Denotification versus Nucleophilic Substitution in Some Platinum(II) Coordinated Olefins Containing an Electron Withdrawing Group

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Two new cationic olefin complexes of platinum(II) with electron-withdrawing substituents on the allylic carbon, [PtCl(η2-CH2=CHCH2X)(tmeya)]+ (X = –C(O)OCH3 (1a), –OC(O)OCH3 (1b)) have been synthesized and their reactivity toward nucleophiles investigated. The reaction of 1a with various nucleophiles, including water, causes allylic deprotonation and formation of the η1-allyl complex [Pt(η1-CH2CHCH2C(O)OCH3)(tmeya)]+ (4a). In nonaqueous media it was possible to identify also a transient alkenyl species, [PtCl(η1-CH=CH2C(O)OCH3)(tmeya)] (2a), formed by loss of a vinylic proton. In contrast, the reaction of 1b with nucleophiles does not lead to deprotonation but to substitution of the acetate group followed by addition to the olefinic double bond. The latter can be intramolecular, as in the case of acetylated compound, leading to [PtCl(η1-CH2CHCH2C(C(O)OCH3)=C(CH3)2)(tmeya)] (5b) or requires a second molecule of nucleophile, as in the case of secondary amines, leading to the Markovnikov and anti-Markovnikov addition products (e.g., [PtCl(η1-CH2CH(NEt2)CH2NEt2)(tmeya)] (6b) and [PtCl(η1-CH2NEt2)] (tmeya)] (6b)).

The activation of unsaturated molecules, promoted by coordination to a metal center, is a topic of great interest in organometallic chemistry, and it is exploited for the production of fine chemicals in several metal-catalyzed reactions. Olefins in particular, when bound to a metal center, become electrophilic and may also show Brønsted acidity.1,3

We are currently investigating the cationic complexes [PtCl(η2-CH2=CHX)(tmeya)]+ (X = H, alkyl, ary1, tmeya = N,N,N,N-tetramethyl-1,2-ethanediamine)2 which, apart from undergoing addition to the olefin of several carbon, nitrogen, and oxygen donor nucleophiles,5 also exhibit acidic character.

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elemental analysis, ESI-MS, and NMR (Figures S1–S4, Supporting Information). They were stable for months in the solid state and for some days, at room temperature, in solutions of acetone or of chlorinated solvents.

The complexes 1a,b were subjected to attack by several nucleophiles (secondary and tertiary amines, methoxide and acetylacetonate anions).

In the case of complex 1a, none of the considered nucleophiles added to the coordinated olefin, but all of them promoted its deprotonation with the exclusive formation of the \( \eta^3 \)-allyl species \([\text{Pt}\{\eta^3-\text{C}_2\text{H}_5\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}(\text{tmeda})]^+\) (4a in Scheme 2). The proton abstraction, however, is less straightforward than possibly suggested by the obtainment of a unique product. The overall reaction pattern, depicted in Scheme 2, could be deduced by \(^1\)H NMR spectroscopy (Figure 1).

When the reaction is carried out in an NMR tube (Figure 1), using NEt\(_3\) (\(pK_a = 10.7\)) as deprotonating agent and acetone-\(d_6\) as solvent, the alkenyl species \([\text{PtCl}\{\eta^1-\text{C}_6\text{H}_5\text{H}=\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{OCH}_3\}(\text{tmeda})]\) (2a) forms soon after the mixing of the reagents. The 16 Hz value for \(\delta\) for the central proton of the allyl moiety has only one \(\delta\) value smaller than 10 Hz (\(\delta\) values: 7.2, 10.2, and 12.3 Hz; see also Figure S5 in the Supporting Information), which is in accord with a syn configuration. Most likely, 4a results from the rearrangement of a \(\eta^1\)-allyl complex, \([\text{PtCl}\{\eta^1-\text{CH}_2\text{CH}=\text{CH}(\text{O})\text{OCH}_3\}(\text{tmeda})]\) (3a), which, however, never reaches a concentration detectable by \(^1\)H NMR. The allylic deprotonation of coordinated terminal alkenes leading to \(\eta^1\)-allyl complexes has seldom been observed in platinum(II) chemistry, since the following evolution to the \(\eta^3\)-allyl species, with the contemporary loss of an anionic ligand, is usually rather fast.\(^{6a}\) There are two possible routes through which 2a could be converted into 3a (dashed arrows in Scheme 2): direct isomerization (via a sigmatropic rearrangement implying a 1,3-hydrogen shift) or back-conversion to 1a followed by allylic deprotonation. The Bronsted acidity of complex 1a is such that it can be deprotonated also by a base weaker than NEt\(_3\), such as \(N\)-methylmorpholine (\(pK_a = 7.41\)), the deprotonation pathway (\(^1\)H NMR, acetone-\(d_6\)) being completely analogous to that observed using NEt\(_3\). In water solution the conversion of 1a into the \(\eta^3\)-allyl complex 4a can take place directly without requiring the addition of a base. Moreover, in this solvent there is no indication of formation of the alkenyl species 2a or observation of deuterium incorporation into 4a. These findings indicate that in the aqueous medium only the direct allylic deprotonation of 1a takes place.

The reactivity of the isomeric complex 1b is completely different from that of 1a. The reaction pattern has been elucidated in the case of two types of nucleophiles: acetylacetonate anion and secondary amines (NHEt\(_2\) and NHMe\(_2\)).

The reaction of 1b with acetylacetone, in the presence of an inorganic carbonate, affords a neutral complex, 5b (Scheme 3), whose structure could be unambiguously determined by combining the results of elemental analysis, ESI-MS, and multinuclear 1D and 2D NMR (Figures S6–S9, Supporting Information).

Figure 1. Portions of the \(^1\)H NMR spectra (300 MHz, acetone-\(d_6\), 298 K) of complex 1a treated with NEt\(_3\): (a) prior to base addition; (b–d) 2 min and 6 and 24 h after base addition, respectively.

Information). Complex $5b$ contains a 2,5-dimethyl-3-acetyl-4,5-dihydrofuran moiety linked to platinum through the deprotonated methyl group at C5. It is formed by loss of an acetate anion and incorporation of a bis-deprotonated acetylacetonate anion. The reaction route is depicted in Scheme 3. In the first step there is a nucleophilic substitution at the allylic carbon, with an acetylacetonate anion replacing the acetate group. Subsequently, the deprotonated enolic tautomer of the substitution product undergoes a cyclization reaction in which the enolate oxygen adds to the coordinated olefinic double bond in a Markovnikov fashion, thus forming the furan ring. In principle, the nucleophilic addition to the olefinic double bond could precede the nucleophilic substitution at the allylic carbon. However, the latter reaction sequence would have led to an isomeric furan ring (2,4-dimethyl-3-acetyl-4,5-dihydrofuran), which has not been observed. Treatment of complex $5b$, either with concentrated aqueous HCl (37%)$^{5a,f,10}$ or with hydrides of different metals, did not cause the selective cleavage of the Pt–C α bond but, instead, caused destruction of the furan ring.

The reactivity of $1b$ toward aliphatic amines (NHEt$_2$ and NHMe$_2$) has been considered. Also with these nucleophiles the first step is substitution at the allylic carbon with displacement of the acetate anion. Subsequently a second molecule of nucleophile adds to the olefinic double bond (Scheme 4).

In the case of NHEt$_2$ the two isomeric species $6b$ and $6b'$, isolated as monoperochlorate salts due to the monoprotonation of the diaminopropyl group, were formed and they were characterized by elemental analysis, ESI-MS, 1R, and multinuclear ($^1$H, $^{13}$C, and $^{195}$Pt) 1D and 2D NMR (Figures S10–S12 and S13-I, Supporting Information). $6b$ was, by far, the dominant species ($6b$:6b' $\approx$ 4:1). 2D ($^1$H, $^1$H) COSY and $^1$H($^{13}$C) HETCOR spectra (Figures S11 and S12) are fully consistent with the presence of a major component containing an $N,N,N',N'$-tetraethyl-1,3-diaminopropyl group α-bound to the metal by its central carbon. For the minor component 6b', although the complete assignment of the NMR resonances was not possible, the presence of a Pt–CH$_2$CH(NEt$_2$)CH$_2$(NEt$_2$) moiety ($N,N,N',N'$-tetraethyl-1,2-diaminopropyl group α-bound to the metal through its terminal carbon atom) was supported by characteristic $C$, $H_2$ (δ$_H$ 0.90 and 1.83 ppm; δ$_C$ -10.3 ppm) and $C_8$H (δ$_H$ 3.94 ppm; δ$_C$ 68.8 ppm) signals. $6b$ corresponds to an anti-Markovnikov type of attack of the amine at the olefin, while $6b'$ corresponds to a Markovnikov type of attack. After standing in solution (CDCl$_3$) for over 1 day, a trace amount of a third species, containing a Pt–CHCH$_2$N moiety, appears (Figure S11). The low-field resonance of the methylene protons (δ$_H$ 4.36 and 4.77 ppm) is highly indicative of an azametallacyclobutane ring with one aminic nitrogen bound to the metal (7b in Scheme 4).$^{5k} 7b$ derives from $6b$ by an intramolecular nucleophilic substitution of amine for chloride.$^{5k}$

The acid hydrolysis of the mixture of $6b$ and $6b'$, performed with concentrated aqueous HCl (37%)$^{5a,f,10}$ afforded (GC–MS data; Figure S14 Supporting Information) diethylallylamine (ca. 75%) and $N,N,N',N'$-tetraethyl-1,2-diaminopropane (ca. 25%). Therefore, while the acid hydrolysis of complex $6b'$ directly cleaves the Pt–C α bond, in contrast, the acid decomposition of compound $6b$ contemplates the initial loss of a NEt$_2$ fragment, with reversal of the platinum-bound diaminopropyl group to a α-bound diethylallylamine, followed by displacement of the allylamine by a chloride. It is tempting to hypothesize that the reversal of the addition reaction in $6b$ is related to an intrinsic instability of the product of anti-Markovnikov attack as compared to the Markovnikov attack. In the reaction of $1b$ with NHMe$_2$, the previously described pattern (substitution of amine for acetate at the allylic carbon and nucleophilic addition of a second molecule of amine to the olefinic double bond in a prevalent anti-Markovnikov fashion) was fully confirmed. However,
differently from the NHEt$_2$ system, in the case of NHMe$_2$ the presence of a perceivable quantity of the ring-closed species [Pt(C$_5$H$_5$-C$_6$H$_5$NHMe$_2$)$_2$(tmeda)]$^+$ with characteristic chemical shifts at 4.57 and 4.93 ppm (C$_6$H$_5$$_2$) was detected (1H NMR) right from the beginning. The amount of the latter species also increased with time. The 195Pt NMR spectrum (CDCl$_3$, 298 K, 20 h of acquisition time) showed the presence of two signals in a ~2:1 ratio (Figure S13-I, Supporting Information). The signal of greater intensity (major component) was at -3355 ppm (a value very close to that of platinum in the 6b and 6b$'$ species obtained with NHEt$_2$ and fully consistent with an open-chain addition product). The signal of lower intensity (minor component) was at -2798 ppm and could be assigned to the ring-closed species of type 7b (Scheme 4). In this system (1b + NHMe$_2$) there was no clear evidence for the formation of the 6b$'$ type of species in addition to 6b.

The intramolecular nucleophilic substitution process, leading to an azametallacyclobutane ring, is favored by the presence of substituents both on the amine γ-nitrogen and on the carbon atoms. A bulky group on the α-carbon with respect to the metal is particularly effective; therefore, 6b is a good candidate to undergo this type of reaction. Apparently the increased bulk on the amine nitrogen, on going from dimethyl- to diethylamine, causes a retardation of the ring-closing process (6b → 7b) in the latter case. Interestingly, while in the case of NHEt$_2$ the ESI-MS spectrum has the highest mass peak at m/z 533 corresponding to monoprotonated 6b and 6b$'$ species, in contrast to the case of NHMe$_2$ (Figure S15, Supporting Information) the highest mass peak is at m/z 440, corresponding to 7b, even though 7b is a minor component with respect to 6b even after standing in solution for 20 h (NMR data). Therefore, the experimental data indicate that the ring-closing process (6b → 7b) takes place more readily in the case of dimethylamine than in the case of diethylamine and this is particularly true in the gas phase (ESI-MS). As already suggested, this could be a consequence of the smaller steric bulk of the dimethylamine favoring the chloride displacement reaction.

Conclusions

This work has shown that the stability of cationic complexes of the type [PtCl(η$^2$-CH$_2$=CHCH$_3$O)(tmeda)]$^+$ is not sensibly affected by the presence, on the allylic carbon, of an electron-withdrawing substituent such as a C- or O-bonded ester group (X = -C(O)OCH$_3$ (1a), -OC(O)CH$_3$ (1b)). The reactivity of the two complexes, however, is very different. In 1a the -C(O)-OCH$_3$ group confers a remarkable Brønsted acidity to the coordinated olefin and all potential nucleophiles deprotonate the platinum-bound alkane rather than add to it. In nonaqueous solvents both vinylclic and allylic deprotonation do occur. While the former shows up in the early stages of the reaction (η$^2$-alkenyl, 2a), the latter prevails at longer reaction time due to its irreversible transformation into an η$^1$-allyl species (4a) (Scheme 2). In both cases the reaction is highly regioselective, affording exclusively (E)-alkenyl or syn-allyl species. Unlike 1a, no deprotonation reaction is observed in the case of complex 1b, where the olefin exhibits two reactive sites: the allylic carbon and the C=C double bond. The incoming nucleophile first attacks the allylic carbon, displacing the acetate group. The newly formed substitution product at the allylic carbon can then evolve in two different ways, depending upon the nature of the attacking nucleophile. In the case of acetylacetonate (acac) there is an intramolecular attack of an acac oxygen at the C=C double bond with formation of a dihydrofuran ring. In the case of secondary amines (NHEt$_2$ and NHMe$_2$) there is the attack of a second molecule of amine at the olefin double bond and formation of a dianinopropyl moiety o-bound to platinum. With time, one amino group of the dianinopropyl derivative can displace the platinum-bound chloride, leading to formation of a cyclo metallated species. The prevalent anti-Markovnikov type of attack observed in the addition of the second molecule of amine suggests that, as in the case of acetylacetonate anion, the acetate substitution occurs as the first step, placing a bulky -CH$_2$NR$_2$ group on the vinyl carbon and directing the nucleophilic addition of the second amine molecule on the distal olefinic carbon, resulting in an anti-Markovnikov type of addition.

Experimental Section

General Procedures. Elemental analyses were performed with a CHN Eurovector EA 3011. 1H, 13C, and 195Pt NMR spectra were recorded with 300 MHz Mercury (Varian) and DPX 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 an internal standard. 1H, 13C inversely detected gradient sensitivity enhanced heterocorrelated 2D NMR spectra for normal coupling (INViEgassi) were acquired 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. For 195Pt NMR spectra, K$_2$PtCl$_4$ was used as the external standard (-1643.00 ppm). IR spectra were recorded as KBr or high-density polyethylene pellets on a Perkin-Elmer Spectrometer. The ESI-MS spectra were recorded with an Agilent 1100 Series LC-MSD Trap System VL. GC-MS spectra were recorded with an Agilent 6890N-5973N MSD instrument.

Solvents and reagents, unless otherwise stated, were commercially available (purchased from Aldrich Chemical Co.) and used as received. Chlorinated solvents were dried over activated molecular sieves beads (4~8 mesh).

| [PtCl(η$^2$-CH$_2$=CHCH$_3$O)(O)ClO$_4$)](tmeda) | Chem. Calcd for C$_{11}$H$_{24}$Cl$_2$N$_2$O$_6$Pt: C, 24.18; H, 4.00; N, 5.13. Found: C, 24.01; H, 4.38; N, 5.17. Peak of greatest intensity in ESI-MS: m/z 446.2 [1a$^+$. NMR (acetone-d$_6$, 298 K, ppm): δ$_{H}$ 3.03 and 3.42 (dd, 1H, each, η$^2$-CH$_2$=CHCH$_3$O(O)-OCH$_3$), 3.76 (s, 3H, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 4.86 and 4.91 (d, 1H, each, J$_{HCH2}$ ca. 60 and ca. 50 Hz, respectively, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 5.38 (m, 1H, ω-CH$_2$=CHCH$_3$O(O)CH$_3$), δ$_{C}$ 38.4 (η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 51.4 (η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 72.0 (ω-CH$_2$=CHCH$_3$O(O)CH$_3$), 117.0 (J$_{PC}$ ca. 1412 Hz, ω-CH$_2$=CHCH$_3$O(O)CH$_3$), 176.0 (J$_{PC}$ ca. 70 Hz, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 96.0 (J$_{PC}$ ca. 185 Hz, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$). 1b(CIO$_4$). Anal. Calcd for C$_{11}$H$_{24}$Cl$_2$N$_2$O$_6$Pt: C, 24.18; H, 4.40; N, 5.13. Found: C, 24.16; H, 4.41; N, 5.10. Peak of greatest intensity in ESI-MS: m/z 446.2 [1b$^+$. NMR (acetone-d$_6$, 298 K, ppm): δ$_{H}$ 2.12 (s, 3H, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 4.42 and 4.73 (d, 1H, each, J$_{HCH2}$ ca. 40 Hz, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 4.95 and 4.99 (d, 1H, each, J$_{HCH2}$ ca. 70 Hz, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 5.31 (m, 1H, J$_{HCH2}$ ca. 60 Hz, η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), δ$_{C}$ 29.3 (η$^2$-CH$_2$=CHCH$_3$O(O)CH$_3$), 62.6 (J$_{PC}$ ca. 144 Hz, ω-CH$_2$=CHCH$_3$O(O)CH$_3$), 95.9 (J$_{PC}$ ca. 192 Hz, ω-CH$_2$=CHCH$_3$O(O)CH$_3$). Reactions of 1a(CIO$_4$) and 1b(CIO$_4$) with Potential Nucleophiles. In a typical experiment 200 mg (0.37 mmol) of cationic complex was suspended in CH$_2$Cl$_2$ (~6 mL) and treated with a |

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2- or 3-fold excess of nucleophile. Acetyl acetonate was produced in situ from acetyl acetone and K$_2$CO$_3$. The reaction mixture was stirred for 24 h in the case of acetyacetone and ~3 h in the case of aliphatic amines. The mother liquor was then filtered on a sintered glass filter and evaporated to dryness under reduced pressure. The oily products were triturated with diethyl ether to obtain solid powders. When necessary, a final washing with water to remove salts was also performed before drying the obtained product in vacuo.

The crude reaction product was purified by chromatography on silica gel (eluent CH$_2$Cl$_2$/acetone, 4/1 v/v); the isolated yield, referenced to platinum, was 75%. Anal. Calcd for C$_{11}$H$_{23}$ClN$_2$O$_6$Pt: C, 25.91; H, 4.55; N, 5.49. Found: C, 25.66; H, 4.60; N, 5.57. Peak of greatest intensity in ESI-MS: m/z 533.2 [6b·H]+ or 6b·H$.^+$·H$^+$. NMR (CDCl$_3$, 298 K, ppm): $\delta_{CH}$ 1.99 (m, 1H, $\eta^1$-CH(CH$_2$NEt$_2$)$_2$); $\delta_C$ 2.0 ($^2$J$_{CH-C}$ = 790 Hz, $\eta^1$-CH(CH$_2$NEt$_2$)$_2$), 62.3 ($\eta^1$-CH(CH$_2$NEt$_2$)$_2$); $\delta_{Pt}$ = 3377. NMR (CDCl$_3$, 298 K, ppm) for 6b: HClO$_4$: $\delta_{CH}$ 0.90 and 1.83 (dd, 2H, $\eta^1$-CH$_2$CH(NEt$_2$)CH$_2$NEt$_2$), 2.61 (m, 2H, $\eta^1$-CH$_2$CH(NEt$_2$)CH$_2$NEt$_2$), 3.94 (m, 1H, $\eta^3$-CH$_2$CH(NEt$_2$)CH$_2$NEt$_2$); $\delta_C$ = 10.3 ($\eta^1$-CH$_2$CH(NEt$_2$)CH$_2$NEt$_2$). 44.4 ($\eta^1$-CH$_2$CH(NEt$_2$)CH$_2$NEt$_2$), 68.8 ($\eta^1$-CH$_2$CH(NEt$_2$)CH$_2$NEt$_2$); $\delta_{Pt}$ = 3290.

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Supporting Information Available: Figures giving selected NMR, ESI-MS, and GC-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.