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Propylene oxidation by palladium nitro and nitrato complexes: in situ NMR and IR studies

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Abstract

The mechanism of the propylene oxidation by $Pd(NO_n)Cl_{2-m}(CH_3CN)_2$ complexes ($n=2,3$; $m=0,1,2$) in chloroform solutions has been studied by ^1H NMR and IR spectroscopy. The main reaction products are acetone and 2-nitropropylene, with their ratio depending on the equilibrium existing in the reaction solutions between palladium complexes containing NO_n ligands bonded to a palladium atom via either an oxygen or a nitrogen atom. Reactivities of the oxygen bonded nitrato and nitrito complexes are significantly higher than that of the nitrogen bonded nitro complex. Various new organopalladium intermediates have been observed and monitored in situ. A reversible insertion of the coordinated propylene into the Pd–O or Pd–N bonds results in nitrato-, nitrito- and nitropalladation intermediates, which then decompose via a β-hydrogen elimination. Two isomers of the nitritopalladation intermediate have been detected, i.e., a palladium metallacycle and an open ring complex, with the latter being much more reactive towards the β-hydrogen elimination than the former. The decomposition of the nitrato- and nitritopalladation intermediates results in the organometallic precursor of acetone, i.e., an acetonylpalladium complex, and then in acetone itself. On the other hand, the nitropalladation intermediate originates 2-nitropropylene. In the presence of dioxygen, which re-oxidizes the nitrosyl groups, the acetone formation becomes a catalytic reaction with respect to both palladium and nitrogen.

Keywords: Propylene; Oxidation; Palladium nitro and nitrato complexes

1. Introduction

Palladium(II) nitro and nitrato complexes oxidize a wide variety of alkenes to carbonyl compounds, epoxides, vinyl derivatives or glycol esters, being reduced themselves to palladium(II) nitrosyl complexes [1–5]. In the presence of dioxygen, which re-oxidizes the nitrosyl groups, these reactions become catalytic with respect not only to palladium but also to nitrogen, thus offering valuable alternatives to the Wacker type commercial catalyst ($PdCl_2$–$CuCl_2$) for aerobic oxidations of alkenes [6–15]. A distinctive feature of the systems based on the palladium-nitro/nitrosyl redox couple is an oxygen atom transfer from a nitro group to alkene [1,3,4]. This interaction may be considered as an intramolecular nucleophilic addition to the coordinated alkene, whereas the standard Wacker oxidation as an intermolecular nucleophilic addition [15]. The key reaction intermediates – σ-organopalladium compounds formed via the insertion of the coordinated alkene into Pd–O or Pd–N bonds – have been observed in situ for various alkenes in [1,16] and in our previous works [17–21]. However, the mechanism of the palladium-catalyzed oxidation of propylene, although a very important reaction, has only little been studied hitherto.

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We report herein new advances in the mechanistic studies by IR and NMR spectroscopy of the oxidation of propylene by $Pd(NO_n)_mCl_{2-m}(CH_3CN)_2$ ($n=2,3$; $m=0,1,2$) complexes. Various organopalladium intermediates have been detected and monitored in situ, mostly for the first time, and a detailed mechanism has been proposed.

2. Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated. Chloroform was purified twice by distillation over phosphorous pentoxide. The syntheses of the complexes $Pd(NO_n)_mCl_{2-m}(CH_3CN)_2$ ($n=2,3$; $m=0,1,2$) were described in [5]. $Pd(N^*O_2)Cl(CH_3CN)_2$ and $Pd(N^*O_3)Cl(CH_3CN)_2$ (50% enriched in ^{18}O) were obtained from $PdCl_2(CH_3CN)_2$ and properly enriched AgN^*O_2 or AgN^*O_3, respectively. ^{18}O-enriched $AgNO_2$ was prepared by stirring for 1 h of the $NaNO_2$ solution in equimolar amounts of $H_2{}^{18}O$, in the presence of trace amounts of HNO_3, followed by the neutralization with NaOH (up to pH 6) and addition of $AgNO_3$. The resulting precipitate was isolated by filtration, washed with $H_2{}^{18}O$ and dried in vacuum over phosphorous pentoxide. $AgN^{18}O_3$ was synthesized through the reaction of AgF and ^{18}O-enriched $LiNO_3$ in acetonitrile. The latter was prepared as follows: $LiNO_3$ (0.9 mmol) was dissolved in 110 μl of $H_2{}^{18}O$ and kept at 25 °C for 24 h, then water was evaporated and a precipitate was dried at 575 °C. In NMR experiments, $Pd(NO_n)_mCl_{2-m}(CD_3CN)_2$ complexes obtained by dissolving the corresponding protio complex in CD_3CN (0.3% of residual protium) followed by solvent evaporating were used.

^1H NMR spectra were recorded on a Bruker CXP-300 or Bruker MSL-400 spectrometer using $CDCl_3$ (0.5% of residual protium) as the solvent and tetramethylsilane (TMS) as the internal reference. The sample temperature was monitored with an accuracy of 1° by a VT-1000 thermocouple. IR spectra were recorded on an IFS-113v (Bruker), Interspec-2020 (Spectrolab) or Specord-75 IR (Karl Zeiss, Jena) spectrometer using in a home-made thermostatic 0.5 mm BaF_2 liquid-cell. In IR and NMR standard experiments, the concentration of complexes was 10 mM for $Pd(NO_2)ClL_2$ and 5 mM for the other complexes, with 5–10 mol of propylene per 1 mol of Pd being introduced into the solution by bubbling at required temperature. In kinetic experiments, the reactions were carried out either in a stirred glass reactor equipped with a sampling system and connected to a gas burette or directly in the probe of the spectrometer. Reactions in the glass reactor were followed by measuring a gas uptake and by a gas–liquid chromatography using a LHM-8MD instrument fitted with a 2 m×3 mm column (15% 1,2,3-tris(β-cyanoethoxy)propane on Polysorb-1) and flame ionization detector.

2.1. Spectroscopic data for propylene ($H^{a(cis)}$-$H^{b(trans)}C{=}CH^cCH^d{}_3$) (**I**)

IR ($CHCl_3$ solution)/cm^{-1}: 1644 [ν(C=C)], 1551, 1373, 996 [δ(=C–H)], 920 [δ(=C–H)]. δ_H: 1.74 (dt, 3H, $^4J_{a-d}=1.9$ Hz, $^4J_{b-d}=1.4$ Hz, $^3J_{c-d}=6.1$ Hz, H^d), 5.82 (m, 1H, $^3J_{a-c}=18.0$ Hz, $^3J_{b-c}=12.0$ Hz, $^3J_{c-d}=6.1$ Hz, H^c), 4.93 (dm, 1H, $^2J_{a-b}=3.0$ Hz, $^3J_{b-c}=12.0$ Hz, $^4J_{b-d}=1.4$ Hz, $H^{b(trans)}$), 5.02 (dp, 1H, $^2J_{a-b}=3.0$ Hz, $^3J_{a-c}=18.0$ Hz, $^4J_{a-d}=1.9$ Hz, $H^{a(cis)}$).

2.2. Spectroscopic data for acetone (**II**)

IR ($CHCl_3$ solution)/cm^{-1}: 1712 [ν(C=O)], 1363 [$\delta_s(CH_3)$], 1090. δ_H: 2.08 (s, 6H).

2.3. Spectroscopic data for 2-nitropropylene [$H^a{}_2C{=}C(NO_2)CH^b{}_3$] (**III**)

IR ($CHCl_3$ solution)/cm^{-1}: 1534 [$\nu_{as}(NO_2)$], 1346 [$\nu_s(NO_2)$]. δ_H: 2.19 (br s, 3H, H^b), 5.57 [br s, 1H, H^a (*trans* to NO_2)], 6.34 [br s, 1H, H^a (*cis* to NO_2)].

2.4. Spectroscopic data for propionic aldehyde [$H^a{}_3CCH^b{}_2COH^c$] (**IV**)

δ_H: 1.03 (t, 3H, $^3J_{a-b}=7.4$ Hz, H^a), 2.40 (qd, 2H, $^3J_{b-c}=1.4$ Hz, H^c), 9.71 (t, 1H, $^3J_{b-c}=1.4$ Hz, H^b).

3. Results and discussion

3.1. Reactivity of the palladium nitro and nitrato complexes in propylene oxidation and reaction products

The reactions of propylene (**I**) with the following complexes: $Pd(NO_2)ClL_2$ (**1**), $Pd(NO_3)ClL_2$ (**2**), $Pd(NO_2)_2L_2$ (**3**), $Pd(NO_2)(NO_3)L_2$ (**4**), and $Pd(NO_3)_2L_2$ (**5**), where $L=CH_3CN$, in chloroform solutions have been studied (Table 1). The main reaction products are acetone (**II**) and 2-nitropropylene (**III**), along with small amounts of propionic aldehyde (**IV**) (up to 2% on reacted **I**). The latter product results from the anti-Markovnikov oxidation of propylene. The product distribution depends on the composition of the palladium complex used. Mononitro (**1**) and mononitrato (**2**) complexes give almost exclusively acetone (93–97%), with no formation of a palladium metal being observed. On the other hand, the reactions with complexes **3**–**5**, containing two NO_n ligands, result in the formation of 20–30% of nitrogenated product **III** and 70–80% of acetone. In the reactions with **3**–**5**, a palladium metal is formed in equimolar amounts based on **III**. The initial

Table 1
Propylene oxidation by palladium complexes in chloroform (L = CH_3CN)

Run	Complex	Rate[a] (mM min^{-1})	TON[b]	Product distribution[c] (mol %)	
				Acetone (**II**)	2-Nitropropylene (**III**)
1	$Pd(NO_2)ClL_2$ (**1**)	0.34	1	93	6
2	$Pd(NO_3)ClL_2$ (**2**)	0.58	2	93	5
3	$Pd(NO_2)L_2$ (**3**)	0.22	2	67	32
4	$Pd(NO_2)(NO_3)L_2$ (**4**)	0.58	3	76	23
5	$Pd(NO_3)_2L_2$ (**5**)	0.66	4	78	20
6[d]	$Pd(NO_2)ClL_2$ (**1**)	0.50	6	97	1

Reaction conditions: [complex] = 5 mM, 25 °C, gas phase: propylene (0.1 MPa), reaction time 6 h.
[a] Initial rate of a gas phase uptake.
[b] Tonover number per mol of palladium complex charged.
[c] Determined by gas chromatography, 1–2% of propionic aldehyde was also formed.
[d] Gas phase: propylene: dioxygen = 1:2 (0.1 MPa), 24 h.

rate of propylene oxidation is also ligand-dependent. Nitrato complexes **2**, **4** and **5** are more active than mononitro complex **1**, while the reactivity of the latter is significantly higher than that of dinitro complex **3**. Under oxygen-free conditions (Table 1, runs 1–5), the acetone formation is accompanied by the reduction of all NO_n^- ligands into nitrosyl groups bonded to palladium(II). Thus, the reaction is catalytic on palladium but not on nitrogen. In the presence of dioxygen, which reoxidizes the nitrosyl groups, it becomes catalytic also on nitrogen giving a turnover number of 6 per one Pd atom for 24h (Table 1, run 6 vs. run 1).

3.2. Reaction intermediates

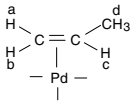
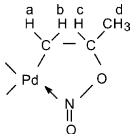
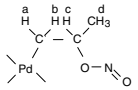
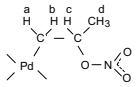
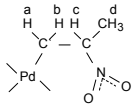
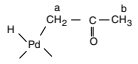
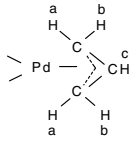
Solid-state IR spectra of mononitro complex **1** show that a nitro group is bonded to palladium mainly via a nitrogen atom (nitro complex). Vibrational frequencies at 1451 ($\nu_{as}(NO_2)$), 1335 ($\nu_s(NO_2)$), 831 ($\delta(NO_2)$) and 605 cm^{-1} ($\rho_w(NO_2)$), assigned to a nitro group and confirmed by ^{18}O labeling, were observed. On dissolving this complex in chloroform, the absorption bands (a.b.'s) of free acetonitrile appear (2292 and 2257 cm^{-1}) and splitting the a.b.'s of coordinated acetonitrile occurs. It could be partially explained by the formation of dimer complexes through chloride bridging [16]. The IR spectrum of **1** in chloroform solutions shows vibrational frequencies of both a nitrogen-bonded (1460, 1466, 1333, 1325 cm^{-1}) and an oxygen bonded (1509, 1517, 1024, 1035 cm^{-1}) NO_2 group. The assignment was confirmed by ^{18}O labeling. On the other hand, dinitro complex **3** has been shown to exist in chloroform solutions mainly as a nitrogen-bonded form. An analysis of the IR and NMR spectra of complexes **1**–**5** in chloroform reveals that various types of palladium species coexist in the solutions, including monomeric and dimeric forms, which are linked by multiple equilibria. A complete report on the study of these equilibria will be published elsewhere.

The reactions of propylene with complexes **1**–**3** in chloroform solutions were monitored by ^1H NMR and IR spectroscopy in situ. It was observed that the addition of propylene to the solutions of the palladium complexes leads to the appearance of various new lines in the IR and ^1H NMR spectra. Based on the analysis of the changes in their intensities with reaction time, some lines were attributed to the final reaction products and the other ones to reaction intermediates. The results of the assignment and the structures proposed for the detected intermediates are given in Table 2 and for the final products in Section 2.

The interaction of propylene with complexes **1**–**3** leads primarily to the corresponding π-complexes (**V**). The intensities of the a.b.'s of coordinated acetonitrile decrease rapidly due to its displacement by propylene, while those of free acetonitrile increase. The stretching frequencies of a C═C fragment, at ca. 100 cm^{-1} below than that of the free propylene (1644 cm^{-1}), appear in the IR spectra. The shift of the adsorption due to C═C depends on the other ligands on palladium (Table 2). In the ^1H NMR spectra, the dynamically averaged resonances of propylene protons are observed due to a rapid, on a NMR timescale, exchange between the free and coordinated propylene. The maximum downfield changes in the averaged resonances compared to those of the free propylene are detected for two vinylic hydrogens: H_c (102 Hz) and H_b (81 Hz), *trans* to the methyl group, vs. 21 Hz for the *cis* vinylic proton H_a and 30 Hz for the hydrogens of the methyl group (see structure **V** in Table 2). As these changes depend on the temperature and on the C_3H_6/Pd ratio, the data in Table 2 are given for the C_3H_6/Pd ratio of 1/1 and the temperature of 0 °C. These results clearly show a distortion occurring in the π-complexes, with shifting the electronic density of the π-bond towards a less sterically hindered face of propylene (*trans* to CH_3).

In the course of the reaction, the intensities of the NMR and IR lines of the initial complexes, π-complexes

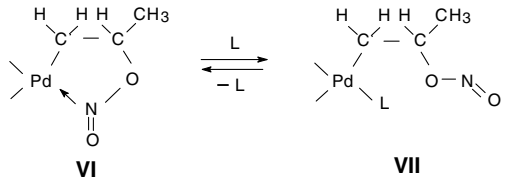
Table 2
^{1}H NMR data, the most characteristic vibrational frequencies and structures proposed for the compounds observed at propylene oxidation

Compound		^{1}H NMR data				IR data	Proposed structure
		Line structure[a]	δ	J_{H-H}(Hz)	Intensity ratio	Absorption bands (cm^{-1}) Attribution	
V[b]	a	d	5.09	$J_{a-c}=16.3$	1	1535–1560	
	b	d	5.20	$J_{b-c}=8.2$	1	ν(C═C)[c],	
	c	br s	6.16	$J_{c-d}=7.1$	1	1437, 1047	
	d	d	1.84		3	1001	
VI	a	dd	3.11	$J_{a-c}=6.4$	1	1626 ν(N═O),	
	b	dd	3.40	$J_{b-c}=4.7$	1	1140, 985	
	c	sextet	4.48	$J_{c-d}=8.7$	1	878	
	d	d	1.52	$J_{c-d}=6.6$	3		
VII	a,b	br s	2.80		2	1614, ν(N═O)	
	c	br q	4.68–5.10	$J_{c-d}=6$	1	1130, 981	
	d	d	1.88		3	885	
VIII	a	br d	2.36	$J_{a-b}=9.7$	1	1627 $\nu_{as}(NO_2)$,	
	b	br d	3.22	$J_{c-d}=6.5$	1	1292 $\nu_s(NO_2)$	
	c	m	4.28		1		
	d	d	1.38		3		
IX	a	m	2.60		1	1548 $\nu_{as}(NO_2)$,	
	b	m	3.00		1	1325 $\nu_s(NO_2)$	
	c	m	4.62		1		
	d	d	1.76	$J_{c-d}=6.52$	3		
X	a	s	3.36		2	1693 ν(C═O),	
	b	s	2.28		3	1356 δ_s (CH_3)	
XI	a	d	3.07	$J_{a-c}=11.8$	2	1460 δ_{as} (CH_2),	
	b	d	4.15	$J_{b-c}=6.8$	2	1385 δ_s (CH_2),	
	c	m	5.48		1	1022 ν_s(CCC),	
						943 ρ_w (CH_2)	

[a] s, singlet; d, doublet; q, quartet; m, multiplet; br, broadened; dd, doublet of doublets.
[b] In the ^{1}H NMR spectra, the dynamically averaged resonances of propylene protons are observed due to a rapid exchange between free and coordinated alkene on the NMR timescale. The data are given for the solution of complex **1** treated with 1 equivalent of propylene at 0 °C.
[c] The C═C stretching frequency for compound **V** depends on the nature of the other ligands on palladium: for **1**, 1541; for **2**, 1550; for **3**, 1548; for **4**, 1557 and for **5**, 1560 cm^{-1}.

V and free propylene decrease, while the lines attributed to reaction products **II**–**IV** and a nitrosyl palladium(II) complex $Pd(NO)ClL_2$ (**6**) appear and their intensities increase with time. The lines appearing and then disappearing in the course of the reaction were attributed to reaction intermediates. To clarify a structure and reactivity of these intermediates, we have monitored the reaction at various temperatures (−30 to +55 °C). During the interaction of propylene with mononitro complex **1**, four compounds with kinetics characteristic for intermediates were registered in the reaction solutions: **VI**, **VII**, **IX** and **X**. It was found that acetone and 2-nitropropylene as well as intermediate **X** are formed with appreciable induction periods, during which near to maximum concentrations of intermediate **VII** are observed.

According to the ^{1}H NMR data (Table 2), intermediates **VI** and **VII** appear to be 1,2-disubstituted propanes containing a CH_2–CH–CH_3 fragment. The most distinctive IR spectral feature of both **VI** and **VII**, showing very similar a.b.'s, is a strong band at 1626 and 1614 cm^{-1}, respectively. This band is attributed to a N═O stretch of organic nitrites [22]. To confirm the structures of **VI** and **VII**, we used the ^{18}O-enriched complex **1** (the $^{18}O/^{16}O$ isotopic ratio of approximately 1/1). Expectedly, the a.b.'s of acetone at 1712 cm^{-1} (ν(C═O)) and palladium nitrosyl complex at 1730 cm^{-1} (ν(N═O)) split into equal intense doublets. The a.b.'s of the nitro groups in complexes **1** and **V** split into three components with the intensity ratio of 1:2:1 corresponding to the vibrational frequencies of nitro groups $N^{18}O_2$, $N^{18}O^{16}O$, and $N^{16}O_2$. However, in the IR spectra of **VI**



Scheme 1.

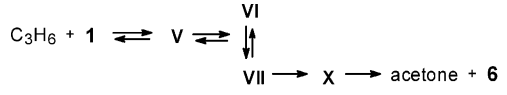
and **VII**, the doublets of approximately equal intensities were observed at 1626/1614 and 1592/1586 cm^{-1}, respectively, corresponding to the stretching frequencies of N═^{16}O and N═^{18}O fragments of nitrito groups.

Based on the data obtained, we propose the structures shown in Scheme 1 for compounds **VI** and **VII**, which are most probably linked by an equilibrium.

When the reaction was carried out in the presence of excess acetonitrile ($Pd/CH_3CN = 1/100$), the shift of the equilibrium in Scheme 1 towards the open ring isomer **VII** was observed due to a higher coordinating ability of acetonitrile vs. chloroform. Broadening the lines and changes in the chemical shift of the hydrogens of the CHONO fragment in **VII** were observed (Table 2). It can be explained by a known *cis*/*trans* isomerization of open ring organic nitrites [23], with the chemical shifts of α-protons in two isomers being substantially different from each other. Dynamically averaged proton resonances are usually observed due to a rapid exchange between *cis* and *trans* isomers on the NMR timescale, which is possible to freeze out only at −60 °C [23]. Metallacycle **VI** has been detected previously under similar conditions [1,16] and the spectral characteristics obtained herein are in agreement with those reported.

Although the structures of intermediates **VI** and **VII** are similar, a kinetic study has shown that their reactivities are quite different. Judging from the kinetic curves, intermediate **VII** seems to be a kinetic precursor of intermediate **X** and is much more reactive than complex **VI**. The sequence of transformations shown in Scheme 2 seems to take place in the solutions.

We monitored the decomposition of the intermediates **VI** and **VII** in the absence of propylene by ^{1}H NMR and IR. The excess propylene was slowly vented by nitrogen after ca. 30 min of reaction at 0 °C. This treatment resulted in the disappearance of the lines attributed to propylene and π-complex **V**. A dominant compound observed in the spectrum after such a procedure was intermediate **VI**. Its *slow* decomposition resulted in π-complex **V** and acetone, which clearly indicates a reversibility of the formation of this intermediate, i.e., a reversibility of a propylene oxypalladation step (see a discussion below). When excess acetonitrile was added after removal of propylene, π-complex **V** and complex **VII** instead of **VI** were mainly detected. Complex **VII** then *rapidly* decomposed giving the initial complex **1**, π-complex **V** and acetone. These experiments provided additional evidence of the higher reactivity of the open ring intermediate **VII** compared with that of its metallacycle isomer **VI**.



Scheme 2.

The structure of intermediate **X** has been proposed based on the analysis of its ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum consists of two singlets at δ 3.36 and 2.28 with the intensity ratio 2:3. In the IR spectrum, two a.b.'s with a dynamics similar to that of the NMR singlets mentioned above are observed: at 1693 and 1356 cm^{-1}, attributed to the C═O and C–H stretches, respectively (cf. with IR data for acetone: 1712 cm^{-1}, ν(C═O), and 1363 cm^{-1}, $\delta_s(CH_3)$). Considering that the decomposition of **X** does give acetone, we suppose that this intermediate is formed from **VII** via a β-hydride shift and contains a Pd–CH_2COCH_3 fragment. Although our attempts to register a signal from the sixth propylene hydrogen have failed, we suppose that it should be bound directly to palladium as a hydride ligand. This suggestion was supported by the following experiments. Either DCl or CD_3COOD were added to the reaction solution when maximum concentrations of **X** were registered. No ^{1}H NMR signals from acetone enriched in deuterium were detected showing that there was no noticeable exchange of propylene hydrogens with D^+. Thus, the "missed" proton unlikely has an acid nature and most probably is a hydride one. The NMR spectrum of **X** is very similar to that observed for the related platinum complex [Pt(CH_2COCH_3)Clbipy] [24]. In our previous study on the ethylene oxidation [17–19], we detected an analogous organometallic precursor of acetaldehyde, HPd–CH_2CHO. The related intermediate containing a fragment Pd–CH_2COPh (δ 3.17, s, 2H) we observed also at styrene oxidation by **1**. To the best of our knowledge, there are no other works available in literature which describe the spectroscopic evidences of the formation of such type of organometallic intermediates at palladium-catalyzed alkene oxidations.

In the course of the reaction of propylene with nitrato complex **2**, intermediate **VIII** was detected by both ^{1}H NMR and IR. The ^{1}H NMR spectrum of **VIII** is rather similar to that of **VI** (Table 2). In its IR spectrum, two main a.b.'s at 1627 and 1292 cm^{-1} of approximately equal intensities, which are characteristic for $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ of organic nitrates [25], are observed. So, we suppose that **VIII** is the product of the nitratopalladation of propylene containing a fragment $PdCH_2CH(ONO_2)CH_3$. To confirm the structure, we used the ^{18}O-enriched $Pd(NO_3)ClL_2$ (the ^{18}O/^{16}O isotopic ratio of approximately 1/1). The a.b.'s of **VIII** split into

three components with the intensity ratio of 1:2:1 corresponding to the vibrational frequencies of nitrate groups $ON^{18}O_2$, $ON^{18}O^{16}O$ and $ON^{16}O_2$. Intermediate **VIII** is formed at a high rate and its maximum concentration is observed in the first spectrum registered (ca. 2 min after the propylene addition), even at low temperature. Then, the concentration of **VIII** decreases and the a.b.'s of acetone and nitro π-complexes **V** appear. The latter then decompose into acetone and nitrosyl palladium (II) complex **6** via the intermediate formation of compounds **VI** and **VII**.

The reaction of propylene with dinitro complex **3** gives ca. 30% of 2-nitropropylene (**III**) along with acetone. Intermediate product **IX**, which seems to be an organometallic precursor of **III**, is detected in the reaction solutions, The ^{1}H NMR spectrum of **IX** consists of three multiplets at δ 2.60, 3.00, 4.62 and a doublet at δ 1.76 with the intensity ratio of 1:1:1:3, indicating that **IX** contains a CH_2–CH–CH_3 fragment. Vibrational frequencies at 1548 and 1325 cm^{-1} in its IR spectrum can be assigned to a nitro group of nitroalkanes ($\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively) [25]. Thus, we suppose that intermediate **IX** is a product of the nitropalladation of propylene containing a fragment $PdCH_2CH(NO_2)CH_3$.

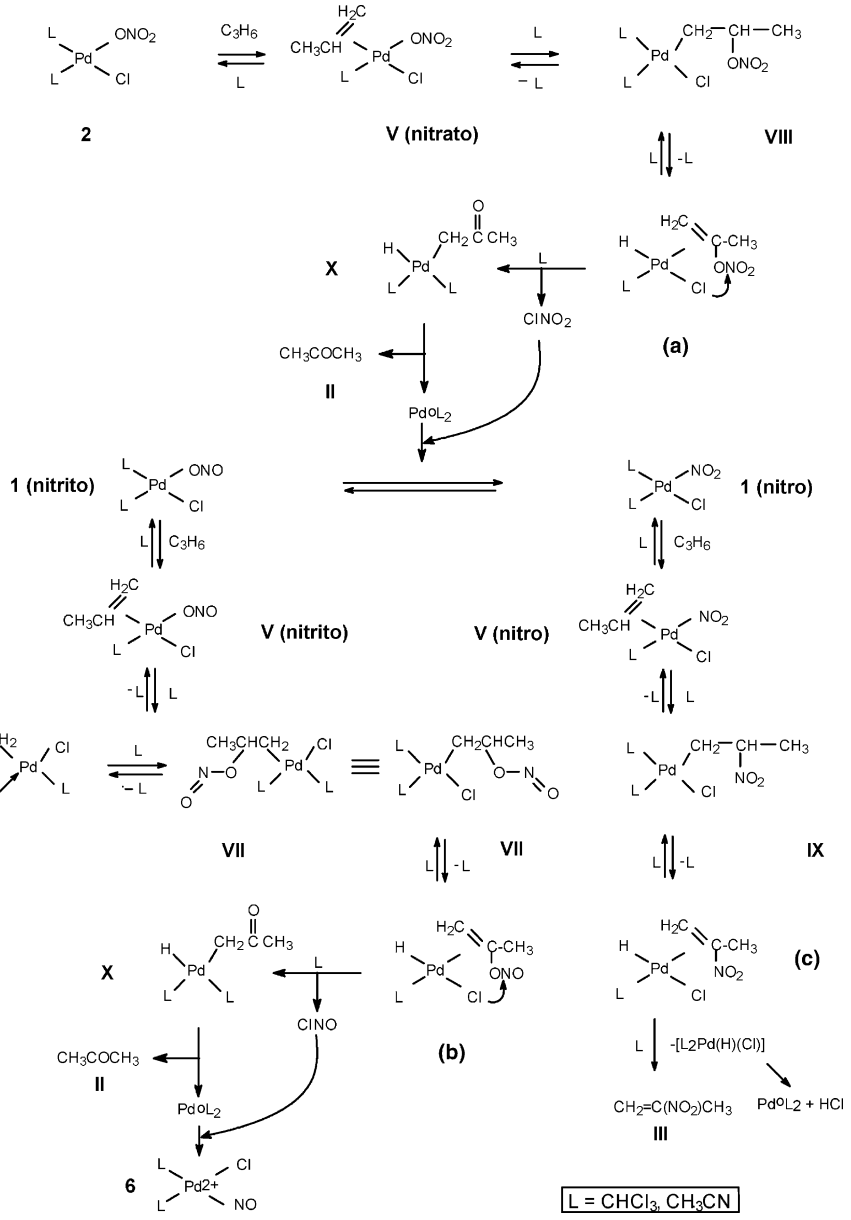
3.3. Mechanism of propylene oxidation by palladium nitrato and nitro complexes

Based on the analysis of the NMR and IR results, we propose a mechanism for propylene oxidation by palladium nitro and nitrato complexes in aprotic solvents (Scheme 3). Propylene successively reduces the nitrate group first to the nitro and then to the nitrosyl group, with acetone being formed via similar routes. In the presence of dioxygen, the re-oxidation of nitrosyl palladium(II) complexes occurs, thus the nitrate and nitro groups act as oxygen transfer ligands and the reaction becomes catalytic not only on palladium but also on nitrogen. In Scheme 3, only monomeric initial complexes are presented for simplification, although, as mentioned above, there are various monomeric and dimeric palladium species with different geometry and reactivity in starting solutions. In the first reaction step, a ligand exchange takes place with the formation of corresponding π-propylene palladium complexes **V** (nitrato, nitro and nitrito). The insertions of the alkene into the Pd–O bonds of nitrato and nitrito complexes or into the Pd–N bond of the nitro complex result in the palladation products **VIII**, **VI/VII** and **IX**, respectively. The nucleophilic attack of an oxygen or a nitrogen atom occurs preferably at the more substituted carbon. Only small amounts (up to 2% on reacted propylene) of the anti-Markovnikov oxidation product, i.e., propionic aldehyde, and no corresponding σ-organopalladium intermediate have been observed.

As it has been shown by ^{1}H NMR and IR, in the absence of propylene, the decomposition of **VI** and **VII** leads to the formation of π-complex **V** along with acetone, which clearly indicates the reversibility of the palladation step. A reaction rate-determining step seems to be the decomposition of these σ-organopalladium compounds via the β-hydride shift. Two isomers of the nitritopalladation product have been detected in the reaction solutions: palladium metallacycle **VI** and open ring complex **VII**, probably, linked by the equilibrium. The kinetic study revealed their quite different reactivities. Open isomer **VII** seems to be a kinetic precursor of intermediate **X** and is much more reactive than **VI**. The analysis of molecular model structures showed that β-hydrogen elimination is sterically more difficult in metallacycle **VI** than in open ring isomer **VII**. It contributes in higher stability of metallacycle **VI** and facilitates its spectral registration.

The decomposition of nitrato- and nitritopalladation products **VIII** and **VI/VII** gives acetone and palladium(II) nitro- or nitrosyl complexes, respectively. This decomposition occurs via the formation of intermediate **X**. This compound, in fact, is the intermediate of the hydrogen atom transfer from the β- to α-carbon atom and the organometallic precursor of acetone. Nitropalladation product **IX** decomposes also via the β-hydrogen elimination resulting in 2-nitropropylene and palladium(II) hydride, which then gives H^+ and Pd(0) due to the intramolecular redox reaction. Thus, the nitro group transfer to the alkene, in contrast to the oxygen atom transfer, is accompanied by the formation of equimolar amounts of the palladium metal. The decomposition of intermediates **VI**–**IX** could be rationalized as follows. Reversible $\sigma - \pi$ rearrangements via a β-hydride shift result in π-palladium hydride complexes **A**, **B** and **C** with coordinated vinyl derivatives (Scheme 3). The latter can be displaced from the coordination sphere of palladium by another ligand. In this way, 2-nitropropylene is formed from **C**. Hydride complexes **A** and **B** are further transformed via the insertion of coordinated vinyl substituted propylene into the Pd–Cl bond, with the nucleophilic Cl^- attacking at the electrophilic nitrogen atom of the nitrato or nitrito group. This results in the aldehyde precursor **X** and nitryl or nitrosyl chlorides ($ClNO_2$ or ClNO). Then, **X** decomposes by a reductive elimination giving acetone and a palladium(0) complex, which is reoxidized back to Pd(II) by $ClNO_2$ or ClNO via their oxidative addition.

Thus, nitryl and nitroxyl chlorides act as reversible oxidants and the reaction of acetone formation is catalytic on palladium, whereas nitrogen is reduced. In the presence of dioxygen, which re-oxidizes the nitrosyl groups, the acetone formation becomes a catalytic reaction with respect to both palladium and nitrogen. At longer reaction time, a catalyst deactivation occurs, most likely due to the formation of stable dimeric π-allyl



Scheme 3. Mechanism of the propylene oxidation by palladium nitrato and nitro complexes in chloroform solutions.

palladium(II) complexes **XI** (Table 2). After the 24-hour reaction in chloroform at 25 °C, **XI** was detected in equimolar amounts to complex **1** charged. The IR data of **XI** are similar to those reported in [26] for $[(\pi\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$. Complex **XI** is rather stable in chloroform solutions, however with the addition of acetic acid, it decomposes giving allyl acetate.

The amounts of acetone vs. 2-nitropropylene formed in these reactions depend on the equilibrium between the palladium complexes with nitrogen vs. oxygen bonded NO_2 groups, i.e., nitro and nitrito complexes, and also on the relative reactivity of these complexes towards propylene. The reactivites of the oxygen-bonded complexes (nitrato and nitrito) have been found to be significantly higher than that of the nitrogen-bonded nitro complex. Dinitro complex **3** shows the less activity because it exists in chloroform solutions mainly in the nitrogen-bonded form, which gives nitrogenated product **III** from propylene. Nitrato complex **2** is more reactive than complex **1**, which can be explained by the presence of the significant amounts of nitro isomer in the chloroform solutions of **1**, whereas complex **2** contains only the oxygen bonded NO_3^- ligand.

4. Conclusions

The propylene oxidation by $Pd(NO_n)Cl_{2-m}(CH_3CN)_2$ complexes in chloroform solutions results mainly in acetone and 2-nitropropylene, with their ratio

depending on the equilibrium between nitrito and nitro palladium complexes. Reactivities of the oxygen bonded nitrato and nitrito complexes are significantly higher than that of the nitrogen bonded nitro complex. Various new organopalladium intermediates have been observed and monitored in situ by ^{1}H NMR and IR. A reversible insertion of the coordinated propylene into the Pd–O or Pd–N bonds results in nitrato-, nitrito- and nitropalladation intermediates, which then decompose via β-hydrogen elimination. Two isomers of the nitritopalladation intermediate have been detected, i.e., a palladium metallacycle and an open ring complex, with the latter being much more reactive towards the β-hydrogen elimination than the former. The decomposition of the nitrato- and nitritopalladation intermediates results in the organometallic precursor of acetone and then in acetone itself. On the other hand, the nitropalladation intermediate originates 2-nitropropylene. In the presence of dioxygen, which re-oxidizes the nitrosyl groups, the acetone formation becomes a catalytic reaction with respect to both palladium and nitrogen.

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