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Titanacyclobutenes or Titanium Vinyl Carbene Complexes? Reactivity of Organotitanium Species Generated by the Reaction of γ-Chloroallyl Sulfides with a Titanocene(II) Reagent

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Abstract: The reactivity of the organotitanium species generated by the reductive titanation of γ-chloroallyl sulfides with the titanocene(II) reagent $[Cp_2Ti\{P(OEt)_3\}_2]$ was studied. The organotitanium species formed from α-monosubstituted γ-chloroallyl sulfides reacted with 1,5-diphenylpentan-3-one and styrene to produce conjugated dienes and vinyl cyclopropanes as major products, thus suggesting the formation of vinyl carbene complexes as intermediates. On the contrary, the organotitanium species generated from acyclic β,γ-disubstituted γ-chloroallyl sulfides revealed titanacyclobutene-like reactivity, and their reaction with 1,5-diphenylpentan-3-one produced homoallyl alcohols. These organotitanium species did not react with styrene, but did react with dichlorophenylphosphine to afford phosphacyclobutenes. In the case of β-monosubstituted, γ-monosubstituted, and α,γ-disubstituted γ-chloroallyl sulfides, the organotitanium species reacted with both 1,5-diphenylpentan-3-one and styrene. The former reaction produced homoallyl alcohols and the latter gave vinyl cyclopropanes or unconjugated dienes. These results suggest that titanacyclobutenes and/or titanium vinyl carbene complexes are produced by the reductive titanation of γ-chloroallyl sulfides depending on their substitution patterns.

Keywords: alkenes · heterocycles · ketones · metallacycles · titanium

Introduction

Whether metallacyclobutenes exist in equilibrium with vinyl carbene complexes is one of the key issues in organo-transition-metal chemistry. Decisive experimental evidence for the equilibrium between titanacyclobutenes **1** and titanium vinyl carbene complexes **2** (Scheme 1) has not yet appeared.

Scheme 1. The equilibrium between titanacyclobutenes **1** and titanium vinyl carbene complexes **2**.

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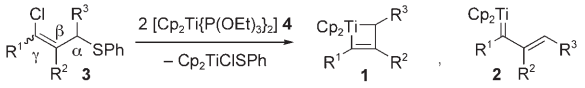
Doxsee et al. suggested the above equilibrium for the isomerization of α-isopropenyl-β-ethyltitanacyclobutene into α-(1-ethylethenyl)-β-methyltitanacyclobutene.[1] The process, however, has not been fully explored. Binger et al. reported the selective formation of these two organotitanium species: α,β-diphenyltitanacyclobutene is exclusively formed by the reaction of 1,2-diphenylcyclopropene with $[Cp_2Ti(PMe_3)_2]$ (Cp = cyclopentadienyl), whereas the γ,γ-diphenylvinylcarbene complex is produced by a similar reaction of 3,3-diphenylcyclopropene.[2] Titanacyclobutenes **1** bearing two identical substituents at the α- and β-positions have been prepared by the reaction of symmetrical alkynes with titanocene methylidene.[3] On the basis of an investigation into their reactivity toward various organic compounds,[3,4] it has been suggested that the titanacyclobutenes **1** formed are not in equilibrium with vinyl carbene complexes **2**. Furthermore, Grubbs and co-workers ruled out the possibility of this process in the insertion reaction of carbon monoxide into α,β-disubstituted titanacyclobutenes on the basis of kinetic studies.[5]

To clarify the structure-dependent reactivity of organotitanium species **1** and **2** toward organic molecules, we have explored a versatile method for the preparation of these spe-

cies. Herein, we describe the formation of organotitanium species by the reductive titanation of γ-chloroallyl sulfides **3** with a titanocene(II) reagent **4** and their dual reactivity as titanacyclobutenes **1** and vinyl carbene complexes **2** depending on the substitution patterns of **3** (Table 1).

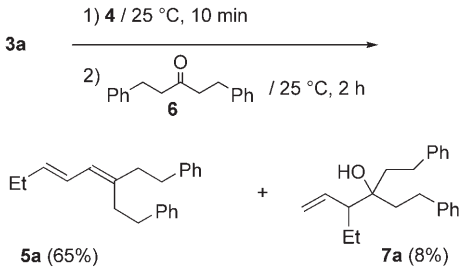
Table 1. The formation of titanacyclobutenes **1** and/or titanium vinyl carbene complexes **2** by the reaction of γ-chloroallyl sulfides **3** with titanocene(II) reagent **4**.



3	R^1	R^2	R^3	Ratio of stereoisomers
3a	H	H	Et	100:0
3b	H	Ph	H	100:0
3c	Me	H	H	82:18
3d	Hex	H	H	95:5
3e	Ph	H	H	92:8
3f	Ph	H	Et	100:0
3g	Ph	H	Ph	100:0
3h	Et	Me	H	59:41
3i	$-(CH_2)_4-$		H	–
3j	Ph	Me	H	96:4
3k	Ph	Et	H	100:0
3l	Me	Ph	H	66:34
3m	Ph	Ph	H	74:26

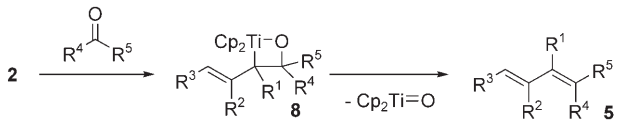
Results and Discussion

The treatment of the organotitanium species generated by the reductive titanation of α-monosubstituted γ-chloroallyl sulfide **3a** (2 equiv) with **4** (6 equiv) at 25 °C produced the organotitanium species that affords the *E*-conjugated diene **5a** stereoselectively on treatment with 1,5-diphenylpentan-3-one (**6**; Scheme 2). It is of interest that homoallyl alcohol **7a** was also produced as a minor product.



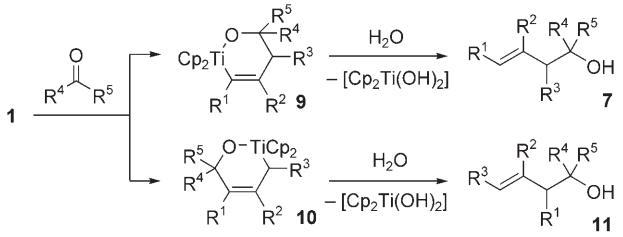
Scheme 2. Reaction of α-monosubstituted γ-chloroallyl sulfide **3a** with 1,5-diphenylpentan-3-one (**6**).

Previously, we reported the formation of conjugated dienes **5** by the reaction of γ-substituted vinyl carbene complexes **2** ($R^1=R^2=H$; R^3=Ph, alkyl) with carbonyl compounds via oxatitanacyclobutane intermediates **8** (Scheme 3).[6] Grubbs and Meinhart demonstrated that the α,β-disubstituted titanacyclobutenes **1** ($R^1=R^2$=Ph, alkyl; $R^3=H$), on the contrary, produce homoallyl alcohols **7** via



Scheme 3. Reaction of titanium vinyl carbene complexes **2** with carbonyl compounds.

six-membered titanacycles **9** when treated with ketones and aldehydes (Scheme 4).[4a] Doxsee and Mouser reported that regioisomers **10** were also formed by the insertion of carbonyl compounds into the titanium–vinyl bond.[4c] Therefore, the formation of **5a** and **7a** suggests that both organotitanium species **1** and **2** would act as the intermediates in the reaction of **3a**, though the formation of **5a** via a *gem*-dititanium species such as [(Cp_2PhSTi)(Cp_2ClTi)CH−CH=CHEt], is not neglected at this stage.

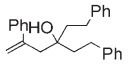
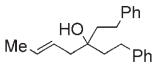
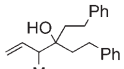
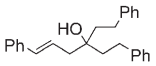
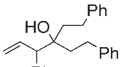
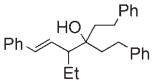
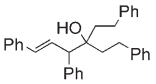
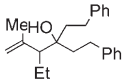
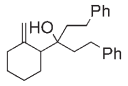
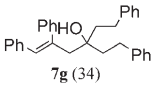


Scheme 4. Reaction of titanacyclobutenes **1** with carbonyl compounds.

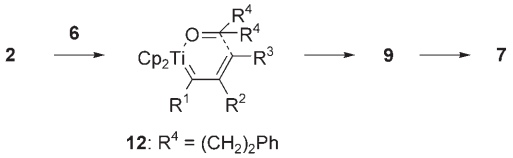
In the reactions of β- and γ-monosubstituted and α,γ- and β,γ-disubstituted γ-chloroallyl sulfides **3** with **6**, however, the exclusive formation of homoallyl alcohols **7** and/or **11** was observed (Table 2). It was found that the substituent R^1 in **7** is absolutely *cis* to R^2 regardless of the stereoisomeric purity of the starting materials **3**. These results indicate that the reactions of all these γ-chloroallyl sulfides **3** follow a pathway that involves the titanacyclobutenes **1** (see Scheme 4). Although their regioselectivity is somewhat complicated, the tendency for α-phenyl-substituted titanacyclobutenes **1** to preferentially produce products **7** from titanium–alkyl bond insertion was observed (Table 2, entries 3, 4, and 8). A similar regioselectivity was observed in the reaction of α,β-diphenyltitanacyclobutene prepared from titanocene methylidene and diphenylacetylene with ketones.[4c] The formation of homoallyl alcohols of the type **7** by the reaction of vinyl carbene complexes **2** with **6** via the six-membered transition states **12** (Scheme 5) should be ruled out on the basis of the formation of another type of homoallyl alcohol **11** and the results of the reaction with styrene (**13**; see below).

Vinyl carbene complexes **2** react with terminal olefins to afford vinyl cyclopropanes,[7] whereas there has been no report on the reaction of titanacyclobutanes **1** with terminal olefins. We then studied the reactivity of the organotitanium intermediates generated from γ-chloroallyl sulfides **3** with different substitution patterns to styrene (**13**).

Table 2. Reaction of γ-chloroallyl sulfides **3** with 1,5-diphenylpentan-3-one (**6**).

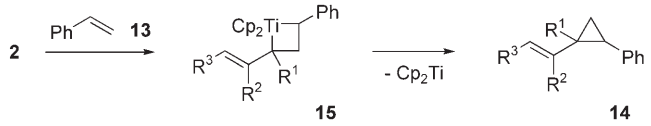
Entry	Sulfide **3**	Products[a]	
1[b]	**3b**	 **7b**[c] (60)	
2[d]	**3c**	 **7c** (24)	 **11a** (38)
3[d]	**3e**	 **7d** (63)	 **11b** (10)
4[d]	**3f**	 **7e** (84)	
5[d]	**3g**	 **7f**[c] (88)	
6[b]	**3h**	 **11c** (55)	
7[b]	**3i**	 **11d** (40)	
8[b]	**3m**	 **7g** (34)	

[a] Yields of the isolated products are given in parentheses. [b] Performed by using procedure B, as described in the Experimental Section. [c] The insertion of **6** into the titanium–alkyl and titanium–vinyl bonds affords the same homoallyl alcohol. [d] Performed by using procedure C, as described in the Experimental Section.



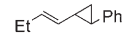
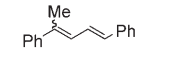
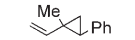
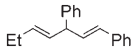
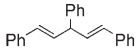
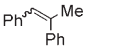
Scheme 5. A possible pathway for the formation of homoallyl alcohols **7** by the reaction of vinyl carbene complexes **2** with **6**.

As is expected from the selective formation of diene **5a** by the reaction of ketone **6**, the treatment of α-substituted γ-chloroallyl sulfide **3a** with the titanocene(II) reagent **4** in the presence of **13** gave vinyl cyclopropane **14a** through the reductive elimination of titanacyclobutane intermediate **15** (Scheme 6; Table 3, entry 1). The most significant finding is that the organotitanium species generated from β-monosubstituted γ-chloroallyl sulfide **3b**, which reacted with **6** via titanacycle **1**, also produced vinyl cyclopropane **14b** on reaction with **13** (Table 3, entry 2). Similarly, the reactions of γ-



Scheme 6. The formation of vinyl cyclopropanes **14** through the reductive elimination of titanacyclobutanes **15**.

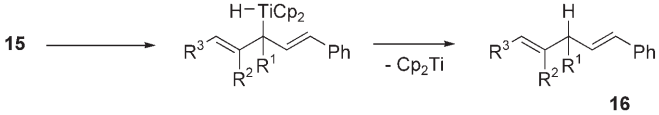
Table 3. Reaction of γ-chloroallyl sulfides **3** with styrene (**13**).

Entry	Sulfide **3**	Products[a]	
1[b]	**3a**	 **14a** (58, 85 : 15[c])	
2[d]	**3b**	 **14b** (24)[c]	 **17** (41, *E* : *Z* = 67 : 33)[f]
3[b]	**3c**	 **14c** (71, 76 : 24[c])	
4[b]	**3d**	 **14d** (60, 96 : 4[c])	
5[b]	**3f**	 **16b** (63)	
6[b]	**3g**	 **16c** (53)	
7[d]	**3i**	 **18** (55, *E* : *Z* = 80 : 20)	
8[g]	**3m**	 **19a** (25, 68 : 32[c])	 **19b** (42)

[a] Yields of the isolated products are given in parentheses. [b] Performed by using procedure D, as described in the Experimental Section. [c] Ratio of isomers. [d] Performed by using procedure E, as described in the Experimental Section. [e] Obtained as a single isomer. [f] Contaminated with a trace amount of (*E*)-1,4-diphenyl-1,4-pentadiene (**16a**). [g] Performed by using procedure F, as described in the Experimental Section.

monosubstituted γ-chloroallyl sulfides **3c** and **3d** also gave vinyl cyclopropanes **14c** and **14d** (Table 3, entries 3 and 4).

The alternative conceivable mode of the reaction via titanacyclobutanes **15** is β-elimination followed by reductive elimination to produce unconjugated dienes **16** (Scheme 7). The concomitant formation of conjugated diene **17** by reaction of **3b** (Table 3, entry 2), therefore, would be rationalized by the isomerization of the initially produced unconjugated diene **16a**. The stereoselective formation of (*E*,*E*)-dienes **16b** and **16c** was indeed observed when the α,γ-dis-



Scheme 7. The formation of unconjugated dienes **16** through the β-elimination of titanacyclobutanes **15**.

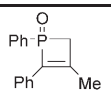
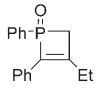
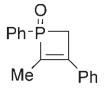
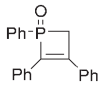
ubstituted sulfides **3f** and **3g** were employed (Table 3, entries 5 and 6). Although the reaction of cyclic γ-chloroallyl sulfide **3i** with **13** gave conjugated diene **18** through the ring-opening of the initially formed vinyl cyclopropane (Table 3, entry 7), neither **14** nor **16** were obtained by reaction of acyclic β,γ-disubstituted sulfides **3h** and **3m** with **13**; for example, only the reduction products **19** were produced in 67% total yield when **3m** was employed (Table 3, entry 8). These results suggest that the organotitanium intermediates generated from acyclic β,γ-disubstituted γ-chloroallyl sulfides behave as α,β-disubstituted titanacyclobutenes in the reaction with **13**.

It has been reported that the α,β-disubstituted titanacyclobutenes **1** are transformed into phospha-,[8] arsa-,[8b] and stiba-[8e] cyclobutenes. As the above results indicate that the treatment of β,γ-disubstituted γ-chloroallyl sulfides **3** with **4** affords the α,β-disubstituted titanacyclobutenes **1** bearing various substituents, we examined their transformation into phosphacycles.

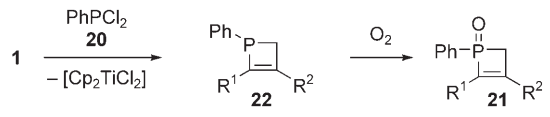
The successive treatment of **3j–m** with **4** at 25°C for 1 h and with dichlorophenylphosphine (**20**) under reflux in THF for 1 h produced the phosphacyclobutene *P*-oxides **21** (see Table 4 and Scheme 8). The formation of **21** is explained by the oxidation of the initially formed phosphacyclobutenes **22** in air[8c] during the work-up and isolation. A similar treatment of the organotitanium species generated from **3** (other than the β,γ-disubstituted species with at least one phenyl group) resulted in messy reactions, and no formation of phosphacycles **21** was observed. These unsuccessful results would be attributable, at least in part, to the equilibration of the titanacycles **1** with the vinyl carbene complexes **2**.

All the above results indicate that the reaction mode of the organotitanium intermediates generated from **3** is dependent on their substitution patterns. In the case of the α-monosubstituted derivatives, the intermediates act as vinyl carbene complexes **2** for both ketone **6** and styrene (**13**), whereas the α,β-disubstituted titanacyclobutenes are predominant intermediates for the reaction of acyclic β,γ-disubstituted γ-chloroallyl sulfides. The organotitanium species generated from other γ-chloroallyl sulfides show dual reactivity as the titanacyclobutenes **1** for **6** and the vinyl carbene complexes **2** for **13**. Such behavior may be explained by the equilibrium between **1** and **2**.

Table 4. Reaction of γ-chloroallyl sulfides **3** with dichlorophenylphosphine (**20**).[a]

Entry	Sulfide **3**	Product **21**[b]
1	**3j**	 **21a** (60)[c]
2	**3k**	 **21b** (60)
3	**3l**	 **21c** (56)[c]
4	**3m**	 **21d** (65)[c]

[a] Performed by using procedure G, as described in the Experimental Section. [b] Yield of the isolated products is given in parentheses. [c] Contaminated with a trace amount of triethylphosphate; the yield was corrected for this contaminant.



Scheme 8. The formation of phosphacyclobutene *P*-oxides **21** by the reaction of titanacyclobutenes **1** with dichlorophenylphosphine (**20**).

Conclusion

The present study has demonstrated that organotitanium species generated by the reaction of γ-chloroallyl sulfides with the titanocene(II) reagent **4** reveal, in principle, dual reactivity as titanacyclobutenes and vinyl carbene complexes. The α,β-disubstituted titanacyclobutenes formed from γ-chloroallyl sulfides are useful for the regioselective preparation of unsymmetrically substituted phosphacyclobutenes.

Experimental Section

THF was distilled from sodium and benzophenone. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. Column chromatography was performed on Merck Si 60. ^{1}H and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded in $CDCl_3$ and chemical shifts (δ) are quoted in parts per million from tetramethylsilane for ^{1}H NMR and from $CDCl_3$ for ^{13}C NMR spectroscopy unless otherwise noted. IR absorptions are reported in cm^{-1}. All the reactions were carried out in an argon atmosphere. γ-Chloroallyl sulfide **3a** was prepared from 3-(trimethylsilyl)-2-propyn-1-ol: The alcohol was transformed into a propargyl sulfide ($PhSSPh–Bu_3P$)[9] and ethylated (LDA—EtBr; LDA = lithium diisopropylamide). Hydroalumination (diisobutylaluminum hydride; DIBAL) of the propargyl sulfide followed by chlorination (*N*-chlorosuccinimide; NCS) [10] and desilylation (KOH/MeOH) gave **3a**. γ-Chloroallyl sulfides **3b** and **3e–m** were prepared from phenylacetaldehyde or ketones in three steps: The carbonyl compounds were converted into β-chloro-α,β-unsaturated aldehydes by using the Vilsmeier reagent.[11] These aldehydes were transformed into alcohols by reduction ($LiAlH_4$) or addition of Grignard reagents. Treatment of the alcohols with $PhSSPh–Bu_3P$ gave **3b** and **3e–m**. Sulfide **3c** was prepared by the treatment of 1,3-dichloro-2-butene with PhSH–KOH. γ-Chloroallyl sulfide **3d** was prepared from 2-heptyn-1-ol by hydroalumination (DIBAL), chlorination (NCS), and the treatment of the resulting alcohol with $PhSSPh–Bu_3P$.

Reaction of γ-chloroallyl sulfides 3 with 1,5-diphenylpentan-3-one (6)

Procedure A: Finely powdered molecular sieves 4 Å (MS4A; 150 mg), magnesium turnings (37 mg, 1.5 mmol), and [Cp_2TiCl_2] (374 mg, 1.5 mmol) were placed in a flask and dried by heating with a heat gun under reduced pressure (2–3 mm Hg). After the mixture was cooled, THF (2.5 mL) and $P(OEt)_3$ (0.51 mL, 3 mmol) were added successively with stirring at 25°C. After 3 h, a solution of **3a** (107 mg, 0.5 mmol) in THF (1.7 mL) was added dropwise over 3 min and the reaction mixture was stirred for 10 min. Then a solution of **6** (60 mg, 0.25 mmol) in THF

(1.7 mL) was added dropwise over 3 min and the reaction mixture was stirred for 2 h at 25 °C. The reaction was quenched by addition of 1 M NaOH, and the insoluble materials were removed by filtration through Celite and washed with diethyl ether. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by PTLC (eluant: pentane and then hexane/AcOEt 9:1) to give (*E*)-3-phenethyl-1-phenyl-3,5-octadiene (**5a**; 47 mg, 65%) and 4-ethyl-3-phenethyl-1-phenyl-5-hexen-3-ol (**7a**; 6 mg, 8%). **5a**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.00$ (t, $J = 7.5$ Hz, 3H), 2.10 (dq, $J = 7.2$, 7.2 Hz, 2H), 2.31–2.39 (m, 2H), 2.44–2.53 (m, 2H), 2.67–2.79 (m, 4H), 5.65 (dt, $J = 15.0$, 7.1 Hz, 1H), 5.88 (d, $J = 10.8$ Hz, 1H), 6.21 (dd, $J = 10.7$, 14.9 Hz, 1H), 7.13–7.33 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.8$, 25.9, 33.1, 34.9, 35.1, 39.3, 125.1, 125.6, 125.8, 125.9, 128.3, 128.4, 135.0, 139.1, 142.1, 142.2 ppm; IR (neat): $\tilde{\nu} = 3061$, 3026, 2961, 2870, 1602, 1496, 1454, 962, 745, 698 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{26}$: C 90.98, H 9.02; found: C 90.64, H 8.89. **7a**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 7.3$ Hz, 3H), 1.18–1.35 (m, 1H), 1.55 (s, 1H), 1.59–1.73 (m, 1H), 1.76–2.04 (m, 4H), 2.09–2.21 (m, 1H), 2.57–2.81 (m, 4H), 5.18 (dd, $J = 2.1$, 16.9 Hz, 1H), 5.26 (dd, $J = 2.1$, 10.1 Hz, 1H), 5.67 (ddd, $J = 10.0$, 10.0, 17.0 Hz, 1H), 7.14–7.36 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.7$, 21.3, 29.6, 29.7, 38.8, 39.3, 54.4, 74.9, 119.0, 125.8, 128.3, 128.39, 128.44, 138.3, 142.7, 142.8 ppm; IR (neat): $\tilde{\nu} = 3582$, 3484, 3062, 3026, 2956, 2871, 1603, 1454, 1378, 1052, 1030, 1004, 940, 915, 748, 699 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{28}O$: C 85.66, H 9.15; found: C 85.56, H 8.94.

Procedure B: A solution of **3b** (156 mg, 0.6 mmol) in THF (2 mL) was added dropwise to a solution of **4** in THF (3 mL) (prepared from MS4A (150 mg), magnesium turnings (44 mg, 1.8 mmol), $[Cp_2TiCl_2]$ (448 mg, 1.8 mmol), and $P(OEt)_3$ (0.61 mL, 3.6 mmol)) over 3 min at 25 °C. The reaction mixture was stirred for 1 h. Then a solution of **6** (72 mg, 0.3 mmol) in THF (2 mL) was added dropwise over 3 min and the reaction mixture heated to reflux for 2 h. The usual work-up and purification by PTLC (hexane/AcOEt 9:1) gave 3-phenethyl-1,5-diphenyl-5-hexen-3-ol (**7b**; 64 mg, 60%). **7b**: m.p. 86–88 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.56$ (s, 1H), 1.67–1.84 (m, 4H), 2.49–2.72 (m, 4H), 2.86 (s, 2H), 5.24 (s, 1H), 5.38 (d, $J = 1.8$ Hz, 1H), 7.00 (d, $J = 6.8$ Hz, 4H), 7.12–7.47 ppm (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 30.3$, 41.2, 44.5, 74.1, 118.1, 125.7, 126.7, 127.7, 128.2, 128.3, 128.6, 142.3, 142.7, 145.6 ppm; IR (KBr): $\tilde{\nu} =$ 3536, 3024, 2925, 1495, 1452, 1383, 1268, 1103, 926, 768, 749, 719, 701 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{28}O$: C 87.60, H 7.92; found: C 87.46, H 8.12.

Procedure C: A solution of **3c** (119 mg, 0.6 mmol) in THF (2 mL) was added dropwise to a solution of **4** in THF (3 mL) (prepared from MS4A (150 mg), magnesium turnings (44 mg, 1.8 mmol), $[Cp_2TiCl_2]$ (448 mg, 1.8 mmol), and $P(OEt)_3$ (0.61 mL, 3.6 mmol)) over 3 min at 25 °C. The reaction mixture was stirred for 10 min. Then a solution of **6** (72 mg, 0.3 mmol) in THF (2 mL) was added dropwise over 3 min and the reaction mixture stirred for 1 h at 25 °C. The usual work-up and purification by PTLC (hexane/AcOEt 9:1) gave (*E*)-3-phenethyl-1-phenyl-5-hepten-3-ol (**7c**; 21 mg, 24%) and 4-methyl-3-phenethyl-1-phenyl-5-hexen-3-ol (**11a**; 34 mg, 38%). **7c**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.53$ (s, 1H), 1.72 (dd, $J = 1.1$, 6.0 Hz, 3H), 1.81–1.85 (m, 4H), 2.30 (d, $J = 7.1$ Hz, 2H), 2.67–2.72 (m, 4H), 5.52 (dtq, $J = 15.1$, 7.2, 1.3 Hz, 1H), 5.62 (dq, $J = 15.1$, 6.0 Hz, 1H), 7.16–7.32 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 18.2, 30.1, 41.1, 42.5, 73.7, 125.6, 125.8, 128.3, 128.4, 130.0, 142.5 ppm; IR (neat): $\tilde{\nu} = 3563$, 3450, 3025, 2935, 1496, 1453, 970, 748, 698 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{26}O$: C 85.67, H 8.90; found: C 85.91, H 9.29. **11a**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.09$ (d, $J = 7.0$ Hz, 3H), 1.48 (s, 1H), 1.79–1.91 (m, 4H), 2.50 (dq, $J = 7.2$, 7.2 Hz, 1H), 2.59–2.79 (m, 4H), 5.15 (d, $J = 10.4$ Hz, 1H), 5.16 (d, $J = 17.0$ Hz, 1H), 5.89 (ddd, $J =$ 8.7, 10.4, 16.9 Hz, 1H), 7.19–7.31 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.5$, 29.7, 29.8, 38.5, 38.8, 45.3, 75.0, 116.6, 125.8, 128.3, 128.4, 128.5, 140.0, 142.59, 142.61 ppm; IR (neat): $\tilde{\nu} = 3582$, 3482, 3062, 3026, 2950, 1496, 1454, 748, 699 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{26}O$: C 85.67, H 8.90; found: C 85.91, H 8.62.

(*E*)-3-Phenethyl-1,6-diphenyl-5-hexen-3-ol (7d) and 3-phenethyl-1,4-diphenyl-5-hexen-3-ol (11b): The reaction was carried out according to procedure C with **3e** (156 mg, 0.6 mmol) and **6** (72 mg, 0.3 mmol). **7d** (67 mg, 63%): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.58$ (s, 1H), 1.56–1.91 (m, 4H), 2.52 (d, $J = 7.5$ Hz, 2H), 2.71–2.77 (m, 4H), 6.28 (dt, $J = 15.8$, 7.7 Hz, 1H), 6.53 (d, $J = 15.8$ Hz, 1H), 7.19–7.39 ppm (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 30.1$, 41.3, 43.1, 74.3, 124.9, 125.9, 126.1, 127.4, 128.3, 128.5, 128.6, 134.0, 137.2, 142.2 ppm; IR (neat): $\tilde{\nu} = 3563$, 3453, 3060, 3025, 2935, 1602, 1495, 1453, 968, 747, 697 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{28}O$: C 87.60, H 7.92; found: C 87.77, H 8.14. **11b** (11 mg, 10%): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.45$ (s, 1H), 1.63–1.82 (m, 2H), 1.92–1.97 (m, 2H), 2.60–2.77 (m, 4H), 3.51 (d, $J = 9.7$ Hz, 1H), 5.20 (d, $J = 17.4$ Hz, 1H), 5.21 (dd, $J = 1.8$, 9.3 Hz, 1H), 6.36 (ddd, $J = 10.1$, 10,1 16.7 Hz, 1H), 7.08–7.34 ppm (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.9$, 38.5, 38.9, 58.1, 75.4, 117.5, 125.8, 125.9, 126.8, 128.27, 128.34, 128.4, 128.45, 128.54, 129.2, 137.6, 140.7, 142.2, 142.3 ppm; IR (neat): $\tilde{\nu} = 3578$, 3463, 3061, 3025, 2945, 2868, 1495, 1453, 748, 700 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{28}O$: C 87.60, H 7.92; found: C 87.23, H 8.20.

(*E*)-4-Ethyl-3-phenethyl-1,6-diphenyl-5-hexen-3-ol (7e): The reaction was carried out according to procedure C with **3f** (173 mg, 0.6 mmol) and **6** (72 mg, 0.3 mmol). **7e** (97 mg, 84%): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.91 (t, $J = 7.3$ Hz, 3H), 1.27–1.45 (m, 1H), 1.57 (s, 1H), 1.67–2.04 (m, 5H), 2.33 (dt, $J = 2.3$, 10.5 Hz, 1H), 2.61–2.85 (m, 4H), 6.07 (dd, $J = 9.9$, 15.8 Hz, 1H), 6.53 (d, $J = 15.9$ Hz, 1H), 7.13–7.43 ppm (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.9$, 21.8, 29.7, 29.8, 38.9, 39.5, 53.6, 75.5, 125.8, 126.2, 127.4, 128.36, 128.40, 128.45, 128.6, 129.9, 133.9, 137.1, 142.6, 142.7 ppm; IR (neat): $\tilde{\nu} = 3572$, 3479, 3083, 3060, 3025, 2955, 2871, 1602, 1495, 1453, 1378, 1030, 973, 945, 748, 696 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{32}O$: C 87.45, H 8.39; found: C 87.38, H 8.48.

(*E*)-3-Phenethyl-1,4,6-triphenyl-5-hexen-3-ol (7f): The reaction was carried out according to procedure C with **3g** (202 mg, 0.6 mmol) and **6** (72 mg, 0.3 mmol). **7f** (114 mg, 88%): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 1.51 (s, 1H), 1.67–1.86 (m, 2H), 1.96–2.05 (m, 2H), 2.64–2.81 (m, 4H), 3.67 (d, $J = 9.7$ Hz, 1H), 6.52 (d, $J = 15.8$ Hz, 1H), 6.76 (dd, $J = 9.7$, 15.8 Hz, 1H), 7.08–7.41 ppm (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 29.99, 30.03, 38.7, 39.1, 57.3, 76.0, 125.86, 125.88, 126.3, 126.9, 127.3, 128. 3, 128.35, 128.43, 128.46, 128.49, 128.6, 129.23, 129.24, 132.5, 137.2, 140.8, 142.09, 142.15 ppm; IR (neat): $\tilde{\nu} = 3572$, 3469, 3082, 3060, 3025, 2945, 2865, 1601, 1495, 1453, 1053, 1030, 969, 909, 746, 696 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{32}O$: C 88.85, H 7.46; found: C 88.79, H 7.81.

(*Z*)-3-Phenethyl-1,5,6-triphenyl-5-hexen-3-ol (7g): The reaction was carried out according to procedure B with **3m** (202 mg, 0.6 mmol) and **6** (72 mg, 0.3 mmol). **7g** (44 mg, 34%): m.p. 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.45$ (s, 1H), 1.82 (t, $J = 8.7$ Hz, 4H), 2.56–2.73 (m, 4H), 2.92 (s, 2H), 6.63 (s, 1H), 6.89–6.92 (m, 2H), 7.08–7.36 ppm (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 30.3$, 41.4, 49.1, 74.9, 125.8, 126.6, 127.5, 127.9, 128.3, 128.4, 128.96, 129.03, 129.1, 131.3, 136.8, 138.7, 141.2, 142.3 ppm; IR (KBr): $\tilde{\nu} = 3462$, 3025, 2938, 1494, 1449, 1189, 1041, 756, 698 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{32}O$: C 88.85, H 7.46; found: C 88.76, H 7.49.

4-Ethyl-5-methyl-3-phenethyl-1-phenyl-5-hexen-3-ol (11c): The reaction was carried out according to procedure B with **3h** (136 mg, 0.6 mmol) and **6** (72 mg, 0.3 mmol). Purification by PTLC (benzene) gave **11c** (53 mg, 55%). **11c**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 7.3$ Hz, 3H,), 1.43–1.67 (m, 3H), 1.78 (s, 3H), 1.80–1.96 (m, 4H), 2.18 (dd, $J =$ 3.1, 11.7 Hz, 1H), 2.58–2.76 (m, 4H), 4.86 (s, 1H), 5.02 (s, 1H), 7.16–7.32 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.6$, 19.6, 30.16, 30.20, 30.8, 39.0, 39.3, 55.8, 75.3, 115.5, 125.79, 125.83, 128.28, 128.33, 128.4, 128.5, 142.5, 142.6, 145.0 ppm; IR (neat): $\tilde{\nu} = 3490$, 3026, 2957, 2872, 1496, 1454, 699 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{30}O$: C 85.66, H 9.38; found: C 85.28, H 9.58.

3-(2-Methylidenecyclohexyl)-1,5-diphenylpentan-3-ol (11d): The reaction was carried out according to procedure B with **3i** (143 mg, 0.6 mmol) and **6** (72 mg, 0.3 mmol). Purification by PTLC (hexane/benzene 1:2) gave **11d** (40 mg, 40%). **11d**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.41$–2.08 (m, 11H), 2.13–2.19 (m, 1H), 2.26–2.38 (m, 1H), 2.42 (t, $J = 5.5$ Hz, 1H), 2.58–2.80 (m, 4H), 4.84 (s, 1H), 4.93 (s, 1H), 7.17–7.32 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 24.0$, 27.8, 27.9, 30.0, 30.1, 35.9, 39.3, 39.6, 49.1, 76.0, 110.9, 125.77, 125.79, 128.3, 128.37, 128.41, 128.44, 142.6,

149.4 ppm; IR (neat): $\tilde{\nu}$ = 3583, 3500, 3062, 3026, 2932, 2857, 1496, 1453, 747, 699 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{30}O$: C 86.18, H 9.04; found: C 85.92, H 9.21.

Reaction of γ-chloroallyl sulfides 3 with styrene (13)

Procedure D: A solution of **3a** (64 mg, 0.3 mmol) in THF (1.2 mL) was added dropwise to a solution of **4** in THF (1.8 mL) (prepared from MS4A (54 mg), magnesium turnings (18 mg, 0.7 mmol), [Cp_2TiCl_2] (187 mg, 0.8 mmol), and $P(OEt)_3$ (0.26 mL, 1.5 mmol) in the presence of **13** (0.14 mL, 1.2 mmol)) over 3 min at 25 °C. The reaction mixture was stirred for 4 h. The usual work-up and purification by PTLC (pentane) gave (*E*)-1-(1-butenyl)-2-phenylcyclopropane (**14a**; 30 mg, 58 %) as a mixture of stereoisomers (85:15). **14a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.4 Hz, 0.45 H), 0.91–1.08 (m, 1 H), 0.97 (t, *J* = 7.4 Hz, 2.55 H), 1.13 (ddd, *J* = 5.2, 5.2, 8.4 Hz, 0.85 H), 1.17–1.24 (m, 0.15 H), 1.57–1.68 (m, 0.85 H), 1.74–1.94 (m, 1.45 H), 2.02 (ddt, *J* = 1.5, 7.4, 13.8 Hz, 1.7 H), 4.76 (ddt, *J* = 8.8, 15.3, 1.5 Hz, 0.15 H), 5.14 (ddt, *J* = 8.2, 15.2, 1.5 Hz, 0.85 H), 5.58 (dt, *J* = 15.2, 6.4 Hz, 1 H), 7.02–7.30 ppm (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.6, 13.8, 14.0, 16.7, 24.9, 25.5, 25.6, 26.5, 125.4, 125.6, 125.7, 127.8, 127.9, 128.3, 129.1, 130.9, 131.0, 132.6, 142.8 ppm; IR (neat): $\tilde{\nu}$ = 3025, 2962, 1604, 1497, 1459, 959, 749, 696 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{16}$: C 90.64, H 9.36; found: C 90.42, H 9.41.

Procedure E: A solution of **3b** (130 mg, 0.5 mmol) in THF (2 mL) was added dropwise to a solution of **4** in THF (3.0 mL) (prepared from MS4A (126 mg), magnesium turnings (43 mg, 1.8 mmol), [Cp_2TiCl_2] (436 mg, 1.8 mmol), and $P(OEt)_3$ (0.6 mL, 3.5 mmol) in the presence of **13** (0.23 mL, 2 mmol)) over 3 min at 25 °C. The reaction mixture was heated to reflux for 4 h. The usual work-up and purification by PTLC (hexane) gave a mixture of 1-phenyl-2-(1-phenylethenyl)cyclopropane (**14b**) and 1,4-diphenyl-1,3-pentadiene (**17**)[12] (74 mg: **14b**: 25 %, **17**: 42 %; *E*/*Z* = 67:33). Mixture of **14b** and **17**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (ddd, *J* = 5.3, 5.3, 8.5 Hz 0.37 H), 1.39 (ddd, *J* = 5.0, 6.2, 8.5 Hz, 0.37 H), 1.92–2.04 (m, 0.74 H), 2.19 (s, 0.63 H), 2.27 (s, 1.26 H), 5.04 (s, 0.37 H), 5.35 (s, 0.37 H), 6.31 (d, *J* = 11.2 Hz, 0.21 H), 6.53 (d, *J* = 15.8 Hz, 0.21 H), 6.61–6.72 (m, 0.84 H), 6.86 (dd, *J* = 11.0, 15.6 Hz, 0.21 H), 7.09–7.55 ppm (m, 10.42 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.9, 16.2, 25.6, 26.4, 27.8, 109.4, 125.6, 125.7, 125.8, 126.1, 126.25, 126.34, 126.7, 127.08, 127. 14, 127.3, 127.4, 127.55, 127.57, 128.17, 128.24, 128.3, 128.39, 128.44, 128.5, 128.6, 131.4, 132.9, 136.8, 137.8, 139.6, 141.1, 141.6, 142.5, 143.0, 148.3 ppm; IR (neat): $\tilde{\nu}$ = 3057, 3028, 1602, 1494, 1443, 1027, 963, 777, 748, 696 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{16}$: C 92.68, H 7.32; found: C 92.52, H 7.52.

1-Ethenyl-1-methyl-2-phenylcyclopropane (14c): The reaction was carried out according to procedure D with **3c** (99 mg, 0.5 mmol) and **13** (0.23 mL, 2 mmol). **14c** (56 mg, 71 %, ratio of stereoisomers = 76:24): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (s, 2.28 H), 1.07–1.14 (m, 1.52 H), 1.18–1.26 (m, 0.48 H), 1.35 (s, 0.72 H), 2.17 (dd, *J* = 11.7, 11.7 Hz, 1 H), 4.83–5.02 (m, 2 H), 5.20 (dd, *J* = 10.5, 17.2 Hz, 0.24 H), 5.61 (dd, *J* = 10.5, 17.1 Hz, 0.76 H), 7.15–7.29 ppm (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.9, 18.8, 19.7, 25.1, 25.5, 30.9, 32.1, 109.8, 111.9, 126.0, 126.1, 129.3, 138.9, 142.3, 147.0 ppm; IR (neat): $\tilde{\nu}$ = 3085, 3062, 2952, 1634, 1604, 1072, 1030, 993, 896, 698 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{14}$: C 91.08, H 8.92; found: C 90.60, H 9.18.

1-Ethenyl-1-hexyl-2-phenylcyclopropane (14d): The reaction was carried out according to procedure D with **3d** (134 mg, 0.5 mmol) and **13** (0.23 mL, 2 mmol). **14d** (69 mg, 60 %, ratio of stereoisomers = 96:4): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 6.9 Hz, 3 H), 0.84–1.37 (m, 12 H), 2.15 (dd, *J* = 7.0, 8.2 Hz, 1 H), 4.88–5.01 (m, 2 H), 5.22 (dd, *J* = 10.5, 17.4 Hz, 0.04 H), 5.81 (dd, *J* = 10.6, 17.2 Hz, 0.96 H), 7.12–7.30 ppm (m, 5 H); ^{13}C NMR (major isomer; 75 MHz, $CDCl_3$): δ = 14.0, 17.0, 22.5, 26.8, 29.4, 30.2, 30.8, 31.67, 31.73, 110.7, 125.8, 127.8, 129.0, 138.8, 144.5 ppm; IR (neat): $\tilde{\nu}$ = 3063, 2999, 2927, 2856, 1634, 1604, 1497, 1455, 992, 896, 780, 698, 447 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{24}$: C 89.41, H 10.59; found: C 89.16, H 10.65.

(1*E*,4*E*)-1,3-Diphenyl-1,4-hepatdiene (16b): The reaction was carried out according to procedure D with **3f** (144 mg, 0.5 mmol) and **13** (0.23 mL, 2 mmol). **16b** (79 mg, 63 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.4 Hz, 3 H), 2.09 (dq, *J* = 7.1, 7.1 Hz, 2 H), 4.16 (m, 1 H), 5.57 (ddt, *J* = 0.8, 15.8, 5.8 Hz, 1 H), 5.70 (ddt, *J* = 6.6, 15.4, 1.2 Hz, 1 H), 6.38–6.42 (m, 2 H), 7.16–7.42 ppm (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 25.6, 51.4, 126.2, 126.3, 127.1, 128.0, 128.5, 130.0, 130.7, 132.8, 133.4, 137.5, 143.6 ppm; IR (neat): $\tilde{\nu}$ = 3026, 2962, 2931, 1493, 1450, 968, 743, 698 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{20}$: C 91.88, H 8.12; found: C 91.73, H 8.18.

(1*E*,4*E*)-1,3,5-Triphenyl-1,4-pentadiene (16c):[13] The reaction was carried out according to procedure D with **3g** (168 mg, 0.5 mmol) and **13** (0.23 mL, 2 mmol). **16c** (77 mg, 53 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35–4.42 (m, 1 H), 6.45–6.50 (m, 4 H), 7.17–7.41 ppm (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.6, 126.3, 126.6, 127.3, 128.1, 128.5, 128.6, 130.8, 131.9, 137.3, 142.8 ppm; IR (neat): $\tilde{\nu}$ = 3081, 3059, 3026, 1599, 1494, 1448, 967, 908, 741, 694 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{20}$: C 93.20, H 6.80; found: C 93.21, H 7.16.

1-Methylidene-2-(1-phenylethylidene)cyclohexane (18): The reaction was carried out according to procedure E with **3i** (119 mg, 0.5 mmol) and **13** (0.23 mL, 2 mmol). (*E*)-**18** (43 mg, 43 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56–1.74 (m, 4 H), 1.88 (s, 3 H), 2.13 (br t, 2 H), 2.27 (br t, 2 H), 6.47 (d, *J* = 15.9 Hz, 1 H), 7.16–7.43 ppm (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5, 22.8, 22.9, 25.5, 33.2, 124.9, 126.1, 126.7, 127.6, 127.9, 128.5, 134.9, 138.6 ppm; IR (neat): $\tilde{\nu}$ = 3041, 2926, 1629, 1598, 1495, 1447, 955, 748, 691 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{18}$: C 90.85, H 9.15; found: C 90.56, H 9.08. (*Z*)-**18** (11 mg, 11 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57–1.73 (m, 7 H), 1.95–2.04 (m, 2 H), 2.04–2.12 (m, 2 H), 4.97 (d, *J* = 1.8 Hz, 1 H), 5.53 (d, *J* = 1.8 Hz, 1 H), 7.21–7.42 ppm (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 23.2, 23.3, 30.4, 31.3, 112.5, 126.2, 127.3, 128.3, 129.8, 132.1, 139.9, 150.2 ppm; IR (neat): $\tilde{\nu}$ = 3080, 3056, 3023, 2925, 2831, 1611, 1492, 1445, 1377, 1028, 897, 778, 708 cm^{-1}.

Procedure F: A solution of **3m** (168 mg, 0.5 mmol) in THF (2 mL) was added dropwise to a solution of **4** in THF (4.8 mL) (prepared from MS4A (126 mg), magnesium turnings (49 mg, 2 mmol), [Cp_2TiCl_2] (498 mg, 2 mmol), and $P(OEt)_3$ (0.68 mL, 4 mmol) in the presence of **13** (0.23 mL, 2 mmol)) over 3 min at 25 °C. The reaction mixture was heated to reflux for 4 h. The usual work-up and purification by PTLC (hexane) gave a mixture of 1,2-diphenyl-1-propene (**19a**) and 2,3-diphenyl-1-propene (**19b**) (66 mg: **19a**: 25 %; ratio of stereoisomers = 68:32, **19b**: 42 %). Mixture of **19a** and **19b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (d, *J* = 1.5 Hz, 0.75 H), 2.27 (d, *J* = 1.1 Hz, 0.36 H), 3.82 (s, 1.26 H), 5.00 (m, 0.63 H), 5.48 (s, 0.63 H), 6.46 (s, 0.25 H), 6.84 (s, 0.12 H), 6.87–7.53 ppm (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.4, 27.1, 41.6, 114.6, 125.97, 126.05, 126.06, 126.09, 126.4, 126.48, 126.53, 126.9, 127.2, 127.4, 127.6, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 128.7, 128.9, 129.1, 137.4, 137.6, 138.3, 138.7, 139.5, 140.8, 142.1, 143.9, 146.9 ppm; IR (neat): $\tilde{\nu}$ = 3082, 3059, 3026, 2913, 1626, 1600, 1495, 1443, 1029, 900, 777, 758, 725, 697 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{14}$: C 92.74, H 7.26; found: C 92.74, H 7.38.

Reaction of γ-chloroallyl sulfides 4 with dichlorophenylphosphine (20)

Procedure G: A solution of **3j** (137 mg, 0.5 mmol) in THF (1.5 mL) was added dropwise to a solution of **4** in THF (4.8 mL) (prepared from MS4A (150 mg), magnesium turnings (49 mg, 2 mmol), [Cp_2TiCl_2] (498 mg, 2 mmol), and $P(OEt)_3$ (0.68 mL, 4 mmol)) over 3 min at 25 °C. The reaction mixture was stirred for 1 h. Then **20** (0.17 mL, 1.3 mmol) was added at 25 °C and the reaction mixture was heated to reflux for 1 h. The reaction was quenched by addition of 1 M NaOH, and the insoluble materials were removed by filtration through Celite and washed with diethyl ether. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and concentrated. After removal of triethyl phosphite and triethyl phosphate under reduced pressure (95 °C, 0.3 mm Hg), the residue was purified by PTLC (hexane/AcOEt 1:2) to give 3-methyl-1,4-diphenyl-1,2-dihydrophosphete *P*-oxide (**21a**; 77 mg) contaminated with a trace amount of triethyl phosphate. The yield was corrected for the contaminant (60 %). **21a**: m.p. 140–143 °C (recrystallized from hexane/AcOEt); ^{1}H NMR (300 MHz, C_6D_6): δ = 1.59 (d, *J* = 3.3 Hz, 3 H), 2.36 (dd, *J* = 12.8, 12.8 Hz, 1 H), 2.83 (dd, *J* = 17.6, 17.6 Hz, 1 H), 6.88–7.11 (m, 6 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 7.88–7.95 ppm (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9 (d, $^3J_{C,P}$ = 34.7 Hz), 44.8 (d, $^1J_{C,P}$ = 59.5 Hz), 127.4, 127.5, 128.2, 128.7, 128.8, 128.9, 130.9, 131.0, 132.08, 132.12 ppm; ^{31}P NMR (121 MHz, C_6D_6; relative to external H_3PO_4): δ = 21.5 ppm; IR (KBr): $\tilde{\nu}$ = 3057, 2925, 1440,

1213, 1196, 1125, 1111, 840, 769, 732, 699 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{15}OP$: C 75.58, H 5.95; found: C 75.91, H 5.98.

3-Ethyl-1,4-diphenyl-1,2-dihydrophosphete *P*-Oxide (21b): The reaction was carried out according to procedure G with **3k** (144 mg, 0.5 mmol) and **20** (0.17 mL, 1.3 mmol). **21b** (81 mg, 60%): m.p. 140–143 °C (recrystallized from hexane/AcOEt); ^1H NMR (300 MHz, C_6D_6): $\delta = 0.76$ (t, $J =$ 7.5 Hz, 3H), 2.20 (dt, $J = 3.8$, 7.5 Hz, 2H), 2.50 (dd, $J = 13.8$, 15.9 Hz, 1H), 2.89 (dd, $J = 15.9$, 19.1 Hz, 1H), 6.88–7.05 (m, 3H), 7.07–7.13 (m, 3H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.89–7.96 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.3$ (d, $^4J_{C,P} = 2.5$ Hz), 24.5 (d, $^3J_{C,P} = 32.3$ Hz), 41.7 (d, $^1J_{C,P} = 59.3$ Hz), 127.5, 124.6, 128.19, 128.21, 128.7, 128.8, 129.0, 130.9, 131.1, 132.07, 132.11 ppm; ^{31}P NMR (121 MHz, C_6D_6; relative to external H_3PO_4): $\delta = 20.7$ ppm; IR (KBr): $\tilde{\nu} = 3056$, 2971, 2933, 2907, 1439, 1206, 1105, 772, 723, 699 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{17}OP$: C 76.10, H 6.39; found: C 76.15, H 6.47.

4-Methyl-1,3-diphenyl-1,2-dihydrophosphete *P*-Oxide (21c): The reaction was carried out according to procedure G with **3l** (137 mg, 0.5 mmol) and **20** (0.17 mL, 1.3 mmol). **21c** (72 mg, 56%): m.p. 105–108 °C (recrystallized from hexane/AcOEt); ^1H NMR (300 MHz, C_6D_6): $\delta = 1.73$ (dt, $J =$ 17.2, 2.2 Hz, 3H), 2.80 (ddq, $J = 14.5$, 14.5, 1.8 Hz, 1H), 3.14 (ddq, $J =$ 14.8, 18.9, 2.5 Hz, 1H), 7.06–7.21 (m, 8H), 7.81–7.88 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.4$, 41.1 (d, $^1J_{C,P} = 58.9$ Hz), 128.17, 128.19, 128.79, 128.82, 128.9, 130.0, 131.0, 131.1, 132.06, 132.10 ppm; ^{31}P NMR (121 MHz, C_6D_6; relative to external H_3PO_4): $\delta = 21.0$ ppm; IR (KBr): $\tilde{\nu} = 3052$, 2956, 2920, 1439, 1207, 1162, 1108, 762, 745, 691 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{15}OP$: C 75.58, H 5.95; found: C 75.97, H 5.98.

1,3,4-Triphenyl-1,2-dihydrophosphete *P*-oxide (21d):[8c] The reaction was carried out according to procedure G with **3m** (168 mg, 0.5 mmol) and **20** (0.17 mL, 1.3 mmol). **21d** (103 mg, 56%): m.p. 125–128 °C (recrystallized from hexane/AcOEt); ^1H NMR (300 MHz, C_6D_6): $\delta = 2.80$ (dd, $J = 14.0$, 15.5 Hz, 1H), 3.29 (dd, $J = 15.6$, 19.6 Hz, 1H), 6.85–7.10 (m, 9H), 7.29 (dd, $J = 1.7$, 8.0 Hz, 2H), 7.39–7.42 (m, 2H), 7.97–8.04 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 42.2$ (d, $^1J_{C,P} = 59.6$ Hz), 127.5, 127.6, 128.11, 128.14, 128.69, 128.72, 128.8, 128.9, 129.1, 130.5, 130.6, 131.0, 131.2, 131.9, 132.19, 132.23, 133.3, 133.8, 147.0, 147.1 ppm; ^{31}P NMR (121 MHz, C_6D_6; relative to external H_3PO_4): $\delta = 18.9$ ppm; IR (KBr): $\tilde{\nu} = 3048$, 2956, 2914, 1439, 1218, 1185, 1108, 767, 749, 734, 693 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{17}OP$: C 79.73, H 5.42; found: C 79.92, H 5.46.

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[1] K. M. Doxsee, J. J. J. Juliette, J. K. M. Mouser, K. Zientara, *Organometallics* **1993**, *12*, 4742–4744.
[2] a) P. Binger, P. Müller, R. Benn, R. Mynott, *Angew. Chem.* **1989**, *101*, 647–648; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 610–611; b) P. Binger, P. Müller, A. T. Herrmann, P. Philipps, B. Gabor, F. Langhauser, C. Krüger, *Chem. Ber.* **1991**, *124*, 2165–2170.
[3] a) F. N. Tebbe, G. W. Parshall, D. W. Ovenall, *J. Am. Chem. Soc.* **1979**, *101*, 5074–5075; b) F. N. Tebbe, R. L. Harlow, *J. Am. Chem. Soc.* **1980**, *102*, 6149–6151; c) T. R. Howard, J. B. Lee, R. H. Grubbs, *J. Am. Chem. Soc.* **1980**, *102*, 6876–6878; d) R. J. McKinney, T. H. Tulip, D. L. Thorn, T. S. Coolbaugh, F. N. Tebbe, *J. Am. Chem. Soc.* **1981**, *103*, 5584–5586; e) J. J. Eisch, A. Piotrowski, *Tetrahedron Lett.* **1983**, *24*, 2043–2046; f) E. V. Anslyn, R. H. Grubbs, *J. Am. Chem. Soc.* **1987**, *109*, 4880–4890; g) J. D. Meinhart, E. V. Anslyn, R. H. Grubbs, *Organometallics* **1989**, *8*, 583–589; h) K. M. Doxsee, J. K. M. Mouser, J. B. Farahi, *Synlett* **1992**, 13–21; i) N. A. Petasis, D.-K. Fu, *Organometallics* **1993**, *12*, 3776–3780; j) K. M. Doxsee, J. J. J. Juliette, J. K. M. Mouser, K. Zientara, *Organometallics* **1993**, *12*, 4682–4686.
[4] a) J. D. Meinhart, R. H. Grubbs, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 171–180; b) K. M. Doxsee, J. K. M. Mouser, *Organometallics* **1990**, *9*, 3012–3014; c) K. M. Doxsee, J. K. M. Mouser, *Tetrahedron Lett.* **1991**, *32*, 1687–1690; d) R. D. Dennehy, R. J. Whitby, *J. Chem. Soc. Chem. Commun.* **1992**, 35–36; e) K. M. Doxsee, J. J. J. Juliette, T. J. R. Weakley, K. Zientara, *Inorg. Chim. Acta* **1994**, *222*, 305–315.
[5] J. D. Meinhart, B. D. Santarsiero, R. H. Grubbs, *J. Am. Chem. Soc.* **1986**, *108*, 3318–3323.
[6] a) Y. Horikawa, M. Watanabe, T. Fujiwara, T. Takeda, *J. Am. Chem. Soc.* **1997**, *119*, 1127–1128; b) T. Takeda, Y. Takagi, N. Saeki, T. Fujiwara, *Tetrahedron Lett.* **2000**, *41*, 8377–8381.
[7] Y. Horikawa, T. Nomura, M. Watanabe, T. Fujiwara, T. Takeda, *J. Org. Chem.* **1997**, *62*, 3678–3682.
[8] a) K. M. Doxsee, G. S. Shen, *J. Am. Chem. Soc.* **1989**, *111*, 9129–9130; b) W. Tumas, J. A. Suriano, R. L. Harlow, *Angew. Chem.* **1990**, *102*, 89–90; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 75–76; c) K. M. Doxsee, E. M. Hanawalt, G. S. Shen, T. J. R. Weakley, H. Hope, C. B. Knobler, *Inorg. Chem.* **1991**, *30*, 3381–3389; d) N. Maigrot, N. Avarvari, C. Charrier, F. Mathey, *Angew. Chem.* **1995**, *107*, 623–625; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 590–592; e) K. M. Doxsee, N. P. Wood, E. M. Hanawalt, T. J. R. Weakley, *Heteroat. Chem.* **1996**, *7*, 383–389; f) N. Avarvari, P. L. Floch, C. Charrier, F. Mathey, *Heteroat. Chem.* **1996**, *7*, 397–402.
[9] I. Nakagawa, T. Hata, *Tetrahedron Lett.* **1975**, *17*, 1409–1412.
[10] G. Zweifel, W. Lewis, *J. Org. Chem.* **1978**, *43*, 2739–2744.
[11] K. Bodendorf, R. Mayer, *Chem. Ber.* **1965**, *98*, 3554–3560.
[12] A. R. Katritzky, D. Cheng, S. A. Henderson, J. Li, *J. Org. Chem.* **1998**, *63*, 6704–6709.
[13] T. Hirao, S. Kohno, J. Enda, Y. Ohshiro, T. Agawa, *Tetrahedron Lett.* **1981**, *22*, 3633–3636.

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