olefin.

Let us consider first the influence of the phenyl substituent X on the isomeric composition of the addition products. As compared to unsubstituted styrene, the Markovnikov/*anti*-Markovnikov ratio is greater for a methoxy group in *para* position (**3c**), while is smaller for a methoxy group in *meta* position (**3d**) or for a purely withdrawing group either in *meta* or *para* position (**3e–g**). It can be noticed how in this series of compounds the decrease of Markovnikov/*anti*-Markovnikov ratio parallels the decrease in $\Delta\delta$ and $\Delta(^1J_{\text{Pt-C}})$ (Table 1). Therefore, it can be concluded that the reaction kinetic is dominated by the degree of olefin slippage in the ground state which is greatest for the 4-methoxy derivative (**1c**). In the last compound the contribution of the η^1 -limiting structure, which places a positive charge on the olefinic carbon atom further away from the metal centre, is stabilized by the conjugative effect of the OMe group in position 4 of the phenyl ring. It is noteworthy that the same methoxy group in *meta* position (**1d**) is unable to exert such a conjugative effect. As a result, a 3-OMe substituent behaves as a purely electron withdrawing group disfavouring the Markovnikov type of addition. The reaction medium appears to have some influence upon the isomeric composition. In general,



Scheme 1. Nucleophilic addition of methoxide anion MeO^- to $[\text{PtCl}(\eta^2\text{-CH}_2=\text{CHR})(\text{tmeda})]^+$.

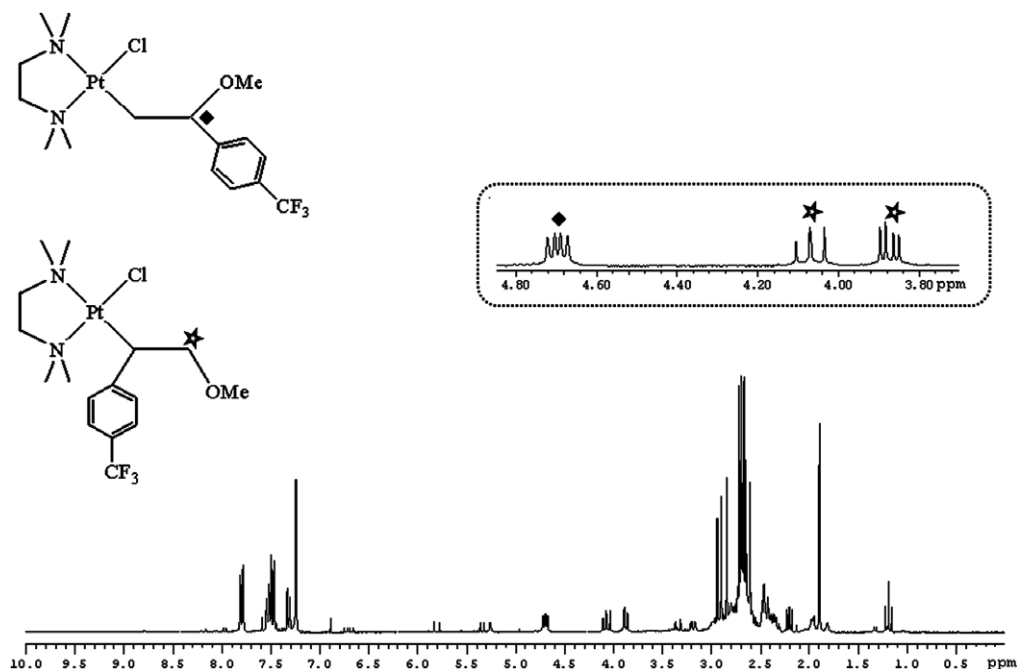


Fig. 1. ^1H NMR spectrum (300 MHz, CDCl_3 , 21 °C) of the addition product of CD_3O^- to $[\text{PtCl}(\eta^2\text{-4-CF}_3\text{-styrene})(\text{tmeda})](\text{ClO}_4)$ (**1e**).

Table 2

Kinetically controlled isomeric composition for the methoxide addition products having Markovnikov (M), $[\text{PtCl}(\text{CH}_2\text{CHR}(\text{OMe}))](\text{tmeda})$, or *anti*-Markovnikov (*anti*-M), $[\text{PtCl}(\text{CHRCH}_2(\text{OMe}))](\text{tmeda})$, configurations

Starting substrate	R	M (%)	<i>anti</i> -M (%)
1b	Ph	60	40
		80	20
1c	4-OMe-Ph	>90	<10
		>95	<5
1d	3-OMe-Ph	–	–
		65	35
1e	4-CF ₃ -Ph	30	70
		60	40
1f	3-CF ₃ -Ph	40	60
		65	35
1g	3-NO ₂ -Ph	40	60
		70	30

Upper and lower entries refer to acetone- d_6 and CDCl_3 solvents, respectively.

acetone appears to disfavour the Markovnikov addition as compared to chloroform; the difference between acetone and chloroform may well depend upon the different solvation properties of the two solvents. Acetone has better solvation capacity and, among other things, this could affect the real size of the reactants [15]. An increase in steric hindrance would disfavour the Markovnikov isomer as compared to the *anti*-Markovnikov one.

2.3. X-ray crystallography

We obtained crystals suitable for X-ray investigation for some of the considered complex species. Among the complexes of type 1, only the one with ethene (**1a**) has been structurally investigated [10a,b]. The structures for the complex cations **1b** and **1c** are reported in Figs. 2 and 3, respectively; significant bond lengths and angles are reported in Table 3.

The olefin molecule binds to the platinum(II) centre in an η^2 -fashion and the coordination sphere has the usual square planar arrangement, when the chlorine atom, the two nitrogen atoms

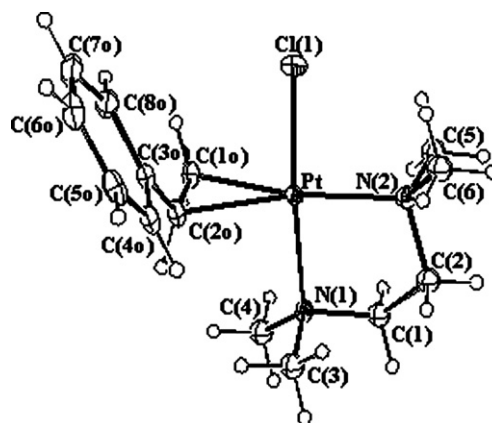


Fig. 2. ORTEP drawing of the complex $[\text{PtCl}(\eta^2\text{-styrene})(\text{tmeda})](\text{ClO}_4)$, **1b** (the counter anion omitted for clarity). Data collection performed at 193 K. Ellipsoids enclose 20% probability.

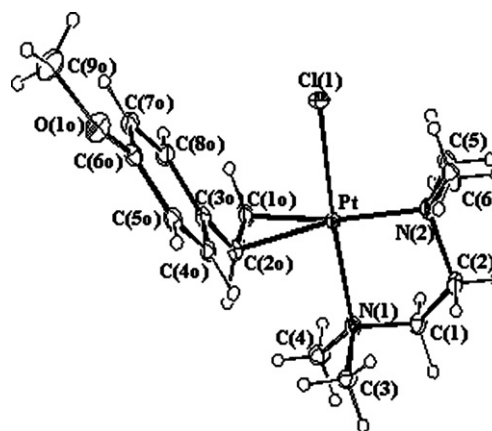


Fig. 3. ORTEP drawing of the complex $[\text{PtCl}(\eta^2\text{-4-OMe-styrene})(\text{tmeda})](\text{ClO}_4)$, **1c** (the counter anion omitted for clarity). Data collection performed at 193 K. Ellipsoids enclose 20% probability.

Table 3Selected bond lengths (Å) and angles (°) for [PtCl(η^2 -styrene)(tmeda)](ClO₄) (**1b**) and [PtCl(η^2 -4-OMe-styrene)(tmeda)](ClO₄) (**1c**)

Vector	1b	1c
Pt–Cl(1)	2.297(3)	2.3028(14)
Pt–N(1)	2.112(9)	2.083(5)
Pt–N(2)	2.097(4)	2.103(2)
Pt–C(1o)	2.160(6)	2.145(2)
Pt–C(2o)	2.223(6)	2.218(3)
N(1)–C(1)	1.508(9)	1.511(5)
N(2)–C(2)	1.498(7)	1.495(4)
C(1)–C(2)	1.498(9)	1.494(5)
C(1o)–C(2o)	1.395(9)	1.386(6)
C(2o)–C(3o)	1.462(9)	1.469(4)
N(1)–Pt–N(2)	85.0(2)	84.7(1)
N(1)–Pt–C(1o)	97.8(2)	97.1(2)
N(1)–Pt–C(2o)	90.1(3)	90.6(1)
N(2)–Pt–C(1o)	160.2(2)	159.1(2)
N(2)–Pt–C(2o)	162.6(2)	163.8(1)
N(1)–Pt–Cl(1)	174.8(2)	174.9(1)
N(2)–Pt–Cl(1)	89.8(1)	90.2(1)
C(1o)–Pt–Cl(1)	87.1(2)	87.8(2)
C(2o)–Pt–Cl(1)	94.8(2)	94.3(9)
C(1)–N(1)–Pt	102.9(5)	104.5(3)
C(3)–N(1)–Pt	110.4(5)	111.0(3)
C(4)–N(1)–Pt	115.9(5)	117.3(3)
C(2)–N(2)–Pt	106.9(3)	107.05(18)
C(5)–N(2)–Pt	107.8(3)	107.04(19)
C(6)–N(2)–Pt	115.5(3)	115.3(2)
C(3)–N(1)–C(1)	109.7(5)	108.8(3)
C(4)–N(1)–C(1)	106.7(6)	106.8(4)
C(4)–N(1)–C(3)	110.8(7)	108.1(3)
C(2)–N(2)–C(6)	107.7(4)	108.2(2)
C(5)–N(2)–C(2)	109.5(4)	109.8(3)
C(5)–N(2)–C(6)	109.3(4)	109.4(2)
C(1o)–C(2o)–C(3o)	125.8(6)	125.7(4)

from tmeda, and the centroid of the olefin double bond are considered. In both cations the metal atom lies exactly in the plane defined by the chlorine and nitrogen donors; the Pt–Cl(1), Pt–N(1) (*cis* to the olefin), and Pt–N(2) (*trans* to the olefin) bond distances are very close to the value found for the ethene derivative [10b] when the estimated standard deviations are taken into account. In the tmeda ligand N–C and C–C distances fall in the normal range. The chelate ring is puckered and both λ and δ conformations are present in the crystal; the puckering, comparable in the two complexes, was measured by the q_2 parameter of Cremer and Pople [16] (0.481(9) and 0.468(5) Å for **1b** and **1c**, respectively).

Bond angles of the coordination sphere are close to the idealized values of 90° and 180° when the Cl(1), N(1) and N(2) atoms are considered, the largest deviation being that of the N(1)–Pt–N(2) bond angle (close to 85°), which is governed by the bite angle of the tmeda ligand. The dihedral angle between the least-square planes defined by Pt, C(1o) and C(2o) and by Cl(1), N(1), and N(2) (from now on referred to as coordination plane) deviates by ~10° from the ideal value of 90° (the corresponding deviation was only 2° in the case of the previously investigated [PtCl(η^2 -CH₂=CH₂)(tmeda)]⁺ (**1a**), where the olefin approached the idealized perpendicular orientation [10b]).

The distance between platinum and the unsubstituted olefinic carbon is significantly shorter than that between platinum and the olefinic carbon bearing the phenyl ring (Table 3); this could be taken as an indication that in the two complexes there is a contribution of the η^1 -limiting formula to the ground state structure.

The C(1o)–C(2o) bond distance, similar for the two compounds, is very close to the values found for the ethene derivative (1.376(3) Å) [10b] and for the Zeise's anion, [PtCl₃(η^2 -C₂H₄)]⁻, (1.375(4) Å) [17]. Bond distances and angles involving the olefin are normal. As generally found in olefin complexes, there is a deviation of the olefin moiety (CH₂=CHR) from planarity. Such a deviation can be

sized by the α angle between the normals to the CH₂ and CHR planes [18]. This angle is 32° in Zeise's anion [17] and in **1a** [10b], and close to 60° in **1b** and **1c**. A greater α (0° is the value for a perfectly planar olefin) indicates greater bending-back of the olefin substituents and, in turn, greater electron back-donation from the metal $d\pi$ to the olefin π^* orbital. The phenyl ring is oriented towards the chlorido ligand (*syn* orientation) and outward with respect to the Me₂N(1) group of tmeda (*anti* orientation); such an orientation avoids steric repulsions that could occur if the phenyl was *syn* to the Me₂N(1) group. Moreover, the phenyl ring is almost coplanar with the olefin, the C(1o)–C(2o)–C(3o)–C(4o) torsion angles being -164.0(4)° and -162.7(2)° for **1b** and **1c**, respectively. Such an orientation, that leads to significant non-bonding interactions between an *ortho* proton of the phenyl ring and the olefin proton on C(2o) (H...H distances of 2.19(4) and 2.15(3) Å for **1b** and **1c**, respectively), can be accounted for on the basis of an electronic conjugation between the phenyl and the olefin π systems. The X-ray structure also reveals a conjugation between the oxygen lone pair of the methoxy substituent and the phenyl π system. Moreover, the short values of the O–Ph (1.352(4) Å) and O–Me (1.434(4) Å) bonds and the large value of the Me–O–Ph angle (118.5(2)°) indicate that the oxygen atom has a sp^2 hybridization and the O–Ph some double bond character. A similar situation has been previously described in some iminoether complexes of platinum [19] and leads to the conclusion that, whenever an oxygen atom is adjacent to an unsaturated system, an oxygen lone pair gets involved in the π bond.

Hydrogen-bond type interactions are found between two methyl groups from tmeda and the *cis* chlorine atom. Both in **1b** and **1c**, the complex cations form columnar arrays with the perchlorate anions hosted in the holes. There are no stacking interactions between the π systems of the phenyl rings.

2.4. DFT calculations

The geometries of the cations of **1b** and **1c** were optimized starting from the X-ray structures (similar calculations were also performed on **1e**, using the coordinates of **1c** for the initial guess). The calculated metric values compare well to the experimental data. For the bond lengths the average deviation is 0.05 Å, while the greatest deviation is ~0.1 Å and involves the Pt–C(2o) bond in **1c**. The metal–carbon bond distances happen to be the least accurate as it can be judged from their large variation as a function of the solvent. For the bond angles, the average deviation is 1°, while the maximum deviation is 4° and it involves the C(1o)–C(2o)–C(3o) bond angle of **1c**. Geometry optimizations of the same cations in the presence of solvents (CHCl₃, CH₂Cl₂, (CH₃)₂CO, and CH₃OH), within the C-PCM approach [20], lead to similar results. Therefore the calculations reproduce well the structural features of these olefin complexes. In particular the calculations reproduce the fact that not all olefins are symmetrically bonded to the metal but a slippage is present in **1b** and **1c** [6].

In order to better analyze the effect of coordination to [PtCl(tmeda)]⁺, we compared free and coordinated olefins. For the three complexes here considered, upon coordination, the C–C bond elongates by 0.06–0.07 Å; while the α angle, which sizes the bending-back of the olefin substituents, is 33–34° (similar to the experimental values found in **1a** and in Zeise's anion but significantly smaller than those found in **1b** and **1c**). A Natural Bond Orbital (NBO) analysis was carried out to study the bonding properties between the olefin and the metal. For the three complexes the donation from the olefin to the metal is found to be significantly stronger than the back-donation from the metal to the olefin. In particular the olefin π orbital donates almost 0.5 electrons to the metal fragment, while the back-donation to π^* is no larger than 0.3 electrons. Within the Perturbation Theory Energy Analysis, the

lowering in energy of the filled metal d_{π} orbital, consequent to the interaction with the empty olefin π^* , increases from 4-OMe-styrene (33.7 kcal/mol) to styrene (38.9 kcal/mol) and to 4-CF₃-styrene (40.6 kcal/mol), in good agreement with the Hammett σ parameters. The donation from the olefin to the metal complex is best understood by looking at the Natural Localized Molecular Orbitals (NLMO) and in particular at the orbital describing the olefinic π bond (Table 4). This orbital has always a larger contribution coming from the unsubstituted carbon and the difference between unsubstituted and substituted carbon increases from 4-CF₃-styrene (6%), to styrene (8%), and to 4-OMe-styrene (13%). Since the back-donation is almost equal for the two carbons, the π donation determines the difference between the electron densities on the two carbons; the substituted carbon being the one with smaller electron density. This analysis thus accounts for a slightly stronger interaction between the metal and the unsubstituted carbon. This difference in Pt–C interactions is however small and is largest in the 4-methoxy substituted styrene for which the calculated difference between the contributions of the two carbons is the highest.

The computational analysis of selectivity requires, in principle, the determination of the transition states for the competing reactions. This is not feasible in the present case because in the *gas phase* the addition of an anionic nucleophile to a cationic species occurs without a transition state. Therefore, since the calculations involving ionic species require the full consideration of all partners (here two cations and two anions) as well as the participation of the solvent, we resort to consider only the properties of the reactants to rationalize the observations. This mode of reasoning has been frequently used with success in particular for the regioselectivity of addition to organic substrates [21]. The nucleophilic addition does not occur to a non-coordinated olefin, but only to olefins coordinated to a metal fragment. The earlier work carried at the extended Hückel level [3] gave a LUMO for the coordinated olefin which was higher in energy than that of the free olefin. This is because the olefinic π^* is destabilized by anti-bonding interaction with occupied metal d orbitals. The explicit consideration of electron density and total charge, at the DFT level, yields a different result. The calculations show that, because of the positive charge on the metal fragment, the LUMO of the complexed olefin is significantly lower in energy than that of the free olefin. Even though the energies of empty orbitals in DFT calculations should not be considered quantitatively, they are qualitatively informative: low lying empty orbitals clearly indicate an increased reactivity towards an incoming nucleophile [22]. In the present case, the η^2 -coordination activates the olefin towards nucleophilic addition. The regioselectivity of the addition reaction is in accord with the electron distribution associated with the NLMO analysis. The donation from the olefinic π orbital to platinum dominates over the back-donation from platinum d_{π} orbitals to the olefin. In the donation the two carbons behave differently and the unsubstituted one, which moves closer to platinum, remains more electron rich and therefore becomes less susceptible of nucleophilic attack. This is specifically the case of the 4-OMe-styrene complex (**1c**) for which the observed regioselectivity is the highest (we refer to the results in dichloromethane because it is a non coordinating solvent). In the

4-CF₃-substituted compound (**1e**) the two carbons contribute almost equally to the donation of the π orbital to Pt and, as a consequence, the observed regioselectivity is the lowest.

3. Conclusions

This investigation has shown that there is a significant participation of the η^1 limiting formula to the ground state geometry of styrene complexes **1b** and **1c**. This conclusion is supported by several evidences: the terminal carbon of the olefin, as compared to the one bearing the phenyl substituent, has a greater shielding, a greater coupling with ¹⁹⁵Pt, and a shorter distance from the metal atom. This slippage of the olefin appears to stem from a phenyl stabilization of the positive charge which accumulates on the distal olefinic carbon (+M effect). The conjugation between the phenyl and the olefin π systems is revealed by the *quasi* planarity of the styrene moiety; this planar conformation is attained notwithstanding the repulsive interactions between the *ortho* protons of the phenyl ring and a proton of the olefin moiety. The presence of a methoxy substituent in *para* position of the phenyl ring (**1c**) substantially contributes to a further stabilization of the η^1 -slipped form. The electron releasing ability of the 4-methoxy substituent is promoted by an oxygen lone pair getting involved in conjugation with the π system of the phenyl ring. This is inferred by several structural features such as the methoxy group coplanar with the phenyl ring, the Me–O–Ph angle close to 120°, and the Me–O and O–Ph distances slightly shorter than average values. In terms of reactivity, the presence of a methoxy substituent in *para* position is sufficient to shift the reaction towards the almost exclusive formation of the Markovnikov addition product (addition of methoxide to the olefinic carbon bearing the phenyl ring). On the other hand, the presence of an electron withdrawing substituent (compounds **1d–g**) reduces the +M effect of the phenyl ring (smaller differences in shielding and coupling with ¹⁹⁵Pt of the two olefinic carbons) and in the reaction with MeO[−] the Markovnikov and the *anti*-Markovnikov addition products form in comparable yields.

DFT calculations have revealed a significant slippage of the η^2 -bonded olefin (unsubstituted carbon closer to the metal center) for the 4-OMe-styrene derivative and, to a lesser extent, for the styrene derivative, in good agreement with the solid state structures. The reactivity of the complexed olefin towards an incoming nucleophile stems from a lowering of the LUMO energy with respect to that of the free olefin. Finally the regioselectivity can be understood on the basis of the interaction between the olefinic π and the empty Pt d orbitals: the carbon which is closer to the metal atom is more electron rich and less susceptible of nucleophilic attack. Despite being only qualitative, this analysis has succeeded in highlighting some principles which control the reactivity and selectivity of nucleophilic addition to coordinated olefins.

4. Experimental

4.1. Reagents and methods

Reagents and solvents were commercially available and used as received without further purification. Elemental analyses were performed with a CHN Eurovector EA 3011. ¹H and ¹³C NMR spectra were recorded with a 300 MHz Mercury Varian and a DPX-WB 300 Avance Bruker instruments equipped with probes for inverse detection and with z gradient for gradient-accelerated spectroscopy. ¹H and ¹³C NMR spectra were referenced to TMS; the residual proton signal of the solvent was used as internal standard. ¹H/¹³C inversely detected gradient-sensitivity enhanced heterocorrelated 2D NMR spectra for normal coupling (INVIEAGSSI) were acquired

Table 4
Contributions from the two vinyl carbon atoms in the orbitals involved in σ donation (π) and π back-donation (d_{π} Pt) as obtained by NLMO analysis

Complex	π		d_{π} Pt	
	%C _{us}	%C _s	%C _{us}	%C _s
1b	41.4	33.5	4.4	5.0
1c	44.0	30.6	3.8	5.0
1e	40.6	34.6	4.7	5.1

C_{us} = C(1o), C_s = C(2o) of X-ray crystal structures.

using standard Bruker automation programs and pulse sequences. Each block of data was preceded by eight dummy scans. The data were processed in the phase-sensitive mode. The ESI-MS spectra were recorded with an Agilent 1100 Series LC-MSD Trap System VL.

4.2. Syntheses

Cationic complexes $[PtCl(\eta^2\text{-olefin})(tmeda)](ClO_4)$, **1**, (olefin = ethene, **1a**; propene, **1a'**; styrene, **1b**; 4-OMe-styrene, **1c**; 3-OMe-styrene, **1d**; 4-CF₃-styrene, **1e**; 3-CF₃-styrene, **1f**; 3-NO₂-styrene, **1g**).

Complexes **1a** [10a], **1a'** [10c] and **1b,c** [10g] were prepared according to already reported procedures. Complexes **1d,g** were prepared similarly to **1b,c** by olefin exchange starting from the cationic complex $[PtCl(\eta^2\text{-propene})(tmeda)](ClO_4)$, **1a'**. In a typical experiment **1a'** (250 mg, 0.5 mmol) was suspended in dichloromethane (3 mL) and treated with a 10 molar excess of the incoming olefin (**d** = 3-OMe-styrene or **g** = 3-NO₂-styrene). After 24 h stirring at room temperature, the solid was recovered on a sintered glass filter, washed with diethyl ether, and dried; it turned to be the desired compound.

$[PtCl(\eta^2\text{-3-OMe-styrene})(tmeda)](ClO_4)$, **1d**: the isolated yield, referred to platinum, was 95% (282 mg). Elemental Anal. Calc. for C₁₅H₂₆Cl₂N₂O₅Pt (580.36): C, 31.04; H, 4.52; N, 4.83. Found: C, 31.33; H, 4.44; N, 4.45%. Peak of greatest intensity in ESI-MS: $m/z = 481 = [M-ClO_4]^+$. NMR (acetonitrile-*d*₃, 21 °C): $\delta(^1H) = 3.2\text{--}2.7$ (16H), CH₃N and CH₂N of tmeda; 3.83 (s, 3H), CH₂=CHC₆H₄OCH₃; 4.7 (d, ³J_{H-H} *cis* = 8 Hz, ²J_{Pt-H} = 61 Hz, 1H), and 5.3 (bd, ³J_{H-H} *trans* = 15 Hz, 1H), CH₂=CHC₆H₄-3-OCH₃; 6.3 (bm, 1H), CH₂=CHC₆H₄-3-OMe; 7–7.4, aromatic H ppm.

$[PtCl(\eta^2\text{-3-NO}_2\text{-styrene})(tmeda)](ClO_4)$, **1g**: the isolated yield, referred to platinum, was 95% (295 mg). Elemental Anal. Calc. for C₁₄H₂₃Cl₂N₃O₆Pt (595.3): C, 28.24; H, 3.89; N, 7.06. Found: C, 28.52; H, 3.98; N, 7.10%. Peak of greatest intensity in ESI-MS: $m/z = 495.9 = [M-ClO_4]^+$. NMR (acetone-*d*₆, 21 °C): $\delta(^1H) = 2.97$ (s, 3H), 3.01 (s, 6H), 3.48 (s, 3H), tmeda CH₃N; 3.01 (m, 1H), 3.23 (m, 1H), 3.5 (m, 1H), and 3.57 (m, 1H), tmeda CH₂N; 5.05 (d, ³J_{H-H} *cis* = 8.2 Hz, ²J_{Pt-H} = 65 Hz, 1H), and 5.62 (d, ³J_{H-H} *trans* = 15.2 Hz, ²J_{Pt-H} = 57 Hz, 1H), CH₂=CHC₆H₄-3-NO₂; 6.61 (m, 1H), CH₂=CHC₆H₄-3-NO₂; 7.7 (t, ³J_{H-H} = 8.0 Hz, 1H), H_{meta}; 8.23 (d, 1H), H_{ortho}; 8.31 (d, 1H), H_{para}; 8.54 (s, 1H), H_{ortho} ppm. $\delta(^{13}C) = 49, 50, 51, \text{ and } 52$, tmeda CH₃N; 62 and 65, tmeda CH₂N; 70.5 (¹J_{Pt-C} = 124 Hz), CH₂=CHC₆H₄-3-NO₂; 96.0 (¹J_{Pt-C} = 139 Hz), CH₂=CHC₆H₄-3-NO₂; 123, C_{ortho}; 124, C_{para}; 129, C_{meta}; 136, C_{ortho} ppm.

Complexes **1e,f** were prepared by olefin exchange starting from the cationic complex **1g**. In a typical experiment **1g** (150 mg, 0.25 mmol), was suspended in dichloromethane (3 mL), and treated with a 13-fold excess of the incoming olefin (**e** = 4-CF₃-styrene or **f** = 3-CF₃-styrene). After 24 h stirring at room temperature, the reaction mixture was filtered on a sintered glass filter to remove un-reacted **1g**. The mother liquor was evaporated to dryness under vacuum and the sticky residue after trituration with diethyl ether gave a yellowish solid which was **1e** or **1f**. The isolated yield, always referred to platinum and after the indicated stirring time, was ca. 50%.

$[PtCl(\eta^2\text{-4-CF}_3\text{-styrene})(tmeda)](ClO_4)$, **1e**: Elemental Anal. Calc. for C₁₅H₂₃Cl₂F₃N₂O₄Pt (618.33): C, 29.14; H, 3.75; N, 4.53. Found: C, 29.49; H, 3.66; N, 4.37%. Peak of greatest intensity in ESI-MS: $m/z = 518.9 = [M-ClO_4]^+$. NMR (acetone-*d*₆, 21 °C): $\delta(^1H) = 2.97$ (s, 3H), 3.02 (s, 6H), 3.48 (s, 3H), tmeda CH₃N; 3.04 (m, 1H), 3.16 (m, 1H), 3.48 (m, 1H), 3.54 (m, 1H), tmeda CH₂N; 5.0 (d, ³J_{H-H} *cis* = 9 Hz, 1H), and 5.54 (d, ³J_{H-H} *trans* = 15 Hz, 1H), CH₂=CHC₆H₄-4-CF₃; 6.56 (m, 1H), CH₂=CHC₆H₄-4-CF₃; 7.72 (d, ³J_{H-H} = 8.7 Hz, 2H), 2H_{ortho}; 7.99 (d, 2H), 2H_{meta} ppm. $\delta(^{13}C) = 49.86, 50.61,$

51.24, and 53.12, tmeda CH₃N; 62.54 and 66.94, tmeda CH₂N; 65, CH₂=CHC₆H₄-4-CF₃; 96.5, CH₂=CHC₆H₄-4-CF₃; 130.3, C_{meta}; 125, C_{ortho} ppm.

$[PtCl(\eta^2\text{-3-CF}_3\text{-styrene})(tmeda)](ClO_4)$, **1f**: Elemental Anal. Calc. for C₁₅H₂₃Cl₂F₃N₂O₄Pt (618.33): C, 29.14; H, 3.75; N, 4.53. Found: C, 29.44; H, 3.48; N, 4.72%. Peak of greatest intensity in ESI-MS: $m/z = 518.9 = [M-ClO_4]^+$. NMR (acetone-*d*₆, 21 °C): $\delta(^1H) = 2.97$ (s, 3H), 3.0 (s, 6H), and 3.41 (s, 3H), tmeda CH₃N; 3.02 (m, 1H), 3.18 (m, 1H), 3.5 (m, 1H), and 3.58 (m, 1H), tmeda CH₂N; 4.98 (d, ³J_{H-H} *cis* = 10 Hz, ²J_{Pt-H} = 64 Hz, 1H) and 5.54 (d, ³J_{H-H} *trans* = 14 Hz, ²J_{Pt-H} = 55 Hz, 1H), CH₂=CHC₆H₄-3-CF₃; 6.56 (m, 1H), CH₂=CHC₆H₄-3-CF₃; 7.63 (t, 1H, ³J_{H-H} = 8.0 Hz), H_{meta}; 7.79 (d, 1H), H_{ortho}; 8.04 (s, 1H), H_{ortho}; 8.11 (d, 1H), H_{para} ppm. $\delta(^{13}C) = 49.6, 50.4, 51.1, \text{ and } 53.3$, tmeda CH₃N; 62.4 and 66.9, tmeda CH₂N; 70.5 (¹J_{Pt-C} = 164 Hz), CH₂=CHC₆H₄-3-CF₃; 97.3 (¹J_{Pt-C} = 137 Hz), CH₂=CHC₆H₄-3-CF₃; 125.98, C_{ortho}; 126.42, C_{para}; 129.43, C_{meta}; 133.77, C_{ortho} ppm.

4.3. Addition products with methoxide anion

The addition product **2b** has already been reported [10c]. Compounds **2c-g** have been prepared as hereafter described. A few mL of CH₂Cl₂ and a known amount of a methanolic solution of KOH (0.12 mmol, 120 μ L of a 1 M solution) were placed in a reaction vessel and treated with a stoichiometric amount (0.12 mmol) of the appropriate cationic complex. In the case of unstable starting complexes (**1e-g**) the reaction vessel was precooled in an ice bath. The mixture was kept under stirring for 2 h during that time dissolution of the cationic complex and precipitation of KClO₄ were observed. The organic phase was repeatedly washed with water (4 \times 0.5 ml), diluted with CH₂Cl₂ up to 20 mL and kept for some hours over anhydrous Na₂SO₄, filtered, and finally evaporated to dryness under vacuum. Trituration with diethyl ether of the obtained sticky residue gave a solid powder of the addition product, which was a mixture of the Markovnikov and anti-Markovnikov isomers. The yield, referred to platinum, was nearly quantitative.

2c, Elemental Anal. Calc. for C₁₆H₂₉ClN₂O₂Pt (511.94): C, 37.54; H, 5.71; N, 5.47. Found: C, 38.1; H, 5.92; N, 5.68%. NMR (CDCl₃, 21 °C): $[PtCl(\eta^1\text{-CH}_2\text{-CH(OCH}_3\text{)}(C_6H_4\text{-4-OCH}_3\text{)})(tmeda)]$, $\delta(^1H) = 1.92$ (s, ³J_{Pt-H} = 50 Hz, 3H), 2.66 (s, 3H), 2.68 (s, 3H), and 2.71 (s, 3H), tmeda CH₃N; 2.6–2.9 (m, 4H), tmeda CH₂N; 1.19 (t, ²J_{H-H} and ³J_{H-H} = 9.5 Hz, ²J_{Pt-H} = 90 Hz, 1H) and 2.23 (dd, ³J_{H-H} = 5.0 Hz, 1H), Pt-CH₂-CH(OCH₃)(C₆H₄-4-OCH₃); 3.27 (s, 3H), Pt-CH₂-CH(OCH₃)-(C₆H₄-4-OCH₃); 3.74 (s, 3H), Pt-CH₂-CH(OCH₃)(C₆H₄-4-OCH₃); 4.56 (dd, 1H), Pt-CH₂-CH(OCH₃)(C₆H₄-4-OCH₃); 6.77 (d, ³J_{H-H} = 8.5 Hz, 2H), 2H_{meta}; 7.55 (d, 2H), 2H_{ortho} ppm. In this case the anti-Markovnikov isomer was very minor (<5%).

2d, Elemental Anal. Calc. for C₁₆H₂₉ClN₂O₂Pt (511.94): C, 37.54; H, 5.71; N, 5.47. Found: C, 37.01; H, 6.02; N, 5.95%. NMR (CDCl₃, 21 °C): $[PtCl(\eta^1\text{-CH}_2\text{-CH(OCH}_3\text{)}(C_6H_4\text{-3-OCH}_3\text{)})(tmeda)]$, $\delta(^1H) = 1.92$ (s, ³J_{Pt-H} = 50 Hz, 3H), 2.67 (s, 3H), 2.69 (s, 3H), and 2.71 (s, 3H), tmeda CH₃N; 2.6–2.9 (m, 4H), tmeda CH₂N; 1.22 (t, ²J_{H-H} and ³J_{H-H} = 9.6 Hz, ²J_{Pt-H} = 90 Hz, 1H), and 2.21 (dd, ³J_{H-H} = 5.0 Hz, 1H), Pt-CH₂-CH(OCH₃)(C₆H₄-3-OCH₃); 3.28 (s, 3H), Pt-CH₂-CH(OCH₃)(C₆H₄-3-OCH₃); 3.76 (s, 3H), Pt-CH₂-CH(OCH₃)(C₆H₄-3-OCH₃); 4.58 (dd, 1H), Pt-CH₂-CH(OCH₃)(C₆H₄-3-OCH₃); 6.66 (dd, ³J_{H-H} = 8.2 Hz, ⁴J_{H-H} = 2.8 Hz, 1H), H_{para}; 6.95 (s, 1H), H_{ortho}; 7.14 (d, ³J_{H-H} = 7.6 Hz, 1H), H_{ortho}; 7.2 (m, 1H), H_{meta} ppm. $[PtCl(\eta^1\text{-CH(OCH}_3\text{)}(C_6H_4\text{-3-OCH}_3\text{)}\text{-CH}_2\text{(OCH}_3\text{)})(tmeda)]$, $\delta(^1H) = 2.60$ (s, 3H), 2.64 (s, 3H), 2.76 (s, 3H), and 2.84 (s, 3H), tmeda CH₃N; 2.6–2.9 (m, 4H), tmeda CH₂N; 3.09 (dd, ³J_{H-H} = 4.1 and 10.5 Hz, 1H), Pt-CH(C₆H₄-3-OCH₃)-CH₂(OCH₃); 3.27 (s, 3H), Pt-CH(C₆H₄-3-OCH₃)-CH₂(OCH₃); 3.74 (s, 3H), Pt-CH(C₆H₄-3-OCH₃)-CH₂(OCH₃); 3.86 (dd, ²J_{H-H} = 10.5 Hz, 1H), and 4.0 (t, 1H), Pt-CH(C₆H₄-3-OCH₃)-CH₂(OCH₃); 6.56 (d, ³J_{H-H} = 6.6 Hz, 1H), H_{para}; 6.95 (s, 1H), H_{ortho}; 7.14 (d, ³J_{H-H} = 7.64 Hz, 1H), H_{ortho}; 7.2 (m, 1H), H_{meta}.

2e, Elemental Anal. Calc. for $C_{16}H_{26}ClF_3N_2OPt$ (549.92): C, 34.95; H, 4.77; N, 5.09. Found: C, 34.80; H, 4.52; N, 5.12%. NMR ($CDCl_3$, 21 °C): $[PtCl\{\eta^1-CH_2-CH(OCH_3)(C_6H_4-4-CF_3)\}(tmeda)]$, $\delta(^1H) = 1.89$ (s, $^3J_{Pt-H} = 50$ Hz, 3H), 2.66 (s, 3H), 2.69 (s, 3H), and 2.71 (s, 3H), $tmeda$ CH_3N ; 2.6–2.9 (m, 4H), $tmeda$ CH_2N ; 1.19 (t, $^2J_{H-H}$ and $^3J_{H-H} = 9.6$ Hz, $^2J_{Pt-H} = 90$ Hz, 1H), and 2.21 (dd, $^3J_{H-H} = 5.0$ Hz, 1H), $Pt-CH_2-CH(OCH_3)(C_6H_4-4-CF_3)$; 3.28 (s, 3H), $Pt-CH_2-CH(OCH_3)(C_6H_4-4-CF_3)$; 4.69 (dd, 1H), $Pt-CH_2-CH(OCH_3)(C_6H_4-4-CF_3)$; 7.48 (d, $^3J_{H-H} = 8.0$ Hz, 2H), $2H_{ortho}$; 7.79 (d, $^3J_{H-H} = 8.2$ Hz, 2H), $2H_{meta}$ ppm. $[PtCl\{\eta^1-CH(C_6H_4-4-CF_3)-CH_2(OCH_3)\}(tmeda)]$, $\delta(^1H) = 2.60$ (s, 3H), 2.84 (s, 3H), 2.9 (s, 3H), and 2.94 (s, 3H), $tmeda$ CH_3N ; 2.6–2.9 (m, 4H), $tmeda$ CH_2N ; 3.18 (dd, 1H, $^3J_{H-H} = 4.0$ and 10.5 Hz), $Pt-CH(C_6H_4-4-CF_3)-CH_2(OCH_3)$; 3.27 (s, 3H), $Pt-CH(C_6H_4-4-CF_3)-CH_2(OCH_3)$; 3.88 (dd, $^2J_{H-H} = 10.5$ Hz, 1H), and 4.07 (t, 1H), $Pt-CH(C_6H_4-4-CF_3)-CH_2(OCH_3)$; 7.3 (d, $^3J_{H-H} = 8.23$ Hz, 2H), $2H_{ortho}$; 7.52 (d, $^3J_{H-H} = 8.0$ Hz, 2H), $2H_{meta}$ ppm.

2f, Elemental Anal. Calc. for $C_{16}H_{26}ClF_3N_2OPt$ (549.92): C, 34.95; H, 4.77; N, 5.09. Found: C, 34.65; H, 4.55; N, 5.23%. NMR ($CDCl_3$, 21 °C): $[PtCl\{\eta^1-CH_2-CH(OCH_3)(C_6H_4-3-CF_3)\}(tmeda)]$, $\delta(^1H) = 1.77$ (s, $^3J_{Pt-H} = 50$ Hz, 3H), 2.65 (s, 3H), and 2.68 (s, 6H), $tmeda$ CH_3N ; 2.6 ÷ 2.9 (m, 4H), $tmeda$ CH_2N ; 1.07 (t, $^2J_{H-H}$ and $^3J_{H-H} = 9.5$ Hz, $^2J_{Pt-H} = 90$ Hz, 1H), and 2.27 (dd, $^3J_{H-H} = 4.5$ Hz, 1H), $Pt-CH_2-CH(OCH_3)(C_6H_4-3-CF_3)$; 3.28 (s, 3H), $Pt-CH_2-CH(OCH_3)(C_6H_4-3-CF_3)$; 4.72 (dd, 1H), $Pt-CH_2-CH(OCH_3)(C_6H_4-3-CF_3)$; 7.35 (m, 2H), H_{meta} and H_{ortho} ; 7.8 (d, $^3J_{H-H} = 7.2$ Hz, 1H), H_{para} ; 8.17 (s, 1H), H_{ortho} ppm. $[PtCl\{\eta^1-CH(C_6H_4-3-CF_3)-CH_2(OCH_3)\}(tmeda)]$, $\delta(^1H) = 2.59$ (s, 3H), 2.64 (s, 3H), 2.83 (s, 3H), and 2.88 (s, 3H), $tmeda$ CH_3N ; 2.6 ÷ 2.9 (m, 4H), $tmeda$ CH_2N ; 3.17 (dd, $^3J_{H-H} = 4.2$ and 10.5 Hz, 1H), $Pt-CH(C_6H_4-3-CF_3)-CH_2(OCH_3)$; 3.27 (s, 3H), $Pt-CH(C_6H_4-3-CF_3)-CH_2(OCH_3)$; 3.87 (dd, $^2J_{H-H} = 10.5$ Hz, 1H), and 4.05 (t, 1H), $Pt-CH(C_6H_4-3-CF_3)-CH_2(OCH_3)$; 7.23 (m, 2H), H_{meta} and H_{ortho} ; 7.6 (s, 1H), H_{ortho} ; 7.67 (d, $^3J_{H-H} = 6.9$ Hz, 1H), H_{para} ppm.

2g, Elemental Anal. Calc. for $C_{15}H_{26}ClN_3O_3Pt$ (526.92): C, 34.19; H, 4.97; N, 7.97. Found: C, 37.96; H, 5.12; N, 5.08%. NMR ($CDCl_3$, 21 °C): $[PtCl\{\eta^1-CH_2-CH(OCH_3)(C_6H_4-3-NO_2)\}(tmeda)]$, $\delta(^1H) = 1.77$ (s, $^3J_{Pt-H} = 50$ Hz, 3H), 2.66 (s, 3H), and 2.68 (s, 6H), $tmeda$ CH_3N ; 2.6 ÷ 2.9 (m, 4H), $tmeda$ CH_2N ; 1.08 (t, $^2J_{H-H}$ and $^3J_{H-H} = 9.5$ Hz, $^2J_{Pt-H} = 90$ Hz, 1H), and 2.28 (dd, $^3J_{H-H} = 4.7$, 1H), $Pt-CH_2-CH(OCH_3)(C_6H_4-3-NO_2)$; 3.31 (s, 3H), $Pt-CH_2-CH(OCH_3)(C_6H_4-3-NO_2)$; 4.75 (dd, 1H), $Pt-CH_2-CH(OCH_3)(C_6H_4-3-NO_2)$; 7.31 (m, 2H), H_{meta} and H_{ortho} ; 7.79 (d, 1H, $^3J_{H-H} = 7.2$ Hz), H_{para} ; 8.17 (s, 1H), H_{ortho} ppm. $[PtCl\{\eta^1-CH(C_6H_4-3-NO_2)-CH_2(OCH_3)\}(tmeda)]$, $\delta(^1H) = 2.58$ (s, 3H), 2.60 (s, 3H), 2.84 (s, 3H), and 2.89 (s, 3H), $tmeda$ CH_3N ; 2.6–2.9 (m, 4H), $tmeda$ CH_2N ; 3.18 (dd, $^3J_{H-H} = 4.1$ and 10.5 Hz, 1H), $Pt-CH(C_6H_4-3-NO_2)-CH_2(OCH_3)$; 3.30 (s, 3H), $Pt-CH(C_6H_4-3-NO_2)-CH_2(OCH_3)$; 3.87 (dd, $^2J_{H-H} = 10.5$ Hz, 1H), and 4.06 (t, 1H), $Pt-CH(C_6H_4-3-NO_2)-CH_2(OCH_3)$; 7.26 (m, 2H), H_{meta} and H_{ortho} ; 7.6 (s, 1H), H_{ortho} ; 7.69 (d, $^3J_{H-H} = 7.2$ Hz, 1H), H_{para} ppm.

4.4. X-ray crystallography

The data sets for compounds **1b** and **1c** were collected through a Bruker SMART CCD area detector diffractometer located at X-ray Crystallography Laboratory, Emory University, Atlanta, Georgia, USA, at 193 ± 2 K. Selected crystallographic data are reported in Table 5. The original data sets were corrected for Lorentz-polarization effects through SAINT32 [23] (**1b,1c**) computer packages. The absorption effects were corrected through the ψ -scan techniques by using the SADABS [24] for **1b** and **1c**. The structure solution was performed through the direct methods implemented in the SHELXS-97 software [25a] under WINGX [26]. All the atoms of the coordination sphere and most of the other non-hydrogen atoms were located from the structure solution whereas the remaining atoms were located from subsequent cycles of Fourier-difference synthesis and least-squares calculations. The hydrogen atoms were located via the HFIX options of SHELXL-97 [25b] and left riding on

Table 5

Selected crystal data and structure refinement parameters for $[PtCl(\eta^1\text{-styrene})(tmeda)](ClO_4)$ (**1b**) and $[PtCl(\eta^2\text{-4-OMe-styrene})(tmeda)](ClO_4)$ (**1c**)

Parameter	Value	
	1b	1c
Empirical formula	$C_{14}H_{24}Cl_2N_2O_4Pt$	$C_{15}H_{26}Cl_2N_2O_5Pt$
Formula weight	550.34	580.37
Temperature (K)	193(2)	193(2)
Crystal system, space group	Monoclinic, Cc	Monoclinic, Cc
<i>a</i> (Å)	16.059(2)	16.0319(19)
<i>b</i>	11.2805(16)	11.4831(13)
<i>c</i>	12.8872(19)	13.0220(15)
α (°)	90	90
β (°)	127.124(2)	126.6400(10)
γ (°)	90	90
Volume (Å ³)	1861.5(5)	1923.6(4)
Z, Calculated density (Mg m ⁻³)	4, 1.964	4, 2.004
Absorption coefficient (mm ⁻¹)	7.844	7.600
Crystal size (mm)	0.24 × 0.22 × 0.13	0.43 × 0.25 × 0.18
Reflections collected/unique [<i>R</i> _{int}]	12,587/4604 [0.0399]	13,608/4687 [0.0265]
Data/restraints/parameters	4369/2/208	4562/2/226
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ , 0.0269; <i>wR</i> ₂ , 0.0630	<i>R</i> ₁ , 0.0157; <i>wR</i> ₂ , 0.0369
<i>R</i> indices (all data)	<i>R</i> ₁ , 0.0288; <i>wR</i> ₂ , 0.0639	<i>R</i> ₁ , 0.0162; <i>wR</i> ₂ , 0.0371
Absolute structure parameter	0.071(8)	−0.003(4)
Largest difference in peak and hole (e Å ⁻³)	1.226 and −0.858	0.932 and −0.571

The wavelength was 0.71073 Å for all data collection.

the atoms to which they are attached. The non-hydrogen atoms were refined as anisotropic, and the hydrogen atoms were treated as isotropic with thermal factors equal to 1.2 times those of the correspondent heavier atoms. Twenty-four cycles of least-squares calculations gave a nice convergence for the model of each of the two structures. The conventional *R*₁ and *wR*₂ factors converged to 0.0269 and 0.0630 for **1b**, and 0.0157 and 0.0361 for **1c**. The analysis of molecular geometry parameters was performed through PARST-97 [27] and the molecular graphics was carried out through ORTEP-32 [28]. All the calculations were performed by using Pentium IV personal computers operating through the Windows-XP system. All data for the structures here reported have been deposited with the Cambridge Crystallographic Data Centre as CCDC reference numbers: 665827 (**1b**) and 665825 (**1c**).

4.5. Computational details

The calculations were performed with the GAUSSIAN03 package [29] at the B3PW91 level [30]. Platinum and chlorine atoms were represented by the relativistic effective core potentials (RECP) from the Stuttgart group and their associated basis sets (SDDALL keyword in GAUSSIAN03) [31], augmented by a *f* polarization function for Pt ($\alpha = 0.993$) [32a] and a *d* for Cl ($\alpha = 0.64$) [32b]. A 6-31G(d,p) basis set was used for all the other atoms (C, N, H, O, F) [33]. The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum had been reached. Geometry optimizations were performed at the B3PW91 level either in the *gas phase* or within the C-PCM methodology (UAKS radii were used) [20]. Natural bonding orbital analysis [34] was performed with the NBO 5.0 version implemented in GAUSSIAN03.

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Appendix A. Supplementary material

CCDC 665827 and CCDC 665825 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.05.040](https://doi.org/10.1016/j.jorganchem.2008.05.040).

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