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Allyl stannanes as electrophiles or nucleophiles in the palladium-catalyzed reactions with alkynes

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Dedicated to Professor J.P. Genêt on the occasion of his 60th birthday in recognition of his contributions in organopalladium chemistry and organic synthesis

Abstract

The reactivity of the allyl stannanes can be inverted by changing the oxidation state of the catalyst from Pd(II) to Pd(0). Whereas with Pd(II) an *anti* nucleophilic attack of the allyl stannane on the alkyne takes place, the reaction with Pd(0) proceeds by oxidative addition to form (η^3-allyl)palladium complexes leading to a formal *syn* addition to the alkyne. This mechanistic proposal is supported by DFT calculations.

Keywords: Palladium; Allyl stannanes; Electrophiles; Nucleophiles

1. Introduction

Allyl stannanes are important reagents in the Stille reaction [1]. In this cross coupling, the organic electrophile R–X (X = halide, triflate) reacts with the $Pd(0)L_n$ complex by oxidative addition to give electrophilic $RPd(L)_2X$ complexes, which transmetallate with the allyl stannanes [2,3].

Recently, Shirakawa et al. found that the palladium(0)-catalyzed reaction of allyl stannanes **1** with alkynes **2** affords allylstannylation products **3** (Scheme 1) [4]. This transformation is also catalyzed by $Ni(cod)_2$ [5]. It was proposed that the palladium-catalyzed allylstannylation of alkynes could proceed by oxidative cyclometallation to form a palladacyclopentene complex **4**, which would undergo β-tin elimination, followed by reductive elimination [4]. An alternative mechanism was also considered, in which an oxidative addition of the allyl stannanes to Pd(0) would give (η^3-allyl)palladium complexes **5a** as key intermediates (Scheme 1) [4,6]. In this transformation, the usually nucleophilic allyl stannanes [7] behave formally as electrophiles. An oxidative addition to form complexes **5b** has been proposed to take place in the Pd(0)-catalyzed carboxylation of allyl stannanes with CO_2 [8]. Complexes of type **5** are believed to be formed by transmetallation of (η^3-allyl)palladium complexes with hexamethylditin [9]. However, palladium complexes of type **5** have never been isolated as stable species [10].

We have recently found that substrates **6** react in the presence of $PdCl_2$, $PtCl_2$, or other electrophilic metal complexes to form dienes **8** (Scheme 2) [11,12]. In this reaction, the metal triggers the *anti* attack of the allyl stannane to the (η^2-alkyne)metal complex as shown in **7** [13,14].

Recently a new cyclization was developed based on the regioselective Pd(0)-catalyzed addition of $R_3Si–SnR'_3$ to alleneynes [15]. This transformation was proposed to proceed by cyclization of the alkynes with allyl stannanes, formed as intermediate species by the Pd(0)-catalyzed stannylation of the allenes. More simply, substrates of type **6** could also undergo cyclization promoted by Pd(0). Therefore, we decided to explore this alternative with the aim to determine if an oxidative

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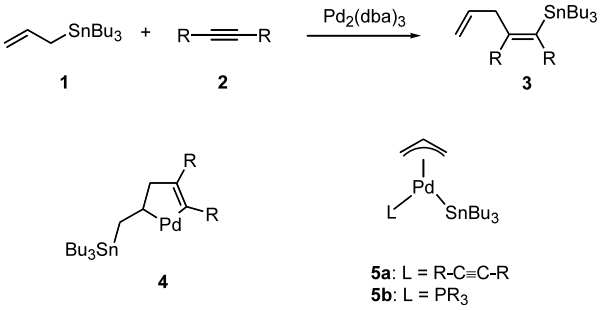
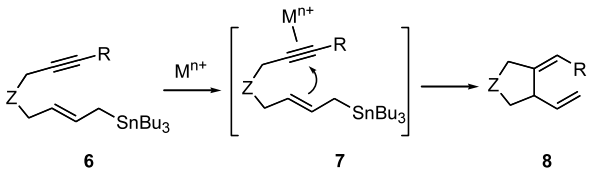


Scheme 1.



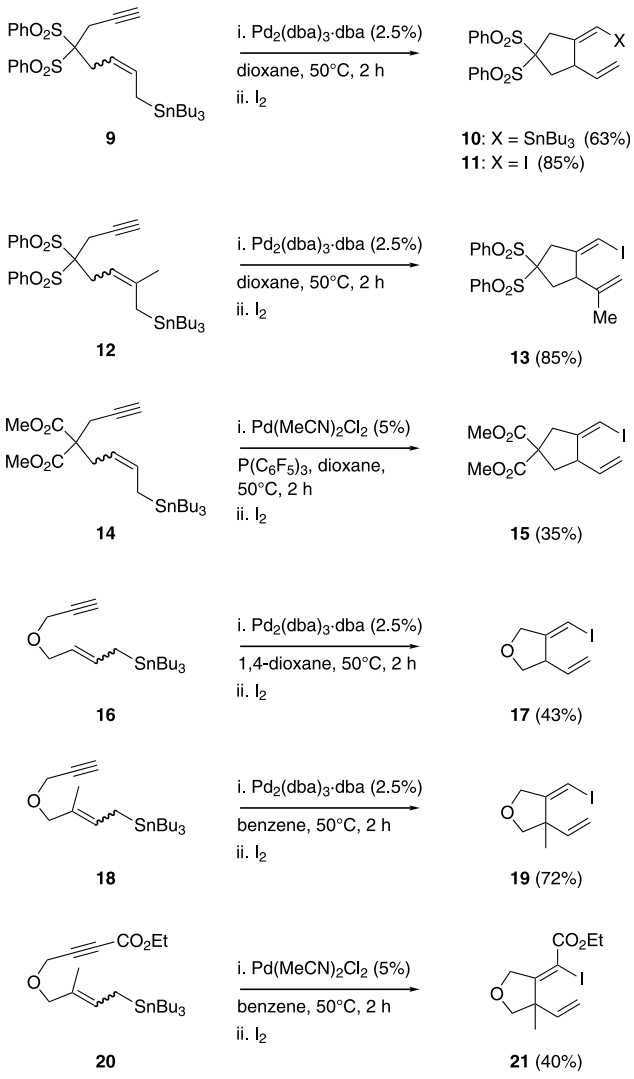
Scheme 2.

addition of allyl stannanes to Pd(0) to give (η^3-allyl)palladium complexes actually takes place.

2. Results and discussion

The cyclization of substrates of type **6** can be performed with Pd(0) catalysts. Thus, disulfone **9** reacted in 1,4-dioxane at 50 °C with $Pd_2(dba)_3 \cdot dba$ (2.5 mol%) to give *Z*-alkenyl stannane **10** in 63% isolated yield (Scheme 3). The reaction of **9** with $Pd(PPh_3)_4$ (5 mol%) gave **10** in 55% yield. Stannanes of type **10** were quite labile and suffered facile protodestannylation. However, treatment of the cyclization mixture with I_2 allowed for the isolation of the corresponding alkenyl iodides. Under these conditions, substrate **9** afforded iodide **11** in 85% yield. The *Z* configuration of **11** was demonstrated by NOE experiments. Similarly, **12** (1.2:1 *E*/*Z*) gave carbocycle **13** (85%). A lower yield (74%) was obtained with $Pd(PPh_3)_4$ (5 mol%).

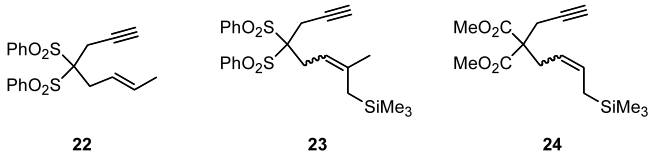
Allyl stannane **14**, which is similar to **9**, failed to undergo cyclization reaction under the above conditions. However, reaction with a catalyst prepared in situ from $Pd(MeCN)_2Cl_2$ and $P(C_6F_5)_3$ (2 equiv/Pd), followed by treatment with I_2 gave **15**, albeit in only 35% yield. Under these conditions it was expected that a Pd(0) complex may be involved, since heating $PdCl_2$ with phosphines is known to give $Pd(0)L_n$ complexes [16]. On the other hand, cyclization of ether **16**, followed by reaction with I_2 afforded heterocycle **17** (43%). Similarly, cyclization of ether **18** (4.3:1 mixture of isomers), followed by reaction with I_2 afforded **19**



Scheme 3.

(72%). Reaction of **18** with $Pd(MeCN)_2Cl_2$ and $P(C_6F_5)_3$ gave **19** in 34% yield. By using $Pd(MeCN)_2Cl_2$ as pre-catalyst, the cyclization of **18** proceeded in 42% yield. Substrate **20**, with the alkyne substituted with an ester group, reacted with the $Pd(MeCN)_2Cl_2$ in benzene to give **21** in 40% yield. The *E* configurations of the exocyclic alkene of **17** was corroborated by NOE experiments. The assignment of the configuration of **21** was based on the observation of a weak correlation peak in the NOESY spectrum between the methyl hydrogens of the ethyl ester and the C-2 methylene hydrogens.

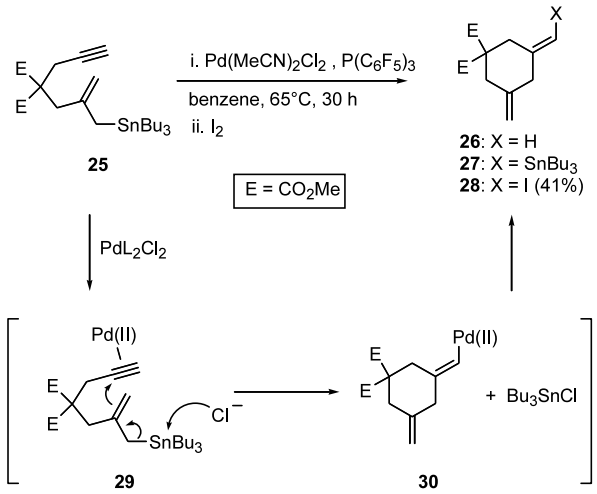
No cyclization reaction was observed with simple 1,6-enynes such as **22** by using $Pd_2(dba)_3 \cdot dba$ as the catalyst. Allyl silanes **23** and **24**, the silyl analogues of **12** and **14**, also failed to cyclize under the conditions of Scheme 3.



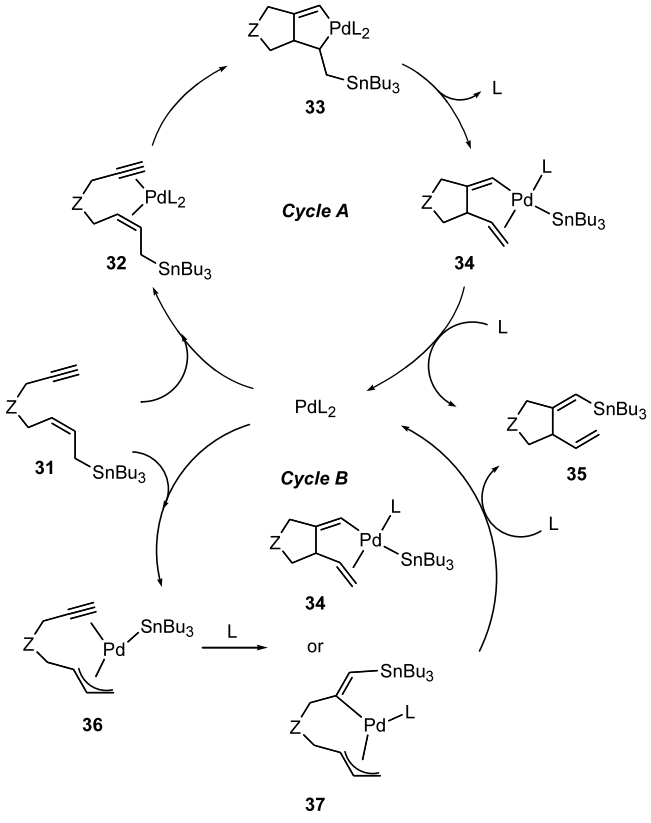
22 23 24

Reaction of **25** with $Pd_2(dba)_3 \cdot dba$ (2.5 mol%) led to destannylated **26** [11b] in 73% yield after 1 h at 65 °C. The same result was obtained in the presence of $P(C_6F_5)_3$ or *i*-Pr_2NEt. Indeed, destannylation of the expected stannane **27** was observed in the crude reaction mixtures. However, reaction with the catalyst prepared in situ from $Pd(MeCN)_2Cl_2$ and $P(C_6F_5)_3$ (two equivalents/Pd), followed by treatment with I_2 gave a 1:3.5 mixture of **26** [11] and **28** (53% yield) (Scheme 4). The configuration of **28** was secured as shown on the basis of NOE experiments. This configuration does not correspond to the most stable isomer, since *Z*-alkenyl iodide **28** is 0.7 (AM1) or 1.2 (PM3) kcal mol^{-1} less stable than the *E*-isomer. Formation of **28**, with a *Z* geometry at the exocyclic alkene, is not consistent with the results of Scheme 3 and suggests that this is an example of a Pd(II)-catalyzed transformation, which proceeds by the *anti* attack of the allyl stannane to the (η^2-alkyne)metal complex, as shown in **29**, to give intermediate **30** [11]. Cleavage of the Pd–C bond by the electrophilic Bu_3SnCl then gives **27**. This result indicates that, although $Pd(0)L_n$ may be formed by the reduction of $Pd(MeCN)_2Cl_2$ by the phosphine [16], nevertheless some of the initially formed $Pd(L)_2Cl_2$ complex is able to trigger the Pd(II)-catalyzed process. This is in agreement with our recent observation of a Pd(II)-catalyzed process under similar conditions [17].

According to the mechanistic proposals made by Shirakawa et al. [4], the results of Scheme 3 can be explained by the oxidative cyclometallation (via intermediates of type **4**) or the oxidative addition (via intermediates of type **5**) mechanisms (Scheme 5). Thus,



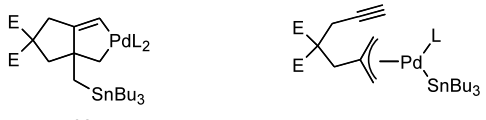
Scheme 4.



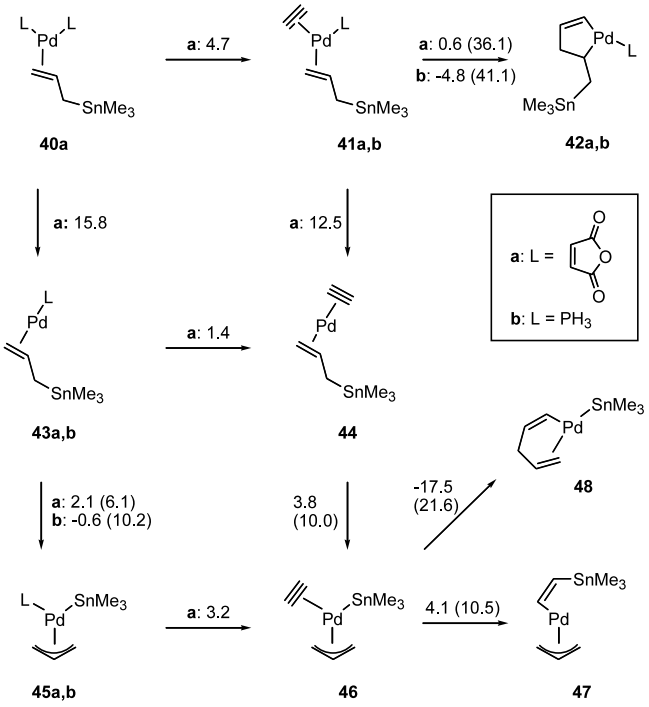
Scheme 5.

allyl stannanes **31** might evolve, via palladium complex **32**, to give bicycle **33**, the result of an oxidative cyclometallation (cycle A). A β-tin elimination would then afford alkenylpalladium complex **34**, which would give the final carbo- or heterocycles **35** by *trans* to *cis* isomerization and reductive elimination. Alternatively, an oxidative addition of **31** to Pd(0) would give an (allyl)(tributylstannyl)–Pd(II) complex **36**. Insertion of the alkyne onto the Pd–C bond or Pd–Sn bond would give complexes **34** or **37**, respectively. Finally, a C–Sn or C–C reductive elimination accounts for the formation of **35** (cycle B, Scheme 5).

In the cyclization of **25** (Scheme 4), the Pd(0)-promoted reaction of **25** would have formed intermediates **38** or **39**. However, **38**, the result of an oxidative cyclometallation, cannot further evolve since the β-tin elimination is not possible. On the other hand, formation of the C–C bond between the η^3-allyl and the alkyne from complex **39** is difficult for geometrical reasons. For these reasons, **25** evolves through a Pd(II)-catalyzed pathway as shown in Scheme 4.



To distinguish between the pathways shown in



Scheme 6. Energies in kcal mol^{-1} at the B3LYP/6-31G(d) and LANL2DZ level including ZPE correction. Values in parentheses correspond to activation energies.

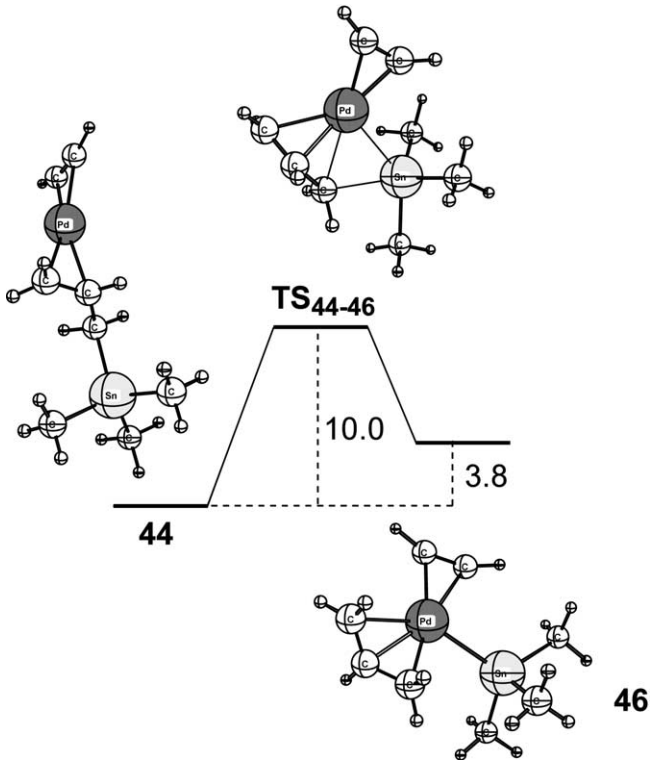


Fig. 1. Reaction coordinate for the transformation of complex **44** into **46** by oxidative addition. Energies (E+ZPE) are given in kcal mol^{-1}.

Scheme 5 we recurred to DFT calculations on model compounds **40**–**48** using maleic anhydride as a model for dba ligand (Scheme 6). The cyclometallation product **42a** was located as a minimum of almost the same energy of **41a** (+0.6 kcal mol^{-1}). However, the corresponding transition state $\mathbf{TS_{41a-42a}}$ lies 36.1 kcal mol^{-1} above **41a**. When $L = PH_3$, the reaction is more favorable thermodynamically, but the activation energy is even higher. These calculations indicate that a cyclometallation of an alkyne with an alkene involving Pd(0) is not a favorable process.

On the other hand, formation of the oxidative product **46** from complex **44** is slightly endothermic (3.8 kcal mol^{-1}) and the activation energy to reach the corresponding transition state $\mathbf{TS_{44-46}}$ is much lower (10.0 kcal mol^{-1}) than that of the cyclometallation process. In this transition state, the allyl stannane, initially in a perpendicular arrangement to the coordination plane, rotates to an arrangement similar to **46** (Fig. 1). The inverse process, which would show a lower activation energy (6.2 kcal mol^{-1}) corresponds to the reductive elimination in the palladium-catalyzed reaction of allyl electrophiles with hexamethylditin [9]. Unexpectedly, starting from **43a** with a more electron-withdrawing maleic anhydride ligand, the oxidative addition to give **45a** was more favorable ($E_a = 6.1$ kcal mol^{-1}). On the other hand, reaction from **43b** is almost thermoneutral, but the activation energy is similar to that of **44** → **46**.

With regards to the insertion, the evolution of **46** to **47** (Fig. 2) was found to take place smoothly with a rather low activation energy (10.5 kcal mol^{-1}). Although the transformation is moderately endothermic (+4.1 kcal mol^{-1}), substitution of the acetylene ligand by buthynedial, to mimic dimethyl acetylenedicarboxylate, led to an exothermic (−5.0 kcal mol^{-1}) insertion of $SnMe_3$ into the alkyne ($E_a = 8.8$ kcal mol^{-1}). This insertion is therefore more facile than the alternative insertion of the allyl into the alkyne to give **48** ($E_a = 21.6$ kcal mol^{-1}), although the transformation is exothermic (−17.5 kcal mol^{-1}).

3. Summary

In summary, these results demonstrate that the reactivity of the allyl stannanes can be inverted by changing the oxidation state of the catalyst from Pd(II) to Pd(0). DFT calculations suggest that the reaction with Pd(0) proceeds by oxidative addition to form (η^3-allyl)palladium complexes. Importantly, the stereochemical outcomes of the Pd(II)- and Pd(0)-catalyzed processes are complementary: intermediates of type **49** are involved with Pd(II) (Scheme 7), while in the present Pd(0)-catalyzed reaction, the intermediate is a palladium(II) complex with the configuration shown in **50**. The stannanes and iodides that result from **50** have signifi-

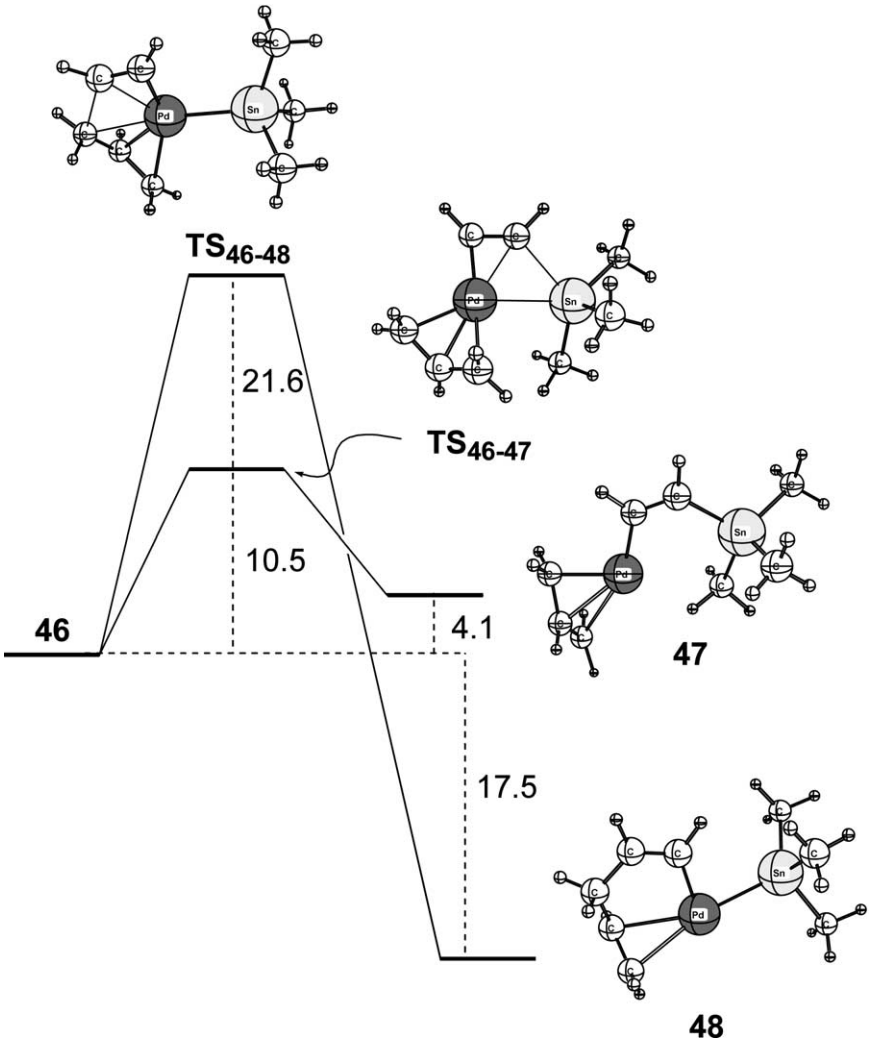
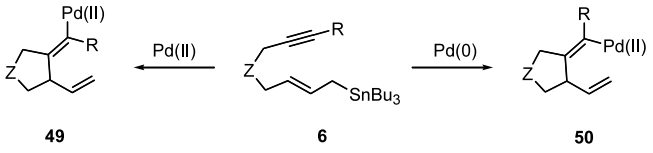


Fig. 2. Alternative pathways for the evolution of complex **46** by insertion reactions. Energies (E+ZPE) are given in kcal mol^{-1}.



Scheme 7.

cant synthetic potential for the construction of functionalized molecules.

4. Experimental

The NMR determinations were carried out at 23 °C. R_f were determined on TLC aluminum sheets coated with 0.2 mm GF_{254} silica gel. Elemental analyses were performed at the SIdI (UAM). All reactions were carried out under an atmosphere of Ar. Solvents were purified, dried by standard methods and degassed prior to use.

4.1. Synthesis of stannanes

Stannanes **9**, **12**, and **14** and silanes **23** and **24** were prepared as previously described [11].

4.2. Synthesis of stannane *16* (Scheme 3)

4.2.1. 4-(Tri-n-butylstannyl)-2-buten-1-ol

(i). To a solution of *cis*-2-buten-1,4-diol (40 g, 454 mmol), pyridine (36.7 ml, 454 mmol), and DMAP (500 mg, 4.1 mmol) in CH_2Cl_2 (100 ml) at 0 °C was added Ac_2O (43.6 ml, 463 mmol) and the mixture was stirred at 23 °C for 16 h. After extractive work-up (CH_2Cl_2) and chromatography (SiO_2; 9:1 to 1:1, hexane–EtOAc) the monoacetate was obtained as a colorless oil (8.55 g, 15%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.82–5.74 (m, 1H), 5.60–5.51 (m, 1H), 4.60 (d, $J = 6.7$ Hz, 2H), 4.18 (d, $J = 6.5$ Hz, 2H), 2.01 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.12 (C), 133.31 (CH), 125.16 (CH), 60.02 (CH_2), 58.09 (CH_2), 20.83 (CH_3). (ii). To a suspension of

CuCN (2.73 g, 30.7 mmol) in THF (50 ml) at −78 °C was added *n*-BuLi (26 ml, 61.51 mmol; 2.4 M in hexanes) and the mixture was stirred at −60 °C for 3 h. The resulting pale yellow solution was cooled down to −78 °C before adding *n*-Bu_3SnH (17.9 g, 61.51 mmol). After 15 min a solution of *cis*-4-acetyloxy-2-buten-1-ol (2.00 g, 15.37 mmol) in THF (10 ml) was added and the mixture was stirred at −40 °C for 16 h. The mixture was warmed up to 23 °C, and a solution of saturated aqueous NH_4Cl (pH 8) was added. After extractive work-up (Et_2O) and chromatography (SiO_2; 10:1, hexane–EtOAc) the stannyl alcohol was obtained as a colorless oil (3.84 g, 70%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.72 (dtt, $J = 10.9$, 9.3, 1.2 Hz, 1H), 5.30 (dtt, $J = 10.9$, 6.7, 1.2 Hz, 1H), 4.17 (br t, $J = 6.7$ Hz, 2H), 1.76 [dd, $J = 9.3$, 1.2 Hz, $^1J(^1H-^{117}Sn) = 25.6$ Hz, $^1J(^1H-^{119}Sn) = 35.2$ Hz, 2H], 1.54–1.19 (m, 12H), 1.14 (t, $J = 5.7$ Hz, 1H), 0.93–0.74 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 132.55 (CH), 122.37 (CH), 58.48 (CH_2), 29.09 [$^3J(^{13}C-Sn) = 10.7$ Hz; CH_2], 27.33 [$^2J(^{13}C-^{119}Sn) = 27.4$ Hz, $^2J(^{13}C-^{117}Sn) = 18.9$ Hz; CH_2], 13.69 (CH_2), 10.98 (CH_3), 9.32 [$^1J(^{13}C-Sn) = 330.4$ Hz; CH_2].

4.2.2. 4-(Tri-n-butylstannyl)-2-buten-1-yl propargyl ether (16)

To a suspension of NaH (111 mg, 2.73 mmol; 60% in mineral oil) in DMF (5 ml) a solution of 4-(tri-*n*-butylstannyl)-2-buten-1-ol (900 mg, 2.49 mmol) in DMF (3 ml) was added at 0 °C and the mixture was stirred at 23 °C for 15 min. Propargyl bromide (444 mg, 2.97 mmol) was added and the mixture was stirred for 16 h at 23 °C. After extractive work-up (Et_2O–H_2O–ice) and chromatography (SiO_2; 10:1, hexane–EtOAc) the title product was obtained as a yellowish oil (342 mg, 35%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.88–5.77 (m, 1H), 5.27–5.17 (m, 1H), 4.14 (d, $J = 2.4$ Hz, 2H), 4.10 (dd, $J = 6.9$, 1.3 Hz, 2H), 2.41 (t, $J = 2.4$ Hz, 1H), 1.79 [dd, $J = 9.3$, 0.8 Hz, $^1J(^1H-^{117}Sn) = 25.6$ Hz, $^1J(^1H-^{119}Sn) = 34.9$ Hz, 2H], 1.53–1.43 (m, 6H), 1.35–1.24 (m, 6H), 0.91–0.84 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 134.25 (CH), 118.83 [$^2J(^{13}C-Sn) = 22.1$ Hz; CH], 80.12 (CH), 74.07 (C), 65.03 (CH_2), 56.86 (CH_2), 29.11 [$^3J(^{13}C-Sn) = 10.5$ Hz; CH_2], 27.33 [$^2J(^{13}C-Sn) = 27.4$ Hz; CH_2], 13.69 (CH_3), 11.18 (CH_2), 9.37 (CH_2). HRMS–EI Calc. for $C_{15}H_{27}OSn$ [$M^+ -$ Bu]: 343.1084. Found: 343.1080.

4.3. Synthesis of stannane 18 (Scheme 3)

4.3.1. 4-(Tri-n-butylstannyl)-2-methyl-2-buten-1-ol

To a suspension of CuCN (603 mg, 6.74 mmol) in THF (20 ml) at −78 °C was added *n*-BuLi (5.6 ml, 13.48 mmol; 2.4 M in hexanes) and the mixture was stirred at −60 °C for 3 h. The resulting pale yellow solution was cooled down to −78 °C before adding *n*-Bu_3SnH (3.924 g, 13.48 mmol). After 15 min 2-methyl-2-vinyloxirane (510 mg, 6.06 mmol) was added and the mixture was stirred at −40 °C for 16 h. The mixture was warmed up to 23 °C, and a solution of saturated aqueous NH_4Cl (pH 8) was added. After extractive work-up (Et_2O) and chromatography (SiO_2; 20:1, hexane/Et_3N), the stannyl alcohol [18] was obtained as a colorless oil (1.84 g, 80%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.65–5.58 (m, 1H), 3.97 (d, $J = 5.6$ Hz, 2H), 1.77–1.23 (m, 17H), 1.09 (t, $J = 5.6$ Hz, 1H), 0.91–0.82 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 128.90 (C), 126.73 [$^2J(^{13}C-Sn) = 22.1$ Hz; CH], 69.80 (CH_2), 29.16 [$^3J(^{13}C-Sn) = 10.5$ Hz; CH_2], 27.35 [$^2J(^{13}C-Sn) = 26.3$ Hz; CH_2], 16.69 (CH_3), 13.52 (CH_3), 10.81 [$^1J(^{13}C-^{119}Sn) = 122.1$ Hz, $^1J(^{13}C-^{117}Sn) = 115.7$ Hz; CH_2], 9.51 [$^1J(^{13}C-^{119}Sn) = 155.7$ Hz, $^1J(^{13}C-^{117}Sn) = 149.4$ Hz; CH_2]. Anal. Calc. for $C_{17}H_{36}OSn \cdot 0.5H_2O$: C, 53.15, H, 9.72. Found: C, 53.59; H, 9.77%.

4.3.2. 4-(Tri-n-butylstannyl)-2-methyl-2-buten-1-yl propargyl ether (18)

To a suspension of NaH (80 mg, 2.00 mmol; 60% in mineral oil) in DMF (5 ml) a solution of 4-(tri-*n*-butylstannyl)-2-methyl-2-buten-1-ol (685 mg, 1.82 mmol) in DMF (3 ml) was added at 0 °C and the mixture was stirred at 23 °C for 15 min. Propargyl bromide (330 mg, 1.82 mmol) was added and the mixture was stirred for 16 h at 23 °C. After extractive work-up (Et_2O–H_2O–ice) and chromatography (SiO_2; 20:1, hexane–EtOAc), the stannane **18** was obtained as a yellowish oil (401 mg, 27%; 63% based on recovered starting material) (4.3:1 mixture of isomers): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.66 (br t, $J = 9.1$ Hz, 1H, major isomer), 5.58 (br t, $J = 8.7$ Hz, 1H, minor isomer), 4.10 (d, $J = 2.8$ Hz, 2H, minor isomer), 4.04 (d, $J = 2.8$ Hz, 2H, major isomer), 3.96–3.92 (m, 2H), 2.40 (t, $J = 2.8$ Hz, 1H, minor isomer), 2.38 (t, $J = 2.8$ Hz, 1H, major isomer), 1.83–1.23 (m, 17 H), 0.96–0.77 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) (mixture of isomers) δ 129.63 [$^2J(^{13}C-Sn) = 23.1$ Hz; CH], 125.08 (C, major isomer), 124.86 (C, minor isomer), 80.37 (CH, minor isomer), 80.24 (CH, major isomer), 76.19 (CH_2), 73.90 (C, minor isomer), 73.74 (C, major isomer), 56.56 [$^4J(^{13}C-Sn) = 7.4$ Hz; CH_2, minor isomer], 56.44 (CH_2, major isomer), 29.14 [$^3J(^{13}C-Sn) = 10.5$ Hz; CH_2], 27.33 [$^2J(^{13}C-Sn) = 27.4$ Hz; CH_2], 13.66 (CH_3), 10.95 (CH_2), 9.51 [$^1J(^{13}C-Sn) = 157.8$ Hz; CH_2, major isomer], 9.37 (CH_2, minor isomer) (several signals of the minor isomer are missing due to overlapping). Anal. Calc. for $C_{20}H_{38}OSn$: C, 58.13, H, 9.27. Found: C, 58.49; H, 9.67%.

4.4. Synthesis of ethyl 4-[4-(tri-n-butylstannyl)-2-methyl-2-buten-1-yloxy]-2-butynoate (**20**) (Scheme 3)

To a solution of *i*-Pr_2NH (1.28 mmol) in THF at −40 °C, *n*-BuLi (1.28 mmol) was added dropwise, and the mixture was stirred at −40 °C for 1 h. To the resulting solution **18** (1.16 mmol), was added at −40 °C. The red solution was stirred for 2 h, and then $ClCO_2Et$ (2.56 mmol) was added rapidly. After 2 h, the reaction was allowed to warm to room temperature (r.t.), and was quenched with NH_4Cl (pH 8). After usual workup (Et_2O) and chromatography (15:1, hexane–EtOAc), stannane **20** was obtained (253 mg, 45%) as a colorless oil: IR (neat) 1717, 1245 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.67 (t, $J = 9.3$ Hz, 1H), 4.22 (q, $J = 7.3$ Hz, 2H), 4.16 (s, 2H), 3.95 (s, 2H), 1.72 (d, $J = 8.9$ Hz, 2H), 1.61 (s, 4H), 1.50–1.41 (m, 4H), 1.33–1.22 (m, 10H), 0.91–0.73 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 153.3, 130.4 [$^2J(^{13}C–Sn) = 22.4$ Hz], 124.7, 83.9, 76.7, 73.7, 62.0, 55.3, 29.7 [$^3J(^{13}C–Sn) = 9.8$ Hz; CH_2], 27.3 [$^2J(^{13}C–Sn) = 26.8$ Hz], 14.0, 13.7, 11.1, 9.6 [$^1J(^{13}C–^{119}Sn) = 157.7$ Hz; $^1J(^{13}C–^{117}Sn) = 150.6$ Hz; CH_2] (one carbon signal was not observed); FAB-MS *m/z* (%): 486 [M^+, 13].

4.5. Synthesis of stannane **25** (Scheme 4)

4.5.1. Dimethyl-1-(2-chloromethyl-2-propenyl)malonate

To a suspension of NaH (705 mg, 17.6 mmol; 60% in mineral oil) in DMF (50 ml) dimethyl malonate (2.28 g, 17.28 mmol) was added at 0 °C and the mixture was stirred at 23 °C for 30 min. 3-Chloro-2-chloromethyl-1-propene (2.28 g, 17.3 mmol) was added and the mixture was stirred for 17 h at 23 °C. After extractive work-up (Et_2O) and chromatography (SiO_2; 5:1, hexane–EtOAc) the malonate was obtained as a colorless oil (1.21 g, 32%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.20 (s, 1H), 5.01 (s, 1H), 4.0 (br s, 2H), 3.74 (s, 6H), 3.67 (t, $J = 7.7$ Hz, 1H), 2.80 (d, $J = 7.7$ Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 169.06 (C), 141.39 (C), 116.68 (CH_2), 52.67 (CH_3), 50.14 (CH), 47.45 (CH_2), 32.03 (CH_2). Anal. Calc. for $C_9H_{13}ClO_4$: C, 48.99; H, 5.94. Found: C, 48.63, H, 6.11%

4.5.2. Dimethyl-1-(2-propenyl-2-tri-n-butylstannyl)malonate

To a suspension of CuCN (974 mg, 10.87 mmol) in THF (30 ml) at −78 °C was added *n*-BuLi (8.7 ml, 21.74 mmol; 2.5 M in hexanes) and the mixture was stirred at −60 °C for 3 h. The resulting pale yellow solution was cooled down to −78 °C before adding *n*-Bu_3SnH (6.32 g, 21.74 mmol). After 15 min a solution of dimethyl-1-(2-chloromethyl-2-propenyl)malonate (1.1 g, 4.98 mmol) in THF (10 ml) was added and the mixture was stirred at −40 °C for 16 h. The mixture was warmed up to 23 °C, and a solution of saturated aqueous NH_4Cl (pH) was added. After extractive work-up (Et_2O) and chromatography (SiO_2; 20:1, hexane–Et_3N) the stannane was obtained as a colorless oil (1.7 g, 72%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.56 [br s, $^4J(^1H–Sn) = 8.9$ Hz, 1H], 4.48–4.42 (m, 1H), 3.73 (s, 6H), 3.63 (t, $J = 7.7$ Hz, 1H), 2.54 (d, $J = 7.7$ Hz, 2H), 1.75 [br d, $J = 0.8$ Hz, $^1J(^1H–Sn) = 29.9$ Hz, 2H], 1.59–1.39 (m, 6H), 1.36–1.23 (m, 6H), 1.35–1.23 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 169.53 (C), 145.96 (C), 106.50 [$^3J(^{13}C–Sn) = 19.9$ Hz; CH_2], 52.48 (CH_3), 50.62 (CH), 37.34 (CH_2), 29.06 [$^3J(^{13}C–Sn) = 9.5$ Hz; CH_2], 27.61 [$^2J(^{13}C–Sn) = 24.2$ Hz; CH_2], 18.74 (CH_2), 13.66 (CH_3), 9.42 [$^1J(^{13}C–Sn) = 151.5$ Hz; CH_2]. Anal. Calc. for $C_{21}H_{40}O_4Sn$: C, 53.07; H, 8.48. Found: C, 52.69; H, 8.59%.

4.5.3. 2-[(Tri-n-butylstannyl)methyl]-1-propen-3-ol [19]

To a solution of *n*-BuLi (54.67 mmol, 23.3 ml; 2.35 M in hexanes) and TMEDA (7.62 g, 65.6 mmol) in Et_2O (26 ml) at 0 °C was added dropwise 2-methyl-1-propen-3-ol (1.71 g, 23.7 mmol). Upon completion of the addition, THF (11 ml) was added and stirring was continued for 24 h at 23 °C. The reaction mixture was cooled to 0 °C, and then *n*-Bu_3SnCl (8.5 g, 26.15 mmol) was added rapidly. The resulting clear solution was stirred at 23 °C for 15 min. The reaction mixture was added to Et_2O (400 ml), washed with saturated aqueous $CuSO_4$, H_2O, and saturated aqueous solution of NaCl. The organic phase was dried over $MgSO_4$. After purification by chromatography (SiO_2; 9:1, hexane–EtOAc) the stannane was obtained as a colorless oil (4.82 g, 56%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.76–4.69 (m, 1H), 4.65–4.59 (m, 1H). 3.96 (br d, $J = 6.4$ Hz, 2H), 1.75 [d, $J = 1.2$ Hz, $^1J(^{13}C–Sn) = 29.3$ Hz, 2H], 1.51–1.40 (m, 6H), 1.36–1.22 (m, 6H), 0.93–0.79 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 149.42 (C), 104.30 [$^3J(^{13}C–Sn) = 17.9$ Hz; CH_2], 67.13 (CH_2), 29.03 [$^3J(^{13}C–Sn) = 8.4$ Hz; CH_2], 27.3 [$^2J(^{13}C–Sn) = 27.4$ Hz; CH_2], 15.03 [$^1J(^{13}C–Sn) = 117.8$ Hz; CH_2], 13.69 (CH_3), 9.51 [$^1J(^{13}C–^{119}Sn) = 159.9$ Hz, $^1J(^{13}C–^{117}Sn) = 152.6$ Hz; CH_2]; FAB-MS *m/z* (%): 385 [$M^+ - 15$, 3], 343 (4), 177 (100).

4.5.4. 2-[(Tri-n-butylstannyl)methyl]-3-chloro-1-propene

To a stirred solution of 2-[(tri-*n*-butylstannyl)methyl]-1-propen-3-ol (600 mg, 1.66 mmol), *i*-Pr_2EtN (858 mg, 6.64 mmol) in THF (10 ml) was added at 0 °C followed by the addition of mesyl chloride (288 mg, 1.98 mmol). The mixture was stirred at 23 °C for 2 h before adding LiCl (352 mg, 8.3 mmol). The mixture was stirred for 16 h at r.t. After extractive work-up (Et_2O–aqueous $NaHSO_3$) and chromatography (SiO_2; 20:1, hexane–Et_3N) the stannane was obtained as a colorless oil (525 mg, 84%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.84 [br

s, $^4J(^1H–Sn) = 8.9$ Hz, 1H], 4.71 [br s, $^4J(^1H–Sn) = 8.9$ Hz, 1H], 3.95 [d, $J = 0.8$ Hz, $^4J(^1H–Sn) = 3.24$ Hz, 2H], 1.89 [d, $J = 0.8$ Hz, $^1J(^1H–Sn) = 29.1$ Hz, 2H], 1.59–1.44 (m, 6H), 1.36–1.24 (m, 6H), 0.99–0.77 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 145.63 [$^2J(^{13}C–Sn) = 21.1$ Hz; C], 109.82 [$^3J(^{13}C–Sn) = 18.9$ Hz; CH_2], 50.14 (CH_2), 29.03 [$^3J(^{13}C–Sn) = 10.5$ Hz; CH_2], 27.33 [$^2J(^{13}C–Sn) = 27.4$ Hz; CH_2], 15.84 [$^1J(^{13}C–Sn) = 115.8$ Hz; CH_2], 13.69 (CH_3), 9.65 [$^1J(^{13}C–^{119}Sn) = 162.1$ Hz; $^1J(^{13}C–^{117}Sn) = 153.6$ Hz; CH_2].

4.5.5. Dimethyl-1-(2-propenyl-2-tri-n-butylstannyl)-1-propargyl malonate (**25**)

4.5.5.1. Method A. To a suspension of NaH (84 mg, 2.1 mmol; 60% in mineral oil) in DMF (10 ml) dimethyl-1-(2-propenyl-2-tri-*n*-butylstannyl) malonate (1.0 g, 2.1 mmol) was added at 0 °C and the mixture was stirred at 23 °C for 15 min. Propargyl bromide (374 mg, 2.52 mmol; 80% in toluene) was added and the mixture was stirred for 4 h at 23 °C. After extractive work-up (Et_2O/H_2O/ice) the organic phase was dried over $MgSO_4$, filtered and the solvent evaporated. Stannane **25** was obtained as a colorless oil (984 mg, 92%).

4.5.5.2. Method B. To a suspension of NaH (47 mg, 1.16 mmol; 60% in mineral oil) in DMF (5 ml), dimethyl-propargyl malonate (180 mg, 1.1 mmol) was added at 0 °C and the mixture was stirred at 23 °C for 30 min. 2-[(Tri-*n*-butylstannyl)methyl]-3-chloro-1-propene (400 mg, 1.1 mmol) was added and the mixture was stirred for 16 h at 23 °C. After extractive workup (Et_2O–H_2O–ice) and chromatography (SiO_2; 20:1, hexane–Et_3N), stannane **25** was obtained as a colorless oil (366 mg, 65%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.66 [d, $J = 1.4$ Hz, $^4J(^1H–Sn) = 9.1$ Hz, 1H], 4.50 [d, $J = 1.4$ Hz, $^4J(^1H–Sn) = 9.1$ Hz, 1H], 3.73 (s, 6H), 2.89 (d, $J = 2.8$ Hz, 2H), 2.72 [s, $^4J(^1H–Sn) = 3.6$ Hz, 2H], 2.02 (t, $J = 2.8$ Hz, 1H), 1.57 [s, $^1J(^1H–Sn) = 30.3$ Hz, 2H], 1.57–1.39 (m, 6H), 1.35–1.21 (m, 6H), 0.98–0.79 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 170.48 (C), 144.09 [$^2J(^{13}C–Sn) = 21.0$ Hz; C], 109.71 [$^3J(^{13}C–Sn) = 10.5$ Hz; CH], 79.45 (CH), 71.67 (C), 57.03 (C), 52.64 (CH_3), 39.15 (CH_2), 29.00 [$^3J(^{13}C–Sn) = 10.5$ Hz; CH_2], 27.36 [$^2J(^{13}C–Sn) = 27.3$ Hz; CH_2], 22.70 (CH_2), 19.99 [$^1J(^{13}C–^{119}Sn) = 351.5$ Hz, $^1J(^{13}C–^{117}Sn) = 332.2$ Hz; CH_2], 13.66 (CH_3), 9.39 [$^1J(^{13}C–^{119}Sn) = 149.9$ Hz, $^1J(^{13}C–^{117}Sn) = 117.9$ Hz; CH_2]; HRMS-EI Calc. for $C_{24}H_{41}0_4Sn$ [$M^+ + 1$]: 523.2026. Found: 523.2037.

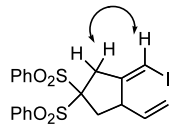
4.6. Palladium(0)-catalyzed cyclizations

4.6.1. General procedure: reaction of **9** with $Pd_2(dba)_3$·dba to give tributyl-(Z)-[4,4-bis(phenylsulfonyl)-2-vinylcyclopentylidenemethyl)]stannane (**10**)

A solution of **9** (90 mg, 0.13 mmol) in 1,4-dioxane (5 ml) was added to a flask containing $Pd_2(dba)_3$·dba (4 mg, 3.6 10^{-3} mmol). The mixture was stirred for 2 h at 60 °C under Ar. After evaporation of the solvent and chromatography (SiO_2; 10:1 hexane–EtOAc), stannane **10** was obtained as a colorless oil (55 mg, 63%): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.07–8.01 (m, 4H), 7.73–7.67 (m, 2H), 7.61–7.53 (m, 4H), 5.70 (br s, 1H), 5.65 (ddd, $J = 16.9$, 9.3, 8.1 Hz, 1H), 5.11–5.04 (m, 2H), 3.60 (dt, $J = 17.8$, 2.0 Hz, 1H), 3.37–3.282 (m, 1H), 2.98 (dt, $J = 17.8$, 1.6 Hz, 1H), 2.86 (ddd, $J = 15.0$, 8.9, 1.2 Hz, 1H], 2.56 (dd, $J = 15.0$, 8.1 Hz, 1H), 1.57–1.39 (m, 6H), 1.36–1.18 (m, 6H), 0.95–0.83 (m, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 156.17 (C), 139.57 (CH), 137.09 (C), 136.18 (C), 134.57 (CH), 134.46 (CH), 131.13 (CH), 131.06 (CH), 126.66 (CH), 123.89 (CH), 116.64 (CH_2), 91.64 (C), 48.46 (CH), 42.22 (CH_2), 38.32 (CH_2), 29.06 (CH_2), 27.33 (CH_2), 13.72 (CH_3), 11.02 (CH_2) (one C is missing due to overlapping).

4.6.2. General procedure: reaction of **9** with $Pd_2(dba)_3$·dba, followed by iodination to give (Z)-1-iodomethylene-4,4-bis(phenylsulfonyl)-2-vinylcyclopentane (**11**)

A solution of **9** (90 mg, 0.13 mmol) in 1,4-dioxane (5 ml) was added to a flask containing $Pd_2(dba)_3$·dba (4 mg, 3.6 10^{-3} mmol). The mixture was stirred for 2 h at 60 °C under Ar. The reaction mixture was cooled down to 0 °C and a solution of I_2 (35 mg, 0.13 mmol) in 1,4-dioxane (3 ml) was added. The mixture was stirred for 2 h at 23 °C. The solvent was evaporated and MeOH (6 ml) and KF (90 mg, 1.55 mmol) were added to the flask. The mixture was stirred at 23 °C for 16 h. The solvent was evaporated and Et_2O was added. The resulting suspension was filtered off and the filtrate was evaporated and purified by chromatography (SiO_2; 7:3 hexane–EtOAc) to yield **11** as a white solid (43 mg, 85%): m.p. 128–130 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.10–8.06 (m, 2H), 7.97–7.95 (m, 2H), 7.76–7.69 (m, 2H), 7.64–7.57 (m, 4H), 6.02 (t, $J = 2.0$ Hz, 1H), 5.67 (ddd, $J = 17.4$, 9.7, 7.7 Hz, 1H), 5.19–5.14 (m, 2H), 3.53 (dt, $J = 17.4$, 2.0 Hz, 1H), 3.27 (m, 1H), 3.02–2.92 (m, 2H), 2.73 (dd, $J = 17.7$, 6.1 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 149.01 (C), 136.01 (C), 135.67 (C), 135.06 (CH), 134.75 (CH), 131.07 (CH), 130.85 (CH), 128.98 (CH), 128.78 (CH), 117.02 (CH_2), 91.89 (C), 82.13 (CH), 73.82 (CH), 49.50 (CH), 40.30 (CH_2), 36.81 (CH_2); HRMS-FAB Calc. for [$M^+ + 1$]: 514.9847. Found: 514.9823. Anal. Calc. for $C_{20}H_{19}IO_4S_2$: C, 46.70, H, 3.72; S, 12.47. Found: C, 46.80; H,3.61; S, 12.58%. The structure was confirmed by the following NOE correlation.



*4.6.3. (Z)-1-Iodomethylene-2-isopropenyl-4,4-bis(phenylsulfonyl)cyclopentane (**13**)*

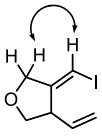
White solid: mp 146–148 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.08–8.05 (m, 2H), 8.00–7.96 (m, 2H), 7.77–7.70 (m, 2H), 7.64–7.56 (m, 4H), 6.15 (br t, $J = 2.6$ Hz, 1H), 4.88–4.81 (m, 1H), 4.81 (br s, 1H), 3.55 (dt, $J =$ 17.4, 2.6 Hz, 1H), 3.27–3.19 (m, 1H), 3.00 (m, 1H), 2.95 (ddd, $J = 15.4$, 9.3, 1.6 Hz, 1H), 2.96 (dd, $J = 15.4$, 7.7 Hz, 1H), 1.67 (br t, $J = 1.0$ Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 148.95 (C), 142.65 (C), 136.99 (C), 135.68 (C), 134.98 (CH), 134.67 (CH), 130.96 (CH), 130.79 (CH), 128.93 (CH), 128.76 (CH), 114.15 (CH_2), 91.90 (C), 74.71 (CH), 53.32 (CH), 41.47 (CH_2), 37.04 (CH_2), 19.16 (CH_3). Anal. Calc. for $C_{21}H_{21}IO_4S_2$: C, 47.73, H, 4.01; S, 12.14. Found: C, 47.39; H, 4.03; S, 12.04%.

*4.6.4. (Z)-Iodomethylene-4,4-bis(methoxycarbonyl)-2-vinylcyclopentane (**15**)*

^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.17 (m, 1H), 5.66 (ddd, $J = 16.6$, 9.7, 6.9 Hz, 1H), 5.14 (dt, $J = 5.7$, 1.2 Hz, 1H), 5.09 (q, $J = 1.6$ Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.33 (q, $J = 6.9$ Hz, 1H), 3.08 (dt, $J = 16.2$, 2.0 Hz, 1H), 2.95 (dt, $J = 15.1$, 1.3 Hz, 1H), 2.77 (dq, $J = 8.5$, 1.2 Hz, 1H), 2.22 (dd, $J = 7.7$, 6.1 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.4, 171.3, 151.4, 136.7, 116.1, 72.9, 59.4, 52.9, 52.8, 48.9, 42.8, 39.5; HRMS-EI Calc. for $C_{12}H_{15}O_4I$ [M^+]: 350.0015. Found: 350.0003.

*4.6.5. (E)-3-Iodomethylene-4-vinyltetrahydrofuran (**17**)*

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.08 (q, $J = 1.8$ Hz, 1H), 5.70 (ddd, $J = 17.4$, 10.1, 7.6 Hz, 1H), 5.18 (dt, $J =$ 17.2, 1.2 Hz, 1H), 5.14 (dt, $J = 10.2$, 1.0 Hz, 1H), 4.31 (dt, $J = 13.0$, 1.7Hz, 1H), 4.21 (dd, $J = 13.0$, 1.7 Hz, 1H), 3.94 (dd, $J = 8.8$, 6.2 Hz, 1H), 3.84 (dd, $J = 8.8$, 3.0 Hz, 1H), 3.32 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 152.5 (C), 134.7 (CH), 116.9 (CH_2), 73.4 (CH_2), 71.8 (CH_2), 69.3 (CH), 51.6 (CH); FAB-MS *m/z* (%): 235 [$M^+ - 1$, 14], 219 (34), 167(100). The structure was confirmed by COSY and NOESY experiments. The following NOE correlation allowed to determine the configuration.

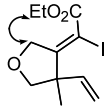


*4.6.6. (E)-3-Iodomethylene-4-methyl-4-vinyltetrahydrofuran (**19**)*

Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.04 (t, $J = 2.0$ Hz, 1H), 5.89 (dd, $J = 17.4$, 10.5 Hz, 1H), 5.24 (dd, $J = 10.5$, 1.2 Hz, 1H), 5.23 (dd, $J = 17.4$, 1.2 Hz, 1H), 4.43 (dd, $J = 12.9$, 2.0 Hz, 1H), 4.40 (dd, $J = 12.9$, 2.0 Hz, 1H), 3.79 (d, $J = 8.7$ Hz, 1H), 3.70 (d, $J = 8.7$ Hz, 1H), 1.43 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 154.42 (C), 139.35 (CH), 115.08 (CH_2), 82.23 (CH_2), 75.06 (CH_2), 66.21 (CH), 50.93 (C), 19.65 (CH_3).

*4.6.7. (Z)-Iodo-(4-methyl-4-vinyldihydrofuran-3-ylidene)acetic acid ethyl ester (**21**)*

IR (neat) 1704, 1244 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.82 (dd, $J = 17.5$, 10.7 Hz, 1H), 5.25 (dd, $J =$ 10.7, 0.5 Hz, 1H), 5.17 (d, $J = 17.2$ Hz, 1H), 4.84 (d, $J =$ 16.6 Hz, 1H), 4.66 (d, $J = 16.6$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.64 (dd, $J = 12.2$, 8.8Hz, 2H), 1.49 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.1 (C), 163.7 (C), 138.9 (CH), 116.4 (CH_2), 81 (CH_2), 79.7 (C), 76 (CH_2), 62.7 (CH_2), 53.7 (C), 19.2 (CH_3), 14.1 (CH_3). The structure was confirmed by COSY, NOESY, HMBC, and HMQC experiments. The following NOE correlation allowed to determine the configuration. HRMS-CI Calc. for $C_{11}H_{16}O_3I$ [$M^+ + 1$]: 323.0144. Found: 323.0131.



*4.6.8. (Z)-3-Iodomethylene-5-methylenecyclohexane-1,1-dicarboxylic acid dimethyl ester (**28**)*

To a flask containing $Pd(MeCN)_2Cl_2$ (2.5 mg, 0.01 mmol) and $(C_6F_5)_3P$ (10.4 mg, 0.02 mmol) a solution of dimethyl-1-(2-propenyl-2-tri-*n*-butylstannyl)-1-propargyl malonate (100 mg, 0.195 mmol) in benzene (5 ml) was added. The mixture was stirred at 70 °C for 30 h. A solution of I_2 (54 mg, 0.21 mmol) in benzene (3 ml) was added at 0 °C and the mixture was stirred for 2 h at 23 °C. The solvent was evaporated and MeOH (6 ml) and KF (50 mg, 0.9 mmol) were added to the flask. The mixture was stirred at 23 °C for 16 h. The solvent was evaporated and Et_2O was added. The resulting suspension was filtered off and the filtrate was evaporated and purified by chromatography (SiO_2; hexane) to yield a mixture of dimethyl 3,5-dimethylenecyclohexane-1,1-dicarboxylate (**27**) and (*E*)-dimethyl 3-iodomethylene-5-methylenecyclohexane-1,1-dicarboxylate (**28**) as a colorless oil (33 mg, 53%, 1:3.5 mixture). **26**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.78 (br s, 4H), 3.70 (s, 6H), 2.84 (s, 2H), 2.74 (s, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 170.90 (C), 142.40 (C), 111.22 (CH_2), 56.81 (C), 52.57 (CH_3), 42.84 (CH_2), 39.21 (CH_2); APCI-MS (*m/z*):

225.3 [$M^+ + 1$]. **28**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.08 (t, $J = 1,2$ Hz, 1H), 4.82 (br s, 2H), 3.73 (s, 6H), 2.97 (br s, 2H), 2.92 (br s, 2H), 2.76 (br s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$; DEPT) δ 150.54 (C), 144.00 (C), 140.94 (C), 112.12 (CH_2), 75.74 (CH), 56.31 (C), 52.69 (CH_3), 44.39 (CH_2), 39.57 (CH_2), 39.17 (CH_2). The structure was confirmed by COSY and NOESY experiments.

5. Calculations

The calculations were performed with Gaussian 98 [20]. The geometries of all complexes here reported were optimized applying density functional theory (DFT) at the generalized gradient approximation using the B3LYP hybrid functional [21]. The standard 6-31G(d) basis set was used for C, H, O, and P. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt [22] and employs a split-valence (double-ξ) basis set, was used for Pd and Sn. Energies include zero-point energy (ZPE) correction. Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies. The starting approximate geometries for the transition states (TS) were graphically located.

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