Hydroformylation of myrcene: metal and ligand effects in the hydroformylation of conjugated dienes

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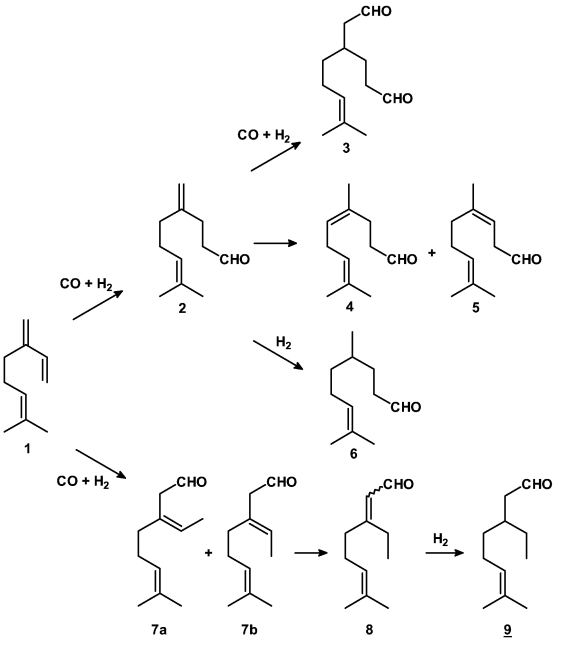
The hydroformylation of myrcene catalyzed by Rh and Pt/Sn catalysts containing different P-donor ligands leads to the formation of a number of mono- and dialdehydes. Nine major products of the reaction have been characterized, showing that they arise from the *n*-alkyl and η^3-allyl intermediates, formed through the reaction of the metal catalysts with the less substituted C=C bond of the substrate. Thus, 4-methylene-8-methyl-7-nonenal is the major aldehyde formed with Pt/Sn catalysts, regardless of the P-donor ligand used. This aldehyde is also the main product of the reaction catalyzed by the Rh/xantphos system (xantphos = 9,9-dimethyl-4,6-bis(diphenylphosphino)xantene). However, with ligands such as bisbi (bisbi = 2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl), also with bite angles around 120°, but with more flexible backbones than xantphos, rhodium catalysts yield mainly *cis*- and *trans*-3-ethylidene-7-methyl-6-octenal. These two aldehydes are also formed in the reactions catalyzed by Rh and P-donor monodentate ligands or the bidentante ones with bite angles around 90° (dppe, dppp). For the last type of ligands, an increase in the flexibility of the backbone reduces the selectivity for the β,γ-unsaturated aldehydes.

Introduction

Hydroformylation of naturally occurring olefins represents a versatile method for the production of aldehydes, which are difficult to obtain by conventional synthetic pathways.[1] Terpenes are an important family of natural products extensively used in the perfume industry.[2] Since aldehydes often show interesting organoleptic properties,[3] the hydroformylation of terpenes has been quite extensively investigated and a considerable amount of information in this field is nowadays available, both in patents and in the open literature.[4,5]

Myrcene **1** is a very abundant acyclic terpene available from hops and other sources. It is used in the synthesis of a variety of commercial products.[6] Judging from the structure, the hydroformylation of myrcene could result in a complex mixture of saturated and unsaturated C_{11}-monoaldehydes and C_{12}-dialdehydes, arising from the hydroformylation (and, eventually, from the isomerization and hydrogenation) of both the 2-substituted butadiene fragment and trisubstituted double bond. Probably for this reason, there has previously been only one report on the hydroformylation of myrcene.[7] In this work, a Rh/PPh_3 catalyst was used in a single experiment, and 3-ethyl-7-methyl-6-octenal **9** (see Scheme 1), formally resulting from the hydroformylation of the disubstituted double bond and the hydrogenation of the monosubstituted double bond, was obtained in a 40% selectivity, along with many secondary products. According to this result and taking into account the well-known reactivity of different substituted olefins in hydroformylation, it is expected that most of the products of the hydroformylation of myrcene should arise from the addition of CO and H_2 to the conjugated diene fragment.

Several reports in the literature deal with the hydroformylation of conjugated dienes, mostly simple ones, such as 1,3-butadiene, isoprene and 1,3-pentadiene. These substrates are more reluctant to be hydroformylated than mono-olefins. A recent study on the competitive hydroformylation of conjugated dienes and olefins shows that trace quantities of dienes compete against an excess of olefins for $RhH(CO)_4$, forming η^3-allyl complexes, while their



Scheme 1

hydroformylation usually occurs at a much slower rate than that of simple olefins.[8]

The homogeneous hydroformylation of conjugated dienes was firstly reported by Natta[9] and Adkins.[10] Later, other groups extensively investigated this reaction.[11] In these studies, a marked tendency for the formation of saturated monoaldehydes was observed. Because of the rather severe conditions used in these reactions, selectivities for any specific product were generally quite low. Only 1,3-butadiene was converted to pentanal with over 90% selectivity using a Rh/dppe catalyst (dppe = 1,2-bis(diphenylphosphino)ethane).[11e] Some rhodium catalytic systems have been also developed to produce β,γ-unsaturated aldehydes (which are attractive synthetic intermediates) from various conjugated dienes. High chemo- and regioselectivities for these products (80–96%) were attained with a Rh vapour-mesitylene cocondensate/dppe system.[12] The hydroformylation of butadiene with a Rh/bubiphos (bubiphos = bis(1,1′-biphenyl-2,2′-diyl)(1,1′-biphenyl-3,3′,5,5′-tetra-*tert*-butyl-2,2′diyl)diphosphite) catalyst was disclosed to yield a 25% selectivity for 1,6-hexanedial.[13] More recently, Ohgomori *et al.* reported that 1,6-hexanedial and 4-pentenal can be obtained in up to a 35% combined yield *via* the hydroformylation of butadiene using Rh catalysts containing bidentate phosphines with natural bite angles within the "intermediate region" (100–110°).[14] According to these authors, diphosphine ligands coordinating the metal as apical-equatorial chelates (ligands with bite angles near 90°) allow butadiene to be coordinated at diequatorial positions, which favors the formation of η^3-allyl complexes leading to β,γ-unsaturated aldehyde, *i.e.*, 3-pentenal. On the other hand, diphosphine ligands with diequatorial coordination (bite angles near 120°) induce an apical–equatorial coordination of butadiene, which through η^4-butadiene rhodium complexes produces the γ,δ-unsaturated aldehyde, *i.e.*, 4-pentenal, and then dialdehyde. Good to excellent regio- and enantioselectivities were obtained with a Rh/binaphos catalyst (binaphos = (2-diphenylphosphino-1,1′-dinaphthalen-2,2′-diyl)(1,1′-dinaphthalene-2,2′-diyl)phosphite)) in the hydroformylation of some conjugated dienes.[15]

In this work we describe a systematic study on the hydroformylation of myrcene catalyzed by different Rh and Pt/Sn catalysts, aiming to obtain new aldehydes of a potential interest for the fine chemicals industry. The effect of the metal and ligand nature on the reaction selectivity is analyzed.

Results and discussion

The hydroformylation of myrcene was studied with the following catalytic systems: Rh and monodentate P-donor ligands, namely PPh_3, tris(*o*-tolyl)phosphine, tris(*o*-trifluoromethylphenyl)phosphine, tris(*p*-trifluoromethylphenyl)phosphine, tris(*o*-*tert*-butylphenyl)phosphite $P(OPh^*)_3$; Rh and bidentate P-donor ligands, namely dppe, 1,3-bis(diphenylphosphino)-propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1,2-bis[(diphenylphosphino)methyl]benzene (dppmb), (*R,R*)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (diop), bubiphos, 9,9-dimethyl-4,6-bis(diphenylphosphino)xantene (xantphos), 2,2′-bis((diphenylphosphino)-methyl)-1,1′-biphenyl (bisbi); $Pt/SnCl_2$ and PPh_3 or diphosphines dppe, dppp, dppb and 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphtyl (naphos). The structures of some of these ligands are depicted in Chart 1.

As expected, several concomitant transformations occur under reaction conditions resulting in a complex mixture of mono- and dialdehydes, as well as the products of the myrcene hydrogenation. The reaction network and identified aldehydes **2**–**9** are represented in Scheme 1, with aldehydes **2**–**8** being new compounds. In general, major hydroformylation products are aldehydes **2**, **7a** and **7b**. These aldehydes are primary reaction

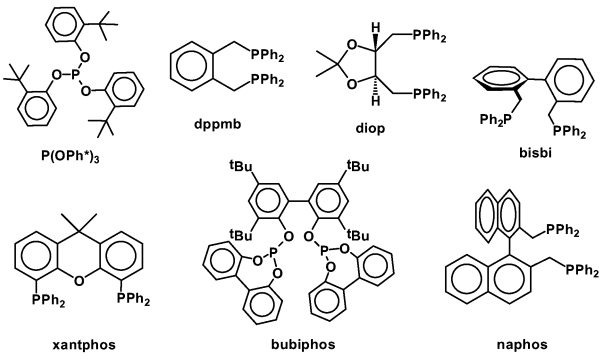
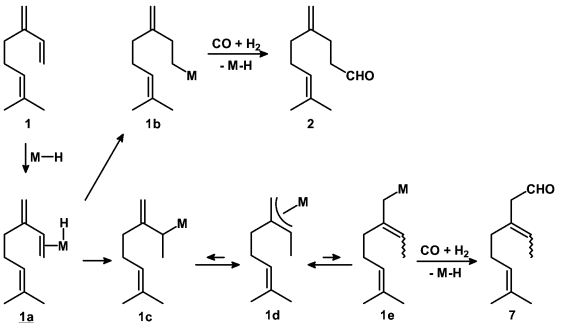


Chart 1

products resulting from the catalyst coordination to the less hindered double bond, Scheme 2. In the subsequent migration step, either *n*-alkyl (**1b**) or *iso*-alkyl (**1c**) intermediates are formed. The first evolves to linear aldehyde **2**, which can further react with CO and H_2 to selectively produce dialdehyde **3**. No aldehydes resulting from the Markovnikov addition of the metal hydride to the methylenic double bond were observed. Instead, under certain reaction conditions (*i.e.*, with Pt/Sn catalysts), the methylenic double bond undergoes isomerization or hydrogenation, rendering products **4** and **5** or **6**, respectively. Aldehyde **6** could also arise from the hydrogenation of the α,β-unsaturated aldehyde produced by further isomerization of **5**. However, this α,β-unsaturated aldehyde was not detected in the reaction mixture.

η^3-Allyl intermediate **1d** is formed by the rearrangement of *iso*-alkyl intermediate **1c**. Since the aldehyde derived from the *iso*-alkyl intermediate was not detected in reaction mixtures, it should be inferred that this rearrangement is faster than the CO insertion. This is consistent with the observation that Rh catalyzed deuteroformylation of 1,3-butadiene has resulted in the formation of 1,5-d_2-3-pentenal.[12] Furthermore, it has been found that $[Rh(\eta^3\text{-allyl})(CO)(PPh_3)_2]$ complexes (η^3-allyl represents a substituted allyl ligand) showing a severely distorted trigonal bipyramidal geometry are stable enough to be characterized by X-ray diffraction.[16] Aldehydes **7a** and **7b** seem to be generated through the CO insertion into η^1-allyl intermediate **1e**, instead of the direct carbonylation of η^3-allyl intermediate **1d**. η^3-Allyl rhodium complexes are known to be rather resistant to CO insertion, but they can readily form η^1-allyl rhodium species.[11e,15b] The formation of η^3-allyl, σ-allyl and acyl rhodium complexes have been recently observed in an HPIR study on the hydroformylation of some conjugated dienes catalyzed by $RhH(CO)_4$.[8]

The *trans* and *cis* isomers of **7** are obtained in a similar proportion. The isomerization of these primary products produces α,β-unsaturated aldehyde **8**, which is much more susceptible to hydrogenation than to hydroformylation and readily



Scheme 2

transformed into partially saturated aldehyde **9**. The latter is the major product found in the previous study on the hydroformylation of myrcene.[7] However, under the conditions used in the present work, both aldehydes **8** and **9** are always minor components of the reaction mixture. Aldehyde **8**, useful as an intermediate for the synthesis of biologically active compounds,[17] can be quantitatively obtained from the mixture of aldehydes **7** in the presence of the $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$/$PPh_3$ catalyst (70 °C, N_2, toluene, 6 h). The hydroformylation and isomerization of myrcene described here seems to be a more convenient synthetic path for aldehyde **8** than that originally reported. Aldehyde **8** can be converted into aldehyde **9** by hydrogenation (70 °C, H_2, 15 bar, toluene) in the presence of the Rh/PPh_3 catalyst mentioned above. However, both the isomerization and hydrogenation of aldehydes **7** are nearly suppressed under a CO atmosphere. This is the reason for the low content of **8** and **9** in the hydroformylation products.

The results on myrcene hydroformylation catalyzed by different rhodium and platinum/tin species are presented in Tables 1–5. Most of the rhodium systems favor the formation of **7a** and **7b** and then small amounts of **8** and **9**, *via* the formation of the η^3-allyl rhodium intermediate. On the contrary, platinum catalysts give rise to aldehyde **2** and then to its derivatives **3**–**6** through the *n*-alkyl intermediate.

Rhodium catalysts

Table 1 collects the data on the hydroformylation of **1** catalyzed by a series of Rh catalysts under the same reaction conditions. The observed selectivity dramatically depends on the ligand used. Thus, diphosphines with bite angle[18] near 90° and very low ring flexibility, such as dppe, show a high selectivity for aldehydes **7a** and **7b**, with small amounts of their isomerization and hydrogenation products **8** and **9** also being formed. The molar ratio between the total amounts of products **7**–**9**, arising from η^3-allyl intermediate **1d**, and those arising from linear σ-alkyl intermediate **1b**, *i.e.*, products **2**–**6**, is indicated as *S*(b/l) in Tables 1–4. This parameter reaches a value close to eight for the dppe catalyst, indicating that ligands coordinating only as axial–equatorial chelates favor the formation of the η^3-allyl rhodium intermediate. An increase in the flexibility of the backbone of the ligands with bite angle angles around 90° (*i.e.*, going from dppe to dppb), significantly decreases the *S*(b/l) parameter. On the other hand, ligands with a bite angle near 120° and with a rigid backbone, such as xantphos,[19] show preferential selectivities for aldehyde **2** and for the other products originating from *n*-alkyl intermediate **1b**. This suggests that the equatorial–equatorial ligand coordination disfavors the formation of the η^3-allyl intermediate.

Interestingly, other ligands, such as bisbi and bubiphos, which also coordinate the metal preferentially in equatorial–equatorial positions (bite angles around 120°),[20] show very low selectivity for aldehyde **2**. As a matter of fact, in both cases, the *S*(b/l) parameter is greater than 3, while it is only 0.5 for the xantphos catalyst. This is an unexpected result, since the three ligands with bite angles near 120° are known to yield similarly high ratios between linear and branched products in the hydroformylation of 1-alkenes.[21] Furthermore, catalysts containing diop and dppmb, bite angles near 100°, produce an *S*(b/l) parameter of around 1. Thus, although these two ligands show lower selectivity for linear aldehydes than bubiphos or bisbi in the case of 1-alkenes, in the hydroformylation of myrcene, they render a higher ratio of the products arising from the *n*-alkyl intermediate than two large bite angle ligands. These results indicate that, for the ligands coordinating the metal in diequatorial positions in catalytically active species, a flexible backbone (such as that of bisbi or bubiphos) facilitates the formation of the η^3-allyl intermediate, while a rigid backbone disfavors this reaction path. Interestingly, the opposite trend is observed for the ligands coordinating rhodium in axial–equatorial positions. It can be speculated that, for the ligands with bite angles near 120°, the flexibility of the backbone is required to produce a low energy path, probably through a Berry or Meakin rearrangement,[22] to convert the η^3-allyl intermediate into the η^1-allyl complex, where the CO insertion can take place. For instance, a square pyramidal intermediate, where the ligand is coordinating in two *trans* basal positions, should be easily accessible for the flexible ligand, such as bisbi, as evidenced by the structure of [Fe(bisbi)$(CO)_3$], which adopts this geometry.[23]

It seems to be expected that rhodium catalysts with PPh_3 (cone angle of 145°) and similar phosphines, which can be considered as equatorial–equatorial ligands[24] with complete flexibility, yield mainly the products derived from the η^3-allyl intermediate in high selectivity. Finally, monodentate ligands with high cone angles, such as tris(*o*-*tert*-butylphenyl)phosphite (cone angle of 175°), tris(*o*-trifluoromethylphenyl)phosphine (cone angle of 231°) and tris(*o*-tolyl)phosphine (cone angle of 194°), as well as the [RhH$(CO)_4$] catalyst, show low or no activity in myrcene hydroformylation, under the reaction conditions of Table 1.

We have further investigated the effect of the reaction conditions on the selectivity of rhodium catalysts with three representative ligands, with respect to their behavior in this reaction, namely xantphos, dppe and PPh_3. Results are summarized in Tables 2, 3 and 4, respectively. For the Rh/

Table 1 Hydroformylation of myrcene (**1**) catalyzed by Rh/P-donor ligands[a]

Ligand[b]	L/Rh[c]	Con.(%) (*t*/h)[d]	**2** (%)	**3** (%)	**7** (%)	Ot. (%)[e]	H. (%)[f]	*S*(b/l)[g]
dppe	2	94(24)	9	1	73	14	3	7.8
dppp	2	43(24)	12	0	78	6	4	6.2
dppb	2	75(24)	31	2	63	2	2	1.9
dppmb	2	62(24)	48	1	48	<1	3	1.0
(*R*, *R*)-diop	2	75(24)	49	0	47	1	3	1.0
bisbi	2	99(24)	17	2	77	3	1	4.3
bubiphos	2	99(17)	2	20	60	8	5	3.2
xantphos	2	64(24)	62	3	28	3	4	0.5
PPh_3	6	99(24)	6	10	73	10	1	4.4
$P(OPh^*)_3$	6	16(72)	11	0	65	5	19	6.2
$P(p\text{-}CF_3C_6H_4)_3$	3	29(24)	11	0	54	5	30	5.0

[a] Reaction conditions: 3.75×10^{-2} mmol of Rh as $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 7.5 ml of toluene; [**1**]/[Rh] = 200; [CO]/[H_2] = 1; 45 bar; 70 °C. [b] See Chart 1. [c] [Ligand]/[Rh]. [d] Conversion determined by gas chromatography for the time indicated in parentheses. [e] Other aldehydes, including **4**, **5**, **6**, **8** and **9**. [f] Products of hydrogenation of **1**. [g] Ratio between the products arising from allylic intermediate **1d** and *n*-alkyl intermediate **1b**: **(7+8+9)/(2+3+4+5+6)** (see text).

Table 2 Hydroformylation of myrcene (**1**) catalyzed by Rh/xantphos[a]

P/bar	T/°C	Con. (%) (t/h)[b]	**2** (%)	**3** (%)	**7** (%)	Ot. (%)[c]	H. (%)[d]	S(b/l)[e]
45	50	17(40)	64	0	28	0	8	0.4
45	70	64(24)	62	3	28	3	4	0.5
45	100	100(24)	11	8	13	65[f]	3	1.1
30	50	58(65)	58	1	33	0	8	0.6
30	70	95(24)	44	5	39	5	78	0.8
60	70	81(24)	63	4	27	2	4	0.4
60	100	91(20)	8	28	17	46[f]	<1	0.8

[a] Reaction conditions: 3.75×10^{-2} mmol of Rh as $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 7.5 ml of toluene; [xantphos]/[Rh] = 2; [**1**]/[Rh] = 200; [CO]/[H_2] = 1. [b] Conversion determined by gas chromatography for the time indicated in parentheses. [c] Other aldehydes, including **4**, **5**, **6**, **8** and **9**. [d] Products of hydrogenation of **1**. [e] Ratio between the products arising from allylic intermediate **1d** and *n*-alkyl intermediate **1b**: (**7** + **8** + **9**)/(**2** + **3** + **4** + **5** + **6**) (see text). [f] Mainly unidentified dialdehydes along with 6–10% of **9**.

xantphos catalyst, little effect of pressure on the reaction selectivity was observed at pressures above 45 bar. However, on raising the temperature from 70 to 100 °C, the selectivity for aldehydes **2** and **3** reduces because of the formation of several unidentified products. This effect seems to be related to the increase in the thermal flexibility of xantphos. For the Rh/dppe catalyst, the S(b/l) ratio also increases with temperature, with the yield of the products originating from the σ-alkyl intermediate being significantly lower at 100 °C. Interestingly, the Rh/PPh_3 catalyst shows the opposite effect, since the temperature increase clearly reduces the proportion of aldehydes **7** with respect to aldehydes **2** and **3**. It should be mentioned also that at a higher P/Rh ratio (15 *vs.* 6), a marked increase in the relative amounts of dialdehyde **3** at the expense of aldehydes **7** is observed, while the reaction becomes slower.

Platinum/tin catalysts

The results on the hydroformylation of myrcene with Pt/$SnCl_2$ catalysts and different P-donor ligands are collected in Table 5. The most distinctive feature of these catalytic systems is an exceptionally high regioselectivity for aldehyde **2** and its derivatives regardless of the P-donor used. Not even trace amounts of β,γ-unsaturated aldehydes **7** have been observed in platinum catalyzed reactions. The steric bulk of both the phosphine (diphosphine) and $SnCl_3^-$ ligands in the platinum complex should favor an anti-Markovnikov H addition, with the formation of less sterically crowded straight-chain σ-alkyl platinum intermediate **1b** leading to aldehyde **2**. Furthermore, the formation of η^3-allyl complexes **1d**, which further give aldehydes **7**, requires more coordination positions and seems to be also sterically disfavored in Pt/Sn/phosphine systems.

In the absence of $SnCl_2$, platinum complexes show no activity in the hydroformylation of myrcene. A synergetic effect of $SnCl_2$ and Pt(II) on hydroformylation has been thoroughly investigated.[25] A recent theoretical study proposes that the most important effect of the $[SnCl_3]^-$ ligand is to stabilize pentacoordinated Pt(II) intermediates and facilitate the olefin insertion due to weakening of the Pt–H bond *trans* to this ligand.[26] The strong *trans*-activation effect of the tin ligand favors the required ligand-exchange reactions.

The hydroformylation of myrcene in all platinum/tin systems studied is accompanied by the hydrogenation and, to a lesser extent, dimerization of the substrate. The product selectivity is strongly influenced by the nature of phosphorous ligand, the phosphine/Pt molar ratio and reaction conditions. The best selectivity was obtained with the PPh_3 ligand. For instance, at 80 °C, 45 bar and PPh_3/Pt = 4, the selectivity for aldehyde products reaches 87%. From these aldehydes, 85% corresponds to aldehyde **2**. Small amounts of aldehydes **4**, **5** and **6**, resulting from the isomerization and hydrogenation of **2**, were also observed. The structures of minor aldehydes **4**,**5** and **6** have been proposed based on GC/MS data and additionally confirmed by the isomerization (50 °C, N_2, toluene) and hydrogenation (10% Pd/C, 50 °C, H_2, 30 bar, toluene) of **2**. On raising the temperature to 100 °C, the rate increases but the chemoselectivity drops drastically due to the extensive hydrogenation and dimerization of the substrate. Surprisingly, the reaction rate and chemoselectivity virtually do not depend on the pressure. Only a slight increase in the relative amounts of minor aldehydes **4**, **5** and **6** at the expense of aldehyde **2** is observed. The best rates were observed at PPh_3/Pt = 2. At this P/Pt ratio, the reaction occurs under relatively mild conditions for Pt catalysts (45 bar, 70 °C), although the selectivity is worse than that at PPh_3/Pt = 4.

We have also tested the hydroformylation of myrcene with Pt/$SnCl_2$ in the presence of various diphosphines: dppe, dppp, dppb and naphos. All these catalysts produce exclusively aldehyde **2** and its derivatives, but they render much lower rates than that with PPh_3. The addition of diphosphines also increases the amounts of hydrogenation products, which leads to a drop in the aldehyde selectivity compared to the catalyst with PPh_3.

Conclusions

We have achieved a good control of the chemo- and regioselectivity of the hydroformylation of myrcene **1**, through the

Table 3 Hydroformylation of myrcene (**1**) catalyzed by Rh/dppe[a]

P/bar	T/°C	Con. (%) (t/h)[b]	**2** (%)	**3** (%)	**7** (%)	Ot. (%)[c]	H. (%)[d]	S(b/l)[e]
45	70	94(24)	9	1	73	14	3	7.8
45	100	96(9)	3	<1	75	19	3	30.3
30	70	39(24)	5	0	61	31[f]	3	15.2
60	70	83(24)	9	0	70	15	6	8.3

[a] Reaction conditions: 3.75×10^{-2} mmol of Rh as $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 7.5 ml of toluene; [dppe]/[Rh] = 2; [**1**]/[Rh] = 200; [CO]/[H_2] = 1. [b] Conversion determined by gas chromatography for the time indicated in parentheses. [c] Other aldehydes, including **4**, **5**, **6**, **8** and **9**. [d] Products of hydrogenation of **1**. [e] Ratio between the products arising from allylic intermediate **1d** and *n*-alkyl intermediate **1b**: (**7** + **8** + **9**)/(**2** + **3** + **4** + **5** + **6**) (see text). [f] Mainly of **8** (17%) along with other monoaldehydes.

Table 4 Hydroformylation of myrcene (**1**) catalyzed by Rh/PPh_3[a]

P/bar	T/°C	P/Rh[b]	Con. (%) (t/h)[c]	**2** (%)	**3** (%)	**7** (%)	Ot. (%)[d]	H. (%)[e]	S(b/l)[f]
45	50	6	91(24)	13	0	83	3	1	6.5
45	70	6	99(24)	6	10	73	10	1	4.4
45	100	6	99(24)	5	14	42	38[g]	21	2.7
30	70	6	98(24)	3	5	78	12	2	10.2
60	70	6	97(24)	2	5	76	16	21	10.7
45	70	15	93(40)	0	37	51	12	0	1.5

[a] Reaction conditions: 3.75×10^{-2} mmol of Rh as $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 7.5 ml of toluene; $[PPh_3]/[Rh] = 2$; $[\mathbf{1}]/[Rh] = 200$; $[CO]/[H_2] = 1$. [b] $[PPh_3]/[Rh]$. [c] Conversion determined by gas chromatography for the time indicated in parentheses. [d] Other aldehydes, including **4**, **5**, **6**, **8** and **9**. [e] Products of hydrogenation of **1**. [f] Ratio between the products arising from allylic intermediate **1d** and *n*-alkyl intermediate **1b**: **(7 + 8 + 9)/(2 + 3 + 4 + 5 + 6)** (see text). [g] Mainly unidentified dialdehydes

appropriate combination of the metal and ligands. Thus, the preferential syntheses of a mixture of *cis*- and *trans*-3-ethylidene-7-methyl-6-octenal **7a**/**7b** and 4-methylene-8-methyl-7-nonenal **2** were attained, both with 75% selectivity, with Rh and Pt/Sn, respectively. 3-Ethyl-7-methyl-2,6-octadienal **8**, useful for the synthesis of biologically active compounds,[17] and 3-ethyl-7-methyl-6-octenal **9**, previously described as the major product of myrcene hydroformylation,[7] are formed only in small amounts under our conditions. Both **8** and **9** can be, however, readily obtained from aldehydes **7**. Furthermore, unsaturated nonanals, *i.e.*, 4,8-dimethyl-4,7-nonadienal **4**, 4,8-dimethyl-3,7-nonadienal **5** and 4,8-dimethyl-7-nonenal **6**, can be prepared from aldehyde **2**. Finally, 3-(4-methyl-3-pentenyl)hexanedial **3** is also accessible through the hydroformylation of **1**, although the rate for this reaction is low.

Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated. $[Rh(\mu\text{-}OMe)(cod)]_2$,[27] $[Rh(\mu\text{-}Cl)(cod)]_2$,[28] xantphos,[19] bisbi,[29] bubiphos,[30] dppmb,[31] $P(p\text{-}CF_3C_6H_4)_3$ and $P(o\text{-}CF_3C_6H_4)_3$[32] and $P(O\text{-}o\text{-}^tBuC_6H_4)_3$[33] were prepared by published methods or by slight modifications of them. Naphos was kindly donated by Prof. B. Hanson (Virginiatech, US). Toluene was purified under reflux with sodium wire–benzophenone for 6 h and then distilled under nitrogen. Myrcene was distilled before use.

The products were analyzed by gas chromatography (GC) using Carbowax 20 M or HP-5 capillary columns and a FID. NMR spectra were obtained in $CDCl_3$ using Bruker 500, 400 and 250 MHz spectrometers, with TMS as internal standard. Mass spectra were obtained on a Hewlett-Packard (5890/Series II or G1800A) instrument operating at 70 eV and fitted with a HP-5 capillary column.

Hydroformylation experiments were carried out in home-made autoclaves with magnetic stirring. To prevent a direct contact with stainless steel, the reaction solution was kept in a glass vessel and the autoclave cap was Teflon-covered. The reaction products were separated by column chromatography (silica) using mixtures of hexane, CH_2Cl_2 and methanol as eluent. The products were identified by MS, ^1H, and ^{13}C-NMR. The assignment of ^1H and ^{13}C-NMR signals was made using bidimensional techniques.

4-Methylene-8-methyl-7-nonenal 2

$PtCl_2(PhCN)_2$ (0.05 mmol), $SnCl_2{\cdot}2H_2O$ (0.05 mmol), PPh_3 (0.20 mmol), myrcene (3.75 mmol) and toluene (7.5 ml) were transferred under nitrogen into the autoclave, which was pressurized to 45 bar total pressure ($CO/H_2 = 1/1$), placed in an oil bath (80 °C) and stirred with a magnetic stirrer. After carrying out the reaction for 48 h and cooling to room temperature, the excess CO and H_2 were slowly vented. Aldehyde **2** was separated by column chromatography (silica) using mixtures of hexane, CH_2Cl_2 and methanol as eluents and identified by GC/MS and ^1H and ^{13}C-NMR spectroscopy. GC yield 40%. MS (m/z/rel.int.): 166/1 (M^+); 133/1; 123/26; 122/18; 107/8; 69/100; 41/50. For ^1H and ^{13}C NMR data see Fig. 1.

3-(4-Methyl-3-pentenyl)hexanedial 3

This product was isolated and characterized as its 2,4-dinitrophenylhydrazone. A catalytic mixture enriched in aldehyde **3** was treated with 2,4-dinitrophenylhydrazine following a described procedure.[34] The product was recrystallized in EtOH and purified by preparative chromatography (silica) to yield an

Table 5 Hydroformylation of myrcene (**1**) catalyzed by $Pt/SnCl_2$/P-donor ligand[a]

Ligand[b]	P/Pt[c]	P/bar	T/°C	Con. (%)[d]	**2** (%)	**(4 + 5)** (%)	**6** (%)	H. (%)[e]	Ot (%)[f]	S_{al}[g]
PPh_3	2	45	70	60	66	6	7	19	2	79
PPh_3	4	45	70	20	68	9	16	7	< 1	93
PPh_3	4	45	80	55	74	7	6	7	6	87
PPh_3	4	45	100	85	43	5	6	40	6	54
PPh_3	4	80	70	18	53	17	24	6	< 1	94
PPh_3	2	60	70	60	63	6	8	23	< 1	77
PPh_3	2	80	70	52	66	8	10	15	1	84
dppe	2	45	70	28	21	6	11	62	< 1	48
dppp	2	45	70	30	32	8	13	47	< 1	53
dppb	2	45	70	28	34	7	12	47	< 1	53
naphos	4	45	80	15	54	6	21	16	3	81

[a] Reaction conditions: 5.0×10^{-2} mmol of $PtCl_2(PhCN)_2$ in 7.5 ml of toluene; $[SnCl_2{\cdot}2H_2O]/[Pt] = 1$; $[\mathbf{1}]/[Pt] = 75$; $[CO]/[H_2] = 1$. [b] See Chart 1. [c] Phosphorus to platinum atomic ratio. [d] Conversion for 48 h, determined by gas chromatography. [e] Products of hydrogenation of **1**. [f] Other products, mainly those of dimerization of **1**. [g] Selectivity for aldehydes.

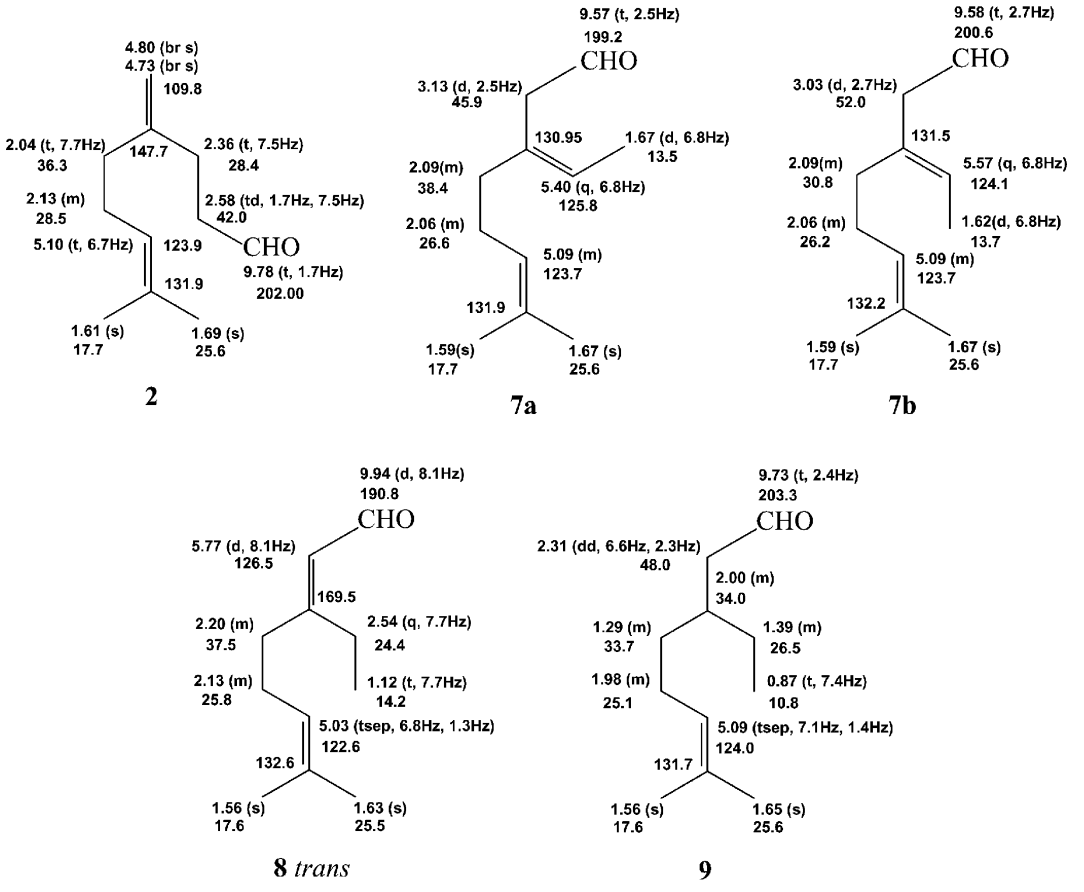
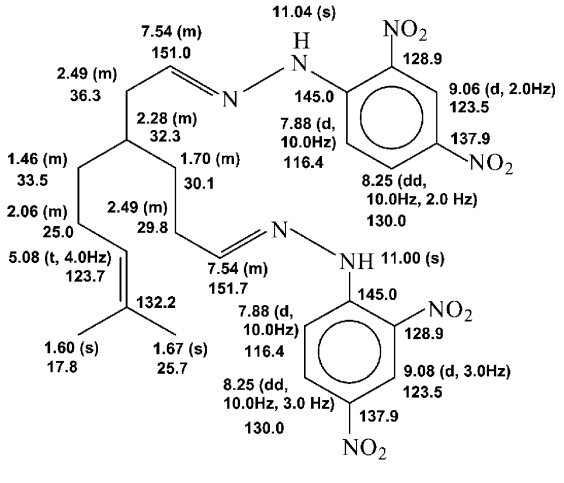


Fig. 1

orange powder, which was analyzed by ^{1}H and ^{13}C NMR. See data in Fig. 2. MS of **3** (*m*/*z*/rel.int.): 196/1 (M^{+}); 178/8; 163/8; 152/9; 135/14; 134/31; 121/23; 109/30; 95/30; 83/38; 69/100; 55/45; 41/89.

4,8-Dimethyl-4,7-nonadienal 4

MS (*m*/*z*/rel.int.): 166/4 (M^{+}); 148/7; 133/8; 122/58; 107/28; 93/32; 91/24; 81/33; 80/43; 79/100; 68/33; 67/60; 55/54; 53/32. A catalytic mixture enriched in aldehyde **2** was heated at 50 °C under N_2 for 4 h. A partial conversion of **2** into a mixture of **4** and **5** was observed by GC/MS.



2,4-dinitrophenylhydrazone of **3**

Fig. 2

4,8-Dimethyl-3,7-nonadienal 5

MS (*m*/*z*/rel.int.): 166/4 (M^{+}); 148/4; 137/22; 123/10; 109/25; 108/28; 95/30; 83/26; 69/100; 67/21; 41/76.

4,8-Dimethyl-7-nonenal 6

MS (*m*/*z*/rel.int.): 153/1 (M^{+}-CH_3); 135/1; 125/10; 109/13; 107/7; 79/10; 69/100; 68/14; 55/7; 53/8. The solution of aldehyde **2** in toluene was heated at 50 °C under H_2 (30 bar) for 12 h, in the presence of 5%Pd/C (2 wt%). A partial conversion of **2** into **6** was observed by GC/MS.

3-Ethylidene-7-methyl-6-octenal *trans* 7a and *cis* 7b

$[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ (0.02 mmol), PPh_3 (0.24 mmol), myrcene (7.50 mmol) and toluene (7.5 ml) were transferred under nitrogen into the autoclave, which was pressurized to 45 bar total pressure ($CO/H_2 = 1/1$), placed in an oil bath (70 °C) and stirred with a magnetic stirrer. After carrying out the reaction for 24 h and cooling to room temperature, the excess CO and H_2 were slowly vented. Aldehydes **7a** and **7b** were separated as a mixture (≈1/1) by column chromatography (silica) using mixtures of hexane, CH_2Cl_2 and methanol as eluents and identified by GC/MS and ^{1}H and ^{13}C-NMR spectroscopy. GC combined yield 72%. **7a**: MS (*m*/*z*/rel.int.): 166/5 (M^{+}); 151/8; 123/17; 122/18; 107/2; 95/4; 81/3; 69/100; 67/8; 53/6; 41/46. **7b**: MS (*m*/*z*/rel.int.): 166/3 (M^{+}); 151/8; 123/15; 122/22; 107/3; 95/4; 81/3; 69/100; 67/8; 53/6; 41/46. For ^{1}H and ^{13}C NMR data see Fig. 1.

3-Ethyl-7-methyl-2,6-octadienal 8

A solution was prepared with 1.0 g of a mixture of aldehydes **7a** and **7b** (6.00 mmol), 9.0 mg of [Rh(μ-OMe)(cod)] (0.02 mmol) and 64.0 mg of PPh_3 (0.24 mmol) in 10 ml of toluene. The mixture was heated at 70 °C. The reaction evolution was followed by GC. After 6–8 h, a nearly complete conversion was obtained. The oily product was purified by distillation in a kugelrohr apparatus at 75 °C (1 mm of Hg). Yield 75%. MS (*m*/*z*/rel.int.): 166/4 (M^+); 151/4; 137/16; 123/7; 108/14; 95/11; 98/16; 83/19; 69/100; 41/57. Aldehyde **8** is obtained as a mixture of *trans* and *cis* isomers (88% *trans*/12% *cis*) as shown by NOESY experiments. For ^1H and ^{13}C NMR data for the major (*trans*) isomer see Fig. 1.

3-Ethyl-7-methyl-6-octenal 9

An autoclave was charged with 0.50 g of aldehyde **8**, 9.0 mg of [Rh(μ-OMe)(cod)] (0.02 mmol) and 64.0 mg of PPh_3 (0.24 mmol) dissolved in 7.5 ml of toluene. The autoclave was closed and pressurized with 15 bar of H_2 at 60 °C. After 4 h, the gas pressure was released and the product was purified by distillation in a kugelrohr apparatus at 77 °C (1 mm of Hg). Yield 90%. MS (*m*/*z*/rel.int.): 168/7 (M^+); 153/7; 150/8; 125/21; 121/26; 95/63; 83/47; 69/100; 67/32; 55/50; 41/80. For ^1H and ^{13}C NMR data see Fig. 1.

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