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PAPER

Modulation of properties in analogues of Zeise's anion on changing the ligand *trans* to ethene. X-Ray crystal structures of *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$ and *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-$†

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To get further insight in the reaction of nucleophilic substitution upon changing the ligand *trans* to a η^2-olefin, the reactivity of some monoanionic platinum(II) complexes (*trans*-$[PtCl_2X(\eta^2\text{-}C_2H_4)]^-$, X = Cl^-, **1**, OH^-, **2**, and $CH_2NO_2^-$, **3**) towards pyridines with different steric hindrance (py, 4-Mepy, and 2,6-Me_2py) has been tested. All crystallographic (**2** and **3** reported for the first time) and spectroscopic data are in accord with a platinum–olefin interaction decreasing in the order **2** > **1** > **3**, paralleling the decreasing electronegativity of the donor atom (O > Cl > C). Not only the platinum-olefin bond but also the bond between platinum and the ligand *trans* to the olefin appear to be strongest in **2** (Pt–O distance at the lower limit for this type of bond). In the reaction with py, the ligand *trans* to the olefin is displaced in **1** and **2**. Moreover the reaction is in equilibrium in the case of sterically hindered 2,6-Me_2py, the equilibrium being shifted moderately or prevalently toward the reagents in the case of **1** and **2**, respectively. In the case of **3**, the reaction with pyridines leads to substitution of the olefin instead of the carbanion. This is in accord with the observation that carbanions strongly weaken the *trans* Pt–olefin bond.

Introduction

Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$, serendipitously prepared by William Zeise in 1825,[1] saw its full characterization only 150 years later, when a neutron diffraction study could precisely locate also the hydrogen atoms.[2] Apart from the historical interest, it was in fact the first organometallic compound to be reported, Zeise's anion is a paradigmatic example of olefin to metal bond [3] and a still important starting material for the synthesis of platinum-based organometallic compounds.[4] Moreover, Zeise's salt can be used to detect the presence of the hepatitis associated antigen (HAA) in humans.[5]

The great reactivity of Zeise's anion, essentially related to the great lability of the chloride *trans* to the olefin,[6] allows to bring in the metal coordination shell, and in very mild reaction conditions, any donor having a reasonable affinity to platinum.[7] Such high reactivity towards nucleophiles depends upon the π-acid character of the ethene molecule which stabilizes the trigonal bipyramidal transition state, where the entering and the leaving ligand and the *trans*-directing olefin occupy the equatorial sites.[8] In the trigonal plane, in fact, apart from the lone pairs of the three donors, there is accumulation of extra electron density due to two filled non bonding d orbitals of platinum. The π-back-donation from the metal to the unsaturated ligand can remove part of this electron density and stabilize the transition state.[9] Moreover, in the five-coordinate transition state the repulsion between bonding and non bonding electron pairs is reduced if the angle between entering and leaving ligands is rather small (< 90°, against a theoretical value of 120°).[9] This last aspect has received full experimental support by the isolation of several five-coordinate complexes of formula $[PtCl_2(\eta^2\text{-}C_2H_4)(N\text{–}N)]$, where the bite angle of the dinitrogen ligand is close to 70°.[10]

In water solution Zeise's anion, **1**, readily undergoes substitution of the chloride *trans* to ethene by a solvent molecule which, in basic conditions, can be deprotonated yielding the mono-anionic hydroxo species *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$, **2**. At high pH values, substitution of another Cl^- by OH^- can take place.[11] In basic alcoholic medium RO^- takes the place of OH^-, **2′**.[4a,c]

Substitution of OH^- (**2**) or RO^- (**2′**) for Cl^- (**1**) should not alter the pattern of nucleophilic substitution at the platinum center, however we noticed different reactivity towards a sterically hindered ligand such as 2,9-dimethyl-1,10-phenanthroline, Me_2phen. While **1** reacts readily with Me_2phen forming

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$[PtCl_2(\eta^2\text{-}C_2H_4)(Me_2phen)]$, in contrast species of type **2** do not react at all.[4a] Moreover, if *trans*-$[PtCl_2(OR)(\eta^2\text{-}C_2H_4)]^-$, **2′**, is transformed into *trans*-$[PtCl_2(OR)(\eta^1\text{-}C_2H_4\text{–}OR)]^{2-}$ by a nucleophilic attack of RO^- onto the coordinated ethene in basic methanol, the dianion, differently from **2′**, reacts readily with Me_2phen to give the stable $[PtCl(\eta^1\text{-}C_2H_4\text{–}OR)(Me_2phen)]$ end product.[4a]

To get further insights in the reaction of nucleophilic substitution upon changing the ligand *trans* to the η^2-olefin, we have tested the reactivity of some monoanionic platinum(II) complexes (*trans*-$[PtCl_2X(\eta^2\text{-}C_2H_4)]^-$, X = Cl^-, **1**, OH^-, **2**, and $CH_2NO_2^-$, **3**) towards aromatic imines with different steric requirements (pyridine, py; 4-methylpyridine, 4-Mepy; and 2,6-dimethylpyridine, 2,6-Me_2py). We also report the X-ray crystal structures of **2** and **3** (the X-ray structure of **1** has been resolved long time ago [2]).

Results and discussion

Synthesis and structural characterization of species 2 and 3

Complexes **1**, **2**, and **3** were isolated as tetraphenylphosphonium (PPh_4) salts in order to increase their solubility in organic solvents. Therefore (PPh_4)**1** was obtained from (PPh_4)Cl and Zeise's salt in water at neutral pH, while the same reaction, performed at pH ≈14, gave (PPh_4)**2**. (PPh_4)**3** was obtained by a reaction of (PPh_4)**2** with a moderate excess of nitromethane in organic solvent.[12]

Relevant NMR data for the three anionic complexes are reported in Table 1. It has to be noted that on going from **1** to **2** (substitution of Cl^- *trans* to ethene by OH^-), the proton and carbon atoms of the unsaturated ligand undergo a significant upfield shift. In contrast, when the Cl^- of **1** is replaced by the $CH_2NO_2^-$ carbanion, to give **3**, the resonances of ethene protons and carbons shift to a lower field. The $^2J_{Pt,H}$ value, similar for **1** and **2**, is significantly smaller in the case of **3**. As far as the ^{195}Pt resonance is concerned, **1** and **3** exhibit an almost coincident value (−2747 and −2749 ppm, respectively) while in **2** the signal is slightly shifted to a higher field (−2772 ppm).

It was possible to obtain crystals of **2** and **3** suitable for X-ray investigation; their structures are depicted in Fig. 1 and 2. Significant bond distances are reported in Table 2 together with the corresponding values for Zeise's salt, K**1**. The coordination shell of platinum has, in both cases, the usual square planar arrangement, when the centroid of the olefin bond is considered. The displacement of the platinum atom from the coordination plane is 0.022 and 0.019 Å for **2** and **3**, respectively. The two mutually *trans* Pt–Cl distances remain practically unaltered in all compounds.

Table 1 Selected ^{1}H, ^{13}C and ^{195}Pt chemical shifts for: $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$, **1** (tetrabutylammonium salt, ref. 13); *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$, **2** ($PPh_4$ salt, this work and ref. 14); *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-$, **3** ($PPh_4$ salt, this work)[a]

	Complex		
	1	**2**	**3**
^{1}H (η^2-C_2H_4)	4.33 ($^2J_{Pt,H}$ = 60)	3.72 ($^2J_{Pt,H}$ = 55)	4.46 ($^2J_{Pt,H}$ = 44)
^{1}H (Pt–O*H*)	—	3.82 ($^2J_{Pt,H}$ = 49)	—
^{13}C (η^2-C_2H_4)	68 ($^1J_{Pt,C}$ = 93)	56 ($^1J_{Pt,C}$ = 68)	83 ($^1J_{Pt,C}$ = 83)
^{1}H (η^1-CH_2-)	—	—	5.26 ($^2J_{Pt,H}$ = 104)
^{13}C (η^1-CH_2-)	—	—	71 ($^1J_{Pt,C}$ = 722)
^{195}Pt	−2747	−2772	−2749

[a] Spectra collected in $CDCl_3$; ^{1}H and ^{13}C NMR chemical shifts are given in ppm by using the residual solvent signal as reference; ^{195}Pt NMR chemical shift is given in ppm by using the standard reference K_2PtCl_6; *J* values are given in Hz.

Table 2 Comparison of selected bond lengths [Å] for: $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$, **1** (potassium salt, ref. 2); *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$, **2** ($PPh_4$ salt, this work); *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-$, **3** ($PPh_4$ salt, this work)

Bond lengths [Å]	**1**	**2**	**3**
Pt–O	—	1.991(10)	—
Pt–C_{ol}	2.135(3) and 2.128(3)	2.096(15) and 2.071(19)	2.200(6) and 2.217(7)
Pt–C_σ	—	—	2.078(7)
Pt–Cl_{trans}	2.340(2)	—	—
Pt–Cl_{cis}	2.303(2) and 2.302(2)	2.287(5) and 2.272(5)	2.293(5) and 2.301(5)
C═C	1.375(4)	1.41(2)	1.354(11)

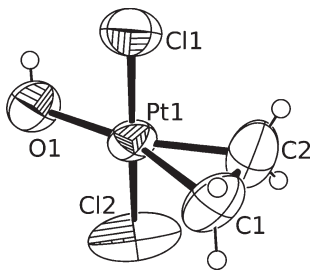


Fig. 1 Single crystal X-ray diffraction molecular structure of (PPh_4) {*trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]$}, ($PPh_4$)**2**. ORTEP drawing, 50% probability ellipsoids, of the *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$ anion. Selected bond lenghts [Å] and angles [°]: Pt1–O1 1.991(10); Pt1–C1 2.096(15); Pt1–C2 2.071(19); Pt1–Cl1 2.287(5); Pt1–Cl2 2.272(5); C1–C2 1.41(2); O1–Pt1–C1 159.3(6); O1–Pt1–C2 161.2(6); C1–Pt1–C2 39.5(7); O1–Pt1–Cl2 90.5(4); O1–Pt1–Cl1 88.9(4); C1–Pt1–Cl1 90.6(6); C1–Pt1–Cl2 90.5(6); C2–Pt1–Cl2 89.7(7); C2–Pt1–Cl1 90.2(7); Cl1–Pt1–Cl2 178.20(19).

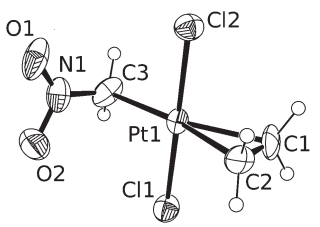


Fig. 2 Single crystal X-ray diffraction molecular structure of (PPh_4) {*trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]$}, ($PPh_4$)**3**. ORTEP drawing, 50% probability ellipsoids, of the *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-$ anion. Selected bond lenghts [Å] and angles [°]: Pt1–C1 2.217(7); Pt1–C2 2.200(6); Pt1–C3 2.078(7); Pt1–Cl1 2.293(5); Pt1–Cl2 2.301(5); C1–C2 1.354(11); N1–O1 1.180(9); N1–O2 1.286(10); N1–C3 1.356 (10); C1–Pt1–C2 35.7(3); C1–Pt1–C3 160.7(3); C1–Pt1–Cl1 90.0(3); C1–Pt1–Cl2 90.5(3); C2–Pt1–C3 163.5(3); C2–Pt1–Cl1 90.2(3); C2–Pt1–Cl2 90.7(3); C3–Pt1–Cl1 91.0(3); C3–Pt1–Cl2 88.3(3); Cl1–Pt1–Cl2 179.06(11); O1–N1–O2 116.3(8); O1–N1–C3 129.1(10); O2–N1–C3 114.4(8).

The Pt–OH bond in **2** (1.991(10) Å) is shorter than in any other reported Pt(II) complex where the *trans* ligand is other than an olefin (*e.g.* hydride (2.16 Å),[15] phenyl (2.094 Å),[16] phosphine (2.042 Å, average),[17] or nitrogen donor (2.028 Å).[18] On the other hand, the Pt–C_σ bond in **3** [2.081(7) Å] lies close to the mean value for platinum–carbon σ-bond distances which may range from 1.903 [19] to 2.432 Å.[20]

The ethene ligand is perpendicular to the coordination plane, the angle between the C═C bond axis and the orthogonal to the coordination plane being only 0.1(9)° in **2** and 0.6(4)° in **3**.[21] The preferred upright orientation of a coordinated olefin in square planar complexes has essentially a steric origin. In fact, an in-plane orientation of the olefin would cause short repulsive contacts with the two adjacent chlorine atoms, as revealed by the significant energy barrier (at least 20 kcal mol^{-1}) for olefin rotation detected in similar species.[22] This interpretation (steric effect favoring the orthogonal disposition of the olefin with respect to the coordination plane in square planar complexes) is fully supported also by the observation that when there is less steric hindrance in the coordination plane, such as in the case of the platinum(II) complex $[Pt\{\eta^3\text{-}CH_2C(Me)CH_2\}(PPh_3)(\eta^2\text{-}CH_2CHPh)]^+$ [23] and, more recently, in the rhodium(I) species $[Rh(PCP)(\eta^2\text{-}C_2H_4)]$ [24] (PCP is a three-coordinate pincer diphosphite ligand), a coplanar arrangement of the coordinated olefin is observed. In the latter complexes the structure of the allyl group (platinum case) and that of the pincer ligand (rhodium case) is such as to leave more room in the coordination plane allowing though the in-plane orientation of the olefin. Accordingly, a very low energy barrier for olefin rotation has been found in the quoted platinum complex.[23]

From the data of Table 2 it appears that on going from **1** to **2**, that is, by substitution of a hydroxyl group for the chloride *trans* to ethene, there is a significant shrinking of the Pt–C_{ol} distances. In contrast, the substitution of a carbanion for the chloride *trans* to ethene, to form **3**, produces considerable elongation of the Pt–C_{ol} bond distances.

Effect of the *trans* ligand upon the platinum–olefin bond

The extent of π-back donation from the metal to a coordinated olefin can be sized by the degree of elongation of the C═C bond of the unsaturated ligand.[25] However this single parameter could not be sufficient for ranking the strength of the π-bond since also pure σ donation from the olefin to the metal can cause a similar effect.[26] Another parameter which could be exploited for sizing the extent of π-back donation is the Pt–C_{ol} bond length. Compared to **1**, complex **2** reveals a significant shortening of the two Pt–C_{ol} bond lengths; therefore it is possible to conclude that, as far as the bonding between the metal and the ethene ligand is concerned, the π-back bonding is greater in **2** than in **1**. This feature is also supported by the NMR data (see above) revealing how the olefin proton and carbon atoms are significantly more shielded in **2** than in **1** (see Table 1).

The lone pairs of anionic oxygen and nitrogen ligands have long been known to engage in repulsion interactions with filled late transition metal d-orbitals.[27] As a consequence the filled d-orbitals are pushed up in energy and these are exactly the orbitals engaged in the back-bonding to the ethene ligand. Thus, it is not surprising that the ethene ligand is strongly bonded with the hydroxo complex. Conversely, the back-bonding of the ethene ligand will reduce the repulsion between the Pt atom and the hydroxo group so that the Pt–OH distance becomes particularly short.

In compound **3** there is a carbanion ($NO_2CH_2^-$) *trans* to the olefin. Carbanions are known to be very strong σ-donors. The carbanion *trans* to the ethene molecule has a dramatic effect on the platinum–olefin bond system and causes a remarkable lengthening of the Pt–C_{ol} bonds (0.10 Å longer than in **1** and 0.14 Å longer than in **2**). Most probably, olefin-to-platinum σ-donation and platinum-to-olefin π-back-donation operate synergistically, therefore a reduction in the olefin-to-platinum σ-bond (due to the strong σ-donor capacity of the *trans* carbanion) can have a strong (weakening) effect on the platinum-to-olefin π-back-donation. Comparing the three *trans* ligands, their σ-donor ability can be confidently rated in the order carbanion > chloride > hydroxyl. The weaker σ-donor ability of chloride, as compared to a carbanion, is also witnessed by the X-ray structure of $[PtCl(\eta^1\text{-}CHRCH_2\text{–}L)(tmen)]^+$, tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine, where the tmen nitrogen *trans* to the η^1-carbon is 0.09 Å longer than that *trans* to chloride.[28] On the other hand the much weaker σ-donor capacity of a hydroxyl, as compared to a carbanion, can be easily deduced by the much greater electronegativity of oxygen with respect to carbon. Therefore, the much smaller σ-donor and π-acceptor capacity of the olefin in **3** can fully account for the remarkable elongation (as compared to **1** and **2**) of the Pt–C_{ol} distances and for the shift to a lower field of the carbon and hydrogen NMR frequencies (the electronic situation more shifted towards that of a regular olefin than towards that of a cyclopropane).[29,30] In summary, all crystallographic and spectroscopic data are in accord with a platinum–olefin interaction decreasing in the order: **2** > **1** > **3**, paralleling the decreasing electronegativity of the donor atoms (O > Cl > C). In **2**, not only the platinum–olefin bond but also the bond between platinum and the ligand *trans* to the olefin appear to be strongest (Pt–O distance at the lower limit for this type of bond).

Reactivity towards an entering nucleophile

The second aim of this work was to investigate how the different ground state stability of the three substrates could influence their reactivity towards a monodentate nucleophile. It has already been mentioned in the Introduction that, while compound **1** readily reacts with chelating, but sterically hindered, neocuproine (Me_2phen) to yield $[PtCl_2(\eta^2\text{-}C_2H_4)(Me_2phen)]$, compound **2** does not react at all.

Therefore the three platinum complexes ($[PtCl_3(\eta^2\text{-}C_2H_4)]^-$, **1**; *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$, **2**; and *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-$, **3**) were reacted with py, 4-Mepy, and 2,6-Me_2py. The reaction course was monitored *via* NMR in organic solvents where all reactants and products are soluble, the results are summarized in Table 3. The expected reaction products, *trans*-$[PtCl_2(L)(\eta^2\text{-}C_2H_4)]$ (L = py, **4a**; 4-Mepy, **4b**; 2,6-Me_2py, **4c**), were independently prepared by a reaction of Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$, with the relevant base (py, 4-Mepy, or 2,6-Me_2py) in water, where complexes of type **4** are practically insoluble and precipitate from solution in almost quantitative yield.[31]

Table 3 Percentage of the product in the reaction of **1**, **2** and **3** with an entering pyridine

	py	4-Mepy	2,6-Me_2py
1	100% **4**	100% **4**	≈ 40% **4**
2	100% **5**[a]	100% **5**[a]	≈ 0% **5**[a]
3	100% **6**	100% **6**	100% **6**

[a] Denotes that **5** is the major reaction product but it is in equilibrium with the precursor **4** (**5** derives from **4** by nucleophylic addition of the released hydroxyl upon the π-ethene).

The reaction of (PPh_4)**1** with L, performed in organic solvent ($CDCl_3$, 294 K), was complete within the mixing time of the reagents (monitored by ^{1}H NMR). However, a quantitative conversion into **4** was achieved only in the case of py and 4-Mepy (eqn (I)), while in the case of 2,6-Me_2py

$$\underset{\mathbf{1}}{[PtCl_3(\eta^2\text{-}C_2H_4)]^-} + L \rightarrow \textit{trans}\text{-}\underset{\mathbf{4}}{[PtCl_2(L)(\eta^2\text{-}C_2H_4)]} + Cl^-$$
$$L = \text{py } (\mathbf{a}); \text{4-Mepy } (\mathbf{b}) \qquad (I)$$

an equilibrium between reagents and products was established and the estimated K value at the working temperature was *ca.* 0.4 (eqn (II)).

$$\underset{\mathbf{1}}{[PtCl_3(\eta^2\text{-}C_2H_4)]^-} + L \rightleftarrows \textit{trans}\text{-}\underset{\mathbf{4}}{[PtCl_2(L)(\eta^2\text{-}C_2H_4)]} + Cl^-$$
$$L = \text{2,6-Me}_2\text{py } (\mathbf{c}) \qquad (II)$$

The reaction of (PPh_4)**2** ($CDCl_3$, 294 K) with py and 4-Mepy also went to completion within the mixing time of the reagents and produced **4** together with *trans*-$[PtCl_2(L)(\eta^1\text{-}C_\alpha H_2C_\beta H_2\text{-}OH)]^-$, **5**, (L = py, **5a**, and 4-Mepy, **5b**. eqn (III)).

Complex **5**, which formally derives from addition of the released OH^- to the coordinated ethene in complex **4**, was in both cases the major component ([**5**]/[**4**] = 5/1). The presence of **5** was recognized by the diagnostic pattern of the ethanide moiety [^{1}H NMR ($CDCl_3$, 294 K): $C_\alpha H_2$ at *ca.* 2.1 ppm ($^2J_{Pt,H}$ *ca.* 85 Hz) and $C_\beta H_2$ at *ca.* 3.2 ppm ($^3J_{Pt,H}$ *ca.* 30 Hz)].

In principle, also a pyridine molecule (L) could add to the coordinated ethene of **4**, and form the zwitterionic species *trans*-$[PtCl_2(L)(\eta^1\text{-}C_\alpha H_2C_\beta H_2\text{-}L)]$, with a similar pattern for the ethanide moiety. These species have been investigated in the past and in the case of 4-MePy even isolated in the solid state; however, they do not survive in solution at temperatures > 243 K.[32] To confirm the nature of species **5**, py or 4-Mepy was added to a solution of independently prepared **4a** or **4b** in $CDCl_3$ at 294 K, no reaction whatsoever was observed (sharp signals of **4** and of free aromatic base were present in the ^{1}H NMR spectra). When the same solution of species **4** was treated with a few drops of KOH in D_2O, signals due to **5** immediately appeared in the organic phase (^{1}H NMR). Species **5** of the present investigation are not indefinitely stable in solution and with time (a few hours at room temperature) they decompose releasing the aromatic base (^{1}H NMR) and forming platinum oligomers (ESI-MS data). This decomposition, however, was not further investigated.

Unlike py and 4-Mepy, 2,6-Me_2py, treated with **2**, does not give the substitution product, neither immediately nor after several hours from the mixing of the reagents (eqn (IV)), showing a strict analogy with Me_2phen previously found not to give reaction products by treatment with the anionic complex **2** in MeOH solution.[4a,c]

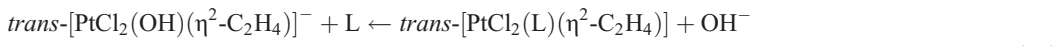
In order to show that the lack of formation of reaction products in the reaction of **2** with sterically hindered aromatic bases (2,6-Me_2py and Me_2phen) is not due to kinetic inertness, but to the shift of the equilibrium in favor of the reactants (eqn (IV)), the complex *trans*-$[PtCl_2(2,6\text{-}Me_2py)(\eta^2\text{-}C_2H_4)]$, **4c**, independently prepared as previously described, was reacted with KOH (made soluble in $CDCl_3$ by the addition of a crown ether). The reverse reaction, with formation of **2** and free 2,6-Me_2py, did occur quantitatively in the mixing time of the reagents.

Finally we tested the reactivity towards the same set of pyridines of (PPh_4)**3**. In all cases the reaction produced, within the mixing time, 100% conversion of the starting substrate into the anionic complex *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(L)]^-$, **6**, (L = py, **6a**; 4-Mepy, **6b**; or 2,6-Me_2py, **6c**) formed by substitution of the aromatic base for ethene (eqn (V)).

Selectivity in the substitution reaction

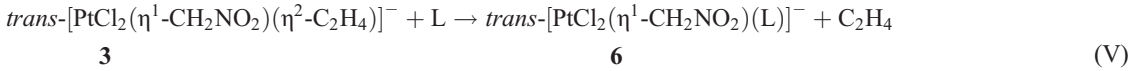
In the nucleophilic substitution at a platinum(II) center, the reaction course is deeply influenced by the nature of the entering ligand, which generally replaces its closest similar (π-acid ligands replace π-acid coordinated groups and σ-donors replace ligands having prevalently a σ-donor character). The reason for such selectivity is that, in the trigonal bipyramidal transition

$$\underset{\mathbf{2}}{\textit{trans}\text{-}[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-} + L \longrightarrow \underset{\mathbf{4}}{\textit{trans}\text{-}[PtCl_2(L)(\eta^2\text{-}C_2H_4)]} + OH^-$$
$$L = \text{Py } (\mathbf{a}); \text{ 4-Mepy } (\mathbf{b}) \qquad \downarrow\uparrow$$
$$\underset{\mathbf{5}}{\textit{trans}\text{-}[PtCl_2(L)(\eta^1\text{-}C_\alpha H_2C_\beta H_2\text{-}OH)]^-} \qquad (III)$$



$$\underset{\mathbf{2}}{trans\text{-}[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-} + L \leftarrow \underset{\mathbf{4}}{trans\text{-}[PtCl_2(L)(\eta^2\text{-}C_2H_4)]} + OH^- \quad \text{(IV)}$$

$L = 2,6\text{-}Me_2py\ (\mathbf{c})$



$$\underset{\mathbf{3}}{trans\text{-}[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-} + L \rightarrow \underset{\mathbf{6}}{trans\text{-}[PtCl_2(\eta^1\text{-}CH_2NO_2)(L)]^-} + C_2H_4 \quad \text{(V)}$$

$L = py\ (\mathbf{a});\ 4\text{-Mepy}\ (\mathbf{b});\ 2,6\text{-}Me_2py\ (\mathbf{c}).$

state, entering, leaving, and *trans* groups share the equatorial plane and ligands with a similar character (σ-donor or π-acceptor) are in stronger competition to one another with one finally losing and leaving the metal core. In accord with this expectation, Vicente & Co.[33] observed that the anionic complex *cis*-$[PtCl_2(CH_2COCH_3)(\eta^2\text{-}C_2H_4)]^-$ (where a σ-carbon and an olefin, having both *trans* labilizing properties, are mutually *cis*) reacts with ligands having a π-acidic character replacing the olefin. In contrast, ligands which are essentially σ-donors replace the chloride lying *trans* to the σ-carbon. In accord with the same view, **1** [34] and **2** (having only one *trans*-labilizing ligand, the olefin) and also **3** (having two *trans*-labilizing groups *trans* to one another) react with π-acid ligands (another olefin) displacing ethene.[35] Always in accord with the same rule, pyridines (which are essentially σ-donors) react with **1** and **2** replacing the σ-donor ligand *trans* to the *trans*-labilizing olefin. Of course, the reaction can be of equilibrium and the equilibrium composition reflects the relative stability of the starting and of the end products. It is interesting to note the deep influence exerted by steric effects upon the stability of pyridine's end products. In the case of 2,6-Me_2py, the steric hindrance exerted by the two methyl substituents in *ortho* position to the N-donor causes destabilization of compound **4c** to such an extent that the starting substrate is still present (partially, **1**, or nearly exclusively, **2**) at the end of the reaction (eqn (II) and (IV)).[32,36] The different extent of formation of **4c** in eqn (II) and (IV) confirms the greater stability of **2** over **1**, already deduced from crystallographic and spectroscopic parameters. The stability of **2** is such that even a bidentate, but sterically hindered, diimine such as neocuproine fails to give reaction products.

It is noteworthy to observe that complex **3** reacts with pyridines (mostly σ-donor ligands) giving an olefin rather than carbanion substitution. Therefore olefin substitution is observed not only in the case of reaction with π-acceptor ligands but also in the case of reaction with σ-donor ligands like pyridines. In the above discussion it was pointed out that a carbanion weakens the interaction between platinum and a *trans* olefin. We can now conclude that the weakening is such that the olefin becomes the most labile ligand and is preferentially displaced not only by π-acceptor but also by σ-donor ligands. Moreover, also an *ortho* disubstituted pyridine, such as 2,6-Me_2py, can give complete displacement of the olefin, further supporting the great destabilization of the platinum-to-olefin bond in **3**.

Conclusions

Our data have highlighted the nature of the Pt–Cl, Pt–OH, and Pt–C_σ bonds *trans* to an olefin (C_σ^- = carbanion). The σ-donor capacity of the ligands can be ranked in the order: $OH^- < Cl^- \ll C_\sigma^-$. A carbanion exerts an exceptionally high weakening effect on the bond between platinum and a *trans*-olefin. As a consequence the olefin is displaced in preference to the carbanion not only by another olefin but also by σ-donors such as pyridines.

The remarkable effect of substituents at the pyridine ring upon the stability of platinum complexes has also been highlighted.

Experimental

Reagents and methods

Reagents and solvents were commercially available and used as received without further purification. Zeise's salt was prepared by a modified procedure [4c] of the method reported by Chock *et al.*[37] The complexes *trans*-$[PtCl_2(\eta^2\text{-olefin})(L)]$, **4**, (L = py, **4a**; 4-Mepy, **4b**; 2,6-Me_2py, **4c**) were prepared in water from Zeise's salt and the appropriate imine according to a reported procedure.[29] Elemental analyses were performed with a CHN Eurovector EA 3011. ^1H, and ^{13}C NMR spectra were recorded with Avance Bruker DPX-WB 300 instrument equipped with probes for inverse detection and with *z* gradient for gradient-accelerated spectroscopy. ^1H and ^{13}C NMR spectra were referenced to TMS; the residual proton and carbon signals of the solvent were used as internal standard. For ^{195}Pt NMR spectra, K_2PtCl_4 (−1643.00 ppm) was used as external standard. $^1H/^{13}C$ inversely detected gradient-sensitivity enhanced heterocorrelated 2D NMR spectra for normal coupling (INVIEAGSSI) were acquired using standard Bruker automation programs and pulse sequences. Each block of data was preceeded 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.

Synthesis of complexes

$(PPh_4)[PtCl_3(\eta^2\text{-}C_2H_4)]$, (PPh_4)1. Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]\cdot H_2O$, (193 mg, 0.50 mmol) was dissolved in 4 mL of water and treated at 273 K with a water solution of $(PPh_4)Cl$ (206 mg, 0.55 mmol, in ~3 mL of solvent). A cream-colored solid instantaneously precipitated. The formed solid was recovered by filtration on a sintered glass filter, washed twice with water and dried *in vacuo*. All manipulations were carried out at room temperature. The yield of (PPh_4)**1**, with respect to platinum, was nearly quantitative. Anal. Calcd (%) for $C_{26}H_{24}Cl_3PPt$ (668.88): C, 46.69; H 3.62. Found: C 46.49; H 3.57. Peaks of greatest intensity in ESI-MS: *m/z* 328 $[M - PPh_4]^-$, and 339 $[M - PtCl_3(\eta^2\text{-}C_2H_4)]^+$. NMR ($CDCl_3$, 300 MHz, 294 K): δ_H

4.32 (pseudo triplet, 4H, $^2J_{Pt,H}$ = 60 Hz, C_2H_4), 7.62–7.93 (m, 20H, P(C_6H_5)$_4$) ppm.

(PPh$_4$){*trans*-[PtCl$_2$(OH)(η^2-C$_2$H$_4$)]}·H$_2$O, (PPh$_4$)2·H$_2$O. The preparation was similar to that of (PPh$_4$)**1**, but in this case Zeise's salt was dissolved in basic water (KOH) at a pH close to 14, while the working temperature was always 273 K. The yield of (PPh$_4$)**2** with respect to platinum was nearly quantitative. Anal. Calcd (%) for $C_{26}H_{25}Cl_2OPPt·H_2O$ (668.45): C, 46.72; H, 4.07; Cl, 10.61. Found: C 46.89; H 3.95; Cl, 10.95. NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 3.71 (pseudo triplet, 4H, $^2J_{Pt,H}$ = 55 Hz, C_2H_4), 3.85 (pseudo triplet, 1H, $^2J_{Pt,H}$ = 49 Hz, O*H*), 7.62–7.93 (m, 20H, P(C_6H_5)$_4$) ppm.

Crystals of (PPh$_4$)**2** were obtained from a solution prepared by dissolving Zeise's salt, K[PtCl$_3$(η^2-C$_2$H$_4$)]·H$_2$O, and (PPh$_4$)Cl in basic methanol (NaOMe). The basic methanol was obtained by reaction of sodium metal with methanol dried over molecular sieves of Type 4A (activated by heating at 393 K for 48 h), the solution was kept at 253 K (NaCl/ice bath) until the evolution of hydrogen ceased and was then let to warm up to 273 K. After removal by filtration of the precipitated KCl, a sample of the resulting solution was placed in a vial, layered under diethyl ether and placed in a deep freezer (253 K). After two weeks, pale yellow needles formed of what turned to be anhydrous (PPh$_4$)**2**.

(PPh$_4$){*trans*-[PtCl$_2$(η^1-CH$_2$NO$_2$)(η^2-C$_2$H$_4$)]}, (PPh$_4$)3. A solution of (PPh$_4$)**2**·H$_2$O (267 mg, 0.4 mmol) in CH_2Cl_2 (5 mL) at room temperature, was reacted with CH_3NO_2 (49 mg, 0.8 mmol, 43 μL). A rapid reaction took place and the color of the solution changed from pale to bright yellow. The solution was evaporated under reduced pressure, leaving a yellow oil from which, after trituration with diethyl ether, a yellow solid was obtained. The yield of (PPh$_4$)**3** with respect to platinum was nearly quantitative. Anal. Calcd (%) for $C_{27}H_{26}Cl_2NO_2PPt$ (693.46): C, 46.76; H 3.78; N, 2.02. Found: C 46.85; H 3.77; N, 2.12. NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 4.45 (pseudo triplet, 4H, $^2J_{Pt,H}$ = 40 Hz, C_2H_4), 5.27 (pseudo triplet, 2H, $^2J_{Pt,H}$ = 104 Hz, -CH_2NO_2) 7.62–7.93 (m, 20H, P(C_6H_5)$_4$) ppm.

Crystals of (PPh$_4$)**3** were obtained from a $CHCl_3$ solution containing (PPh$_4$)**2**·H$_2$O and a slight excess of CH_3NO_2. After 10 min at room temperature (298 K), the solution was layered under pentane and placed in a deep freezer (253 K). After several days bright yellow crystals of (PPh$_4$)**3** formed.

Reactions of platinum complexes with pyridines

All reactions were performed in NMR tubes at 294 K using $CDCl_3$ as solvent. 1 mL of a 0.03 M solution of the aromatic imine [L = py (**a**); 4-Mepy (**b**); 2,6-Me$_2$py (**c**)] was placed in an NMR tube and, after recording the ^{1}H NMR spectrum, was treated with a stoichiometric amount of the appropriate platinum complex. The resulting mixture was shaken until homogeneous solution was obtained and then the ^{1}H NMR spectrum was recorded.

The reaction products obtained in the different cases are reported in Table 3.

In the case of complex **1** all imines (L) gave an instantaneous substitution reaction with formation of *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(L)], **4**. The transformation was complete in the case of py and 4-Mepy and partial (≈ 40%) in the case of 2,6-Me$_2$py.

***trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(py)], 4a.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 4.80 (pseudo triplet, $^2J_{Pt,H}$ = 61 Hz, C_2H_4), 7.13 (t, 2H, H_{meta}), 7.71 (t, 1H, H_{para}), 9.12 (d, 2H, H_{ortho}) ppm.

***trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(4-Mepy)], 4b.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 2.45 (s, 3H, 4-*Me*-py), 4.77 (pseudo triplet, 4H, $^2J_{Pt,H}$ = 58 Hz, C_2H_4), 7.29 (d, 2H, H_{meta}), 8.73 (d, 2H, H_{ortho}) ppm.

***trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(2,6-Me$_2$py)], 4c.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 3.2 (s, 6H, Me_2-py), 4.81 (pseudo triplet, $^2J_{Pt,H}$ = 57.0 Hz, C_2H_4), 7.19 (d, 2H, H_{meta}), 7.63 (t, 1H, H_{para}) ppm.

In the case of complex **2**, py and 4-Mepy gave an instantaneous and complete substitution product with the released OH^- taken up by the olefin (*trans*-[PtCl$_2$(η^1-CH$_2$CH$_2$–OH)(L)]$^-$, **5**). No reaction was observed with 2,6-Me$_2$py. In our opinion the lack of reactivity was caused by a shift of the equilibrium

Table 4 Crystallographic data for (PPh$_4$)**2** and (PPh$_4$)**3**

	(PPh$_4$)**2**	(PPh$_4$)**3**
Empirical formula	$C_{26}H_{25}Cl_2OPPt$	$C_{27}H_{26}Cl_2NO_2PPt$
Formula weight	650.42	693.45
T/K	293(2)	150(2)
Wavelength [Å]	0.71069	0.71069
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*Cc*
Unit cell dimensions		
a/Å	7.956(2)	17.8100(4)
b/Å	11.887(2)	7.41700(10)
c/Å	13.184(2)	19.2250(6)
α (°)	91.152(16)	90.000
β (°)	90.206(18)	91.915(2)
γ (°)	100.160(16)	90.000
Volume [Å^3]	1227.0(4)	2538.14(10)
Z	2	4
Density (calculated) [Mg m^{-3}]	1.76	1.815
Absorption coefficient [mm^{-1}]	6.017	5.827
F(000)	632	1352
Crystal size [mm^3]	0.25 × 0.225 × 0.15	0.15 × 0.13 × 0.1
Theta range for data collection	1.74 to 22.97°.	4.33 to 29.22°.
Index ranges	$-8 \leqq h \leqq 8, -13 \leqq k \leqq 13, 0 \leqq l \leqq 14$	$-23 \leqq h \leqq 23, -9 \leqq k \leqq 9, -24 \leqq l \leqq 26$
Reflections collected	3575	9451
Independent reflections	3400 [*R*(int) = 0.0175]	4760 [*R*(int) = 0.0345]
Data/restraints/parameters	3400/0/281	4760/26/308
Goodness-of-fit on F2	1.52	1.023
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.059, wR_2 = 0.1287	R_1 = 0.0339, wR_2 = 0.0735
R indices (all data)	R_1 = 0.0781, wR_2 = 0.1335	R_1 = 0.0382, wR_2 = 0.077
Absolute structure parameter		0.569(9)
Largest diff. peak and hole/e Å^{-3}	1.613 and −2.003	1.401 and −1.209

towards the reagents, see Results and discussion section; to prove this complex **4c** (≈ 2 mg), independently prepared, was reacted with KOH (≈ 5 mg) made partially soluble in $CDCl_3$ (600 μL, NMR tube) by addition of 18-Crown-6 ether (≈ 5 mg). Formation of **2** and free 2,6-Me_2py, did occur almost quantitatively.

***trans*-[$PtCl_2(\eta^1$-$CH_2CH_2OH)$(py)]$^-$, 5a.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 2.16 (pseudo triplet of triplets, 2H, $^2J_{Pt,H}$ = 87 Hz, $^3J_{H,H}$ = 12 Hz, $C_\alpha H_2$), 3.24 (pseudo triplet of triplets, 2H, $^3J_{Pt,H}$ = 27 Hz, $^3J_{H,H}$ = 12 Hz, $C_\beta H_2$), 7.13 (t, 2H, H_{meta}), 7.72 (t, 1H, H_{para}), 9.12 (d, 2H, H_{ortho}) ppm.

***trans*-[$PtCl_2(\eta^1$-$CH_2CH_2OH)$(4-Mepy)]$^-$, 5b.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 2.11 (pseudo triplet of triplets, 2H, $^2J_{Pt,H}$ = 84 Hz, $^3J_{H,H}$ = 13 Hz, $C_\alpha H_2$), 2.19 (s, 3H, 4-*Me*-py), 3.21 (pseudo triplet of triplets, $^3J_{Pt,H}$ n.d., $^3J_{H,H}$ = 13 Hz, $C_\beta H_2$), 6.94 (d, 2H, H_{meta}), 8.91 (d, 2H, H_{ortho}) ppm.

In the case of complex **3**, all imines (L) gave an instantaneous and complete reaction with formation of *trans*-[$PtCl_2(\eta^1$-$CH_2NO_2)$(L)]$^-$, **6**.

***trans*-[$PtCl_2(\eta^1$-$CH_2NO_2)$(py)]$^-$, 6a.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 5.40 (pseudo triplet, 2H, $^2J_{Pt,H}$ = 104 Hz, -CH_2NO_2), 7.15 (t, 2H, H_{meta}), 7.65 (t, 1H, H_{para}),8.98 (d, 2H, H_{ortho}) ppm.

***trans*-[$PtCl_2(\eta^1$-$CH_2NO_2)$(4-Mepy)]$^-$, 6b.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 5.40 (pseudo triplet, 2H, $^2J_{Pt,H}$ = 104 Hz, -CH_2NO_2), 2.23 (s, 3H, 4-*Me*-py), 7.20 (d, 2H, H_{meta}), 8.60 (d, 2H, H_{ortho}) ppm.

***trans*-[$PtCl_2(\eta^1$-$CH_2NO_2)$(2,6-Me_2py)]$^-$, 6c.** NMR ($CDCl_3$, 300 MHz, 294 K): δ_H 5.38 (pseudo triplet, 2H, $^2J_{Pt,H}$ = 104 Hz, -CH_2NO_2), 2.48 (s, 6H, 2,6-Me_2-py), 6.92 (d, 2H, H_{meta}), 7.43 (t, 1H, H_{para}) ppm.

X-Ray structure determinations. Data collection for (PPh_4)**2** was performed on a Nonius CAD4 automatic diffractometer at room temperature. The intensities were corrected for Lorentz-polarization and empirical correction for absorption, using Ψ scan, was applied.[38] For complex (PPh_4)**3** the data were collected on an Oxford Diffraction Excalibur 3 diffractometer equipped with CCD area detector at 150 K. The program CrysAlis CCD[39] was used. Data reductions (including absorption corrections) were carried out with the program CrysAlis RED.[40] Data collection details are given in Table 4.

The structures were solved by direct methods using SIR97[41] and refined by full-matrix F^2 refinement using SHELX97,[42] with anisotropic thermal parameters assigned to all non-hydrogen atoms. All the calculations were performed using the package WINGX.[43] In (PPh_4)**3** a merohedral twin is present and the twin component was found to be 0.569(9).

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