

The effect of oxygen on the regioselectivity in the rhodium catalysed hydrosilylation of 1,3-dienes †

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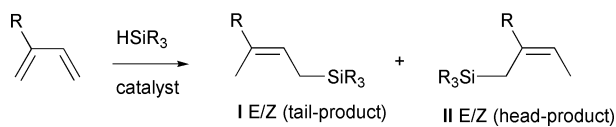
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The regioselectivity of the hydrosilylation of substituted 1,3-dienes catalysed by several rhodium complexes in the presence and absence of oxygen was studied. In addition to the already known accelerating effect, the presence of oxygen strongly affected the product distribution. For 2-substituted 1,3-dienes in the presence of oxygen the regioselectivity was in the range of 1 : 6 to 1 : 10 in favour of the head-product, while the absence of oxygen changed the ratios to 1 : 1 to 3 : 1 in favour of the tail-product. When HSiPh_3 was used in the presence of oxygen a single isomer was isolated in 87% yield, while in the absence of oxygen a mixture of products was produced. Control experiments indicated that a heterogeneous/colloidal catalytic system may be responsible for the preferred head-product formation.

Introduction

Allylic silanes are useful synthetic intermediates in organic synthesis, for example as components in the Hosomi–Sakurai reaction and the [3 + 2] cycloaddition of unsaturated ketones to give five membered rings.^{1–3} The silanes may also act as masked hydroxy groups as they can be oxidized to give alcohols according to the procedure developed by Tamao *et al.* and Fleming *et al.*^{4,5} The transition metal-catalysed hydrosilylation of alkenes is an attractive way of attaching silicon substituents to the carbon skeleton, *e.g.* the hydrosilylation of 1,3-dienes may give allylic silanes *via* a 1,4-addition of the hydrosilane. When an unsymmetrical diene is used, four different isomers may be produced *via* the 1,4-addition (Scheme 1).

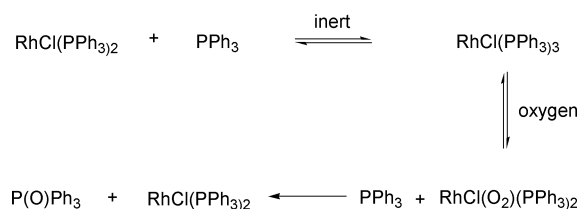


Scheme 1 Hydrosilylation of an unsymmetrical diene.

Depending on the catalyst, various *E–Z* mixtures of **I** (tail-product) and **II** (head-product) may be produced. It has been shown that when rhodium- or palladium-based catalysts are used, a mixture of **I** and **II** is obtained *via syn*-addition of the hydrosilane.⁶ The isomer ratio is dependent on many factors such as solvent, hydrosilane and temperature but mainly on the catalyst metal. For example, Pd-based catalysts give predominantly the (*Z*)-**II** isomer, while Rh-based catalysts can give either (*E*)-**I** or (*Z*)-**II** as the main product.^{7,8}

Oxygen and organic peroxides have been used to enhance the catalytic activity of certain metal complexes such as Rh, Ru and Pt.^{9–13} Parish *et al.* showed that under strictly deoxygenated conditions $\text{RhCl}(\text{PPh}_3)_3$ was inactive as a catalyst in the hydrosilylation of alkenes and alkynes. When a catalytic amount of oxygen or a peroxide was present, the complex became catalytically active. This co-catalytic effect was explained as a result of oxidation of a phosphine ligand to give an unsaturated rhodium complex (Scheme 2).⁹

A similar displacement of a coordinated ligand has been observed in the *tert*-butylhydroperoxide (TBHP)-initiated



Scheme 2 Activation of Wilkinson's catalyst by oxygen.⁹

oxidation of $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ to give $[\text{RhCl}(\text{PPh}_3)_2]_2$ and carbon dioxide.¹⁴ It is also known that several transition metals form discrete complexes with oxygen thereby changing the catalytic properties of the metal.^{15–18}

Lewis *et al.* have pointed out that in many homogeneous catalytic systems containing Rh, Pt, Ir and Pd complexes the actual catalytic species is a colloid.^{16,19–21} Whether the catalyst is homogeneous or colloidal, electronic effects of the coordinated ligands such as O_2 would be expected, which was stressed by Lewis *et al.* for the platinum catalysed hydrosilylation of olefins.¹⁶

Our earlier applications of catalytic 1,3-hydrosilylations resulted in only modest regiocontrol.²² Moreover, in trying to improve the selectivity we encountered considerable irregularities; the regioselectivity varied strongly from experiment to experiment for no apparent reason. During our studies, we also observed results that deviated somewhat from those in the literature. Ojima *et al.* had previously reported a 72 : 28 ratio between **I** and **II**, in the $\text{RhCl}(\text{PPh}_3)_3$ catalysed hydrosilylation of isoprene with HSiMe_2Ph .^{7,23} However, we observed that this reaction gave essentially only **I** (>99%) under certain conditions, which unfortunately could not be consistently reproduced. After extensive experimentation we found that the presence of oxygen had a considerable effect on the regiochemistry.

In this paper we wish to report the effect of molecular oxygen on the regioselectivity in the Rh-catalysed, and in one case the Ir-catalysed, hydrosilylation of unsymmetrical 1,3-dienes.

Results and Discussion

The results of the hydrosilylation of isoprene under an argon (Ar-conditions) and an oxygen atmosphere (O_2 -conditions), respectively, are shown in Table 1 for a number of different

† Electronic supplementary information (ESI) available: NMR spectra. See <http://www.rsc.org/suppdata/p1/b1/b106143g/>

Table 1 Different silanes used in the RhCl(PPh₃)₃-catalysed hydrosilylations of isoprene under deoxygenated and oxygenated conditions

Entry	Hydrosilane	Conditions	Ratio I : II	Yield (%)
1	HSiEt ₃	80 °C, 15 h, Ar	55 : 45	>90
2	HSiEt ₃	80 °C, 2 h, O ₂	15 : 85	>90
3	HSiMe ₂ Ph	80 °C, 2 h, Ar	75 : 25 ^a	92
4	HSiMe ₂ Ph	80 °C, 2 h, O ₂	10 : 90 ^a	94
5	HSiPh ₃	110 °C, 12 h, Ar	Mixture ^b	85
6	HSiPh ₃	110 °C, 12 h, O ₂	5 : 95	87
7	HSi(OMe) ₃	90 °C, 4 h, Ar	76 : 24	85
8	HSi(OMe) ₃	90 °C, 4 h, O ₂	13 : 87	84
9	HSi(OMe) ₃	110 °C, 4 h, Ar	55 : 45	>80
10	HSi(OMe) ₃	110 °C, 4 h, O ₂	10 : 90	>80

^a The reproducibility in a number of experiments was within $\pm 2\%$.

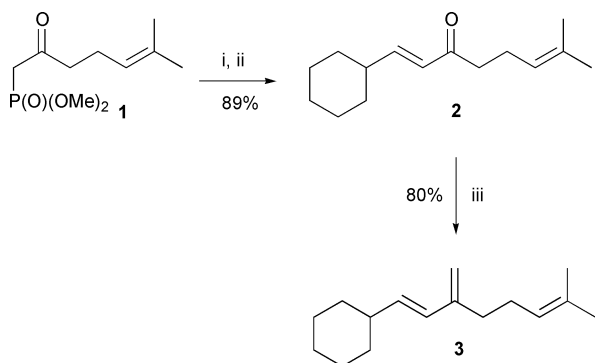
^b Mixture of several products, presumably *via* 1,2- and 1,4-additions. Several signals in the olefin region in the ¹H NMR spectrum were observed.

silanes. Under oxygen-free conditions our results were in good agreement with those of Ojima *et al.*^{7,23} The isomer ratio I : II was 75 : 25 for HSiMe₂Ph. In these experiments the solvent was thoroughly degassed by purging with argon.

The experiments under an oxygen atmosphere were standardised as follows: O₂ was bubbled through a suspension (heptane) or a solution (benzene) of RhCl(PPh₃)₃ for 30 seconds. The reddish mixtures were then heated at about 90 °C for 60 min. During this time the colour changed to yellow–orange in benzene (homogeneous) and pale yellow in heptane (heterogeneous). No further investigation were made to explain these colour changes. After cooling, the appropriate hydrosilane and diene were added. Heating this mixture gave products which were analysed by GLC. All hydrosilanes tested showed the same general trend regarding isomer distribution under the various conditions. Under an inert atmosphere isomer I was favoured (at worst a 1 : 1 mixture was obtained), while II predominated under O₂-conditions. The ratio ranged from 1 : 6 (HSiEt₃, Table 1, entry 2) to 1 : 9 (HSiMe₂Ph, Table 1, entry 4). When HSiPh₃ (Table 1, entry 6) was used the only isolated product was II (87%).

Other substituted dienes also gave II as the major product under O₂-conditions, while complex mixtures of 1,2- and 1,4-addition products were produced under Ar-conditions (Table 2). Both myrcene (Table 2, entry 1) and epoxy myrcene (Table 2, entry 2) as well as isoprene (Table 1, entry 3) gave a similar 75 : 25 isomer ratio between I and II under Ar-conditions, while under O₂-conditions a 1 : 9 ratio was observed for all three substrates.

In all cases studied, under O₂-conditions, the *Z*-configuration of the allylic silanes was observed except for penta-1,3-diene, which gave a considerable amount of the *E*-isomer and also a change in stereoisomer distribution from *E–Z* 1 : 2 under Ar-conditions to *E–Z* 4 : 1 under O₂-conditions (Table 2, entry 3). The 1,3-disubstituted butadiene 3, synthesised from 1 in 74% overall yield *via* a HEW–Wittig reaction sequence (Scheme 3),

**Scheme 3** Synthesis of triene 3: i, NaH, DME, 0 °C; ii, cyclohexanecarbaldehyde, 70 °C; iii, MePPh₃⁺ Br⁻, BuLi, THF, 50 °C.

gave under Ar-conditions a mixture of isomers, while the head-product 4 was formed as the major isomer in 80% yield (Table 2, entry 5) under O₂-conditions. An interesting observation was that cyclohexenone was hydrosilylated to give the silyl enol ether with a sterically hindered silane such as HSiPh₃ (Table 2, entry 6) in the presence of oxygen. Under Ar-conditions Wilkinson's catalyst was previously (also in our hands) shown to be ineffective in this transformation and only one successful report has, to our knowledge, appeared in the literature.²⁴ Further substrates are under investigation.

Several other catalytic systems followed the general trend in isomeric distribution under the O₂-conditions (Table 3), *i.e.* II was the major product. It should be noted that when CO-containing rhodium complexes such as RhCl(CO)(PPh₃)₂ (Table 3, entry 2) and RhH(CO)(PPh₃)₃ (Table 3, entry 7) or the Rh^{III} complexes Rh(acac)₃ (Table 3, entry 4) and RhCl₃·H₂O (Table 3, entry 5) were used, isomer II was the main product even under Ar-conditions in the hydrosilylation of isoprene with HSiMe₂Ph. Under O₂-conditions II predominated even more. Despite the low solubility of RhCl₃·H₂O in the solvents used, a good yield of the corresponding allylic silane was achieved.

The metalhydrido complex RhH(PPh₃)₄ (Table 3, entry 6) behaved like Wilkinson's catalyst and gave a ratio of 75 : 25 between I and II under Ar-conditions. Under O₂-conditions the ratio changed to 10 : 90.

An interesting observation was that, under Ar-conditions, the thiocarbonyl complex RhCl(CS)(PPh₃)₂ (Table 3, entry 3) gave isomer I as the main product, while the carbonyl analogue gave II. Under O₂-conditions the isomer ratios were essentially the same for both of these catalysts. The iridium complex [Ir(COD)Cl]₂ was less selective, but also with this catalyst we observed a predominance of II under O₂-conditions (Table 3, entry 8).

At this point a proper mechanistic study has not been undertaken, although a few remarks can be made: it is known that RhCl(PPh₃)₃ in methylene chloride reacts with oxygen to give two complexes, [RhCl(O₂)(PPh₃)₃·2CH₂Cl₂] and [RhCl(O₂)(PPh₃)₂·CH₂Cl₂]₂.^{17,18} These complexes gave in our hands isomer I as the major product in the reaction between isoprene and dimethylphenylsilane under an inert atmosphere. This excluded that these complexes were the major catalytic species under O₂-conditions. The change in the Rh : PPh₃ ratio due to oxidation of PPh₃ to P(O)Ph₃ was probably not responsible for the selectivity either, as shown by the following results. Addition of PPh₃ to [RhClCOD]₂ in lower ligand to metal ratios than 3 : 1 still gave I as the major isomer; addition of 0, 2, 4 or 6 equivalents of the phosphine with respect to the Rh-complex gave I and II in the ratios 50 : 50, 58 : 42, 74 : 26 and 75 : 25, respectively. The lower concentration of PPh₃ could explain a part of the observed selectivity change, but in the light of the fact that even the phosphine-free Ir(COD)₂Cl₂ gave more of isomer II under the O₂-conditions, this is probably not the sole reason.

The question of radical reactions was also considered. However, the presence of a radical scavenger (galvinoxyl) gave no inhibition, which should exclude a radical chain mechanism. Still, a metal centered radical mechanism cannot be excluded, but it is not likely to operate, since the use of (Me₃Si)₃SiH, introduced by Giese *et al.* as an efficient radical generating species and also used in radical hydrosilylation of alkenes,²⁵ did not lead to any consumption of the silane in the hydrosilylation of isoprene under O₂-conditions.

As a further mechanistic possibility colloidal catalysis was considered and examined as follows. The mercury inhibition test for colloidal catalysis^{26,27} resulted in a moderate change of the product ratio between I and II in the hydrosilylation of isoprene with HSiMe₂Ph from 17 : 83 in the absence of mercury to 38 : 62 in its presence. A sluggish conversion of the starting

Table 2 Different substrates in Rh-catalysed hydrosilylations with HSiMe₂Ph. **A:** inert conditions. **B:** under oxygen. For details, see the Experimental section

Entry	Substrate	Conditions	Products	Yield (%)
1		A or B	+	>80
			A: 75 B: 10	25 ^a 90 ^a
2		A or B	+	75
			A: 75 B: 10	25 ^a 90 ^a
3		A or B	+	>85
			A: 1 B: 4	2 1
4		A or B	+ small amount <5% of unknown isomer	>90 ^a
5		A or B		80
			A: mixture of isomers B: head-product 4 ^a + 10% of a minor isomer	
6		A or B		70
			A: no reaction B: silylenol ether	

^a The *E/Z* distribution was not determined. However, only one of the two possible stereoisomers was indicated by ¹³C NMR.

Table 3 Different rhodium complexes used as catalysts in the hydrosilylation of isoprene with HSiMe₂Ph under deoxygenated and oxygenated conditions, respectively

Entry	Catalyst	Ratio of I : II		Yield I + II (%)
		Inert	Oxygen	
1	RhCl(PPh ₃) ₃	75 : 25	10 : 90	>99
2	RhCl(CO)(PPh ₃) ₂	33 : 67	14 : 86	>90
3	RhCl(CS)(PPh ₃) ₂	70 : 30	13 : 87	>90
4	Rh(acac) ₃	>5 : 95	>5 : 95	>90
5	RhCl ₃ ·H ₂ O	28 : 72	14 : 86	>90
6	RhH(PPh ₃) ₄	75 : 25	11 : 89	>90
7	RhH(CO)(PPh ₃) ₃	10 : 90	10 : 90	>90
8	Ir(COD) ₂ Cl ₂	50 : 50	20 : 80	>90

materials in the reaction which contained mercury, indicated that a more active heterogeneous/colloidal system was inhibited by the mercury. As total conversion of the starting materials was achieved, a parallel homogeneous system is likely to be operating.

Next, a rhodium colloid ("rhodium red" 2.5 nm amorphous particles) was prepared according to a procedure published by Lewis *et al.*²⁰ By using this colloid as a catalyst in the hydrosilylation of isoprene, **II** was formed as the major isomer, again indicating that the active catalyst could be either a colloid or a heterogeneous phase. However, Crivello and Fan showed that substrates containing both an alkene and an epoxide underwent ring-opening polymerization in the presence of a naked colloidal rhodium catalyst,²⁸ which indicates that in our experiments such a colloid should not be acting since

we obtained a good yield of the hydrosilylation product of epoxy myrcene (Table 2, entry 2).

The suggestion by Berberova *et al.*^{29,30} that transition metal catalysed hydrosilylation (platinum) may proceed *via* a radical cation is probably not true in our case. Catalysts of the platinum group rapidly oxidise hydrosilanes to their corresponding radical cations. In the absence of a substrate, fast evolution of hydrogen gas usually occurs and the hydrosilane is consumed. However, in our case, addition of the hydrosilane before the substrate *did* produce the allylic silane in high yield. Moreover, no evolution of hydrogen gas was observed. Further, the insignificant inhibition of the reaction using a radical scavenger suggests that the main reaction does not involve radicals.

Conclusions

We observed that the rhodium catalysed hydrosilylation of 2-substituted-1,3-dienes under an oxygen atmosphere gave the head-product as the major isomer, while the oxygen free conditions gave mainly the tail-product. To our knowledge this is the first observation that the presence of oxygen can change the product distribution in hydrosilylations, although its activating effect was known. In addition, the Rh/oxygen procedure may be an efficient way of synthesising sterically hindered allylsilanes and silyl enol ethers and be a useful catalytic system in polymer chemistry for the hydrosilylation of unsaturated polymers.

Although no rigorous investigation has been made regarding the nature of the catalytic species, it seems likely that the head-selective catalyst is of colloidal/heterogeneous nature, resembling the effects of soluble Rh^{III}-complexes.

Application of the Rh/oxygen conditions in the hydrosilylation of more highly functionalised structures will be reported elsewhere.

Experimental

All reactions were carried out under either an oxygen or an argon atmosphere. The hydrosilanes and [RhCl₃·3H₂O] were used as delivered without further purifications. [Rh₂Cl₂(COD)₂],³¹ [Rh₂Cl₂(PPh₃)₄],³² [Rh(PPh₃)₃Cl],³² [RhCl(CO)(PPh₃)₂],³³ [RhCl(CS)(PPh₃)₂],³⁴ [RhH(PPh₃)₄],³⁵ [RhH(CO)(PPh₃)₃],³⁵ (Rh(acac)₃)³⁶ and (Ir₂Cl₂(COD)₂)³⁷ and epoxy myrcene³⁸ were prepared according to literature procedures. All other dienes were commercially available. ¹H NMR and ¹³C NMR spectra were recorded on a Varian XL 300 or on a Bruker DRX 400 NMR spectrometer. Coupling constants *J* are given in Hz. IR analyses were performed on a Perkin-Elmer 254 spectrophotometer. GLC analyses were performed on a Varian 3400 gas chromatograph using a SPB-5 column (Supelco, 30 m × 0.25 mm id × 0.25 μm thickness). The *E-Z* distribution of the products in Table 3 were not determined. However, only one of the two possible stereoisomers was indicated by ¹³C NMR.

The reactions were carried out using the same general methods as detailed below for the hydrosilylation of isoprene with HSiMe₂Ph (Method A: Ar-conditions, Method B: O₂-conditions). The reaction vessels used in the catalytic runs were thoroughly washed with acid and base to minimize the risk of contamination of the finely divided rhodium particles. A blank reaction (using the standard conditions, see below but without added catalyst) confirmed that no reaction took place in the absence of added catalyst.

Typical conditions for the hydrosilylations

Method A. Benzene (15 mL) was thoroughly degassed by being purged with argon. RhCl(PPh₃)₃ (10 mg, 0.01 mmol), HSiMe₂Ph (0.50 g, 3.6 mmol) and isoprene (0.50 mL, 5.1

mmol) were added sequentially, after which the reaction vessel was sealed with a screw cap and heated at 60 °C. After 2 h the reaction mixture was allowed to cool to rt. Removal of the catalyst by filtration through a column of silica gel and evaporation of the solvent afforded the crude product which was analysed by GLC. Isolated yields based on the silane are given in Tables 1 and 3. No sign of decomposition of the catalyst was noticed and, indeed, a small amount of the solution could be used as a catalyst for a subsequent reaction.

Method B. Oxygen gas was bubbled through a solution of RhCl(PPh₃)₃ (10 mg, 0.01 mmol) in benzene (15 mL) for 30 s. The reaction vessel was sealed and heated at 90 °C. After 60 min the reaction mixture was allowed to cool to rt and HSiMe₂Ph (0.50 g, 3.6 mmol) and isoprene (0.50 mL, 5.1 mmol) were added sequentially. After 2 h at 60 °C the reaction mixture was allowed to cool to rt. Removal of the catalyst by filtration through a column of silica gel and evaporation of the solvent afforded the crude product which was analysed by GLC. Isolated yields based on the silane are given in Tables 1 and 3. As above, no sign of decomposition of the catalyst was noticed and a small amount of the solution could be used as a catalyst for a subsequent reaction.

(*Z*)-1-(Triphenylsilyl)-2-methylbut-2-ene

(Table 1, entry 6, method B). The (*Z*)-configuration was determined by NOE spectroscopy showing the contact between H-1 and H-4. δ_H 1.25 (3 H, d, *J* 6.7), 1.57 (3 H, s), 2.42 (2 H, s), 5.15 (1 H, q, *J* 6.7), 7.46–7.35 (9 H, m) and 7.61–7.55 (6 H, m); δ_C 13.7, 19.9, 26.5, 118.4, 127.8, 129.5, 135.2, 135.9; mp 49–51 °C. HRMS (CI mode, CH₄): C₂₃H₂₄Si (M); found: *m/z* 328.1647. Calc.: *m/z* 328.1647.

The following substances were prepared according to the general procedures described above and isolated as mixtures of regio isomers. The ratio between **I** and **II** was determined by GLC (Tables 1 and 2): 1-[dimethyl(phenyl)silyl]-3-methylbut-2-ene,⁷ 1-triethylsilyl-3-methylbut-2-ene,³⁹ 1-trimethoxysilyl-3-methylbut-2-ene, 1-triethoxysilyl-3-methylbut-2-ene,⁷ (*Z*)-1-[dimethyl(phenyl)silyl]-2-methylbut-2-ene,⁷ (*Z*)-1-triethylsilyl-2-methylbut-2-ene,³⁹ (*Z*)-1-trimethoxysilyl-2-methylbut-2-ene, (*Z*)-1-triethoxysilyl-2-methylbut-2-ene,^{40,41} (*E*)-3,7-(dimethyl)-1-[dimethyl(phenyl)silyl]octa-2,6-diene,⁷ (*Z*)-3-[dimethyl(phenyl)silylmethyl]-7-methylocta-2,6-diene,⁷ 1-[dimethyl(phenyl)silyl]pent-2-ene (mixture of stereoisomers),⁴² (*Z*)-1-[dimethyl(phenyl)silyl]-2-methylpent-2-ene and 1-(triphenylsilyloxy)cyclohexene.²⁴

(*Z*)-2,3-Epoxy-6-[dimethyl(phenyl)silylmethyl]-2-methyloct-6-ene

(Table 2, entry 2, method B). δ_H 0.32 (6 H, s), 1.20 (3H, s), 1.27 (3 H, s), 1.46 (3 H, d, *J* 7.3), 1.50–1.67 (2 H, m), 1.74 (2 H, d, *J* 6.0), 1.87–2.05 (2 H, m), 2.60 (1 H, t, *J* 7.2), 5.15 (1 H, q, *J* 7.3), 7.33–7.37 (3 H, m) and 7.50–7.55 (2 H, m); δ_C –2.4, –2.3, 13.9, 18.7, 20.4, 24.9, 27.5, 35.6, 58.3, 64.2, 116.5, 127.8, 129.0, 133.5, 136.3 and 139.4. HRMS (CI mode, CH₄): C₁₈H₂₈OSi (M); found: *m/z*, 288.1914. Calc.: *m/z* 288.1909.

(*E*)-2,3-Epoxy-8-[dimethyl(phenyl)silyl]-2,6-dimethyloct-6-ene

(Table 2, entry 2, method A). δ_H 0.26 (6 H, s), 1.25 (3 H, s), 1.29 (3 H, s), 1.51 (2 H, s), 1.66 (3 H, d, *J* 8.4), 2.05–2.20 (2 H, m), 2.68 (1 H, t, *J* 6.4), 5.22 (1 H, t, *J* 8.4), 7.33–7.38 (3 H, m) and 7.50–7.55 (2 H, m); δ_C –3.2, –3.2, 15.8, 17.8, 18.7, 24.9, 27.8, 36.6, 58.2, 64.1, 120.2, 127.7, 128.9, 132.3, 133.5 and 139.1.

Dimethyl 6-methyl-2-oxohept-5-enylphosphonate 1⁴³

A solution of *n*-BuLi (22 mL, 35 mmol, *c* = 1.6 M) in hexane was slowly added to a stirred solution of dimethyl methylphosphonate (4.4 g, 35 mmol) in dry THF (50 mL) under an

atmosphere of argon at $-65\text{ }^{\circ}\text{C}$. After 15 min, a solution of ethyl 5-methylhex-4-enoate (3.0 g, 19 mol) in dry THF (10 mL) was added and the reaction mixture was stirred at this temperature for another 60 min. Ether (100 mL) and brine (50 mL) were then added and after acidification with 2 M HCl the phases were separated. The aqueous phase was extracted with ether ($2 \times 50\text{ mL}$) and the combined organic phases were washed with brine ($2 \times 50\text{ mL}$) and dried (Na_2SO_4). Filtration and concentration of the solvent at reduced pressure afforded crude **1**. Column chromatography (EtOAc) gave **1** (2.7 g, 62%) as a colourless oil; R_f 0.23 (EtOAc); δ_{H} 1.59 (3 H, br s), 1.65 (3H, d, J 1.1), 2.24 (2 H, m), 2.62 (2 H, t, J 7.3), 3.06 (2 H, d, J 22.7), 3.75 (3 H, s), 3.78 (3 H, s) and 5.0 (1 H, apparent tq, J 7.2 and 1.4); δ_{C} 17.8, 22.3, 25.8, 40.9, 42.1, 44.3, 53.2 (d, J 7.0), 122.4, 133.2, 201.8 (d, J 6.0). HRMS (CI mode, CH_4): $\text{C}_{10}\text{H}_{19}\text{O}_4\text{P}$ (M); found: m/z , 234.1020. Calc.: m/z 234.1021. (Analytical data were missing in ref. 43.)

(1E)-1-Cyclohexyl-7-methyl-3-oxoocta-1,6-diene 2

NaH (0.34 g, 8.5 mmol, 60% in mineral oil) was added to a solution of **1** (2.0 g, 8.5 mmol) in dry DME (80 mL) under argon at $0\text{ }^{\circ}\text{C}$. The cooling bath was removed, and the mixture stirred for 10 min, after which the temperature was raised to $70\text{ }^{\circ}\text{C}$. A solution of cyclohexanecarbaldehyde (0.96 g, 8.5 mmol) in dry DME (5 mL) was then added rapidly. The reaction mixture was stirred at $70\text{ }^{\circ}\text{C}$ for 10 min and then cooled. Ether (80 mL) was added and the solution was washed with brine ($2 \times 50\text{ mL}$) and dried (Na_2SO_4). Filtration and evaporation of the solvent followed by column chromatography (heptane–EtOAc 5 : 1) of the residue afforded **2** (1.7 g, 89%) as a colourless oil. R_f 0.27 (heptane–EtOAc 5 : 1); δ_{H} 1.37–1.08 (5 H, m), 1.62 (3 H, s), 1.68 (3 H, s), 1.81–1.68 (5 H, m), 2.14 (1 H, m), 2.29 (2 H, m), 2.56 (2 H, m), 5.10 (1 H, apparent tq, J 7.2 and 1.4), 6.04 (1 H, dd, J 16.0 and 1.4) and 6.76 (1 H, dd, J 16.0 and 6.8); δ_{C} 17.9, 23.2, 25.9, 25.9, 26.1, 32.0, 40.3, 40.8, 123.2, 128.0, 132.8, 152.5 and 201.1. HRMS (EI+): $\text{C}_{15}\text{H}_{24}\text{O}$ (M); found: m/z 220.1826. Calc.: m/z 220.1827.

(1E)-1-Cyclohexyl-7-methyl-3-methyleneocta-1,6-diene 3

n-Butyllithium (3.8 mL, 6.1 mmol, 1.6 M in hexane) was added to a slurry of methyltriphenylphosphonium bromide (2.2 g, 6.1 mmol) in dry THF (30 mL) under argon. The reaction mixture was stirred at room temperature for 10 min. Then the temperature was raised to $50\text{ }^{\circ}\text{C}$ and **2** (1.3 g, 5.8 mmol) in dry THF (10 mL) was added rapidly. The mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 10 min and then at $20\text{ }^{\circ}\text{C}$ for 30 min. Ether (50 mL) and brine (30 mL) were added followed by separation of the phases. The organic phase was washed with brine ($2 \times 30\text{ mL}$), dried (Na_2SO_4), filtered and concentrated at reduced pressure. Column chromatography of the residue (heptane–EtOAc 9 : 1) afforded **3** as a colourless oil (1.1 g, 83%). R_f 0.55 (heptane–EtOAc 9 : 1); δ_{H} 1.35–1.05 (5 H, m), 1.62 (3 H, s), 1.71 (3 H, s), 1.78–1.60 (5 H, m), 2.0 (1 H, m), 2.25–2.13 (4 H, m), 4.87 (1 H, br s), 4.91 (1 H, d, J 2.0), 5.17 (1 H, m), 5.67 (1 H, dd, J 16.0 and 7.0), 6.04 (1 H, d, J 16.0); δ_{C} 17.9, 25.9, 26.3, 27.2, 32.5, 33.2, 41.2, 113.3, 124.6, 129.6, 131.8, 136.2, 146.5. HRMS (EI+): $\text{C}_{16}\text{H}_{26}$ (M); found: m/z 218.2031. Calc.: m/z 218.2035.

(2Z)-1-Cyclohexyl-7-methyl-3-[dimethyl(phenyl)silylmethyl]-octa-2,6-diene 4

A catalyst solution was prepared according to the general description method B and then **3** (100 mg, 0.46 mmol) and HSiMe_2Ph (63 mg, 0.46 mmol) were added sequentially. The reaction mixture was heated at $90\text{ }^{\circ}\text{C}$ for 30 min. After cooling, ether (20 mL) and brine were added, the phases were separated and the organic phase was washed with brine ($2 \times 10\text{ mL}$) and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure and filtration through a short plug of silica afforded a

mixture of two products **4** and a minor isomer (9 : 1 ratio) in 80% yield. R_f 0.77 (heptane).

Major isomer **4**: δ_{H} 0.32 (6 H, s), 0.87 (2 H, m), 1.30–1.11 (4 H, m), 1.59 (3 H, br s), 1.69 (3 H, d, J 1.1), 1.76 (2 H, br s), 1.78–1.62 (7 H, m), 1.89 (2 H, apparent t, J 7.2), 2.06 (2 H, apparent q, J 7.3), 5.07 (2 H, m), 7.39–7.34 (3 H, m), 7.65–7.50 (2 H, m); δ_{C} -2.0 , 17.9, 20.7, 26.0, 26.7, 26.9, 27.1, 33.5, 36.5, 38.9, 39.4, 121.6, 124.8, 127.9, 129.1, 131.4, 133.7, 136.4 and 139.9. HRMS (EI+): $\text{C}_{24}\text{H}_{38}\text{Si}$ (M); found: m/z 354.2735. Calc.: m/z 354.2743.

Minor isomer: δ_{C} -1.4 –1, 23.1, 26.0, 26.4, 26.5, 33.2, 33.4, 33.6, 38.9, 39.7, 40.6, 40.8, 125.1, 127.8, 128.8, 129.0, 131.2, 133.8, 135.7.

The dependence of the regioselectivity on the PPh_3 : Rh ratio

Different quantities (n) of PPh_3 ($n = 0, 0.04, 0.08$, and 0.12 mmol) were added to a solution of $[\text{RhCl}(\text{COD})_2]$ (10 mg, 0.02 mmol) in benzene (5 mL). The vessels were supplied with H_2 (3 atm) for 1 h and were then degassed with argon. Next, HSiMe_2Ph (0.20 g, 1.5 mmol) and isoprene (0.21 mL, 2.2 mmol) were added and these reaction mixtures were heated at $60\text{ }^{\circ}\text{C}$ for 1 h and then worked up as described above. The chromatographed products were all obtained in quantitative yields. The isomer ratios between **I** and **II** were as follows: for $n = 0$, 50 : 50, $n = 0.04$, 58 : 42, $n = 0.08$, 74 : 26, $n = 0.12$, 75 : 25 as analyzed by GLC.

Mercury inhibition studies as a test for colloids^{26,27}

A standard solution was prepared as follows. $\text{RhCl}(\text{PPh}_3)$ (10 mg, 0.01 mmol) in benzene (5 mL) was treated with oxygen for 30 s and then heated at $70\text{ }^{\circ}\text{C}$ for 60 min. Part of this solution (2.5 mL) was transferred to another vessel, Hg (3.0 g) was added and the reaction was stirred for 10 min. This treatment was to remove colloids. Then isoprene (0.44 g, 6.5 mmol) and HSiMe_2Ph (0.58 g, 4.2 mmol) were added to each catalyst preparation and the reaction vessels were heated at $60\text{ }^{\circ}\text{C}$ for 2 h. The product distribution was monitored by GLC. Addition of mercury changed the isomer ratio **I** : **II** from 17 : 83 to 38 : 62, which indicated that a heterogeneous/colloidal catalyst could be operating, at least to some extent. Also the conversion of the substrates was slower under the Hg-conditions indicating the presence of a more sluggish catalytic homogeneous system operating in parallel with a heterogeneous/colloidal system.

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