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REGIOSELECTIVE INTRODUCTION OF *O*-NUCLEOPHILES INTO β-MYRCENE AND *trans*-OCIMENE USING PALLADIUM(II) COMPLEXES

MITSURU TAKAHASHI, HISAO URATA, HIROHARU SUZUKI*, YOSHIHIKO MORO-OKA,* and TSUNEO IKAWA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227 (Japan)

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Summary

O-Nucleophiles, RO^- (R = H, Me, Et, i-Pr, and Ac), are introduced regioselectively into the terminal positions of β-myrcene and *trans*-ocimene in the presence of $(CH_3CN)_2PdCl_2$ in HMPA to form acyclic η^3-allylpalladium complexes. The decomposition of hydroxymethyl-η^3-allylpalladium complexes under basic conditions gives monoterpene alcohols and aldehydes.

Introduction

Regioselective introduction of an oxygen atom or a hydroxy group into the terminal position of the 1,3-diene moiety of myrcene or ocimene is one of the simplest and most direct methods of preparing monoterpene aldehydes and alcohols such as citral, geraniol, nerol, and citronellol. The application of organometallics, especially palladium complexes to such transformations, has been examined, and several η^3-allylpalladium complexes of myrcene and ocimene were prepared in the presence of nucleophiles [1]. Among the possible reaction sites for the nucleophilic attack on β-myrcene in the presence of a palladium(II) salt (Scheme 1), site C seems to be preferred electronically to sites A and B.

McQuillin and co-workers reported that nucleophilic attack of chloride and alkoxide anions mainly occurs at site C to give η^3-allylic palladium complexes with a five-membered ring structure [1]. The only example of *anti*-Markownikoff 1,2-addition of the nucleophile to β-myrcene has been reported by Tamaru et al. in the 1,2-hydrosulfonylation of β-myrcene to give C–C bond formation [2]. In a previous paper [3], we reported the novel method for the regioselective introduction of an *O*-nucleophile into the terminal position of β-myrcene to give the acyclic η^3-allylpalladium complexes. We describe herein the detailed analysis of the reaction of β-myrcene and *trans*-ocimene with various *O*-nucleophiles in the presence of pal-

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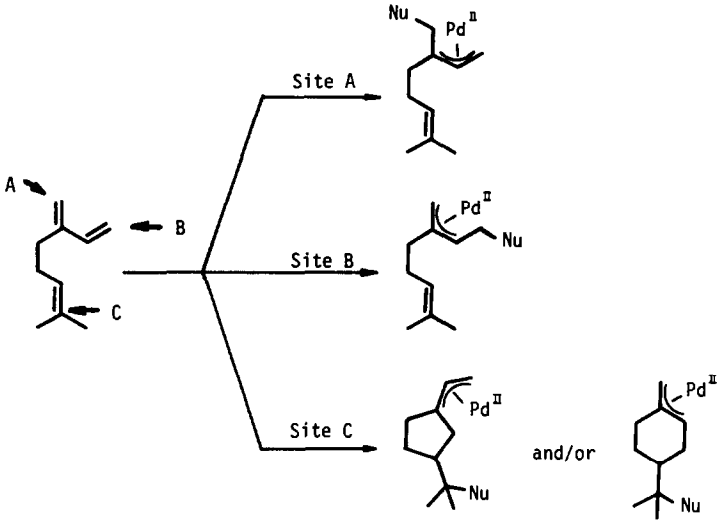


SCHEME 1. Nucleophilic attack toward the palladium(II) complex of β-myrcene.

ladium(II) salts. The decomposition of the η^3-allylpalladium complexes to give monoterpene alcohols is also mentioned.

Results and discussion

Reaction of the O-nucleophile with β-myrcene in the presence of $(CH_3CN)_2PdCl_2$

Reactions of β-myrcene with *O*-nucleophiles were conducted in a mixed (v/v = 1/10) solvent of ROH (R = H, Et, i-Pr, and Ac) and aprotic polar solvent at room temperature under an atmosphere of dry nitrogen. Products were separated and purified by column chromatography on silica gel. The results of the reaction are summarized in Table 1.

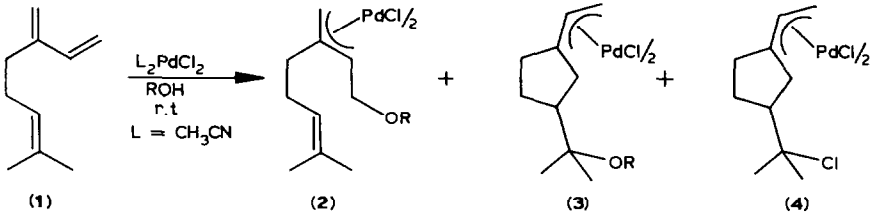
The structure of the η^3-allylpalladium complexes **2**, **3**, and **4** were identified by means of ^{1}H NMR and IR spectroscopy, and elemental analysis. For example, the ^{1}H NMR spectrum of **2a** showed three allylic protons (H(a), H(b), and H(c)) as a singlet at δ 3.72, 2.79, and 3.65, respectively (Fig. 1), and the tri-substituted olefinic proton H(d) (δ 5.15, m) remained unaltered after complexation to form **2a**.

The spectral and physical constants of product **2** as well as of **3** and **4** are given in the Experimental.

As shown in Table 1, the present reaction is greatly affected by the solvent used. The reaction in the mixed solvent acetone/water or in alcohol gave only a mixture of cyclic η^3-allylpalladium complexes, **3** and **4**. Addition of a base such as Li_2CO_3 suppressed the formation of **4** and afforded **2** in a low yield. The yield of **2** was increased by using dimethylformamide as solvent, but the reaction still remained non-selective. Regioselective introduction of *O*-nucleophiles at the terminal carbon atom of **1** (site B) was realized by using hexamethylphosphoric triamide as solvent. Although the reaction rate was retarded, the acyclic η^3-allyl complex **2** was formed exclusively in the attack of every *O*-nucleophile examined. Hexamethylphosphoric triamide is basic enough to capture the hydrogen chloride formed during the reaction, and hence the nucleophilic attack of the chloride ion could be suppressed.

TABLE 1

ATTACK OF THE *O*-NUCLEOPHILE AT *β*-MYRCENE TO FORM *π*-ALLYLPALLADIUM COMPLEXES



(1) (2) (3) (4)

Nucleophile (ROH)	Solvent [a]	Base added	Time (h)	Isolated yield (%)		
				2	3	4
a, R = H	H_2O-HMPA	–	5.0	75	4	4
	H_2O-acetone	–	0.2	–	30	60
	H_2O-acetone	Li_2CO_3	3.0	25	30	6
	H_2O-DMF	Li_2CO_3	6.0	33	6	7
b, R = Me	MeOH	–	0.5	–	76	12
	MeOH	Li_2CO_3	1.0	49	17	–
	MeOH-HMPA	–	3.0	56	–	–
c, R = Et	EtOH	–	1.0	–	35	26
	EtOH-HMPA	–	4.0	57	–	5
d, R = i-Pr	i-PrOH	–	4.0	–	43	48
	i-PrOH-HMPA	–	24.0	44	–	15
e, R = Ac	HOAc	–	0.2	–	30	51
	HOAc-HMPA	Li_2CO_3	24.0	64	–	–

[a] The ratio for the mixed solvent was nucleophile/solvent = 1/10.

The high polarity of this solvent may force the carbon skeleton of *β*-myrcene to unfold, and consequently the *O*-nucleophile may attack the sterically less-hindered site.

Reaction of the O-nucleophile with trans-ocimene in the presence of $(CH_3CN)_2PdCl_2$

Since *trans*-ocimene easily dimerizes in the presence of palladium(II) salts, the reactions were conducted at low temperature (−5°C ~ room temperature). The products of the reaction of *trans*-ocimene with water in the presence of $(CH_3CN)_2PdCl_2$ were separated into three fractions by column chromatography. The complex with R_f 0.3 was recrystallized from dichloromethane/diethyl ether, and was identified as **6** by means of ^1H NMR and IR spectroscopy, and elemental

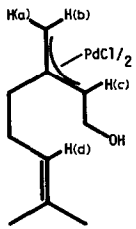


Fig. 1. Structure of complex **2a**.

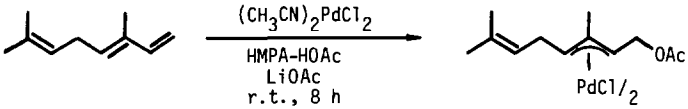
analysis. The ^1H NMR spectrum of complex **6** exhibited multiplet peaks at δ 3.45 ~ 3.85 assignable to the *anti*-protons (H(a) and H(b)) of the η^3-allylic ligand, as well as a doublet peak corresponding to the methylene protons attached to the hydroxy group (δ 3.73). The IR spectrum ($CHCl_3$) of **6** showed absorptions at 3500 (ν(O–H)) and 1015 cm^{-1} (ν(C–O)) characteristic of the primary alcohol. These results agree with the proposed structure of complex **6**. The yellow oily product of R_f 0.25 was tentatively identified as a mixture of *syn*- and *anti*-η^3-allylic complexes and their diastereomers, **7**, for the following reasons. The ^1H NMR spectrum exhibited three peaks for the methyl protons (δ 1.20, 1.23, and 1.40) attached to the η^3-allyl carbon and three alcoholic proton signals (δ 2.36, 2.77, and 3.07), as well as a signal for the terminal Me_2C=CH group and a complex ABX spectrum for the η^3-allylic protons. Another by-product with R_f 0.7 did not show any bands assignable to ν(O–H) in the IR spectrum.

When $(CH_3CN)_2PdBr_2$ was used instead of $(CH_3CN)_2PdCl_2$, the η^3-allylic complexes corresponding to **6** and **7** were well separated by column chromatography.

The results of the hydroxylation of *trans*-ocimene are summarized in Table 2.

The yield of **6** did not change, regardless of the nature of the solvent used, although the regioselectivity (**6**/(**6** + **7**)) was improved by the use of a polar solvent from 0.35 (in acetone, −5°C) to 0.78 (in HMPA, room temperature).

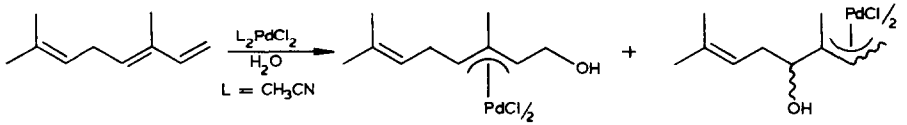
Regioselective introduction of an acetoxy group to the terminal position of *trans*-ocimene was achieved by treating *trans*-ocimene with acetic acid in hexamethylphosphoric triamide in the presence of $(CH_3CN)_2PdCl_2$ at room temperature (eq. 1).



(5) (8, 54%) (1)

TABLE 2

REACTION OF *trans*-OCIMENE WITH WATER IN THE PRESENCE OF $(CH_3CN)_2PdCl_2$



(5) (6) (7)

Solvent	H_2O/solvent	Temp. (°C)	Time (h)	Isolated yield (%)	
				6	7
Acetone	1/5	−5	8.0	26	49
Acetone [a]	1/5	−5	8.0	33	32
DMF	1/5	−5	8.0	30	35
HMPA	3/2	−5	6.0	33	18
HMPA	1/5	−5	8.0	37	12
HMPA	1/5	r.t.	8.0	35	10
HMPA [b]	1/10	r.t.	10.0	35	19

[a] Li_2CO_3 was added. [b] $(CH_3CN)_2PdBr_2$ was used instead of $(CH_3CN)_2PdCl_2$. Products were bromide-bridged dinuclear π-allylpalladium complexes corresponding to **6** and **7**.

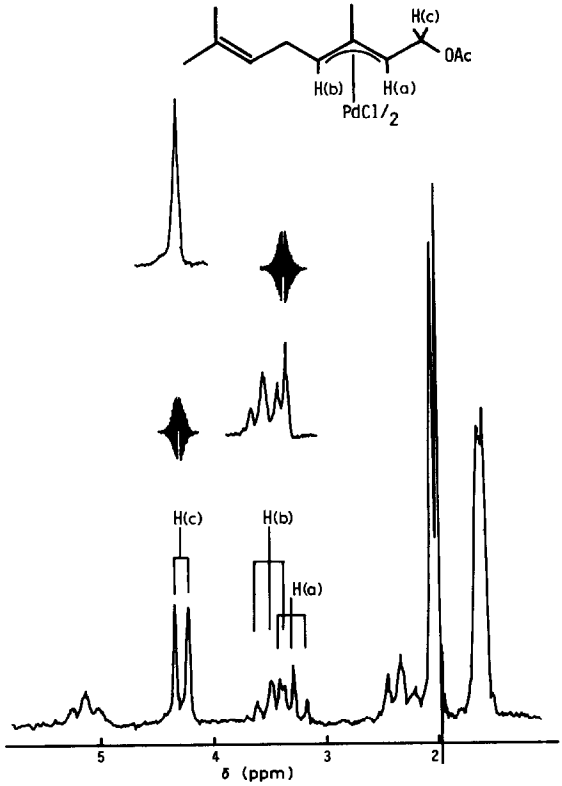
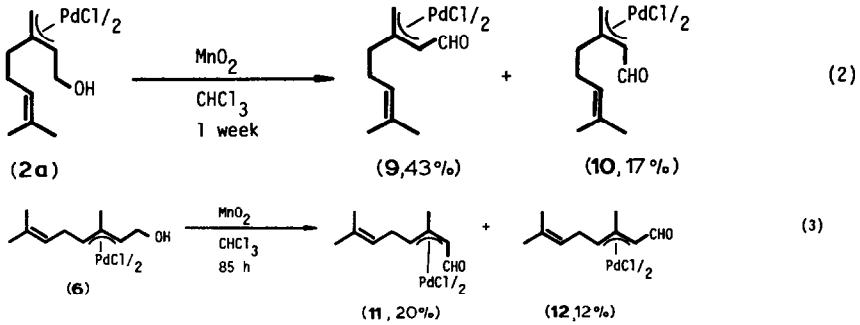


Fig. 2. ^{1}H NMR spectrum of complex **8** in $CDCl_3$.

The formation of the regioisomeric complex corresponding to **7** was not observed in this reaction. The acetoxy anion must therefore attack *trans*-ocimene exclusively at the terminal sp^2 carbon owing to steric requirements.

Oxidation of **2a** *and* **6**

Oxidation of the 1-hydroxymethyl-η^3-allylic complexes **2a** and **6** was performed by the use of MnO_2 in chloroform. Treatment of **2a** with large excess amounts of MnO_2 in chloroform at room temperature yielded a mixture of the *anti*- and *syn*-1-formyl-η^3-allylic palladium complexes, **9** and **10**, in a 60% combined yield (**9**/**10** = 5/2) (eq. 2).



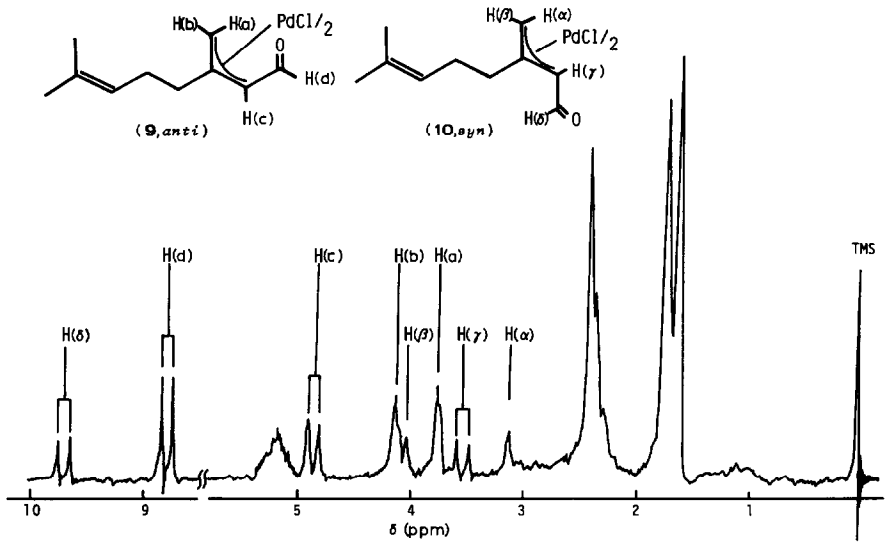


Fig. 3. ^{1}H NMR spectrum of a mixture of **9** and **10** in $CDCl_3$.

In a similar manner, the η^3-allylic complex **6** derived from *trans*-ocimene was transformed to the corresponding 1-formyl-η^3-allylic palladium complexes, **11** and **12** (eq. 3).

In both cases, *anti*-1-formyl-η^3-allylic palladium complexes, which were stabilized by the coordination of the formyl group to the palladium(II) centre, were predominantly formed.

Although it was a considerably slow process, oxidation with MnO_2 was so selective that no products other than the above-mentioned 1-formyl-η^3-allylic complexes were formed.

Reductive demetallation of 2a and 6

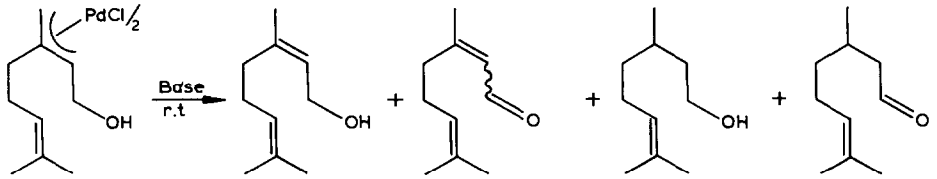
Treatment of **2a** with bases such as NaOMe, NaH, or $NaBH_4$ gave terpene alcohols and aldehydes together with the deposition of palladium(0) powder. The results of the reductive demetallation of **2a** with various bases are summarized in Table 3.

Under conditions where a methoxide or a hydroxide anion served as a reducing agent, nerol (**13**) and citral ($E/Z = 1.0 \sim 1.5$) (**14**) were obtained. Especially in the case of hydroxide anion (runs 3 and 4), nerol was predominantly formed, but was still far from being selectively formed. Reduction by use of a metal hydride afforded citronellol (**15**) and citronellal (**16**), together with nerol and citral. The notable fact that nerol was exclusively formed by the reductive demetallation of **2a**, except in run 5, is consistent with the *syn*-form of **2a**.

The η^3-allyl complex **6** derived from *trans*-ocimene was reduced in a similar manner to give geraniol (**17**), isogeraniol (**18**), and citral (**14**) (Table 4).

Although the small experimental scale and the separation of the products by column chromatography on silica gel lowered the isolated yield, the absence of nerol in the products was confirmed by GLC analysis of the crude products. This result also strongly suggests that the η^3-allyl complex **6** is a *syn*-isomer.

TABLE 3. REDUCTION OF **2a** BY THE USE OF BASES



(2a) (13) (14) (15) (16)

Run	2a (mmol)	Solvent (ml)	Base (mmol)	Time (h)	Product ratio (%)					Combined yield (%)	isolated (GLC)
					13	14	(E/Z)	15	16		
1	1.50	MeOH (20)	NaOMe (7.8)	3.0	55	45	(1.5)	0	0	81	(89)
2	1.04	MeOH (20)	K_2CO_3 (4.0)	2.5	53	47	(1.5)	0	0	49	
3	0.75	H_2O/MeOH (10/15)	KOH (10)	1.0	79	21	(1.0)	0	0	39	
4	0.75	H_2O/MeOH (10/10)	NaOH (10)	0.5	83	17	(1.0)	0	0	46	
5	0.47	DME (9)	NaH (5.0)	5.0	66 [a]	0		10	24		(92)
6	0.47	MeOH (15)	$NaBH_4$ (1.0)	3.5	71	18	(0.4)	6	5		(82)
7 [b]	1.00	DME (15)	$LiAlH_4$ (1.0)	6.0	71	17	(0.5)	0	12	59	
8 [c]	1.15	DME (15)	$LiAlH_4$ (10.1)	0.5	5	0		84	11	38	

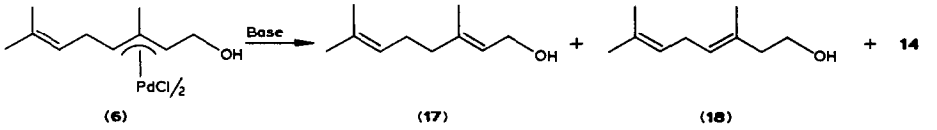
[a] $E/Z = 1/5$. [b] The reaction was conducted at 0°C. [c] The reaction was conducted at −10°C.

Experimental

Solvents were dried over appropriate drying agents and were freshly distilled prior to use. β-Myrcene and *trans*-ocimene (purity 95%) were obtained from Nissan Kagaku Co., and were used without further purification. Dichlorobis(acetonitrile)palladium, $(CH_3CN)_2PdCl_2$, was prepared according to the standard method [4].

TABLE 4

REDUCTION OF **6** BY THE USE OF BASES



(6) (17) (18)

Base	Solvent	Temp. (°C)	Time (h)	Isolated yield (%)		
				17	18	14 (Z/E)
NaOMe	MeOH	r.t.	4.0	21	28	13 (1/3)
KOH (aq.)	MeOH	r.t.	1.5	12	16	0
$LiAlH_4$	THF	0	2.0	10	25	0

^{1}H NMR spectra were measured on a Hitachi High Resolution NMR Spectrometer R24B or a JEOL Model JNM-PS-100 in CCl_4 or $CDCl_3$, with tetramethylsilane (TMS) as the internal standard. IR spectra and melting points were recorded on a Shimadzu IR-27G and a Yanagimoto-MP apparatus, respectively. GLC analyses were performed by a Shimadzu GC-6A instrument at 115°C with a 1 m × 3 mm ∅ glass column packed with 20% PEG 6000 on Celite 545.

All reactions were carried out under a nitrogen atmosphere.

Reaction of β-myrcene with water in HMPA

To a solution of $(CH_3CN)_2PdCl_2$ (0.81 g, 3.1 mmol) in 20 ml of hexamethylphosphoric triamide (HMPA) were added water (2 ml) and β-myrcene (0.61 g, 4.5 mmol). The mixture was stirred for 5 h at room temperature. The resulting mixture was extracted three times with benzene. The combined organic layer was washed with water and dried over $CaCl_2$. After removal of the solvent under reduced pressure, the yellow oily residue was separated by column chromatography on silica gel with benzene/ethyl acetate (5/1) into three fractions, **2a**, **3a**, and **4** in 75, 4, and 4% yields, respectively.

2a: Yellow needles; m.p. 86.5–88.5°C; IR (CCl_4): 3640, 3550 (O–H), and 1050 cm^{-1} (C–O); (KBr): 3250 (O–H), 995 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$): δ 1.63 (3H, s), 1.70 (3H, s), 2.35 (4H, m), 2.50 (1H, s, OH, D_2O-exchangeable), 2.79 (1H, s), 3.65 (3H, s), 3.72 (1H, s), 5.15 (1H, m). Found: C, 40.88; H, 6.11; Cl, 11.54. $C_{10}H_{17}OPdCl$ calcd.: C, 40.70; H, 5.81; Cl, 12.01%.

3a: M.p. 72–74°C; IR (KBr): 3350 (O–H), 1120 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$): δ 1.20, 1.22 (6H, each s), 1.75 (1H, br s), 1.50–2.55 (7H, m), 3.05 (1H, d, J = 13 Hz), 3.90 (1H, d, J = 7 Hz), 5.25 (1H, m). Found: C, 41.23; H, 6.17; Cl, 12.87. $C_{10}H_{17}OPdCl$ calcd.: C, 40.70; H, 5.81; Cl, 12.01%.

4: M.p. 149–152°C; IR (KBr): 3060, 3020 (C–H), and 1494 cm^{-1} (C–H); ^{1}H NMR ($CDCl_3$): δ 1.57 (6H, s), 1.5–3.0 (7H, m), 3.05 (1H, d, J = 13 Hz), 3.95 (1H, d, J = 7 Hz), 5.25 (1H, m). Found: C, 38.64; H, 5.27; Cl, 21.98. $C_{10}H_{16}PdCl$ calcd.: C, 38.31; H, 5.14, Cl, 22.61%.

In a similar manner, a series of complexes, **2b–2e** and **3b–3e**, was synthesized. The physical, spectral, and analytical data of the new compounds ontained in this study are as follows:

2b: M.p. 112–113°C; IR (KBr): 3050 (C–H) and 1088 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$): δ 1.60 (3H, s), 1.72 (3H, s), 2.1–2.5 (4H, m), 2.76 (1H, s), 3.35 (3H, s), 3.55 (3H, s), 3.75 (1H, s), 5.10 (1H, m). Found: C, 43.18; H, 6.30; Cl, 12.76. $C_{11}H_{19}OPdCl$ calcd.: C, 42.74; H, 6.19; Cl, 11.47%.

2c: Yellow needles, m.p. 114–115°C; IR (KBr): 3060 (C–H) and 1090 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$): δ 1.20 (3H, t, J = 7 Hz), 1.62 (3H, s), 1.70 (3H, s), 2.30 (4H, m), 2.76 (1H, s), 3.60 (5H, m), 3.76 (1H, s) 5.13 (1H, m). Found: C, 44.40; H, 6.71; Cl, 11.45. $C_{12}H_{21}OPdCl$ calcd.: C, 44.60; H, 6.55; Cl, 10.97%.

2d: Yellow needles, m.p. 100–103°C; IR (KBr); 3060 (C–H), 1150, 1125, and 1042 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$): δ 1.15 (6H, d, J = 6 Hz), 1.62 (3H, s), 1.70 (3H, s), 2.30 (4H, m), 2.76 (1H, s), 3.60 (4H, m), 3.75 (1H, s), 5.15 (1H, m). Found: C, 46.32; H, 6.91; Cl, 10.06. $C_{13}H_{23}OPdCl$ calcd.: C, 46.31; H, 6.88; Cl, 10.51%.

2e: Yellow needles, m.p. 121–122.5°C; IR (KBr): 3050 (C–H), 1735 (C=O), and 1230 cm^{-1} (C–O); ^{1}H NMR ($CDCl_3$): δ 1.65 (3H, s), 1.75 (3H, s), 2.16 (3H, s), 2.3–2.5 (4H, m), 2.90 (1H, s), 3.62 (1H, dd, J = 10 and 13 Hz), 4.49 (1H, dd, J = 7

and 13 Hz), 5.25 (1H, m). Found: C, 42.54; H, 5.72; Cl, 10.43. $C_{12}H_{19}O_2PdCl$ calcd.: C, 42.75; H, 5.68; Cl, 10.52%.

3b: M.p. 132–134°C; IR (KBr): 3020 (C–H) and 1080 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.10 (6H, s), 1.5–2.3 (7H, m), 3.0 (1H, d, $J = 12$ Hz), 3.86 (1H, d, $J = 7$ Hz), 5.25 (1H, m). Found: C, 43.14; H, 6.49. Cl, 11.53. $C_{11}H_{19}OPdCl$ calcd.: C, 42.74; H, 6.19; Cl, 11.47%.

3c: M.p. 112–114°C; IR (KBr): 3050 (C–H) and 1075 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.08 (9H, m), 1.5–2.3 (7H, m), 3.0 (1H, d, $J = 13$ Hz), 3.35 (2H, q, $J = 7$ Hz), 3.84 (1H, d, $J = 7$ Hz), 5.20 (1H, m). Found: C, 44.31; H, 6.58; Cl, 11.69. $C_{12}H_{21}$ OPdCl calcd.: C, 44.60; H, 6.55; Cl, 10.97%.

3d: M.p. 115–116°C; IR (KBr): 3040 (C–H) and 1020 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.06–1.12 (12H, m), 1.5–2.3 (7H, m), 3.0 (1H, d, $J = 13$ Hz), 3.5–4.0 (2H, m), 5.20 (1H, m). Found: C, 46.94; H, 7.11; Cl, 12.03. $C_{13}H_{23}OPdCl$ calcd.: C, 46.31; H, 6.88; Cl, 10.51%.

3e: M.p. 116–118°C; IR (KBr): 3050 (C–H), 1735 (C=O), and 1255 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.45 (6H, s), 1.5–2.3 (7H, m), 1.95 and 2.0 (3H, m), 3.05 (1H, d, $J = 13$ Hz), 3.92 (1H, d, $J = 7$ Hz), 5.30 (1H, m). Found: C, 42.74; H, 5.74; Cl, 10.95. $C_{12}H_{19}O_2PdCl$ calcd.: C, 42.75; H, 5.68; Cl, 10.52%.

Reaction of trans-ocimene with water in HMPA

To a mixed solution of $(CH_3CN)_2PdCl_2$ (1.06 g, 4.1 mmol) in water (3 ml) and HMPA (15 ml) was added *trans*-ocimene (0.61 g, 4.5 mmol). The reaction mixture was stirred at room temperature for 8 h, and then extracted with benzene and washed with water. Drying over $CaCl_2$ followed by the removal of the solvent under reduced pressure gave yellow oily products. Purification by column chromatography on silica gel with benzene/ethyl acetate (5/1) afforded **6** (R_f 0.3) and **7** (R_f 0.25) in 35 and 10% yield, respectively, together with an unidentified compound (R_f 0.7).

6: M.p. 150–151°C; IR (KBr): 3510, 3450 (O–H), and 995 cm^{-1} (C–O); ($CHCl_3$): 3500 (O–H) and 1015 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.66 (3H, s), 1.72 (3H, s), 2.2 (3H, s), 2.42 (3H, br t), 3.45–3.80 (4H, m), 5.2 (1H, br t). Found: C, 40.91; H, 6.02; Cl, 12.15. $C_{10}H_{17}OPdCl$ calcd.: C, 40.70; H, 5.81; Cl, 12.01%.

7: Yellow oil; IR ($CHCl_3$): 3510 (O–H) and 1060 cm^{-1} (C–O). Found: C, 40.62; H, 5.90; Cl, 12.85. $C_{10}H_{17}OPdCl$ calcd.: C, 40.70; H, 5.81; Cl, 12.01%.

Reaction of trans-ocimene with acetic acid in HMPA

To a mixed solution of $LiOAc \cdot 2H_2O$ (0.21 g, 2.0 mmol) in acetic acid (2 ml) and HMPA (15 ml) were added a solution of $(CH_3CN)_2PdCl_2$ (0.53 g, 2.1 mmol) in HMPA (5 ml) and then *trans*-ocimene (0.41 g, 3.0 mmol). The reaction mixture was stirred at room temperature for 8 h, extracted with benzene, and washed with water. Drying over $CaCl_2$ followed by the removal of the solvent under reduced pressure gave a yellow oil. Purification by column chromatography on silica gel with benzene/ethyl acetate (10/3) afforded **8** in a 54% yield. The ^1H NMR spectrum of complex **8** (Fig. 2) agreed with the proposed structure.

8: M.p. 134–136°C; IR (KBr): 1730 (C=O) and 1220 cm^{-1} (C–O); ^1H NMR ($CDCl_3$): δ 1.65 (3H, s), 1.70 (3H, s), 2.03 (3H, s), 2.10 (3H, s), 2.40 (2H, t, $J = 6.5$ Hz), 3.34 (1H, t, $J = 7$ Hz); 3.52 (1H, t, $J = 6.5$ Hz), 4.32 (2H, d, $J = 7$ Hz), 5.18 (1H, br t). Found: C, 43.17; H, 5.75; Cl, 10.85. $C_{12}H_{19}O_2PdCl$ calcd.: C, 42.75; H, 5.68; Cl, 10.52%.

*Reaction of **2a** with MnO_2*

To a solution of **2a** (0.30 g, 0.5 mmol) in 10 ml of chloroform was added MnO_2

(0.87 g, 10 mmol). The reaction mixture was stirred at room temperature for 1 week. Removal of MnO_2 by filtration followed by concentration of the filtrate under reduced pressure gave yellow oily products. Purification and separation by column chromatography on silica gel with benzene/ethyl acetate (10/1) yielded a mixture of **9** and **10** in a 60% yield. The ratio of **9** (*anti-form*) to **10** (*syn-form*) was determined to be 5/2 by means of ^1H NMR spectroscopy (Fig. 3).

9 and **10**: IR (CCl_4): 1685 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 1.61 (3H, s) 1.70 (3H, s), 2.2–2.5 (4H, m), 3.10 (0.3H, s), 3.52 (0.3H, d, J = 6.5 Hz), 3.73 (0.7H, br s), 4.00 (0.3H, s), 4.10 (0.7H, br s). 4.83 (0.7H, d, J = 6 Hz), 5.15 (1H, m), 8.80 (0.7H, d, J = 6 Hz), 9.73 (0.3H, d, J = 6.5 Hz).

*Reaction of **6** with MnO_2*

To a solution of **6** (0.3 g, 0.5 mmol) in 10 ml of chloroform was added MnO_2 (0.87 g, 10 mmol). The reaction mixture was stirred at room temperature for 85 h. Removal of MnO_2 by filtration followed by the concentration of the filtrate under reduced pressure gave a yellow oil. Purification and separation by column chromatography on silica gel with benzene/ethyl acetate (5/1) afforded a mixture of **11** (*anti-form*) and **12** (*syn-form*) in 20 and 12% yields, respectively.

11 and **12**: IR ($CHCl_3$): 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 1.7 (6H, br s), 2.15 (1.8H, s), 2.37 (3.2H, m), 3.38 (0.4H, d, J = 6 Hz), 3.83 (0.4H, t, J = 7 Hz), 4.52 (0.6H, t, J = 7 Hz), 4.75 (0.6H, d, J = 6 Hz), 5.20 (1H, m), 8.85 (0.6H, d, J = 6 Hz), 9.92 (0.4H, d, J = 6 Hz).

*Demetallation of **2a** with sodium methoxide*

To a solution of **2a** (0.91 g, 1.5 mmol) in 20 ml of methanol was added sodium methoxide (0.42 g, 7.8 mmol), and the mixture was stirred at room temperature for 3 h. GLC analysis showed the formation of nerol (51%) and citral (45%, Z/E = 2/3). Nerol (45%) and citral (36%) were isolated by column chromatography on silica gel using benzene as eluent.

*Demetallation of **2a** with NaH*

To a suspension of NaH (0.25 g, 5.16 mmol) in 5 ml of dimethoxyethane (DME) was added a solution of complex **2a** (0.28 g, 0.48 mmol) in 4 ml of DME, and the reaction mixture was stirred at room temperature for 1.5 h. GLC analysis showed the formation of nerol (51%), citronellol (9%), citronellal (23%), and geraniol (10%).

*Demetallation of **6** with sodium methoxide*

To a solution of **6** (0.35 g, 0.6 mmol) in 20 ml of methanol was added sodium methoxide (0.17 g, 3.2 mmol), and the mixture was stirred at room temperature for 4 h. The resulting mixture was extracted three times with di-isopropyl ether, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel with benzene to afford geraniol (21%), isogeraniol (28%), and citral (13%, Z/E = 1/3).

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