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Note

Phase dependent η^2 -alkene versus η^1 -alkyl transformation in platinum(II) complexes

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Abstract

Addition products of some nucleophiles to the coordinated olefin in $[Pt(\eta^2 - olefin)Cl(tmen)]^+$ (1) (tmen = *N,N,N',N'*-tetramethylethylenediamine) have shown to undergo a chemical transformation in the solid phase. The acetylacetonate (acac) addition product $[Pt{CH(H,Ph)CH(Ph,H)(acac)}Cl(tmen)]$ (2) is formed as a mixture of Marcovnikov and *anti*-Marcovnikov isomers; in the solid state slow isomerization to the pure Marcovnikov isomer takes place. The complex $[Pt{CH_2CH_2OC(O)CH_3}Cl(tmen)]$ (3), obtained by addition of acetate anion to 1, in the solid state slowly dissociates into its constituent species. Heterometallacycles $[Pt{CH(H,Me)-CHMeONO}(tmen)]^+$ (4) formed by *endo* nucleophilic attack of an oxygen of the nitro ligand on the *cis* alkene ligand can be detected in solution; however, they lose stability in the solid state where they revert to the acyclic species. The hydroxyl compound $[Pt(CH_2CH_2OH)Cl(tmen)]$ (5), formed by addition of OH⁻ to 1, undergoes, in the solid state, a condensation reaction to give the dimeric ether species [(tmen)ClPtCH_2CH_2OCH_2CH_2PtCl(tmen)] (6) and a water molecule. Moreover, the 5 to 6 transformation is catalyzed by carbon dioxide. All data are in accord with the solid state increasing the stability of the η^2 -olefin species and free nucleophile over the η^1 -alkyl addition product, a role for enthropic factors is envisaged. (C) 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The addition of nucleophiles to coordinated η^2 -olefins leads to η^1 -alkyl species, the stability of which depends upon several factors such as basicity of the added nucleophiles, charge of the complex, and substituents on the olefin (Scheme 1) [1–4].

In our current studies on the chemistry of the cationic complexes $[Pt(\eta^2-olefin)Cl(tmen)]^+$ (1) (tmen = N, N, N', N'-tetramethylethylenediamine) [5–10], and in particular of their reactivity towards nucleophiles, we have come across a number of cases in which there was a reaction taking place in the solid state. The description of these findings, which are indicative of a phase-dependent conformational preference, are hereafter described.

2. Experimental

2.1. Starting materials

Commercial reagent-grade chemicals were used without further purification. N,N,N',N'-tetramethylethylenediamine

2.2. Preparation of compounds

distillation from potassium hydroxide.

was purchased from Aldrich and purified before use by

2.2.1. η^2 -Olefin complexes

The complexes $[Pt(\eta^2-ethene)X(tmen)](ClO_4)$ (X = Cl, NO₂; tmen = N, N, N', N'-tetramethylethylenediamine) were prepared according to Refs. [6] and [7]. All other cationic species were prepared by olefin exchange. In a typical experiment 1 mmol of the ethene complex was suspended in dichloromethane (5 ml) and treated with an excess of the exchanging olefin under stirring for 2 days at room temperature. Owing to their low solubility, the reaction products were recovered quantitatively by filtration of the mother liquor. In the case of E- and Z-2-butene the olefin exchange afforded a crude reaction product which contained some non-olefin containing species. The raw material was then treated with a base (KOH in methanol) to form the methoxide addition product [Pt(CHMeCHMeOMe)(NO₂)(tmen)] which is very soluble in methanol. The solution was filtered and treated with aqueous $HClO_4$ to restore the $\eta^2\mbox{-olefin}$ complex which precipitates as a white solid. It is necessary to use an E-2-butene which contains less than 1% of the Zisomer, otherwise a significant amount of complex contain-

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ing the Z-2-butene is also formed. The yield of the isolated product was 65% referred to platinum in both cases. *Anal.* Calc. for $C_{10}H_{24}ClN_3O_6Pt$: C, 23.4; H, 4.7; N, 8.2. Found (*E*-2-butene): C, 23.2; H, 4.7; N, 8.1; (*Z*-2-butene): C, 23.3; H, 4.7; N, 8.1%.

2.3. Addition products

[Pt{CH(H,Ph)CH(Ph,H)(acac)}Cl(tmen)] (2). The cationic complex, [Pt(η^2 -styrene)Cl(tmen)](ClO₄) (1 mmol) was treated with acetylacetone (1 mmol) in a few ml of anhydrous dichloromethane in the presence of sodium carbonate (2 mmol). After 24 h stirring at room temperature, the solution was filtered and the solvent evaporated. The oily residue, upon trituration with pentane and diethyl ether, gave a pale yellow solid which proved to be a mixture of Markovnikov and *anti*-Markovnikov isomers of **2**. *Anal*. Calc. for C₁₉H₃₁ClN₂O₂Pt: C, 41.5; H, 5.7; N, 5.1. Found: C, 41.3; H, 5.7; N, 5.0%.

 $[Pt{CH_2CH_2OC(O)CH_3}Cl(tmen]$ (3), was prepared according to Ref. [6].

[Pt(CH₂CH₂OH)Cl(tmen)] (**5**). [Pt(η^2 -ethene)Cl(tmen)]-(ClO₄) (0.5 mmol) was reacted with KOH (2 mmol) in 5 ml of water; after 0.5 h stirring, the mother liquor was filtered and extracted with dichloromethane. The CH₂Cl₂ fractions were allowed to stand (1 h) over anhydrous Na₂SO₄; the solution was filtered and the solvent evaporated under reduced pressure to leave a white solid of **5**. To obtain **5** free from **6** (see below), all reported manipulations were carried out in argon atmosphere and the used solvent were flushed with the same gas (to exclude any carbon dioxide). The yield, referred to platinum, was 80%. *Anal.* Calc. for C₈H₂₁ClN₂OPt: C, 24.5; H, 5.4; N, 7.1. Found: C, 24.7; H, 5.5; N, 7.1%.

[(tmen)ClPtCH₂CH₂OCH₂CH₂PtCl(tmen)] (**6**). [Pt(η^2 ethene)Cl(tmen)](ClO₄) (0.5 mmol) was reacted with finely ground KOH (2 mmol) in a chlorinated solvent (either dichloromethane or 1,2-dichloroethane, 5 ml). After 24 h stirring, the mother liquor was filtered and the solvent evaporated under reduced pressure to leave **6** as a white solid. The yield, referred to platinum, was 80%. *Anal*. Calc. for C₁₆H₄₀Cl₂N₄OPt: C, 25.1; H, 5.3; N, 7.3. Found: C, 24.9; H, 5.4; N, 7.1%.

2.4. Physical measurements

IR spectra in the range 4000–600 cm^{-1} were recorded as KBr pellets, Nujol mulls or solution spectra (in chlorinated solvents, using a cell of 0.1 mm thickness with NaCl

windows) on a Perkin-Elmer FT 1600 spectrophotometer. ¹H NMR spectra were obtained with a Bruker AM 300 spectrometer.

3. Results and discussion

Addition of a nucleophile to a metal coordinated olefin takes place with a high degree of regioselectivity according to the Markovnikov rule (preferred attack on the more substituted carbon). When also the incoming nucleophile is encumbered, the *anti*-Markovnikov addition product gains stability [11].

Therefore, the styrene complex $[Pt(\eta^2-CH_2CHPh)Cl-$ (tmen)⁺ reacts with acetylacetonate to give **2** as a mixture of Markovnikov (~75%) and anti-Markovnikov isomers $(\sim 25\%)$ (Scheme 2) [10]. ¹H NMR spectra of aged samples of 2, dissolved in CDCl₃ just before the registration of the spectrum, are reported in Fig. 1 as a function of aged time¹. The most significant part of the spectrum (in the region between 3.5 and 4.5 ppm downfield from TMS) is related to the signals of the residual proton on the attacking carbon of the acetylacetonate anion (in γ position with respect to platinum). This particular proton gives rise to a neat doublet in the case of the Markovnikov addition product (coupling with the single proton on the β carbon) and a doublet of doublets in the anti-Markovnikov addition product (coupling with the two protons on the β carbon which are unequivalent because of the diastereotopic splitting induced by the asymmetric carbon in α position). The γ proton in the two isomers resonates at sufficiently different fields to allow, on the basis of the integration ratio, a quantitative measure of their relative concentrations. The spectra show a progressive lowering with time of the intensity of the signals assignable to the anti-Markovnikov addition product and their complete disappearance after storage of the solid sample at 20°C for 14 weeks (Fig. 1).

The observed chemical transformation taking place in the solid state requires detachment of the added carbanion and its subsequent readdition in the thermodynamically more favored site. This rearrangement cannot be detected in solution where irreversible decomposition to other species takes place in a few days. In contrast, dissociation of the carbanion in the solid phase leaves the nucleophile in close



¹The complete solubilization of all the samples excludes the presence of decomposition products.



Fig. 1. ¹H NMR spectra (CDCl₃) of samples of [Pt{CH(H,Ph)CH(Ph,H)-(acac)}Cl(tmen)], **2**, registered immediately after dissolution: (1) soon after preparation; (2) after two days; (3) after 55 days; (4) after 89 days. ((A) γ proton of the Markovnikov isomer; (B) γ proton of the *anti*-Markovnikov isomer; (C) β proton of the Markovnikov isomer which is coupled to three different nuclei (the γ and the two diastereotopic α protons)).

proximity to the reactive cationic complex allowing its prompt readdition before decomposition patterns become effective.

It has been reported in the literature that the photodecarboxylation of 3-indolacetic acid using phenanthridine as sensitizer occurs with high yield and selectivity if the reaction is performed in the solid state and at low temperature (-70° C). Higher temperature, or performing the reaction in solution, severely lowers the selectivity [12]. The pictured situation is understood on the basis of the presence of an intermediate radical species; the lower the temperature, the less mobile is the radical though the more straightforward and cleaner the observed reaction. The analogy with the system we have described is quite evident.

We have also found that the complex $[Pt{CH_2CH_2O-C(O)CH_3}Cl(tmen)]$ (3) [6], obtained by addition of acetate anion to 1, in the solid state slowly dissociates into its constituent species, as it can be monitored by IR spectra in the solid [6]. The absorption bands at 1730 and 1245 cm⁻¹, present in the freshly prepared sample and assignable to the ester group, lose intensity with time while absorptions of

free acetate anion at 1570 and 1450 cm^{-1} gradually appear and grow. These aged samples, when redissolved in chlorinated solvents, did show complete restoring of the ester function. Thus, the stability of the compound is phase dependent: in solution the addition product is the preferred one, in the solid state the detached form gains stability. Both events could be favored by enthropic factors: desolvation of the ions (cationic complex and anionic nucleophile) in solution and dissociation into two separate units in the solid.

A further example of phase dependent conformational preference came from the different behavior in the solid and in solution of the cationic species [Pt(η^2 $olefin)(NO_2)(tmen)]^+$ (4) having NO_2^- , instead of Cl⁻, as anionic ligand. When the olefin is propene or *E*-2-butene, the ¹H NMR spectra in CD₂Cl₂ were consistent with the presence of a heterometallacycle formed by endo-nucleophilic attack of an oxygen of the nitro ligand on the cis alkene ligand [9]. The heterometallacycle is the only species present in solution in the case of propene. It represents ca. 50% of the total (the remaining 50% is the η^2 -olefin species) in the case of *E*-2-butene, and it is not detectable when the olefin is either ethene or Z-2-butene. The formation of the heterometallacycle was also supported by FTIR spectra of the same solutions used for ¹H NMR, which showed a band at 1582 cm⁻¹ (propene), or 1588 cm⁻¹ (E-2-butene) assignable to the N=O stretching of a -N(O)OR group (this band was missing in the case of ethene and Z-2-butene). However, the bands at 1400 and 1340 cm^{-1} , characteristic of a terminal nitro ligand, missing in the case of propene, were of moderate intensity in the case of E-2-butene, and were the strongest of the spectrum in the case of ethene and Z-2butene. When the IR spectra were recorded in the solid phase (Nujol mulls) all the series of cationic complexes did not show any absorption in the region of 1600 cm^{-1} , but only those assignable to a terminal NO₂ group. Therefore, the endo-addition with the formation of the heterometallacycle is favored in solution, while only the η^2 -alkene complex is present in the solid state.

We have also observed the spontaneous condensation of two molecules of [Pt(CH₂CH₂OH)Cl(tmen)] (5) (formed by addition of OH⁻ to 1), [6] to give the dimeric species [(tmen)ClPtCH₂CH₂OCH₂CH₂PtCl(tmen)] (6) and a water molecule. The reaction is reversible and the equilibrium is shifted towards the monomer as the water content of the medium increases. Pure 5 can be prepared only in water, while in aprotic solvents or in the solid phase the 5 to 6condensation reaction takes place. Furthermore, this transformation is catalyzed by carbon dioxide. For instance, a solid sample of complex 5 kept under argon atmosphere remains unaltered for several days. The same sample in open air undergoes 50% conversion to 6 after one week at 20°C, a much faster dimerization reaction (80% transformation after 5 h at 20° C) is observed under a pressure of CO₂ (2.5 atm). No significant catalytic effect is observed in solution (CDCl₃ saturated with CO₂ at 1 atm) where a sample of 5 shows only 15% conversion after three days





at 20°C (in absence of CO_2 the conversion is slightly less than 10%).

A possible mechanism for the catalysis is depicted in Scheme 3 and implies an electrophilic attack of carbon dioxide upon the hydroxyl group and formation of hydrogen carbonate anion and parent cationic complex 1, the latter can then react with the hydroxyl of 5 to give 6 releasing a proton (the proton and the hydrogen carbonate can give back carbon dioxide and water). This reaction pattern is very similar to the classical mechanism of formation of an ether from an alcohol in the presence of an electrophile. In our case the electrophile is CO₂. Stronger electrophiles, such as H⁺, would have shifted the equilibrium towards the formation of a single species (1), thus not allowing the condensation reaction; in contrast CO₂ leads to an equilibrium between 1 and 5, so allowing the interaction of these two species to form the dimeric complex 6. The role played by CO₂ is quite evident and its higher efficacy in the solid state is not surprising according to the examples we have just described; the solid phase, in fact, appears to favor the first step reported in the scheme.

4. Conclusions

The several examples reported in this work indicate that the solid phase stabilizes the η^2 -coordination mode, thus favoring the shift of existing equilibria or allowing chemical transformations promoted by the dihapto species. The observed phase-dependent conformational preference also indicates that crystal packing effects can act in opposite direction than solvation effects.

The transformations here described (which take place smoothly and require a very limited amount of energy) should deserve some attention also in relation to the growing interest, as witnessed by several recent reports, in reactions occurring in the solid phase that can be useful from a synthetic point of view either for their stereo- or chemo-selectivity [13–15].

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