New $[Ru_3(CO)_{12}]$-Based Catalysts with Imidazolinium Salt, Diimine, or Bis(oxazoline) Ligands and Ruthenium Bis(oxazoline) Complex for Tandem Isomerisation/Claisen Rearrangement of Dienyl Ethers − X-ray Structure of [RuCl{(*R*,*R*)-bis(isopropyloxazoline)}(*p*-cymene)]BF_4

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The reaction of various 1,7-dienes in the presence of the three-component catalyst **A**: $[Ru_3(CO)_{12}]$/imidazolinium salt/Cs_2CO_3 (1:1:2) leads to the tandem alkene isomerisation/Claisen rearrangement affording γ,δ-unsaturated aldehydes. Other three component catalysts: $[Ru_3(CO)_{12}]$/diimine/Cs_2CO_3 and $[Ru_3(CO)_{12}]$/benzoxazoline or chiral bis(oxazoline)/Cs_2CO_3 offer new active catalytic systems for these tandem reactions. Two ruthenium complexes containing optically active bis(oxazoline), [RuCl{(*R*,*R*)-bis(oxazoline)}(*p*-cymene)]BF_4, were prepared and the X-ray structure of one of them (**18**) was established. The combination of chiral **18**/imidazolinium salt/Cs_2CO_3 (1:1:2) catalysed the above reaction of 1,6-dienes and the results suggest initial catalytic isomerisation followed by a thermal Claisen rearrangement.

Introduction

The [3,3]-sigmatropic rearrangement of allyl vinyl ethers constitutes a powerful method for accessing γ,δ-unsaturated aldehydes[1] since its discovery by Claisen.[2] This reaction is often limited by the difficulty of introducing the vinyl ether group. The most general routes to vinyl ethers involve organometallic intermediates or acid-catalysed reactions.[3] An alternative method is emerging. It is based on selective isomerisation of allyl groups into vinyl heteroatom intermediates. Ruthenium complexes, such as ruthenium hydride[4] or ruthenium carbonyl[5] derivatives have been used for selective alkene isomerisation. This isomerisation process was also applied to enantioselective catalysis.[6] Recently alkene metathesis ruthenium catalysts have shown a propensity to isomerise alkenes, but leading to competition between isomerisation and metathesis.[7,8]

The $[RuCl_2(PPh_3)_3]$-catalysed Claisen rearrangement of diallyl ethers occur at a high temperature (150 °C),[9] whereas selected iridium[10] and rhodium[11] complexes tend to promote this transformation under milder conditions. It is worth noting that an indenylidene ruthenium catalyst has performed ring closing metathesis (RCM), isomerisation and a Claisen rearrangement, successively.[8]

By contrast we found that ruthenium catalysts prepared in situ for the RCM of 1,6-dienes and 1,6-enynes[12−14] did not perform RCM of 1,7-dienyl ethers but selectively led to tandem isomerisation/Claisen rearrangement affording γ,δ-unsaturated aldehydes[15] [Equation (1)]. The in situ generated catalyst, was originally prepared with $[RuCl_2(p\text{-cymene})]_2$ as a ruthenium source,[12] but the combination of $[Ru_3(CO)_{12}]$, with an imidazolinium salt appeared to be more efficient as reported in our preliminary communication.[15]

(1)

We now wish to report (i) the detailed study of in situ prepared catalysts for isomerisation/Claisen rearrangement of 1,7- and 1,6-dienyl ethers into γ,δ-unsaturated aldehydes, (ii) we show that new $[Ru_3(CO)_{12}]$-based catalysts containing sterically hindered diimine or the bis(oxazoline) ligand, and bis(oxazoline)ruthenium complex as the ruthenium source and imidazolinium salt in the presence of Cs_2CO_3, are active catalysts for these tandem catalytic reactions. (iii) The synthesis of new chiral bis(oxazoline)ruthenium arene derivatives, used as catalyst precursors, is described with the X-ray structure of one of them.

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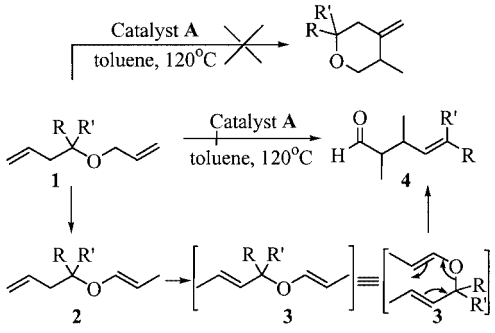
Results and Discussion

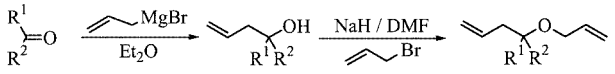
1. Catalytic Reaction Principle and Influence Factors

Recently, in a preliminary study[15] it was revealed that the in situ prepared three-component catalyst for the ring closing metathesis (RCM) reaction of 1,6-dienes and 1,6-enynes: $[RuCl_2(p\text{-cymene})]_2$/a hindered imidazolinium chloride/Cs_2CO_3, when applied to allyl homoallyl ethers with a 1,7-diene structure, the latter were catalytically transformed into γ,δ-unsaturated aldehydes rather than the expected RCM six-membered cyclic compounds. The new three-component system consisting of **A** = $[Ru_3(CO)_{12}]$, 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride, and cesium carbonate appeared to be the most active catalyst for this transformation of 1,7-dienes **1** into unsaturated aldehydes **4** (Scheme 1). The reaction takes place via a double C=C isomerisation of allyl and homoallyl branches via the intermediates **2** and **3**, followed by a Claisen rearrangement to give **4**.



Scheme 1

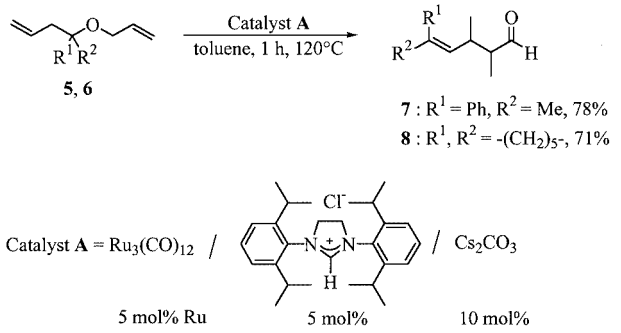
The use of the three-component catalytic system **A** has now been applied to the selective transformation of various 1,7-dienes. The etherated dienes **5** and **6** were easily prepared from the corresponding ketones, in two steps, by addition of allylmagnesium bromide, followed by allylation of the corresponding homoallyl alcohols (Scheme 2).



5 : R^1 = Ph, R^2 = Me, 57%
6 : R^1, R^2 = -$(CH_2)_5$-, 82%

Scheme 2

In the presence of the catalytic system **A** based on $[Ru_3(CO)_{12}]$ (1.67 mol %, that is 5 mol % of ruthenium atoms), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (5 mol %) and cesium carbonate (10 mol %) in toluene, these dienes have been totally converted into their corresponding γ,δ-unsaturated aldehydes after 1 hour at 120 °C (Scheme 3). The aldehydes **7** and **8** were obtained in 78% and 71% yield, respectively, as a mixture of diastereoisomers due to the formation of stereogenic centres, and their



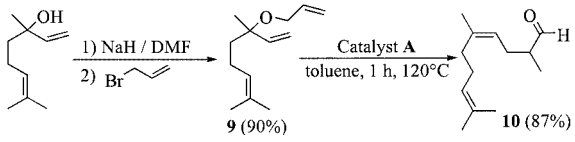
Scheme 3

NMR spectroscopic analyses were in accordance with those in the literature.[10b]

The absence of one of the three components of the catalytic system A gave no conversion, not even isomerisation. This observed reaction indicates that the isomerisation of the terminal alkene branches is faster than the RCM and cycloisomerisation reactions leading to six-membered rings. The RCM involving disubstituted C=C bonds is known to be disfavoured, thus in that case, after isomerisation no competition occurs between isomerisation and metathesis, and hence high selectivity in aldehyde formation is observed.

It is noteworthy that the above in situ generated ruthenium catalyst **A** selectively isomerises terminal alkene branches, by displacing the C=C bond towards the heteroatom, to produce a vinyl ether group.

The influence of the catalyst concentration and temperature has been investigated. This study was performed on the 1,6-diene **9** which is more easily transformed into the corresponding γ,δ-unsaturated aldehyde **10**, than the dienes **5** and **6**. It involves one simple allyl to vinyl isomerisation followed by a Claisen rearrangement (Scheme 4).



Scheme 4

The commercially available linalol was first converted by allylation in 90% yield to the 1,6-diene **9**. In the presence of the catalytic system **A,** using 5 mol % of ruthenium, this diene was transformed into the aldehyde **10**[16] at various temperatures. The transformation of **9** into aldehyde **10** was very slow at 60 °C, it reached completion at 80 °C for 3 h and alternatively within 1 h at 120 °C (see Table l).

A minimum temperature of 80 °C was required to reach completion (Table 1). By performing the transformation at 80 °C, but varying the diene/catalyst ratio, it was observed that decreasing this ratio under 5 mol % (3%, 0.5%) led to longer reaction times (Entries 3,5,6). Thus, for further tandem isomerisation/Claisen reaction of unsaturated ethers, 5 mol % of ruthenium catalyst was used between 80 °C and

Table 1. Influence of temperature, time and ruthenium loading on the transformation **9** → **10**

Entry	Mol-% [Ru]	Temp. (°C)	Reaction time (h)	Conversion (%)
1	5	40	16	0
2	5	60	16	22
3	5	80	3	100
4	5	120	1	100
5	3	80	60	80
6	0.5	80	96	20

120 °C, and a reaction time of 1−3 h was expected according to the nature of the substrate.

2. Use of Dinitrogen Chelating Ligands in Ruthenium Catalyst Precursors

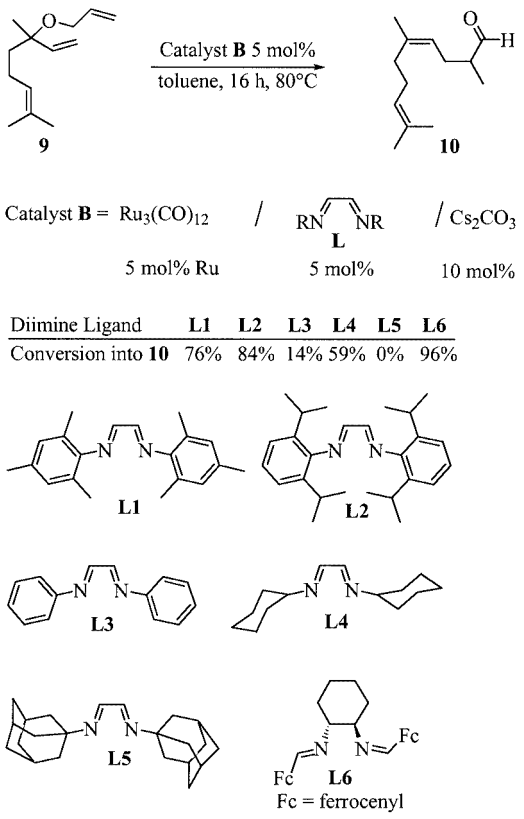
With the objective of finding new efficient catalysts for the above tandem catalytic reactions several catalytic modifications were investigated. Since well-defined chelating dinitrogen containing ruthenium complexes of type [RuCl{bis(oxazoline)}(arene)]$^+$ X^- have already shown some activity for this reaction,[17] we have explored the catalyst modification based on [$Ru_3(CO)_{12}$], as a ruthenium source, by replacing the bulky imidazolinylidene precursor by a sterically hindered diimine or bis(oxazoline)ligand.

2.1 Diimine Ruthenium Precursors

Catalyst **B** was generated in situ by a combination of [$Ru_3(CO)_{12}$] (5 mol % of Ru atoms), diimine **L** (5 mol %) and Cs_2CO_3 (10 mol %) and was evaluated on the transformation of the diene **9** into the aldehyde **10** in toluene at 80 °C and the conversions were monitored using proton NMR spectroscopy by measuring the **10/9** ratio (Scheme 5). Several diimines **L1**−**L6**[18] containing bulky R groups were evaluated.

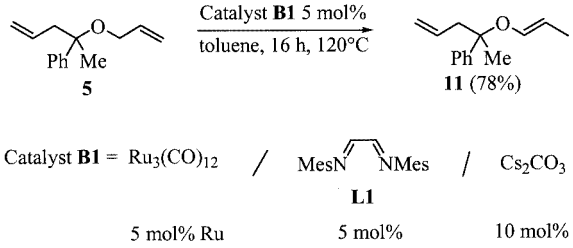
The results show that the diimines lead to an in situ generated catalyst performing the tandem reactions at 80 °C for 16 h. The nature of the diimine drastically influences the catalytic activity. The diimines $\mathbf{L_6}$ (96%) $\mathbf{L_2}$ (84%) and $\mathbf{L_1}$ (76%) offer the best catalyst efficiencies. Especially when the reaction is performed at 120 °C, the ferrocenyl containing diimine $\mathbf{L_6}$ leads to the best activity and the corresponding catalyst **B** completely converts **9** into **10** within 6 hours.

However, the resulting catalyst **B** requires a longer reaction time to reach suitable conversion into aldehyde **10** than catalyst **A**; catalyst **B** requires 16 h at 80 °C with the most activating diimine. These results indicate that the preliminary catalytic alkene isomerisation and the overall tandem reaction are not at all restricted to imidazolinium ruthenium intermediates. Moreover they show that the presence of cesium carbonate does allow the reaction to proceed. Cs_2CO_3 was originally used for the deprotonation of the imidazolinium salt to generate an imidazolinylidene ligand. In the absence of Cs_2CO_3 in catalyst **B** no isomerisation takes place. Although its role is not elucidated, cesium carbonate thus has a crucial influence on the ruthenium-catalysed isomerisation reaction.



Scheme 5

It is noteworthy that profit can be taken from the slightly lower catalytic activity of catalyst **B** to perform the selective isomerisation without Claisen rearrangement. The isomerisation of the diene **5**, containing a phenyl and methyl groups at the homoallylic position, is more difficult to perform than that of **9**. The reaction of **5** with catalyst **B,** containing the $\mathbf{L_1}$ diimine, in toluene, at 120 °C for 16 h does not afford the expected unsaturated aldehyde **7** but is completely transformed into the vinyl homoallyl ether **11** resulting simply from the allyl to vinyl isomerisation (Scheme 6). Thus, the phenyl group inhibits the homoallyl to allyl isomerisation with catalyst **B** that readily takes place with catalyst **A** (Scheme 3). This experiment shows that the *O*-allyl branch of the 1,7-diene **1** is first isomerised to give an intermediate of type **2** and that the ease of the second isomerisation further controls the Claisen rearrangement. It also reveals the interest of less active catalysts to perform only one reaction step.

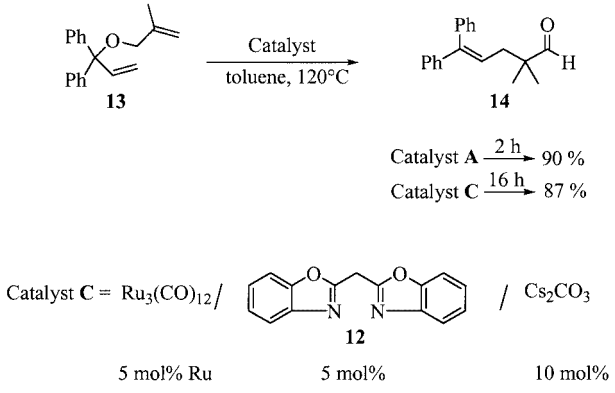


Scheme 6

The large influence of the nature of the ligand on catalyst activity and the ease of generating these catalysts in situ suggest that the association of various ruthenium sources with various ligands, should be investigated to reveal new active catalysts.

2.2 Bis(oxazoline) Ruthenium Precursors

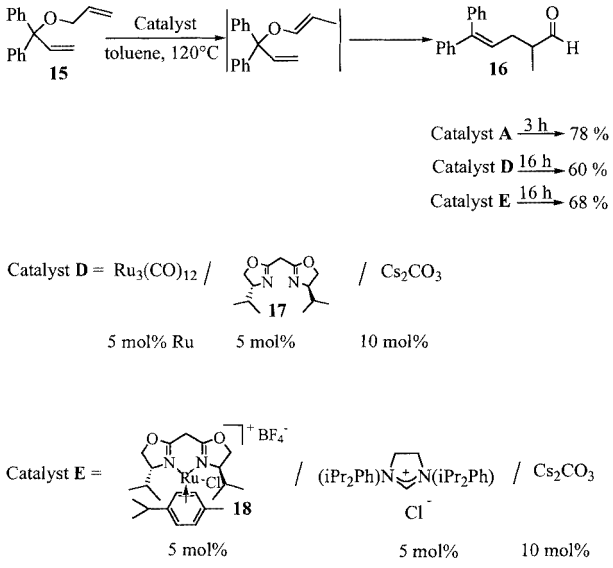
Achiral or chiral bis(oxazolines) are commonly used as chelating nitrogen ligands in catalysis nowadays,[19] because they are easily prepared and have been shown to significantly modify the catalytic metal site with respect to phosphane or carbene ligands.[20] Thus, catalyst **C** analogous to catalyst **B**, by replacing the diimine **L** by the benzoxazoline derivative **12**,[21] has been evaluated for the transformation of 1,6-diene **13** into aldehyde **14** (Scheme 9). The results show that the bis(oxazoline)ligand **12** associated with $[Ru_3(CO)_{12}]$ in the presence of Cs_2CO_3 promotes the tandem reactions with an activity analogous to that of the most active diimine-containing catalysts. The efficiency of catalyst **C** is analogous to that of catalyst **B**, as the transformation was complete after 16 h at 120 °C and led to the isolation of 87% of aldehyde **14**[22] (Scheme 7).



Scheme 7

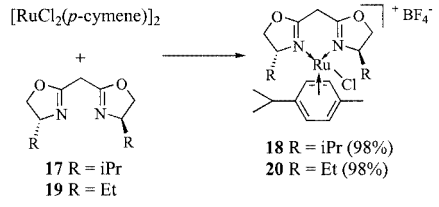
An advantage to generating a catalyst in situ, from a metal source and a ligand, is related to the easy access of the chiral version of the catalyst. Catalysts of type **C** could thus easily be transformed into chiral catalysts using an optically active bis(oxazoline). The transformation of the 1,6-diene **15** into the aldehyde **16**, containing only one chiral centre, was first considered.

The interest in using a chiral catalyst was to investigate whether, after isomerisation, the Claisen step leading to the creation of a chiral centre, was influenced by the catalyst or essentially a thermal process. An enantiomeric excess is expected to be observed in the first process and not in the second. The achiral catalyst **A** performed the tandem reaction at 120 °C, and after 3 h the racemic aldehyde **16** was isolated (78%) (Scheme 8). Then catalyst **C** was modified into catalyst **D** by the introduction of the optically active (*R*,*R*)-bis(oxazoline)**17**,[19] instead of **12**. Catalyst **D** gave an activity similar to that of catalyst **C** and afforded 60% of aldehyde **16**. The isolated aldehyde **16** *showed no enantiomeric excess,* thus indicating that the chiral catalyst **D** gave no stereochemical induction, unless the racemization of the aldehyde takes place (Scheme 8).



Scheme 8

The bis(oxazoline) **17** was then used to prepare a well-defined ruthenium(II) (arene) complex according to the procedure we previously used for *achiral* bis(oxazoline)ruthenium complexes.[17] Two equiv. of the bis(oxazoline) **17** were reacted with the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ in methanol at room temperature with two equiv. of NH_4BF_4 and the orange complex **18** was isolated in 98% yield (Scheme 9). Analogously, the optically active bis(oxazoline) **19**[19f] led to the ruthenium complex **20.**



Scheme 9

Complex **18** does not catalyse the **15** → **16** transformation, even in the presence of two equiv. of Cs_2CO_3. By contrast complex **18** with one equiv. of imidazolinium salt and two equiv. of Cs_2CO_3 (Catalyst **E**), allowed the transformation of **15** into **16**, isolated in 68% yield after 1 h at 120 °C (Scheme 8). It is worth noting that with the well-defined chiral ruthenium complex **18**, the resulting aldehyde **16,** did not exhibit an enantiomeric excess.

The above results show that a bis(oxazoline) associated with $[Ru_3(CO)_{12}]$ and a bis(oxazoline)ruthenium complex associated with an imidazolinium salt performed the isomerisation of 1,6-dienes, in the presence of Cs_2CO_3. But no enantiomeric excess was observed when a chiral centre was formed in the presence of an optically active catalytic species. This suggests that the ruthenium complex, associated with Cs_2CO_3, plays an isomerisation catalyst role and when the required 1,5-diene is formed in situ, a thermal Claisen

rearrangement takes place, unless the imidazolylidene ligand displaces the chiral ligand from the ruthenium site.

3. Crystal Structure of Complex 18

The structure of these bis(oxazoline)ruthenium complexes is confirmed by the crystal structure of the complex **18**. The ORTEP is presented in Figure 1 and the principal bond lengths and angles are reported in Table 2. The crystal data and structure refinement are gathered in Table 3.

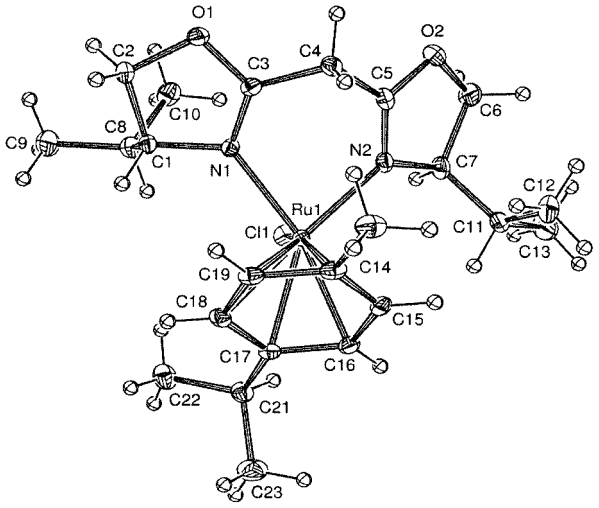


Figure 1. X-ray structure of complex **18**

Table 2. Selected bond lengths and angles

Bond lengths	Å	Angles	°
Ru(1)−N(2)	2.129(2)	C(3)−C(4)−C(5)	110.9(2)
Ru(1)−N(1)	2.130(2)	N(1)−C(3)−C(4)	125.8(2)
N(1)−C(3)	1.285(4)	N(2)−C(5)−C(4)	126.2(2)
N(2)−C(5)	1.279(4)		

The structure shows the chirality of the complex with a classical piano stool geometry. This structure reveals that the bis(oxazoline) ligand presents only slight distortions due to the coordination to the metal centre. Indeed, the C(3)−C(4)−C(5) angle of 110.9° is close to the expected value for an sp^3 carbon atom and the N(1)−C(3)−C(4) and N(2)−C(5)−C(4) angles (125.8(2) and 162.2(2)°) correspond to the value of an sp^2 carbon atom. The two oxazoline rings are nearly in the same plane and the distortion between the two planes is around 10°. The ruthenium-nitrogen bonds have similar distances to those of related complexes.[23]

Conclusion

The above results show that tandem isomerisation/Claisen reactions of etherated 1,7-dienes and 1,6-dienes are catalysed by in situ prepared ruthenium catalysts to selectively produce γ,δ-unsaturated aldehydes. The best catalyst appears to consist of the combination of [$Ru_3(CO)_{12}$], an imidazolinium salt that is a bulky heterocyclic carbene precursor and Cs_2CO_3. However the combination of [$Ru_3(CO)_{12}$], a bulky diimine or bis(benzoxazoline) ligand, in the presence of Cs_2CO_3 results in a slightly less efficient catalyst, which is still able to operate at 80 °C. The use of the optically active bis(oxazoline) ligand or complex in the formation of a chiral centre, in the unsaturated aldehyde product, gave no enantiomeric excess, and thus there is no evidence that the Claisen rearrangement step is also catalysed by the chiral ruthenium catalyst under these conditions. The ease of in situ preparation of such catalysts from a ruthenium source and a variety of ligands open the route to the use of high throughput experiment tools to discover new or more efficient catalysts.

Table 3. Crystal data and structure refinement of **18**·$(CH_3)_2CO$

Chemical formula[a]	$RuC_{23}H_{36}BClO_2$, BF_4, C_3H_6O
Formula mass	653.95
Wavelength (Å)	0.71073
T (K)	120(1)
Crystal size (mm)	0.25 × 0.22 × 0.12
Crystal system	orthorhombic
a (Å)	10.9218(2)
b (Å)	13.6861(2)
c (Å)	19.8514(4)
V (Å^3)	2967.3(9)
Z	4
$D_{calcd.}$ (mg m^{-3})	1.464
μ (mm^{-1})	0.673
F(000)	1352
2Θ range (deg)	1.0−27.48
No. of reflections collected	23815
No. of indep. reflections	6792
R_{int}	0.038
Refined method	full-matrix least-square on F^2
Refined parameters	344
Goodness of fit on F^2	1.097
Final R indices [$I > 2\sigma(I)$]	
$R1$[a], $wR2$[b]	0.0312, 0.0682
(all data)	0.0388, 0.0724
Largest diff. peak/hole (e·Å^{-3})	1.136/−0.503

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Experimental Section

General Experimental Procedures: All experiments were carried out in Schlenk tubes under nitrogen. Diethyl ether and tetrahydrofuran were dried by refluxing over sodium/benzophenone under argon, while toluene was dried with sodium, and dichloromethane was purified over calcium hydride. Methanol was used without further purification and degassed before use.

^1H and ^{13}C NMR spectra were recorded with a Bruker AC 200 MHz spectrometer. GC-MS were performed with a CE Instrument GC 8000 Top (capillary column OV1, 25 m × 0.35 mm, 0.1−0.15 μm) chromatograph linked to an Automass II Finnigan MAT (70 eV) apparatus. Infra-red spectra were recorded in KBr pellets using a Nicolet 205 FT-IR. UV/Visible spectra were recorded with a KONTRON UVIKON 941 spectrometer in diluted dichloromethane (*ca*, 10^{-4} mol·L^{-1}). Microanalyses were performed by the Service Central d'Analyses du CNRS (Vernaison, France).

General Procedures. Procedure A − Synthesis of the Homoallylic Alcohols via Allylmagnesium Addition to a Ketone: In a two-necked flask under nitrogen, equipped with a reflux condenser, magnesium turnings (2 equiv.) were heated under vacuum for 5 minutes by means of a heat gun. After cooling to room temperature, diethyl ether (1 mL per 2 mmol of magnesium) was added. Allyl bromide (1.2 equiv.) was then slowly added to the vigorously stirred mixture and the flask was introduced into an ice bath as soon as the diethyl ether ebullition started. After the addition was complete the reaction mixture was stirred for 1 h at 0 °C. The ketone (1 equiv.) was then added dropwise in diethyl ether (1 mL per 3 mmol of ketone). The reaction mixture was stirred for 30 minutes at 0 °C, followed by 4 h at room temperature. After addition of a 1 N HCl solution and extraction with diethyl ether, the corresponding homoallylic alcohol was obtained and used without purification.

Procedure B − Alcohol Allylation Reaction: Sodium hydride (1.2 equiv.) and dry dimethylformamide (1.5 mL per mmol of alcohol) were introduced into a Schlenk tube under nitrogen. The alcohol (1 equiv.) in dimethylformamide (1 mL per mmol of alcohol) was slowly added at 0 °C. After 30 minutes, allyl bromide (1.3 equiv.) was added dropwise and the stirring was continued at 0 °C for 30 minutes and at room temperature for 4 h. After hydrolysis extraction with diethyl ether and drying over $MgSO_4$, the crude product was then purified by flash chromatography over silica gel using a low polar mixture of diethyl ether and heptane.

Procedure C − Synthesis of the Allylic Alcohols via Vinylation of Aldehydes and Ketones: A Schlenk tube under nitrogen containing anhydrous $CeCl_3$ (0.1 equiv.) was first heated at 150 °C for 5 minutes and then cooled down to room temperature. Tetrahydrofuran (2 mL per mmol of ketone or aldehyde) was introduced followed by the ketone or the aldehyde (1 equiv.) and the reaction mixture was stirred at room temperature for 30 minutes. After cooling to 0 °C, vinylmagnesium bromide (1.0 M solution in tetrahydrofuran, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature 16 h. After quenching by slow addition of a 1 N HCl solution and extraction with diethyl ether, the corresponding allylic alcohol was obtained and used in the following step without purification.

Procedure D − General Procedure using the $[Ru_3(CO)_{12}]$-Based Catalyst for Tandem Isomerisation/Claisen Reaction: $[Ru_3(CO)_{12}]$ (5/3 mol % = 5 mol % of Ru atoms), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (5 mol %), cesium carbonate (10 mol %) and toluene (7.5 mL per mmol of diene) were introduced into a Schlenk tube under nitrogen. The reaction mixture was stirred for 5 minutes at room temperature and the diene was then added. After 1 hour of heating at 120 °C, the solvent was removed under reduced pressure and the crude product was extracted with heptane, filtered and the solvents evaporated to dryness. After chromatography on silica using a mixture of diethyl ether/heptane as eluent and/or bubble-to-bubble distillation the corresponding aldehyde was isolated as a colourless oil as a mixture of diastereoisomers.

Preparation of the 1,7-Dienes

2-Allyloxy-2-phenylpent-4-ene (5):[10b]

Following Procedure A: Allyl bromide (1.92 mL, 20.6 mmol) was added to a solution of magnesium turnings (0.83 g, 34.2 mmol) in diethyl ether (15 mL). Acetophenone (2.0 mL, 17.3 mmol) in diethyl ether (6 mL) was then added. Subsequent treatment gave the corresponding homoallylic alcohol as a yellow oil, which was used without purification for the next step.

Following Procedure B: Homoallylic alcohol (17.3 mmol) in dimethylformamide (17 mL) was added to a solution of sodium hydride (60% in mineral oil, 0.82 g, 20.6 mmol) in of dimethylformamide (30 mL). After addition of allyl bromide (2.0 mL, 22.5 mmol) and subsequent treatment, the crude was purified by flash chromatography over silica gel using diethyl ether/heptane (1:40) as eluent to afford the corresponding 1,7-diene **5** as a colourless oil (2.01 g, 57% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.53 (s, 3 H, CH_3), 2.53−2.64 [m, 2 H, CH_2C(Ph)(Me)OR], 3.61−3.85 (m, 2 H, OCH_2CH=CH$_2$), 4.94−5.45 [m, 4 H, 2 × (CH=CH_2)], 5.58−5.98 [m, 2 H, 2 × (CH=CH$_2$)], 7.20−7.48 (m, 5 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.5 (CH_3), 47.9 [CH$_2$C(Ph)(Me)OR], 63.9 (OCH$_2$CH=CH$_2$), 78.9 [C(Ph)(Me)], 115.6 (OCH$_2$CH=CH$_2$), 117.7 [C(Ph)(Me)CH$_2$CH=CH$_2$], 126.3, 127.1, 128.3 (CH arom.), 134.3 (OCH$_2$$C$H=CH$_2$), 135.7 [C(Ph)(Me)CH$_2$$C$H=CH$_2$], 145.1 (C arom.) ppm. MS (EI): *m*/*z* (%) = 202 (<1) $[M]^+$, 161 (35), 143 (11), 129 (52), 115 (25), 105 (15), 103 (18), 91 (19), 77 (48), 65 (15), 63 (15), 57 (15), 51 (35), 43 (100), 41 (56).

1-Allyl-1-allyloxycyclohexane (6):[10b]

Following Procedure A: Allyl bromide (0.96 mL, 10.3 mmol) was added to a solution of magnesium turnings (0.42 g, 17.1 mmol) in diethyl ether (10 mL). Cyclohexanone (0.9 mL, 8.6 mmol) in diethyl ether (3 mL) was then added. Subsequent treatment gave the corresponding homoallylic alcohol as a yellow oil, which was used without purification for the next step.

Following Procedure B: Homoallylic alcohol (8.6 mmol) in dimethylformamide (9 mL) was added to a solution of sodium hydride (60% in mineral oil, 0.41 g, 10.3 mmol) in dimethylformamide (15 mL). After addition of allyl bromide (1.0 mL, 11.3 mmol) and subsequent treatment, the crude was purified by flash chromatography over silica gel using diethyl ether/heptane (1:40) as eluent to afford the corresponding 1,7-diene **6** as a colourless oil (1.32 g, 85% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.61−1.79 (m, 10 H, 5 × CH_2), 2.31−2.43 [m, 2 H, CH_2C(Cy)OR], 3.85−3.91 (m, 2 H, OCH_2CH=CH$_2$), 4.95−5.34[m, 4 H, 2 × (CH=CH_2)], 5.55−6.02 [m, 2 H, 2 × (CH=CH$_2$)] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.0 (2 × *m*-CH_2 of Cy), 26.7 (*p*-CH_2 of Cy), 34.5 (2 × *o*-CH_2 of Cy), 51.2 [CH$_2$C(Cy)OR], 61.3 (OCH$_2$CH=CH$_2$), 74.8 [C(Cy)], 114.6 (OCH$_2$CH=CH$_2$), 116.9 [C(Cy)CH$_2$CH=CH$_2$], 134.3 (OCH$_2$$C$H=CH$_2$), 136.9 [C(Cy)CH$_2$$C$H=CH$_2$] ppm. MS (EI): *m*/*z* (%) = 180 (<1) $[M]^+$, 147 (14), 133 (24), 119 (11), 105 (12), 93 (26), 91 (31), 79 (58), 77 (29), 67 (40), 65 (19), 55 (19), 53 (25), 41 (100), 39 (44).

Tandem Isomerisation/Claisen Rearrangement Reactions

2,3-Dimethyl-5-phenylhex-4-enal (7):[10b]

Following Procedure D: $[Ru_3(CO)_{12}]$ (26.3 mg, 5 mol % of ruthenium), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (52.7 mg, 5 mol %), Cs_2CO_3 (80.5 mg, 10 mol %), toluene (25 mL) and diene **5** (0.5 g, 2.47 mmol) were stirred at 120 °C for 1 h. After treatment and distillation, the aldehyde **7** was obtained as a colourless oil as a mixture of diastereoisomers (0.39 g, 78% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.08−1.19 [m, 6 H, 2 × [CH(CH_3)], 2.07 [s, 3 H, (CH_3)(Ph)C=CH], 2.28−2.43 [m, 1 H, CH(CH$_3$)CH-(CH$_3$)CHO], 2.89−3.05 [m, 1 H, CH(CH$_3$)CH(CH$_3$)CHO], 5.52−5.66 [m, 1 H, (CH$_3$)(Ph)C=CH)], 7.22−7.39 (m, 5 H, Ph), 9.40−9.70 (m, 1 H, CHO) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.2 [CH(CH$_3$)CHO], 16.3 [CH(CH$_3$)CH(CH$_3$)CHO], 18.9 [(CH$_3$)-(Ph)C=CH], 34.0 [CH(CH$_3$)CH(CH$_3$)CH], 52.3 [CH(CH$_3$)CH-(CH$_3$)CH], 125.7, 126.9, 128.2 (CH arom.), 130.2 [(CH$_3$)(Ph)C=C], 136.2 [(CH$_3$)(Ph)C=CH], 143.5 (C arom.), 205.2 (CHO) ppm.

MS (EI): *m*/*z* (%) = 202 (8) $[M]^+$, 145 (64), 143 (12), 131 (12), 129 (30), 118 (100), 117 (52), 115 (34), 91 (65), 79 (13), 77 (44), 65 (22), 63 (13), 53 (13), 51 (26), 41 (35), 39 (31).

4-Cyclohexylidene-2,3-dimethylbutyraldehyde (8):[10b]

Following Procedure D: [$Ru_3(CO)_{12}$] (26.3 mg, 5mol % of ruthenium), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (52.7 mg, 5 mol %), Cs_2CO_3 (80.5 mg, 10 mol %), toluene (25 mL) and diene **6** (0.45 g, 2.47 mmol) were stirred at 120 °C for 1 h. After treatment and distillation, the aldehyde **8** (0.32 g, 71% yield) was obtained as a colourless oil as a mixture of diastereoisomers. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91−1.10 [m, 6 H, CH(C*H*$_3$)-CH(C*H*$_3$)CHO], 1.40−1.85 (m, 10 H, 5 × C*H*$_2$), 2.25−2.50 [m, 1 H, CH(CH$_3$)C*H*(CH$_3$)CHO], 2.62−2.82 [m, 1 H, C*H*(CH$_3$)-CH(CH$_3$)CHO], 5.69−5.91 [m, 1 H, (Cy)C=C*H*], 9.55−9.60 (m, 1 H, C*H*O) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.1 [CH(*C*H$_3$)CHO], 17.3 [CH(*C*H$_3$)CH(CH$_3$)CHO], 22.8 (2 × *m*-*C*H$_2$ of Cy), 26.2 (*p*-*C*H$_2$ of Cy), 33.2 [*C*H(CH$_3$)CH(CH$_3$)CHO], 33.5 [(*E*)-*o*-*C*H$_2$ of Cy], 41.2 [(*Z*)-*o*-*C*H$_2$ of Cy], 52.3 [CH(CH$_3$)*C*H(CH$_3$)CH], 123.7 [(Cy)C=*C*H], 140.5 [(Cy)*C*=CH], 205.7 (*C*HO) ppm. MS (EI): *m*/*z* (%) = 180 (1) $[M]^+$, 162 (10), 81 (74), 79 (26), 77 (21), 69 (17), 67 (69), 65 (15), 55 (100), 53 (31), 51 (11), 43 (16), 41 (92), 39 (43).

Preparation of the 1,6-Dienes

3-Allyloxy-3,7-dimethylocta-1,6-diene (9):

Following Procedure B: Linalol (6.5 mmol) in dimethylformamide (7 mL) was added to a solution of sodium hydride (60% in mineral oil, 0.31 g, 7.8 mmol) in dimethylformamide (15 mL). After addition of allyl bromide (0.73 mL, 8.4 mmol) and subsequent treatment, the crude was purified by flash chromatography over silica gel using diethyl ether/heptane (1:30) as eluent to afford the corresponding 1,6-diene **9** (1.13 g, 90% yield) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22 (s, 3 H, C*H*$_3$), 1.49−1.58 [m, 5 H, CH$_2$C*H*$_2$CH=C(CH$_3$)$_2$, (*E*) CH$_2$CH$_2$CH=C(C*H*$_3$)$_2$], 1.63−1.69 [m, 3 H, (*Z*) CH$_2$CH$_2$CH=C(C*H*$_3$)$_2$], 1.92−2.05 [m, 2 H, C*H*$_2$CH$_2$CH=C(CH$_3$)$_2$], 3.80 (dt, ^3J = 5.2, ^4J = 1.6 Hz, 2 H, OC*H*$_2$CH=CH$_2$), 5.04−5.30 [m, 5 H, C*H*=C(CH$_3$)$_2$, C(CH$_3$)(R)$_2$-CH=C*H*$_2$, OCH$_2$CH=C*H*$_2$], 5.70−5.99 [m, 2 H, C(CH$_3$)(R)$_2$C*H*=CH$_2$, OCH$_2$C*H*=CH$_2$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.7 (*C*H$_3$), 22.3 [(*E*)-CH$_2$CH$_2$CH=C(*C*H$_3$)$_2$], 22.4 [CH$_2$*C*H$_2$CH=C(CH$_3$)$_2$], 25.7 [(*Z*)-CH$_2$CH$_2$CH=C(*C*H$_3$)$_2$], 39.8 [*C*H$_2$CH$_2$CH=C(CH$_3$)$_2$], 63.5 (O*C*H$_2$CH=CH$_2$), 77.5 [*C*(CH$_3$)(R)$_2$CH=CH$_2$], 114.5 [C(CH$_3$)(R)$_2$CH=*C*H], 115.5 (OCH$_2$CH=*C*H$_2$), 124.5 [*C*H=C(CH$_3$)$_2$], 131.4 [CH=*C*(CH$_3$)$_2$], 136.0 (OCH$_2$*C*H=CH$_2$), 143.0 [C(CH$_3$)(R)$_2$*C*H=CH$_2$] ppm. MS (EI): *m*/*z* (%) = 194 (<1) $[M]^+$, 136 (25), 121 (44), 111 (50), 107 (15), 95 (23), 93 (36), 91 (17), 82 (13), 80 (100), 71 (12), 69 (49), 67 (39), 55 (44), 53 (22), 42 (40), 40 (34).

{1-[Isoprop-2-enyl)oxy]-1-(phenyl)prop-2-enyl}benzene (13):

Following Procedure C: Benzophenone (3.0 g, 16.5 mmol) was added to $CeCl_3$ (0.41 g, 1.65 mmol) in tetrahydrofuran (30 mL) at room temperature. Vinylmagnesium bromide (20.0 mL, 20.0 mmol) was then added at 0 °C. Subsequent treatment afforded the corresponding allylic alcohol as a pale yellow oil used without purification for the next step.

Following Procedure B: Allylic alcohol (16.5 mmol) in dimethylformamide (15 mL) was added to a solution of sodium hydride (60% in mineral oil, 0.86 g, 19.8 mmol) in dimethylformamide (25 mL). After the addition of 2-methylpropenyl chloride (2.2 mL, 19.8 mmol) and subsequent treatment, the crude was purified by flash chromatography over silica gel using diethyl ether/heptane (1:20) as eluent to afford an orange oil which was then bubble-to-bubble distilled to give the corresponding 1,6-diene **13** (3.74 g, 86% yield) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, C*H*$_3$), 3.94−4.00 [m, 2 H, OC*H*$_2$C(CH$_3$)=CH$_2$], 5.15−5.63 [m, 4 H, C(CH$_3$)=C*H*$_2$, C(Ph)$_2$CH=C*H*$_2$], 6.69−6.84 [m, 1 H, C(Ph)$_2$C*H*=CH$_2$], 7.42−7.55 (m, 6 H, H arom.), 7.62−7.72 (m, 4 H, H arom.) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6 (*C*H$_3$), 68.0 [O*C*H$_2$C(CH$_3$)=CH$_2$], 84.8 [*C*(Ph)$_2$(R)$_2$], 111.1 [C(Ph)$_2$CH=*C*H$_2$], 117.0 [OCH$_2$C(CH$_3$)=*C*H$_2$], 127.8, 128.5, 128.7 (*C*H arom.), 141.0 [C(Ph)$_2$*C*H=CH$_2$], 143.4 (*C* quat. arom.), 144.9 [OCH$_2$*C*(CH$_3$)=CH$_2$] ppm. MS (EI): *m*/*z* (%) = 264 (1) $[M]^+$, 193 (32), 191 (15), 178 (18), 165 (14), 144 (12), 116 (19), 115 (100), 106 (43), 103 (19), 91 (40), 77 (45), 55 (69), 41 (13), 39 (25).

(1-Allyloxy-1-phenylprop-1-enyl)benzene (15):

Following Procedure C: Benzophenone (1.67 g, 9.2 mmol) was added to $CeCl_3$ (0.23 g, 0.92 mmol) in tetrahydrofuran (20 mL) at room temperature. Vinylmagnesium bromide (11.1 mL, 11.1 mmol) was then added at 0 °C. Subsequent treatment afforded the corresponding allylic alcohol as a pale yellow oil used without purification for the next step.

Following Procedure B: Allylic alcohol (9.2 mmol) in 10 mL of dimethylformamide was added to a solution of sodium hydride (60% in mineral oil, 0.44 g, 11.1 mmol) in dimethylformamide (15 mL). After addition of allyl bromide (1.1 mL, 12.0 mmol) and subsequent treatment, the crude was purified by flash chromatography over silica gel using diethyl ether/heptane (1:20) as eluent to afford an orange oil which was then bubble-to-bubble distilled to give the corresponding 1,6-diene **15** (1.88 g, 82% yield) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.84−3.90 (m, 2 H, OC*H*$_2$CH=CH$_2$), 5.20−5.53 [m, 4 H, CH=C*H*$_2$, C(Ph)$_2$CH=C*H*$_2$], 5.95−6.12 (m, 1 H, OCH$_2$C*H*=CH$_2$), 6.49−6.63 [m, 1 H, C(Ph)$_2$C*H*=CH$_2$], 7.29−7.50 (m, 10 H, H arom.) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 64.8 (O*C*H$_2$CH=CH$_2$), 84.2 [*C*(Ph)$_2$(R)$_2$], 115.3 [C(Ph)$_2$CH=*C*H$_2$], 116.2 (OCH$_2$CH=*C*H$_2$), 127.1, 127.8, 127.9 (*C*H arom.), 135.6 (OCH$_2$*C*H=CH$_2$), 140.2 [C(Ph)$_2$*C*H=CH], 144.0 (*C* quat. arom.) MS (EI): *m*/*z* (%) = 250 (<1) $[M]^+$, 211 (15), 210 (65), 192 (17), 165 (17), 133 (25), 115 (23), 106 (40), 104 (21), 91 (38), 79 (40), 77 (18), 63 (14), 55 (100), 51 (43), 39 (10).

Tandem Isomerisation/Claisen Rearrangement Reactions

2,5,9-Trimethyldeca-4,8-dienal (10):[16]

Following Procedure D: [$Ru_3(CO)_{12}$] (27.4 mg, 5mol % of ruthenium), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (54.9 mg, 5mol %), Cs_2CO_3 (83.8 mg, 10mol %), toluene (25 mL) and diene **9** (0.5 g, 2.6 mmol). After 1 h at 120 °C, treatment and distillation, the aldehyde **10** (0.435 g, 87% yield) was obtained as a colourless oil as a mixture of diastereoisomers. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 [d, ^3J = 7.6 Hz, 3 H, CH(C*H*$_3$)CHO], 1.15−1.24 [m, 1 H, C*H*(CH$_3$)CHO], 1.50−1.66 [m, 9 H, CH=C(C*H*$_3$)CH$_2$CH$_2$CH=C(C*H*$_3$)$_2$], 1.90−2.10 [m, 4 H, C*H*$_2$C*H*$_2$CH=C(CH$_3$)$_2$], 2.21−2.39 [m, 2 H, C*H*$_2$CH(CH$_3$)CHO], 4.95−5.06 [m, 2 H, C*H*=C(CH$_3$)CH$_2$CH$_2$C*H*=C(CH$_3$)$_2$], 9.56 (d, ^4J = 1.5 Hz, 1 H, C*H*O) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.6/12.8 [CH(*C*H$_3$)CH], 17.2/17.3 [(*E*)-CH$_2$CH$_2$CH=C(*C*H$_3$)$_2$], 23.1 [CH=C(*C*H$_3$)], 26.1/26.2 [(*Z*)-CH$_2$CH$_2$CH=C(*C*H$_3$)$_2$], 28.6/28.8 [CH$_2$*C*H$_2$CH=C(CH$_3$)$_2$], 31.7 [*C*H$_2$CH$_2$CH=C(CH$_3$)$_2$], 39.4 [*C*H$_2$CH(CH$_3$)CHO], 46.4/46.5 [*C*H(CH$_3$)CH], 120.7/121.1 [*C*H=C(CH3)], 123.8/123.9 [*C*H=C(CH$_3$)$_2$], 131.0/131.3 [CH=*C*(CH$_3$)$_2$], 137.2/137.3 [CH=*C*(CH3)], 204.30/204.35 (*C*HO) ppm. MS (EI):

m/*z* (%) = 194 (1.5) $[M]^+$, 107 (10), 95 (12), 81 (16), 69 (100), 67 (14), 55 (30), 53 (14), 43 (30), 41 (85), 39 (22).

2,2-Dimethyl-5,5-diphenylpent-4-enal (14):[22]

Following Procedure D: $[Ru_3(CO)_{12}]$ (10.0 mg, 5mol % of ruthenium), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (16.2 mg, 5mol %), Cs_2CO_3 (30.7 mg, 10mol %), toluene (7.5 mL) and diene **13** (250 mg, 0.94 mmol). After 1 h at 120 °C, treatment and distillation, the aldehyde **14** (225 mg, 90% yield) was obtained as a colourless oil as a mixture of diastereoisomers. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12 (s, 6 H, 2 × CH_3), 2.39 (d, ^3J = 7.6 Hz, 2 H, CH_2), 6.09 [t, ^3J = 7.6 Hz, 1 H, $(Ph)_2C{=}CHCH_2$], 7.18−7.30 (m, 6 H, C*H* arom.), 7.38−7.49 (m, 4 H, C*H* arom.), 9.48 (s, 1 H, C*H*O) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2 (2 × CH_3), 36.6 (CH_2), 46.5 [$C(CH_3)_2$], 123.6 [$(Ph)_2C{=}CHCH_2$], 127.0, 127.1, 128.0, 128.2, 129.7 (*C*H arom.), 139.5, 142.2 (*C* arom.), 144.3 [$(Ph)_2C{=}CH$], 205.5 (*C*HO) ppm. MS (EI): *m*/*z* (%) = 264 (2) $[M]^+$, 193 (43), 180 (100), 178 (36), 165 (37), 115 (87), 91 (38), 51 (10), 43 (14), 41 (16), 39 (14).

2-Methyl-5,5-diphenylpent-4-enal (16):

Following Procedure D: $[Ru_3(CO)_{12}]$ (4.3 mg, 5mol % per ruthenium atom), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (8.5 mg, 5mol %), Cs_2CO_3 (13.0 mg, 10mol %), toluene (5 mL) and diene **15** (100 mg, 0.40 mmol). After 3 h at 120 °C, treatment and distillation, the aldehyde **16** (78 mg, 78% yield) was obtained as a colourless oil as a mixture of diastereoisomers. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14 (d, ^3J = 6.9 Hz, 3 H, CH_3), 2.16−2.39 [m, 1 H, C*H*(CH_3)], 2.44−2.64 (m, 2 H, CH_2), 6.08 [t, ^3J = 7.5 Hz, 1 H, $(Ph)_2C{=}CHCH_2$], 7.19−7.44 (m, 10 H, C*H* arom.), 9.63 (d, ^3J = 1.4 Hz, 1 H, C*H*O) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.1 (CH_3), 30.5 (CH_2), 46.7 [C*H*(CH_3)], 125.5 $[(Ph)_2C{=}CHCH_2]$, 127.1, 128.1, 128.3, 129.7 (*C*H arom.), 139.6, 142.1 (*C* arom.), 144.9 $[(Ph)_2C{=}CH]$, 204.4 (*C*HO) ppm. MS (EI): *m*/*z* (%) = 250 (39) $[M]^+$, 219 (24), 204 (18), 203 (19), 193 (100), 191 (55), 189 (45), 177 (17), 167 (20), 166 (37), 152 (33), 129 (25), 128 (38), 116 (38), 105 (16), 103 (15), 89 (26), 77 (27), 65 (25), 51 (17), 39 (20).

{1-Methyl-1-[prop-1-enyloxy]but-3-enyl}benzene (11) Using Catalyst B1 with the Diimine L1: $[Ru_3(CO)_{12}]$ (13.2 mg, 5mol % per ruthenium atom), bis(imine) **L1** (18.1 mg, 5mol %), cesium carbonate (40.3 mg, 10mol %) and of toluene (10 mL) were introduced into a Schlenk tube under nitrogen. The reaction mixture was stirred at room temperature for 5 minutes and the diene **5** (250 mg, 1.24 mmol) was then added. After heating at 120 °C for 16 hours, the solvent was removed under reduced pressure and NMR spectroscopic analysis of the crude gave a complete conversion into the homoallyl vinyl ether **11**. The crude was dissolved in heptane, filtered and the solvents evaporated to dryness. This material was then purified by a bubble-to-bubble distillation to afford the corresponding compound **11** (195 mg, 78%) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.55−1.62 [m, 3 H, C(Ph)(CH_3)], 1.65−1.72 (m, 3 H, OCH=CHCH_3), 2.52−2.65 [m, 2 H, OC(Ph)(Me)CH_2CH=CH_2], 4.33−4.49 (m, 1 H, OCH=C*H*CH_3), 4.96−5.10 (m, 2 H, CH=CH_2), 5.54−5.76 [m, 1 H, OC(Ph)(Me)CH_2C*H*=CH_2], 5.81−5.92 (m, 1 H, OC*H*=$CHCH_3$), 7.20−7.38 (m, 5 H, Ph) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.8 (OCH=CH*C*H_3), 25.4 (CH_3), 47.1 [CH_2C(Ph)(Me)OR], 76.2 [*C*(Ph)(Me)], 97.8 (OCH=*C*HCH_3), 117.3 [C(Ph)(Me)CH_2CH=*C*H], 126.1, 126.8, 127.8 (*C*H arom.), 133.9 [C(Ph)(Me)CH_2*C*H=CH], 143.7 (O*C*H=$CHCH_3$), 144.8 (*C* arom.) ppm. MS (EI): *m*/*z* (%) = 202 (7) $[M]^+$, 143 (13), 131 (13), 129 (45), 115 (100), 113 (37), 91 (69), 78 (21), 65 (24), 63 (14), 53 (16), 51 (31), 41 (38), 39 (37).

2,2-Dimethyl-5,5-diphenylpent-4-enal (14) by Using Catalyst D and the 2,2′-Bis(oxazoline) Ligand 17: $[Ru_3(CO)_{12}]$ (10.6 mg, 5mol % ruthenium atom), 2,2′-bis(oxazoline) **17**[19d] (11.9 mg, 5 mol %), cesium carbonate (32.5 mg, 10 mol %) and toluene (10 mL) were introduced into a Schlenk tube under nitrogen. The reaction mixture was stirred at room temperature for 5 minutes and the diene **13** (250 mg, 1.01 mmol) was then added. After heating at 120 °C for 16 hours, the solvent was removed under reduced pressure and NMR spectroscopic analysis of the crude gave 60% of conversion into the aldehyde **14**.

General Procedure for the Preparation of [RuCl{bis(oxazoline)}(*p*-cymene)][BF_4]: A solution of bis(oxazoline) ligand (2 equiv.) in MeOH (10 mL) was added to $[RuCl_2(p\text{-cymene})]_2$ (1 equiv.) and NH_4BF_4 (2 equiv.), and the resulting suspension was stirred at room temperature for 2 h. An orange-brown solution was obtained, which was then evaporated and the crude residue dissolved in CH_2Cl_2. Filtration through celite gave a brown solution, which was evaporated, and the crude complex was washed with diethyl ether (2 × 15 mL) and dried under vacuum. The scale and the yields for individual complexes are shown below.

[RuCl{(*R*,*R*)-4,4′-Diisopropyl-2,2′-methylenebis(1,3-oxazoline)}(*p*-cymene)][BF_4] (18): Complex **18** was prepared in methanol (10 mL) from $[RuCl_2(p\text{-cymene})]_2$ (100 mg, 0.163 mmol), (*R*,*R*)-4,4′-diisopropyl-2,2′-methylenebis(1,3-oxazoline) (**17**) (77 mg, 0.32 mmol) and NH_4BF_4 (34 mg, 0.32 mmol) in a 94 mg yield (98%). Recrystallisation in a mixture of acetone/heptane afforded complex **18** as orange needles. $C_{23}H_{36}BClF_4N_2O_2Ru$: calcd. C 46.36, H 6.09, N 4.70, Cl 5.95; found C 46.45, H 6.33, N 4.51, Cl 5.95. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.52, 0.87, 1.00, 1.07 [4 × d, 12 H, ^3J = 6.6, ^3J = 7.2, ^3J = 7.0, ^3J = 6.8 Hz, 2 $CH(CH_3)_2$], 1.31 [d, ^3J = 7.0 Hz, 6 H, $CH(CH_3)_2$ of *p*-cymene], 2.30 (s, 3 H, $CH_3C_6H_4$), 2.28−2.33 [m, 1 H, C*H*$(CH_3)_2$], 2.60−2.66 [m, 1 H, C*H*$(CH_3)_2$], 3.01−3.09 [m, 1 H, C*H*$(CH_3)_2$ of *p*-cymene], 3.45, 4.00 (AB, 2 H, J_{AB} = 19.7 Hz, CH_2), 4.30−4.92 [m, 6 H, OCH_2C*H*(*i*Pr)N], 5.40−6.05 (m, 4 H, C*H* *p*-cymene) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.4, 14.7 [$CH(CH_3)_2$], 18.4 ($CH_3C_6H_4$), 18.9, 19.5 [$CH(CH_3)_2$], 20.9, 22.9 [$CH(CH_3)_2$ of *p*-cymene], 27.0 (CH_2), 28.1, 28.6, 30.9 [C*H*$(CH_3)_2$], 69.4, 70.3 [2 × *C*H(*i*Pr)], 71.3, 71.7 [OCH_2-CH(*i*Pr)], 79.4, 80.8, 83.8, 85.7 (4 *C*H *p*-cymene), 99.5, 110.0 (2 × *C* *p*-cymene), 165.4, 165.6 (2 × *C*=N) ppm. IR: $\tilde{\nu}$ = 1173 (ν B−F), 1540 (ν C=C), 1602 (ν C=N), 1670 (ν C=N) cm^{-1}. UV: λ (ε, $L{\cdot}mol^{-1}{\cdot}cm^{-1}$) = 422 (910) nm, 325 (1245), 278 (5465) 246 n(5465), 230 (5326).

[RuCl{(*S*,*S*)-4,4′-Diethyl-2,2′-methylenebis(1,3-oxazoline)}(*p*-cymene)][BF_4] (20): Complex **20** was prepared in methanol (10 mL) from $[RuCl_2(p\text{-cymene})]_2$ (100 mg, 0.163 mmol), (*S*,*S*)-4,4′-diethyl-2,2′-methylenebis(1,3-oxazoline) (**19**)[19f] (69 mg, 0.32 mmol) and NH_4BF_4 (34 mg, 0.32 mmol) in a 91 mg yield (98%). $C_{21}H_{32}BClF_4N_2O_2Ru$: calcd. C 44.42, H 5.68, N 4.93; found C 44.17, H 5.76, N 4.93. ^{1} H NMR (200 MHz, $CDCl_3$): δ = 0.79 (t, ^3J = 7.4 Hz, 3 H, CH_3CH_2), 0.96 (t, ^3J = 7.4 Hz, 3 H, CH_3CH_2), 1.28 [d, ^3J = 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.57 (m, 2 H, CH_3CH_2), 2.11 (m, 2 H, CH_3CH_2), 2.19 (s, 3 H, $CH_3C_6H_4$), 2.91 (m, 1 H, C*H*Me_2), 3.49, 3.68 (AB, 2 H, J_{AB} = 20.0 Hz and J_{AB} = 20.1 Hz, CH_2), 4.27−4.88 [m, 6 H, OCH_2C*H*(Et)N], 5.51−5.61 (m, 4 H, C_6H_4) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.8, 9.4 (CH_3CH_2), 18.4 ($CH_3C_6H_4$), 21.3, 22.7 [$CH(CH_3)_2$], 27.1, 27.2, 27.3 (2 × CH_3CH_2, CH_2), 31.1 (*C*HMe_2), 68.5, 72.2 (2 × *C*HEt), 74.0, 74.2 (OCH_2CHEt), 80.6, 82.5, 83.1, 83.8 (4 *C*H *p*-cymene), 98.4, 108.0 (2 *C* *p*-cymene), 165.1, 165.4 (*C*=N) ppm. IR: $\tilde{\nu}$ = 1097 (ν B−F), 1534 (ν C=C), 1601 (ν C=N), 1670 (ν C=N) cm^{-1}. UV: λ (ε,

$L \cdot mol^{-1} \cdot cm^{-1}$) = 421 nm (1012), 322 (1587), 278 (7524), 245 (6780), 230 (7252).

2,2-Dimethyl-5,5-diphenylpent-4-enal (14) by Using Catalyst E with Complex (18) as the Metal Source: Complex **18** (29.7 mg, 5 mol %), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (21.3 mg, 5 mol %), cesium carbonate (32.5 mg, 10 mol %) and toluene (10 mL) were introduced into a Schlenk tube under nitrogen. The reaction mixture was stirred at room temperature for 5 minutes and the diene **13** (250 mg, 1.01 mmol) was then added. After heating at 120 °C for 16 hours, the solvent was removed under reduced pressure and NMR spectroscopic analysis of the crude gave 90% of conversion into the aldehyde **14**. After a column chromatography over silica gel using a mixture diethyl ether/heptane (1/20), the aldehyde **14** (170 mg) was isolated in 68% yield.

X-ray Crystallographic Study of Complex 18: Crystallographic and data collection information as well as a description of the structural analyses and refinements are summarised in Table 3. Single crystals of **18** were obtained by slow diffusion of heptane into an acetone solution of the complex. Data were collected with a Nonius−Kappa CCD diffractometer with graphite-monochromatised Mo-K_α radiation. The cell parameters were obtained with Denzo and Scalepack[24] using 10 frames (psi rotation: 1° per frame). The data collection[25] ($2\Theta_{max}$ = 54°, 128 frames via 21.7° omega rotation and 50 s per frame, *hkl* range: h −14,14; k −17,17; l −25,25) gives 23815 reflections. The data reduction[24] leads to 6792 independent reflections from which 6112 with $I > 2.0\sigma(I)$. The structure was solved with SIR-97,[26] which reveals the non-hydrogen atoms of the structure. After anisotropic refinement, many hydrogen atoms could be found with a Fourier Difference. The whole structure was refined with SHELXL-97[27] by the full-matrix least-squares techniques.

Atomic scattering factors were obtained from International Tables for X-ray Crystallography.[28] ORTEP views were realised with PLATON98.[29]

CCDC-210758 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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