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Stoichiometric and catalytic hydroxy-palladation of conjugated dienes

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Abstract

Palladium-catalyzed oxidation of 4-methyl- and 2,4-dimethyl-1,3-pentadiene under chloroacetoxylation conditions in the presence of small amounts of water gave (*E*)-1-chloro-4-methyl-2-penten-4-ol (**3a**) and (*E*)- and (*Z*)-1-chloro-2,4-dimethyl-2-penten-4-ol (**3b**), respectively. The analogous oxidation of 2,5-dimethyl-2,4-hexadiene gave 3-acetoxy-2,5-dimethyl-4-hexen-2-ol (**5**) as the main product. These catalytic reactions proceed via an initial hydroxypalladation where water attacks the most substituted terminus of the diene. It was demonstrated in stoichiometric reactions that conjugated dienes readily can be hydroxypalladated. Nine different acyclic dienes reacted with $PdCl_2(CH_3CN)_2$ in aqueous acetone in the presence of $KHCO_3$ and gave in each case stable 4-hydroxy-η^3-allyl complexes, which were isolated in high yields and characterized.

It is well known that palladium has the ability to activate olefins and dienes for nucleophilic addition [1]. In case of conjugated dienes it is possible to add two nucleophiles in a catalytic process by using a suitable oxidant. We have recently been concerned with a catalytic system consisting of a palladium(II) salt with *p*-benzoquinone as the oxidant and the reactions are performed in acetic acid. This system transforms 1,3-dienes in a stereo- and regio-selective fashion to the corresponding 1-acetoxy-4-substituted-2-alkenes. The substituent (X^-) in the 4-position of the product can be varied just by adding the corresponding lithium salt (LiX). This principle has so far been applied to three different 1,4-functionalizations and the products are the result of either an acetoxychlorination [2], a diacetoxylation [3], or an acetoxytrifluoro-acetoxylation [4] of the 1,3-diene (eq. 1). The reactions

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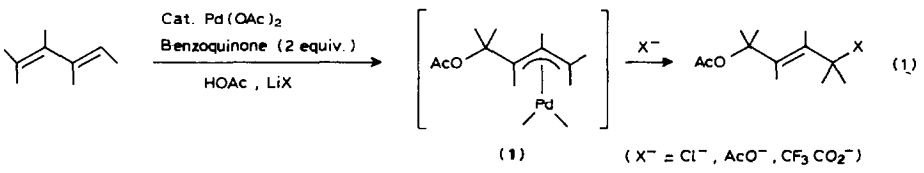
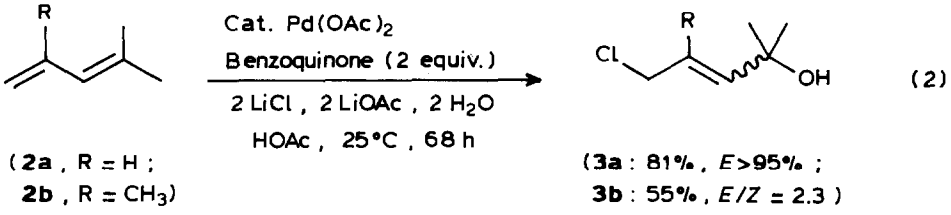
probably proceed via a common intermediate, a 4-acetoxy-π-allylpalladium complex **1**.



During our studies of the acetoxychlorination reaction [2] we unexpectedly observed addition of water instead of acetate when dienes lacking hydrogens at one of the termini were oxidized. We now would like to report a palladium catalyzed nucleophilic addition to conjugated dienes which involves a regioselective hydroxypalladation in the first step and also a general synthesis of bis(4-hydroxy-π-allylpalladium chloride) complexes.

Results and discussion

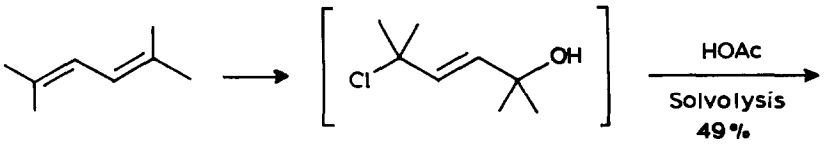
When 4-methyl-1,3-pentadiene (**2a**) was allowed to react under normal acetoxychlorination conditions we isolated, instead of the expected acetoxy-chloro adduct, the chloroalcohol **3a** in 61% yield [5*]. The olefin geometry was exclusively of *E* configuration (> 95%) judged by the olefinic coupling constant (*J* 15.4 Hz) in the ^{1}H NMR spectrum. 2,4-Dimethyl-1,3-pentadiene (**2b**) reacted in an analogous way and the chloroalcohol **3b** was isolated in 55% yield but in this case as a 2.3/1 mixture of *E* and *Z* isomers (eq. 2).



The assignment of configuration of the tri-substituted double bond in *E*- and *Z*-**3b** respectively, is based on the fact that ^4J(H,H) allylic coupling constants usually are larger for protons in a cisoid versus a transoid relationship [6]. Furthermore, the ^{13}C chemical shifts for the vinylic methyl group in *E*- and *Z*-**3b** are 14.93 and 22.65 ppm respectively. This supports the assignment made since methyl groups on tri-substituted double bonds are shifted to higher field for the *E*-isomers [7]. The even more sterically hindered 2,5-dimethyl-2,4-hexadiene underwent a palladium-catalyzed nucleophilic addition but in this case the acetoxyalcohol **5** was formed together with the dienylacetate **6** in 49% isolated yield (eq. 3).

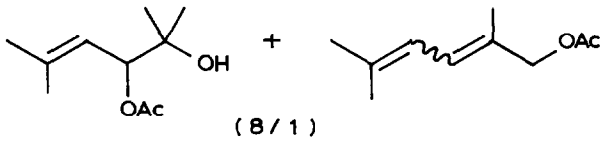
The results presented above demonstrated a chemoselectivity in the formation of the intermediate π-allylpalladium complex. Despite the fact that the molar ratio between acetic acid and water (water is present due to the use of $LiOAc \cdot 2H_2O$) is 17/1 under the reaction conditions used, water is selectively added to the most

* This and other references marked with asterisks indicate notes occurring in the list of references.



(4)

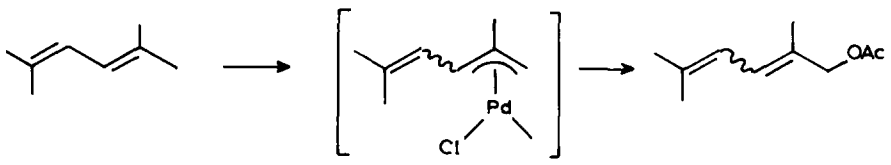
(3)



(8 / 1)

(5) (6: E/Z = 2.7/1)

substituted terminus of the diene, suggesting that mesomer **7b** is a significant contributor to the intermediate cationic dienepalladium complex **7**, Scheme 1. The π-allylcomplex **8** thus formed would then be attacked by a chloride at C(1) remote from the hydroxy group and the chloroalcohol is formed. In the case of 2,5-dimethyl-2,4-hexadiene the anticipated chloroalcohol **4** was not detected since the tertiary and allylic chloro group in **4** most likely will be rapidly displaced solvolytically and the isolated acetoxyalcohol **5** is formed [8*]. The formation of **6** is probably the result of a nucleophilic attack on the π-allyl complex **9** (eq. 4) [9*].

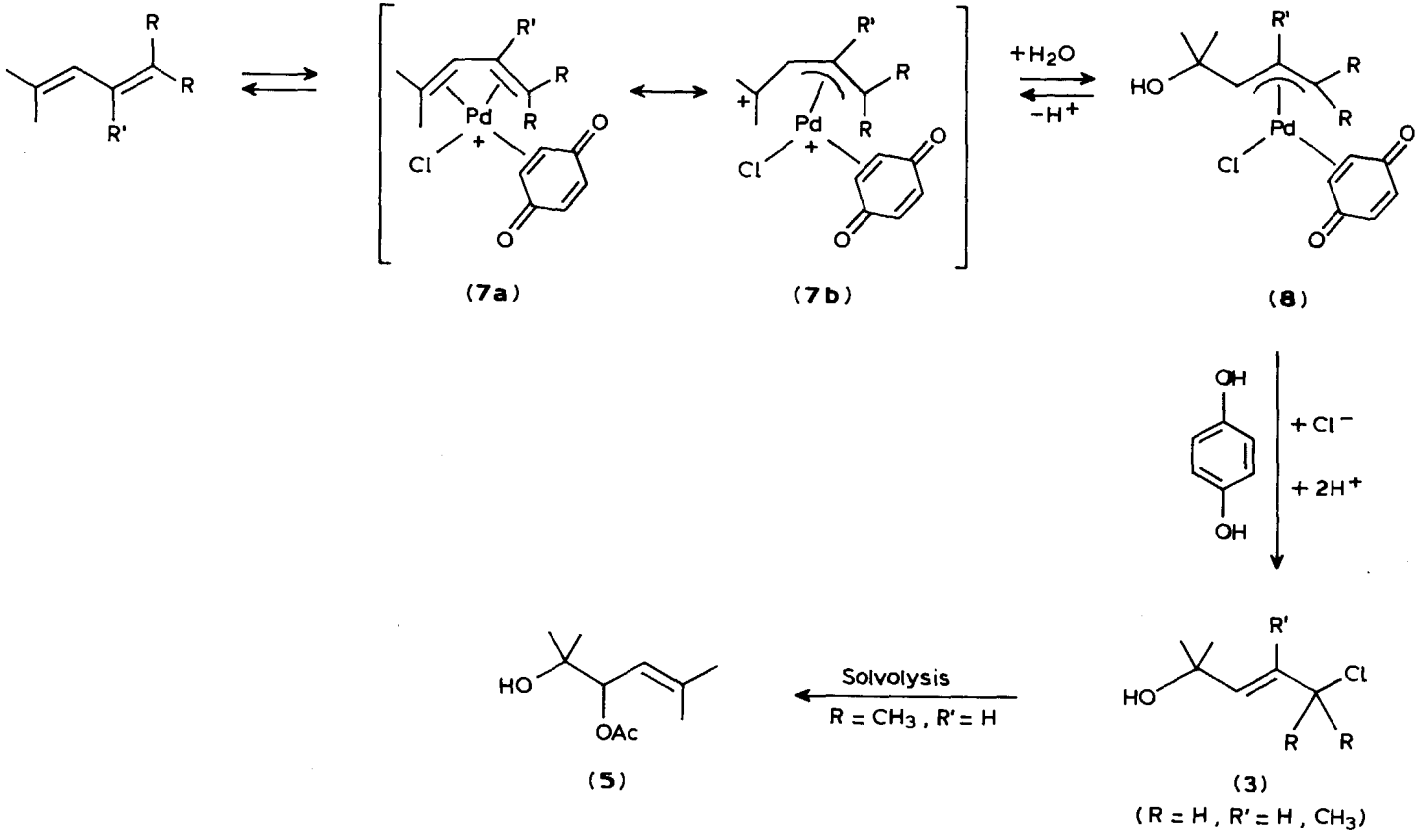


(4)

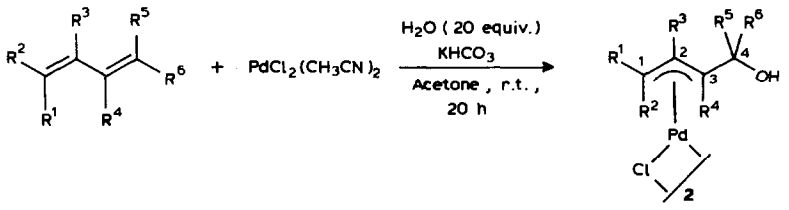
(9) (6: E/Z = 2.7/1)

The special selectivity for adding two nucleophiles sequentially to a diene can be rationalized as follows. The overall process can be divided into two separate steps: a reversible formation of the intermediate π-allyl complex **8** and an irreversible nucleophilic attack on **8** to form the products. The first step operates with a carbonium ion-like behavior and a relative stable carbo-cation **7** is formed reversible. This accounts for the regioselectivity observed. There are three different nucleophiles (Cl^-, OAc^-, H_2O) in the solution that may attack **7**. Since this attack is a reversible process [2] the result will be that the most thermodynamically stable complex is formed. This explains why the hydroxy-π-allylpalladium complex **8** is favored [10]. The second step, a nucleophilic attack on a π-allyl ligand, is reminiscent of an S_N2 reaction and the best nucleophile, in this case a chloride, will displace palladium.

These ideas are strongly supported by the results from stoichiometric addition of water to a series of 1,3-dienes. This type of reaction, where nucleophilic attack on 1,3-dienes is promoted by palladium is well known [11] but there are only a few examples where water has been used as nucleophile [12]. We have now found that very efficient addition of water may be obtained by reacting 1,3-dienes with


R
R
R'
Pd
Cl
+
O
O
(7a)
(7b)
+H2O
-H+
HO
(8)
OH
OH
+Cl−
+2H+
(3)
(R = H, R' = H, CH3)
Cl
Solvolysis
R = CH3, R' = H
OAc
(5)

Scheme 1



(5)

bis(acetonitrile)palladium dichloride at 25°C and water (ca. 20 equiv.) in acetone containing solid $KHCO_3$ [13*].

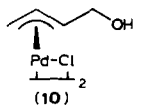
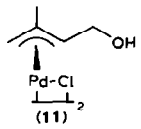
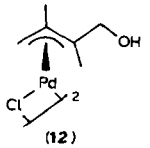
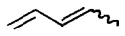
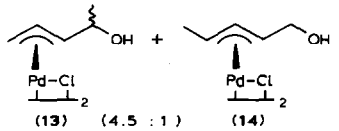
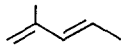
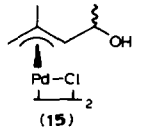
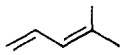
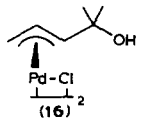
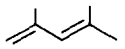
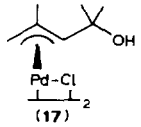
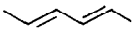
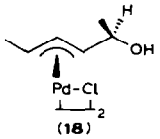
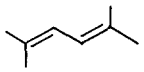
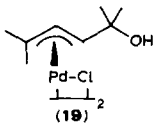
The products are stable η^3-allyl complexes (eq. 5) which are easily purified by chromatography. The results are summarized in Table 1. All acyclic dienes tried, gave good to excellent yields of η^3-allyl complexes but 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene all failed under these conditions, precipitation of palladium(0) and presumably oxidation being serious problems.

The stoichiometric reactions of 4-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and 2,5-dimethyl-2,4-hexadiene show that addition of water to form a tertiary alcohol is indeed very efficient (entries 6, 7, and 9) and the respective η^3-allyl complexes **16**, **17**, and **19** are formed in high yields. The exclusive formation of **16** and **17** (entry 6 and 7) also supports the idea of carbonium ion character at C(4), which completely overcomes any steric effects. This dominance of electronic factors appears to be generated and also unsymmetric dienes with one monosubstituted terminus react preferentially at this position rather than at the unsubstituted terminus. This is demonstrated by the reaction of 1,3-pentadiene (entry 4) which gives a product mixture that contains about 80% **13a** and **13b** from attack at the more substituted terminus and only 20% of the linear isomer **14**. 2-Methyl-1,3-pentadiene (entry 5) shows an even higher preference for reaction at the more substituted position and in this case **15a** and **15b** are the major products together with trace amounts of the regio isomer from reaction at the less substituted terminus. In part this preference for reaction at the more substituted terminus is due to the fact that there is also a preference for formation of 2-methyl-substituted η^3-allyl complexes. This is demonstrated by the reaction of isoprene which gives complex **11** as the major product together with smaller amounts of the regioisomeric complex. The major directing effect for addition of water, however, appears to be the preference for reaction at the most substituted terminus of the 1,3-diene.

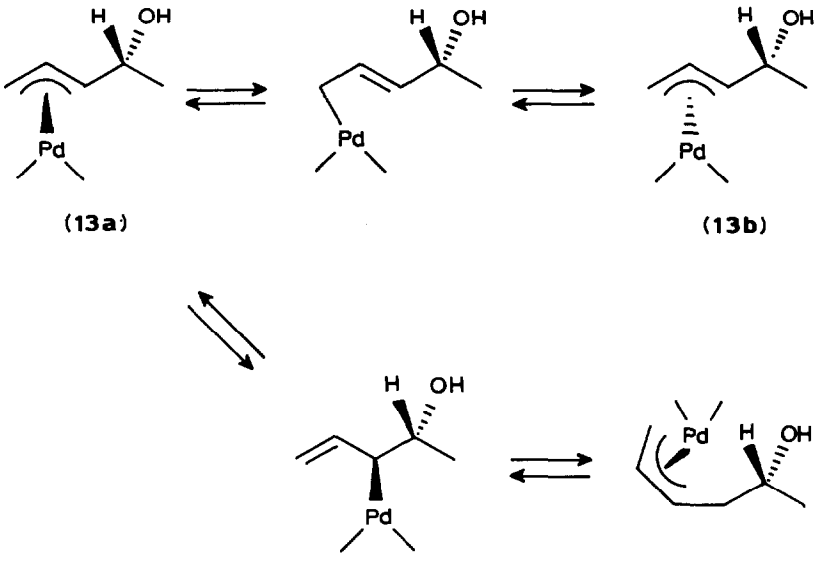
The isomeric pairs **13a**, **13b** and **15a**, **15b** were initially thought to be *syn-anti* isomers. However, the ^1H NMR data for **13a** and **13b**, especially the large coupling constant between H(2) and H(3), 11 and 10.5 Hz, clearly show that both have a *syn*-configuration. As a consequence, they must be diastereoisomers. Also **15a** and **15b** are probably diastereoisomers as suggested by their very similar ^{13}C NMR spectra, particularly the fact that both C(4) shifts are ca. 66 ppm, very close to the values for C(4) of **13a** and **13b** (68 and 66 ppm). An earlier study of the geranyl-neryl system shows an *anti*-carbon at C(3) is shifted to 3–5 ppm higher field than the corresponding *syn*-carbon [14].

The diastereoisomers **13a** and **13b** are formed in about equal amounts from either *E*- or *Z*-pentadiene, while the ratio between **15a** and **15b** is about 3.5/1. In contrast, (*E*,*E*)-2,4-hexadiene (entry 8) gave only one diastereomer, probably **18** from stereospecific *trans* addition of water and palladium [15]. The most reasonable

Table 1. Hydroxypalladation of conjugated dienes [a]

Entry	Diene	Reaction time (h)	Product	Yield[b]
1		29	 (10)	87[c]
2		26	 (11)	92[d]
3		15.5	 (12)	90
4	 E or Z	24.5	 (13) (4.5 : 1) (14)	88[e]
5		26	 (15)	92[f]
6		26	 (16)	95
7		18	 (17)	87
8		20.5	 (18)	99 (88)[g]
9		26	 (19)	99

[a] Unless otherwise stated, the reactions were performed under the following conditions: diene (1 mmol), bis(acetonitrile)palladium dichloride (1.25 mmol), water (20 mmol), and $KHCO_3$ (1.25 mmol) in acetone at 20 °C. [b] All yields refer to pure compounds isolated by column chromatography. [c] Butadiene (20 mmol) was used. [d] Isoprene (2 mmol) was used and the product was contaminated with 12% of 4-hydroxy-3-methyl-2-butenylpalladium chloride. [e] Complex **13** is a 1/1 mixture of two diastereomers **13a** and **13b** and the product was also contaminated with complex **14** (18%). [f] Complex **15** is a (3.5/1) mixture of two diastereomers **15a** and **15b**. [g] Bis(acetonitrile)palladium dichloride (1.00 mmol) was used.



Scheme 2

explanation is that the initial diastereomer **13a** (and **15a**) is isomerized via an η^3-η^1 equilibrium involving the unsubstituted σ-allyl terminus as depicted in Scheme 2. In contrast, the equilibrium involving the more substituted σ-allyl terminus is slow (as shown for the neryl-geranyl system) [14] and thermodynamically disfavored since it would lead to a less stable *anti* configuration. For complex **18**, in which both η^3-allyl termina are substituted, the isomerization pathway depicted in Scheme 2 would lead to less stable *anti*-isomer. This explains why only one diastereomer **18** is formed.

Conclusions

Conjugated dienes which have a fully substituted terminus undergo a regioselective palladium(II)-catalyzed 1,4-addition of H_2O and Cl^- to give tertiary alcohols. The mechanism involves a thermodynamically controlled formation of a 4-hydroxy-π-allylpalladium complex followed by a kinetic S_N2-type displacement of palladium by chloride. The mechanism is supported by the preparation of dimeric 4-hydroxy-π-allylpalladium chloride complexes from the reaction of dienes (9 different) with $PdCl_2$ in aqueous acetone.

Experimental

Infrared spectra (IR) were recorded on a Perkin–Elmer 420 spectrometer. NMR spectra were obtained with a Bruker WP 200 MHz or a Bruker AM 400 MHz spectrometer. Chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS) for ^1H spectra and relative to internal $CDCl_3$ (77.00 ppm) for ^{13}C spectra. ^{13}C multiplicities were obtained by proton off resonance decoupling. High pressure liquid chromatography (HPLC) was performed on a Waters M-45 instru-

ment with a microporasil column (silica, 10 μm packing, 0.4 × 30 cm) and a differential refractometer as detector. Bulb-to-bulb distillations were performed with a Büchi Kugelrohr apparatus. Flash chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck). 1,3-Butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, (*E*)-1,3-pentadiene, (*Z*)-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, (*E,E*)-2,4-hexadiene, and 2,5-dimethyl-2,4-hexadiene were purchased from Aldrich Chemicals. Lithium acetate dihydrate, lithium chloride, *p*-benzoquinone were from Kebo AB.

(E)-1-Chloro-4-methyl-2-penten-4-ol (3a). $Pd(OAc)_2$ (76 mg, 0.3 mmol), LiCl (336 mg, 8 mmol), $LiOAc \cdot 2H_2O$ (816 mg, 8 mmol), and *p*-benzoquinone (864 mg, 8 mmol) were dissolved in HOAc (16 ml) at 25 °C. Pentane (20 ml) and 4-methyl-1,3-pentadiene (328 mg, 4 mmol) were added and the biphasic reaction mixture was stirred at a moderate rate at 25 °C for 68 h. Brine (16 ml) was added and after 5 minutes of additional stirring the pentane phase was collected and the aqueous phase was extracted with ether/pentane (3 × 50 ml, 1/1). The combined organic phases were washed successively with water (2 × 10 ml), aqueous K_2CO_3 (20 ml, saturated), 2 *M* NaOH (10 ml), and then stirred over 2 *M* NaOH (10 ml, saturated with $NaBH_4$) for 15 minutes. The organic phase was collected, dried ($MgSO_4$), concentrated, and bulb-to-bulb distillation (120 °C, 1 mmHg) gave 329 mg (61%) of **3a** (> 95% *E*) as a colorless liquid which was contaminated with *O*-acetyl-**3a** (8%) according to ^1H NMR. **3a**: ^1H NMR (200 MHz): 5.91 (d, $J_{2,3}$ 15.36 Hz, 1H, H(3)), 5.83 (dt, $J_{2,3}$ 15.36 and $J_{1,2}$ 6 Hz, 1H, H(2)), 4.66 (d, $J_{1,2}$ 5.8 Hz, 2H, H1), 1.5 (s, 1H, OH), 1.34 (s, 6H, H(5) and H(6)); ^{13}C NMR (50.3 *M* Hz) 142.4 (d), 122.8 (d), 70.48 (s, C(4), 44.72 (t, C(1)), 29.51 (q, C(5) and C(6)) ppm; IR (neat, NaCl): 3490 (s), 2970, 1370, 1250, 1140, 970 cm^{-1}; HPLC, $V_r/V_o = 4.2$ (EtOAc/hexane = 12/88). Anal. Found (For **3a** isolated by prep HPLC): C, 53.53; H, 8.31. $C_6H_{11}ClO$ calcd.: C, 53.54; H, 8.24%.

(E)- and (Z)-1-Chloro-2,4-dimethyl-2-penten-4-ol (3b). The procedure for preparation of **3a** was followed but 2,4-dimethyl-1,3-pentadiene (440 mg, 4 mmol), $Pd(OAc)_2$ (90 mg, 0.4 mmol), and pentane (50 ml) were used. Workup and concentration gave 432 mg of a crude product which according to ^1H NMR and HPLC consists of (*E*)- and (*Z*)-**3b** (76%, $E/Z = 2.3$), *O*-acetyl-**3b** (19%, $E/Z = 14$), and 5,5,7-trimethyl-5,8-dihydro-1,4-dihydroxy-naphthalene (**20**) (5%). For analytical purposes (*E*)-**3b**, (*Z*)-**3b**, *O*-acetyl-**3b**, and **20** were separated by preparative HPLC.

E-**3b**: HPLC, $V_r/V_o = 5.0$ (EtOAc/hexane = 10/90); ^1H NMR (200 MHz) 5.67 (tq, $J_{3,6}$ 1.32 and $J_{1,3}$ 0.91 Hz, 1H, H(3)), 3.96 (d, $J_{1,3}$ 0.91 Hz, 2H, H(1), 1.98 (d, $J_{3,6}$ 1.32 Hz, 3H, H(6)), 1.5 (s, 1H, OH), 1.38 (s, 6H, H5 and H(7)) ppm; ^{13}C NMR (100.6 MHz) 137.09 (C(3)), 133.25 (C(2)), 70.84 (C(4)), 53.22 (C(1)), 30.77 (C(5) and C(7)), 14.93 (C(6)) ppm.

Z-**3b**: HPLC, $V_r/V_o = 3.0$ (EtOAc/hexane = 10/90); ^1H NMR (200 MHz) 5.47 (q, $J_{3,6}$ 1.46 Hz, 1H, H(3)), 4.47 (s, $W_{0.5}$ 0.6 Hz, 2H, H(1)), 1.82 (d, $J_{1,3}$ 1.46 Hz, 3H, H(6)),1.5 (s, 1H, OH), 1.37 (s, 6H, H(5) and H(7)) ppm; ^{13}C NMR (100.6 MHz) 137.16 (C(3)), 133.13 (C(2)), 71.37 (C(4)), 43.79 (C(1)), 31.61 (C(5) and C(7)), 22.65 (C(6)) ppm.

(*E*)-*O*-acetyl-**3b**: HPLC, $V_r/V_o = 1.6$ (EtOAc/hexane = 10/90); ^1H NMR (200 MHz, in mixture with the *Z* isomer) 5.74 (tq, $J_{1,3}$ 0.8 and $J_{3,6}$ 1.3 Hz, 1H, H(3)), 3.96 (d, $J_{1,3}$ 0.8 Hz, 2H, H(1)), 2.00 (s, 3H, OAc), 1.84 (d, $J_{3,6}$ 1.3 Hz, 3H, H(6)), 1.54 (s, 6H, H5 and H7) ppm.

(*Z*)-*O*-acetyl-**3b**: HPLC, $V_r/V_o = 1.6$ (EtOAc/hexane = 10/90); ^{1}H NMR (200 MHz, in mixture with the *E* isomer) 5.60 (q, $J_{3,6}$ 1.5 Hz, 1H, H(3)), 4.20 (s, $W_{0,5}$ 0.8 Hz, 2H, H(1)), 2.04 (s, 4H, OAc), 1.82 (d, $J_{3,6}$ 1.5 Hz, 3H, H(6)), 1.55 (s, 6H, H(5) and H(7)).

20: HPLC, $V_r/V_o = 8.1$ (EtOAc/hexane = 10/90); ^{1}H NMR (200 MHz, in mixture with **3b** and *O*-acetyl-**3b**) 6.5–6.4 (AB-spectrum, J_{AB} 8.5 Hz, δ_A 6.51 and δ_B 6.45, 2H, H(2) and H(3)), 5.24 (bs, 1H, H(6)), 4.9 (bs, 2H, OH), 3.10 (bs, 2H, H(8)), 1.81 (bs, 3H, vinylic Me), 1.43 (s, 6H, Me(2)) ppm. IR (neat, NaCl, crude product): 3400(s), 2980, 2930, 2870, 1450, 1370, 1270, 1240, 1150, 690 cm^{-1}. Anal. Found (for *E*-**3b**): C, 56.42; H, 8.66. $C_7H_{13}ClO$ calcd.: C, 56.57; H, 8.82%.

3-Acetoxy-2,5-dimethyl-4-hexen-2-ol (5). The procedure for preparation of **3a** was followed but 2,5-dimethyl-2,4-hexadiene (440 mg, 4 mmol) was used and H_2O (1.1 ml, 60 mmol) was added to the reaction mixture. Workup, concentration and bulb-to-bulb distillation (150 °C, 1 mmHg) gave 363 mg (49%) of **5** as a colorless liquid contaminated with 1-acetoxy-2,5-dimethyl-2,4-hexadiene (**6**) (13%, $E/Z = 2.7$) according to ^{1}H NMR. For analytical purposes **5** and **6** were separated by preparative HPLC.

5: HPLC, $V_r/V_o = 7.5$ (EtOAc/hexane = 12/88): ^{1}H NMR (200 MHz) 5.35 (d, $J_{3,4}$ 9.70 Hz, 1H, H(3)), 5.20 (dsept, $J_{3,4}$ 9.70 and J_4(allylic) 1.4 Hz, 1H, H(4)), 2.08 (s, 3H, OAc), 1.78 and 1.77 (two d, J_4 (allylic) 1.4 Hz, 6H, vinylic CH_3's), 1.8 (bs, 1H, OH), 1.20 and 1.19 (two s, 6H, Me_2) ppm; ^{13}C NMR (50.3 MHz) 170.4 (s, CH_3COO), 139.8 (s, C(5)), 119.6 (d, C(4)), 77.35 (d, C(3)), 72.61 (s, C(2)), 26.23 (q), 26.05 (q), 21.23 (q), 18.69 (q) ppm.

E- and *Z*-**6**; ^{1}H NMR (200 MHz): 6.3–5.95 (AB-spectrum, J_{AB} 11 Hz, 2H, H(3) and H(4)), 4.53 (s, 2H, H1 in *E*-**6**), 2.07 (s, 3H, OAc); 1.83 (s, 3H, H(7)) 1.77 (s, 6H, H(6) and H(8)) ppm; IR (neat **5**, NaCl); 3420, 2970, 2920, 1720, 1440, 1370, 1250, 1020, 960 cm^{-1}. Anal. Found (for **5**): C, 64.32; H, 9.69. $C_8H_{18}O_3$ calcd.: C, 64.49; H, 9.74%.

Di-μ-chlorobis[(1,2,3)-4-hydroxy-2-buten-1-yl]dipalladium (10) [12a]. Butadiene (1.27 g, 24 mmol) was added from syringe at 0 °C to a yellow slurry of bis(acetonitrile)palladium dichloride (259 mg, 1.00 mmol) and potassium bicarbonate (120 mg, 1.20 mmol) in acetone (10 ml). A yellow-orange solution was formed which was reacted at 20 °C with water (360 μl, 20.0 mmol). After 28 h at 20 °C, the precipitate which had formed mainly potassium chloride, was removed by filtration through celite, which was then washed with ethyl acetate (50 ml). The combined solutions were concentrated at water-aspirator pressure and the residue was flash chromatographed on a 13 × 2.5 cm column, using ethyl acetate ethanol 9/1 as eluant. After removal of the solvent, **10** was obtained as yellow crystals (186 mg, 87%): m.p. ca. 53 °C (decomp.) ^{1}H NMR (200 MHz) 5.60 (ddd, $J_{1\text{-}anti,2}$ 12.1, $J_{2,3}$ 11.0 and $J_{1\text{-}syn,2}$ 6.9 Hz, 1H, H(2)), 4.06 (d, $J_{1\text{-}syn,2}$ 6.7 Hz, 1H, H1-*syn*), 3.97 (dt, $J_{2,4}$ 11.0 and $J_{3,4}$ 4.0 Hz, 1H, H(3)), 3.80 (ddd, J_{gem} 15.0, $J_{4,OH}$ 6.0 and $J_{3,4}$ 3.2 Hz, 1H, one of CH_2O), 3.57 (ddd, J_{gem} 15.0, $J_{4,OH}$ 7.3 and $J_{3,4}$ 4.5 Hz, 1H, one of CH_2O), 3.00 (d, $J_{1\text{-}anti,2}$ 12.1 Hz, 1H, H1-*anti*), 2.09 (bt, $J_{3,5} \approx J_{3,4}$ 6–7 Hz, 1H, exchangeable with D_2O, OH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): 115.21 (d, C(2)), 89.57 (d, C(3)), 64.26 (t, C(1)), 60.18 (t, C(4)); IR (KBr): 3330, 3230, 2910, 2850, 1440, 1365, 1285, 1230, 1095, 1000, 975, 950, 870, 855, 665 cm^{-1}. Anal. Found: C, 22.85; H, 3.44. C_4H_7ClOPd calcd.: C, 22.56; H, 3.31%.

Di-μ-chlorobis[(2,3,4-)-5-hydroxy-3-hexen-2-yl]dipalladium (18) [13]. To a yellow

slurry of bis(acetonitrile)palladium dichloride (325 mg, 1.25 mmol) and potassium bicarbonate (120 mg, 1.20 mmol) in acetone (10 ml), at 20 °C, was added a solution of (*E,E*)-2,4-hexadiene (82 mg, 1.00 mmol) and H_2O (360 μl, 20.0 mmol) in acetone (6 ml). A red-brown solution with a white precipitate was formed within seconds. The reaction mixture was stirred for 20.5 h at 20 °C and then filtered through a Celite pad and the pad was washed with EtOAc (50 ml). The filtrate was concentrated at water-aspiratory pressure to afford 391 mg of a red-brown oil. The oil was immediately taken up in a few ml of EtOAc and flash chromatographed on a 15 × 2.5 cm column eluated with EtOAc to yield 238 mg (0.99 mmol, 99%) of **18** [11b] as yellow crystals; m.p. > 96 °C, ^{1}H NMR (200 MHz): 5.47 (t, $J_{2,3} = J_{3,4} = 11.0$ Hz, 1H, H(3)), 4.01 (m, $W_{0.5}$ 17 Hz, 1H, H(5)), 3.90 (dq, $J_{2,3}$ 11.3 and $J_{1,2}$ 6.2 Hz, 1H, H(2)), 3.82 (dd, $J_{3,4}$ 10.9 and $J_{4,5}$ 3.0 Hz, 1H, H(4)), 2.48 (d, $J_{OH,5} = 4.2$ Hz. exchangeable with D_2O, 1H, OH), 1.38 and 1.34 (two d, J 6.4 Hz, 6H, H(1) and H(6)) ppm; ^{13}C NMR (50 MHz); 107.54 (d, C(3)), 86.84 (d, C(4)), 79.41 (d, C(2)), 66.12 (d, C(5)), 21.77 (q), 18.04 (q) ppm, IR (KBr): 3360, 3320, 2975, 2930, 2875, 1405, 1390, 1375, 1270, 1150, 1060, 1030, 990, 935, 840 cm^{-1}. Anal. Found: C, 30.04; H, 4.54. $C_6H_{11}ClOPd$ calcd.: C, 29.90; H, 4.60%.

The following complexes were prepared by the same procedure: *Di-μ-chlorobis[(1,2,3-η)-4-hydroxy-2-methyl-2-buten-1-yl]dipalladium (11)* was prepared from isoprene and isolated in 91% yield. The product from flash chromatography was contaminated with about 10% of *syn* and *anti* forms of the regioisomer. Pure **11** was obtained by preparative HPLC: ^{1}H NMR (200 MHz), 3.85 (s, 1H, H(1-*syn*)), 3.82–3.66 (m, 3H, H(3) and H(4)), 2.87 (s, 1H, H(1-*anti*)), 2.30 (br s, $W_{0.5}$ 15 Hz, 1H, exchangeable with D_2O, OH), 2.16 (s, 3H, CH_3) ppm; ^{13}C NMR (50 MHz): 124.91 (s, C(2)), 81.85 (d, C(3)), 62.11 (dd, C(1)), 60.75 (t, C(4)), 18.61 (q, CH_3) ppm.

Di-μ-chlorobis[(1,2,3-η)-2,3-dimethyl-4-hydroxy-2-buten-1-yl]dipalladium(12) was prepared from 2,3-dimethyl-1,3-butadiene and 90% of pure **12** was obtained after flash chromatography; M.p. 42–48 °C; ^{1}H NMR (200 MHz): 3.89 (d, J_{gem} 1.5 Hz, 1H, H(1-*syn*)), 3.47 (dd, J_{gem} 12.3 and $J_{4,OH}$ 2.5 Hz, 1H, one of CH_2OH), 3.32 (d, J_{gem} 1.5 Hz, 1H, H(1-*anti*)), 3.19 (dd, J_{gem} 12.3 and $J_{4,OH}$ 8 Hz, 1H, one of CH_2OH), 2.61 (dd, $J_{4,OH}$ 3 and $J_{4,OH}$ 8 Hz, 1H, OH), 2.15 (s, 3H, CH_3 – C(2)), 1.47 (s, 3H, CH_3 – C(3)) ppm; ^{13}C NMR (50 MHz): 121.35 (s, C(2)), 92.53 (s, C(3)), 70.96 (t, C(1)), 59.90 (t, C(4)), 20.65 (q), 19.64 (q) ppm; IR (KBr): 3400, 2960, 2900, 1450, 1430, 1240, 1025, 990, 885, 735, 715 cm^{-1}. Anal. Found: C, 29.86; H, 4.52. $C_6H_{11}ClOPd$ calcd.: C, 29.90; H, 4.60%.

A mixture of di-μ-chlorobis[(1,2,3-η)-4-hydroxy-2-penten-1-yl]dipalladium (13) and di-μ-chlorobis(2,3,4-η)-4-hydroxy-3-penten-2-yl]dipalladium (14) was obtained from (*E*)-1,3-pentadiene or (*Z*)-1,3-pentadiene. The total yield after flash chromatography was 88% which consisted of **13** (82%) and **14** (18%). For analytical purposes **13** and **14** were separated by preparative HPLC. The regioisomer **13** is a 1/1 mixture of diastereomers **13a** and **13b**.

13a: ^{1}H NMR (200 MHz, assigned in mixture with **13b**) 5.44 (ddd, $J_{2,1\text{-}anti}$ 12.0, $J_{2,3}$ 10.5, and $J_{2,1\text{-}syn}$ 6.8 Hz, 1H, H(2)), 4.05 (d, $J_{2,1\text{-}syn}$ 6.8 Hz, 1H, H(1-*syn*)), 3.96–3.80 (m, 2H, H(3) and H(4)), 2.99 (d, $J_{2,1\text{-}anti}$ 12.0 Hz, 1H, H(1-*anti*)), 2.62 (bd, $J_{4,OH} = 3$ Hz, 1H, exchangeable with D_2O, OH), 1.39 (d, $J_{4,5}$ 6.4 Hz, 3 H, H(5)).

13b: ^{1}H NMR (200 MHz, assigned in mixture with **13a**) 5.62 (ddd, $J_{2,1\text{-}anti}$ 12.2,

$J_{2,3}$ 10.3, and $J_{2,1\text{-}syn}$ 6.9 Hz, 1H, H(2)), 4.05 (d, $J_{2,1\text{-}syn}$ 6.9 Hz, 1H, H(1-*syn*)), 3.96–3.80 (m, 2H, H(3) and H(4)), 2.98 (d, $J_{2,1\text{-}anti}$ 12.2 Hz, 1H, H(1-*anti*)), 2.18 (d, $J_{4,OH}$ 4 Hz, 1H, exchangeable with D_2O, OH), 1.39 (d, $J_{4,5}$ 6.4 Hz, 3H, H(5)) ppm.

14: ^1H NMR (200 MHz) 5.44 (t, $J_{2,3} = J_{3,4} = 11$ Hz, 1H, H(3)), 3.89 (dq, $J_{2,3}$ 11 and $J_{1,2}$ 6 Hz, 1H, H(2)), 3.81–3.71 (m, 2H, H(3) and, one of H(5), 3.52 (dd, J_{gem} 15.3 and $J_{4,5}$ 5.5 Hz, 1H, one of H(5)), 1.62 (brs, $W_{0,5}$ 19 Hz, 1H, exchangeable with D_2O, OH), 1.34 (d, $J_{1,2}$ 6.2 Hz, 3H, H(1)) ppm; ^{13}C NMR (50 MHz, mixture of **13a**, **13b**, and **14**): 108.55(d), 107.56 (d), 106.22(d), 91.18(d), 91.08(d), 80.91(d), 79.34(d), 68.16(d), 66.07(d), 61.76(d,d), 60.84(d,d), 60.56(d), 23.07(q), 21.99(q), 18.17(q) ppm. IR (KBr, mixture of **13** and **14**): 3260, 2970, 2920, 1450, 1375, 1265, 1140, 1035, 735 cm^{-1}.

Di-μ-chlorobis[(1,2,3-η)-4-hydroxy-2-methyl-2-penten-1-yl]dipalladium (15) was obtained from (*E*)-2-methyl-1,3-pentadiene in 92% yield after flash chromatography. The product **15** consists of two diastereomers **15a** and **15b** in a 3.6/1 ratio.

15a: ^1H NMR (200 MHz, assigned in mixture with **15b**): 4.06 (quint of d, $J_{3,4} = J_{4,5} = 7$ and $J_{4,OH} = 3$ Hz, 1H, H(4)), 3.83 (s, 1H, H(1-syn)), 3.62 (d, $J_{3,4}$ 7.4 Hz, 1H, H(3)), 2.94 (d, $J_{OH,4} = 3$, 1H, exchangeable with D_2O, OH), 2.82 (s, IH, H(1-*anti*), 2.12 (s, 3H, $CH_3 - C(2)$), 1.34 (d, $J_{4,5}$ 6.4 Hz, 3H, H(5)) ppm; ^{13}C NMR (50 MHz): 126.53 (s, C(2)), 88.63 (d, C(3)), 66.22 (d, C(4)), 62.11 (dd, C(1)), 21.53(q), 18.61 (q) ppm.

15b: ^1H NMR (200 MHz, assigned in mixture with **15a**): 4.22 (m, 1H, H(4)), 3.82 (s, 1H, H(1-*syn*)), 3.56 (d, $J_{3,4}$ 5.9 Hz, 1H, H(3)), 2.82 (s, 1H, H(1-*anti*), 2.31 (s, 3H, CH_3–C(2)), 2.16 (d, $J_{4,OH}$ 4 Hz, 1H, exchangeable with D_2O, OH), 1.45 (d, $J_{4,5}$ 6.5 Hz, 3H, H(5)) ppm; ^{13}C NMR (assigned in mixture with **15a**): 124.75 (s, C(2)), 85.20 (d, C(3)), 66.04 (d, C(4)), 64.04 (dd, C(1)), 19.20(q), 18.23(q) ppm. IR(KBr): 3515, 2970, 2910, 2890, 1440, 1430, 1380, 1270, 1050, 870 cm^{-1}. Anal. Found: C, 30.02; H, 4.54. $C_6H_{11}ClOPd$ calcd.: C, 29.90; H, 4.60%.

Di-μ-chlorobis[(1,2,3-η)-4-methyl-4-hydroxy-2-hexen-1-yl (16) was obtained from 4-methyl-1,3-pentadiene in 95% yield after flash chromatography as brown crystals; m.p. 110 °C (decomp.); ^1H NMR (200 MHz): 5.60 (dt, $J_{1,2}$ 6.8 Hz and $J_{2,3} = J_{2,1\text{-}anti} = 12$ Hz, 1H, H(2)), 4.05 (d, $J_{2,3}$ 12 Hz, 1H, H(3)), 4.04 (d, $J_{2,1\text{-}syn}$ 6.8 Hz, 1H, H(1-*syn*)), 2.90 (d, $J_{2,1\text{-}anti}$ 12.0 Hz, 1H, H(1-*anti*)), 2.3 (s, 1H, OH), 1.42 (s, 6H, H5) ppm; ^{13}C NMR (100.6 MHz, DEPT): 107.18 (CH, C(2)), 96.72 (CH, C(3)), 70.88 (C(4)), 61.25 (CH_2, C(1)), 29.60 and 28.96 (two CH_3, C(5) and C(6)) ppm; IR (KBr): 3460, 2980, 2915, 1465, 1445, 1370, 1250, 1150, 950, 890 cm^{-1}.

Di-μ-chlorobis[(1,2,3-η)-2,4-dimethyl-4-hydroxy-2-penten-1-yl]dipalladium (17) was obtained from 2,4-dimethyl-1,3-pentadiene in 87% yield after flash chromatography. M.p. > 110 °C (decomp.): ^1H NMR (200 MHz) 3.75 and 3.63 (two 2, 2H, H(1-*syn*) and H(3)), 2.69 (s, 1H, H(1-*anti*)), 2.36 (s, 3H, $CH_3 - C(2)$), 2.23 (s, 1H, exchangeable with D_2O,OH), 1.51 and 1.44 (two 2, 6H, H(5)) ppm; ^{13}C NMR (50 MHz): 124.16 (s, C(2)), 92.38 (d, C(3)), 70.72 (s, C(4)), 63.07 (dd, C(1)), 31.85(q), 26.49(q), 19.24(q) ppm; IR (KBr): 3515, 2975, 2940, 1450, 1425, 1375, 1340, 1285, 1225, 1165, 1125, 1050, 1040, 1005, 955, 875, 835, 780 cm^{-1}. Anal. Found: C, 32.72; H, 5.07. $C_7H_{13}ClOPd$ calcd.: C, 32.97; H, 5.14%.

Di-μ-chlorobis[(2,3,4-η)-2,4-dimethyl-4-hydroxy-3-hexen-2-yl]dipalladium (19) was obtained from 2,4-dimethyl-2,4-hexadiene and was isolated in 99% yield after flash chromatography. M.p. 150 °C (decomp.); ^1H NMR (200 MHz); 5.11 (d, $J_{3,4}$ 11.8 Hz, 1H, H(3)), 4.11 (d, $J_{3,4}$ 11.7 Hz, 1H, H(4)), 2.44 (s, 1H, exchangeable with

D_2O, OH), 1.43 (s, 9H), 1.26 (s, 3H) ppm; ^{13}C NMR (50 MHz): 103.38 (d, C3), 92.23 (s, C2), 89.07 (d, C4), 70.96 (s, C5), 30.00 (q), 29.05 (q), 21.35(q), 22.54(q) ppm; IR (KBr): 3520, 2980, 2900, 1470, 1440, 1385, 1375, 1360, 1340, 1290, 1235, 1155, 1120, 1065, 955, 940, 920, 880, 820, 780 cm^{-1}. Anal. Found: C, 35.48; H, 5.48. $C_8H_{15}ClOPd$ calcd.: C, 35.71; H, 5.62%.

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