Facile Chloropalladation of Vinylcyclopropanes. Isolation of Ring-Opened 1,2,5-η^3-σ,π Chelates as Kinetic Precursors to 1–3-η^3-π-Allyl Final Products

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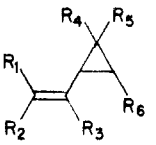
Reactions of vinylcyclopropane (**1a**), isopropenylcyclopropane (**1c**), and α-cyclopropyl-4-fluorostyrene (**1d**) (all are vinylcyclopropanes) with $PdCl_2(PhCN)_2$ in low polarity aprotic media (e.g., $CDCl_3$) leads to rapid cyclopropane chloropalladation with formation of 1,2,5-η^3-σ,π chelates. In one case (**1a**) the precursor to chloropalladation—a π complex that may involve Pd(II)–cyclopropane interaction also—is observed by ^1H and ^{13}C NMR. The 1,2,5-η^3-σ,π complexes rearrange in solution over periods of hours to days to 1–3-η^3-π-allyls. In the case of the 1,2,5-η^3-σ,π complex from **1a**, namely, **6**, allyl formation is accompanied by rearrangement (hydrogen shift). Compound **6** rearranges to a π-allyl also in the solid state, but in this case the hydrogen shift path is not followed. Dynamic NMR experiments conducted on **6** lead to the conclusion that very fast chloropalladation/dechloropalladation occurs in solution, in such a way that the carbon alternately getting and losing chlorine dynamically inverts its configuration. This observation leads to a better understanding of earlier published results for chrysanthemate ester isomerizations catalyzed by $PdCl_2(PhCN)_2$. In the course of the present work, the molecular structures of the following two compounds were determined by X-ray diffraction: bis(μ-chloro)bis(1,2,5-η^3-2-methyl-3-chloro-1-penten-5-yl)dipalladium(II) (**5**) and (acetylacetonato)(1–3-η^3-2-methyl-5-chloro-1-penten-3-yl)palladium(II) (**9**). Crystal data for compound **5**: space group $P\bar{1}$ (no. 2); a = 5.487 (3) Å, b = 11.959 (2) Å, c = 6.902 (2) Å; α = 89.06 (2)°, β = 107.2 (3)°, γ = 106.3 (3)°; V = 414.1 (5) Å^3; Z = 2. The refinement for **5** was based on 1263 reflections with $I > 3\sigma(I)$ with a final R = 3.4% and R_w = 5.2%. Crystal data for compound **9**: space group $P2_1/c$ (no. 14); a = 4.529 (2) Å, b = 17.026 (3) Å, c = 16.580 (3) Å; β = 92.49 (3)°; V = 1277 (1) Å^3; Z = 4. The refinement for **9** was based on 1740 reflections with $I > 3\sigma(I)$ with final R = 3.4% and R_w = 4.4%.

Introduction

Largely as a result of the lability of the three-membered ring vinylcyclopropane (**1a**) and its monocyclic and polycyclic derivatives have received much attention from both



1a: $R_1 = R_6 = H$
b: $R_1 = R_2 = R_4 = R_5 = CH_3$; $R_3 = H$; $R_6 = CO_2H$
c: $R_1 = R_2 = R_4 = R_5 = R_6 = H$; $R_3 = CH_3$
d: $R_1 = R_2 = R_4 = R_5 = R_6 = H$; $R_3 = p\text{-}FC_6H_4$

the organic and the organometallic viewpoints. Early interest in the butadiene–vinylcyclopropane analogy[1-3] and in the vinylcyclopropane to cyclopentene rearrangement[4] led to observations of the influences of both transition metals and non-transition metals on vinylcyclopropane coordination chemistry,[5] rearrangments,[6] ring-opening reactions,[7] and cyclizations to cyclopentenes.[8] The vinylcyclopropane moiety is found in the natural and synthetic chrysanthemate insecticides[9] (ester derivatives of chrysanthemic acid, **1b**). We[10] and others[11] have observed that complexes of palladium dichloride catalyze the conversion of *cis*-chrysanthemate esters to the isomeric trans esters. In the late 1960s, palladium dichloride was reported by two groups[1-3] to cleave the ring in vinylcyclopropanes to give palladium π-allyls. In an effort to relate our observations on the palladium dichloride catalysis of chrysanthemate ester isomerization to the palladium dichloride ring openings of vinylcyclopropanes, we have investigated the time course of reactions of dichlorobis(benzonitrile)palladium(II) (**2**) and dichlorobis(acetonitrile)palladium(II) (**3**) with vinylcyclopropanes **1a**, **1c**, and **1d**. We have ob-

$PdCl_2(C_6H_5CN)_2$ **2** $PdCl_2(CH_3CN)_2$ **3**

served three sequentially formed and structurally distinct products in the reactions of $PdCl_2(RCN)_2$ with the vinylcyclopropanes. These products are described as π-bonded (ring intact), σ,π-bonded (ring opened), and π-allyl (ring opened) (see Schemes I and II). In one case (**1a**) evidence for cyclopropane coordination to Pd(II) is presented, and an intermediate of structure close to this is believed to dynamically mediate the interconversions of the observed structure types.

Prior to this work, only the π-allylic (thermodynamic) products from the chloropalladation of vinylcyclopropanes had been observed,[1-3] although the σ,π product from **1a** was isolated but its correct structure was not recognized.[1,2]

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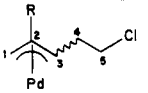
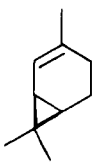
Table I. ^{13}C NMR Results (ppm) for Vinylcyclopropanes 1a, 1c, and 1d and Their $PdCl_2$ Complexes in $CDCl_3$ (50 MHz, Reference Me_4Si)

										
	R = CH_3 (1c)	R = H (1a)	R = p-FC_6H_4 (1d)	R = CH_3 (5)	R = H[a] (6)	R = H[b] (7)	R = CH_3 [8(syn)]	R = H[c] [10(syn)]	R = p-FC_6H_4 12(syn)	R = p-FC_6H_4 12(anti)
C_1	107.6	111.5	108.9	77.1	82.0	74.1	60.9	60.0	61.8	58.8
C_2	146.6	142.5	137.5	127.3	111.0	99.5	124.8	111.1	126.7	122.3
C_3	17.4	14.7	15.7	58.6	62.0	54.8	77.4	80.6	78.8	75.4
C_4	5.1	6.7	6.6	29.2	34.0	23	32.6	35.0	32.8	34.0
C_5	5.1	6.7	6.6	35.4	34.0	33	42.6	42.4	42.8	43.5

[a] From solid ^{13}C NMR. [b] Acetylacetonate derivative of 6. [c] Prepared from 5-chloro-1-pentene.

During the course of this work, Bäckvall and co-workers[12-14] reported that chloropalladation of the vinylcyclopropane moiety in [(+)-car-2-ene] (4) leads also to isolated π-allylic products.



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Experimental Section

General Data. The ^1H NMR spectra were recorded at 200 MHz on a JEOL FX200 spectrometer and at 300 MHz on a Nicolet 300 spectrometer. The ^{13}C spectra in solution were recorded at 50 MHz on the FX200, while the solid ^{13}C spectrum was obtained at 50 MHz by using an in-house built instrument at the California Institute of Technology-NSF Regional NMR Center. Both ^1H and ^{13}C chemical shifts are referenced to tetramethylsilane. ^{13}C and ^1H NMR results are in Tables I and II, respectively. X-ray intensity data were collected at room temperature on an Enraf-Nonius CAD-4 automated diffractometer. Infrared spectra were recorded on a Perkin-Elmer 283 instrument. Reagent grade solvents were used at all times. Palladium chloride was purchased from D. F. Goldsmith Metal Chemical Corp. or was obtained as a loan from Johnson, Matthey, Inc. Dichlorobis(benzonitrile)palladium(II) was prepared by the Kharasch procedure.[15] Bis(μ-chloro)dichlorobis(ethylene)dipalladium(II) was prepared by a literature procedure.[16] Isopropenylcyclopropane (1c) was purchased from Wiley Organics, vinylcyclopropane (1a) was prepared by a literature method,[17] and α-cyclopropyl-4-fluorostyrene (1d) was purchased from the A. Bader Library of Rare Chemicals, Aldrich Chemical Co. 5-Chloropent-1-ene was obtained from Wiley Organics and was used as received. [(+)-Car-2-ene] was purchased from Fluka Chemical Co.

Elemental analysis was performed by MicAnal, Tucson, Az. Molecular weight measurement was done by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of Compounds. α-Cyclopropyl-4-fluorostyrene (1d). The material received from Bader was contaminated with ca. 50% of the cyclopentene isomer. Samples of pure α-cyclopropane-4-fluorostyrene were obtained by dechloropalladation of its palladium π-allyl complex. The latter was prepared by reacting a solution of the mixture obtained from Bader with complex 2 in $CDCl_3$ until rearrangement to the π-allyl complexes was complete. Under these conditions 2 reacts only with 1d and not with the cyclopentene isomer. Thus through repeated crystallizations, pure π-allyl complexes are obtained, and then these are reacted with a large excess of aqueous cyanide ion to liberate pure 1d.

Bis(μ-chloro)bis(1,2,5-η^3-2-methyl-3-chloro-1-penten-5-yl)dipalladium(II) (5), was prepared by chloropalladation of isopropenylcyclopropane (1c). Complex 2 (5.80 g, 32.7 mmol) dissolved in a minimum of $CDCl_3$ was filtered through a cotton plug and was added to a cold solution (ice–acetone bath) of isopropenylcyclopropane (1c) (1.28 g, 15.6 mmol). The mixture was stirred in the cold bath for 90 min. A white solid precipitated which was filtered and washed four times with 10-mL portions of chilled pentane. A total of 2.76 g (10.7 mmol, 68%) of 5 was obtained. Anal. Calcd for $C_{12}H_{20}Pd_2Cl_4$: C, 27.76; H, 3.86. Found: C, 27.71; H, 3.82.

Bis(μ-chloro)bis(1,2,5-η^3-3-chloro-1-penten-5-yl)dipalladium(II) (6). Method A. Solid 2 (0.153 g, 0.40 mmol) was added to a solution of 58 μL of 1a (0.60 mmol) in 2 mL of dichloromethane. The solution was stirred for 75 min. A white precipitate formed (6) which was filtered and washed several times with 2-mL portions of CH_2Cl_2 [yield 0.078 g (0.16 mmol, 80%)].

Method B. In a nitrogen-filled glovebag bis(μ-chloro)dichlorobis(ethylene)dipalladium(II) (1.01 g, 2.5 mmol) suspended in 15 mL of dichloromethane was treated with 700 μL of 1a (7.2 mmol). After 30 min, a white solid formed, which was filtered, washed with CH_2Cl_2, and dried [yield 840 mg of 6 (68%)].

The observed melting point for 6 was 111–113 °C, in good agreement with literature data (110 °C[1]). Molecular weight: 483 g/mol, $CHCl_3$, 24 °C; 500 g/mol, CH_2Cl_2, 37 °C (solution molecular weight measurements were made less than 4 min after sample dissolution, calcd 491.8 g/mol for $C_{10}H_{16}Cl_4Pd_2$). IR: NaCl pellet, 1515 and 1530 cm^{-1}; Nujol, 280, 240 cm^{-1}. The maximum solubility of complex 6 is ~0.01 M in either $CDCl_3$ or CH_2Cl_2.

Because of lability of 6 in solution, suitable crystals for X-ray analysis could not be obtained. We therefore characterized 6 in solution by ^1H NMR (Table II) and in the solid state by CP/MAS ^{13}C NMR (^{13}C data in Table I, solution ^{13}C NMR was not feasible because of lability/poor solubility). During the course of ^1H homonuclear decoupling experiments, it was observed through spin saturation transfer effects that (at least) one pair of protons in 6 is involved in site exchange. Thus, in C_6D_6 at 300 MHz, irradiation at δ 0.47 [4(up)] causes a 58% reduction in the intensity of the peak at δ 1.42 [4(down)]. The T_1 values were also measured (inversion–recovery: T_1[4(up)] = 1.3 s; T_1[4(down)] = 1.1 s.

(Acetylacetonato)(1,2,5-η^3-3-chloro-1-penten-5-yl)palladium(II) (7). Complex 6 (0.0405 g, 0.165 mmol), was treated in chloroform solution with thallium acetylacetonate (0.0442 g, 0.146 mmol). The reaction mixture was stirred for 5 min and was then filtered to remove the thallium chloride precipitate. The solvent was removed in the rotary evaporator, and a pale yellow solid (7) was obtained (0.0476 g, 0.154 mmol, 93%).

Bis(μ-chloro)bis(1-3-η^3-2-methyl-5-chloro-1-penten-3-yl)dipalladium(II) [8(syn)]. Complex 5 (0.286 g, 1.10 mmol) was dissolved in chloroform (~30 mL) and allowed to stand for 4 days at room temperature, at which time the ^1H NMR showed the presence of a single product. A red-orange solution was obtained which was then concentrated in the rotary evaporator and chromatographed on a Florisil column with dichloromethane as eluent. A single orange fraction was collected, and the solvent

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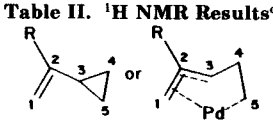
Table II. ^{1}H NMR Results[a]



compd	hydrogens on C1	hydrogens on C2	hydrogens on C3	hydrogens on C4	hydrogens on C5	R
1a	5.08 (d, H_{anti}, J = 17) 4.85 (d, H_{syn}, J = 11)	5.35 (m)	1.42 (m)	0.72 (m, 2 H) and 0.40 (m, 2 H)		...
1c	4.70 (s) 4.66 (s)	...	1.40 (m)	0.62 (m, 2 H) and 0.45 (m, 2 H)		1.60 (s, CH_3)
1d	5.24 (s) 4.92 (s)	...	1.62 (m)	0.86 (m, 2 H) and 0.60 (m, 2 H)		7.58 (m, 2 H) 7.03 (m, 2 H)
5	4.64 (s) 4.31 (s)	...	4.43 (dd, $J_{3,4u}$ = 13, $J_{3,4d}$ = 6)[b]	3 H multiplet at δ 2.40–1.89 1 H multiplet at δ 1.29–1.15		2.21 (s)
6	4.79 (d, H_{anti}, J = 14) 4.53 (d, H_{syn}, J = 8)	5.88 (8 line m, J_{anti} = 14, J_{syn} = 8, $J_{2,3}$ = 5)	4.62 (pentuplet, $J_{3,2}$ = 5, $J_{3,4u}$ = 13, $J_{3,4d}$ = 6)	2 H multiplet at δ 2.15 1 H multiplet at δ 2.03 1 H multiplet at δ 1.17		...
5 (300 MHz, C_6D_6)	3.98 (s) 3.96 (s)		3.68 (Js same as **5** in $CDCl_3$)	1.44, 4u ($J_{4u,5d}$ = $J_{4u,4d}$ = $J_{4u,3}$ = 13, $J_{4u,5u}$ = 8) 0.60, 4d ($J_{4d,5d}$ = $J_{4d,3}$ = 6, $J_{4d,4u}$ = 13)	1.7, 5u ($J_{5u,5d}$ = 8, $J_{5u,4u}$ = 8) 1.85, 5d ($J_{5d,5u}$ = 8, $J_{5d,4u}$ = 13, $J_{5d,4d}$ = 6)	1.96 (s)
6 (300 MHz, C_6D_6)	4.11 (d, H_{syn}, J = 8) 3.97 (d, H_{anti}, J = 14)	5.33 (Js same as **6** in $CDCl_3$)	3.67 (pentuplet, Js same as **6** in $CDCl_3$)	1.42, 4u [All Js identical with those in **5** (C_6D_6)] 0.47, 4d	1.77, 5u [all Js identical with those in **5** (C_6D_6)] 1.87, 5d	...
7[c]	4.58 (d, J_{anti}, J = 14) 4.4 (d, H_{syn}, J = 9)	5.72 (m)	4.65 (m)	multiplet (3 × 1 H) at δ 2.2–1.7[b] 1 H multiplet at δ 1.25		...
8(syn)	3.78 (s, H_{syn}) 2.78 (s, H_{anti})	...	3.53 (t, J = 6.5)	2.3–1.9 (m, 2 H)	3.80 (m, 2 H)	2.15 (s, CH_3)
8(syn) (200 MHz, C_6D_6)	3.44 (s, H_{syn}) 2.22 (s, H_{anti})	...	3.08 (dd, Js = 7.1, 6.3)	1.97 (dd, 1 H, Js = 16.6, 6.3) 1.50 (m, 1 H)	3.48 (m, 2 H)	1.40 (s, CH_3)
9[d] (200 MHz, C_6D_6)	3.37 (s, H_{syn}) 2.31 (s, H_{anti})	...	2.96 (dd, Js = 8, 6)	2.16–1.8 (m, 1 H) 1.74–1.52 (m, 1 H)	3.75–3.68 (m, 2 H)	1.55 (s, CH_3e
10	4.07 (d, H_{syn}, J = 7) 2.95 (d, H_{anti}, J = 12	5.40 (Js = 12, 12, 7)	3.85–3.68 (m, 1 H)	2.27 (m, 1 H) 2.07 (m, 1 H)	3.85–3.68 (m, 2 H)	...
11	4.75 (s, H_{anti}) 4.68 (s, H_{syn})	...	5.05 (dd, Js = 12, 6)	3 H multiplet at δ 2.5–2.1 1 H multiplet at δ 1.5–1.35		7.5 (m, 2 H) 7.15 (m, 2 H)
12(syn)	3.88 (s, H_{syn}) 3.10 (s, H_{anti})	...	3.95 (t, 1 H, J = 6.3)	2.0 (m, 2 H)	3.72 (m, 2 H)	7.55 (m, 2 H) 7.1 (m, 2 H)
12(anti)[e]	4.30 (s, H_{syn}) 3.48 (s, H_{anti})	...	4.81 (t, 1 H, J = 6.3)	2.1 (m, 2 H)	3.72 (m, 2 H)	7.55 (m, 2 H) 7.1 (m, 2 H)

[a] δ referenced to Me_4Si; J in Hz; 200 MHz in $CDCl_3$ unless otherwise stated. [b] Superscripts u (up) and d (down) refer to hydrogens as shown in the ORTEP drawings. [c] For **7**: acac methine, δ 5.3; acac CH_3 (6 H) under the broad δ 2.2–1.7 multiplet. [d] For **9**: acac methine, δ 5.33; acac CH_3, δ 2.0 (s, 3 H), 1.92 (s, 3 H). [e] **13** and **14**—see Experimental Section.

was evaporated in vacuo. A total of 0.0971 g (0.374 mmol, 34%) of orange-yellow solid [8(syn)] was obtained. Anal. Calcd for $C_{12}H_{20}Pd_2Cl_4$: C, 27.76; H, 3.86. Found: C, 27.65; H, 3.69.

(Acetylacetonato)(1-3-η^3-2-methyl-5-chloro-1-penten-3-yl)palladium(II) (9). The π-allyl complex 8 (0.0971 g, 0.374 mmol) dissolved in chloroform was treated with 1 equiv of thallium acetylacetonate (0.1130 g, 0.372 mmol). The reaction mixture was stirred for 5 min and was then filtered to remove the thallium chloride precipitate. The solvent was removed with the rotary evaporator to obtain 0.110 g (0.341 mmol, 91%) of a white solid (9). Complex 9 was characterized by X-ray diffraction (vide infra).

Bis(μ-chloro)bis(1-3-η^3-5-chloro-1-penten-3-yl)dipalladium(II) (10). Palladium chloride (1.018 g, 5.74 mmol), sodium carbonate (10.0 g, 9.4 mmol), and 5-chloropent-1-ene (1.51 g, 14.4 mmol) in chloroform (50 mL) were stirred at room temperature for 48 h. The mixture was filtered, and dark yellow solution was obtained. The solution was concentrated on the rotary evaporator and chromatographed on a Florisil column with dichloromethane as eluent. A bright yellow fraction was collected. Concentration and addition of pentane led to a light yellow crystalline powder (10), 0.296 g (1.21 mmol, 21%). Anal. Calcd for $C_{10}H_{16}Pd_2Cl_4$: C, 24.45; H, 3.26. Found: C, 24.74; H, 3.31.

Bis(μ-chloro)bis[1,2,5-η^3-2-(*p*-fluorophenyl)-3-chloro-1-penten-5-yl]dipalladium(II) (11). This complex was not isolated but was observed by ^{1}H NMR in $CDCl_3$ solution. Solutions of olefin **1d** (0.40 mL, 0.11 M) and nitrile complex **2** (0.25 μL, 0.21 M) were mixed, and at 7-min reaction time, practically complete formation of 11 was observed.

Bis(μ-chloro)bis[1-3-η^3-2-(*p*-fluorophenyl)-5-chloro-1-penten-3-yl]dipalladium(II) [12(syn,anti)]. Compound **1d** (0.0717 g, 0.443 mmol) was reacted with **2** (0.117 g, 0.453 mmol) in chloroform. The solution was allowed to stand at room temperature for 2 days and was then concentrated and chromatographed on Florisil (elution with dichloromethane). The solvent was evaporated, and a bright yellow solid was obtained (0.0850 g, 0.250 mmol, 57%). Every attempt to separate syn from anti failed. Anal. Calcd for $C_{22}H_{22}F_2Pd_2Cl_4$: C, 38.89; H, 3.24. Found: C, 39.05; H, 3.29.

Bis(μ-chloro)bis[1-3-η^3-(1-chloromethyl)-1-buten-3-yl]dipalladium(II) (13). Complex **6** (10 mg) was stirred at 50 °C with 1.0 mL of C_6D_6. After 3 h all of white solid **6** had dissolved and the solution formed was orange. Stirring was continued at 50 °C for an additional 2 h for a total of 5 h. At this time the ^{1}H NMR (200 MHz) of the C_6D_6 solution showed the total absence of **6**, a few percent unidentified material, and ca. 95% **13**. ^{1}H NMR of **13** (200 MHz, C_6D_6): δ 4.37 (dd, H_2, $J_{2,3}$ = 12 Hz, $J_{2,11}$ = 10 Hz), 3.65 (dd, 1 H [chloromethyl], J_{gem} = 12 Hz, J_{toH_1} = 3.8 Hz), 3.55 (dd, 1 H [chloromethyl], J_{gem} = 12 Hz, J_{toH_1} = 10 Hz), 3.16 (dd, H_3, $J_{3,2}$ = 12 Hz, J_{toCH_3} = 6.3 Hz), 3.00 (td, H_1, $J_{1,2}$ = 10 Hz, J_{toCH_2Cl} = 3.8, 10 Hz), 0.93 (d, CH_3, $J_{CH_3,3}$ = 6.3 Hz). The ^{13}C NMR of **13** in $CDCl_3$ follows (assigned by using INEPT[18] pulse sequence): δ 111.6 (C_2); 81.9, 74.0 (C_1, C_3); 43.1 ($ClCH_2$); 17.8 (CH_3).

In order to structurally relate the product of thermal rearrangement of **6** in C_6D_6 to that of rearrangement of **6** in $CDCl_3$, the rearrangement was carried out in C_6D_6 (above), the solvent was removed, and the residue was taken up in $CDCl_3$. The resultant 200-MHz ^{1}H spectrum in $CDCl_3$ indicates that the product is the same (**13**) when the thermal rearrangement is carried out in C_6D_6 or in $CDCl_3$.

All attempts to isolate analytically pure **13** from cold solvents or from mixed solvents led to some decomposition (detected by ^{1}H NMR). Attempted derivative formation by bridge-splitting agents even as weakly basic as pyridine led to immediate decomposition to $PdCl_2(py)_2$ and a mixture of *cis* and *trans*-1,3-pentadienes.

Complex **13** also forms in $\leq$3 min on mixing complex **2** (0.32 M) and a mixture of *cis*- and *trans*-1,3-pentadienes (0.20 M) in $CDCl_3$ at room temperature. The rearrangement of complex **6** (ca. 0.01 M in $CDCl_3$) to allyl **13** was found to have a half-life of 16 h at room temperature.

Catalysis of 6 → 13 + 10 by Complex 2. Reaction of excess complex **2** (125 mg, 0.326 mmol) in 1.0 mL $CDCl_3$ with **1a** (14 mg, 0.20 mmol) resulted in conversion of 50% of **6** (original concentration 0.20 M) to a 1:1 mixture of **13** and **10** in 2.5 h at room temperature. Completion of the reaction after 18 h resulted in a 1.4:1 mixture of **10/13**.

In a control experiment it was found that under conditions with no excess **2** (0.20 M in $CDCl_3$ of both **2** and vinylcyclopropane) that no detectable allyl had formed after 3.7 h. In this same experiment a major portion of the super-saturated **6** precipitated at the 2.5-h point.

Rearrangment of 6 in the Presence of PhCN. Rearrangment of **6** (ca. 0.01 M) in the presence of 1 M PhCN in $CDCl_3$ was found to produce only allyl **13** at a rate indistinguishable from that of the **6** → **13** rearrangement in the absence of PhCN.

Attempted Interconversion of Allyls 10 and 13. Under the conditions of our experiments (up to 0.2 M concentration in $CDCl_3$), it is found that the conversions **10** → **13** or **13** → **10** do not occur in $CDCl_3$, $CDCl_3$/PhCN, or $CDCl_3/PdCl_2(PhCN)_2$.

Observation of "Pre-Ring-Opened" Complex of 2 and Vinylcyclopropane (1a). The rapid "NMR titration" described in a later section was utilized to demonstrate observable complexation of **1a** by **2** to form an adduct **14** prior to ring opening. During the titration it was observed that the resonance for H_2 of **1a** moved from δ 5.35 to δ 5.95 (with some broadening), that $H_{1,syn}$ and $H_{1,anti}$ were essentially unaffected, that all hydrogens on C_4, C_5 broadened slightly and moved stepwise to the same chemical shift at δ 1.2, and that H_3 moved to δ 1.6. At the end of the experiment (ca. 20 min) peaks for ring-opened **6** were noticeable.

^{13}C NMR of Adduct 14. To complex **2** (76.7 mg, 0.20 mmol) in 1.0 mL of CD_2Cl_2 (99.6%) was added 19.4 μL of **1a** (13.6 mg, 0.20 mmol). The solution in the NMR tube was cooled in $\leq$5 min to −21 °C in the NMR instrument (Nicolet 300, 75-MHz ^{13}C). After 75-min data acquisition at −21 °C, the following peaks (which were not assignable to PhCN or $PdCl_2(PhCN)_2$) were observed: δ 79.5 (C_1), 135.5 (C_2), 18.3 (C_3), 12.5 (C_4, C_5, br). Note that essentially all the PhCN present is uncoordinated. Only a trace $PdCl_2(PhCN)_2$ was detected. The assignments are made by analogy to a Ag^+·vinylcyclopropane experiment to be described next. Two other low-temperature experiments in $CDCl_3$ gave essentially the same results. In all experiments 20–30% conversion to **6** at the end of the experiment was observed.

NMR of 1:1 Ag(F_3CSO_3) and 1a. Af(F_3CSO_3) (56.7 mg, 0.221 mmol) was added to 400 μL of $CDCl_3$ in an NMR tube, and there appeared to be no dissolution. Addition of 22 μL of **1a** (15.4 mg, 0.226 mmol) to the tube led to immediate dissolution of the Ag(F_3CSO_3) upon shaking (a colorless solution). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.93 (m, H_2), 5.22 (d, H_{1anti}, $J_{1anti,2}$ = 16.5 Hz), 5.04 (d, H_{1syn} $J_{1syn,2}$ = 9.0 Hz), 1.57 (m, H_3), 0.93 (m, 2 H), 1.63 (m, 2 H). Homonuclear decoupling also revealed $J_{2,3}$ = 9.0 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, assignments made by off-resonance decoupling): δ 97.7 (C_1), 142.8 (C_2), 15.5 (C_3), 9.6 (C_4, C_5).

Rearrangement of 6 to 10 in the Solid State. It was observed that a sample of solid **6** which had been stored at room temperature for 1 year was converted quantitatively to **10** (after 1 year the ^{1}H NMR was identical with that of **10** prepared from 5-chloro-pent-1-ene). At the same time it was noted that a one-year-old sample of **6** which was stored in the freezer at −26 °C was indeed still **6**. A few milligrams of **6** was heated to 50 °C for 4 days (in the dark). After 4 days, ^{1}H NMR of the soluble portion of the product showed a 50:50 mixture of **6/10** (no **13**). Finally, rearrangment of homogeneous solutions of **6** leads essentially exclusively to allyl **13**, while rearrangment of dissolved **6** (ca. 0.5 mL, 0.01 M) with excess solid **6** present (ca. 10 mg of solid *6*) gave a 1:1 mixture of **10/13** after 5 days at room temperature.

^{1}H NMR Titrations. (a) Isopropenylcyclopropane (1c). A total of 0.4 mL of a solution 4.18×10^{-1} M in $CDCl_3$ of **1c** was placed in an NMR sample tube, and the instrument (JEOL FX200) was tuned with this sample. Ten 0.1-mL portions of a solution 2.05×10^{-1} M **2** in $CDCl_3$ were added to the **1c** solution. After each addition, five-pulse 1K spectra were acquired with a pulse angle of 45°. Each spectrum was stored in the memory, and data were manipulated after titration was completed. The time interval between each spectrum was approximately 2 min. **(b) Vinylcyclopropane (1a).** The titration was carried out in the same manner as before but with 0.4 mL of 2.0×10^{-1} M of **1a** and 10 50-μL portions of 2.5×10^{-1} M **2**. A similar titration

(18) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760–762.

Table III. Summary of Crystallographic Data for Bis(μ-chloro)bis(1,2,5-η³-2-methyl-3-chloro-1-penten-5-yl)dipalladium(II) (5) and for (Acetylacetonato)(1-3-η³-2-methyl-5-chloro-1-penten-3-yl)palladium(II) (9)

	5	9
formula	$Pd_2Cl_4C_{12}H_{20}$	$PdClC_{11}H_{17}O_2$
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
M_r, daltons	518.9	323.11
a, Å	5.487 (3)	4.529 (2)
b, Å	11.959 (2)	17.026 (3)
c, Å	6.902 (2)	16.580 (3)
α, deg	89.06 (2)	
β, deg	107.20 (3)	92.49 (3)
γ, deg	106.30 (3)	
V, Å³	414.1 (5)	1277 (1)
z	2	4
d_{calcd}, g/cm³	2.080	1.680
d_{obsd}, g/cm³	2.08 (1)[a]	1.68 (1)[a]
crystal size, mm³	0.05 × 0.07 × 0.4	0.076 × 0.114 × 0.711
radiation	graphite-monochromated Mo Kα (λ = 0.7107 Å)	graphite monochromated Mo Kα (λ = 0.7107 Å)
scan type	ω–2θ	ω–2θ
scan width (ΔW), deg	1.0 + 0.35 tan θ	1.0 + 0.35 tan θ
max counting time, s	$2 \le 2\theta \le 35°$, 60 s; $34.8 \le 2\theta \le 42°$, 120 s; $41.8 \le 2\theta \le 50°$, 240 s	$2 \le 2\theta \le 40°$, 120 s; $40 \le 2\theta \le 45°$, 180 s; $44.8 \le 2\theta \le 50°$, 240 s
collection range	$2 \le 2\theta \le 50°$	$2 \le 2\theta \le 50°$
no. of unique data	1456	1899
no. of unique data $I > 3\sigma(I)$	1263	1740
no. of variables	122	204
R	0.034[b]	0.034[b]
R_w	0.052[c]	0.044[c]
esd	1.381[d]	1.40[d]
largest parameter shift	0.14[d]	0.85[d]
largest peak, e/Å³	1.371[e]	0.583[e]

[a] By flotation in a mixture of CCl_4 and CH_2Br_2. [b] $R = \sum||F_o| - |F_c||/\sum F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 4F^2/L^2\sigma(I)$, where L is the reciprocal Lorentz–polarization correction, and $\sigma(I) = [P + 4B + (0.045I)^2]^{1/2}$. Here P is the number of counts during the scan, t is the scan counting time in seconds, B is the sum of the background counts. [d] From final refinement. [e] From final difference Fourier.

of **1a** with nitirle complex **3** was also done. **(c) α-Cyclopropane-4-fluorostyrene (1d).** The titration was carried out as for **1c**. Added to 0.40 mL of 0.114 M **1d** were 10 20-μL portions of 0.21 M **2**. **(d) [(+)-Car-2-ene] (4).** The experiment is similar to **1c**. Added to 0.40 mL [(+)-car-2-ene] in $CDCl_3$ (0.41 M) were 10 20-μL portions of 0.21 M **2** in $CDCl_3$.

Crystal Growth. Single crystals of complex **5** suitable for X-ray diffraction studies were obtained by diffusion of pentane vapor into a solution of **5** in chloroform at 5 °C. After 2 days very pale yellow, thin platelets were obtained. Crystals of **9** were obtained in the same way, except that diffused solvent was petroleum ether. In 3 days at 5 °C very thin colorless needles were obtained.

X-ray Diffraciton Studies. A summary of crystallogrpahic data and data collection conditions for **5** and **9** is presented in Table III. Each crystal structure was determined by using the same basic procedure. Preliminary cone axis, zero-layer precession, and Weissenberg photographs were obtained by using Cu Kα radiation. The space groups were determined from the observed systematic absences in the photographic data. Intensity data were collected at room temperature by using an Enraf-Nonius CAD-4 automated diffractometer. The cell constants were obtained from least-squares refinement of 12 (for **5**) and 22 (for **9**) carefully centered reflections. Data reduction, structure solution, and refinement were accomplished by using the Enraf-Nonius structure determination programs (SDP version 18.2). Each structure was solved by the heavy-atom method, and full-matrix least squares was used for the refinements. Hydrogen atoms in both structure factors were located from difference maps. In structure **9** the hydrogens on C5 refine to give large isotropic thermal parameters (ca. 10). Thus all the hydrogen thermal parameters were set equal to that of the attached atom and were not refined. Selected distances and angles are found in the figure captions. Tables of additional distances, angles, planes, positional and thermal parameters, torsion angles, and structure factors are included as supplementary material.

Results

Isopropenylcyclopropane (1c). Reaction of **1c** with nitrile complex **2** in low polarity solvents yielded in minutes

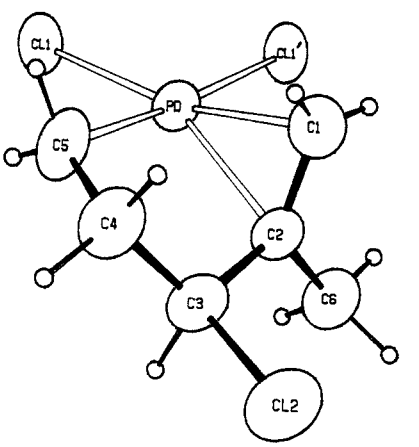


Figure 1. View of bis(μ-chloro)bis-(1,2,5-η³-2-methyl-3-chloro-1-penten-5-yl)dipalladium(II) (**5**). Only a monomeric unit augmented by an additional bridging chloride is shown. A center of symmetry midway between the chlorines generates the remainder of the dimer. The vector which is perpendicular to the square plane is tilted 35° from horizontal toward the viewer. Important distances (Å): Pd–C1, 2.142 (6); Pd–C2, 2.185 (5); Pd–C5, 2.016 (6); Pd–Cl1′ (trans to C_5), 2.506 (1); Pd–Cl1 (trans to C1=C2), 2.361 (1); C3–Cl2, 1.807 (6), C1–C2, 1.278 (9). Best planes (deg): Pd–C1–C2/Pd–Cl–Cl, 73.5.

a colorless solid, **5** (consult Schemes I and II for summary of results and structures). The molecular structure of **5** (Figure 1) was found to be that of a centrosymmetric dimeric 1,2,5-η³-σ,π chelate which results from chloropalladation of the cyclopropane ring. The ^{13}C and ^1H NMR results (Tables I and II) for **5** in solution are fully consistent with the molecular structure in the solid state.

In order to monitor the reaction of **2** with **1c**, prior to the ring-opening step, an ^1H NMR titration was carried out as described in the Experimental Section. No changes in the ^1H chemical shifts of **1c** are observed as increasing

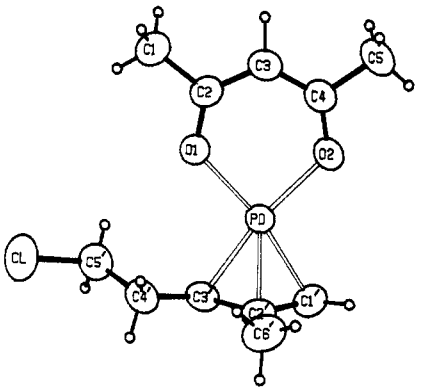


Figure 2. (Acetylacetonato)(1-3-η^3-2-methyl-5-chloro-1-penten-3-yl)palladium(II) (**9**) viewed directly above the coordination plane. Important distances (Å): Pd–C1′, 2.099 (5); Pd–C2′, 2.121 (4); Pd–C3′, 2.109 (4); Pd–O1, 2.078 (3); Pd–O2, 2.089 (3); C1′–C2′, 1.410 (7); C2′–C3′, 1.409 (6); C5′–Cl, 1.787 (6). Important angles (deg): O1–Pd–O2, 90.4 (1); O1–Pd–C3′, 99.6 (1); O2–Pd–C1′, 101.0 (2); C1′–C2′–C3′, 115.3 (4); C2′–C3′–C4′, 123.7 (4); Pd–C2′–C6′, 121.4 (3); Pd–C3′–C4′, 121.3 (3). Best planes (deg): Pd–O1–O2/C1′–C2′–C3′, 111.7; C1′–C2′–C6′/C1′–C2′–C3′, 10.1.

equivalents of **2** are added. We observe only the disappearance of **1c** and the appearance of **5**.

Complex **5** rearranges in solution in days at room temperature (weeks at 5 °C), first to a mixture of syn and anti π-allyl products 8(syn) and 8(anti). The product isolated at equilibrium is 8(syn). Early in the **5** → 8(syn) + 8(anti) rearrangement, the presence of the two isomeric π-allyls was determined by ^{1}H NMR. Formation of 8(anti) was most clearly observed at early stages in the rearrangment at 5 °C as a second pair of singlets for the allylic hydrogens on C_1 at lower field than those for 8(syn) (thus for 8(anti) in $CDCl_3$, singlets at δ 3.95 and 3.23). Low-field shifts for the hydrogens on C_1 are characteristic of anti palladium π-allyls.[19] Rearrangement of **5** at 5 °C for 16 days in $CDCl_3$ led to a 36:56:18 mixture of **5**/8(syn)/8(anti). In 24 days at 5 °C there was no **5**, ca. 95% 8(syn), and 5% 8(anti). Observation of the same rearrangement at room temperature showed simultaneous formation of 8(syn) and 8(anti). At 40 °C, only 8(syn) is observed. At room temperature, the first half-life of the **5** → **8** rearrangement is about 45 h (starting with 10 mg of **5** in 400 μL of $CDCl_3$). Subsequent half-lives for disappearance of **5** at room temperature are shorter (e.g., the second is ca. 17 h). The reaction is complete at 48 h. The room-temperature **5** → **8** rearrangement is catalyzed by complex **2**. Thus, for a solution of 10 mg of **5** and 5 mg of **2** in 400 μL of $CDCl_3$, the first half-life for the rearrangement is 7 h and the reaction is 90% complete in 24 h. In all cases at equilibrium, only 8(syn) is present.

A solid sample of **5** was heated to 45 °C for 5 days, after which the ^{1}H NMR showed no change or decomposition.

The structure assigned to 8(syn) by NMR was confirmed by X-ray determination of the molecular structure of the acetylacetonate derivative **9** (Figure 2).

Vinylcyclopropane (1a). The reaction of **1a** with nitrile complexes **2** and **3** proceeds through a detected intermediate π complex **14**. Thus room-temperature titration of **1a** with **2** or **3** with simultaneous observation of the ^{1}H NMR indicated "time-of-mixing" complexation with significant changes in both vinyl and cyclopropane ^{1}H chemical shifts. The behavior of the ^{1}H shifts (gradual change in δs rather than growth of separate resonances) indicates fast exchange for **1a** between **14** and "free". The ^{13}C NMR of the same π complex (1:1 stoichiometry for **1a**:**2**) was observed at −21 °C, where the major chemical shift change observed was for vinyl C_1 ($\Delta\delta$ = 28.1 ppm to high field). A comparable experiment with $Ag(F_3CSO_3)$ and **1a** in a 1:1 mole ratio led to smaller ^{1}H complexation shifts and a $\Delta\delta$ for C_1 of 13.8 ppm to high field.

At room temperature complex **14** rapidly (minutes) rearranges to chloropalladation product **6** whose structure is assigned on the basis of elemental analysis, solution molecular weight measurements, and detailed interpretation of the ^{1}H and ^{13}C NMR. Complex **6** rearranges in $CDCl_3$ solution (ca. 0.01 M, room temperature) to π-allyl **13** with a half-life of 16 h. Allyl **13** also forms rapidly from *cis*- and *trans*-penta-1,3-dienes and **2**. In the presence of nitrile complex **2** (0.13 *M*) acting as a catalyst, complex **6** (0.2 M) rearranges to a mixture of allyls **10** and **13**. The first half-life for consumption of **6** under these conditions was 2.5 h. A companion experiment 0.2 M in **6** with no excess $PdCl_2(PhCN)_2$ (but 0.4 M in PhCN) showed essentially no allyl formed at 3.7 h. In the companion experiment almost all of the **6** present precipitated at 2.5 h. No precipitate was observed in the presence of excess $PdCl_2(PhCN)_2$ during which rapid consumption of **6** was occurring. In a third experiment, a saturated solution of **6** in $CDCl_3$ (~0.01 M) was made 1 M in PhCN. Only allyl **13** was formed with a half-life unchanged from the pure **6** rearrangement (~16 h). Equation 1 summarizes these results. It is also established (Experimental Section) that **10** and **13** do not interconvert under the conditions of our experiments.

$$\underset{95\%}{\mathbf{13}} \xleftarrow[\text{cat.}]{\text{no}} \mathbf{6} \xrightarrow[\text{cat.}]{PdCl_2(PhCN)_2} \underset{58\%}{\mathbf{10}} + \underset{42\%}{\mathbf{13}} \qquad (1)$$

Complex **6** exhibits a dynamic ^{1}H NMR effect in which protons 4(up), 4(down) are found to be involved in site exchange. With use of eq 2[20a] and the experimental sat-

$$M_{z_{A\infty}} = \frac{(1+\eta)R_A M_{oA}}{R_A + k_A} \qquad (2)$$

uration and T_1 data (Experimental Section), the rate constant k_A for 4(up) → 4(down) [or 4(down) → 4(up)] is found to be 2 s^{-1} (22 °C). The other parameters in eq 2 are defined as follows: $M_{z_{A\infty}}$ = equilibrium longitudinal magnetization at site A when site B is saturated; M_{oA} = equilibrium longitudinal magnetization at site A when the decoupling field is off-resonance; η = nuclear Overhauser factor (estimated to be 0.5[20b]); $R_A = 1/T_{1A}$.

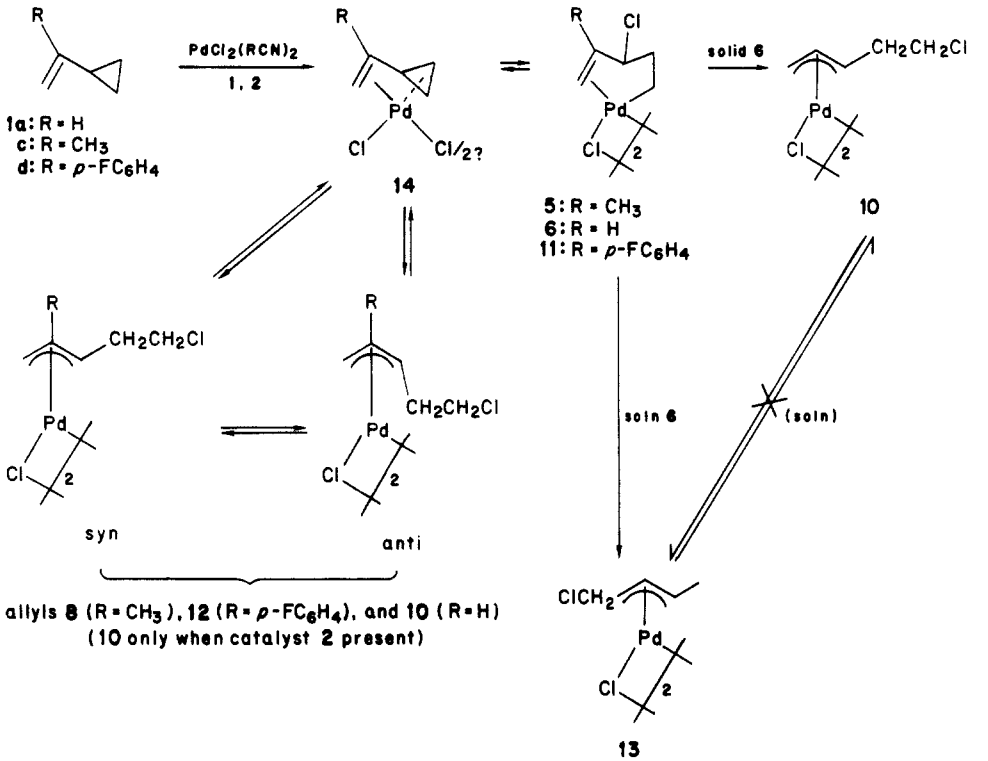
The various observations described in the Experimental Section indicate that complex **6** rearranges in the solid state also but that the solid-state rearrangement produces only allyl **10**. The solid-state rearrangement has not been studied in detail, but it is clear that the half-life is probably at least a month at room temperature.

α-Cyclopropane-4-fluorostyrene (1d). Cyclopropane **1d** reacts with **2** to form σ,π complex **11** with a half-life for formation of **11** of ≤2 min. After 7 min, complex **11** and small amounts of the allyl isomers **12**(syn) and **12**(anti) are present. The NMR titration of **1d** with **2** showed only peaks for **1d** and for **11**, as was the case for isopropenylcyclopropane. Thus **1d** coordinates and undergoes chloropalladation as fast steps, with no accumulation of a π complex.

(19) Comparison of syn/anti palladium allyl ^{1}H NMR: (a) Lukas, J.; Ramakers-Blom, J. E.; Hewitt, T. G.; De Boer, J. J. *J. Organomet. Chem.* **1972**, *46*, 167–177. (b) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93* 2642–2653 (steric factors and mechanistic factors in syn, anti isomerizations of π-allyls). (c) Rowe, J. M.; White, D. A. *J. Chem. Soc. A* **1967**, 1451–1455.

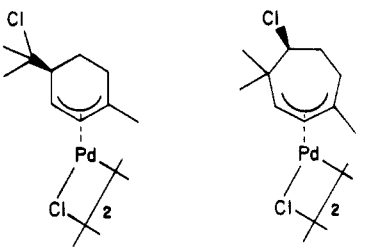
(20) (a) Martin, M. L.; Martin, G. J.; Depuech, J. J. *Practical NMR Spectroscopy*; Heyden & Son: Philadelphia, 1980; pp 315–321. (b) Ibid., p 23 (theoretical maximum for η = 0.5).

Scheme I



After 2 days at room temperature, the **1d**/**2** reaction mixture is converted completely to a 67:33 mixture of **12**(syn)/**12**(anti). The syn:anti ratio is constant for at least 3 days longer. All attempts to separate **12**(syn) from **12**(anti) failed. However, the mixture was isolated analytically pure.

[(+)-Car-2-ene] (4). The only experiment conducted with **4** was the NMR titration. It was observed that as **2** was added, **4** was immediately consumed with concomitant immediate formation of the two π-allyls (**15**,**16**) reported by Bäckvall and co-workers.[12-14] After 30 min and completion of the titration the observed ratio of **15**:**16** was ca. 2:1. No [(+)-car-2-ene] or other products were observed at this time.

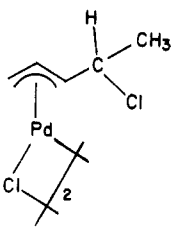


15 **16**

Discussion

In marked contrast to the chrysanthemic acid esters, which have small binding constants to $PdCl_2(RCN)_2$ and which do not accumulate ring-opened products during cis–trans isomerization, the vinylcyclopropanes **1a**, **1c**, and **1d** exhibit time-of-mixing strong binding to Pd(II) followed by rapid (minutes) chloropalladation with cyclopropane ring opening. The first-formed ring opened products are not π-allyls as would have been expected.[1-3] Rather the kinetic preference in these systems leads to the 1,2,5-η^3-σ,π chelates **5**, **6**, and **11**. Each of **5**, **6**, and **11** rearranges further to the ultimate π-allyl products **8**, **13** (or **10**), and **12**, respectively. The results are summarized in Scheme I.

Prior to our work, reactions of both **1a** and **1c** with bis(μ-chloro)bis(ethylene)dipalladium(II) in dichloromethane had been carried out by Ketley, Braatz, and coworkers.[1,2] In the case of **1a**, the earlier workers did not correctly assign the structure of **6** (a simple olefin π complex was assumed), although they did isolate **6** and they observed that it seemed unusually stable for a simple π complex (stable to water at room temperature). The same workers rearranged **6** under conditions (benzene, 35–40 °C) identical with some of our experiments and, on the basis of 60-MHz NMR (^{1}H) results, concluded that the allyl product was a mixture of **10** (40%) and **17** (60%). In



17

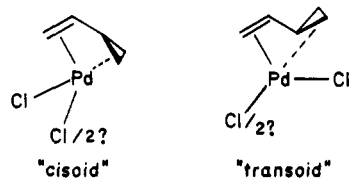
contrast, we observe only traces of **10** in the solution rearrangements, and the major product (≥95% solution rearrangements) is assigned structure **13** on the basis of detailed analysis of high-field ^{1}H and ^{13}C NMR spectra. We note here the observation by Rowe and White[19c] that *cis*- or *trans*-1,3-pentadiene reacts in seconds with $PdCl_4^{2-}$ in cold methanol to give a methoxyallyl with a structure analogous to **17** but that in warm methanol (60 °C) addition of pentadiene to $PdCl_4^{2-}$ gives the methoxyallyl with structure analogous to **13** (and when acetate is used as the nucleophile, only the "**13**-like" structure is observed). The same workers[19c] report that the "**17**-like" methoxyallyl is unstable as a solid. It appears that in methanol the "**17**-like" methoxyallyl is the kinetic product of palladium-mediated attack on pentadiene and that "**17**-like" methoxyallyl rapidly rearranges to "**13**-like" methoxyallyl. Kinetic constraints similar to the methanol system may operate in the chloropalladation to produce **13** (Scheme

II). We have not however detected any **17**.

In only one case (**1a**) was an intermediate of type **14** detected. Similar intermediates are presumed for **1c** and **1d**, where the first observed products are σ,π complexes **5** and **11**. The ^1H and ^{13}C NMR results for **14** (from **1a**)—particularly compared with those for the adduct of $Ag(F_3CSO_3)$ and **1a** (Experimental Section)—lead to the definite conclusion that the Pd–olefin interaction is strong in **14**. The large cyclopropane hydrogen shifts in **14** suggest possible edge or corner coordination of cyclopropane to Pd(II) in **14**; however, the small ^{13}C shifts which are observed imply that any such interaction is rather weak in **14**.

The chloropalladation step (**14** → **5**, **6**, or **11**) leads to kinetically preferred 1,2,5-η^3 chelates. The structure of **5** (Figure 1) was determined crystallographically to support this conclusion. Comparison of NMR spectra of **5**, **6**, and **11** indicates clearly that **5** and **11** are also 1,2,5-η^3 chelates. The kinetic preference for the 1,2,5-η^3 structures may be related to the relatively widespread occurrence of this type of chelate in Pd(II) and Pt(II) chemistry. In at least one case, it is found that the 1,2,5-η^3 and 1–3-η^3 isomers can be nearly equally stable.[21] It is also possible that Cl^- is electronically directed to C_3 by the electronegative (and when coordinated to Pd(II) an even more electronegative group) vinyl group.

In our view, the most straightforward way to isomerize the σ,π chelate structures to the π-allyl structures is be reversal to **14** follwed by chloropalladation in the reverse sense (Pd to C_3, Cl to C_5). This path is followed principally for R = CH_3 and *p*-FC_6H_4, and in both of these cases the anti isomer is observed to accumulate during the early states of rearrangement. The anti isomers should form from a transoid conformation as shown:

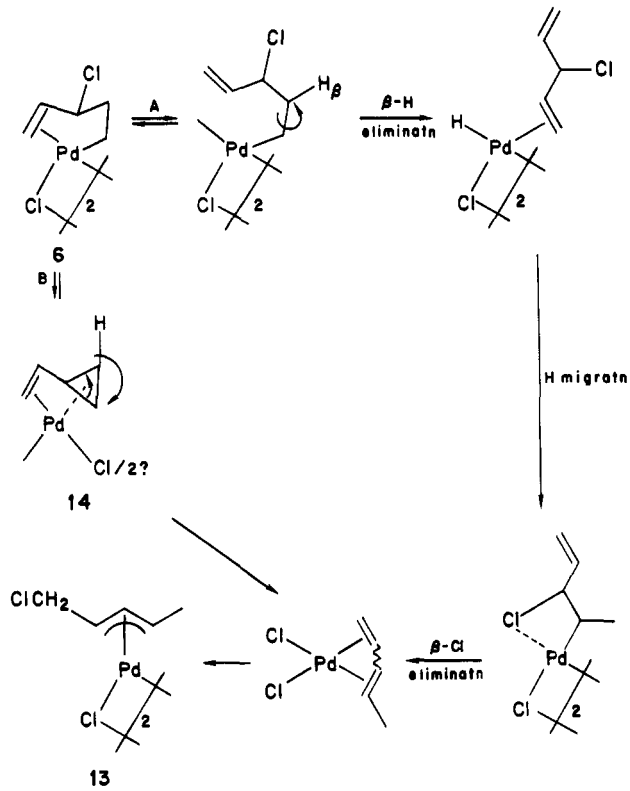


Thus, anti and syn could form competitively from **14** and could equilibrate through **14** or through the more traditional η^1-allyl pathway.[19b] We observe further that only the bulky *p*-FC_6H_4 at C_2 allows **12** (anti) to remain at equilibrium.[19b]

The chemistry of compound **6** differs from that of **5** and **11** in several interesting ways. First, allyl **13** formed from **6** (in solution, no catalyst) must be obtained via a path that involves a hydrogen shift. Second, compound **6** rearranges in the solid state only to **10**, which does not require a hydrogen shift. Third, in the presence of **2** as a solution catalyst, **6** forms both **10** and **13** (under our experimental conditions, there is no interconversion of **10** and **13**). And fourth, compound **6** in solution undergoes a facile rearrangement whose net effect is exchange of protons 4(up) and 4(down) (spin saturation transfer is not observed under our conditions for **5** or **11**).

We will discuss the exchange process first. Interchange of the roles of 4(up), 4(down) with a rate constant of 2 s^{-1} is an experimental indication that there is rapid inversion of configuration at C_3 (i.e., the position of chlorination). This rapid inversion of configuration could be accomplished by facile dechloropalladation/chloropalladation. For example, the drawing of **6** (Figure 1) indicates that the Pd–carbon σ bond is in position to displace chlorine with

Scheme II



inversion at C_3. This displacement is exactly the "reversal to **14**" that we cited above. If the chloropalladation step (**14** → **6**) is cis, i.e., retention at both cyclopropane carbons, then the combination of trans-dechloropalladation/cis-chloropalladation[22] is equivalent to dynamic inversion at C_3 (of course, cis-dechloropalladation/trans-chloropalladation or even randomly coupled events would have the same effect and may be just as likely). Thus, the exchange process observed for **6** is seen as experimental evidence for 1,2,5-η^3-σ,π → **14** reversibility, although in the case of **6** (without catalyst) it is found that **14** is not on the path to product.

In Scheme II we present the proposed pathway from **6** to **13**. The required hydrogen migration along path A is accomplished by β-hydrogen elimination/readdition to terminal carbon. Formation of the methyl group is followed by two steps which are expected to be quite fast. Indeed, we have shown that the last step, which is chloropalladation of pentadiene, is complete in ≤3 min at room temperature. Formation of coordinated pentadiene may also proceed along path B, where cyclopropane involvement with palladium induces charge on carbon with migration of hydrogen.

In the presence of nitrile complex **2** as a catalyst, **6** rearranges both to **13** and to **10** and both pathways are catalyzed! Several possibilities for the nature of the catalysis are suggested. Complex **2** may act as a Lewis acid (attack by **2** on chlorine lone pair at C–Cl) to promote dechloropalladation in **6**. Complex **2** may "insert" an extra $PdCl_2$ unit in the bridge[23] of **6** to change bridge-cleavage kinetics on the way back to **14**, or **2** may initate an alkyl-exchange process which has allyl formation (**10**, **13**) as side reactions. We have also observed catalysis by **2** of the **5** → **8** rearrangement, and the catalyzed reaction here leads

(21) Pd–1,2,5-η^3-cyclooctenyl: Woolcock, J. C. Ph.D. Dissertation, The University of California, Riverside, 1984.

(22) Bäckvall and co-workers have summarized the stereochemical implications of inversion/retention at the nucleophilic/electrophilic centers.[14]

(23) See for an example and leading references: Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013–1017.

only to **8** (the catalyzed reaction gives a cleaner product than uncatalyzed, as there is a small amount of decomposition if the uncatalyzed reaction has to run several days to completion).

The rearrangement of **6** in the solid state only to isomer **10** is in marked contrast to the uncatalyzed solution path only to **13**. Presumably, the multistep proposal in Scheme II is too complex to operate in the constrained crystalline environment, where it is much more reasonable to envision a thermal dechloropalladation—perhaps to a palladium-coordinated vinylcyclopropane/chloride ion pair which collapses to **10**. Overall, this is a remarkable example of phase-induced selectivity.

In order to compare our monocyclic vinylcyclopropanes to the work on the bicyclic vinylcyclopropane [(+)-car-2-ene] (**4**) reported by Bäckvall and co-workers,[12-14] we carried out the NMR titration (**4** + **2**) described above. We observe rapid formation of π-allyls **15** and **16** only. Thus, any 1,2,5-η^3 structure possible in the [(+)-car-2-ene] system either is not on the path to **15** and **16** or is much more labile than those we report here.

Finally, it is appropriate to close the discussion with comments on the relation of the "simple" vinylcyclopropane chemistry to that observed earlier[10,11] in the isomerization of the chysanthemate esters, where **2** and **3** were found to act as catalysts to isomerize cis isomers to trans, via inversion at the carbon (which correlates with our C3) bound to the *gem*-dimethylvinyl group. First, the small binding constants of the chrysanthemates compared to **1a**, **1c**, **1d** are not surprising since the vinyl group is trisubstituted in the chysanthemates. A small binding constant can be tolerated if a fast rearrangement takes place within the low concentration of material bound to the catalyst. Indeed, we have interpreted the dynamic NMR result for **6** to indicate that inversion at C_3 has a rate constant of about 2 s^{-1}, thus indicating that a 1,2,5-η^3-chelate analogous to **6** but formed from a chrysanthemate ester could invert rapidly at C_3 via chloropalladation/dechloropalladation as described above. We also note that a 1,2,5-η^3 chelate derived from a chrysanthemate precursor would be expected to be unstable in any likely conformation. With reference to Figure 1, in a 1,2,5-η^3 chelate derived from a chrysanthemate ester both C_4 and C_1 would carry *gem*-dimethyl groups. In the conformation shown (Figure 1) there would be a serious 1–4 methyl–methyl repulsion. Relaxation to another conformation (rotation around C_4–C_3) leads to an increase in methyl–chlorine repulsions. The overall crowded character of the 1,2,5-σ,π chelate when four methyls and a carboxy group are present no doubt leads to instability with respect to ring closure to the trans chrysanthemate.

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Registry No. **1a**, 693-86-7; **1c**, 4663-22-3; **1d**, 827-87-2; **2**, 14220-64-5; **4**, 4497-92-1; **5**, 100898-93-9; **6**, 100927-31-9; **7**, 100898-94-0; *syn*-**8**, 100898-95-1; **9**, 100898-96-2; **10**, 12288-36-7; **11**, 100898-97-3; *syn*-**12**, 100898-98-4; *anti*-**12**, 100938-00-9; **13**, 100898-99-5; **14**, 100899-00-1; $PdCl_2$, 7647-10-1; bis(μ-chloro)dichlorobis(ethylene)dispalladium(II), 12122-75-7; 5-chloropent-1-ene, 928-50-7; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8; Ag^+-vinylcyclopropane, 100899-01-2.

Supplementary Material Available: For complexes **5** and **9**, tables of bond distances, bond angles, planes, positional parameters, temperature factors, torsion angles, and structure factors (23 pages). Ordering information is given on any current masthead page.