Intramolecular Coupling of Allyl Carboxylates with Allyl Stannanes and Allyl Silanes: A New Type of Reductive Elimination Reaction?

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Abstract: The palladium-catalyzed intramolecular coupling of allyl stannanes with allyl carboxylates provides a general synthesis of five- and six-membered-ring carbocycles. The intramolecular coupling leads selectively to *trans* five-membered carbocycles and *cis* six-membered carbocycles, regardless of the *cis* or *trans* configuration of the allylic functions in the starting material. For example, the stereoselective synthesis of 10-*epi*-elemol demonstrated the *cis* configuration of the six-membered carbocycles. The related Oppolzer cyclization leads to lower yields, or fails completely, with substrates substituted at C-3 of the allyl and/or alkene terminus. The palladium-catalyzed intramolecular coupling of allyl silanes with allyl trifluoroacetates allows the synthesis of *trans* five-membered-ring carbocycles and requires the use of a bicyclic phosphite as the ligand. DFT calculations suggest that the preferred pathway for the intramolecular allyl/allyl coupling is by formation of the C–C bond between the C-3 termini of the allyl ligands of bis(η^3-allyl)palladium complexes.

Keywords: cross-coupling · density functional calculations · palladium · silanes · stannanes

Introduction

The Stille coupling of allyl stannanes with allyl carboxylates[1, 2] or allyl bromides[3, 4] allows the synthesis of 1,5-dienes.[5, 6, 7] In a variation of this reaction the allyl stannane is generated in situ by the palladium(0)-catalyzed reaction of an allyl acetate with hexa-*n*-butyldistannane.[8] Palladium-catalyzed coupling of allyl silanes with allyl electrophiles is an interesting alternative to the use of more toxic stannane electrophiles.[9]

Clean allylic inversion on the allyl stannane was observed in this coupling,[1, 2] which led to the proposal that the reaction might proceed by an external attack of the stannane on the intermediate (η^3-allyl)palladium complex, as has been observed for the reaction of this organometallic reagents with soft nucleophiles.[10] Allylic inversion on the nucleophile was also demonstrated in the coupling with allyl silanes.[9c] A different reaction pathway seems to be involved in the palladium-catalyzed coupling reactions of allylic species in the absence of phosphane ligands.[11] Thus, addition of π-acceptor ligands, such as maleic anhydride or fumaronitrile, has been shown to promote the C–C bond formation by the reductive elimination of the bis(η^3-allyl)palladium intermediates. Additionally, allyl stannanes have been proposed to undergo oxidative addition to palladium(0) complexes.[12] Despite the importance of allyl/allyl coupling in organic synthesis, a detailed mechanistic study of this palladium-catalyzed reaction has not been carried out.

The intramolecular reaction of allyl stannanes **I** or allyl silanes **II** with allyl carboxylates could proceed via (η^1-allyl)(η^3-allyl)palladium complex **III**[13] or bis(η^1-allyl)palladium complexes **IV** and **V** to give carbocycle **VI** after reductive elimination (Scheme 1). The actual situation could be more complex, since additional regioisomers and/or stereoisomers of **III**–**V** could also exist in the equilibrium. The reaction of monophosphanes (PR_3) to bis(η^3-allyl)palladium complexes leads to (η^1-allyl)(η^3-allyl)(PR_3)palladium complexes, which decompose to form dinuclear Pd^I derivatives.[14] Addition of diphosphanes to bis(η^3-allyl)palladium complexes gives bis(η^1-allyl)palladium diphosphane complexes, which undergo smooth reductive elimination at low

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Supporting information for this article is available on the WWW under http://www.chemeurj/org or from the author. Experimental details, characterization data for compounds in Schemes 1–5, and atomic coordinates for structures in Figures 1 and 2.

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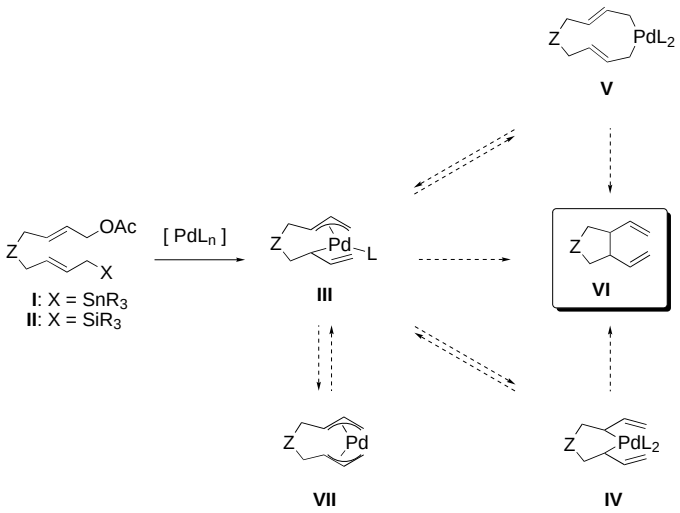
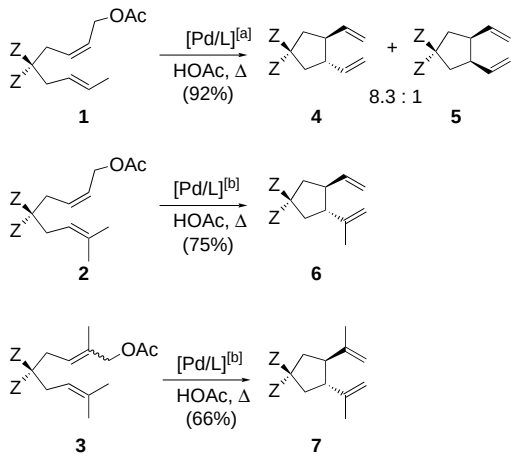


Scheme 1. Possible reductive elimination pathways for the formation of carbocycles **VI**.



Scheme 2. Formation of five-membered ring carbocycles by Oppolzer cyclization. [a] $Z = SO_2Ph$; $[Pd/L] = [Pd_2(dba)_3 \cdot dba]$ (5 mol%)/PPh_3 (20 mol%), HOAc under reflux. Reaction time = 19 h. [b] Reaction time = 15 h. dba = *trans,trans*-dibenzylideneacetone.

temperatures.[15] Bis(η^1-allyl)palladium diphosphane complexes of type **V**, but with only two methylene groups at the tether, have been prepared as stable species by the addition of diphosphanes to complexes of type **III** with a PPh_3 ligand.[16] In that case, reductive elimination to form a relatively strained cyclobutane is not observed.[16] The direct reductive elimination from bis(η^3-allyl)palladium **VII** appears to be less likely, since complexes of this type have recently been prepared by Yamamoto et al. and did not show any tendency to undergo reductive elimination.[17, 18]

A limitation of the allyl/allyl coupling is that a β-hydride intramolecular transfer reaction takes place preferentially to give dienes with substrates bearing hydrogen atoms in the vicinity of the allyl groups.[19] An alternative synthesis of the 1,2-dialkenyl carbo- and heterocycles is based on the intramolecular insertion of alkenes into (η^3-allyl)palladium complexes (the Oppolzer cyclization reaction).[20] This reaction has been shown to proceed through cationic (η^3-allyl)(η^2-alkene)palladium complexes.[21]

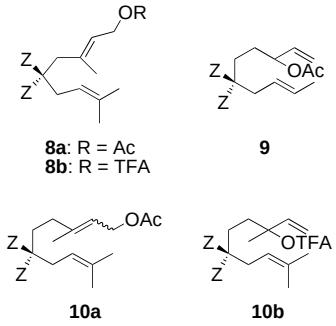
Herein, we compare the efficiency of the intramolecular coupling of allyl carboxylates with allyl stannanes[22] to that of allyl silanes for the formation of five- and six-membered carbocycles. We also compare these approaches with the synthesis of the same carbocycles by means of the Oppolzer cyclization. For the sake of simplicity and because of their easy handling, we focused our work on 1,1-bis(phenylsulfonyl) derivatives. We also address theoretically the nature of the palladium intermediate (**III**–**V**, or **VII**) involved in the formation of the carbocycles.

Results and Discussion

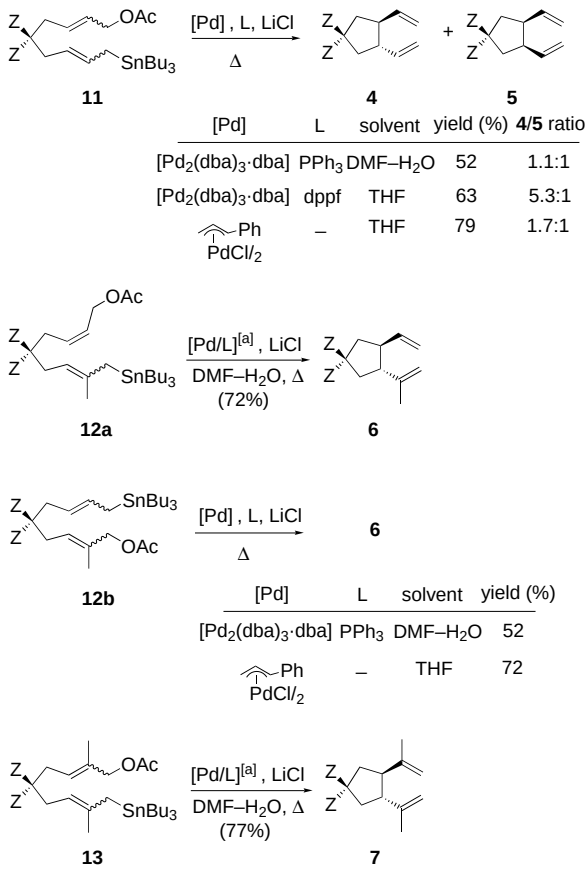
Carbocyclization by Oppolzer cyclization: The Oppolzer cyclization is known to favor formation of *trans* dialkenyl five-membered carbocycles.[20, 23] Accordingly, the reaction of allyl acetate **1** with a catalyst formed from $[Pd_2(dba)_3 \cdot dba]$ (2.5 mol%) and PPh_3 (10 mol%) in refluxing HOAc gave a 8.3:1 mixture of *trans*-**4** to *cis*-**5** isomers in 92% yield (Scheme 2).

Substrates **2** and **3** were cyclized under these conditions to form **6** and **7** in 75 and 66% yield, respectively. The lower yields of these last two carbocyclizations are presumably due to the introduction of an additional methyl group on the alkenyl moiety, which leads to less efficient intramolecular insertion reactions.[21]

Although formation of six-membered carbocycles by using the Oppolzer cyclization was possible with monosubstituted alkenes,[24] substrates **8**–**10** with di- or trisubstituted alkenes failed to cyclize with palladium catalysts under all the conditions examined.[25] The use of a better leaving group in **8b** and **10b** did not improve this lack of reactivity.



Cyclization of allyl stannanes with allyl acetates: The intramolecular coupling could be efficiently carried out without any significant elimination by using a palladium catalyst prepared from $[Pd_2(dba)_3 \cdot dba]$ and PPh_3 (2 equiv. per Pd) in the presence of LiCl (3 equiv)[26] in 0.5% aqueous DMF at 80 °C. Similar results were obtained by using *N*-methylpyrrolidone (NMP) as the solvent and $[Pd(PPh_3)_4]$ and $[Pd_2(dba)_3 \cdot dba]/PCy_3$ as the catalysts. However, under these standard conditions, cyclization of **11** gave a mixture of *trans*-**4** and *cis*-**5** in moderate yield (52%) but with very poor stereoselectivity (Scheme 3). While the use of P(2-fur)$_3$ or 1,3-(diphenylphos-

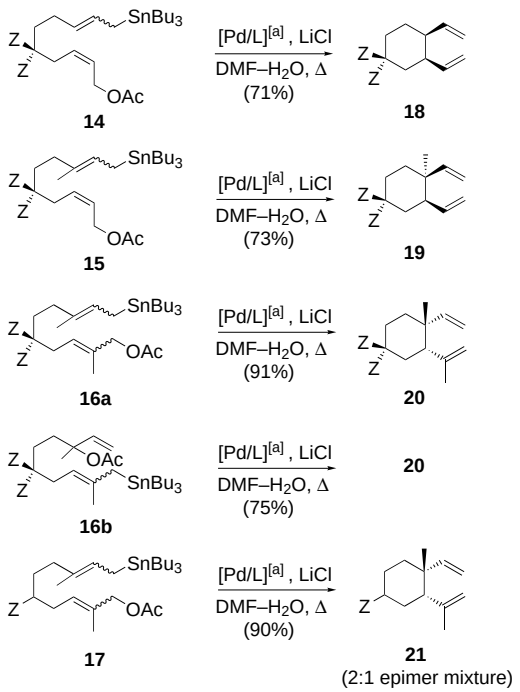


Scheme 3. Formation of five-membered ring carbocycles by intramolecular coupling of allyl acetates with allyl stannanes. $Z = SO_2Ph$. [a] [Pd/L] = $[Pd_2(dba)_3 \cdot dba]$ (5 mol %)/PPh_3 (20 mol %) or dppf (10 %), LiCl (3 equiv.), 0.5 % aqueous DMF, 80 °C, 17 h.

phanyl)propane (dppp) failed to improve this result, a reaction with 1,1′-(diphenylphosphanyl)ferrocene (dppf) as the ligand in THF led to a better isolated yield (63 %) with good selectivity (**4**:**5** = 5.3:1). Under "ligandless" conditions, the yield increased up to 79 %, although the stereoselectivity was lower (1.7:1).

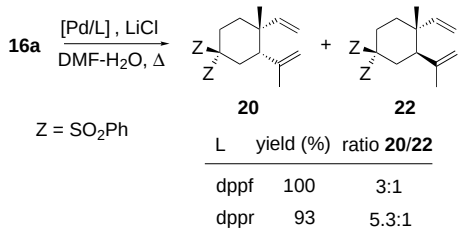
The cyclization of substrates **12a** and **12b** with an additional methyl group at the C-2 position of the allyl stannane or allyl acetate gave carbocycle **6** in 72 and 52 % yields, respectively. In this last cyclization, the use of a palladium pre-catalyst without phosphane ligands led to a better isolated yield (72 %). The palladium-catalyzed carbocyclization of more substituted **13** provided **7** in good yield (77 %) (Scheme 3).

In contrast with the cyclizations of Scheme 3 that are *trans*-selective, the cyclization of substrates **14**–**17** under the standard conditions gave in all cases *cis*-1,2-dialkenylcyclohexanes (Scheme 4). Thus, **14** gave exclusively *cis*-**18** in 71 % yield. The formation of carbocycle **19** with a quaternary center proceeded in similar yield (73 %) from **15**. Similarly, **20** was obtained by starting from either **16a** (92 %) or **16b** (75 %); in the latter starting material the locations of the allylic acetate and allyl stannane are exchanged. Substrate **17** was also cyclized without the benefit of the Thorpe–Ingold effect to furnish **21** in 90 % yield as a 2:1 mixture of epimers at C-1.



Scheme 4. Formation of six-membered ring carbocycles by intramolecular coupling of allyl acetates with allyl stannanes. $Z = SO_2Ph$. [a] [Pd/L] = $[Pd_2(dba)_3 \cdot dba]$ (5 mol %)/PPh_3 (20 mol %), LiCl (3 equiv), 0.5 % aqueous DMF, 80 °C, 17 h.

The cyclization of **16a** was studied in more detail. This reaction could also be performed in the absence of PPh_3, although the reaction required a stoichiometric amount of palladium. Monodentate phosphanes (PCy_3, $P(2\text{-fur})_3$, (diphenylphosphanyl)ruthenocene), phosphites ($P(OMe)_3$, $P(OiPr)_3$, $P(OPh)_3$, $P(OCH_2)_3CEt$),[27] and $AsPh_3$ gave exclusively *cis*-**20**. The cyclization did not take place with other common bidentate ligands bis(diphenylphosphanyl)methane (dppm), 1,3-bis(diphenylphosphanyl)propane (dppp), and 1,4-bis(diphenylphosphanyl)butane (dppb)), while 1,2-bis(diphenylphosphanyl)ethane dppe led to **20** in only 47 % yield. Interestingly, the reaction could be carried out with dppf or the related dppr (1,1′-bis(diphenylphosphanyl)ruthenocene)[28] as the ligands to give a 3:1 (93 %) or 5.3:1 (93 %) mixture of **20** and its *trans* isomer **22** (Scheme 5).



Scheme 5. Cyclization of **16a** to give **20** and **22**.

The configurations of **18**–**21** were determined on the basis of NOE experiments, and by comparison with the NMR data of **22**. The configuration of **20** was confirmed by its transformation into natural product 10-*epi*-elemol (**23**),[29] a member of the elemane family of sesquiterpenes with *cis*-1,2-dialkenyl groups (Scheme 6). Thus, reductive desulfona-

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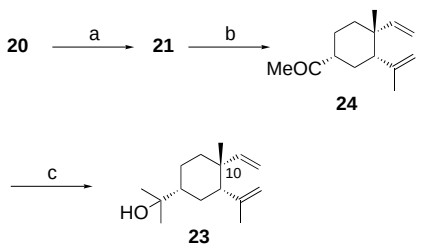
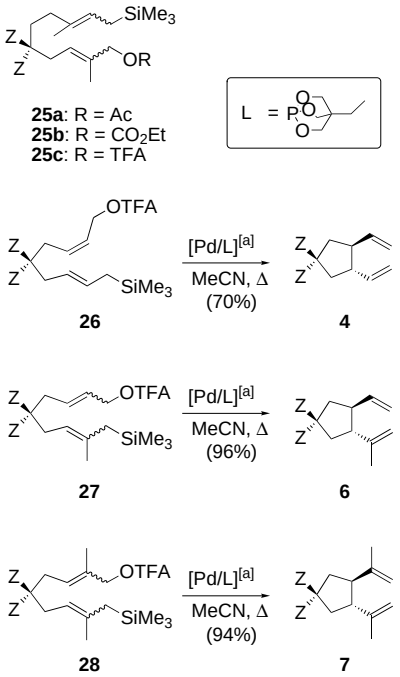


Scheme 6. Synthesis of *epi*-elemol. Reagents and conditions: a) Na(Hg), MeOH, MeCN (74%); b) 1) *n*-BuLi; Ac_2O; 2) Na(Hg), Na_2HPO_4 (95%); c) MeMgBr, THF (82%).

tion of **20** afforded **21** (74%), whose lithium anion was acetylated to give, after reductive desulfonation, **24** as a 9:1 mixture of α-ketone epimers (95%). Final reaction of **24** with methylmagnesium bromide afforded racemic **23**, whose NMR data were identical to those described.[28, 30]

Importantly, the use of the starting substrates in Schemes 3 and 4 as mixtures of regioisomers is inconsequential with regard to the stereoselectivity of the cyclization process. This fact and the fact that regioisomers **12a**,**b** and **16a**,**b** gave the same carbocycles **6** and **20**, respectively, strongly suggest that an equilibrium of allyl palladium complexes such as the one shown in Scheme 1 takes place in the process.

Cyclization of allyl silanes with allyl trifluoroacetates: No cyclization could be effected by the intramolecular attack of allyl silanes on allyl acetates. Thus, the trimethylsilyl analogues of substrates **11**–**13** failed to react with palladium catalysts. Similarly, substrates **25a**–**c** could not be cyclized under any of the conditions examined (Scheme 7). However,



Scheme 7. Formation of five-membered ring carbocycles by intramolecular coupling of allyl trifluoroacetates with allyl silanes. [a] [Pd/L] = $[Pd_2(dba)_3 \cdot dba]$ (5 mol%)/$P(OCH_2)_3CEt$ (20 mol%), acetonitrile, 60°C, 17 h.

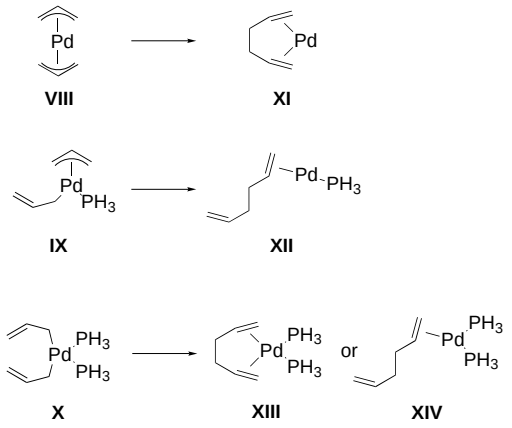
the cyclizations of trifluoroacetates **26**–**28** could be carried out by using a palladium complex formed in situ from $[Pd_2(dba)_3 \cdot dba]$ and bicyclic phosphite $P(OCH_2)_3CEt$[25] as the ligand in acetonitrile at 60°C (Scheme 7). Addition of LiCl was not required in this coupling reaction. In this case, carbocycles **4**, **6**, and **7** were obtained in good to excellent yields exclusively as the *trans* isomers.

The carbocyclizations of allyl silanes, although less general than the reaction of allyl stannanes, proceed with high stereoselectivity. In contrast to the Oppolzer cyclization, in the cyclizations of allyl silanes and allyl stannanes, methyl substitution at the C-2 or C-3 positions on either the nucleophilic or the electrophilic allyl moieties is acceptable, and the corresponding carbocycles are obtained in better yields than with the unsubstituted substrates.

Mechanism of the allyl/allyl coupling: The reductive elimination step: Intramolecular transmetalation[31] of the (η^3-allyl)palladium complexes formed by the oxidative addition of the allyl carboxylates to palladium(0) would initially form complexes of type **III** (Scheme 1). Subsequent rapid equilibration might form bis(η^1-allyl)palladium complexes **IV** and/or **V**, as well as bis(η^3-allyl)palladium complexes **VII**. To determine the nature of the key intermediate(s) involved in the C–C forming step by coupling of the allyl groups, we decided to study the reductive elimination step using high-level computational methods. In this regard, it is important to note that Yamamoto has recently demonstrated that the reductive elimination of bis(η^3-allyl)palladium complexes is triggered by the addition of PPh_3 as the ligand, although the actual number of phosphane ligands (one or two) on palladium was not ascertained in that study.[17]

In principle, the reductive elimination process might take place starting from bis(η^3-allyl)-, (η^1-allyl)(η^3-allyl)-, or bis(η^1-allyl)palladium complexes. Hence, complexes **VIII**–**X** were used as models for the reagents involved in the reductive elimination in the density functional theory (DFT) studies leading to (1,5-hexadiene)palladium complexes **XI**–**XIV**, respectively (Scheme 8).

The possible mechanisms for the reductive elimination were compared by determining the corresponding activation energies. The results from bis(η^3-allyl)palladium (**VIII**)[32] and



Scheme 8. Reductive elimination form complexes **VIII**–**X**.

(η^1-allyl)(η^3-allyl)palladium **IX** complexes are summarized in Figures 1 and 2. The reductive elimination from bis(η^3-allyl)-palladium (**VIII**) to **XI** is a high-energy process proceeding through symmetrical $\mathbf{TS_1}$ ($E_a = 36.6$ kcal mol^{-1}), which is in accord with the experimental evidence (Figure 1).[17, 18] On the other hand, a more favorable pathway was found for the transformation of (η^1-allyl)(η^3-allyl)palladium complex **IX** into **XII** proceeding through transition state $\mathbf{TS_2}$ ($E_a =$ 23.4 kcal mol^{-1}) (Figure 2).

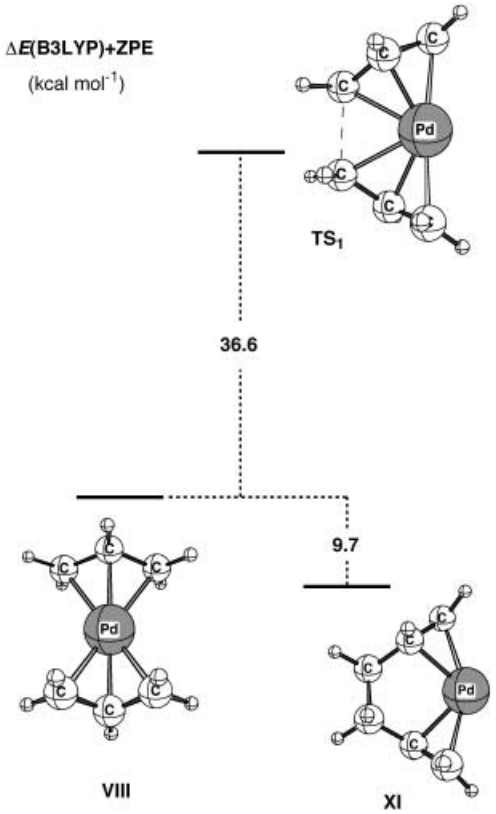


Figure 1. Reaction coordinate for the reductive elimination of palladium complex **VIII**.

The reactions of lowest activation barriers correspond to the elimination from bis(η^1-allyl)palladium complex **X** (Figure 3). In this case, three main possible mechanisms can be envisaged depending on which carbon atoms of the two allyl moieties are involved in the C–C bond formation (C1–C1′, C1–C3′, or C3–C3′). Additionally, two possible arrangements of the η^1-allyl ligands (*syn* and *anti*) are possible for the C3–C3′ coupling. The resulting 1,5-hexadiene can be obtained mono- or biscoordinated to [Pd(PH$_3$)$_2$] as in **XIII** and **XIV** or free to yield [Pd(PH$_3$)$_2$] (**XV**) (Figure 3); all these are exothermic processes. For this reason, IRC studies were not performed from transition states $\mathbf{TS_3}$, $\mathbf{TS_4}$, or $\mathbf{TS_5}$. Under equilibrium conditions, species **XIV** would be favored.

The four possible transition states have an arrangement of ligands around Pd that lies between the square-planar one observed in the reagents and the usual tetrahedral coordination for palladium(0) species. As can be seen in Figure 2, the formation of a bond between C3 and C3′ is significantly preferred, regardless of the *syn* or *anti* arrangement of both

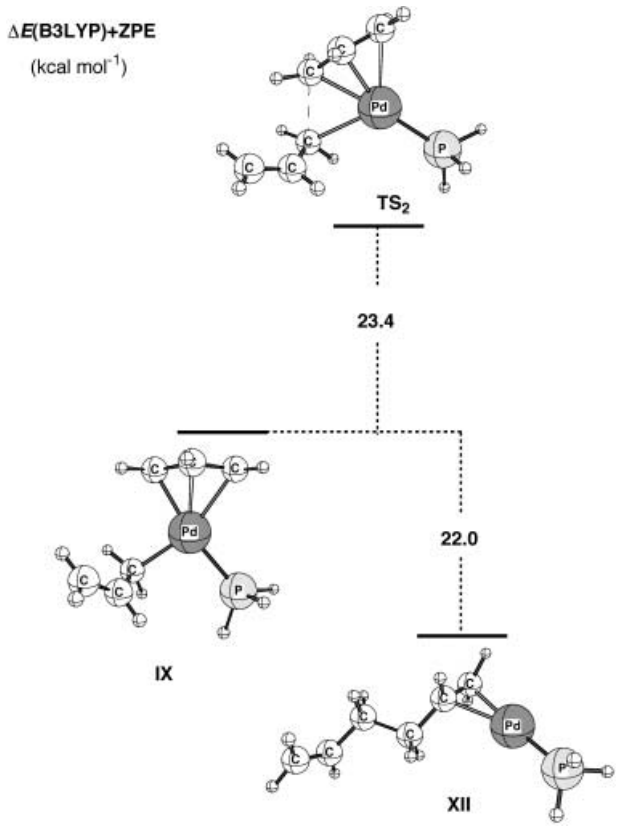


Figure 2. Reaction coordinate for the reductive elimination of palladium complex **IX**.

allyl moieties ($E_a = 11.1$ and 8.5 kcal mol^{-1}, respectively), compared with the formation of C1–C1′ or C1–C3′ bonds ($E_a = 20.9$ and 22.8 kcal mol^{-1}, respectively). The preference for the formation of C3–C3′ bond was studied by natural bonding orbital (NBO) analysis. This study shows that in both transition states $\mathbf{TS_3}$ (*anti* and *syn*) there is significant C–C double bond formation between C1 and C2, as well as between C1′ and C2′. The emerging π orbitals interact with one of the Pd lone pairs. Thus, C2 and C2′ participate in bonding to the metal, leading to lower energies for transitions states $\mathbf{TS_3}$.

On the other hand, the relatively high activation barrier for allyl-allyl coupling from complex **IX** (23.4 kcal mol^{-1}) may explain why this type of complex preferentially reacts with suitable electrophiles by reactions which proceed through significantly lower computed activation energies.[18, 33]

The formation of **IX** from **VIII**, and **X** from **IX** by reaction with PH_3 is calculated to be slightly endothermic (+0.4 and +2.4 kcal mol^{-1}, respectively)[34] (Scheme 9). Hence, considering the difference between the activation energies for all the elimination reactions starting from **VIII**–**X**, it can be concluded that in the presence of phosphanes, the reaction would preferably occur from bis(η^1-allyl)palladium complexes of type **X**, even if these are the minor species in the equilibria. In fact, addition of phosphanes to (η^3-allyl)palladium complexes leads to rapid ligand exchange[35] and, in some cases, (η^1-allyl)(η^3-allyl)palladium(phosphane) complexes are the prevailing species, which do not undergo reductive elimination.[13]

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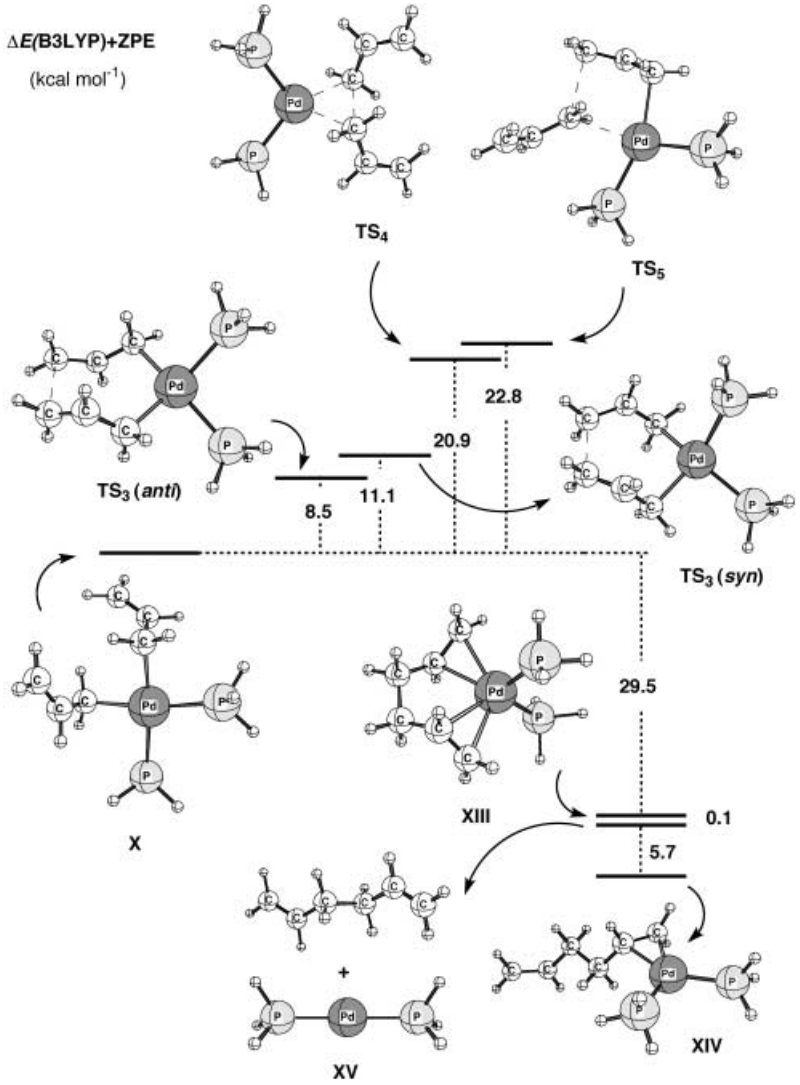
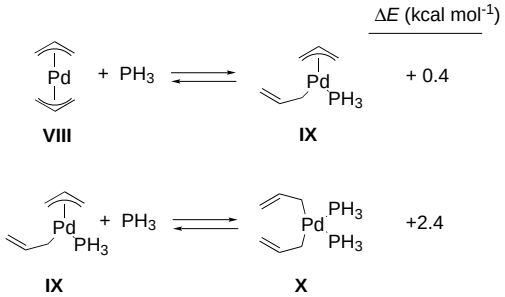


Figure 3. Reaction coordinate for the reductive elimination of palladium complex **X**.



Scheme 9. Equilibria between (η^1-allyl)- and (η^3-allyl)palladium complexes. Energies include zero-point correction.

Conclusion

The intramolecular coupling of allyl stannanes with allyl carboxylates is a quite general procedure for the synthesis of five- and six-membered-ring carbocycles. The intramolecular coupling of allyl silanes allows the synthesis of five-membered-ring carbocycles and requires the use of the more reactive allyl trifluoroacetates. The related Oppolzer cyclization, in which the C–C bond formation takes place by insertion of a (η^3-allyl)palladium complex into an alkene, leads to lower yields, or fails completely, with substrates substituted at the C-3 position of the allyl and/or the alkene terminus. Interestingly, the intramolecular coupling leads selectively to *trans* five-membered carbocycles and *cis* six-membered carbocycles, regardless of the *cis* or *trans* configuration of the allylic functions in the starting material.

Theoretical work indicates that the preferred pathway for the intramolecular allyl/allyl coupling is the formation of the C–C bond between the C-3 terminus of the allyl ligands of a bis(η^1-allyl)palladium complexes, which is in agreement with the fact that the cyclization of substrates **11** and **16a** proceeds in the presence of bidentate ligands such as dppf and dppr. These results point to the formation of bis(η^1-allyl)palladium macrocycles of type **IV** (Scheme 1) (or its *cis*,*trans* and *cis*,*cis* stereoisomers) as the most reactive species for the last step in the cyclization reactions when phosphane complexes are present in the reaction medium. It is important to stress that these conclusions pertain to the coupling in the presence of donor phosphane ligands. In the absence of such ligands,[11] other mechanisms might operate.

Experimental Section

General procedure for the cyclization of allyl carboxylates with alkenes (Oppolzer cyclization): A solution of the corresponding acetate (0.1 mmol), [$Pd_2(dba)_3 \cdot dba$] (0.005 mmol), and PPh_3 (0.02 mmol) in HOAc was heated at 80–120 °C for the stated reaction times. After extractive workup with EtOAc, the solvent was evaporated. The residue was purified by chromatography (hexane/EtOAc 9:1) to give the carbocycle (Scheme 2).

General procedure for the cyclization of allyl stannanes: A solution of the corresponding stannane (0.1 mmol), [$Pd_2(dba)_3 \cdot dba$] (0.005 mmol), PPh_3 (0.02 mmol), and LiCl (0.3 mmol) in a mixture of DMF/H_2O (99.5:0.5) was stirred for 17–19 h at 80 °C. After extractive workup (Et_2O), the solvent was evaporated. The residue was stirred in MeOH with KF for 12 h at 23 °C, and the residue was purified by chromatography (hexane/EtOAc 9:1) to give the carbocycle (Schemes 3 and 4).

General procedure for the cyclization of allylsilanes: A solution of the corresponding silane (0.1 mmol), [$Pd_2(dba)_3 \cdot dba$] (0.005 mmol), and $P(OCH_2)_3CEt$ (0.02 mmol) in MeCN (5 mL) was stirred for 14 h at 60 °C.

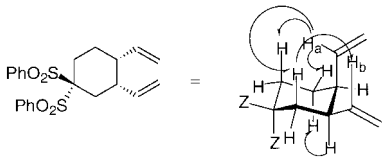
The solvent was then evaporated, and the residue was purified by chromatography (hexane/EtOAc 9:1) to give the carbocycle (Scheme 7).

***trans*-1,1-Bis(phenylsulfonyl)-3,4-diethynylcyclopentane (4)**: White solid; m.p. 139–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.09-8.02$ (m, 4H), 7.76–7.69 (m, 2H), 7.65–7.58 (m, 4H), 5.57 (ddd, $J = 17.1, 10.3, 6.9$ Hz, 2H), 5.05 (dd, $J = 10.3, 1.5$ Hz, 2H), 4.99 (dd, $J = 17.1, 1.5$ Hz, 2H), 2.71 (dd, $J = 14.1, 5.8$ Hz, 2H), 2.45–2.31 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 137.49, 136.34, 134.65, 131.43, 131.37, 128.76, 116.88, 91.55, 49.44, 37.93$ ppm; elemental analysis calcd (%) for $C_{21}H_{22}O_4S_2$ (402.5): C 62.66, H 5.51, S 15.93; found: C 62.60, H 5.57, S 16.02.

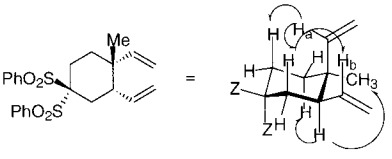
***cis*-1,1-Bis(phenylsulfonyl)-3,4-diethynylcyclopentane (5)**:[36] White solid; m.p. 78–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.07$ (br d, $J = 7.3$ Hz, 4H), 7.71 (m, 2H), 7.60 (m, 4H), 5.71 (ddd, $J = 16.9, 10.5, 8.1$ Hz, 2H), 5.01 (dd, $J = 10.5, 1.6$ Hz, 2H), 4.97 (dd, $J = 16.9, 1.6$ Hz, 2H), 3.01 (td, $J = 13.0, 8.1$ Hz, 2H), 2.67 (dd, $J = 15.4, 7.3$ Hz, 2H), 2.58 ppm (dd, $J = 15.8, 7.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 137.38, 136.07, 134.64, 134.51, 131.38, 131.32, 128.76, 128.68, 116.21, 93.87, 47.41, 36.92$ ppm; HRMS (FAB): *m*/*z* calcd for $C_{21}H_{22}O_4S_2$ $[M+H]^+$: 408.1037; found: 408.1028.

***trans*-1,1-Bis(phenylsulfonyl)-3-ethenyl-4-(1-methylethenyl)cyclopentane (6)**: White solid; m.p. 90–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.09$ (d, $J = 7.6$ Hz, 4H), 7.73 (br t, $J = 7.6$ Hz, 2H), 7.61 (br t, $J = 7.8$ Hz, 4H), 5.53 (ddd, $J = 17.3, 10.3, 7.5$ Hz, 1H), 5.01 (d, $J = 10.3$ Hz, 1H), 4.99 (d, $J = 17.3$ Hz, 1H), 4.80 (s, 1H), 4.70 (s, 1H), 2.68 (dd, $J = 14.7, 6.9$ Hz, 1H), 2.63 (dd, $J = 15.1, 7.2$ Hz, 1H), 2.51 (ddd, $J = 18.6, 11.4, 7.2$ Hz, 1H), 2.44 (dd, $J = 15.0, 11.9$ Hz, 1H), 2.38 (dd, $J = 14.7, 11.4$ Hz, 1H), 2.31 (ddd, $J = 18.8, 11.7, 6.9$ Hz, 1H), 1.61 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.51, 137.72, 136.37, 134.64, 131.38, 128.78, 116.57, 113,23, 91.19, 52.44, 47.02, 38.01, 37.06, 19.24$ ppm; elemental analysis calcd (%) for $C_{22}H_{24}O_4S_2$ (416.6): C 63.44, H 5.81, S 15.39; found: C 63.21, H 5.61, S 15.39. ^{1}H NMR significant signals of *cis* isomer: $\delta = 5.63$ (ddd, $J = 17.0, 9.6, 7.3$ Hz, 1H), 4.97 (dd, $J = 16.8, 1.9$ Hz, 1H), 4.91 (dd, $J = 10.0, 1.9$ Hz, 1H), 4.63 (s, 1H), 3.20 (m, 1H).

***trans*-1,1-Bis(phenylsulfonyl)-3,4-di(1-methylethenyl)cyclopentane (7)**: White solid; m.p. 165–167 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.08$ (d, $J = 5.3$ Hz, 4H), 7.74 (t, $J = 7.9$ Hz, 2H), 7.62 (t, $J = 7.9$ Hz, 4H), 4.77 (br s, 2H), 4.67 (br s, 2H), 2.65–2.53 (m, 2H), 2.52–2.44 (m, 4H), 1.60 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.79, 136.40, 134.64, 131.38, 128.79, 113.14, 90.80, 49.92, 37.12, 18.80$ ppm; elemental analysis calcd (%) for $C_{23}H_{26}O_4S_2$ (430.6): C 64.16, H 6.09, S 14.86; found: C 64.30, H 6.18, S 13.47.



***cis*-1,1-Bis(phenylsulfonyl)-3,4-diethynylcyclohexane (18)**: White solid; m.p. 98–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.13-8.10$ (m, 2H), 8.10–8.00 (m, 2H), 7.77–7.71 (m, 2H), 7.66–7.59 (m, 4H), 5.82 (ddd, $J = 16.6, 10.9, 8.3$ Hz, 1H), 5.70 (ddd, $J = 17.3, 10.5, 6.9$ Hz, 1H), 5.09 (dm, $J = 16.6$ Hz, 1H), 5.04 (dm, $J = 17.3$ Hz, 1H), 5.12–5.03 (m, 2H), 3.19–3.13 (m, 1H), 2.58–2.54 (m, 1H), 2.53–2.49 (m, 2H), 2.40 (dd, $J = 15.24, 13.0$ Hz, 1H), 2.28–2.22 (m, 1H), 2.28–2.22 (m, 1H), 2.21–2.17 (m, 1H), 1.88–1.80 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.53, 136.32, 136.04, 135.06, 134.53, 134.39, 131.60, 131.13, 128.55, 117.69, 114.84, 88.02, 40.55, 38.79, 27.26, 26.19, 21.34$ ppm; HRMS (FAB): *m*/*z* calcd for $[C_{22}H_{24}S_2O_4]^+$: 417.112 $[M+1]^+$; found: 417.119. The structure of **18** was confirmed by COSY and NOESY experiments. Selected NOE enhancements are shown in the drawing.



(3*R,4*S**)-1,1-Bis(phenylsulfonyl)-3,4-diethynyl-4-methylcyclohexane (19)**: White solid; m.p. 123–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.09$ (dd, $J = 8.5, 1.2$ Hz, 2H), 8.00 (dd, $J = 8.5, 1.2$ Hz, 2H), 7.74–7.67 (m, 2H), 7.63–7.56 (m, 4H), 5.91 (dd, $J = 17.5, 11.1$ Hz, 1H), 5.59 (ddd, $J = 17.5, 9.9, 8.5$ Hz, 1H), 5.09 (dd, $J = 17.5, 2.0$ Hz, 1H), 5.08 (dd, $J = 10.1, 2.4$ Hz, 1H), 5.07 (dd, $J = 10.8, 1.6$ Hz, 1H), 4.99 (dd, $J = 17.4, 1.6$ Hz, 1H), 2.80 (ddd, $J = 12.1, 8.2, 3.8$ Hz, 1H), 2.58 (ddd, $J = 15.4, 14.0, 5.0$ Hz, 1H), 2.41 (dd, $J = 15.4, 12.9$ Hz, 1H), 2.25 (m, 1H), 2.18 (dd, $J = 14.5, 10.1$ Hz, 1H), 2.11 (ddd, $J = 15.3, 2.4, 1.8$ Hz, 1H), 1.69 (ddd, $J = 14.5, 6.1, 3.0$ Hz, 1H), 1.08 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.05, 137.94, 136.35, 136.10, 134.51, 134.34, 131.55, 131.30, 131.13, 128.54, 117.10, 115.21, 87.90, 45.99, 37.43, 34.19, 28.08, 26.71, 22.70$ ppm; HRMS (FAB): *m*/*z* calcd for $[C_{23}H_{26}S_2O_4]$: 431.127 $[M+1]^+$; found: 431.135. The structure of **19** was confirmed by COSY and NOESY experiments. Selected NOE enhancements are shown in the drawing.

(3*R,4*S**)-1,1-Bis(phenylsulfonyl)-4-ethenyl-4-methyl-3-(methylethenyl)-cyclohexane (20)**: White solid; m.p. 160–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.11-8.07$ (m, 2H), 8.04–8.00 (m, 2H), 7.74–7.67 (m, 2H), 7.61–7.31 (m, 4H), 6.12 (dd, $J = 17.3, 11.1$ Hz, 1H), 5.03 (dd, $J = 11.1, 1.3$ Hz, 1H), 5.00 (dd, $J = 17.3, 1.3$ Hz, 1H), 4.86 (q, $J = 1.3$ Hz, 1H), 4.74 (br s, 1H), 2.86 (dd, $J = 13.6, 3.0$ Hz, 1H), 2.71 (t, $J = 15.1$ Hz, 1H), 2.58 (ddd, $J = 15.6, 14.0, 5.2$ Hz, 1H), 2.31–2.10 (m, 2H), 2.05 (dt, $J = 15.0, 1.8$ Hz, 1H), 1.67 (br s, 3H), 1.60 (ddd, $J = 13.6, 5.2, 2.8$ Hz, 1H), 1.07 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.84, 140.22, 136.28, 136.18, 134.48, 134.32, 131.57, 131.12, 128.52, 128.47, 114.31, 114.25, 88.37, 48.68, 38.00, 36.55, 27.46, 26.30, 23.04, 22.38$ ppm; elemental analysis calcd (%) for $C_{24}H_{28}O_4S_2$ (444.6): C 64.83, H 6.35, S 14.42; found: C 64.42, H 6.12, S 14.51.

(3*R,4*R**)-1,1-Bis(phenylsulfonyl)-4-ethenyl-4-methyl-3-(methylethenyl)-cyclohexane (22)**: Significant NMR signals: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.82$ (dd, $J = 17.4, 10.9$ Hz, 1H), 4.94 (dd, $J = 9.3, 1.2$ Hz, 1H), 4.90 (m, 1H), 6.64 (m, 1H), 1.60 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.81, 145.33, 134.40, 131.29, 113.34, 111.36, 88.18, 46.04, 34.72, 29.67, 24.91, 15.73$ ppm.

(1*R,3*S**,4*R**)- and (1*R**,3*R**,4*S**)-1-Ethenyl-2-methylethenyl-1-methyl-4-phenylsulfonylcyclohexane (21)**: A mixture of **20** (100 mg, 0.22 mmol) and Na(Hg) (6%, 128 mg, 0.67 mmol) in 1:1 MeOH/MeCN (5 mL) was stirred at 23 °C for approximately 30 min (until metallic Hg was observed). The mixture was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by chromatography (hexane/EtOAc 9:1) to give **21** (37 mg, 54%; 74% based on recovered starting material) as a colorless oil (3:2 mixture of C-4 epimers) and recovered **20** (25 mg). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.90-7.85$ (m, 2H), 7.70–7.50 (m, 3H), 6.16 (dd, $J = 17.2, 10.8$ Hz, 1H; major isomer), 6.10 (dd, $J = 17.7, 10.3$ Hz, 1H; minor isomer), 5.11–4.90 (m, 2H), 4.84–4.78 (m, 1H), 4.69 (br s, 1H; minor isomer), 4.62 (br s, 1H; major isomer), 3.23 (quint, $J = 5.9$ Hz, 1H; minor isomer), 3.10–2.95 (m, 2H; major isomer), 2.51 (dd, $J = 8.6, 4.8$ Hz, 1H; minor isomer), 2.02–1.60 (m, 6H), 1.65 (br s, 3H), 1.05 (s, 3H; minor isomer), 0.99 ppm (s, 3H; major isomer); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 145.37, 143.90, 140.85, 137.41, 133.57, 129.07, 128.84, 128.67, 113.83, 113.72, 112.03, 63.62, 59.47, 53.98, 48.39, 39.71, 38.69, 38.41, 33.27, 27.07, 26.85, 26.34, 25.49, 24.19, 22.45, 21.37, 20.42$ ppm; elemental analysis calcd (%) for $C_{18}H_{24}O_2S$ (304.5): C 71.01, H 7.95, S 10.53; found: C 70.89, H 8.03, S 10.92.

(1*R,3*S**,4*R**)-1-Ethanoyl-4-ethenyl-4-methyl-3-methylethenylcyclohexane (24)**: A solution of *n*BuLi (0.31 mL, 2.3 M in hexane, 0.72 mmol) was slowly added to a solution of **21** (200 mg, 0.66 mmol) in THF (5 mL) at −78 °C. Ac_2O (201 mg, 1.97 mmol) was added to the resulting pale yellow solution, and the mixture was stirred for 1 min. The mixture was diluted with Et_2O, washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by chromatography (hexane/EtOAc 9:1) to give an inseparable mixture of acetylated derivatives and starting material **21**. This mixture was dissolved in 1:1 MeOH/MeCN (5 mL) in the presence of Na(Hg) (6%, 18 mg, 0.79 mmol) and Na_2HPO_4 (226 mg, 1.59 mmol) and was stirred at 23 °C for approximately 1 h. The mixture was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by chromatography (hexane/EtOAc 10:1) to give **24** (53 mg, 39%; 95% based on recovered starting material) as a 9:1 mixture of C-1 epimers (C-7 epimers, elemol numbering). ^{1}H NMR (200 MHz, $CDCl_3$): (major isomer) $\delta = 6.25$ (dd, $J = 17.4, 11.4$ Hz, 1H), 5.03 (dd, $J = 11.4, 1.6$ Hz, 1H), 4.97 (dd, $J = 17.4, 1.6$ Hz, 1H), 4.80 (m, 1H), 4.65 (m, 1H), 2.54–2.38 (m, 1H), 2.15 (s, 3H), 2.05–1.90 (m, 1H), 1.85–1.30 (m, 6H), 1.68 (br s, 3H), 1.02 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 211.56, 146.61, 141.93, 113.04$ (2C), 54.83, 52.00, 40.72, 38.92, 36.60, 29.67, 28.09,

  0947-6539/02/0816-3626 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 16

27.24, 24.25, 22.50 ppm; elemental analysis calcd (%) for $C_{14}H_{22}O$ (206.3): C 81.50, H 10.75; found: C 81.49, H 10.87.

(±)-10-*epi*-Elemol (23): Methylmagnesium bromide (0.05 mL, 3 M in THF, 0.15 mmol) was added to a solution of **24** (15 mg, 0.07 mmol) in THF (5 mL) at 0 °C. The mixture was stirred at 23 °C for 1 h. The mixture was treated with water (1 mL), diluted with Et_2O, washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by chromatography (hexane/EtOAc 10:1) to give **23** (13 mg, 82 %) as a colorless oil and as a 9:1 mixture of C-7 epimers. ^{1}H NMR (200 MHz, $CDCl_3$): (major isomer) $\delta =$ 6.26 (dd, $J = 17.5$, 11.1 Hz, 1H), 5.02 (dd, $J = 11.4$, 1.6 Hz, 1H), 4.97 (dd, $J =$ 17.4, 1.6 Hz, 1H), 4.77 (br s, 1H), 4.64 (br s, 1H), 1.97 (dd, $J = 11.5$, 3.5 Hz, 1H), 1.90–1.20 (m, 7H), 1.68 (br s, 3H), 1.19 (s, 6H), 1.01 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.54$, 142.71, 112.45, 112.42, 72.72, 55.52, 49.48, 41.55, 38.95, 28.76, 27.20, 27.05, 23.05, 22.56 ppm.

Computational methods: The calculations were performed with the Gaussian 98 series of programs.[37] The geometries of all complexes were optimized at the DFT level using the B3LYP hybrid functional.[38] The standard 6–31G(d) basis set was used for C, H, O, and Cl, and the LANL2DZ relativistic pseudopotential was used for Pd. Harmonic frequencies were calculated at the same level of theory to characterize the stationary points and to determine the zero-point energies (ZPE). Intrinsic reaction coordinate calculations (IRC) were performed from **TS_1**, **TS_2**, and **TS_5** to ensure that the transition states found actually connect the proposed reagents and products. Natural bonding orbital (NBO) analysis was used to study transition states **TS_3** and **TS_4**.

Acknowledgements

We are grateful to the DGES (Projects BQU2001–0193-C02–01 and PB97–0002-C2–02) for supporting this research and to the Ministerio de Educación, Cultura y Deportes, the Comunidad Autónoma de Madrid, and the Gobierno Vasco for predoctoral fellowships to M.M., J.M.C., and E.G.-B., respectively. We thank Dr. D. Peña (Universidad de Santiago de Compostela) for work on the stereoselectivity of the cyclization of **11**, Dr. M. Alcamí (Departamento de Química, Universidad Autónoma de Madrid) for helpful comments, and Prof. K. Szabó for information on his calculations of the formation **VIII** from **VII** and PMe_3. We also acknowledge the Centro de Computación Científica (UAM) for computation time and Johnson Matthey PLC for a generous loan of $PdCl_2$.

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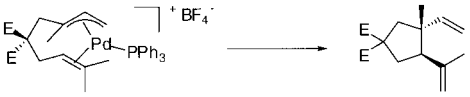

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Received: March 13, 2002 [F3942]

  0947-6539/02/0816-3628 $ 20.00+.50/0