Vinylic Deprotonation in the Coordination Sphere of Platinum(II): Regioselective Formation of Alkenyl Complexes

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Reaction of [PtCl(η^2-CH_2=CHAr)(tmeda)](ClO_4) (**1**) [Ar = C_6H_5 (**1a**), 4-$CH_3OC_6H_4$ (**1b**), 3-$NO_2C_6H_4$ (**1c**); tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with triethylamine, or even with inorganic carbonate, leads to the abstraction of a vinylic proton and formation of the (alkenyl)platinum species [PtCl{(*E*)-CH=CHAr}(tmeda)] (**2**) in high yield. The initially formed (*E*) isomer, in solution of chlorinated solvents, partly isomerizes into the (*Z*) form [equilibrium ratio (*E*)/(*Z*) ≈ 4:1]; the isomerization reaction is rather slow and is catalyzed by visible light. The nature of the phenyl substituent (electron donor OMe or electron-withdrawing NO_2 group) does not appear to affect the rate of deprotonation. The nature and stereochemistry of the formed (alkenyl)platinum species has been elucidated through 1D and 2D ^1H and ^{13}C NMR spectroscopy.

Introduction

In a recent paper we described the allylic deprotonation of the alkene in cationic [PtCl(η^2-alkene)(tmeda)]$^+$ complexes (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). The reaction requires the use of a noncoordinating base (NEt_3) and, under suitable conditions, it can lead to the removal of two allylic protons and formation of a dimeric species with an η^1,η^3-allyl bridging ligand.[1] We have extended the investigation to styrene analogues of the previous compounds, [PtCl(η^2-styrene)(tmeda)](ClO_4), for which only vinylic protons can be removed. The Brönsted acidity of vinylic protons has already been reported for styrenes coordinated to a metal center and in a cationic substrate.[2−6] There is, however, only one report concerning platinum complexes, which involves dicationic species that are known to be rather reactive towards deprotonation.[7]

Results and Discussion

[PtCl(η^2-CH_2=CHPh)(tmeda)](ClO_4) (**1a**) is readily deprotonated by a base in chlorinated solvents. The reaction is fast and quantitative in the presence of a moderate excess of triethylamine (3 h, 25 °C, **1a**/NEt_3 = 1:2.5), but slower in the presence of anhydrous sodium carbonate in heterogeneous conditions (ca. 80% yield at 25 °C after 3 d). Moreover, it is completely regioselective and leads to the exclusive formation of the (*E*) isomer [PtCl{(*E*)-CH=CHPh}(tmeda)] [(*E*)-**2a**] (Scheme 1).

The stereochemistry of **2a** was unequivocally determined on the basis of NMR spectroscopic data. The signals of the vinylic protons appear at δ = 6.46 and 7.31 ppm with $^3J_{H,H}$ = 16.3 Hz which is typical for protons that are mutually *trans* with respect to a carbon−carbon double bond.[8] ^{13}C and $^1H/^{13}C$ INVERSE HETCOR spectra set the signals of the vinylic carbon atoms at δ = 121.3 and 135.8 ppm with $J_{Pt,C}$ = 1009 Hz for the former and < 60 Hz for the latter (Figure 1 and Table 1). The more shielded and strongly Pt-coupled carbon atom is the one directly bound to the metal center. It is worth noting that this carbon atom carries the less shielded proton (δ = 7.31 ppm).

Complex (*E*)-**2a** in chloroform solution partially isomerizes to the (*Z*) form. The transformation is photocatalyzed since at ambient temperature (ca. 25 °C) the equilibrium is attained in the dark after ca. 100 d and if the sample is exposed to visible light after ca. 35 h. At equilibrium the (*E*)/(*Z*) ratio is ca. 4:1. In the (*Z*) isomer the two vinylic protons have $^3J_{H,H}$ = 10.7 Hz consistent with their mutual *cis* position.[9] All other proton resonances change slightly on going from the (*E*) to the (*Z*) form, with the only exception being the phenyl *ortho*-proton signals which are shifted by more than 1 ppm at lower field [δ = 7.27 and 8.50 ppm for the (*E*) and (*Z*) isomer, respectively]. In the (*Z*) isomer the phenyl ring is *cis* to the platinum atom with respect to

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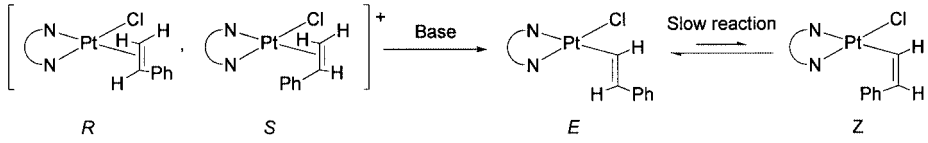

Scheme 1. Deprotonation and isomerization reactions

the olefin double bond, the *ortho* protons are close to and deshielded by the metal center.[10]

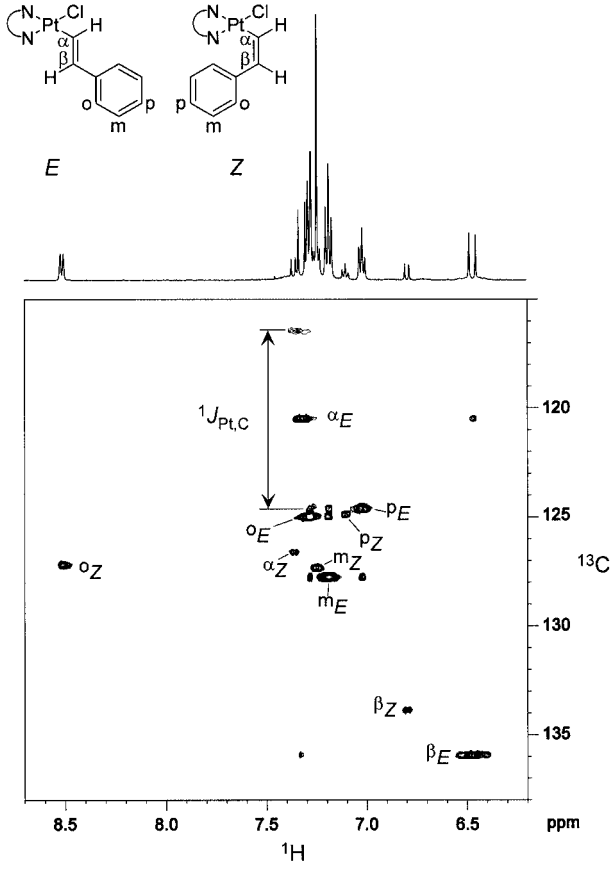

Figure 1. Aromatic portion of the $^1H/^{13}C$ HETCOR spectrum (500 MHz, $CDCl_3$, 25 °C) for an equilibrated solution of (*E*)- and (*Z*)-**2a**; some two-bond carbon-to-hydrogen correlation peaks are also visible

An interesting aspect of the present reaction is its complete stereoselectivity leading to the exclusive formation of the (*E*) isomer. The (*E*) isomer is also thermodynamically preferred because of smaller intramolecular steric interactions. However, the kinetic preference for the (*E*) isomer is greater than the thermodynamic preference for the same isomer, therefore, starting from the pure (*E*) isomer (kinetically determined composition), a significant amount of the (*Z*) form (ca. 20%) is also found at equilibrium.

The behavior of [PtCl(η^2-4-MeO-styrene)(tmeda)](ClO_4) (**1b**) in which the phenyl ring carries an electron-donor substituent, and that of [PtCl(η^2-3-NO_2-styrene)(tmeda)](ClO_4) (**1c**) carrying an electron-withdrawing substituent, is practically the same as that of **1a**. Therefore, the presence of substituents of different types on the styrene phenyl ring does not appear to significantly affect the rate of deprotonation.

Treatment of the alkenyl complexes with mineral acids ($HClO_4$, 0.02 M in water) reverses the reaction, reforming the parent η^2-alkene complexes.

In a thorough work by Gladysz on C−H bond activation of coordinated olefins in cationic complexes of rhenium(II) promoted by K(*t*BuO), the attention was focused on the two different deprotonation pathways involving either allylic or vinylic protons.[3d] It was shown that both types of deprotonation can take place depending upon the experimental conditions. Vinylic deprotonation was preferred in THF or DMSO, while allylic deprotonation was preferred in *t*BuOH. A greater thermodynamic stability of the alkenyl species (sp^2 carbon atom bound to the metal atom), as compared to the η^1-allyl complex (sp^3 carbon atom bound to the metal atom), was given as a rationale for the observed preference in THF and DMSO. On the contrary, the formation of large hydrogen-bonded aggregates of solvent molecules, around the tBuO$^-$ anion, was proposed to be responsible for the enhanced selectivity for less hindered allylic protons in *tert*-butyl alcohol. The relevance of steric

Table 1. ^1H NMR spectroscopic data (300 MHz, $CDCl_3$, 25 °C) for [PtCl(η^1-$C_\alpha H{=}C_\beta HAr$)(tmeda)] complexes **2**; coupling constants in Hz are reported in parentheses ($^3J_{H,H}$), brackets [$J_{Pt,H}$] and braces {$J_{Pt,C}$}; *ortho*, *meta*, and *para* protons of the aryl substituents are indicated by *o*, *m* and *p*, respectively

	Pt−$C_\alpha H_\alpha{=}C_\beta H_\beta$−Ar				Ar			tmeda	
Compound	H_α	H_β	C_α	C_β	*o*	*m*	*p*	CH_2	NCH_3
(*E*)-**2a**	7.31 (16.3) [48]	6.46 (16.3) [50]	121.3 {1009}	135.8 {< 60}	7.27	7.18	7.01	2.62, 2.83	2.77, 2.91
(*Z*)-**2a**	7.35 (10.7)	6.79 (10.7)	126.8	134	8.50	7.24	7.10	2.60, 2.71	2.82, 2.97
(*E*)-**2b**	7.06 (16.2) [46]	6.38 (16.2) [50]	117.6 {1009}	134.0 {79}	7.18	6.74	3.74 (OCH_3)	2.60, 2.81	2.76, 2.90
(*Z*)-**2b**	7.14 (10.7)	6.71 (10.7)	122.5	133.0	8.43	6.80	3.78 (OCH_3)	2.60, 2.68	2.81, 2.95
(*E*)-**2c**	7.61 (16.4) [48]	6.57 (16.4) [53]	125.9	134.2	7.53, 8.11	7.31	7.84	2.65, 2.85	2.79, 2.94

factors was also supported by the observation that vinylic deprotonation in *t*BuOH increased as the number of substituents on the allylic carbon increased.

In our investigations (ref.[1] and present work), we always use a very bulky base (NEt_3) since the use of less bulky nucleophiles such as OH^-, OMe^- or even $NHEt_2$ leads to stable addition products {[PtCl{η^1-$CH_2CHR(X)$}(tmeda)]; R = H, alkyl or aryl; X = OH, OMe or $NHEt_2$} which have no tendency, whatsoever, to lose HX and form allyl- or alkenylplatinum species.[11] Also triethylamine can add to the coordinated olefin, leading to the formation of an alkylplatinum derivative, but only in the case of unsubstituted ethylene.[11] Having used a bulky base it is obvious that, in the presence of allylic protons (more exposed to the solvent than vinylic protons), these are preferentially removed leading to formation of allylplatinum species. Only in the absence of allylic protons (such as in the case of styrene), will vinylic deprotonation take place. Moreover, it is very likely that both allylic and vinylic deprotonations take place through a direct attack of the base (NEt_3) on the leaving proton. The understanding of the reaction on the basis of a simple Brönsted acid-base model is also supported by the observation that mineral acids can protonate the alkenyl species leading back to the π-olefin complex.

The kinetic preference for the (*E*) isomer is also worthy of further discussion. The alkene complex [PtCl(η^2-CH_2=CHAr)(tmeda)]$^+$ is present in solution in two enantiomeric forms having opposite configurations at the =CHAr stereocenter (Scheme 1). The proton abstraction by an achiral base (such as NEt_3) will occur at a similar rate for the two enantiomers and the (*E*) or (*Z*) configuration of the formed alkenyl complex will depend exclusively upon the *trans* or *cis* position of the abstracted proton with respect to the Ar substituent. The kinetic preference for the (*E*) isomer indicates that the proton is removed exclusively in the position *trans* to Ar, which is more exposed to the solvent and more susceptible to undergo attack by a bulky nucleophile. In this context it could be worth mentioning that acidity data for the free styrene indicate that the most acidic protons are not those on the unsubstituted atom, but on the carbon atom bearing the phenyl substituent.[13,14]

The formation of an alkenyl complex by deprotonation of a coordinated alkene is unprecedented in platinum chemistry except for a recent report on dicationic platinum species of formula [Pt(PNP)(alkene)]$^{2+}$ [PNP = 2,6-bis(diphenylphosphanylmethyl)pyridine]. In methanol the styrene derivative exhibited a spontaneous deprotonation leading to formation of the alkenyl complex [Pt(PNP)(HC=CHPh)]$^+$ which precipitated from solution.[7] The authors did not specifically discuss the (*E*) or (*Z*) configuration of the obtained alkenyl complex; however, their NMR spectroscopic data are in full agreement with those found in our case for the (*E*) isomer. Moreover, since the (*E*) isomer is usually preferred, also on a thermodynamic basis, it is not clear if the obtained isomer was also the one preferred on a kinetic basis. Our alkene complexes, being monocationic, have a smaller propensity to undergo deprotonation than the dicationic complex mentioned above and require the use of a base. Moreover, in the case of the dicationic alkene complex, the formed alkenyl species, being insoluble in methanol, precipitated from the solution and this could have favored its formation.

Conclusion

This study, besides providing a quick and clean route to the synthesis of (*E*)-alkenyl complexes, has also given valuable information on the possible reaction mechanism. Abstraction of the proton *trans* to the phenyl substituent leads to the exclusive formation of the (*E*) isomer. The (*E*) isomer is also thermodynamically favored but not to the extent of precluding the formation of a small amount of (*Z*) isomer (ca. 20%) at equilibrium. The equilibration reaction is rather slow (at room temperature in the dark it requires some weeks) and can be accelerated by visible light. There appears to be a direct correlation between overall charge of the complexes and deprotonation propensity of the coordinated alkene.

Experimental Section

General Methods: The reagents and solvents employed are commercially available and were used as received without further purification. The complex [PtCl(η^2-propene)(tmeda)](ClO_4) was prepared as already reported.[11] All complexes described in this work gave satisfactory elemental analysis. ^1H and ^{13}C NMR spectra were recorded with DRX500 Avance and DPX300 Avance Bruker instruments 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 signal of the solvent was used as internal standard. Standard Bruker automation programs and pulse sequences were used for $^1H/^{13}C$ inversely detected gradient-sensitivity enhanced heterocorrelated 2D NMR for normal coupling (INVIEAGSSI). ^1H 2D NOESY experiments were performed at room temperature by collecting a 512 × 1024 matrix with 64 scans per t_1, and a mixing time of 1200 ms. Each block of data was preceded by eight dummy scans. The data were processed in the phase-sensitive mode.

Preparation of Alkene Complexes: [PtCl(η^2-CH_2=CHC_6H_4X)(tmeda)](ClO_4) [X = H, (**1a**), 4-OCH_3 (**1b**), 3-NO_2 (**1c**)]. Complexes **1a**−**c** were prepared by propene exchange in the cationic complex [PtCl(η^2-propene)(tmeda)](ClO_4).[11] In a typical experiment [PtCl(η^2-propene)(tmeda)](ClO_4) (250 mg, 0.51 mmol) was suspended in 4 mL of dichloromethane and treated with a 10-fold excess of the incoming olefin (**a** = styrene, **b** = 4-MeO-styrene, **c** = 3-NO_2-styrene). After 24 h of stirring at room temperature, the solid was recovered on a sintered glass filter, washed with diethyl ether and dried. The yield was always above 90%.

Preparation of Alkenyl Complexes: [PtCl(η^1-CH=CHC_6H_4X)(tmeda)] {X = H [(*E*)-**2a**], 4-OCH_3 [(*E*)-**2b**], 3-NO_2 [(*E*)-**2c**]}, by deprotonation with NEt_3. In a typical experiment the styrene complex **1** (0.4 mmol) was suspended in dichloromethane (8 mL) and triethylamine was added whilst stirring at room temperature (2.5-fold the stoichiometric amount). The mixture was left stirring for several hours, while dissolution of the solid was observed. The resulting solution was concentrated under vacuum; the viscous resi-

due was triturated with diethyl ether and dried. The obtained solid was then washed with water (to remove the alkylammonium salt) and dried again under vacuum leaving a pale yellow compound which was identified as the alkenyl complex **2**. The isolated yield, based on platinum, was ca. 85% for (*E*)-**2a** and (*E*)-**2b** and ca. 50% for (*E*)-**2c**, which required purification of the crude reaction product (Sefadex; eluent chloroform/acetone, 98:2, v/v). All manipulations were carried out by shielding the reaction vessel from light. The alkenyl complexes (*E*)-**2** were also prepared by deprotonation of the corresponding alkene complexes with Na_2CO_3. In a typical experiment **1** (0.25 mmol) was suspended in chloroform (5−6 mL), where it is sparingly soluble, treated with powdered Na_2CO_3 (0.50 mmol), and the mixture stirred for 70 h at 25 °C. After filtration, the mother liquor was concentrated under vacuum and the viscous residue was triturated with diethyl ether and dried. The obtained solid was the alkenyl species **2**, the yield (always based on platinum) was 80% for (*E*)-**2a** and 85% for (*E*)-**2b**.

The Reverse Reaction: The alkenyl species (*E*)-**2** (0.10 mmol) was treated with an aqueous solution (6 mL) containing $HClO_4$ (0.02 M). After 48 h of stirring, the solid was recovered by filtration of the mother liquor, washed with very small amounts of cold water, and dried in a dessicator. It always corresponded to the parent π-alkene complex.

(*E*)/(*Z*) Isomerization of the Alkenyl Ligand: NMR tubes containing $CDCl_3$ solutions (0.7 mL of a 6 mM solution) of the (*E*)-alkenyl species, were exposed to a neon lamp (75 W) and the ^1H NMR spectrum scanned every 4−6 h. The intensity ratio of two well-separated signals, one belonging to the (*E*) and the other to the (*Z*) isomer [the high-field vinylic signal of the (*E*) isomer and the *ortho*-phenyl signals of the (*Z*) form], was plotted against time. A constant ratio was reached at about 35 h for all compounds.

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