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Preparation of 2-Alkenylsilanes and 2-Alkenylstannanes by the Reaction of 2-Alkenyl-1,1-cyclopropanedicarboxylate Esters with $PhMe_2SiAlEt_2$ and $(Ph_3Sn)_2Zn$. Generation of 2-Alkenyl-3-cyclopentene-1,1-dicarboxylates via Alkenyl-Substituted π-Allylpalladium Complexes Derived from Dienylsilanes and $[PdCl_2(CH_3CN)_2]$

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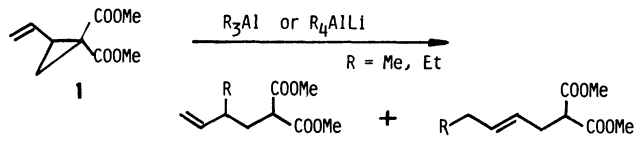
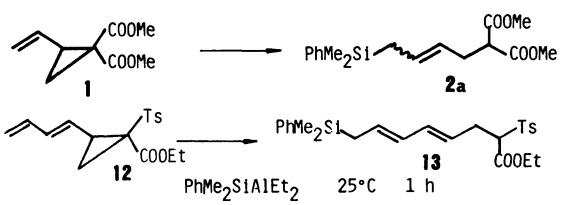
Reaction of 2-vinyl-1,1-cyclopropanedicarboxylate with $PhMe_2SiAlEt_2$, $PhMe_2SiZnEt_2Li$, or $(Ph_3Sn)_2Zn$ gave 1,7-homoconjugate addition products, 2-alkenylsilanes or 2-alkenylstannanes. In a similar fashion, 2-(1,3-butadienyl)-1,1-cyclopropanedicarboxylate provided the corresponding 1,9-homoconjugate adducts, dienylsilanes or dienylstannanes. The adducts were converted into π-allylpalladium complexes by means of $[PdCl_2(CH_3CN)_2]$. Treatment of the alkenyl-substituted π-allylpalladium complexes derived from dienylsilanes and $[PdCl_2(CH_3CN)_2]$ with bases such as PPh_3 or Na_2CO_3 gave 2-alkenyl-3-cyclopentene-1,1-dicarboxylates. In contrast, the reaction of the π-allylpalladiums generated from 2-alkenylsilanes and $[PdCl_2(CH_3CN)_2]$ with the bases resulted in the formation of original vinylcyclopropane derivatives.

Scheme 1 refers to the reaction of organoaluminum reagents with vinylcyclopropanes activated by two electron-withdrawing group. The regiochemistry in the homoconjugate addition of an alkyl group to 2-vinyl-1,1-cyclopropanedicarboxylic ester (**1**) is controlled by the nature of organoaluminum reagents.[1] Here we wish to report the reactions of Scheme 2, in which organometallic reagents such as $PhMe_2SiAlEt_2$,[3] $PhMe_2SiZnEt_2Li$,[3] and $(Ph_3Sn)_2Zn$[4] react with vinylcyclopropanes regioselectively to give 1,7-homoconjugate addition products, 2-alkenylsilanes and 2-alkenylstannanes. Similarly, 2-(1,3-butadienyl)cyclopropanes provide the corresponding dienylsilanes upon treatment with silylmetal reagents.

For example, the vinylcyclopropane **1** was allowed to react with 2.0 equivalents of $PhMe_2SiAlEt_2$ derived from $PhMe_2SiLi$ and Et_2AlCl in tetrahydrofuran. The reaction took place smoothly and was completed usually in 1 h at 0 °C. Dilution of the reaction mixture with dichloromethane, followed by workup (NaF and H_2O) and isolation by silica-gel column chromatography, gave a stereoisomeric mixture of (*E*)-2-alkenylsilane and the (Z)-isomer (**2a**, E : Z = 81 : 19, Run 1 in Table 1). Ate complexes such as $PhMe_2SiAlMe_3Li$,[3] $PhMe_2SiZnEt_2Li$,[3] $PhMe_2SiBEt_3Li$,[5] $(PhMe_2Si)_3MnMgMe$,[6] and $Ph_3SiAlMe_3Li$ are also effective for the regioselective formation of 1,7-homoconjugate adducts with an exception of the reaction of 2-styryl-1,1-cyclopropane dicarboxylate (**8**) (Run 10 in Table 1). The use of $(Ph_3Sn)_2Zn$ instead of silyl reagents produced 2-alkenylstannanes (Runs 6 and 7 in Table 1). In the same way, 2-(1,3-butadienyl)cyclopropanes gave the corresponding dienylsilanes upon treatment with these silylmetal reagents. The regiochemisty of the reaction heavily depends on the nature of the substrates. The 2-(1,3-butadienyl)-cyclopropane (**12**) gave 1,9-homoconjugate adduct mainly, whereas the 2-(4-phenyl-1,3-butadienyl)-cyclopropane (**14**) and 2-(3-methyl-1,3-butadienyl)-cyclopropane (**17**) afforded regioisomeric mixtures. The new method was successfully extended to the ring opening of vinylaziridines and dienylaziridines.



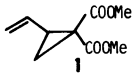
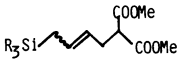
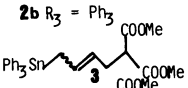
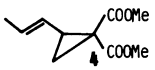
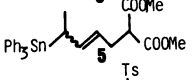
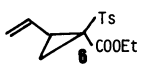
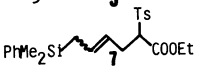
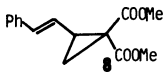
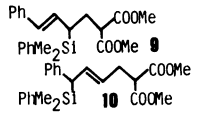
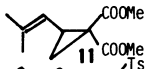
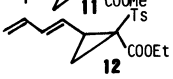
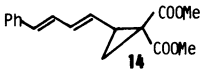
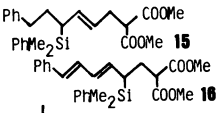
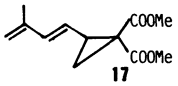
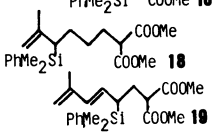
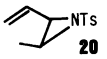
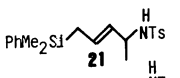
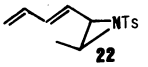
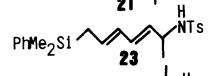
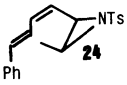
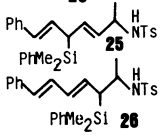
Scheme 1.

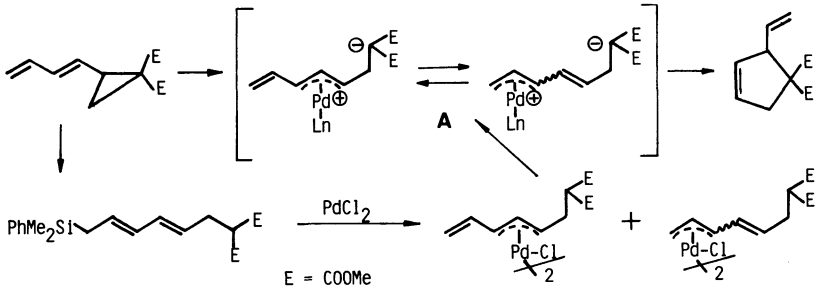


Scheme 2.

Two necessary factors for successful homoconjugate addition are as follows: (a) The presence of two activating groups and (b) a vinyl or dienyl group on the cyclopropane ring. Ethyl chrisanthemate did not undergo conjugate addition, and the attempted reaction of dimethyl 1,1-cyclopropanedicarboxylic ester resulted in the recovery of the starting material. Dimethyl 2-(2-methyl-1-propenyl)-1,1-cyclopropanedicarboxylate remained unchanged upon treatment with $PhMe_2SiAlEt_2$ (Run 11 in Table 1). Steric hindrance of geminal dimethyl groups explains the absence of the attack of $PhMe_2Si$ anion on the vinyl moiety.

Table 1. Homoconjugate Addition of Silylmetal Reagents to Vinylcyclopropanes and Dienylcyclopropanes

Run	Substrate	Reagent	Product	Y/% (E/Z)
1	 1	$PhMe_2SiAlEt_2$		100 (81/19)
2		$PhMe_2SiBEt_3Li$		100 (88/12)
3		$(PhMe_2Si)_3MnMgMe$	**2a** R_3 = $PhMe_2$	78 (90/10)
4		$Ph_3SiAlEt_2$	**2b** R_3 = Ph_3	100 (69/31)
5		$Ph_3SiAlMe_3Li$	 **3**	70 (70/30)
6	 4	$(Ph_3Sn)_2Zn$		81 (82/18)
7		$(Ph_3Sn)_2Zn$	 **5**	74 (90/10)
8	 6	$PhMe_2SiAlEt_2$	 **7**	98 (79/21)
9		$PhMe_2SiAlBu_3Li$		93 (73/27)
10	 8	$PhMe_2SiAlEt_2$	 **9** **10**	60 9/10=28/72
11	 11	$PhMe_2SiAlEt_2$	No Reaction	
12	 12	$PhMe_2SiZnEt_2Li$	 **13**	75
13	 14	$PhMe_2SiZnEt_2Li$	 **15** **16**	48 15/16=1/1
14	 17	$PhMe_2SiAlMe_3Li$	 **18** **19**	37 18/19=31/69
15	 20	$PhMe_2SiAlMe_3Li$	 **21**	81 (100/0)
16	 22	$PhMe_2SiAlMe_3Li$	 **23**	82 E, E only
17	 24	$PhMe_2SiAlEt_3Li$	 **25** **26**	86 25/26=4/6

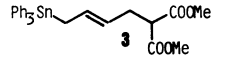
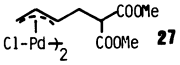
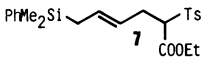
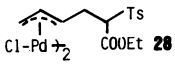
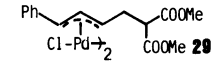
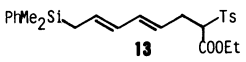
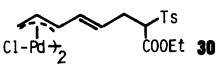
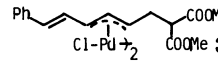
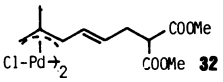
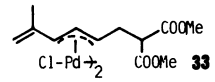
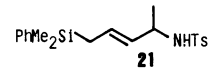
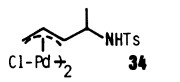
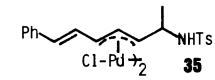


Scheme 3.

Previously, we reported[7,8] that 1,3-butadienylcyclopropanes in Scheme 3 activated by two electron-withdrawing groups smoothly rearranged to vinylcyclopentenes in the presence of a Pd(0) catalyst. 1-Tosyl-2-(1,3-butadienyl)aziridines reacted similarly to give pyrroline derivatives. A zwitterion **A** plays a critical role in the rearrangement. We next examined the synthesis of five-membered ring compounds via the π-allylpalladium complexes which were readily prepared from the above-mentioned alkenylsilanes and $[PdCl_2(CH_3CN)_2]$.

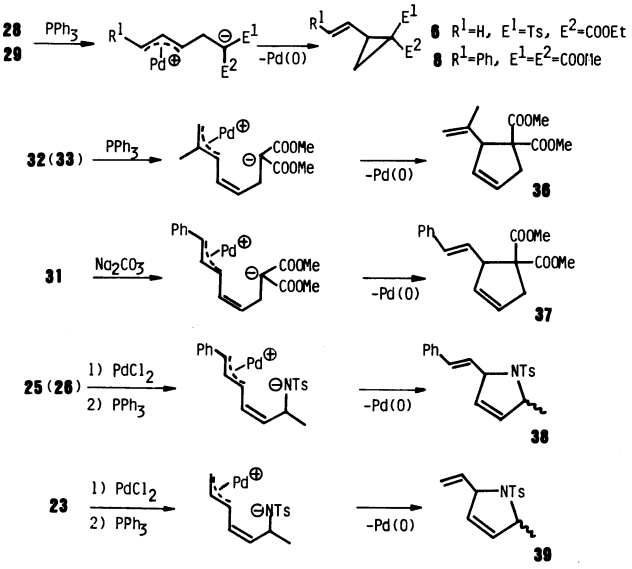
Treatment of the 2-alkenylsilanes **3**, **7**, **9(10)**, and

Table 2. Synthesis of π-Allylpalladium Complexes

Alkenylsilane (Alkenylstannane)	Product	Y/%
 **3**	 **27**	21
 **7**	 **28**	46
9, 10 (9/10 = 72/28)	 **29**	80
 **13**	 **30**	40
15, 16 (15/16 = 1/1)	 **31**	35
18, 19 (18/19 = 31/69)	 **32**	50
	 **33**	32/33 = 3/1
 **21**	 **34**	47
25, 26 (25/26 = 40/60)	 **35**	—

21 and 2,4-dienylsilanes **13**, **15(16)**, **18(19)**, and **25(26)** with one equivalent of $[PdCl_2(CH_3CN)_2]$ in tetrahydrofuran at 25 °C provided π-allylpalladium complexes[9] after purification by silica-gel column chromatography[10] (Table 2).

Exposure of the π-allylpalladiums **28** and **29** to PPh_3 resulted in the formation of the original alkenylcyclopropane derivatives **6** (40%) and **8** (46%) along with unidentified complex products containing isomeric methyl 2-methoxycarbonyl-6-phenylhexadienoate or ethyl 2-tosylhexadienoate. No trace of cyclopentene derivatives was observed. In contrast, treatment of a mixture of **32** and **33** in DMSO with PPh_3 or Na_2CO_3 gave the cyclopentene derivative **36** in 70% or 80% yield, respectively. Similarly, treatment of the crude π-allylpalladium **35** generated from a mixture of **25** and **26** with PPh_3 also produced the pyrroline derivative **38**. Naturally, the prerequisite to the cyclization into five-membered rings should be a U shaped configuration of the zwitterion **A** as shown in Scheme 4. The simple π-allylpalladium complexes such as **27**, **28**, and **29** can not take this form but give vinylcyclopropanes only. On the other hand, the conjugation of C=C bond to the π-allylpalladium moiety enables the aliphatic chain to assume the U shape and leads to the cyclization to five-membered rings. The observed behavior of the isolated π-allylpalladium complexes in the present work does support this idea.



Scheme 4.

Experimental

Distillation of the products was performed by use of Kugelrohr (Büchi), and boiling points are indicated by an airbath temperature without correction. All melting points were obtained on a Yanaco MP-50929 melting point apparatus and are uncorrected, too. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian XL-200 spectrometer, $CDCl_3$ was used as solvent unless otherwise noted, chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Purification of 2-alkenylstannanes was performed by column chromatography on neutral alumina (Merck Art. 1077 (95 g), H_2O (5 g)), and other products were purified by silica-gel column chromatography.

Dimethyl 2-Vinyl-1,1-cyclopropanedicarboxylate (1). The compound was prepared by the reported procedure.[11]

Syntyesis of *cis*-1-Tosyl-3-methyl-2-vinylaziridine (20). This was synthesized in 40% overall yield from 1,3-pentadiene by oxyamination:[12] Mp 90—92 °C (crystallizes after distillation at 110 °C/0.2 Torr (1 Torr = 133.322 Pa)); ^{1}H NMR δ = 1.20 (d, J = 5.8 Hz, 3H), 2.44 (s, 3H), 3.03 (dq, J = 7.0, 5.8 Hz, 1H), 3.33 (d, J = 7.0, 6.9 Hz, 1H), 5.30 (dd, J = 9.9, 1.8 Hz, 1H), 5.39 (dd, J = 17.2, 1.8 Hz, 1H), 5.61 (ddd, J = 17.2, 9.9, 6.9 Hz, 1H); ^{13}C NMR δ = 12.2, 21.6, 40.8, 45.7, 121.3, 127.2, 127.6, 129.5, 129.6, 144.3; IR (nujol) 1596, 1323, 1161, 1091, 927, 841, 678 cm^{-1}; Found: C, 60.69; H, 6.35; N, 5.64%. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90%.

General Procedure for the Preparation of Cyclopropanecarbaldehydes and Aziridinecarbaldehyde. These materials were prepared by means of oxidative cleavage of the corresponding olefinic compounds.[13] In a typical procedure a hexane solution of OsO_4 (0.06 mmol) was added to a solution of **20** (2.1 g, 9.0 mmol) in THF (55 ml) and water

(18 ml) at room temperature under argon atmosphere. The color of the solution turned dark brown after stirring for 5 min. Then powdered sodium periodate (5.2 g, 24.3 mmol) was added and the stirring was continued overnight. The mixture was diluted with hexane and the precipitate was filtered off. The filtrate was washed twice with aqueous sodium thiosulfate solution (1 M, 1 M = 1 mol dm^{-3}, 50 ml × 2), and aqueous layer was extracted with dichloromethane (30 ml). Combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by column chromatography (hexane-ethyl acetate, 3 : 1) afforded 1.7 g (80%) of *cis*-2-formyl-3-methyl-1-tosylaziridine: Mp 50 °C (crystallizes after distillation at 120 °C/0.2 Torr); ^{1}H NMR δ=1.41 (d, J=6.0 Hz, 3H), 2.48 (s, 3H), 3.0—3.4 (m, 1H), 3.20 (dq, J=7.0, 6.0 Hz, 1H), 7.43 (d, J=8.3 Hz, 2H), 7.89 (d, J=8.3 Hz, 2H), 9.35 (d, J=5.5 Hz, 1H); ^{13}C NMR δ=12.9, 21.5, 40.8, 46.4, 127.8, 129.7, 129.8, 145.1, 195.3; IR (neat) 1727, 1595, 1326, 1162, 1090, 878, 714, 670 cm^{-1}.

Dimethyl 2-Formyl-1,1-cyclopropanedicarboxylate. Ozonolysis of **1** following the reported procedure[5] gave the title compound in 65% yield.

Ethyl 2-Formyl-1-tosyl-1-cyclopropanecarboxylate. This material was prepated in 87% yield from ethyl 1-tosyl-2-vinyl-1-cyclopropanecarboxylate[14] with $NaIO_4$ and OsO_4.

***cis*-3-Methyl-2-(4-phenyl-1,3-butadienyl)-1-tosylaziridine (24) (General Method for the Preparation of Dienylcyclopropanes[5] and Dienylaziridines).** To an ethereal suspension of cinnamyltriphenylphosphonium chloride (0.62 g, 1.5 mmol) was added potassium *t*-butoxide (0.12 g, 1.1 mmol) at 0 °C under argon atmosphere. The resulting red suspension was stirred for additional 10 min and then allowed to stand still. The supernatant was transferred using a hypodermic syringe into an ethereal solution of 1-tosyl-2-formyl-3-methylaziridine. After stirring for 30 min, the reaction mixture was poured into aqueous ammonium chloride (30 ml), extracted with hexane, and washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated in vacuo. Purification by column chromatography afforded **24** as a colorless oil (0.12 g, 54% yield): Bp 140 °C/760 Torr (decomp); ^{1}H NMR δ=1.22 (d, J=5.7, 3H), 2.37 (s, 3H), 3.14 (dq, J=5.7, 7.2 Hz, 1H), 3.74 (ddd, J=8.1, 7.2, 1.0 Hz, 1H), 5.21 (dd, J=10.9, 8.1 Hz, 1H), 6.41 (dd, J=11.1, 10.9 Hz, 1H), 6.61 (d, J=15.5 Hz, 1H), 7.12 (ddd, J=15.5, 11.1, 1.0 Hz, 1H), 7.2—7.5 (m, 7H), 7.85 (d, J=8.3 Hz, 2H); ^{13}C NMR δ=12.7, 21.5, 41.1, 41.9, 121.7, 123.1, 126.7, 127.6, 128.1, 128.6, 129.7, 135.4, 135.5, 135.7, 136.7, 144.3; IR (neat) 3026, 1591, 1493, 1450, 1396, 1323, 1156, 1091, 1046, 935, 875, 713, 693, 669 cm^{-1}; Found: C, 70.66; H, 6.48; N, 3.83%. Calcd for $C_{20}H_{21}NO_2S$: C, 70.77; H, 6.24; N, 4.13%.

***cis*-2-(1,3-Butadienyl)-3-methyl-1-tosylaziridine (22).** (E : Z=22 : 78): Mp 78—80 °C (crystallizes after distillation at 150 °C/0.1 Torr); ^{1}H NMR δ=1.19 (d, J=5.9 Hz, 0.66H), 1.21 (d, J=5.9 Hz, 2.34H), 2.43 (s, 3H), 3.0—3.2 (m, 1H), 3.37 (dd, J=7.3, 7.3 Hz, 0.22H), 3.64 (ddd, J=8.3, 7.1, 1.2 Hz, 0.78H), 5.1—5.7 (m, 3.22H), 6.2—6.5 (m, 0.22H), 6.25 (dd, J=11.9, 10.1 Hz, 0.78H), 6.68 (dddd, J=16.6, 11.2, 10.1, 1.1 Hz, 0.78H), 7.33 (d, J=8.4 Hz, 2H), 7.82 (d, J=8.4 Hz, 2H); ^{13}C NMR δ=12.6, 21.5, 40.9, (41.2), 41.6, (45.2), (118.6), 120.7, 122.2, (124.6), (127.0), (127.2), 127.6, (129.5), 129.6, (131.1), 135.5, 135.6, (136.7), 144.3; IR (Nujol) 1596 (w), 1319, 1159, 1090, 910, 868, 677; Found: C, 63.61; H, 6.70; N, 5.58%. Calcd for $C_{14}H_{17}NO_2S$: C, 63.85; H, 6.51; N, 5.32%.

A Typical Procedure for Generation of Silylmetal Reagents. A THF solution of $PhMe_2SiLi$ (1.0 mmol) was added to a solution of Et_2AlCl (1.0 mmol) in THF (2 ml) at 0 °C under argon atmosphere and the resulting solution was stirred for 10 min. Other silylmetal reagents such as $PhMe_2SiBEt_3Li$,[6] $(PhMe_2Si)_3MnMgMe$,[7] and $PhMe_2SiAlEt_3Li$ were also prepared according to the procedures described before.

Reaction of Dimethyl 2-Vinyl-1,1-cyclopropanedicarboxylate (1) with $PhMe_2SiAlEt_2$. To a THF solution of $PhMe_2SiAlEt_2$ (0.94 mmol) was added a solution of **1** (80 mg, 0.43 mmol) in THF (2 ml) at 0 °C under argon atmosphere. After stirring for 1 h, the reaction mixture was diluted with dichloromethane (15 ml) and anhydrous sodium fluoride (0.42 g) was added. Then water (0.2 ml) was added dropwise and the resulting white suspension was vigorously stirred for 10 min. Filtration through a short column of anhydrous sodium sulfate and concentration followed by column chromatography gave 80 mg (100%) of dimethyl 5-(dimethylphenylsilyl)-3-pentene-1,1-dicarboxylate (**2a**) (E : Z=81 : 19): Bp 125 °C/0.1 Torr; ^{1}H NMR δ=0.21 (s, 4.9H), 0.28 (s, 1.1H), 1.66 (dd, J=7.9, 0.8 Hz, 1.62H), 1.75 (dd, J=8.7, 1.1 Hz, 0.38H), 2.53 (dd, J=7.6, 7.6 Hz, 0.38H), 2.57 (dd, J=7.6, 7.6 Hz, 1.62H), 3.25 (t, J=7.6 Hz, 0.19H), 3.66 (t, J=7.6 Hz, 0.81H), 3.70 (s, 4.9H), 3.71 (s, 1.1H), 5.1—5.3 (m, 1H), 5.4—5.6 (m, 1H), 7.3—7.6 (m, 5H); ^{13}C NMR δ=−3.6, (−3.4), (17.7), 21.8 (26.4), 32.0, (47.8), 51.6, (52.2), 52.3, (122.7), 124.2, 127.7, (127.8), (128.3), 128.9, (129.0), (129.1), 129.5, 133.5, 138.5, (143.0), 169.3, (169.5); IR (neat) 2952, 1752, 1737, 1437, 1249, 1156, 837, 731, 699 cm^{-1}; Found: C, 63.98; H, 7.71%. Calcd for $C_{17}H_{24}O_4Si$: C, 63.72; H, 7.55%.

Preparation of Dimethyl 5-(Triphenysilyl)-3-pentene-1,1-dicarboxylate (2b). (E : Z=70 : 30). This compound was obtained (78 mg, 70%) by the reaction between vinylcyclopropane **1** (92 mg, 0.50 mmol) and $Ph_3SiAlMe_3Li$ (1.0 mmol) prepared from Ph_3SiLi[15] and Me_3Al: Bp 250 °C/0.1 Torr; ^{1}H NMR δ=2.29 (d, J=7.9 Hz, 1.4H), 2.37 (d, J=7.4 Hz, 0.6H), 2.46 (dd, J=7.3, 7.3 Hz, 0.6H), 2.50 (dd, J=7.3, 7.3 Hz, 1.4H), 3.07 (t, J=7.3 Hz, 0.3H), 3.23 (t, J=7.3 Hz, 0.7H), 3.59 (s, 4.2H), 3.66 (s, 1.8H), 5.2—5.4 (m, 1H), 5.5—5.8 (m, 1H), 7.3—7.7 (m, 15H); ^{13}C NMR δ=(13.8), 19.4, (25.8), 32.1, 51.9, 52.3, 125.8, 127.8, 128.6, 129.5, 134.5, 135.7, 169.3; IR (neat) 3066, 3046, 3018, 2950, 1753, 1736, 1429, 1234, 1156, 1111, 967, 734, 700 cm^{-1}; Found: C, 73.09; H, 6.23%. Calcd for $C_{27}H_{28}O_4Si$: C, 72.94; H, 6.23%.

Preparation of Dimethyl 5-(Triphenylstannyl)-3-hexene-1,1-dicarboxylate (5). A hexane solution of diethylzinc (1.5 M, 0.24 ml, 0.35 mmol) was added to a THF solution of triphenylstannane (0.25 g, 0.70 mmol) at 0 °C under argon atmosphere. After stirring for 15 min, a solution of **4** (70 mg, 0.35 mmol) in THF (2 ml) was added. The reaction mixture was stirred for 30 min and poured into aqueous ammonium chloride (10 ml). Aqueous layer was extracted with dichloromethane. Organic layers were combined, washed with aqueous ammonium chloride and dried over anhydrous sodium sulfate. The solvent was removed and the residue was submitted to preparative TLC on silica

gel (hexane-ethyl acetate, 5 : 1) to give **5** (0.14 g, 74%, E : Z = 90 : 10) as a white solid: mp 63—66 °C (CH_2Cl_2); ^{1}H NMR δ=1.32 (dd, J=7.3, 1.5 Hz, 0.3H), 1.48 (d, J=7.3 Hz, 2.7H), 2.5—2.9 (m, 3H), 3.63 (s, 2.7H), 3.64 (s, 2.7H), 3.66 (s, 0.3H), 3.72 (s, 0.3H), 5.2—5.4 (m, 1H), 5.9—6.2 (m, 1H), 7.3—7.5 (m, 15H); ^{13}C NMR δ=16.9, 26.6, 32.1, 52.2, 52.3, 120.2, (128.0), 128.5, (128.8), 128.9, (136.9), 137.2, (137.4), 137.6, (137.8), 137.9, 138.1, 169.4; IR (neat) 2920, 2825, 1750, 1727, 1460, 1426, 1237, 1207, 1071, 971, 723, 697 cm^{-1}; Found: C, 61.29; H, 5.42%. Calcd for $C_{28}H_{30}O_4Sn$: C, 61.23; H, 5.51%.

Ethyl 6-(Dimethylphenylsilyl)-2-tosyl-4-hexenoate (7). (E : Z = 79 : 21): Bp 190 °C/0.1 Torr; ^{1}H NMR δ=0.21 (s, 4.74H), 0.27 (s, 1.26H), 1.12 (t, J=7.1 Hz, 2.37H), 1.13 (t, J=7.1 Hz, 0.63H), 1.63 (d, J=8.3 Hz, 1.58H), 1.73 (d, J=8.3 Hz, 0.42H), 2.44 (s, 3H), 2.5—2.8 (m, 2H), 3.75 (dd, J=8.6, 6.9 Hz, 0.21H), 3.88 (dd, J=11.2, 4.0 Hz, 0.79H), 4.0—4.2 (m, 2H), 5.0—5.2 (m, 1H), 5.4—5.6 (m, 1H), 7.1—7.6 (m, 9H); ^{13}C NMR δ=−3.6, 13.8, 21.6, 21.9, 30.1, 61.9, 70.8, 121.7, 127.7, 129.0, 129.3, 129.6, 131.1, 133.4, 134.1, 138.2, 145.3, 165.5; IR (neat) 2954, 1739, 1597, 1427, 1370, 1326, 1249, 1248, 1085, 837, 815, 731, 664, 572 cm^{-1}; Found: C, 64.33; H, 7.13%. Calcd for $C_{23}H_{30}O_4SSi$: C, 64.15; H, 7.02%.

A Mixture of Dimethyl (*E*)-3-(Dimethylphenylsilyl)-5-phenyl-4-pentene-1,1-dicarboxylate (9) and Dimethyl (*E*)-5-(Dimethylphenylsilyl)-5-phenyl-3-pentene-1,1-dicarboxylate (10) and (9 : 10 = 72 : 28): Bp 190 °C/0.1 Torr; ^{1}H NMR δ=0.21 (s, 0.84H), 0.24 (s, 0.84H), 0.33 (s, 2.16H), 0.35 (s, 2.16H), 1.9—2.1 (m, 1.44H), 2.25 (dd, J=11.0, 10.0 Hz, 0.72H), 2.62 (dd, J=7.5, 7.3 Hz, 0.56H), 3.08 (d, J=10.0 Hz, 0.28H), 3.37 (t, J=7.3 Hz, 0.72H), 3.49 (dd, J=9.5, 4.5 Hz, 0.28H), 3.61 (s, 2.16H), 3.65 (s, 0.84H), 3.70 (s, 2.16H), 3.71 (s, 0.84H), 5.29 (dt, J = 15.2, 7.5 Hz, 0.28H), 5.88 (dd, J=15.2, 10.0 Hz, 0.28H), 5.97 (dd, J=15.6, 9.0 Hz, 0.72H), 6.23 (d, J=15.6 Hz, 0.72H), 7.0—7.7 (m, 10H); ^{13}C NMR δ=−5.2, −4.5, (−4.41), (−4.36), 28.6, (32.05), 32.14, (42.5), 51.1, (52.0), 52.3, 52.4, (77.7), (124.2), (124.7), 125.7, 126.7, (127.3), 127.4, 127.8, 128.1, (128.4), 128.4, (129.1), 129.3, 129.6, 130.1, (132.9), 134.0, 134.2, (136.5), 137.7, 141.7, (169.3), (169.45), 169.54, 170.1; IR (neat) 2952, 1751, 1736, 1435, 1250, 1153, 832, 814, 700 cm^{-1}; Found: C, 69.78; H, 7.14%. Calcd for $C_{23}H_{28}O_4Si$: C, 69.66; H, 7.12%.

Ethyl 8-(Dimethylphenylsilyl)-2-tosyl-4,6-octadienoate (13): Bp 210 °C/0.1 Torr; ^{1}H NMR δ=0.2—0.3 (m, 6H), 1.1—1.2 (m, 3H), 1.6—1.9 (m, 2H), 2.46 (s, 3H), 2.5—2.9 (m, 2H), 3.8—4.3 (m 3H), 4.7—6.3 (m, 4H), 7.2—7.9 (m, 9H); ^{13}C NMR δ=−3.4, 13.9, 13.9, 21.7, 22.6, 30.1, 62.1, 70.4, 70.5, 73.0, 121.7, 127.0, 127.6, 127.7, 127.8, 128.6, 128.95, 129.04, 129.2, 129.3, 129.4, 129.5, 129.6, 131.2, 132.5, 133.9, 134.1, 134.9, 145.3, 165.5; IR (neat) 2956, 1738, 1598, 1428, 1327, 1148, 1085, 989, 835, 815, 700, 667 cm^{-1}; Found: C, 65.51; H, 7.10%. Calcd for $C_{25}H_{32}O_4SSi$: C, 65.75; H, 7.06%.

A Mixture of Dimethyl 5-(Dimethylphenylsilyl)-7-phenyl-3,6-heptadiene-1,1-dicarboxylate (15) and Dimethyl 3-(Dimethylphenylsilyl)-7-phenyl-4,6-heptadiene-1,1-dicarboxylate (16) (15 : 16 = 1 : 1): Bp 200 °C/0.2 Torr; ^{1}H NMR δ=0.30 (s, 1.5H), 0.31 (s, 1.5H), 0.31 (s, 1.5H), 0.33 (s, 1.5H), 1.8—2.0 (m, 1.0H), 2.20 (dd, J=11.4, 9.9 Hz, 0.5H), 2.62 (dd, J=7.3, 7.0 Hz, 1.0H), 2.76 (ddd, J=8.8, 4.4, 4.2 Hz, 0.5H), 3.38 (t, J=7.3 Hz, 0.5H), 3.4−3.5 (m, 0.5H), 3.64 (s, 1.5H), 3.68 (s, 3.0H), 3.70 (s, 1.5H), 5.21 (dt, J=16.2, 7.0 Hz, 0.5H), 5.5—5.6 (m, 0.5H), 5.63 (dd, J=16.2, 6.7 Hz, 0.5H), 6.04 (dd, J=15.2, 10.2 Hz, 0.5H), 6.1—6.2 (m, 1.0H), 6.39 (d, J=15.6 Hz, 0.5H), 6.73 (dd, J=15.6, 10.2 Hz, 0.5H), 7.0—7.6 (m, 10H); ^{13}C NMR δ=−5.2, −4.8, 28.6, 32.2, 39.6, 51.1, 52.1, 52.4, 52.5, 123.7, 125.7, 126.0, 126.5, 127.1, 127.6, 127.7, 127.8, 128.4, 128.6, 129.2, 129.48, 129.53, 130.6, 132.0, 134.05, 134.10, 134.7, 169.3, 169.5, 170.2; IR (neat) 3020, 2952, 1752, 1736, 1434, 1249, 1154, 1114, 832, 812, 735, 698 cm^{-1}; Found: C, 70.53; H, 7.22%. Calcd for $C_{25}H_{30}O_4Si$: C, 71.05; H, 7.16%.

Reaction of Dimethyl 2-(3-Methyl-1,3-butadienyl)-1,1-cyclopropanedicarboxylate (17) with $PhMe_2SiAlEt_3Li$. Treatment of **17** (0.13 g, 0.58 mmol) with $PhMe_2SiAlMe_3Li$ (1.5 mmol) afforded a mixture of dimethyl (3*E*)-5-(dimethylphenylsilyl)-6-methyl-3,6-heptadiene-1,1-dicarboxylate (**18**) and (4*E*)-3-(dimethylphenylsilyl)-6-methyl-4,6-heptadiene-1,1-dicarboxylate (**19**) (**18** : **19** = 31 : 69, 76 mg, 37%): bp 130 °C/0.1 Torr; ^{1}H NMR δ=0.28 (s, 0.93H), 0.28 (s, 0.93H), 0.29 (s, 2.07H), 0.30 (s, 2.07H), 1.58 (s, 0.93H), 1.78 (s, 2.07H), 1.80 (d, J=10.1 Hz, 0.31H), 1.8—2.0 (m, 0.69), 2.1—2.3 (m, 0.69H), 2.5—2.7 (m, 1.31H), 3.3—3.5 (m, 1H), 3.66 (s, 2.07H), 3.70 (s, 2.07H), 3.71 (s, 0.93H), 3.72 (s, 0.93H), 4.47 (bs, 0.31H), 4.66 (m, 0.31H), 4.81 (bs, 1.38H), 5.17 (dt, J=15.1, 7.1 Hz, 0.31H), 5.34 (dd, J=15.8, 9.3 Hz, 0.69H), 5.64 (dd, J=15.1, 10.1 Hz, 0.31H), 5.97 (d, J=15.8 Hz, 0.69H), 7.3—7.6 (m, 5H); ^{13}C NMR δ=−5.2, −4.5, (−4.3), 18.8, 28.5, 31.6, (32.1), (43.7), 52.0, (52.1), (52.3), 52.4 (108.5), 113.9, (123.4), 127.5, 127.7, (128.8), 128.95), (129.02), 129.2, 129.8, (129.9), (132.6), 132.7, (133.5), 134.0, 134.1, (136.6), 141.9, 169.4, (169.6), 170.2; IR (neat) 2954, 1754, 1737, 1435, 1250, 1155, 1115, 833, 816, 776, 735, 701 cm^{-1}; Found: C, 66.43; H, 7.87%. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83%.

(2*E*)-1-(Dimethylphenylsilyl)-4-tosylamino-2-pentene (21): Bp 170—180 °C/0.1 Torr; ^{1}H NMR δ=0.20 (s, 6H), 1.11 (d, J=6.7 Hz, 3H), 1.54 (d, J=7.9 Hz, 2H), 2.40 (s, 3H), 3.77 (ddq, J=7.0, 6.7, 6.7 Hz, 1H), 4.62 (d, J=7.0 Hz, 1H), 5.02 (ddt, J=15.2, 6.7, 1.2 Hz, 1H), 5.38 (ddt, J=15.2, 7.9, 1.0 Hz, 1H), 7.25 (d, J=8.1 Hz, 1H), 7.3—7.5 (m, 5H), 7.73 (d, J=8.1 Hz, 2H); ^{13}C NMR δ=−3.6, 21.4, 21.5, 22.3, 51.6, 127.1, 127.6, 127.7, 129.0, 129.4, 129.7, 133.5, 138.0, 138.2, 143.0; IR (neat) 3272, 2956, 1657, 1598, 1426, 1325, 1249, 1159, 1113, 1095, 1066, 965, 836, 813, 698, 663 cm^{-1}; Found: C, 64.11; H, 7.33; N, 3.68%. Calcd for $C_{20}H_{27}NO_2SSi$: C, 64.30; H, 7.28; N, 3.75%.

(2*E*,4*E*)-1-(Dimethylphenylsilyl)-6-tosylamino-2,4-heptadiene (23): Bp 220 °C/0.1 Torr (partially decomposed); ^{1}H NMR δ=0.26 (s, 6H), 1.18 (d, J=6.7 Hz, 3H), 1.74 (d, J=7.8 Hz, 2H), 2.40 (s, 3H), 3.94 (ddq, J=7.2, 6.5, 6.7 Hz, 1H), 4.28 (d, J=7.2 Hz, 1H), 5.20 (dd, J=15.1, 6.5 Hz, 1H), 5.59 (dt, J=15.0, 7.8 Hz, 1H), 5.74 (dd, J=15.0, 9.5 Hz, 1H), 5.92 (dd, J=15.1, 9.5 Hz, 1H), 7.28 (d, J=8.2 Hz, 2H), 7.3—7.6 (m, 5H), 7.75 (d, J=8.2 Hz, 2H); IR (neat) 3270, 2956, 1736, 1427, 1327, 1249, 1158, 1116, 1094, 833, 813, 700, 665 cm^{-1}; Found: C, 65.70; H, 7.38; N, 3.30%. Calcd for $C_{22}H_{29}NO_2SSi$: C, 66.12; H, 7.31; N, 3.50%.

Reaction of 2-(4-Phenyl-1,3-butadienyl)-3-methyl-1-tosylaziridine (24) with $PhMe_2SiAlEt_3tLi$. Reaction between **24** (89 mg, 0.26 mmol) and $PhMe_2SiAlEt_3Li$ (1.0 mmol)

afforded a mixture of 3-(dimethylphenylsilyl)-1-phenyl-6-tosylamino-1,4-heptadiene (**25**) and 5-(dimethylphenylsilyl)-1-phenyl-6-tosylamino-1,3-heptadiene (**26**) (**25** : **26**=40 : 60, 63 mg, 46%): bp 250 °C/0.1 Torr; ^{1}H NMR δ= 0.24 (s, 2.4H), 0.26 (s, 1.8H), 0.27 (s, 1.8H), 1.11 (d, J = 6.7 Hz, 1.8H), 1.13 (d, J=6.7 Hz, 1.2H), 2.2—2.4 (m, 0.4H), 2.32 (s, 1.8H), 2.43 (s, 1.2H), 2.61 (dd, J=7.8, 6.7 Hz, 0.6H), 3.5—3.7 (m, 0.4H), 3.84 (ddq, J=7.2, 6.7, 6.7 Hz, 0.6H), 4.30 (d, J=7.2 Hz, 0.6H), 4.50 (d, J=8.9 Hz, 0.4H), 4.93 (ddd, J =15.4, 6.7, 1.0 Hz, 0.6H), 5.3—5.5 (m, 0.4H), 5.51 (ddd, J =15.4, 8.9, 1.0 Hz, 0.6H), 5.9—6.2 (m, 1.2H), 6.2—6.6 (m, 1.2H), 7.1 — 7.8 (m, 9.0H); ^{13}C NMR δ=−5.2, −4.7, (−4.2), (−3.9), (19.7), 21.4, (21.5), 22.2, (36.5), 39.6, (50.4), 51.6, (123.9), 124.0, (125.6), 125.7, (126.5), 126.6, (127.0), 127.1, (127.5), 127.7, (127.9), 128.5, 128.8, 128.9, 129.4, 129.5, (129.59), (129.64), 130.1, (131.7), (133.0), (133.3), (133.8), 134.1, 136.4, (136.5), (137.3), 137.9, 138.1, (138.2), (139.1), 143.0, (143.1); IR (neat) 3446 (br, w), 3270, 2956, 1736, 1598, 1427, 1325, 1249, 1160, 1114, 1094, 1071, 969, 812, 698, 664; Found: C, 70.08; H, 7.08; N, 2.78%. Calcd for $C_{28}H_{33}NO_2SSi$: C, 70.69; H, 6.99; N, 2.94%.

General Method for the Preparation of π-Allylpalladium Complexes from 2-Alkenylsilanes and 2,4-Dienylsilanes with [PdCl$_2$(CH$_3$CN)$_2$]. The preparation of di-μ-chloro-bis[1,3-η-[5,5-bis(methoxycarbonyl)-2-pentenyl]-palladium(II)] (**27**) is representative. To a THF solution (2 ml) of dimethyl 5-(triphenylstannyl)-3-pentene-1,1-dicarboxylate (**3**) (0.20 g, 0.37 mmol) was added in one portion bis(acetonitrile)dichloropalladium(II) (0.10 g, 0.40 mmol) at room temperature under argon atmosphere. The resulting orange-yellow suspension was stirred for 1 h. The reaction mixture was subjected to column chromatography[15] (hexane-ethyl acetate, 1 : 1). Crude product was repurified by column chromatography to give 26 mg (0.07 mmol, 21% yield) of **27** as yellow crystals from CH_2Cl_2: mp 153.5—154 °C; ^{1}H NMR δ= 2.1—2.4 (m, 2H), 2.87 (d, J = 12.0 Hz, 1H), 3.6—3.8 (m, 2H), 3.73 (s, 3H), 3.75 (s, 3H), 3.94 (d, J = 6.7 Hz, 1H), 5.35 (ddd, J=12.0, 6.9, 6.7 Hz, 1H); ^{13}C NMR δ=31.2, 50.3, 52.6, 52.6, 59.8, 80.0, 111.2, 168.6, 168.8; IR (Nujol): 1731, 1294, 1212, 1154, 1025 cm^{-1}; Found: C, 33.35; H, 4.06%. Calcd for $C_{18}H_{26}Cl_2O_8Pd_2$: C, 33.05; H, 4.01%.

Di-μ-chloro-bis[1-3-η-(5-ethoxycarbonyl-5-tosyl-2-pentenyl)palladium(II)] (28) (Mixture of Diastereomers (6 : 4)): Mp 60 °C (CH_2Cl_2); ^{1}H NMR δ=1.14 (t, J=7.3 Hz, 1.2H), 1.18 (t, J=7.2 Hz, 1.8H), 2.1—2.6 (m, 2H), 2.46 (s, 3H), 2.87 (d, J= 11.9 Hz, 0.6H), 2.92 (d, J= 11.9 Hz, 0.4H), 3.54 (dt, J=11.1, 6.3 Hz, 0.6H), 3.83 (dt, J=11.1, 6.3 Hz, 0.4H), 3.95 (d, J=6.3 Hz, 0.6H), 3.98 (d, J=6.3 Hz, 0.4H), 4.13 (q, J=7.3 Hz, 0.8H), 4.15 (q, J=7.2 Hz, 11.2H), 4.26 (dd, J=7.3, 6.7 Hz, 0.4H), 4.36 (dd, J=11.0, 3.9 Hz, 0.6H), 5.33 (ddd, J=11.9, 11.1, 6.3 Hz, 0.6H), 5.36 (ddd, J =11.9, 11.1, 6.3 Hz, 0.4H), 7.39 (d, J=8.3 Hz, 2H), 7.78 (d, J=8.3 Hz, 2H); ^{13}C NMR δ=(13.8), 13.9, 21.7, (29.2), 29.4, 60.3, (60.4), 62.4, 68.5, (69.0), 76.3, 77.8, (78.8), (111.0), 111.4, 129.2, (129.3), 129.8, (134.1), 145.6, 165.2; IR (neat) 2980, 2934, 1736, 1597, 1446, 1370, 1325, 1247, 1148, 1084, 1046, 814, 716, 668 cm^{-1}; Found: C, 41.16; H, 4.29%. Calcd for $C_{30}H_{38}Cl_2O_8S_2Pd_2$: C, 41.20; H, 4.38%.

Di-μ-chloro-bis[1-3-η-[5,5-bis(methoxycarbonyl)-1-phenyl-2-pentenyl]palladium(II)] (29, 80% from a mixture of **9** and **10**): Mp 195 °C (decomp) (CH_2Cl_2); ^{1}H NMR δ=2.2—2.4 (m, 2H), 3.6—3.9 (m, 2H), 3.73 (s, 6H), 4.47 (d, J= 11.4 Hz, 1H), 5.70 (dd, J= 11.4, 10.8 Hz, 1H), 7.2—7.4 (m, 5H); ^{13}C NMR δ=31.3, 50.5, 52.7, 52.7, 77.7, 78.8, 106.9, 128.0, 128.4, 129.0, 168.7, 168.9; IR (Nujol) 1750, 1733, 1282, 1222, 1147, 690 cm^{-1}; Found: C, 44.67; H, 4.31%. Calcd for $C_{30}H_{34}O_8Cl_2Pd_2$: C, 44.69; H, 4.25%.

Di-μ-chloro-bis[1-3-η-(7-ethoxycarbonyl-7-tosyl-2,4-heptadienyl)palladium(II)] (30) (1 : 1 Diastereomeric Mixture, Very Unstable): Mp 80 °C (decomp) (CH_2Cl_2); ^{1}H NMR δ=1.14 (t, J=7.0 Hz, 1.5H), 1.16 (t, J=7.0 Hz, 1.5H), 2.46 (s, 3H), 2.5—2.7 (m, 2H), 2.89 (d, J=11.7 Hz, 1H), 3.86 (d, J=6.7 Hz, 1H), 3.98 (dd, J=9.1, 6.0 Hz, 1H), 4.0—4.5 (m, 3H), 5.23 (ddd, J=11.7, 10.2, 6.7 Hz, 1H), 5.73 (dd, J=15.5, 9.5 Hz, 1H), 5.8—6.1 (m, 1H), 7.37 (d, J=7.9 Hz, 2H), 7.75 (d, J=7.9 Hz, 2H); IR (benzene) 1736, 1597, 1326, 1147, 1084 cm^{-1}.

Di-μ-chloro-bis[3-5-η-[7,7-bis(methoxycarbonyl)-1-phenyl-1,3-hephadienyl]palladium(II)] (31) (from a mixture of 15 and 16): Mp 80 °C (decomp) (CH_2Cl_2); ^{1}H NMR δ=1.5—1.7 (m, 1H), 2.1—2.3 (m, 1H), 3.5—3.8 (m, 2H), 4.47 (dd, J=15.6, 10.3 Hz, 1H), 5.31 (dd, J=11.5, 10.3 Hz, 1H), 6.31 (dd, J=15.6, 10.3 Hz, 1H), 6.99 (d, J=15.6 Hz, 1H), 7.2—7.6 (m, 5H); IR (CH_2Cl_2) 2922, 2842, 1730, 1433, 1261 cm^{-1}.

A Mixtrure of Di-μ-chloro-bis[1-3-η-[7,7-bis(methoxycarbonyl)-2-methyl-2,4-heptadienyl] palladium(II)] (32) and Di-μ-chloro-bis[3-5-η-[7,7-bis(carbomethoxy)-2-methyl-1,3-heptadienyl]palladium(II)] (33) (32 : 33 = 3 : 1): Mp 80 °C (decomp) (CH_2Cl_2); ^{1}H NMR δ=1.97 (s, 0.75H), 2.1—2.4 (m, 0.25H), 2.13 (s, 2.25H), 2.46 (dd, J= 7.3, 7.3 Hz, 0.25H), 2.53 (dd, J= 7.3, 7.1 Hz, 1.50H), 2.74 (s, 0.75H), 3.49 (t, J=7.3 Hz, 0.75H), 3.5—3.6 (m, 0.25H), 3.7—3.8 (m, 0.25H), 3.74 (s, 0.75H), 3.75 (s, 4.50H), 3.77 (s, 0.75H), 3.80 (s, 0.75H), 4.19 (d, J=10.3 Hz, 0.75H), 4.25 (d, J=11.1 Hz, 0.25H), 5.26 (dd, J=11.4, 11.1 Hz, 0.25H), 5.42 (s, 0.25H), 5.53 (s, 0.25H), 5.89 (dd, J=15.4, 10.4 Hz, 0.75H), 6.12 (dt, J=15.4, 7.1 Hz, 0.75H); ^{13}C NMR δ=18.8, 32.8, 49.3, 50.5, 50.9, 52.58, 52.63, 52.7, 60.2, 67.2, 76.6, 83.8, 102.6, 120.1, 129.6, 135.0, 135.1, 169.0, 169.1; IR (neat) 2952, 2254, 2236, 1732, 1436, 1343, 1266, 1230, 1157, 1026, 969, 914, 731 cm^{-1}; Found: C, 39.15; H, 4.83%. Calcd for $C_{24}H_{34}Cl_2O_8Pd_2$: C, 39.26; H, 4.67%.

Di-μ-chloro-bis[1-3-η-(4-tosylamino-2-pentenyl)palladium(II)] (34) (55 : 45 Diastereomeric Mixture): Mp 58 °C (CH_2Cl_2); ^{1}H NMR δ= 1.21 (d, J = 7.0 Hz, 1.65H), 1.26 (d, J=6.7 Hz, 1.35H), 2.43 (s, 3H), 2.94 (d, J=11.8 Hz, 0.45H), 2.97 (d, J=12.2 Hz, 0.55H), 3.3—3.6 (m, 1H), 3.60 (dd, J=10.8, 2.2 Hz, 0.55H), 3.73 (dd, J=11.1, 3.1 Hz, 0.45H), 4.01 (d, J = 6.7 Hz, 0.45H), 4.07 (d, J = 6.7 Hz, 0.55H), 4.96 (d, J=8.8 Hz, 0.55H), 5.33 (ddd, J=11.8, 11.1, 6.7 Hz, 0.45H), 5.38 (d, J=8.0 Hz, 0.45H), 5.60 (ddd, J= 12.2, 10.8, 6.7 Hz, 0.55H), 7.32 (d, J=8.3 Hz, 2H), 7.79 (d, J = 8.3 Hz, 1.10H), 7.80 (d, J = 8.3 Hz, 0.90H); ^{13}C NMR (benzene) δ=14.7, 20.0, 21.3, 21.6, 50.4, 50.8, 60.6, 60.9, 61.3, 87.9, 88.9, 108.6, 109.1, 127.3, 127.7, 127.8, 128.3, 128.8, 130.4, 139.7, 140.2, 143.5, 143.6; IR (benzene) 3274 (br.m), 1597, 1412, 1332, 1158, 1091, 967, 814 cm^{-1}; Found: C, 39.38; H, 4.59; N, 4.01%. Calcd for $C_{24}H_{32}Cl_2N_2O_4S_2Pd_2$: C, 37.91; H, 4.24; N, 3.68%.

Di-μ-chloro-bis[3-5-η-(1-phenyl-6-tosylamino-1,3-heptadienyl)palladium(II)] and Its Unidentified Isomers

(35): The compound is so unstable and the crude product was used directly for further transformation (see below).

4,4-Bis(methoxycarbonyl)-3-isopropenylcyclopentene (36). Treatment of **32** (36 mg, 0.08 mmol) with PPh_3 (87 mg, 0.3 mmol) in DMSO (2 ml) at 60 °C for 1 h gave **36** (15 mg, 70% yield) which was identical with a sample prepared by the Pd(0) promoted vinylcyclopropane-cyclopentene rearrangenent method.[5] The use of Na_2CO_3 (10 equiv) and anhydrous LiCl (10 equiv)[16] instead of PPh_3 also gave **36** in 80% yield.

4,4-Bis(methoxycarbonyl)-3-styrylcyclopentene (37). Na_2CO_3 (35 mg, 0.35 mmol) and LiCl (15 mg, 0.35 mmol) were added to a solution of **31** (15 mg, 0.035 mmol) in DMSO (1 ml) and the resulting mixture was heated at 60 °C for 3 h to give **37**[5] (11 mg, 95% yield).

General Procedure for the Transformation of Dienylsilanes into Pyrroline Derivatives via Alkenyl-substituted π-Allylpalladiums. The crude product **35** (^{1}H NMR δ=1.5—1.7 (m, 1H), 2.1—2.3 (m, 1H), 3.5—3.8 (m, 2H), 4.47 (dd, J=11.5, 10.3 Hz, 1H), 5.31 (dd, J=11.5, 10.3 Hz, 1H), 6.31 (dd, J=15.6, 10.3 Hz, 1H), 6.99 (d, J=15.6 Hz, 1H), 7.2—7.6 (m, 5H)) derived from a mixture of **25** and **26** (32 mg, 0.07 mmol) and $[PdCl_2(CH_3CN)_2]$ (20 mg, 0.08 mmol) was dissolved in 2 ml of dimethyl sulfoxide under argon atmosphere. To this yellow solution was added triphenylphosphine (15 mg, 0.057 mmol). The reaction mixtrure was heated at 63 °C overnight. Resulting dark brown suspension was poured into water and extracted with ether. Purification by preparative TLC on silica gel (hexane-ethyl acetate, 5 : 1) gave 1-tosyl-2-(*E*)-2-styryl-5-methyl-3-pyrroline (**38**, cis : trans = 85 : 15, 0.012 mmol, 18% overall yield from dienylsilane) as colorless crystals: mp 145 °C (CH_2Cl_2); ^{1}H NMR δ=1.42 (d, J=6.5 Hz, 2.55H), 1.55 (d, J=6.3 Hz, 0.45H), 2.33 (s, 0.45H), 2.37 (s, 2.55H), 4.58 (ddq, J=1.8, 0.9, 6.5 Hz, 0.85H), 4.6—4.8 (m, 0.15H), 5.05 (dm, J=7.1 Hz, 0.85H), 5.1—5.2 (m, 0.15H), 6.06 (dd, J=15.9, 7.1 Hz, 1H), 6.50 (d, J=15.9 Hz, 0.15H), 6.51 (d, J=15.9 Hz, 0.85H), 7.10 (d, J=8.0 Hz, 0.30H), 7.1—7.4 (m, 6.7H), 7.64 (d, J = 8.0 Hz, 0.30H), 7.74 (d, J = 8.4 Hz, 1.70H); ^{13}C NMR δ= 21.5, 23.8, 63.5, 68.9, 126.6, 127.4, 127.5, 127.7, 128.4, 129.6, 120.0, 131.0, 131.3, 135.8, 136.4, 143.3; IR (CCl_4) 2990, 1740, 1720, 1587, 1492, 1444, 1344, 1167, 1091 cm^{-1}; Found: C, 70.70; H, 6.29; N, 3.88%. Calcd for $C_{20}H_{21}NO_2S$: C, 70.77; H, 6.24; N, 4.13%.

2-Ethenyl-5-methyl-1-tosyl-3-pyrroline (39). (cis: trans = 84 : 16): Mp 63—64 °C (crystallizes after distillation at 150 °C/0.1 Torr); ^{1}H NMR δ=1.38 (d, J=6.5 Hz, 2.52H), 1.43 (d, J=6.3 Hz, 0.48H), 2.41 (s, 3H), 5.51 (ddq, J=1.9, 3.6, 4.5 Hz, 0.84H), 4.6—4.8 (m, 0.16H), 4.8—4.9 (m, 0.84H), 4.9—5.0 (m, 0.16H), 5.13 (dt, J=10.1, 1.1 Hz, 1H), 5.29 (dt, J=10.1, 1.1 Hz, 1H), 5.4—5.7 (m, 2H), 5.83 (ddd, J=17.1, 10.1, 6.7 Hz, 1H), 7.29 (d, J=8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ= (20.1), 21.5, (21.7), 23.8, (63.0), 63.6, 69.2, (69.8), 115.8, (116.0), (116.7), (117.0), 127.3, 127.4, (127.6), (127.7), 129.2, 129.6, 131.0, (131.6), (135.4), 138.8, 143.3; IR (Nujol) 1343, 1182, 1163, 1126, 1091, 1044, 926, 806, 668, 656, 595 cm^{-1}; Found: C, 63.64; H, 6.60; N, 5.09%. Calcd for $C_{14}H_{17}NO_2S$: C, 63.85; H, 6.51; N, 5.32%.

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