The unexpected reactivity of Zeise's anion in strong basic medium discloses new substitution patterns at the platinum centre†

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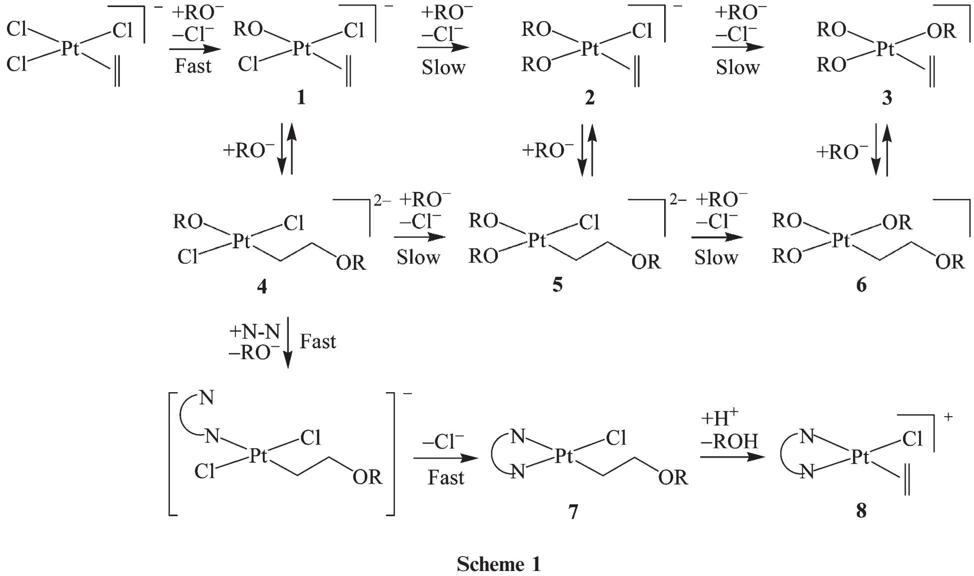
Zeise's anion in strongly basic hydroxylated solvents undergoes unprecedented nucleophilic addition of OR$^-$ (R = H, Me, Et) to the η^2-ethene giving *trans*-[PtCl$_2$(η^1-C$_2$H$_4$OR)(OR)]$^{2-}$ which readily reacts with bidentate nitrogen donors N–N to give Cl$^-$ and OR$^-$ substitution and formation of [PtCl(CH$_2$CH$_2$OR)(N–N)]. Protonolysis of this stable organometallic species offers a versatile route to cationic [PtCl(η^2-C$_2$H$_4$)(N–N)]$^+$ complexes.

The special reactivity of olefins η^2-coordinated to late transition metals can promote Wacker type hydroxylation and alkoxylation reactions[1–4] and homogeneous polymerization of α-olefins.[5–7] Some of the previous reactions also involve intermediate species containing alkoxo and hydroxo ligands with an unusual combination of soft metal centres and hard ligands.

One of the first recognized key step in the Wacker process is the attack of OH$^-$ on the η^2-olefin of the Pd analogue of Zeise's anion, [PtCl$_3$(η^2-C$_2$H$_4$)]$^-$.[8] Hydrolysis of Zeise's anion in water or alcoholic solvents has been reported to give a stepwise substitution of the chlorides leading to compounds **1–3** (R = H, Me,[9,10] Scheme 1). However no direct attack of the alkoxide on the olefin with formation of a σ-alkyl (Pt–CH$_2$CH$_2$OR) has been reported. Apparently only in the case of platinum(IV) species such an addition reaction could take place.[10]

We discovered that when Zeise's anion is dissolved in strongly basic methanol, addition of methoxide to the η^2-ethene takes place besides multiple chloride substitution (Scheme 1). Hence dissolution into a CD$_3$OD solution containing NaOCD$_3$ results in the immediate disappearance of the starting Zeise's anion and formation of a *ca.* 1 : 1 mixture of **1** and **4** (Fig. 1). On standing in solution, within a few minutes **1** and **4** undergo further transformations with formation of new species containing either η^2-bonded ethene (**2** and **3** in Scheme 1) or a σ-bonded alkyl (**5** and **6** in Scheme 1). Longer reaction times result in decomposition with formation of metallic Pt.[11,12]

Interestingly, addition of an aliphatic diamine (*N,N,N′,N′*-tetramethyl-1,2-diaminoethane, **Me$_4$en**, **a**) or an aromatic diimine (2,2′-dipyridyl, **dip**, **b**; 1,10-phenathroline, **phen**, **c**; or 2,9-dimethyl-1,10-phenathroline, **Me$_2$phen**, **d**) to the mixture of **1** and **4**, formed by Zeise's anion in basic methanol, results in the quantitative formation of [PtCl(η^1-C$_2$H$_4$OMe)(N–N)] (**7a–d**) which generally precipitates from the solution.[13] Monitoring the reaction by ^{1}H NMR has revealed immediate disappearance of **4** and slow progressive consumption of **1**. This suggests that compound **4** reacts instantaneously with the bidentate N-donor ligand whereas **1** is rather inert and its disappearance with time could be mediated



Scheme 1

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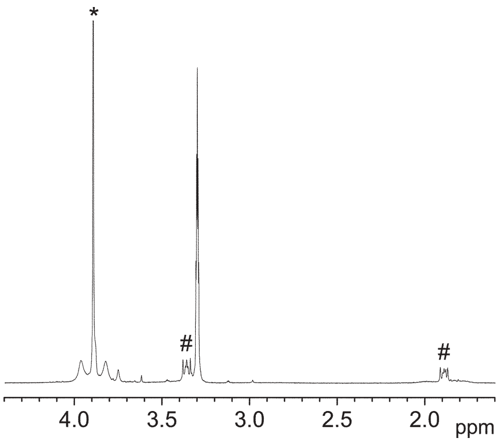

Fig. 1 ^1H NMR spectrum obtained soon after dissolution of Zeise's salt in strongly basic CD_3OD ($[CD_3O^-] \approx 1$ M, 20 °C). Ethene signals of **1** (*) and **4** (#) are labelled.

by conversion into **4** (Fig. 2). Therefore a much greater reactivity of compound **4** (σ-bonded alkyl) with respect to compound **1** (η^2-coordinated olefin) is observed.

How to explain the different reactivities of species **1** and **4** with chelating N-donor ligands? The *trans* effect of an η^2-olefin stems from its ability to remove electron charge from the metal centre, so stabilizing the five-coordinate transition state occurring in ligand substitution at 4-coordinate square planar substrates (entering and leaving groups and the ligand *trans* to the leaving group in the trigonal plane and the two ligands *cis* to the leaving group in the axial sites).[14] In contrast, in the case of compound **4** the *trans* effect stems from the strong σ-donor ability of the alkyl ligand which labilizes the *trans* MeO^- ligand and favours its dissociation while the entering nucleophile (the N-donor) is approaching. Probably the steric hindrance of the entering nitrogen ligands used in this investigation, together with the high electron density of the coordinated methoxy group, disfavour the essentially associative mechanism occurring in the reaction of **1** with respect to the largely dissociative mechanism occurring in the reaction of **4**.

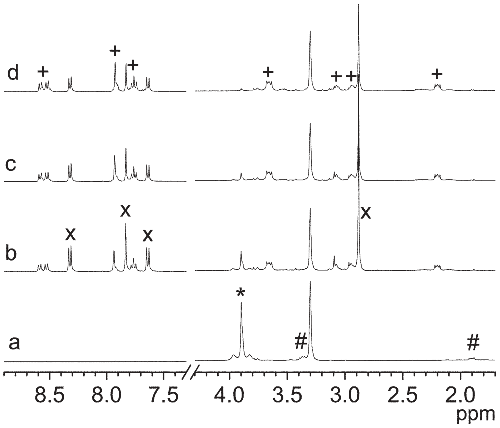

Fig. 2 ^{1}HNMR spectra of Zeise's salt in basic CD_3OD ($[CD_3O^-] \approx$ 1 M, 20 °C) before (a) and after the addition of **Me_2phen** [soon after mixing the reactants (b), after 5 min (c) and after 20 min (d)]. Signals of **1** (*), **4** (#), **7** (+), and free **Me_2phen** (×) are labelled. Methyl signals of coordinated **Me_2phen** (around 3.0 ppm) are broad and weak due to proton exchange with deuterium of the solvent.

After substitution of the methoxy group by the first end of the bidentate ligand, the following reaction could be expected to be different for the two cases. In the case of **1** it is expected that, due to the ability of the η^2-bonded olefin to withdraw electron density from the metal centre, the second N-donor of the bidentate ligand also coordinates to the metal atom, giving rise to the formation of a five-coordinate trigonal bipyramidal species in which the two N-donors and the olefin define the trigonal plane and the two *trans* chlorides the apical positions.[15] In the case of **Me_2phen** such a five-coordinate species[16] is extremely stable even under the experimental conditions used in the present investigation (strongly basic methanol solution); therefore its absence indicates that **Me_2phen** is totally unable to displace the methoxy group from compound **1**. On the other hand, in the case of **4**, after substitution of the methoxy group by the first nitrogen of the bidentate ligand, the second nitrogen cannot simply bind to the metal centre forming a stable 5-coordinate species because of the poor electron withdrawing ability of the σ-alkyl. Instead, the second N-donor of the ligand can displace one *cis* chloride forming compound **7**.

Reaction of species **7a–c** with non coordinating acids results in the quantitative formation of cationic complexes **8a–c**. While **8a** has been prepared long ago,[17,18] **8b** and **c** are obtainable only through the procedure described here, which represents the way to produce a class of versatile and very electrophilic complexes.[19]

This represents a case example of the dual character of the labilizing effect of *trans* ligands which can depend upon their ability to stabilize a five-coordinate transition state (η^2-olefin) or to labilize the *trans* ligand (σ-alkyl). In the case of substitution of a MeO^- by a N-donor ligand only *trans* labilizing ligands of the second type are able to speed up the reaction. What is amazing in the system under investigation is that it is possible to shift the properties of the *trans*-labilizing ligand simply by changing the pH.

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11 A solution of NaOMe was prepared by dissolving metallic sodium in anhydrous MeOH (the evolution of hydrogen gas reveals the oxidation of metallic sodium to Na^+). Upon addition of Zeise's salt (molar ratio MeO^-/Pt in the range 10–50) immediate disappearance of the proton signals of Zeise's anion (4.38 ppm, $^2J_{Pt-H} = 66$ Hz, Fig. 1) and appearance of a new η^2-ethene signal (3.90 ppm, $^2J_{Pt-H} = 60$ Hz) assignable to complex **1** were observed. In addition to the signals of compound **1**, a second spin system (1.89 ppm, $^2J_{Pt-H} \approx 80$ Hz, $C_\alpha H_2$; 3.36 ppm, $C_\beta H_2$; Fig. 1) assignable to a $PtC_\alpha H_2C_\beta H_2OMe$ moiety (compound **4** in the scheme) is observed. If, instead of using NaOMe,

the methanol is made basic by addition of 1 M KOH, compound **1** dominates while compound **4** is formed in trace amount. This result is in line with the greater basicity of OMe^- as compared to OH^-. For longer reaction times at room temperature, two additional resonances (3.75 and 3.62 ppm)[10] assignable to η^2-species such as *cis*-$[PtCl(OR)_2(C_2H_4)]^-$ and $[Pt(OR)_3(C_2H_4)]^-$ (**2** and **3** in the scheme) and two resonances (1.83 and 1.77 ppm, respectively, $^2J_{Pt-H} \approx$ 70–80 Hz) assignable to η^1-bonded ethene species such as *cis*-$[PtCl(\eta^1\text{-}C_2H_4OR)(OR)_2]^{2-}$ and $[Pt(\eta^1\text{-}C_2H_4OR)(OR)_3]^{2-}$ (**5** and **6** in the scheme) are visible before extensive decomposition to platinum metal takes place.

12 $(PPh_4)\{$*trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]\}$ can be obtained as a precipitate by addition of $(PPh_4)Cl$ to a freshly prepared solution of Zeise's salt in basic water ([KOH] $\approx$ 1 M).

13 The yields of isolated products (see also supplementary material) are 94, 87, 96, and 45% for **7a**, **7b**, **7c**, and **7d**, respectively. However also in the case of **7d** where the isolated yield is lowest, its formation in solution is almost quantitative (see Fig. 2).

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