Allylsilanes as Carbon Nucleophiles in the Palladium-Catalyzed 1,4-Oxidation of Conjugated Dienes

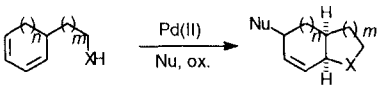
Ana M. Castaño, B. Anders Persson, and Jan-E. Bäckvall*

Abstract: Palladium-catalyzed oxidation of cyclic 1,3-dienes **3**, **5**, **9**, **11**, and **13**, with an allylsilane group in the side chain, led to an intramolecular 1,4-*syn*-addition to the conjugated diene through a carbocyclization. Acyclic trienesilanes **7** also underwent analogous 1,4-oxidations. The reaction was carried out in acetone–acetic acid (2:1) with a slight excess of LiCl. *p*-Benzoquinone was employed as the oxidant and Li_2PdCl_4 as the catalyst. The reaction proceeds through an intramolecular *trans* addition of the allylsilane to a (π-diene)palladium complex to produce a bicyclic (π-allyl)palladium intermediate. Subsequent *trans* attack by chloride at the π-allyl intermediate gives the product. The intermediate (π-allyl)palladium complex was isolated and fully characterized. It was unambiguously demonstrated that the allylsilane had attacked the coordinated double bond *trans* to palladium (*trans*-carbopalladation). The use of $CuCl_2$ as the oxidant, instead of *p*-benzoquinone, gave a less stereoselective addition, but interestingly, with the opposite stereochemistry.

Keywords
allylsilanes · catalysis · cyclizations · oxidations · palladium

Introduction

Palladium-catalyzed reactions by nucleophilic addition to (π-olefin)- and (π-allyl)palladium complexes have become important in organic synthesis.[1–5] These reactions are often associated with high stereo- and regioselectivities, and, in addition, they proceed under mild reaction conditions. Our research group has been particularly engaged in the investigation of palladium-catalyzed oxidations,[6–12] and a few years ago we developed the palladium-catalyzed 1,4-oxidation of conjugated dienes.[2b, 7b, 8] This class of reaction, which involves nucleophilic addition to intermediate (π-olefin)- and (π-allyl)-palladium complexes, leads to an overall 1,4-functionalization of the conjugated diene. Recent extension to intramolecular versions also allows the use of a variety of different oxygen and nitrogen nucleophiles in this oxidation reaction (Scheme 1).[7a, 7b, 9, 10] The latter reaction was successfully employed in the construction of stereo-defined heterocyclic systems.[9, 10]



Scheme 1. Palladium-catalyzed 1,4-oxidation.

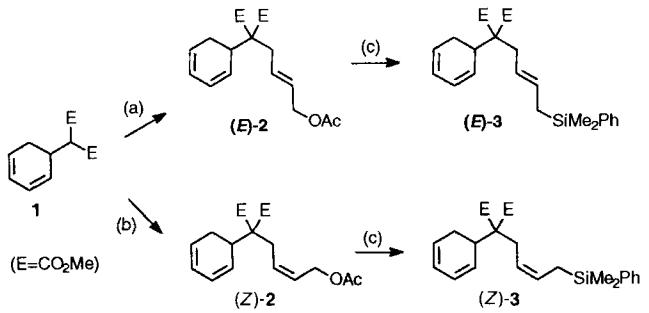
[*] J.-E. Bäckvall, A. M. Castaño, B. A. Persson
Department of Organic Chemistry, University of Uppsala
Box 531, S-751 21 Uppsala (Sweden)
Fax: Int. code +(18) 50-8542

Despite extensive efforts to use carbon nucleophiles, it was not until recently that we were able to obtain carbon–carbon bond formation in the palladium-catalyzed 1,4-oxidation.[11–13] In one approach C–C bond formation was achieved by insertion of a diene into an vinylpalladium species generated in situ.[11, 14] This led to an oxidative 1,4-*anti*-vinylchlorination of the conjugated diene. Another approach involved the use of allylsilanes as masked carbanions. Allylsilanes are known to react with a number of electrophiles (e.g. carbonyl compounds) in an S_E2 manner, under acidic or nucleophilic catalysis.[15, 16] An interesting feature of the latter carbon nucleophiles is that they tolerate weak acids, which is a requirement in the benzoquinone-based palladium-catalyzed 1,4-oxidations.[8, 17] In a preliminary study, we found that allylsilanes can be used as allyl carbanions in an intramolecular 1,4-oxidation of conjugated dienes.[12] Apparently, on coordination to palladium(II) the diene becomes electrophilic enough to react with the allylsilane. We now give a full account of this new palladium-catalyzed carbocyclization; the mechanism is discussed, further examples are reported, and alternative oxidants are compared. We also provide conclusive evidence for an external *anti*-attack by the allylsilane on a (π-diene)palladium complex.[18]

Results and Discussion

A. Preparation of Starting Materials: The requisite allylsilanes (*E*)- and (*Z*)-**3** were obtained from **1**[10c] via the allylic acetates (*E*)- and (*Z*)-**2**, respectively (Scheme 2). Reaction of **1** with the appropriate (*E*)- and (*Z*)-1-acetoxy-4-halo-2-butene[8b, 19] gave

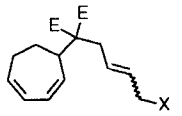
0947-6539/97/0303-0482 $ 15.00+.25/0



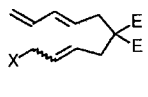
Scheme 2. Synthesis of the starting materials. Reagents and conditions: a) NaH (1.3 equiv), $Pd(OAc)_2$ (4%), PPh_3 (12%), (*E*)-$ClCH_2CH{=}CHCH_2OAc$ [19a] (1.5 equiv), THF, RT, 1.5 h, 82%; b) NaH (1.3 equiv), (*Z*)-$BrCH_2CH{=}CHCH_2OAc$ [19b] (1.4 equiv), THF, RT, 1.5 h, 85%; c) $PhMe_2SiLi$ (2 equiv), CuCN (1.4 equiv), THF, −60 °C, 4 h, 84% for (*E*)-**3**, 56% for (*Z*)-**3**.

(*E*)- and (*Z*)-**2**, respectively. In the reaction of (*E*)-1-acetoxy-4-chloro-2-butene with **1** it was necessary to use Pd^0-catalysis at low temperature, since the noncatalyzed reaction, which required elevated temperature, led to an intramolecular Diels–Alder reaction of the product. Subsequent reaction of the allylic acetates (*E*)- and (*Z*)-**2** with $PhMe_2SiLi$ in the presence of CuCN[20, 21] afforded allylsilanes (*E*)- and (*Z*)-**3**, respectively.

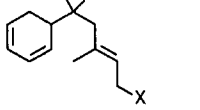
By using an analogous procedure both (*E*) and (*Z*) isomers of allylsilanes **5** and **7** were prepared via **4** and **6**.[22] The substituted allylsilanes **9**, **11**, and **13** were synthesized to study the effect of substitution and the possibility of achieving a 6-*endo*-mode cyclization, respectively.



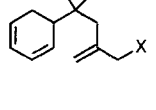
(*E*)-**4**, X = OAc, (83%)
(*Z*)-**4**, X = OAc, (85%)
(*E*)-**5**, X = $SiMe_2Ph$, (48%, 81% brsm)
(*Z*)-**5**, X = $SiMe_2Ph$, (70%)



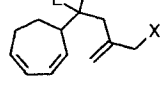
(*E*)-**6**, X = OAc, (88%)
(*Z*)-**6**, X = OAc, (87%)
(*E*)-**7**, X = $SiMe_2Ph$, (60%)
(*Z*)-**7**, X = $SiMe_2Ph$, (69%, 83% brsm)



(*E*)-**8**, X = OAc, (89%)
(*E*)-**9**, X = $SiMe_2Ph$, (41%)

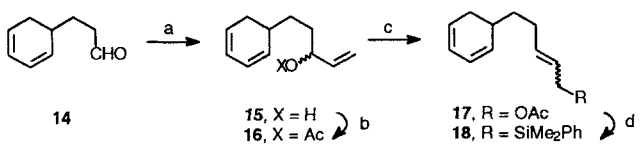


10, X = OAc, (79%)
11, X = $SiMe_2Ph$, (60%)



12, X = OAc, (75%)
13, X = $SiMe_2Ph$, (80%)

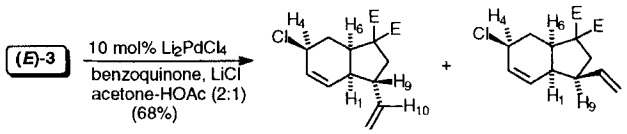
In order to study the effect on the cyclization of *gem*-disubstitution in the tether,[23] unsubstituted allylsilane **18** was prepared from the known aldehyde **14**,[10c] via **16** and **17**, as shown in Scheme 3. Palladium(II)-catalyzed isomerization[24] of **16** gave a



Scheme 3. Synthesis of allylsilane **18**. Reagents and conditions: a) $H_2C{=}CHMgBr$, THF, −50 °C; b) Ac_2O, Et_3N, cat. DMAP, CH_2Cl_2, 54% two steps; c) $Pd(MeCN)_2Cl_2$ (5%), THF, RT, 42%; d) see Scheme 2c, 17% (44% brsm) [22].

mixture of isomers (**16**/**17** ≈ 1:1) from which **17** could be enriched (**16**/**17** ≈ 1:9) by means of chromatography. Subsequent silylation gave **18** ((*E*)/(*Z*) > 95/5). When **16** was subjected to the silylation reaction, an approximately 1:1 mixture of (*E*)- and (*Z*)-**18** was obtained in 85% yield.

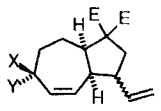
B. Palladium-Catalyzed Carbocyclization: The reaction of (*E*)-**3** with a catalytic amount of Li_2PdCl_4 (10 mol%) in the presence of *p*-benzoquinone (1.5 equiv) and LiCl (2 equiv) in acetone–acetic acid (2:1) gave, after 16 h at room temperature, a mixture of two isomeric allylic chlorides **19** ($\alpha:\beta = 3:1$)[25] in 68% isolated yield (Scheme 4,[22] Table 1, entry 1). The relative



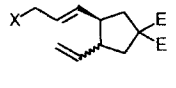
Scheme 4. Cyclization of (*E*)-**3** to give a mixture of two isomeric allylic chlorides **19**. NOE data: **19**α = H1–H6 11.5%, H4–H6 6.8%, H1–H10 7.9%; **19**β = H1–H6 > 5%, H4–H6 6.5%, H1–H9 9.0%.

stereochemistry of both products was determined by NOE measurements (Scheme 4), and it was found that the addition of carbon and Cl^- across the diene was completely stereoselective and only the 1,4-*syn*-addition products were observed. From the NOE data obtained, it is evident that H_1, H_4, and H_6 are on the same side of the ring system in both isomers. Furthermore, it was found that the major isomer has the vinyl group *cis* to H_1 (α). Under the same reaction conditions, (*Z*)-**3** reacted to give **19**, also in a highly stereoselective 1,4-*syn*-addition process (Table 1, entry 2). Interestingly, the ratio between the α and β isomers was opposite to that obtained from (*E*)-**3**, and now the β isomer predominated ($\alpha:\beta = 1:3$).[26]

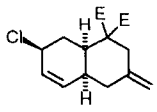
Allylsilanes **5**, **7**, **9**, **11**, **13**, and **18** were cyclized under similar conditions to give the chlorides **20**–**27** and **32**. Selected results



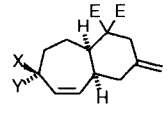
20, X = Cl, Y = H
21, X = H, Y = Cl



22, X = Cl
23, X = OAc



25



26, X = Cl, Y = H
27, X = H, Y = Cl

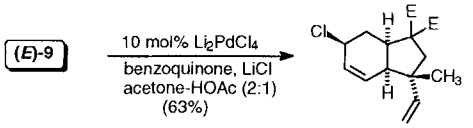
are presented in Table 1. Both 5-*exo* and 6-*endo* cyclizations took place to give the desired allylic chlorides in moderate to good yields. The best results, with regard to yield and selectivity, were obtained with the cyclohexadiene derivatives **3**, **9**, and **11** (Table 1, entries 1, 2, 7 and 8). In these cases, only 1,4-*syn*-addition was observed. A methyl substituent on the double bond of

Table 1. Pd^{II}-catalyzed carbocyclization of ω-dienyl allylsilanes [a].

Entry	Silane	Oxidant	Acetone /HOAc	Products (ratio) [b]	*syn*:*anti* [b,c]	Yield/% [d]
1	(*E*)-**3**	BQ [e]	2:1	**19** (α:β 3:1) [f]	>98% *syn*	68
2	(*Z*)-**3**	BQ	2:1	**19** (α:β 1:3) [f]	>98% *syn*	72
3	(*E*)-**5**	BQ	2:1	**20** (α:β 1.4:1)+**21**	84 : 16	54
4	(*Z*)-**5** [k]	BQ	1.5:1	**20** (α:β 2.6:1)+**21**	84:16	66 [l]
5	(*E*)-**7**	$CuCl_2$	0:1	**22** [g,h]		50
6	(*Z*)-**7**	$CuCl_2$	1:1	**22** [i,j]	–	60
7	(*E*)-**9**	BQ	2:1	**24** (α:β 94:6) [m]	>98% *syn*	63
8	**11**	BQ	2:1	**25**	>98% *syn*	77
9	**13** [k]	BQ	1.5:1	**26** + **27**	84 : 16	53

[a] Unless otherwise stated, the silane, Li_2PdCl_4 (10%), LiCl (2 equiv), and the oxidant (1.5 equiv of 1,4-benzoquinone or 2.5 equiv of $CuCl_2$) were stirred in acetone–HOAc (proportion) at RT under N_2 for 12–40 h. Dienes **3** were added slowly to the reaction mixture. [b] Ratio by ^{1}H NMR. [c] Refers to the stereochemistry of 1,4-addition across the diene system. In all cases the bridgehead protons were *cis* to each other. [d] Isolated (not corrected for conversion) nonoptimized yields. [e] BQ = 1,4-benzoquinone. [f] Small amounts of Diels–Alder adduct (5–7%) were detected. [g] Acetate **23** was also isolated in 20% yield. [h] A 1.3:1 diastereomeric mixture. [i] 5 equiv of LiCl was used. [j] A 1:4 diastereomeric mixture (the major isomer was identical to the minor isomer from (*E*)-**7**). [k] LiCl was added slowly (12 h) to the reaction mixture as a solution in HOAc and 2.5 equiv of BQ was used. [l] 80% conversion according to ^{1}H NMR. [m] Only the α isomer was isolated and characterized.

the allylsilane has an interesting effect on the stereochemistry of the vinyl group. Thus, (*E*)-**9** afforded **24** and the stereochemistry of the vinyl group is now over 94% α (Scheme 5). This is in sharp contrast to the result from the reaction of (*E*)-**3** where the α/β ratio is 3:1. It is interesting to note that, in the transformation of (*E*)-**9** to **24**, the relative stereochemistry of four stereogenic centers is generated in one reaction.

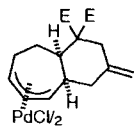


24 (>94% α-vinyl)

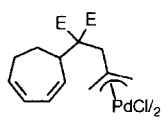
Scheme 5. Exclusive 1,4-*syn*-addition in the reaction of (*E*)-**9**.

In the reactions of the cycloheptadiene silanes **5** and **13** some *anti*-addition products **21** and **27** were observed along with **20** and **26**, respectively. Control experiments showed that both **20** and **26** isomerized to the corresponding 1,4-*anti* derivatives under the reaction conditions. This undesired process could be decreased by adding the LiCl slowly to the reaction mixture. In this way, an improvement in the selectivity was achieved (from 2:1 to 5:1 for (*Z*)-**5** and from 1.2:1 to 5:1 for **13**).

When the reaction of **5** was monitored by ^{1}H NMR spectroscopy, the ratio **20**:**21** was 11:1 at 60% conversion and decreased to 5:1 at 95% conversion. Similarly, when the intermediate (π-allyl)palladium complex **28**, prepared by reaction of **13** with 1 equiv of Li_2PdCl_4 in acetone–HOAc, was treated with LiCl in the presence of *p*-benzoquinone, a 9:1 ratio of **26**:**27** was obtained after 50% conversion (8 h reaction).[27] When the reaction was allowed to reach full conversion, the ratio was approximately 1:1. Interestingly, when (π-allyl)palladium complex **28** was prepared in MeOH at 0 °C, a significant amount of the (π-allyl)palladium complex **29**, formed by transmetalation of the allylsilane to Pd^{II} was obtained.[28] The latter complex did



28

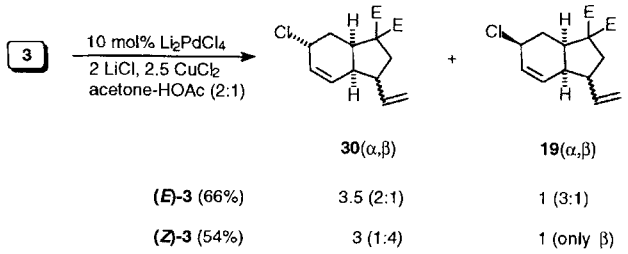


29

not give rise to cyclization after prolonged stirring in $CDCl_3$ at room temperature. No formation of **29** was observed when the reaction was carried out in acetone–HOAc.[28, 29]

For the acyclic substrate **7**, $CuCl_2$ was used as oxidant instead of *p*-benzoquinone, since the latter gave large amounts of Diels–Alder adduct with this diene (25–30%). With $CuCl_2$ as the oxidant, (*E*)- and (*Z*)-**7** afforded chlorides **22** in 50 and 60% yield, respectively (Table 1, entries 5 and 6). For (*E*)-**7** pure HOAc gave a more efficient reaction, but in this case acetate **23** was obtained as side product (20%).

Although $CuCl_2$ has been reported to promote nonstereoselective oxidative cleavage of (π-allyl)palladium complexes,[8b, 10b] it was also used in the reactions of allylsilanes **3** and **9**. Surprisingly, a reversed stereoselectivity of the 1,4-addition was observed, and now the 1,4-*anti* addition product predominated (Scheme 6).[30] Oxidative cleavage of palladium–carbon



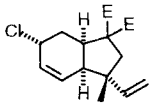
	30(α,β)	**19**(α,β)
(*E*)-**3** (66%)	3.5 (2:1)	1 (3:1)
(*Z*)-**3** (54%)	3 (1:4)	1 (only β)

Scheme 6. Stereoselectivity of the 1,4-addition reaction of **3** mediated by $CuCl_2$.

bonds by $CuCl_2$ has been studied,[6, 31] and it has been shown that the stereochemistry of the process depends on the substrate employed. Thus, $CuCl_2$ cleavage of primary alkyl–palladium bonds proceeds preferentially with inversion[6] in the presence of chloride anions, whereas the cleavage of secondary palladium–carbon bonds is less stereospecific.[6a, 31] In one case it was demonstrated that the $CuCl_2$ cleavage occurs with anchimeric assistance, indicating that carbonium ion character is important in the cleavage process.[6a, 6c] Recently, an S_N1–S_Ni mechanism has been invoked to explain the observed retention in some $CuCl_2$ oxidative cleavage reactions of Pd–C bonds.[31a] The results obtained by the route given in Scheme 6 are consistent with either a carbocation intermediate or an S_N1–S_Ni process, since in the former case attack would occur from the least hindered side, which leads to predominant retention.[31b]

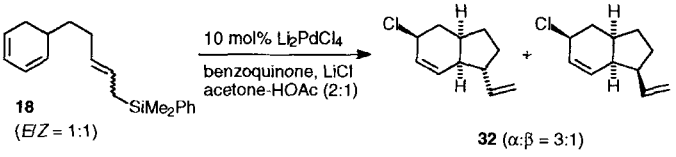
The use of $CuCl_2$ as the oxidant in the palladium-catalyzed oxidation of allylsilane **9** gave a similar result, and allyl chloride **31** was isolated in 57% yield contaminated with **24** ($\approx$30%).

Allylsilane **18** also gave rise to the cyclic allylic chlorides **32** under standard conditions with benzoquinone as the oxidant (Scheme 7). The 1:1 mixture of (*E*)- and (*Z*)-**18** gave an α/β ratio of approximately 3:1.[32] Inter-

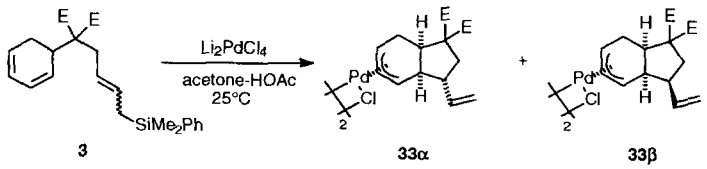


31 (>90% α-vinyl)

 0947-6539/97/0303-0484 $ 15.00+.25/0 Chem. Eur. J. 1997, 3, No. 3



Scheme 7. Cyclization of **18** to give a mixture of two isomeric allylic chlorides **32**.

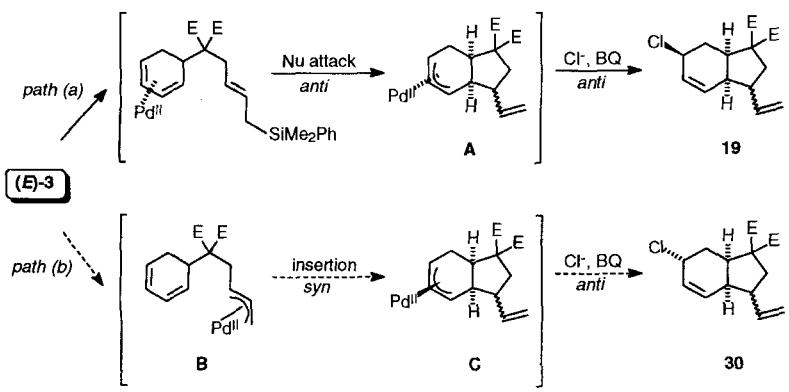


Scheme 9. Synthesis of the intermediate (π-allyl)palladium complexes **33**.

estingly, when the mixture enriched in (*E*)-**18** (>95% (*E*)) was employed in the reaction, the α/β ratio was approximately 1:1. This indicates that the presence of geminal ester substituents on substrates **3** has an influence on the α/β selectivity.[26] We were not able to obtain isomerically pure (*Z*)-**18**, but these data indicate a high α-selectivity (>90% α-vinyl) for (*Z*)-**18**. Surprisingly, the product **32** turned out to be less stable than expected and decomposed during attempted chromatographic purification on silica. Similarly, the intermediate (π-allyl)palladium complexes were quite unstable.

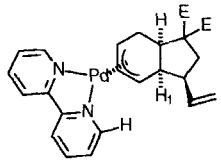
C. Mechanism: A priori, two mechanisms can be considered for the palladium-catalyzed 1,4-carbocyclization. The *syn* stereochemistry between the chloro group and C-9 in **19** is explained by an external *anti* attack by the allylsilane on the coordinated diene to give an intermediate (π-allyl)palladium complex **A**, followed by an external, benzoquinone-induced *anti* attack by chloride[33] (Scheme 8, path a). This is the first example of nucleophilic attack by an allylsilane on an olefin coordinated to a metal.[16] The formation of **19** as the only product also rules out a pathway involving transmetalation from the allylsilane to Li_2PdCl_4 with generation of a (π-allyl)palladium complex in the side chain **B**, followed by *syn* insertion of the diene to give **C**.[28] Again, *anti* attack by chloride on **C** would lead to an overall *anti*-1,4-addition across the diene (Scheme 8, path b).

In order to obtain further support for the mechanism suggested in Scheme 8, the intermediate (π-allyl)palladium complexes were prepared from the dienyl silanes (*E*)- and (*Z*)-**3**. Reaction of (*E*)- and (*Z*)-**3** with 1 equiv of Li_2PdCl_4 in acetone–acetic acid (2:1) afforded (π-allyl) complexes **33**α and **33**β in a ratio of 2.7:1 and 1:3, respectively (Scheme 9). The ratio between the α- and β-vinyl isomers are in agreement with the product ratios obtained from (*E*)- and (*Z*)-**3** in the catalytic reaction. Futhermore, when the reaction was monitored by NMR spectroscopy, the only products observed were complexes **33**.

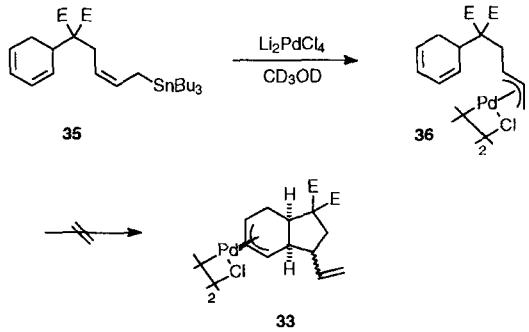


Scheme 8. Mechanism of Pd-catalyzed 1,4-addition of allylsilane (*E*)-**3** (E = CO_2-Me) (ligands on palladium have been omitted for clarity).

Complexes **33**α and **33**β were characterized by ^{1}H NMR spectroscopy. The *syn* relationship between Pd and the bridgehead protons was unambiguously established by the use of 2,2′-bipyridine as a reporter ligand on palladium.[9e, 34] An NOE enhancement between the *ortho* proton of the bipyridine ligand and H_1 (3.4%) in complex **34** was observed.[35]



Further results obtained from the reaction of the stannane **35**[36] with Pd^{II} salts also supports the mechanism proposed and rules out path (b). The reaction of **35** with 1 equiv of Li_2PdCl_4 in CD_3OD at 25 °C yielded π-allyl complex **36** within 5 min (Scheme 10). Attempts to insert the diene unit to give



Scheme 10. Attempted cyclization of the (π-allyl)palladium complex **36**.

the cyclic π-allyl complex **33** were unsuccessful, and prolonged heating in HOAc in the presence of excess of LiCl led only to decomposition. This shows that the hypothetical reaction **B** → **C** in path (b) of Scheme 8 does not take place under the usual reaction conditions. Thus, even if small amounts of complex **B** are formed, no product from path (b) would be formed. When the reaction of allylstannane **35** was carried out with $Pd(OAc)_2$ in HOAc with the aim of suppressing the transmetalation process,[37] three different compounds were obtained immediately, the major of them being **36**.[38]

Conclusions

In this study, a new method for palladium-catalyzed carbocyclization has been developed. We have shown that allylsilanes can be used as carbon

nucleophiles in Pd^{II}-catalyzed 1,4-oxidations of 1,3-dienes, and this leads to highly stereoselective 1,4-*syn*-addition to the diene. This study provides the first example of nucleophilic attack by an allylsilane on an olefin coordinated to a metal. Direct evidence for a trans carbopalladation of the double bond is established.

Experimental Section

All reactions were carried out in oven-dried glassware under N_2 atmosphere, unless otherwise stated. Solvents were dried by standard methods. Chromatographic purification was carried out with columns packed with flash-grade silica gel. NMR spectra were recorded on Varian spectrometers (400 and 300 MHz for ^{1}H NMR and 100.6 and 75 MHz for ^{13}C NMR) with $CDCl_3$ as a solvent unless otherwise stated. Mass spectra were recorded in a Finingan MAT INCOS 50 instrument at 70 eV. Dimethyl 2,4-cyclohexadienylmalonate (**1**) [10c,39], dimethyl 2,4-cycloheptadienylmalonate [40], (*E*)-1-acetoxy-4-chloro-2-butene [19a], and (*E*)-1-acetoxy-4-chloro-3-methyl-2-butene [41] were prepared according to reported procedures. (*Z*)-1-Acetoxy-4-bromo-2-butene [42] and 2-bromomethylprop-2-en-1-yl acetate [43] were prepared from (*Z*)-4-acetoxy-2-buten-1-ol [42] and 2-hydroxymethylprop-2-en-1-yl acetate [44], respectively, following the procedure reported by Nicolaou [19b]. Dimethyl 2,4-(pentadienyl)malonate was prepared by reaction of divinylcarbinol mesylate with the sodium dimethyl malonate anion in DMF at 50 °C, or by Pd^0-catalyzed reaction of (*E*)-2,4-pentadienyl acetate with the sodium dimethyl malonate anion [45]. NaH (80 or 60%) was washed with pentane prior to use. The rest of the reagents were used without further purification.

Preparation of (*E*)-allyl acetates—general procedure [40]: A solution of dienylmalonate (2.0 mmol) in dry THF (7.5 mL) was added to a suspension of NaH (1.1 equiv) in THF (3 mL) under N_2 and the mixture stirred 15–20 min at RT. $Pd(OAc)_2$ (4%) and PPh_3 (12%) were added and, after 15–20 min of stirring, (*E*)-1-acetoxy-4-chloro-2-butene (1.5 equiv) in THF (5 mL) was added. The suspension obtained was stirred 1–2 h at RT, and then brine and Et_2O were added. The phases were separated and the aqueous phase extracted with Et_2O (×3). The combined organic phases were washed with brine and dried (Na_2SO_4–$MgSO_4$). After evaporation, the residue was chromatographed.

Dimethyl (2,4-cyclohexadienyl)((*E*)-4-acetoxy-2-butenyl)malonate ((*E*)-**2**): Chromatography (pentane/Et_2O 4:1) yielded (*E*)-**2** as a colorless oil (82%). ^{1}H NMR: δ = 5.95 (dddd, J = 9.5, 5.0, 2.4, 1.0 Hz, 1H), 5.87 (m, 1H), 5.78–5.66 (m, 4H), 4.50 (d, J = 5.0 Hz, 2H), 3.73 (s, 3H), 3.72 (s, 3H), 3.10 (m, 1H), 2.79–2.64 (m, 2H), 2.35 (dddd, J = 17.3, 9.0, 5.0, 1.5 Hz, 1H), 2.21 (dddd, J = 17.3, 8.3, 3.8, 2.2 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR: δ = 170.7, 170.6, 129.9, 128.1, 126.0, 125.9, 125.1, 123.6, 64.6, 60.9, 52.3, 52.2, 36.7, 35.7, 24.5, 20.9 (one *C*OO overlapping); GC–MS (*m/z*): 322 (M^+, 14), 262 (36), 184 (100), 59 (43); Anal. calcd for $C_{17}H_{22}O_6$: C, 63.33; H, 6.88; found: C, 63.06; H, 6.83.

Dimethyl (2,4-cycloheptadienyl)((*E*)-4-acetoxy-2-butenyl)malonate ((*E*)-**4**): Chromatography (pentane/Et_2O 3:1) gave (*E*)-**4** as a colorless oil (83%, as a 5:1 mixture of isomers from the starting malonate. Enriched fractions in (*E*)-**4**: 47%, ≈12:1). ^{1}H NMR: δ = 5.88–5.57 (m, 6H), 4.48 (dd, J = 6.2, 1.0 Hz, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 2.90 (br d, J = 9.5 Hz, 1H), 2.75 (dd, J = 14.6, 7.6 Hz, 1H), 2.68 (dd, J = 14.9, 7.3 Hz, 1H), 2.40 (m, 2H), 2.1–2.0 (m, 1H, overlapping), 2.03 (s, 3H), 1.55 (m, 1H, overlapping with H_2O); ^{13}C NMR: δ = 171.01, 170.95, 170.7, 134.4, 132.7, 130.4, 128.0, 124.8, 124.6, 64.6, 61.7, 52.22, 52.19, 44.8, 37.0, 32.0, 30.4, 20.9; GC–MS (*m/z*): 336 (M^+, 2), 277 (7), 276 (6), 59 (100); Anal. calcd. for $C_{18}H_{24}O_6$: C 64.27, H 7.19; found: C 64.14, H 7.17.

Dimethyl (2,4-pentadienyl)((*E*)-4-acetoxy-2-butenyl)malonate ((*E*)-**6**): Chromatography (pentane/Et_2O 3:1) yielded (*E*)-**6** as a colorless oil (88%, including 11% of the (*Z*) isomer and 7% of dimethyl divinylmalonate, originating from the starting malonate). ^{1}H NMR: δ = 6.27 (dtd, J = 16.9, 10.5, 0.6 Hz, 1H), 6.07 (ddquint, J = 15.0, 10.4, 0.6 Hz, 1H), 5.72 (m, 2H), 5.48 (m, 2H), 5.12 (br dd, J = 16.8, 1.7 Hz, 1H), 5.02 (br dd, J = 10.0, 1.6 Hz, 1H), 4.48 (ap.d, J = 5.0 Hz, 2H), 3.71 (s, 6H), 2.63 (m, 4H), 2.03 (s, 3H); ^{13}C NMR: δ = 171.0, 170.7, 136.5, 135.2, 129.2, 128.6, 127.4, 116.7, 64.5, 57.7, 52.5, 36.0, 35.6, 20.9; GC–MS (*m/z*): 310 (M^+, 2), 190 (12), 67 (100), 59 (75) (one *C*OO overlapping); Anal. calcd. for $C_{16}H_{22}O_6$: C 61.92, H 7.14; found: C 62.09, H 7.18.

Dimethyl (2,4-cyclohexadienyl)((*E*)-4-acetoxy-2-methyl-2-butenyl)malonate ((*E*)-**8**): Chromatography (pentane/Et_2O 3:2) gave (*E*)-**8** as a colorless oil (89%). ^{1}H NMR: δ = 5.96–5.69 (m, 4H), 5.36 (tq, J = 7.0, 1.4 Hz, 1H), 4.52 (d, J = 7.0 Hz, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.08 (m, 1H), 2.77 (part A of an AB system, d, J = 13.8 Hz, 1H), 2.69 (part B of an AB system, d, J = 13.8 Hz, 1H), 2.35 (dddd, J = 17.3, 8.9, 5.0, 1.6 Hz, 1H), 2.22–2.08 (m, 1H), 2.03 (s, 3H), 1.64 (br s, 3H); ^{13}C NMR: δ = 170.9, 170.7, 137.3, 126.2, 126.0, 125.0, 123.8, 123.5, 60.9, 52.1, 52.0, 42.6, 37.6, 24.5, 20.9, 17.2 (one *C*OO overlapping).

Preparation of (*Z*) allyl acetates—general procedure: A solution of dienylmalonate (1.5 mmol) in dry THF (3 mL) was added to a suspension of NaH (1.1 equiv) in THF (2 mL) under N_2. After 15–20 min of stirring at RT, (*Z*)-1-acetoxy-4-bromo-2-butene (1.4 equiv) in THF (3 mL) was added, and the reaction mixture was stirred at RT for 3–5 h. Workup as given for the Pd^0-catalyzed reactions.

Dimethyl (2,4-cyclohexadienyl)((*Z*)-4-acetoxy-2-butenyl)malonate ((*Z*)-**2**): Chromatography (pentane/Et_2O 4:1) gave (*Z*)-**2** as a colorless oil (85%). ^{1}H NMR: δ = 5.93 (m, 1H), 5.85 (m, 1H), 5.75–5.53 (m, 4H), 4.61 (br d, J = 6.4 Hz, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 3.11 (m, 1H), 2.75 (m, 2H), 2.31 (dddd, J = 17.4, 9.2, 5.0, 1.5 Hz, 1H), 2.19 (m, 1H), 2.05 (s, 3H); ^{13}C NMR: δ = 170.8, 170.7, 170.6, 128.4, 126.9, 126.0, 125.8, 125.3, 123.6, 60.5, 60.1, 52.4, 52.3, 36.8, 30.7, 24.5, 20.9; GS–MS (*m/z*): 322 (M^+, 2), 262 (14), 59 (100); IR (neat): $\tilde{\nu}$ = 3040, 2950, 1755–1715 (multiple), 1435, 1370, 1285–1160, 1030, 685 cm^{-1}; Anal. calcd for $C_{17}H_{22}O_6$: C 63.33, H 6.88; found: C 63.18, H 6.86.

Dimethyl (2,4-cycloheptadienyl)((*Z*)-4-acetoxy-2-butenyl)malonate ((*Z*)-**4**): Chromatography (pentane/Et_2O 4:1) yielded (*Z*)-**4** as a colorless oil (85%). ^{1}H NMR: δ = 5.83–5.70 (m, 4H), 5.63–5.60 (m, 2H), 4.59 (ap.d, J = 5.1 Hz, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 2.92 (br d, J = 9.0 Hz, 1H), 2.77 (m, 2H), 2.40 (m, 2H), 2.1–2.0 (m, 1H, overlapping with CH_3COO), 2.04 (s, 3H), 1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 170.8, 132.4, 128.7, 126.7, 125.0, 124.5, 61.2, 60.1, 52.3 (2C), 44.8, 32.1, 32.0, 30.5, 20.9 (one *C*OO overlapping); GC–MS (*m/z*): 336 (M^+, 10), 276 (14), 216 (95), 91 (100); IR (neat): $\tilde{\nu}$ = 3020, 2955, 2890, 1765–1705 (multiple), 1465–1420, 1290–1160, 1125, 1025, 960, 685 cm^{-1}; Anal. calcd for $C_{18}H_{24}O_6$: C 64.27, H 7.19; found: C 64.11, H 7.15.

Dimethyl (2,4-pentadienyl)((*Z*)-4-acetoxy-2-butenyl)malonate ((*Z*)-**6**): Chromatography (pentane/Et_2O 3.5:1) yielded (*Z*)-**6** as a colorless oil (87%). ^{1}H NMR: δ = 6.27 (dtd, J = 16.9, 10.0, 0.6 Hz, 1H), 6.08 (ddquint, J = 15.0, 10.2, 0.7 Hz, 1H), 5.66 (m, 1H), 5.54–5.47 (m, 2H), 5.12 (ddm, J = 16.9, 1.7 Hz, 1H), 5.02 (ddm, J = 10.2, 1.7 Hz, 1H), 4.59 (ap.dd, J = 6.7, 1.6 Hz, 2H), 3.72 (s, 6H), 2.69 (dm, J = 7.9 Hz, 2H), 2.67 (dd, J = 7, 1.4 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR: δ = 171.0, 170.7, 136.5, 135.3, 127.8, 127.5, 116.6, 60.1, 57.7, 52.4, 36.2, 30.9, 20.8 (one *C*OO overlapping); Anal. calcd for $C_{16}H_{22}O_6$: C 61.93, H 7.14; found: C 61.66, H 7.07.

Preparation of "*endo*-Acetates": **10** and **12** were prepared by the same procedure as for the (*E*)-allyl acetates using 2-bromomethylprop-2-en-1-yl acetate as the alkylating reagent.

Dimethyl (2,4-cyclohexadienyl)(3-acetoxy-2-methylene-propyl)malonate (**10**): Chromatography (pentane/Et_2O 3:1) gave **10** as a colorless oil (79%). ^{1}H NMR: δ = 5.93 (m, 1H), 5.85 (m, 1H), 5.79–5.69 (m, 2H), 5.14 (ap.q, J = 1 Hz, 1H), 4.98 (ap.q, J = 1 Hz, 1H), 4.45 (br s, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.12 (m, 1H), 2.81 (part A of an AB system, d, J = 14.6 Hz, 1H), 2.72 (part B of an AB system, d, J = 14.6 Hz, 1H), 2.33 (dddd, J = 17.4, 8.9, 5.2, 1.4 Hz, 1H), 2.22–2.08 (m, 1H), 2.08 (s, 3H); ^{13}C NMR: δ = 170.7, 170.7, 170.5, 139.6, 126.0, 125.9, 125.2, 123.6, 117.2, 66.8, 60.8, 52.3, 52.2, 37.8, 36.5, 24.5, 20.9; Anal. calcd for $C_{17}H_{22}O_6$: C 63.34, H 6.88; found: C 63.36, H 6.93.

Dimethyl (2,4-cycloheptadienyl)(3-acetoxy-2-methylene-propyl)malonate (**12**): Chromatography (pentane/Et_2O 4.5:1) yielded **12** as a white solid (75%). M.p.: 69 °C (Et_2O–pentane); ^{1}H NMR: δ = 5.89–5.80 (m, 2H), 5.77 (m, 2H), 5.15 (q, J = 1.2 Hz, 1H), 4.97 (q, J = 1.2 Hz, 1H), 4.45 (m, 2H), 3.72

0947-6539/97/0303-0486 $ 15.00+.25/0 Chem. Eur. J. 1997, 3, No. 3

(s, 3H), 3.71 (s, 3H), 2.93 (brd, J = 9.0 Hz, 1H), 2.84 (dd, J = 14.3, 0.9 Hz, 1H), 2.79 (dd, J = 14.3, 0.7 Hz, 1H), 2.41 (m, 2H), 2.11 (m, 1H), 2.08 (s, 3H), 1.52 (m, 1H); ^{13}C NMR: δ = 171.03, 171.02, 170.5, 139.5, 134.6, 132.5, 124.9, 124.5, 117.7, 66.9, 61.7, 52.3, 52.2, 45.3, 37.6, 32.2, 30.8, 20.9; Anal. Calc. for $C_{18}H_{24}O_6$: C 64.27, H 7.19; found: C 64.07, H 7.09.

5-(5-Acetoxy-3-pentenyl)-1,3-cyclohexadiene (17): Vinylmagnesium bromide (1.1 equiv) was added dropwise to a solution of aldehyde **14** (50 mg, 0.37 mmol) in THF (2 mL) at −50 °C (N_2). The reaction mixture was allowed to warm to −30 °C over a period of 30 min and quenched with saturated aq. NH_4Cl. Et_2O and H_2O were added and the phases separated. The aqueous phase was extracted with further Et_2O (×2) and the combined phases were washed with brine, dried ($MgSO_4$–Na_2SO_4), and evaporated to give alcohol **15** (≈1:1 mixture of isomers) as a colorless oil. **15** was used in the next step without further purification. ^{1}H NMR of **15** [46]: δ = 5.91–5.83 (m, 2H), 5.77 (m, 1H), 5.69 (m, 1H), 5.23 (ddm, J = 17.0, 1 Hz), 5.12 (ddm, J = 10.3, 1 Hz), 4.09 (m, 1H), 2.28 (m, 2H), 1.98 (m, 1H), 1.62–1.46 (m, 4H).

Et_3N (1.3 equiv) was added to a solution of dienol **15**, Ac_2O (1.3 equiv) and DMAP (0.1 equiv) in CH_2Cl_2 (3 mL) at 0 °C (N_2). The reaction mixture was stirred at 0 °C for 1–2 h and 1.2 M HCl was then added. The layers were separated and the aqueous phase was extracted with more CH_2Cl_2. The combined organic phases were washed with brine, dried (Na_2SO_4) and evaporated. The residue was chromatographed (pentane–Et_2O = 20:1) to give a ≈1:1 isomeric mixture of acetates **16** as a colorless oil, 54% yield from **14**. ^{1}H NMR of **16** [46]: δ = 5.90–5.75 (m, 4H), 5.66 (m, 1H), 5.23 (dm, J = 17.0 Hz, 1H), 5.23–5.16 (m, 3H), 2.27 (m, 2H), 2.06 (s, 3H), 1.96 (m, 1H), 1.72–1.56 (m, 2H), 1.52–1.32 (m, 2H); ^{13}C NMR for **16** [47]: δ = 170.3, 136.4, 130.8, 125.9 (125.8), 124.0 (123.9), 116.8, 74.9, 32.5, 31.5 (31.4), 29.7, 28.5, 21.2. Allylic acetate **16** dissolved in THF was added to $Pd(MeCN)_2Cl_2$ (0.05 equiv) and the mixture was stirred at RT for 16 h [48]. Evaporation of solvent followed by chromatography (pentane/Et_2O 95:5) gave **17** (42%) contaminated with ≈10% of **16**. ^{1}H NMR of **17** [49]: δ = 5.87 (m, 2H), 5.75 (m, 2H), 5.67 (m, 1H), 5.58 (dtt, J = 15.3, 6.4, 1.4 Hz, 1H), 4.50 (dq, J = 6.4, 1.0 Hz, 2H), 2.26 (m, 2H), 2.10 (m, 1H), 2.06 (s, 3H), 1.96 (m, 1H), 1.70–1.38 (m, 3H); ^{13}C NMR for **17**: δ = 170.9, 136.2, 131.0, 125.8, 124.0, 123.9, 123.8, 65.2, 33.5, 32.2, 29.5, 28.5, 21.0.

Preparation of allylsilanes—general procedure [20]: Phenyldimethylchlorosilane (2.0 mmol) was added to a suspension of finely divided lithium metal (10 mmol) in THF (5 mL) under N_2 and the mixture was stirred overnight at RT. The brownish solution was transferred through a canula to a suspension of CuCN (1.4 mmol) in THF (2.5 mL) at 0 °C under N_2, and after stirring 1.5 h at 0 °C, the dark brown suspension was cooled down to −60 °C and the allylic acetate (1.0 mmol) in THF (1.5 mL) was added. The reaction mixture was stirred between −60 and −50 °C until no starting material remained or the reaction was complete (monitored by TLC). The cooling bath was removed and saturated aqueous NH_4Cl and 2 M NH_4OH were added and the mixture stirred for 1 h. Et_2O was added and the phases separated. The aqueous phase was further extracted with Et_2O (×4) and the combined organic phases washed with brine, dried (Na_2SO_4–$MgSO_4$), evaporated and the residue chromatographed.

Dimethyl (2,4-cyclohexadienyl)((*E*)-4-dimethylphenylsilyl-2-butenyl)malonate ((*E*)-**3**): Chromatography (pentane/Et_2O 12.5:1) yielded (*E*)-**3** as a colorless oil (84%). ^{1}H NMR: δ = 7.48 (m, 2H), 7.35 (m, 3H), 5.90 (m, 1H), 5.84 (m, 1H), 5.75–5.69 (m, 2H), 5.48 (brdt, J = 15.0, 7 Hz, 1H), 5.09 (brdt, J = 15.0, 7.5 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.03 (m, 1H), 2.65 (dd, J = 14.9, 7.5 Hz, 1H), 2.58 (dd, J = 14.8, 8.1 Hz, 1H), 2.31 (dddd, J = 17.5, 8.6, 4.9, 1.4 Hz, 1H), 1.67 (brd, J = 8.1 Hz, 2H), 0.26 (s, 3H), 0.25 (s, 3H); ^{13}C NMR: δ = 171.1, 138.6, 133.6, 130.6, 129.0, 127.7, 126.5, 126.0, 124.8, 123.6, 122.4, 60.8, 52.2, 52.0, 36.1, 35.7, 24.3, 22.1, 15.3, −3.4 (one *C*OO overlapping; one Si*C*H$_3$ overlapping); GC–MS (*m*/*z*): 320 (11), 189 (8), 151 (7), 145 (68), 135 (100); Anal. calcd for $C_{23}H_{30}O_4Si$: C 69.31, H 7.59; found: C 69.19, H 7.56.

Dimethyl (2,4-cycloheptadienyl)((*E*)-4-dimethylphenylsilyl-2-butenyl)malonate ((*E*)-**5**): Chromatography (pentane/Et_2O 17:1) yielded (*E*)-**5** as a colorless oil (48%, 81% based on recovered starting material). ^{1}H NMR: δ = 7.50 (m, 2H), 7.34 (m, 3H), 5.82–5.74 (m, 4H), 5.45 (dtt, J = 15.0, 8.0, 1.3 Hz, 1H), 5.17 (dtt, J = 15.0, 7.5, 1.3 Hz, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 2.89 (brd, J = 9.0 Hz, 1H), 2.67 (dd, J = 7.2, 0.7 Hz, 2H), 2.40 (m, 2H), 2.03 (m, 1H), 1.66 (dd, J = 8.0, 0.7 Hz, 2H), 1.50 (m, 1H), 0.25 (s, 3H), 0.24 (s, 3H); ^{13}C NMR: δ = 171.3, 171.3, 138.8, 134.4, 133.5, 133.1, 130.5, 128.9, 127.7, 124.6, 124.5, 122.9, 61.7, 52.1 (2C), 44.0, 37.5, 32.2, 30.3, 22.0, −3.42, −3.44; GC–MS (*m*/*z*): 334 (15), 135 (100); Anal. calcd for $C_{24}H_{32}O_4Si$: C 69.87, H 7.82; found: C 69.73, H 7.64.

Dimethyl (2,4-pentadienyl)((*E*)-4-dimethylphenylsilyl-2-butenyl)malonate ((*E*)-**7**): Chromatography (pentane/Et_2O 15:1) yielded (*E*)-**7** as a colorless oil (60%). ^{1}H NMR: δ = 7.50 (m, 2H), 7.36 (m, 3H), 6.27 (dtd, J = 16.8, 10.6, 0.4 Hz, 1H), 6.00 (brdd, J = 15.1, 10.5 Hz, 1H), 5.52–5.42 (m, 2H), 5.12–4.98 (m, 3H), 3.66 (s, 6H), 2.57 (m, 4H), 1.67 (d, J = 7.4 Hz, 2H), 0.26 (s, 6H); ^{13}C NMR: δ = 171.3, 138.6, 136.7, 134.8, 133.6, 130.9, 129.0, 128.2, 127.8, 122.4, 116.1, 58.2, 52.2, 36.1, 35.7, 22.1, −3.4 (one *C*OO overlapping; one Si*C*H$_3$ overlapping); GC–MS (*m*/*z*): 308 (15), 135 (100); Anal. calcd for $C_{22}H_{30}O_4Si$: C 68.36, H 7.83; found: C 68.18; H, 7.71.

Dimethyl (2,4-cyclohexadienyl)((*E*)-4-dimethylphenylsilyl-2-methyl-2-butenyl)malonate ((*E*)-**9**): Chromatography (pentane/Et_2O 10:1) gave (*E*)-**9** as a colorless oil (41%). ^{1}H NMR: δ = 7.50 (m, 2H), 7.35 (m, 3H), 5.95–5.79 (m, 3H), 5.76–5.68 (m, 1H), 5.28 (t, J = 8.5 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.02 (m, 1H), 2.75 (part A of an AB system, d, J = 14.7 Hz, 1H), 2.68 (part B of an AB system, d, J = 14.7 Hz, 1H), 2.38 (dddd, J = 17.5, 8.9, 5.2, 1.4 Hz, 1H), 2.19–2.07 (m, 1H), 1.65 (d, J = 8.5 Hz, 2H), 1.42 (s, 3H), 0.27 (s, 3H), 0.26 (s, 3H); ^{13}C NMR: δ = 171.3, 138.8, 133.5, 128.9, 127.8, 127.2, 126.8, 126.2, 125.9, 124.7, 123.6, 60.3, 52.04, 51.97, 42.9, 36.2, 24.4, 18.4, 16.6, −3.2 (one *C*OOMe overlapping; one Si*C*H$_3$ overlapping); Anal. calcd for $C_{24}H_{32}O_4Si$: C 69.87, H 7.82; found: C 69.65, H 7.86.

Dimethyl (2,4-cyclohexadienyl)((*Z*)-4-dimethylphenylsilyl-2-butenyl)malonate ((*Z*)-**3**): Chromatography (pentane/Et_2O 13:1) yielded (*Z*)-**3** as a colorless oil (56%). ^{1}H NMR: δ = 7.51 (m, 2H), 7.36 (m, 3H), 5.91 (m, 1H), 5.84 (m, 1H), 5.71 (m, 2H), 5.52 (dtt, J = 10.7, 8.5, 1.5 Hz, 1H), 5.15 (m, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.08 (m, 1H), 2.57 (m, 2H), 2.29 (dddd, J = 17.3, 9.2, 5.5, 1.6 Hz, 1H), 2.17 (m, 1H), 1.73 (dd, J = 8.2, 0.8 Hz, 2H), 0.28 (s, 6H); ^{13}C NMR: δ = 171.2, 171.1, 138.5, 133.5, 129.0, 128.7, 127.8, 126.4, 126.0, 124.9, 123.6, 121.2, 60.4, 52.2, 52.1, 36.2, 30.1, 24.4, 17.8, −3.3 (one Si*C*H$_3$ overlapping); GC–MS (*m*/*z*): 320 (5), 189 (47), 151 (15), 135 (100); Anal. calcd for $C_{23}H_{30}O_4Si$: C 69.31, H 7.59; found: C 69.51, H 7.66.

Dimethyl (2,4-cycloheptadienyl)((*Z*)-4-dimethylphenylsilyl-2-butenyl)malonate ((*Z*)-**5**): Chromatography (pentane/Et_2O 18:1) yielded (*Z*)-**5** as a colorless oil (54%, 98% based on recovered starting material). ^{1}H NMR: δ = 7.50 (m, 2H), 7.35 (m, 3H), 5.88–5.73 (m, 4H), 5.50 (dtt, J = 11.0, 8.5, 1.5 Hz, 1H), 5.23 (dtt, J = 11.0, 7.3, 1.5 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.91 (brd, J = 9.0 Hz, 1H), 2.63 (ddd, J = 15.0, 7.5, 1.5 Hz, 1H), 2.57 (ddd, J = 15.0, 7.5, 1.6 Hz, 1H), 2.39 (m, 2H), 2.04 (dt, J = 13.2, 4.5 Hz, 1H), 1.70 (brd, J = 8.5 Hz, 2H), 1.52 (dddd, J = 13.4, 10.7, 9.2, 5.5 Hz, 1H), 0.27 (s, 6H); ^{13}C NMR: δ = 171.42, 171.38, 138.6, 134.4, 133.5, 133.2, 129.0, 128.4, 127.7, 124.6, 124.6, 121.7, 61.3, 52.1 (2C), 44.5, 32.1, 31.4, 30.3, 17.7, −3.3 (one Si*C*H$_3$ overlapping); GC–MS (*m*/*z*): 334 (6), 189 (2), 187 (19), 135 (100); Anal. calcd for $C_{24}H_{32}O_4Si$: C 69.87, H 7.82; found: C 69.73, H 7.64.

Dimethyl (2,4-pentadienyl)((*Z*)-4-dimethylphenylsilyl-2-butenyl)malonate ((*Z*)-**7**): Chromatography (pentane/Et_2O 15:1) yielded (*Z*)-**7** as a colorless oil (69%, 82% based on recovered starting material). ^{1}H NMR: δ = 7.50 (m, 2H), 7.35 (m, 3H), 6.27 (dtd, J = 16.9, 10.2, 0.6 Hz, 1H), 6.06 (ddm, J = 15.2, 10.5 Hz, 1H), 5.59–5.46 (m, 2H), 5.16–5.08 (m, 2H), 5.01 (dd, J = 10.3, 1.6 Hz, 1H), 3.70 (s, 6H), 2.64 (dd, J = 7.6, 1.0 Hz, 2H), 2.54 (dd, J = 7.4, 1.6 Hz, 2H), 1.73 (dd, J = 8.6, 1.5 Hz, 2H), 0.28 (s, 6H); ^{13}C NMR: δ = 171.4, 138.6, 136.7, 135.0, 133.6, 129.1, 129.0, 128.1, 127.8, 121.0, 116.2, 58.0, 52.3, 36.0, 30.3, 17.9, −3.3 (one *C*OO overlapping; one Si*C*H$_3$ overlapping); Anal. calcd for $C_{22}H_{30}O_4Si$: C 68.36, H 7.83; found: C 68.21, H 7.89.

Dimethyl (2,4-cyclohexadienyl)(3-dimethylphenylsilyl-2-methylene-propyl)malonate (11): Chromatography (pentane/Et_2O 8:1) gave **11** as a colorless oil (60%). ^{1}H NMR: δ = 7.51 (m, 2H), 7.36 (m, 2H), 5.95–5.81 (m, 2H), 5.78–5.67 (m, 2H), 4.62 (s, 2H), 3.68 (s, 3H), 3.67 (s, 3H), 3.14 (m, 1H), 2.61 (part A of an AB system, d, J = 14.4 Hz, 1H), 2.53 (part B of an AB system, d, J = 14.4 Hz, 1H), 2.29 (dddd, J = 17.6, 8.8, 5.2, 1.4 Hz, 1H), 2.11 (m, 1H), 1.70 (s, 2H), 0.32 (s, 6H); ^{13}C NMR: δ = 170.9, 142.0, 138.7, 133.6, 129.0, 127.7, 126.4, 126.1, 124.9, 123.6, 112.5, 60.7, 52.1, 52.0, 40.5, 37.3, 26.6, 24.5, −3.1 (one *C*OO overlapping; one Si*C*H$_3$ overlapping).

Dimethyl (2,4-cycloheptadienyl)(3-dimethylphenylsilyl-2-methylene-propyl)-malonate (13): Chromatography (pentane/Et_2O 17.5:1) yielded **13** as a colorless oil (80%). ^1H NMR: $\delta = 7.49$ (m, 2H), 7.35 (m, 3H), 5.81 (m, 2H), 5.74 (m, 2H), 4.61 (m, 1H), 4.58 (m, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 2.94 (br d, $J = 9.3$ Hz, 1H), 2.63 (part A of an AB system, dd, $J = 14.2$, 0.8 Hz, 1H), 2.57 (part B of an AB system, dd, $J = 14.2$, 0.9 Hz, 1H), 2.06 (br dt, $J = 13.1$, 4.6 Hz, 1H), 1.72 (part A of an AB system, dd, $J = 13.6$, 0.9 Hz, 1H), 1.68 (part B of an AB system, dd, $J = 13.6$, 0.9 Hz, 1H), 1.44 (m, 1H), 0.30 (s, 3H), 0.30 (s, 3H); ^{13}C NMR: $\delta = 171.3$, 171.2, 141.9, 138.8, 134.6, 133.6, 133.2, 129.0, 127.7, 124.5, 124.4, 113.0, 61.6, 52.1, 52.0, 44.6, 41.6, 32.3, 30.6, 26.6, −3.08, −3.12; Anal. calcd for $C_{24}H_{32}O_4Si$: C 69.87, H 7.82; found: C 70.14, H 8.01.

5-((*E*)-4-Dimethylphenylsilyl-2-butenyl)-1,3-cyclohexadiene ((*E*)-18): Chromatography (pentane) gave **18** ((*E*)/(*Z*) > 95:5 starting from **17** and (*E*)/(*Z*) ≈ 1:1 starting from **16**) as a colorless oil (17%, 44% brsm starting from **17**; 85% starting from **16**). ^1H NMR: $\delta = 7.50$ (m, 2H), 7.35 (m, 3H), 5.86 (m, 2H), 5.76 (m, 1H), 5.67 (m, 1H), 5.38 (dtt, $J = 15.2$, 7.7, 1,1 Hz, 1H), 5.23 (dtt, $J = 15.2$, 6.5, 1.1 Hz), 2.24 (m, 2H), 1.97 (m, 3H), 1.65 (dq, $J = 7.7$, 1.1 Hz, 2H), 1.50–1.30 (m, 2H), 0.26 (s, 6H); ^{13}C NMR: $\delta = 133.6$, 131.6, 129.3, 128.9, 127.7, 125.9, 125.7, 124.0, 123.5, 34.6, 32.0, 30.0, 28.5, 21.6, −3.4. Distinguishable peaks for (*Z*)-**18** in mixture with (*E*)-**18**: ^1H NMR: $\delta = 1.73$ (dm, $J = 8.3$ Hz, 2H); ^{13}C NMR: $\delta = 133.6$, 131.5, 128.9, 128.0, 124.9, 123.6, 34.32, 32.5, 28.5, 24.3, 17.6.

Carbocyclization of dienyl allylsilanes in the presence of Pd^{II} and benzoquinone: In a typical example, (*E*)-**3** (100 mg, 0.25 mmol) in acetone (0.5 mL) was added over a period of 3.75 h to a solution of Li_2PdCl_4 (0.10 equiv, 6.5 mg, 0.025 mmol), LiCl (2.0 equiv, 21 mg, 0.50 mmol), and *p*-benzoquinone (1.5 equiv, 41 mg, 0.38 mmol) in acetone–HOAc (1:1, 1 mL) under N_2. The reaction mixture was stirred at RT for 12 h. Et_2O and water were added and the layers separated. The organic phase was consecutively washed with water (× 1) and 2M NaOH until washings were colorless. The aqueous phase was extracted with Et_2O (× 3) and the combined organic phases were washed with brine, dried ($MgSO_4$–Na_2SO_4) and evaporated. The residue was chromatographed (pentane–Et_2O = 15:1) to give **19** (α:β = 3:1) as a colorless oil (51 mg, 68%). **19α** could be purified by chromatography from this reaction, and **19β** from the reaction of (*Z*)-**3**.

[1(*S*)*,4(*S*)*,6(*R*)*,9(*R*)*]-4-Chloro-7,7-di(methoxycarbonyl)-9-vinyl-bicyclo-[4.3.0]non-2-ene (19α): white solid. M.p. 50–52 °C; ^1H NMR: $\delta = 5.78$ (ap.dq, $J = 10.1$, 1.2 Hz, 1H, H-3), 5.73 (ddd, $J = 10.1$, 4.0, 1.7 Hz, 1H, H-2), 5.64 (ddd, $J = 16.9$, 10.0, 0.8 Hz, 1H, H-10), 5.05 (ddd, $J = 16.9$, 1.6, 1.0 Hz, 1H, H-11 (*trans*)), 5.01 (ddd, $J = 10.0$, 1.6, 0.7 Hz, 1H, H-11 (*cis*)), 4.55 (m, 1H, H-4), 3.75 (s, 3H), 3.73 (s, 3H), 3.10 (ddd, 1H, H-6), 2.92 (dd, $J = 14.3$, 8.7 Hz, 1H, H-8β), 2.58 (m, 1H, H-9), 2.35 (m, 1H, H-1), 1.94 (m, 1H, H-5α), 1.82 (dd, $J = 14.3$, 8.9 Hz, 1H, H-8α), 1.60 (ddd, $J = 14.2$, 12.0, 10.8 Hz, 1H, H-5β); ^{13}C NMR: $\delta = 172.6$, 170.3, 139.4, 129.8, 129.2, 115.6, 62.6, 55.5, 52.8, 52.5, 48.4, 44.6, 43.3, 39.5, 32.9; Anal. calcd for $C_{15}H_{19}ClO_4$: C 60.38, H 6.42; found: C 60.23, H 6.37.

[1(*S*)*,4(*S*)*,6(*R*)*,9(*S*)*]-4-Chloro-7,7-di(methoxycarbonyl)-9-vinyl-bicyclo-[4.3.0]non-2-ene (19β): white semisolid. ^1H NMR: $\delta = 5.82$ (dm, $J = 10.0$ Hz, 1H, H-3), 5.66 (dt, $J = 17.2$, 9.3 Hz, 1H, H-10), 5.59 (ddd, $J = 10.0$, 4.2, 2.0 Hz, 1H, H-2), 4.97 (ddd, $J = 17.2$, 1.5, 0.9 Hz, 1H, H-11 (*trans*)), 4.97 (ddd, $J = 9.4$, 1.5, 0.6 Hz, 1H, H-11 (*cis*)), 4.47 (m, 1H, H-4), 3.75 (s, 3H), 3.74 (s, 3H), 2.99 (m, 1H, H-1), 2.91 (m, 1H, H-6), 2.78 (quint, $J = 9.0$ Hz, 1H, H-9), 2.38 (m, 2H, H-8), 1.91 (dtm, $J = 12.4$, 4.8 Hz, 1H, H-5α), 1.45 (ddd, $J = 14.0$, 12.2, 10.5 Hz, 1H, H-5β); ^{13}C NMR: $\delta = 171.6$, 169.6, 140.5, 129.8, 129.1, 115.2, 63.5, 54.8, 52.9, 52.6, 43.0, 42.9, 39.6, 37.5, 33.7; Anal. calcd for $C_{15}H_{19}ClO_4$: C 60.38; H, 6.42; found: C 60.46, H 6.52; LMRS (of a mixture of both isomers)(*m/z*): 300 ($M^+ + 2$, 0.5), 298 (M^+, 2), 263 (13), 238 (7), 137 (100), 135 (57).

[1(*S*)*,4(*S*)*,6(*R*)*,9(*R*)*]-4-Chloro-7,7-di(methoxycarbonyl)-9-methyl-9-vinyl-bicyclo[4.3.0]non-2-ene (24): Chromatography (pentane/Et_2O 15:1) gave **24** as a mixture of isomers (α:β = 94:6) in 63% yield. Recrystallization (pentane) afforded isomerically pure **24α** as a white solid. M.p. 82 °C; ^1H NMR: $\delta = 5.86$ (br d, $J = 10.2$ Hz, 1H, H-3), 5.77 (dd, $J = 17.4$, 10.6 Hz, 1H, H-10), 5.62 (ddd, $J = 10.2$, 4.7, 2.1 Hz, 1H, H-2), 4.91 (dd, $J = 17.4$, 0.8 Hz, 1H, H-11 (*trans*)), 4.87 (dd, $J = 10.6$, 0.8 Hz, 1H, H-11*c*), 4.53 (m, 1H, H-4), 3.74 (s, 3H), 3.70 (s, 3H), 3.05 (ddd, $J = 14.4$, 7.0, 4.2 Hz, 1H, H-6), 2.75 (m, 1H, H-1), 2.58 (part A of AB system, d, $J = 14.6$ Hz, 1H, H-8β), 2.37 (part B of AB system, dd, $J = 14.6$, 0.9 Hz, 1H, H-8α), 1.88 (m, 1H, H-5α), 1.62 (m, 1H, H-5β), 1.09 (s, 3H); ^{13}C NMR: $\delta = 172.0$, 169.7, 147.8, 130.2, 127.9, 109.6, 62.1, 55.2, 52.8, 52.7, 45.3, 45.1, 44.9, 43.6, 33.1, 26.3.

[1(*S*)*,4(*S*)*,6(*R*)*]-4-Chloro-7,7-di(methoxycarbonyl)-9-methylene-bicyclo-[4.4.0]dec-2-ene (25): Chromatography (pentane/Et_2O 15:1) gave **25** as a white solid. M.p. 71–72 °C (77%); ^1H NMR: $\delta = 5.77$ (ddd, $J = 10.1$, 4.9, 1.7 Hz, 1H, H-2), 5.69 (br d, $J = 10.1$ Hz, 1H, H-3), 4.73 (ap.q, $J = 1.7$ Hz, 1H, H-11), 4.70 (ap.q, $J = 1.7$ Hz, 1H, H-11), 4.63 (m, 1H, H-4), 3.75 (s, 3H), 3.69 (s, 3H), 2.76 (part A of AB system, d, $J = 14.0$ Hz, 1H, H-8β), 2.65 (m, 2H, overlapping with AB system, H-1, H-6), 2.56 (part B of AB system, d, $J = 14.0$ Hz, 1H, H-8α), 2.26 (ddd, $J = 13.4$, 4.8, 1.9 Hz, 1H, H-10α), 1.98 (m, 2H, H-5β, *H*-10β), 1.72 (dd, $J = 12.6$, 6.0 Hz, 1H, H-5α); ^{13}C NMR: $\delta = 170.4$, 170.3, 142.8, 133.6, 128.2, 110.8, 60.5, 56.4, 52.9, 52.7, 37.0, 36.3, 35.2, 35.1, 31.2 (one *C*OOMe overlapping).

[1(*S*)*,4(*S*)*,6(*R*)*]-4-Chloro-9-vinyl-bicyclo[4.3.0]non-2-ene (32): Kügelrohr distillation, (30 °C, 0.5 mmHg) afforded **32** (mixture of α/β isomers [32]) as a colorless oil: ^1H NMR [49]: $\delta = 5.92$–5.66 (m, 3H), 5.08–4.94 (m, 2H), 4.53 (m, 1H), 2.30 (m, 2H), 2.15 (m, 1H), 2.06–1.90 (m, 3H), 1.66 (m, 1H), 1.50 (m, 1H), 1.40 (m, 1H). Distinguishable peaks for **32α** (major isomer when using (*E*)-**18**/(*Z*)-**18** = 1:1): ^1H NMR: $\delta = 5.73$ (ddd, $J = 17.1$, 10.2, 8.2 Hz, 1H), 5.05 (ddd, $J = 17.1$, 1.9, 0.9 Hz, 1H), 4.99 (ddd, $J = 10.2$, 1.9, 0.7 Hz, 1H); ^{13}C NMR: $\delta = 56.1$, 49.4, 44.8, 38.9, 36.8, 32.6, 30.5.

With the cycloheptadienyl derivatives **5** and **13** no slow addition of diene was needed. A solution of LiCl (1.8 equiv) in HOAc was slowly added (12 h) to a solution of diene, benzoquinone (2.5 equiv) and LiCl (0.2 equiv) in acetone–HOAc (5:1) in order to decrease the isomerization of the allylic chloride. Longer reaction times were required (24 h) and inseparable mixtures of isomers were obtained. Spectral data are from enriched mixtures [50].

[1(*S*)*,4(*S*)*,7(*R*)*,10(*R*)*]-4-Chloro-8,8-di(methoxycarbonyl)-10-vinyl-bicyclo[5.3.0]dec-2-ene (20α): ^1H NMR: $\delta = 5.69$ (dddd, $J = 11.5$, 7.8, 2.0, 1.0 Hz, 1H, H-3), 5.65 (ddd, $J = 17.0$, 10.0, 7.8 Hz, 1H, H-11), 5.46 (ddd, $J = 11.7$, 4.9, 1.2 Hz, 1H, H-2), 5.06 (ddd, $J = 17.0$, 1.8, 1.0 Hz, 1H, H-12*t*), 5.00 (ddd, $J = 11.0$, 1.8, 0.9 Hz, 1H, H-12*c*), 4.78 (m, 1H, H-4), 3.73 (s, 3H), 3.72 (s, 3H), 2.92 (ddd, $J = 12.3$, 8.0, 3.0 Hz, 1H, H-7), 2.77 (br quint, $J = 8.5$ Hz, 1H, H-10), 2.70 (dd, $J = 13.6$, 8.0 Hz, 1H, H-9), 2.68 (m, 1H, H-1), 2.12 (m, 1H, H-5β), 2.03 (dddd, $J = 14.5$, 10.5, 4.3, 3.0 Hz, 1H, H-5α), 1.84 (m, 1H, H-6β), 1.81 (dd, $J = 13.7$, 8.8 Hz, 1H, H-9′), 1.53 (m, 1H, H-6α). ^{13}C NMR: $\delta = 172.6$, 171.0, 140.1, 131.5, 129.3, 115.5, 64.2, 59.2, 52.7, 52.4, 49.1, 48.0, 47.7, 38.6, 34.9, 22.7.

20β: ^1H NMR: $\delta = 5.87$ (ddd, $J = 17.0$, 10.3, 6.6 Hz, 1H, H-11), 5.62 (m, 1H, H-3), 5.44 (ddd, $J = 11.7$, 4.8, 1.6 Hz, 1H, H-2), 5.09 (ap.dt, $J = 10.3$, 1.5 Hz, 1H, H-12*c*), 5.03 (ap.dt, $J = 17.1$, 1.5 Hz, 1H, H-12*t*), 4.91 (m, 1H, H-4), 3.74 (s, 3H), 3.73 (s, 3H), 3.20 (ap.quint, $J = 8.4$ Hz, 1H, *H*-7), 3.15 (m, 1H, H-1), 2.64 (m, 1H, H-10), 2.58 (dd, $J = 13.3$, 11.8 Hz, 1H, H-9), 2.31 (br dd, $J = 13.4$, 6.6 Hz, 1H, H-9′), 2.12 (m, 2H, H-5,5′), 1.64 (m, 2H, H-6,6′); ^{13}C NMR: $\delta = 172.9$, 170.9, 138.4, 130.4, 128.3, 116.0, 63.6, 61.1, 52.9, 52.5, 48.7, 44.3, 44.0, 37.7, 33.9, 22.8.

21β (major isomer of the α-Cl isomers): ^1H NMR: $\delta = 5.90$ (ddd, $J = 17.0$, 10.4, 4.5 Hz, 1H, H-11), 5,68 (m, 1H, H-3), 5.53 (ddd, $J = 11.2$, 4.5, 0.7 Hz, 1H, H-2), 5.15 (dt, $J = 10.5$, 1.4 Hz, 1H, H-12*c*), 5.09 (dt, $J = 17.1$, 1.5 Hz, 1H, H-12*t*), 4.51 (m, 1H, H-4), 3.74 (s, 3H), 3.68 (s, 3H), 3.36 (dt, $J = 11.8$, 7.2 Hz, 1H, H-7), 3.29 (m, 1H, H-1), 2.63–2.59 (m, 2H, H-9, H-10), 2.34 (m, 1H, H-5β), 2.28 (m, 1H, *H*-9), 1.99 (m, 1H, H-5α), 1.94 (m, 1H, H-6α), 0.95 (m, 1H, H-6β). [*anti* isomer has as the clearer signal H-4 (m) $\delta = 4.92$]; ^{13}C NMR: $\delta = 173.1$, 171.3, 137.3, 129.4, 128.5, 116.4, 65.8, 59.0, 52.9, 52.3, 48.6, 44.1, 43.3, 37.9, 34.1, 25.0.

[1(*S*)*,4(*S*)*,7(*R*)*]-4-Chloro-8,8-di(methoxycarbonyl)-10-methylene-bicyclo-[5.4.0]undec-2-ene (26): The mixture of *syn*, *anti* isomers precipitates after a lengthy period at −18 °C. Recrystallization (hexane/EtOAc 98:2) afforded isomerically pure **26** as a white solid. M.p. 83–84 °C; ^1H NMR: $\delta = 5.82$ (ddt, $J = 12.2$, 6.6, 0.9 Hz, 1H, H-3), 5.68 (dd, $J = 12.2$, 7.4 Hz, 1H, H-2), 4.78 (m, 1H, H-4), 4.73 (d, $J = 1.6$ Hz, 1H, H-12), 4.72 (d, $J = 1.6$ Hz, 1H, H-12′), 3.74 (s, 3H), 3.69 (s, 3H), 2.83 (dt, $J = 14.0$, 1.5 Hz, 1H, H-9), 2.81 (m, 1H, *H*-1), 2.68 (br d, $J = 11$ Hz, 1H, H-7), 2.62 (dq, $J = 14.1$, 1.5 Hz, 1H, H-9′), 2.27 (m, 1H, H-6β) [51], 2.25 (m, 1H, H-5β) [51], 2.19 (m, 1H, H-1) [51]· 2.12 (br dd, $J = 13.9$, 4 Hz, 1H, H-11α), 1.93 (m, 1H, H-5α), 1.25 (m,

0947-6539/97/0303-0488 $ 15.00+.25/0 Chem. Eur. J. 1997, 3, No. 3

1H, H-6α); ^{13}C NMR: δ = 171.0, 143.4, 135.7, 129.3, 110.8, 61.7, 59.1, 52.8, 52.7, 41.5, 40.5, 36.7, 35.1, 35.0, 21.3 (one COO overlapping); Anal. calcd. for $C_{16}H_{21}ClO_4$ (mixture of isomers): C 61.44, H 6.77; found: C 61.28, H 6.76.

Carbocyclization of dienyl allylsilanes in the presence of Pd^{II} and $CuCl_2$: In a typical example, (*Z*)-**7** (100 mg, 0.26 mmol), Li_2PdCl_4 (0.10 equiv, 6.7 mg, 0.026 mmol), LiCl (5.0 equiv, 55 mg, 1.3 mmol), and $CuCl_2$ (2.5 equiv, 88 mg, 0.64 mmol) in acetone–HOAc (1:1, 1.5 mL) were stirred at RT under N_2 for 44 h. Et_2O and H_2O were added and the layers separated. The aqueous phase was extracted with Et_2O (×3) and the combined organic phases were washed with brine, dried ($MgSO_4$–Na_2SO_4) and evaporated. The residue was chromatographed (pentane/Et_2O 16:1) to give inseparable chlorides **22** (4:1 mixture of isomers) as a pale yellow oil (45 mg, 60%) [49].

1,1-Di(methoxycarbonyl)-3-(3-chloro-1-propenyl)-4-vinylcyclopentane (22):
Major isomer: ^{1}H NMR: δ = 5.72–5.54 (m, 3H), 5.03–4.97 (m, 2H), 4.01 (d, *J* = 5.8 Hz, 2H), 3.73 (s, 6H), 2.82–2.75 (m, 2H), 2.51–2.46 (m, 2H), 2.24–2.16 (m, 2H); ^{13}C NMR: δ = 172.9, 172.6, 137.7, 135.1, 127.0, 115.8, 58.9, 52.9, 52.8, 47.1, 45.4, 45.0, 38.9, 38.8.

Minor isomer (major when using (*E*)-**7**): ^{1}H NMR: δ = 5.72–5.54 (m, 3H), 5.03–4.97 (m, 2H), 4.01 (d, *J* = 5.8 Hz, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 2.59–2.53 (m, 2H), 2.37–2.28 (m, 2H), 2.07–2.00 (m, 2H); ^{13}C NMR: δ = 172.7 (2C), 138.7, 135.8, 127.1, 115.8, 58.2, 52.8 (2C), 49.6, 47.8, 44.9, 40.0, 40.0; LMRS (of the mixture of **22**) (*m*/*z*): 288 (M^++2, 0.5), 286 (M^+, 1.6), 251 (5), 226 (9), 59 (100); Anal. calcd for $C_{14}H_{19}ClO_4$ (mixture of isomers): C 58.64, H 6.68; found: C 58.81; H, 6.69.

1,1-Di(methoxycarbonyl)-3-(3-acetoxy-1-propenyl)-4-vinylcyclopentane (23):
Major isomer [49]: (from (*E*)-**7**): ^{1}H NMR: δ = 5.68–5.52 (m, 3H), 5.04–4.97 (m, 2H), 4.55–4.46 (m, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 2.60–2.54 (m, 2H), 2.36–2.28 (m, 2H), 2.1–2.0 (m, 2H, overlapping with CH_3COO), 2.07 (s, 3H); ^{13}C NMR: δ = 172.8 (2C), 172.7, 138.8, 136.0, 125.1, 115.7, 64.8, 58.2, 52.8 (2C), 49.6, 48.1, 38.9, 38.8, 21.0.

Minor isomer [49] (from (*E*)-**7**): ^{1}H NMR: δ = 5.68–5.52 (m, 3H), 5.04–4.97 (m, 2H), 4.55–4.46 (m, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 2.82–2.75 (m, 2H), 2.52–2.46 (m, 2H), 2.25–2.16 (m, 2H), 2.07 (s, 3H); ^{13}C NMR: δ = 173.0, 172.7, 170.7, 137.9, 135.3, 125.0, 115.6, 64.9, 59.0, 52.8 (2C), 47.1, 45.6, 40.0 (2C), 21.0.

Reaction of 3 with $CuCl_2$ as the oxidant, as described above, yielded mixtures of **30α**, **30β**, **19α**, and **19β** [52]:

30α: ^{1}H NMR: δ = 5.91 (dd, *J* = 10, 4.8 Hz, 1H, H-3), 5.87 (dd, *J* = 10, 4.5 Hz, 1H, H-2), 5.67 (m, 1H, H-10), 5.08–4.99 (m, 2H, H-12*c*,*t*), 4.57 (m, 1H, *H*-4), 3.75 (s, 3H), 3.74 (s, 3H), 3.45 (ap.dt, *J* = 13, 5 Hz, 1H, H-6), 2.87 (m, 2H, H-9, H-9′), 2.50–2.45 (m, 2H), H-1, H-10), 1.82 (m, 1H, H-5), 1.76 (dd, *J* = 13.5, 3.8 Hz, 1H, H-5′); ^{13}C NMR: δ = 172.6, 170.7, 139.5, 131.3, 126.5, 115.6, 62.7, 53.1, 52.8, 52.4, 48.5, 45.0, 39.6, 38.1, 30.5.

30β: ^{1}H NMR: δ = 5.95 (ddd, *J* = 9.8, 5.5, 2.2 Hz, 1H, H-3), 5.73 (dd, *J* = 9.8, 4.5 Hz, 1H, H-2), 5.56 (ddd, *J* = 16.9, 10.0, 9.0 Hz, 1H, H-10), 4.98 (brd, *J* = 16 Hz, 1H, H-11*t*), 4.95 (brd, *J* = 11 Hz,1H, H-11*c*), 4.58 (m, 1H, H-4), 3.76 (s, 3H), 3.75 (s, 3H), 3.33 (*m*, 1*H*, H-6), 3.13 (*m*, 1H, H-1), 2.83 (ap.quint, *J* = 9.0 Hz, 1H, H-9), 2.38 (dd, *J* = 14.0, 8.3 Hz, 1H, H-8), 2.32 (dd, *J* = 14.1, 10.6 Hz, 1H, H-8), 1.79 (m, 1H, H5α), 1.69 (ddd, *J* = 14.0, 12.8, 4.0 Hz, 1H, H-5β); ^{13}C NMR: δ = 171.9, 170.0, 140.2, 131.3, 126.8, 115.2, 63.6, 52.9 (2C), 52.6, 43.7, 40.4, 38.33, 38.25, 31.4.

Reaction of 9 with $CuCl_2$ as the oxidant, as described above, gave **31** as a 9:1 mixture of isomers (α:β), contaminated with **24** (ca. 30%). **31**: ^{1}H NMR [49]: δ = 5.99 (ddd, *J* = 9.8, 5.3, 2.1 Hz, 1H), 5.79 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.74 (dd, *J* = 9.9, 4.7 Hz, 1H), 4.91 (dd, *J* = 17.4, 0.7 Hz, 1H), 4.88 (dd, *J* = 10.6, 0.7 Hz, 1H), 4.63 (m, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.43 (m, 1H), 2.89 (ddd, *J* = 7.5, 4.8, 2.1 Hz, 1H), 2.52 (part A of AB system, d, *J* = 14.5 Hz, 1H), 2.36 (part B of AB system, dd, *J* = 14.5, 1.0 Hz, 1H), 1.81–1.75 (m, 2H), 1.00 (s, 3H); ^{13}C NMR: δ = 172.1, 170.2, 147.8, 130.2, 127.2, 109.8, 62.5, 53.2, 52.6, 45.9, 45.7, 38.6, 31.1, 25.9.

(π-Allyl)palladium complex 28: Prepared from **13** as described below for preparation of **33**. Obtained as a mixture of dimeric diastereoisomers (≈1:1). ^{1}H NMR: δ = 5.20 (brs, 1H, H-3, *isomer 1*), 5.12 (brt, *J* = 7 Hz, 1H, H-3, *isomer 2*), 4.88–4.72 (m, 4H, H-2, H-4, H-12, H-12′), 3.73 (brs, 6H, CO_2CH_3), 3.39 (brs, 1H, H-7), 2.79 (d, *J* = 13.6 Hz, 1H, H-9), 2.69 (brs, 1H, H-1), 2.30 (m, 2H, H-9, H-11), 2.10–1.82 (m, 3H, H-11, H-5, H-5′), 1.33 (m, 1H, H-6), 1.06 (brd, *J* = 14 Hz, 1H, H-6′).

(π-Allyl)palladium complex 29: ^{1}H NMR: δ = 5.90–5.77 (m, 3H), 5.74–5.68 (m, 1H), 3.83 (d, *J* = 2 Hz, 1H), 3.78 (d, *J* = 2 Hz, 1H), 3.75 (s, 3H), 3.75 (s, 3H), 2.97 (d, *J* = 4 Hz, 2H), 2.94 (m, 1H), 2.86 (d, *J* = 4 Hz, 2H), 2.42 (m, 2H), 2.10 (m, 1H), 1.62–1.51 (m, 1H).

(π-Allyl)palladium complexes 33: The complexes **33** were prepared by reaction of **3** with 1 equiv of Li_2PdCl_4 in deuterated acetone–acetic acid (2:1) at 25 °C. The reaction was followed by ^{1}H NMR. Only complexes **33** were detected.
33α (prepared from (*E*)-**3**, major isomer): ^{1}H NMR [53]: δ = 5.72 (ddd, *J* = 17.1, 10.2, 7.7 Hz, 1H, H-10), 5.47 (td, *J* = 6.5, 1.1 Hz, 1H, H-3), 5.05 (ddd, *J* 16.9, 1.7, 1.0 Hz, 1H, H-11*t*), 4.97 (ddd, *J* = 10.1, 1.8, 0.7 Hz, 1H, H-11*c*), 4.91 (m, 1H, H-4), 4.87 (ddd, *J* = 6.5, 3.7, 1.1 Hz, 1H, H-2), 3.79 (m, 1H, H-6), 3.66 (s, 3H), 3.66 (s, 3H), 2.76 (dd, *J* = 13.9, 8.5 Hz, 1H, H-8β), 2.45 (m, 1H, H-1), 2.0–1.9 (overlapping m, 1H, H-5α), 1.75 (dd, *J* = 13.8, 8.4 Hz, 1H, H-8α), 1.08 (m, 1H, H-5β).

33β (prepared from (*Z*)-**3**, major isomer): ^{1}H NMR: δ = 5.80 (ddd, *J* = 16.8, 10.2, 1.8 Hz, 1H, H-10), 5.50 (td, *J* = 6.5, 0.9 Hz, 1H, H-3), 5.05 (dm, *J* = 16.7 Hz, 1H, H-11*t*), 5.07 (dm, *J* = 10.0 Hz, 1H, H-11*c*), 4.90 (m, 1H, H-4), 4.74 (brdd, *J* = 6.5, 2.9 Hz, 1H, H-2), 3.68 (s, 3H), 3.66 (s, 3H), 3.56 (m, 1H, H-6), 2.93 (m, 1H, H-1), 2.76 (m, 1H, H-9), 2.36 (dd, *J* = 14.0, 10.5 Hz, 1H, H-8), 2.16 (dd, *J* = 14.0, 7.4 Hz, 1H, H-8), 2.0–1.9 (overlapping m, 1H, H-5), 1.30 (m, 1H, H-5).

The bipyridine complex **34** prepared from **33β** [54] showed NOE between the *ortho* proton in the bipyridine ligand and H-1 (3.4%). A small NOE was also observed between the *ortho* proton and H-5α (0.8%). ^{1}H NMR [55] δ = 8.95 (brs, 2H, Ar H-6,6′), 8.54 (dt, *J* = 7.9, 0.9 Hz, 2H, Ar H-3,3′), 8.28 (td, *J* = 7.9, 1.6 Hz, 2H, Ar H-4,4′), 7.75 (ddd, *J* = 7.8, 5.0, 1.0 Hz, 2H, Ar H-5,5′), 6.05 (td, *J* = 6.5, 0.9 Hz, 1H, H-3), 5.95 (ddd, *J* = 17.0, 10.3, 8.5 Hz, 1H, H-10), 5.25 (m, 1H, H-4, overlapping *H*-11 (*cis*)), 5.22 (dm, *J* = 10.1, 1H, H-11 (*cis*)), 5.17 (dm, *J* = 16.9 Hz, 1H, H-11 (*trans*)), 5.07 (dd, *J* = 6.8, 3.2 Hz, 1H, *H*-2), 3.71 (s, 3H), 3.65 (s, 3H), 3.43 (ap.q, *J* = 7.5 Hz, 1H, H-6), 3.05 (m, 1H, H-1), 2.89 (ap.quint, *J* = 9 Hz, 1H, H-9), 2.49 (dd, *J* = 14.0, 10.0 Hz, 1H, H-8), 2.27 (dd, *J* = 14.0, 7.5 Hz, 1H, H-8′), 2.17 (ddd, *J* = 17.0, 7.5, 4.1 Hz, 1H, H-5), 1.63 (ddd, *J* = 17.0, 8.0, 3.5 Hz, 1H, H-5′).

Dimethyl (2,4-cyclohexadienyl)((*Z*)-4-tributyltin-2-butenyl)malonate (35): Prepared from (*Z*)-**2** according to reference [36], (37%). ^{1}H NMR: δ = 5.93 (m, 1H), 5.85 (m, 1H), 5.78–5.62 (m, 3H), 4.91 (m, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 3.12 (m, 1H), 2.66 (m, 2H), 2.33 (dddd, *J* = 17.5, 8.0, 5.0, 1.4 Hz, 1H), 2.21 (dddd, *J* = 17.4, 13.5, 3.7, 2.5 Hz, 1H), 1.72 (d, *J* = 9.1 Hz, 1H), 1.47 (m, 6H), 1.30 (m, 6H), 0.89 (m, 15H); ^{13}C NMR: δ = 171.3, 171.2, 132.2, 126.5, 126.0, 124.9, 123.6, 116.7, 60.5, 52.2, 52.1, 36.2, 30.1, 29.2, 27.4, 24.5, 13.7, 10.7, 9.4.

(π-Allyl)palladium complex 36: The complex **36** was formed (in less than 5 min) by reaction of **35** with 1 equiv of Li_2PdCl_4 in deuterated methanol. The reaction was followed by ^{1}H NMR. ^{1}H NMR [55] δ = 6.05 (m, 1H, H-9), 5.86 (ddt, *J* = 8.7, 5.0, 1.3 Hz, 1H, H-8), 5.74 (brt, *J* = 7.5 Hz, 1H, H-10), 5.51 (ddd, *J* = 13.0, 11.0, 7.2 Hz, 1H, H-2), 5.97 (d, *J* = 8.8 Hz, 1H, H-7), 4.76 (d, *J* = 7.3 Hz, 1H, H-1(*syn*)), 4.06 (td, *J* = 11.2, 3.6 Hz, 1H, H-3), 3.81 (s, 3H), 3.79 (s, 3H), 3.76 (d, *J* = 13 Hz, 1H, H-1 (*anti*)), 3.27 (brd, *J* = 7.1 Hz, 1H, H-6), 2.75 (dd, *J* = 15.1, 3.5 Hz, 1H, H-4), 2.13 (dd, *J* = 15.1, 11.4 Hz, 1H, H-4′), 1.94 (dtm, *J* = 17.7 Hz, 1H, H-11), 1.29 (m, 1H, H-11′, overlapping Sn-byproduct); ^{13}C NMR: δ = 171.1, 170.7, 130.1, 123.7, 116.4, 103.7, 95.5, 84.1, 79.8, 66.8, 53.8, 53.7, 37.3, 30.9, 25.3.

Acknowledgments. Financial support from the Swedish Natural Science Research Council and from Ministerio de Educación y Ciencia from Spain (fellowship to A. M. C.) is gratefully acknowledged. We thank Johnson Matthey for a loan of palladium chloride.

Received: September 9, 1996 [F459]

[1] J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, Chichester, **1995**.

[2] a) B. M. Trost, T. R. Verhoeven in *Comprehensive Organometallic Chemistry, Vol. 8* (Eds.: G. Wilkinson, F. G. A. Stone), Pergamon, Oxford, **1982**, p. 799; b) J. E. Bäckvall, In *Advances in Metal-Organic Chemistry, Vol. 1* (Ed.: L. Liebeskind), JA1 Press, London, **1989**, pp. 135–175; c) L. S. Hegedus, in *Comprehensive Organic Synthesis, Vol. 3* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 551–583.

[3] J. E. Bäckvall and D. Tanner, "Palladium-Mediated Synthesis of Alkaloids", in *Studies in Natural Products Chemistry. Vol. 16* (Ed.: Atta-Ur-Rahman), Elsevier, **1995**, pp. 415–452.

[4] B. M. Trost, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1173.

[5] A. Heumann, M. Réglier, *Tetrahedron*, **1995**, *51*, 975.

[6] a) J. E. Bäckvall, *Acc. Chem. Res.* **1983**, 16, 335; b) J. E. Bäckvall, B. Åkermark, S. O. Ljunggren, *J. Am. Chem. Soc.* **1979**, 101, 2411; c) J. E. Bäckvall, R. E. Nordberg, *ibid.* **1980**, 102, 393.

[7] a) J. E. Bäckvall, in *Organometallic Reagents in Organic Synthesis*; Academic: London, **1994**, 81–97; b) J. E. Bäckvall, *Pure Appl. Chem.* **1992**, *64*, 429–437.

[8] a) J. E. Bäckvall, S. E. Byström, R. E. Nordberg, *J. Org. Chem.* **1984**, *49*, 4619–5631; b) J. E. Bäckvall, J. E. Nyström, R. E. Nordberg, *J. Am. Chem. Soc.* **1985**, *107*, 3676–3786; c) J. E. Bäckvall, J. O. Vågberg, *J. Org. Chem.* **1988**, 53, 5695.

[9] a) J. E. Bäckvall, P. G. Andersson, *J. Am. Chem. Soc.* **1990**, *112*, 3683; b) J. E. Bäckvall, P. G. Andersson, *J. Org. Chem.* **1991**, *56*, 2274; c) P. G. Andersson, J. E. Bäckvall, *J. Am. Chem. Soc.* **1992**, *114*, 8696–8698; d) J. E. Bäckvall, P. G. Andersson, *ibid.* **1992**, *114*, 6374–6381; e) J. E. Bäckvall, K. L. Granberg, P. G. Andersson, R. Gatti, A. Gogoll, *J. Org. Chem.* **1993**, *58*, 5445.

[10] a) P. G. Andersson, Y. I. M. Nilsson, J. E. Bäckvall, *Tetrahedron* **1994**, *50*, 559–572; b) Y. I. M. Nilsson, A. Aranyos, P. G. Andersson, J. E. Bäckvall, J. L. Parrain, C. Ploteau, J. P. Quintard, *J. Org. Chem.* **1996**, *61*, 1825; c) J. E. Bäckvall, P. G. Andersson, G. B. Stone, A. Gogoll, *ibid.* **1991**, *56*, 2988–2993; d) P. G. Andersson, J. E. Bäckvall, *ibid.* **1991**, *56*, 5349.

[11] a) J. E. Bäckvall, Y. I. M. Nilsson, P. G. Andersson, R. G. P. Gatti, J. Wu, *Tetrahedron Lett.* **1994**, *35*, 5713–5716; b) Y. I. M. Nilsson, R. G. P. Gatti, P. G. Andersson, J. E. Bäckvall, *Tetrahedron*, **1996**, *52*, 7511.

[12] A. M. Castaño, J. E. Bäckvall, *J. Am. Chem. Soc.* **1995**, *117*, 560–561.

[13] The use of C-nucleophiles in the Pd^{II}-promoted nucleophilic additions to olefins has only been described with stoichiometric amounts of palladium. For a recent review see: Ref. [2c]; see also: G. J. Laidig, L. S. Hegedus, *Synthesis* **1995**, 527.

[14] For a related palladium(II)-catalyzed C–C bond formation by insertion of an olefin into a vinylpalladium species generated in situ see: a) S. Ma, X. Lu, *J. Chem. Soc. Chem. Commun.* **1990**, 733; b) S. Ma, X. Lu, *J. Org. Chem.* **1991**, *56*, 5120; c) J. Ji, X. Lu, *Synlett*, **1993**, 745.

[15] For some recent reviews on allylsilanes, see: a) *The Chemistry of Organic Silicon Compounds*, Part 2 (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**; b) I. Fleming, J. Dunogues, R. Smithers, *Org. React.* **1989**, *37*, 57–575; c) I. Fleming, *Tetrahedron* **1988**, *44*, 3761–4292.

[16] A. Hosomi, H. Sakurai, *J. Am. Chem. Soc.* **1977**, *99*, 1673–1674 and references therein.

[17] H. Grennberg, A. Gogoll, J. E. Bäckvall, *Organometallics* **1993**, *12*, 1790.

[18] Allylsilanes have been shown to react with cationic (pentadienyl, trienyl, and allylic) organometallic complexes: a) L. A. P. Kane-Maguire, E. D. Honig, D. A. Swigart, *Chem. Rev.* **1984**, *84*, 525–543; b) M. Franck-Neumann, P. Bissinger, P. Geoffroy, *Tetrahedron Lett.* **1993**, *34*, 4643–4646; c) B. M. Trost, E. Keinan, *ibid.* **1980**, *21*, 2595–2598; d) M. Terakado, M. Miyazawa, K. Yamamoto, *Synlett* **1994**, 134–136.

[19] a) J. E. Nyström, T. Rein, J. E. Bäckvall, *Org. Synth.* **1989**, *67*, 105–113; b) Prepared from (*Z*)-4-acetoxy-2-buten-1-ol: K. C. Nicolaou, C. A. Veale, S. E. Webber, H. Katerinopoulos, *J. Am. Chem. Soc.* **1985**, *107*, 7515–7518.

[20] a) D. J. Ager, I. Fleming, S. K. Patel, *J. Chem. Soc. Perkin Trans. 1* **1981**, 2520–2526; I. Fleming, D. Higgins, N. J. Lawrence, A. P. Thomas, *J. Chem. Soc. Perkin Trans. 1* **1992**, 3331–3349; b) G. Majetich, J. Defauw, *Tetrahedron* **1988**, *44*, 3833–3849.

[21] For a recent review on the preparation of allylic silanes, see: T. K. Sarkar, *Synthesis* **1990**, 969 and 1101.

[22] Abbreviations: brsm = based on recovered starting material; E = CO_2Me.

[23] For an excellent study on the effect of *gem*-dialkyl substitution in cyclization reactions see: M. E. Jung, J. Gervay, *J. Am. Chem. Soc.* **1991**, *113*, 224–232.

[24] L. E. Overman, F. M. Knoll, *Tetrahedron Lett.* **1979**, 321–324.

[25] Descriptors α and β refer to the orientation of the vinyl substituent at C-9 relative to the plane of the molecule.

[26] An increase in the size of the ester groups in **3** to E = CO_2iPr did not change the α:β selectivity from that observed for (*E*)- and (*Z*)-**3** (E = CO_2Me).

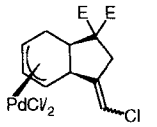
[27] Only the (π-allyl)palladium complexes **28** with palladium on the *exo* face was observed in the ^{1}H NMR spectrum. The complex consists of dimeric diastereoisomers (1:1).

[28] Allylsilanes react with Pd^{II} complexes forming the corresponding (π-allyl)-palladium complex, by transfer of the allyl group: J. M. Kliegman, *J. Organomet. Chem.* **1971**, *29*, 73–77; T. Hayashi, M. Konishi, M. Kumada, *J. Chem. Soc. Chem. Commun.* **1983**, 736–737; S. Ogoshi, W. Yoshida, K. Ohe, S. Murai, *Organometallics* **1993**, *12*, 578–579 and references therein.

[29] Allylsilanes react in Pd^0-catalyzed cross-coupling reactions in which the allyl group is transferred to palladium in an arylpalladium(II) species: Y. Hatanaka, K.-i. Goda, T. Hiyama, *Tetrahedron Lett.* **1994**, *35*, 1279–1282; Y. Hatanaka, Y. Ebina, T. Hiyama, *J. Am. Chem. Soc.* **1991**, *113*, 7075–7076; L. F. Tietze, R. Schimpf, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1089; L. F. Tietze, T. Raschke, *Synlett* **1995**, 599.

[30] Control experiments in the absence of Pd^{II} led mainly to the recovery of the starting material (≈50%), contaminated with unknown by-products and very small amounts of **30**.

[31] a) G. Zhu, S. Ma, X. Lu, Q. Huang, *J. Chem. Soc. Chem. Commun.* **1995**, 271–273; b) When (π-allyl)palladium complex **37** [11], which has Pd at the "*endo*" face, was oxidized with $CuCl_2$ in the presence of Cl^-; ≈20% of addition of Cl^- from the most hindered face (*endo*, S_N1-S_Ni process) was obtained, the major product arising from addition of Cl^- from the least encumbered side (*exo*, *anti* to Pd) [31c]; c) A. Castaño, unpublished results.



37 (E = CO_2Me)

[32] The relative stereochemistry of the products could not be assigned in the chlorides and was determined in the bipyridine triflate complex.

[33] It is known that quinone-induced chloride attack on (π-allyl)palladium complexes occurs *anti*, see Refs. [7] and [8b].

[34] a) A. Albinati, C. J. Ammann, R. W. Kunz, P. S. Pregosin, *Organometallics* **1991**, *10*, 1800–1806; b) A. Gogoll, H. Grennberg, *Magn. Reson. Chem.* **1993**, *31*, 954; c) A. Gogoll, J. Gomes, M. Bergkvist, H. Grennberg, *Organometallics* **1995**, *14*, 1354; d) J. L. Bookham, W. McFarlane, *J. Chem. Soc. Chem. Commun.* **1993**, 1352.

[35] The formation of **33**α and **33**β as the only observable products eliminates an additional alternative pathway for formation of **19**, namely, chloropalladation of the diene and subsequent attack by the silane on the (π-allyl)palladium complex (cf. Ref. [18c,d]).

[36] Prepared in 37% yield from the allylic acetate (*Z*)-**2** by reaction with $(Bu_3Sn)(Bu)Cu(CN)Li_2$: B. H. Lipshutz, E. L. Ellsworth, S. T. Dimock, D. C. Reuter, *Tetrahedron Lett.* **1989**, *30*, 2065–2068.

[37] The corresponding transmetalation of allylsilanes to Pd^{II} salts is known to be less effective in HOAc than in methanol, and $Pd(OAc)_2$ is not a very suitable source of palladium for this reaction (see Ref. [29a]).

[38] The other two compounds have not been characterized. One of the other products has a vinyl group, but it is not clear whether it is a π-allyl complex or if it comes from protonolysis of the allyltin.

[39] The procedure described in Ref. [10c] gave a 7:1 mixture of isomers. The undesired isomer gives rise to an allylic silane that does not react in the carbocyclization reaction. The yields are not corrected to its presence. In some cases, DBU was used instead of iBu_3N, and none of the other regioisomer was observed, however, ca. 30% of the conjugated isomer was formed.

[40] J. E. Bäckvall, J. O. Vågberg, C. Zercher, J. P. Genêt, A. Denis, *J. Org. Chem.* **1987**, *52*, 5430–5435.

[41] J. E. Nyström, J. E. Bäckvall, *J. Org. Chem.* **1983**, *48*, 3947.

[42] Described in: F. Camps, V. Gasol, A. Guerrero, *Synthesis* **1987**, 511.

[43] Described in: G. Magnusson, F. Lindqvist, *J. Chem. Soc. Chem. Commun.* **1990**, 1080.

[44] Prepared from the commercially available 2-methylene-1,3-propanediol.

[45] Y. M. L. Nilsson, P. G. Andersson, J. E. Bäckvall, *J. Am. Chem. Soc.* **1993**, *115*, 6609.

[46] All signals correspond to both diastereoisomers.

[47] Shifts in brackets correspond to the other set of signals, not necessarily to the other isomer, as they have not been assigned.

[48] A mixture **16**/**17** (≈1:1) was obtained, contaminated with small amounts of internal Diels–Alder reaction product.

[49] Spectral data from mixture of isomers.

[50] Some assignments were carried out with the help of 1DTOCSY experiments.

[51] Chemical shifts determined from the cross-peak of a relay experiment.

[52] Spectral data of **30**α and **30**β from the mixture of isomers. In some cases, the coupling constants were measured from 1DTOCSY spectra.

[53] Chemical shifts referred to acetone shift at $\delta = 2.05$.

[54] Prepared using Ag(OTf) instead of Tl(OTf), see Ref. [34].

[55] Chemical shifts referred to methanol shift at $\delta = 4.87$.

0947-6539/97/0303-0490 $ 15.00+.25/0