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Palladium catalyzed transformations of monoterpenes: stereoselective deuteriation and oxidative dimerization of camphene

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Abstract

Camphene undergoes a highly regio and stereoselective palladium catalyzed deuteriation in deuteriated acetic acid solutions of $Pd(OAc)_2$. NMR reveals that an outward oriented vinylic hydrogen is selectively exchanged for ^2H, resulting in 90% camphene-d_1 (ca. 100% stereoselectivity) and 10% camphene-d_2 at 75% conversion of camphene (6 h, 25 °C). Neither π-allyl nor π-olefin palladium complexes are formed in detectable concentrations during the reaction, whereas palladium hydride (singlet at −6.86 ppm) and palladium deuteride (singlet at −6.78 ppm) intermediates have been detected by ^1H and ^2H NMR, respectively. At higher temperature, oxidative coupling of camphene readily occurs giving the (*E*,*E*)-diene, i.e., bis(3,3-dimethyl-2-norbornylidene)ethane, which formally originates by abstracting the outward oriented vinylic hydrogens and coupling the resulting fragments of two camphene molecules. The reaction is catalytic at palladium in the $Pd(OAc)_2$–$LiNO_3$(cat)–O_2 and $Pd(OAc)_2$–benzoquinone systems. Similar mechanisms for the deuteriation and oxidative coupling of camphene are proposed, which involve the formation of σ-vinyl palladium hydride intermediates. No deuteriation neither oxidative coupling of limonene, myrcene and β-pinene were observed under the same conditions.

Keywords: Palladium; Camphene; Deuteriation; Oxidative coupling

1. Introduction

Palladium complexes are widely used in organic chemistry due to their capacity to mediate numerous transformations of organic molecules, often in a catalytic mode [1–3]. In particular, a great variety of valuable products can be achieved by palladium catalyzed oxidations of alkenes. Although the applications of metal complex catalysis to the functionalization of natural products have become a growing field of chemistry in recent years, examples of the palladium catalyzed oxidations of naturally occurring alkenes are rather scarce. Monoterpenes are particularly important precursors of valuable oxygenated products, since terpene aldehydes, ketones, alcohols and esters usually show interesting organoleptic properties and form the largest group of modern fragrance ingredients [4–7]. We have previously studied palladium catalyzed oxidations of some monoterpenes using both dioxygen and hydrogen peroxide as final oxidants [8–12]. Limonene and β-pinene were selectively oxidized into allylic acetates in $PdCl_2$(cat)/$CuCl_2$(cat)/O_2 and $Pd(OAc)_2$(cat)/H_2O_2 systems, respectively [8,9]. A conventional Wacker catalyst ($PdCl_2$/$CuCl_2$) promoted oxidative cyclization of myrcene giving new acetates with a cyclopentane skeleton [11].

The products of the oxidation of limonene, β-pinene and myrcene reported in the works cited above seem to arise via the intermediate formation of π-allyl palladium complexes. In the case of camphene, we do not expect allylic oxidation products, since the only allylic hydrogen in this molecule is at a bridgehead position and not easily abstracted. Indeed, the oxidation of camphene

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with hydrogen peroxide catalyzed by $Pd(OAc)_2$ resulted in glycol derivatives [9], whereas a Pd(II)/NO_n^- ($n = 2, 3$) catalytic system promoted oxidative coupling of camphene with further oxidation of a resulting diene by dioxygen [10,12]. Direct coupling of olefins is not general reaction and only a few examples have been reported so far [13–18]. The scope of this reaction is usually limited to some terminal disubstituted alkenes and alkenes carrying electron-withdrawing groups, such as vinyl acetate.

In this paper, we report the results of NMR studies of the interaction of camphene with $Pd(NO_2)Cl(CH_3CN)_2$ and $Pd(OAc)_2$ in chloroform and acetic acid solutions, respectively. We have found that camphene undergoes a highly regio and stereoselective palladium catalyzed deuteriation, with stereospecific replacement of the outward oriented olefinic hydrogen by deuterium. This method represents a useful tool in the synthesis of the isotopically labeled substrate for mechanistic and kinetic studies. The results clarify the mechanism of the deuteriation as well as the oxidative coupling of camphene.

2. Experimental

All reagents were purchased from commercial sources and used as received, unless otherwise indicated. Racemic camphene was purchased from Aldrich and distilled before use. $Pd(NO_n)Cl(CH_3CN)_2$ ($n = 2, 3$) were synthesized from $PdCl_2(CH_3CN)_2$and $AgNO_n$ in analogy with [21]. The reactions were carried out in a stirred glass reactor and followed by measuring the dioxygen uptake (if any) and/or by gas chromatography (GC) (Shimadzu 14B, Carbowax 20 M). NMR spectra were recorded at 25 °C using a Bruker DRX-400 spectrometer, operating at 400 MHz for ^1H, 61.4 MHz for ^2H or 100.6 MHz for ^{13}C. Chemical shifts are referenced to tetramethylsilane as internal standard. $CDCl_3$ (99.8 at.% D) and CD_3COOD (99.5 at.% D) were used as solvents in NMR experiments. T_1 measurements used the inversion-recovery method with 20 s relaxation delays.

NMR data for camphene (**1**) and camphene-d_1 are presented in Table 1. Those for diene **2** have been previously published in [12].

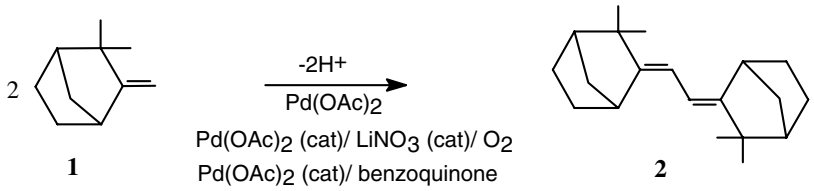
3. Results and discussion

Camphene (**1**) readily reacts with $Pd(NO_2)Cl(CH_3CN)_2$ and $Pd(NO_3)Cl(CH_3CN)_2$ in chloroform or acetic acid solutions at 60 °C giving mainly a product of oxidative dimerization, i.e., bis(3,3-dimethyl-2-norbornylidene)ethane (**2**) (Scheme 1) ([camphene] = 0.10 mol l^{-1}; [Pd] = 0.01 mol l^{-1}). In the absence of dioxygen, the total amounts of the product correspond to the reduction of all NO_n^- ligands in nitrosyls followed by the precipitation of a palladium black. In the presence of dioxygen in acetic acid solutions, the reaction becomes catalytic in both palladium and nitrate, with further oxidation of the diene occurring when $LiNO_3$ is added into the solution [10]. Oxidative coupling of camphene into diene **2** (previously described in [19,20]) can be also performed using catalytic amounts of $Pd(OAc)_2$ and benzoquinone as reoxidant in acetic acid solutions. Two isomers of diene **2** are formed in comparable amounts (ca. 40/60) from racemic camphene in this reaction, both having an (*E*,*E*)-configuration, i.e., *meso* and *dl* stereoisomers [12]. Thus, the palladium catalyzed oxidative coupling of camphene is a highly stereoselective reaction. The (*E*,*E*)-diene **2** formally originates by abstracting the outward oriented vinylic hydrogens in two camphene molecules and coupling the resulting fragments. Two

Table 1
NMR data for camphene and camphene-d_1 deuteriated at position 8a

Atom[a]	Camphene		Camphene-d_1	
	δ (^1H)[b]	δ (^{13}C)	δ (^1H)[b]	δ (^{13}C)
1	1.89 (br.d)	49.21	1.89 (br.d)	49.21
2		42.55		42.52
3		167.09		166.99
4	2.65 (br.d)	47.98	2.65 (br.d)	47.92
5endo	1.21–1.25 (m)	29.68	1.21–1.25 (m)	29.68
5exo	1.68–1.74 (m)		1.68–1.74 (m)	
6endo	1.68–1.74 (m)	24.55	1.68–1.74 (m)	24.55
6exo	1.38–1.48 (m)		1.38–1.48 (m)	
7a	1.21–1.25 (m)	38.11	1.21–1.25 (m)	38.11
7b	1.62–1.66 (m)		1.62–1.66 (m)	
8a	4.71 (s)	99.82		99.55 (t, $^1J_{C-D} = 24$)
8b	4.50 (s)		4.48 (s)	
9	1.05 (s)	28.79	1.05 (s)	28.79
10	1.02 (s)	26.20	1.02 (s)	26.20

[a] Usual numbering for camphene is presented in Scheme 2.
[b] Resonance multiplicities, coupling constants (Hz) in parentheses: (s) singlet, (d) doublet, (t) triplet, (m) multiplet, (br) broadened.



Scheme 1.

possible mechanisms of oxidative coupling of alkenes are generally discussed [2,10,17,22]: via oxypalladation of the olefinic bond (e.g., palladium acetate addition) forming a σ-alkyl palladium intermediate and via palladation at a vinylic carbon resulting in a σ-vinyl palladium intermediate, but no mechanistic studies have been reported so far.

Using NMR spectroscopy, we have studied the interaction of camphene and the palladium (II) complexes $PdCl_2(CH_3CN)_2$, $Pd(NO_2)Cl(CH_3CN)_2$ and $Pd(OAc)_2$, in chloroform and acetic acid solutions. Addition of $PdCl_2(CH_3CN)_2$ to the chloroform solution of camphene resulted in no detectable changes in chemical shifts, widths and relative intensities of its NMR signals, even after 6 h ([camphene] = 0.02 mol l^{-1}; [Pd] = 0.01 mol l^{-1}). Measurements of spin-lattice relaxation times (T_1) of the hydrogen signals also showed that no significant differences in the camphene molecule arise from any presence of the palladium complex in the solution, for no selective relaxation of olefinic hydrogens was observed. The following values of T_1(s) were obtained (the corresponding values in the absence of the palladium complex are given in parentheses): 5.618 (5.429) for H-1; 6.362 (5.737) for H-4; 5.447 (5.021) for H-8a; 5.270 (4.829) for H-8b; 3.773 (3.212) for H-9 and 3.596 (3.115) for H-10. Monitoring the interaction between camphene (0.10 mol l^{-1}) and $Pd(NO_2)Cl(CH_3CN)_2$ (0.01 mol l^{-1}) in chloroform solutions at 25 °C by ^{1}H NMR revealed a slow reaction with the formation of diene **2** (signals from vinylic hydrogens at 5.73/5.71 ppm and from H-4 at 3.09/3.08 ppm for two isomers). No changes in the spectrum of camphene and no signals attributable to the reaction intermediates were observed. Thus, in chloroform solutions, neither π-allyl nor π-olefin palladium complexes are formed from camphene in significant concentrations during the reaction. Moreover, the concentrations of any intermediates leading to camphene coupling are also too low for these to be detected by NMR.

However, the ^{1}H and ^{13}C-NMR spectra of camphene change dramatically with time in acetic acid solutions of $Pd(OAc)_2$. The formation of diene **2** is a very slow reaction at room temperature, with about 10% of camphene being converted to **2** over 30 h under the conditions given in Table 2. Significant changes in the relative intensities of the ^{1}H signals of camphene and the appearance of new ^{1}H and ^{13}C signals prompted us to suggest a relatively fast replacement of hydrogen atoms for deuterium in the camphene molecule. NMR data for starting and monodeuteriated camphene are presented in Table 1. Table 2 gives the kinetic data for this deuteriation reaction. After the addition of $Pd(OAc)_2$ to the deuteriated acetic acid solution of camphene, the intensities of the signals from both vinylic hydrogens (at 4.71 and 4.50 ppm) each rapidly decrease compared to other signals of camphene, resulting in their almost complete disappearance. The signals from the other hydrogens of camphene remain virtually unchanged. Simultaneously, only one new signal appears in the olefinic region of the

Table 2
Deuteriation of camphene catalyzed by $Pd(OAc)_2$[a]

Time (h)	Conversion[b] (%)	Relative intensities of signals from				Selectivity (%)	
		H-4	Camphene		Camphene-d_1[c]	Camphene-d_1[c]	Camphene-d_2[d]
			H-8a	H-8b	H-8b		
0	0	1	0	0	0	0	0
1	20	1	0.80	0.80	0.20	100	0
1.5	35	1	0.65	0.65	0.30	89	11
3	60	1	0.40	0.40	0.53	88	12
5	70	1	0.30	0.30	0.63	90	10
6	75	1	0.25	0.25	0.68	90	10
30[e]	90	1	0.10	0.10	0.64	71	17

[a] Conditions: [camphene] = 0.10 mol l^{-1}, [$Pd(OAc)_2$] = 0.05 mol l^{-1}, 25 °C, solvent: CD_3COOD.
[b] Conversion of camphene.
[c] Deuteriated exclusively at position 8a.
[d] Deuteriated at positions 8a and 8b (described previously in [27]).
[e] Camphene-d_1 deuteriated at position 8b (2% of reacted camphene, signal from H-8a at 4.69 ppm) and diene **2** (10% of reacted camphene) are detected.

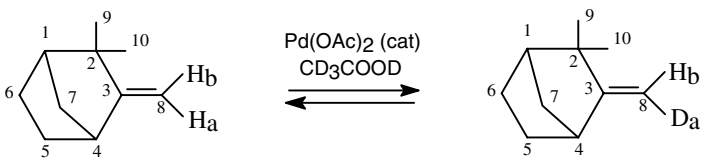
^{1}H NMR spectrum (at 4.48 ppm). This is assigned to H-8b of the deuteriated camphene (Table 1). The signal is shifted upfield from the unlabeled camphene by 0.02 ppm, which is consistent with an α-upfield shift (see below) due to deuterium also at C-8. For 6 h, the combined integral of the two very close signals at 4.48 and 4.50 ppm remains almost equal to the integral of the signal from H-4 (2.65 ppm) as well as to that from H-1 (1.90 ppm). Therefore, the signals at 4.48 and 4.50 ppm together correspond quantitatively to only one hydrogen in the camphene molecule, when both its unlabeled and deuteriated forms are taken into consideration. On the other hand, the relative intensity of the signal from the other vinylic hydrogen (4.71 ppm) decreases rapidly over 3 h, to 40% of the intensity of the signal from H-4 (Table 2). The percentage of the unlabeled camphene compared to all isotopomers was only 10% after 30 h of the reaction, as can be seen from the integrals of its H-8a and H-8b signals (Table 2).

Assignment of the signals from vinylic hydrogens H-8a and H-8b was carried out by NOE-difference experiments. A strong NOE between hydrogens of methyl group H-10 (s, 1.02 ppm) and the vinylic hydrogen H-8b (s, 4.50 ppm) is observed, but not between H-10 and H-8a (s, 4.71 ppm). Therefore, H-8b is spatially proximate to the methyl group, whereas H-8a is outward oriented (Scheme 2). Thus, deuterium is incorporated stereoselectively in the H-8a position of the camphene molecule, as shown in Scheme 2. Further evidence for the deuteriation of camphene came from inspection of the ^{13}C-NMR spectra. Splitting the three signals (from C-2, C-3 and C-4) and the rise of a new 1:1:1 triplet centered at 99.55 ppm were detected in the ^{13}C-NMR spectra of camphene in deuteriated acetic acid containing $Pd(OAc)_2$. The intensities of these four new signals increase with time, whereas the intensities of the original signals from the unlabeled camphene decrease. The triplet at 99.55 ppm with carbon–deuterium coupling constant of 24 Hz is assigned to the vinylic carbon C-8 of the monodeuteriated camphene. It is shifted upfield by 0.27 ppm from C-8 of the unlabeled camphene, which is consistent with an α-isotope shift (typically 0.25 ppm [23]). The singlet at 166.99 ppm, assigned to vinylic carbon C-3, is upfield from C-3 of the unlabeled camphene by 0.1 ppm, which is also in agreement with a β-upfield shift (typically 0.1 ppm [23]) caused by a single deuterium at C-8. The signals from both carbon atoms in γ-positions to C-8 are also shifted upfield by 0.03–0.06 ppm from the corresponding signals of the unlabeled camphene.

^{2}H NMR spectroscopy also indicates the incorporation of only one deuterium atom at position 8a. A signal from ^{2}H-8a appears at 4.75 ppm, downfield as expected from H-8a (4.71 ppm). Deuteriation of camphene takes place only in the presence of $Pd(OAc)_2$, with no palladium black formation being observed even at longer reaction times. The solutions of camphene in deuteriated acetic acid without $Pd(OAc)_2$were monitored by NMR for 30 h and no changes in the ^{1}H and ^{13}C-NMR spectra were detected.

Thus, the palladium catalyzed deuteriation of camphene occurs exclusively at vinylic carbon C-8. The outward oriented (more accessible) hydrogen is selectively exchanged resulting in 90% camphene-d_1 deuteriated exclusively at H-8a position and only about 10% camphene-d_2 deuteriated at both 8a and 8b positions (75% conversion of camphene, 6 h, 25 °C). At longer reaction times (20–30 h) a small but reproducible signal at 4.69 ppm, assigned to hydrogen H-8a in camphene-d_1 deuteriated at 8b position, can also be detected. About 10% of camphene is converted in diene **2** in 30 h under the conditions used. At higher temperatures, the reaction is faster and palladium metal precipitates in the absence of suitable reoxidants. Judging from the relative integrals of the signals from H-4 (at 3.09 and 3.08 ppm for two isomers of **2**) and from the vinylic hydrogens H-8 (at 5.73 and 5.71 ppm, using for **2** the same numbering as for camphene in Scheme 2), diene **2** formed from the camphene enriched in deuterium at 8a position in the solutions of deuteriated acetic acid has no significant percentage of the incorporated deuterium.

Neither π-allyl nor π-olefin palladium complexes are formed in detectable concentrations in the acetic acid solutions of $Pd(OAc)_2$. No changes in chemical shifts, widths and relative intensities of the NMR signals from camphene have been observed, except the decrease in the integrals of the signals from the vinylic hydrogens, discussed above. However, we have detected the formation of palladium hydride and deuteride intermediates. When the reaction is run in deuteriated acetic acid, ^{2}H NMR



camphene camphene-d_1

Scheme 2.

spectra show the resonance at −6.78 ppm assigned to the palladium deuteride, while in nondeuteriated acetic acid (containing 2% CD_3COOD), the palladium hydride appears as a singlet at −6.86 ppm in ^1H NMR spectra.

No deuteriation of other monoterpenes, such as limonene, myrcene and β-pinene, has been observed under the same conditions. All these alkenes have disubstituted terminal double bonds, however, as mentioned above, their palladium catalyzed oxidations involve the formation of π-allyl palladium complexes, with no products of oxidative coupling being detected at all.

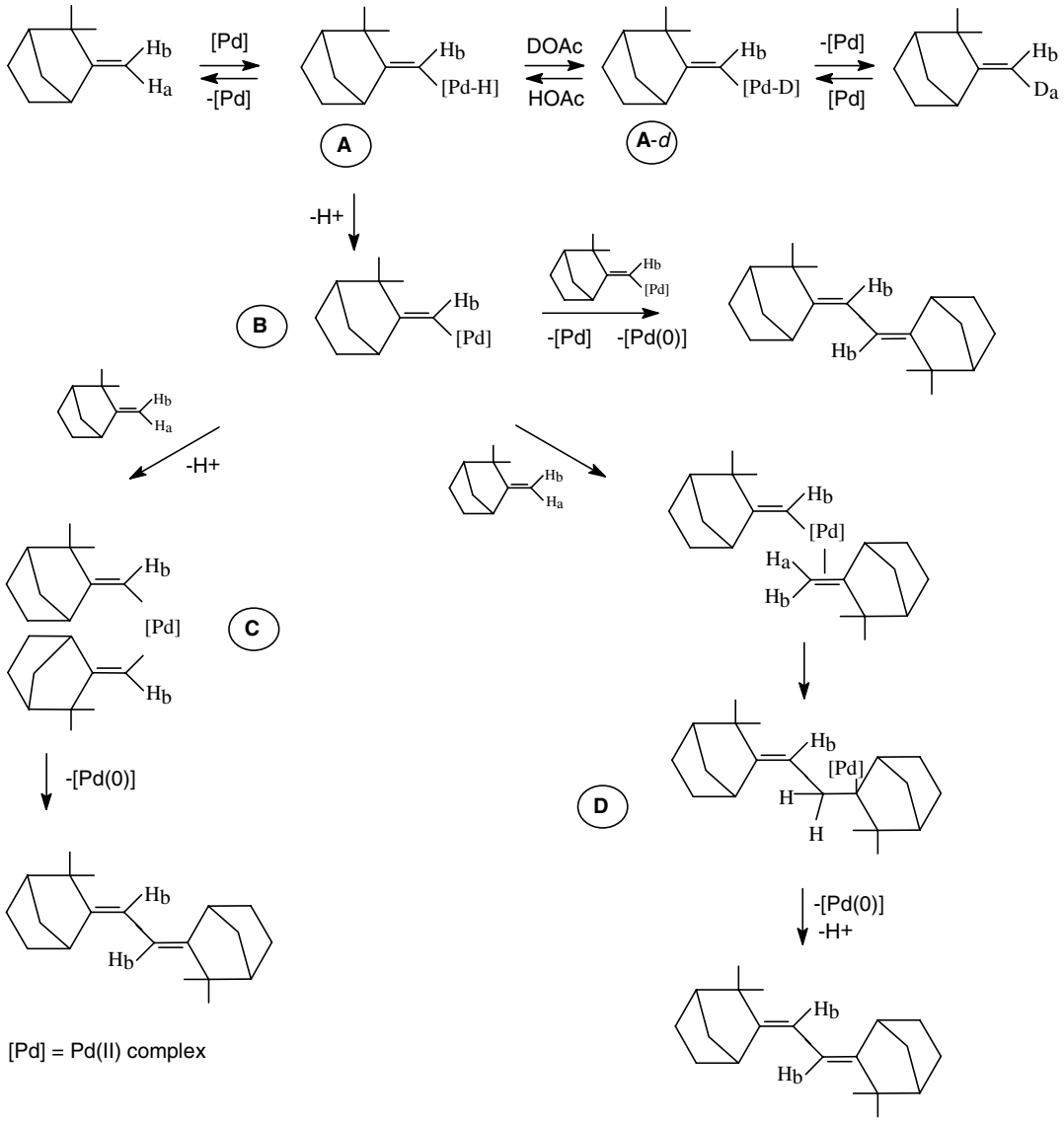
In previous work [10], we suggested a mechanism for palladium catalyzed oxidative coupling of camphene similar to that proposed in [17] for oxidative coupling of other alkenes. The formation of a π-olefin palladium complex was suggested followed by the Markovnikov type insertion of the coordinated camphene into a Pd–O bond resulting in a σ-organopalladium C_{10}-intermediate containing a [>C(X)–CH_2(Pd)] (X=NO_3^- or OAc^-) fragment. The latter then reacts with another molecule of camphene, which inserts into the Pd–C bond in an anti-Markovnikov fashion, giving a C_{20}-intermediate containing a [>C(X)–CH_2–CH_2–C(Pd)<] fragment. The stereochemistry of the final diene **2** [>C=CH–CH=C<] should be determined in the decomposition step of this palladium alkyl C_{20}-intermediate via a dehydropalladation (β-hydrogen abstraction). Usually either *cis* or *trans* alkene can be formed in such a step. To explain the selective formation of (*E, E*)-isomer of diene **2**, we had to suggest that a large steric hindrance of the two bulky isocamphane fragments makes both the PdH and the HX eliminations highly stereoselective. However, it should be mentioned that the elimination of HX from the intermediate [>C(X)–CH_2–CH_2–C(Pd)<] remains quite unusual.

Based on the analysis of the data obtained in the present work, we now assume that another mechanism, involving the formation of σ-vinyl palladium intermediates, is more likely to operate in the oxidative coupling of camphene. Both reactions occurring with camphene in acetic acid solutions in the presence of palladium (II) complexes, i.e., deuteriation and oxidative coupling, formally consist of the abstraction and nucleophilic substitution of the vinylic hydrogen. They each show very high stereoselectivities, with the outward oriented hydrogen almost exclusively abstracted from the camphene molecule. It seems reasonable to suggest that both transformations involve the formation of similar organopalladium intermediates. Deuteriation of camphene at C-8 cannot be explained within the framework of the mechanism proposed previously for the oxidative dimerization of camphene, where the metal alkyl bond is formed between the palladium and the α-carbon of the alkene. This deuteriation could only occur via the anti-Markovnikov deuteriopalladation of the olefinic bond (Pd–D addition) giving a [>C(Pd)–CH_2D] fragment followed by a dehydropalladation (Pd–H abstraction). However, a free palladium hydride/deuteride is very unlikely to exist in acetic acid under the conditions used. Moreover, a stereospecific substitution of only one vinylic hydrogen is not expected within this mechanism. Indeed, a newly formed methyl group in the [>C(Pd)–CH_2D] intermediate is free to rotate and on re-forming the double bond of camphene any hydrogen (deuterium) atom can be removed from this freely rotating methyl group giving a palladium hydride (deuteride) species. Successive deuterio(hydro)palladations/dehydro(deuterio)palladations would result in a non-selective incorporation of deuterium at C-8 position with the formation of camphene-d_1 and then, camphene-d_2.

The mechanism depicted in Scheme 3 seems to be more consistent with our results. A key intermediate is a σ-vinyl palladium compound **A**, probably formed by oxidative addition of camphene to the palladium (II) complex. The more accessible outward oriented H is replaced by PdH. The formal oxidation state of palladium in this complex is +4 and reductive elimination giving the σ-vinyl palladium (II) intermediate **B** and a proton (HOAc) would be expected. However, as described above, ^2H NMR in deuteriated acetic acid shows the formation of a palladium deuteride. We therefore posit the palladium hydride/deuteride intermediates **A** and **A**-*d* in Scheme 3, as the sources of these upfield resonances. They must be present in detectable concentrations during the reaction, with the intermediate palladium hydride **A** undergoing protium/deuterium exchange with the deuteriated acetic acid resulting in deuteride **A**-*d*. Decomposition of the latter by reductive elimination gives camphene-d_1 and regenerates the palladium (II) complex. It should be mentioned that palladium (IV) complexes resulted from the oxidative addition of organic halides to palladium (II) complexes have been isolated and characterized [24].

The $^1H/^2H$ exchange in intermediate **A** can be rationalized either as a conventional proton exchange with the labeled protic solvent, if the hydrogen in **A** shows an acidic character, or via the formation of a nonclassical hydrogen bond (''hydridic–protonic'' or ''dihydrogen'' bond), recently reviewed in [25], as shown in Scheme 4. Exchange of a hydridic hydrogen in a $[(PPh_3)_3PdH]^+$ complex with a proton from a solvent in aqueous solutions of CF_3COOH has been observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy [26].

Intermediate **B** can react further with another molecule of camphene resulting in the divinyl palladium (II) complex **C**, which undergoes intramolecular coupling of two vinylic ligands into diene **2** extruding Pd(0). An alternative for the diene **2** formation can be oxidative coupling of two vinyl palladium (II) complexes **B** releasing Pd(0) and Pd(II). The activation of the second molecule of camphene can also occur via its carbopalladation: a migratory insertion of the Pd(II)-π-



Scheme 3.

$$\text{Pd-H + DOAc} \rightleftharpoons \text{Pd-H} \cdots \text{DOAc} \rightleftharpoons \text{Pd-(HD)}^{+} \cdots \text{OAc}^{-} \rightleftharpoons \text{Pd-D} \cdots \text{HOAc} \rightleftharpoons \text{Pd-D + HOAc}$$

Scheme 4.

coordinated camphene into the σ-vinyl palladium complex giving intermediate **D**. Dehydropalladation of the latter re-forms the olefinic bond and releases Pd(0) and H^+. In such a step, it is again difficult to explain the selective elimination of only hydrogen H-8a, thus this route for the formation of diene **2** appears less probable. Since Pd(0) is ultimately produced along with camphene coupling product **2**, this reaction needs a suitable oxidant to regenerate Pd(II) for a catalytic cycle. Nitrate or nitrite ions as well as benzoquinone can be used for this purpose [10,12]. However, a conventional wacker catalyst, $PdCl_2/CuCl_2$, promotes acid-catalyzed skeletal rearrangements of camphene accompanied by the addition of acetic acid, to give nonoxidative products, mainly bornyl acetate [9].

4. Conclusions

$Pd(OAc)_2$ effectively catalyzes a highly regio and stereoselective deuteriation of camphene in deuteriated acetic acid solutions. The outward oriented vinylic hydrogen is substituted by deuterium resulting in 90% camphene-d_1 (ca. 100% stereoselectivity) and 10% camphene-d_2 at 75% conversion of camphene (6 h, 25 °C). This stereospecific isotopic labeling could be a

useful method in the synthesis of the labeled substrate for mechanistic and kinetic studies. Neither π-allyl nor π-olefin palladium complexes are formed in detectable concentrations during the reaction, whereas palladium hydride and deuteride intermediates have been observed in the reaction solutions. Similar mechanisms for the deuteriation and oxidative coupling of camphene, both palladium (II) catalyzed, have been proposed, which involve the formation of σ-vinyl palladium hydride intermediates.

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