Chloropalladation of Phenyl-Substituted Methylenecyclopropanes

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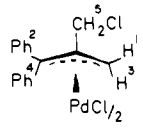
Abstract: The chloropalladation reactions of methylenecyclopropanes bearing phenyl substituents on the cyclopropane ring are shown to involve 1,3 addition of the elements of Pd–Cl to the organic molecule, with cleavage of the 2,3 σ bond of the ring. Chloropalladation of 2,2-diphenylmethylenecyclopropane in $CDCl_3$ or C_6D_6 solution gives a 1:1 mixture of **1** and **4** as the kinetic products; **4** subsequently isomerizes to **1**. In methanol solution, solvolysis of **4** to give **5** occurs more rapidly than isomerization to give **1**. The mechanisms of isomerization and solvolysis are discussed, and kinetic data for the isomerization have been obtained. Similar results are obtained in the chloropalladation of 2,2-diphenylmethylenecyclopropane-*3,3-d*$_2$. 2-Phenylmethylenecyclopropane is chloropalladated to give **9**, **10**, and **11**; in contrast to **4**, **9** only isomerizes to an equilibrium mixture of **10** and **11** in refluxing CH_3CN. In refluxing methanol, **9** is solvolyzed to **12** without isomerization. It is concluded that the mechanism of chloropalladation of phenyl-substituted methylenecyclopropanes is identical with that observed in alkyl analogues.

The organometallic chemistry of methylenecyclopropanes and the chloropalladation of alkyl-substituted methylenecyclopropanes have been discussed in detail in the preceding paper.[2] In particular, the chloropalladation reaction was shown to involve a net 1,3-suprafacial addition of the elements of Pd–Cl as the ring underwent a stereospecific disrotatory opening. A molecular orbital treatment indicated that such a ring opening was orbital symmetry allowed, provided that the olefin axis was perpendicular to the square plane of coordination, and experiments using bicyclic methylenecyclopropanes indicated that transfer of Cl from Pd to C occurred very early in the ring-opening process.

The original investigation of 1,3 chloropalladation was stimulated by the report that 2,2-diphenylmethylenecyclopropane underwent chloropalladation with $PdCl_2(PhCN)_2$ in benzene solution to yield a single product **1** in which Cl apparently had migrated



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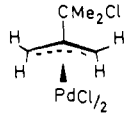

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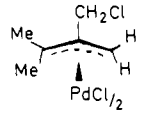

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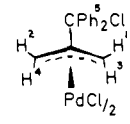
exclusively to the unsubstituted ring-carbon atom.[3] In contrast, chloropalladation of 2,2-dimethylmethylenecyclopropane gave a 9:1 mixture of **2** and **3**, which were shown to be the kinetic products of the reaction.[2] The apparent difference in the regiochemistry of these two chloropalladations prompted us to reinvestigate the chloropalladation reactions of 2,2-diphenylmethylenecyclopropane and 2-phenylmethylenecyclopropane under a variety of conditions. Some of these results have been the subject of a preliminary communication.[4]

Results

^{1}H NMR monitoring of the reaction between equimolar amounts of 2,2-diphenylmethylenecyclopropane and $PdCl_2(PhCN)_2$ in $CDCl_3$ solution revealed the rapid formation of two isomeric chloropalladation products in a 1.0:1.0 ratio. One of these products was identified as **1** by comparison of its ^{1}H NMR spectrum (Table I) with that previously reported.[3] The second product exhibited a ^{1}H NMR spectrum that was compatible only with structure **4**; two singlet resonances were observed for the syn



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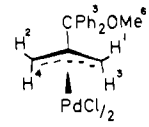

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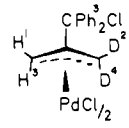
and anti protons of the η-allyl ligand.[5] On standing in $CDCl_3$ solution, isomer **4** was cleanly and quantitatively transformed into **1**, and evaporation of the solution afforded high yields of the latter compound, as previously reported.[3] Kinetic studies of the isomerization of **4** → **1** were carried out by ^{1}H NMR monitoring at different temperatures. The isomerization was cleanly first order in Pd (half order in dimer concentration) over four to five half-lives, and the activation parameters $\Delta H^{\ddagger} = 55$ kJ mol^{-1}, $\Delta S^{\ddagger} = -55$ cal K^{-1} were obtained by conventional methods.[7] Similarly, chloropalladation of 2,2-diphenylmethylenecyclopropane using $PdCl_2(PhCN)_2$ in C_6D_6 solution gave an identical 1.0:1.0 mixture of **1** and **4**, which slowly converted to pure **1**.

In contrast, the reaction of 2,2-diphenylmethylenecyclopropane with either $PdCl_2(PhCN)_2$ or Na_2PdCl_4 in methanol solution produced a 1.0:1.0 mixture of **1** and **5**; the latter compound was identified readily by comparison of its ^{1}H NMR spectrum with that of **4**. This mixture showed no evidence of further rearrangements after 48 h in $CDCl_3$ solution at 25 °C.

Chloropalladation of 2,2-diphenylmethylenecyclopropane-*3,3-d*$_2$ using $PdCl_2(PhCN)_2$ in either $CDCl_3$ or C_6D_6 solution gave initially only a 1.0:1.0 mixture of **6** and **7**; on standing in solution,



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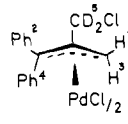

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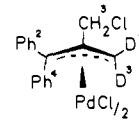

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compound **6** isomerized to a 1.0:1.0 mixture of **7** and **8**, producing a final product mixture of **7** and **8** in a 3.0:1.0 ratio. Notably, no **8** was observed in the initial product mixture.

Under similar conditions, the chloropalladation of 2-phenylmethylenecyclopropane using $PdCl_2(PhCN)_2$ in either CH_2Cl_2, C_6H_6, or CH_3OH solution yielded a mixture of three isomeric

(1) Alfred P. Sloan Research Fellow 1980–1984.
(2) Albright, T. A.; Clemens, P. R.; Hughes, R. P.; Hunton, D. E.; Margerum, L. D. *J. Am. Chem. Soc.*, preceding paper in this issue.
(3) Noyori, R.; Takaya, H. *J. Chem. Soc. D* **1969**, 525.
(4) Dallas, B. K.; Hughes, R. P. *J. Organomet. Chem.* **1980**, *184*, C67–C69.
(5) The ^{1}H NMR spectra of η^3-allylic ligands are particularly useful for structural diagnosis. For examples, see ref 6.
(6) (a) Faller, J. W.; Tully, M. T.; Laffey, K. J. *J. Organomet. Chem.* **1972**, *37*, 193–199. (b) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642–2653.
(7) A convenient discussion appears in Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962.

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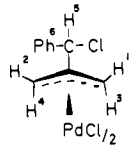
Table I. ^{1}H NMR Data for η^3-Allylic Palladium Products[a]

compd	H^1	H^2	H^3	H^4	H^5	H^6	H^7
1[b,c]	4.14 (s)	7.30 (m)	3.50 (s)	7.30 (m)	3.98 (d), J = 12 4.30 (d), J = 12		
7[b,c]	4.14 (s)	7.30 (m)	3.50 (s)	7.30 (m)			
4[b,c]		3.84 (s)		3.02 (s)	7.30 (m)		
6[b,c]		3.84 (s)		3.02 (s)	7.30 (m)		
8[b,c]		7.30 (m)		7.30 (m)	3.98 (d), J = 12 4.30 (d), J = 12		
5[b,c]		3.95 (s)		2.91 (s)	7.30 (m)	3.08 (s)	
9[b,d]	4.26 (d), J = 1	3.83 (d), J = 1	2.99 (s)	2.89 (s)	5.53 (s)	7.2–7.4 (m)	
9[d,e]	3.01 (s)	2.54 (s)	2.25 (s)	2.11 (s)	4.90 (s)	7.2–7.5 (m)	
10[b,d]	4.05 (s)	7.2–7.4 (m)	3.03 (s)	4.65 (s)	4.40 (d), J = 11 4.16 (d), J = 11		
10[d,e]	3.58 (s)	7.2–7.5 (m)	2.30 (s)	3.93 (s)	3.80 (d), J = 14 3.40 (d), J = 14		
11[b,d]	4.15 (s)	5.96 (s)	3.57 (s)	7.2–7.4 (m)	4.15 (s)		
11[d,e]	3.63 (s)	5.50 (s)	3.17 (s)	7.2–7.5 (m)	3.27 (s)		
12[b,d]	4.14 (s)	3.88 (s)	2.90 (s)	2.83 (s)	4.72 (s)	7.2–7.5 (m)	3.51 (s)

[a] Chemical shift in parts per million downfield from internal Me_4Si; coupling constants in hertz. Proton numbering shown in drawings in the text. [b] $CDCl_3$ solution. [c] 60 MHz. [d] 270 MHz. [e] C_6D_6 solution.

products, identified by their 270-MHz ^{1}H NMR spectra (Table I) as **9**, **10**, and **11**, in a ratio of 3:1:2 measured in $CDCl_3$ solution.



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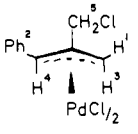

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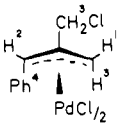
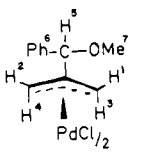


11

In C_6D_6 solution, the ratio of **9**:**10**:**11** was 2:1:1, indicating facile interconversion between **10** and **11** but not between **9** and either **10** or **11**. Isomer **9** was readily identified by the fact that the chiral center at the *C*HPhCl carbon renders the two syn protons diastereotopic and results in a large chemical shift difference; a similar, though less pronounced, effect is transmitted to the corresponding anti protons.[8] Distinction between isomers **10** and **11** is on the basis of the chemical shift difference between the *anti*-CHPh proton in **10** and the corresponding *syn*-CHPh proton in **11**.[9] Notably, the diastereotopic CH_2Cl protons in **10** appear as an AB quartet (as they do in compound **1**), whereas the corresponding protons in **11** resonate as a singlet, presumably because the anti Ph substituent in **11** does not exert sufficient perturbation of their environment.

The mixture of **9**, **10**, and **11** remained unchanged after 24 h in refluxing benzene; however, in refluxing CH_3CN, isomer **9** was quantitatively converted to an equilibrium mixture of **10** and **11**. In refluxing CH_3OH solution, isomer **9** was transformed cleanly into **12**, whereas **10** and **11** remained unchanged. The ratio of



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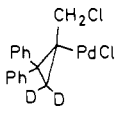
12:**10**:**11** was identical with the original ratio of **9**:**10**:**11**, indicating no conversion of **9** → **10** + **11** under these conditions. Compound **12** was identified easily by comparison of its ^{1}H NMR spectrum with that of **9**. Notably, no **12** was observed in the chloropalladation of 2-phenylmethylenecyclopropane in CH_3OH solution.

(8) For other examples of this phenomenon, see: Ban, E.; Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1974**, *69*, 455–472.

(9) For a discussion of similar chemical shift differences in η-1,2-diphenylallyl compounds of palladium, see ref 6a.

Discussion

Chloropalladation of 2,2-diphenylmethylenecyclopropane-*3,3-d*$_2$ affords only **6** and **7** as the kinetic products. This observation rules out a cyclopropyl–palladium intermediate **13**, which could



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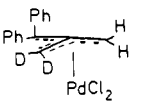

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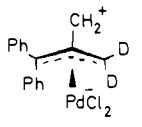

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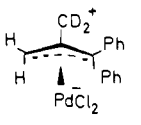

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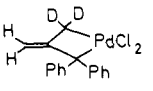

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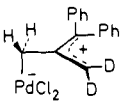


18

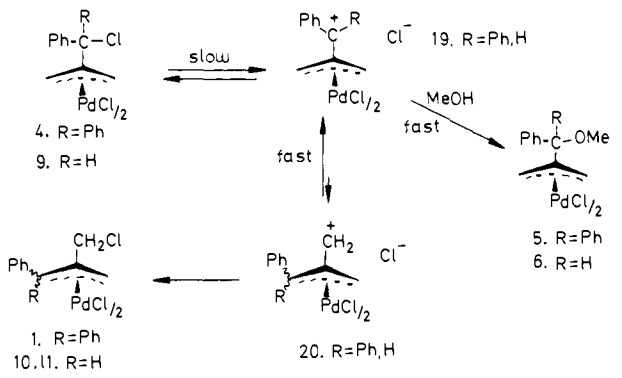
obtain by addition of the elements of Pd–Cl to the coordinated olefin in a manner similar to that observed in the hydridoplatination of methylenecyclopropanes.[10] The absence of **8** in the initial product mixture also allows the exclusion of a symmetrically bound η^4-trimethylenemethane intermediate **14** or of rapidly equilibrating η^3-trimethylenemethane species **15** and **16**,[11] since both would result in the CH_2 and CD_2 termini becoming indistinguishable to a migrating Cl. Evidence for the involvement of η^3-trimethylenemethane species *after* the intial chloropalladation step is discussed below. While formation of a metallacyclic species **17**, followed by reductive elimination of a C–Cl bond, cannot be excluded definitively by this result, such a pathway has been ruled out unambiguously for alkyl-substituted analogues[2] and therefore seems unlikely in this system.

(10) (a) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc. Dalton Trans.* **1978**, 1736–1738. (b) Attig, T. G. *Inorg. Chem.* **1978**, *17*, 3097–3102. (c) Brock, C. P.; Attig, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 1319–1326. See also the discussion in ref 2.

(11) Extended Hückel calculations reveal that the η^3-trimethylenemethane coordination mode is of lower energy than η^4-coordination in these systems and that interconversion between isomeric η^3-forms by metal migration should be extremely facile.[12]

(12) Albright, T. A. *J. Organomet. Chem.* **1980**, *198*, 159–168.

Scheme I



We had postulated previously that a zwitterionic intermediate such as **18** might play a crucial role in 1,3-chloropalladation reactions.[4,13] However, our experimental results using alkyl-substituted methylenecyclopropanes indicate that transfer of Cl must occur very early in the ring-opening process and that a fully ring-opened zwitterion such as **18** cannot represent either an intermediate or transition state for 1,3 chloropalladation.[2] Failure to trap an intermediate such as **18** by conducting chloropalladation reactions in methanol solution also indicates that an intermediate containing significant carbonium ion character is unlikely. It seems probable that the mechanism of 1,3 chloropalladation of aryl-substituted methylenecyclopropanes is identical with that described for alkyl analogues.

It is noteworthy that the regiochemistry of Cl transfer in the chloropalladation of 2,2-diphenylmethylenecyclopropane differs significantly from that observed in the corresponding reaction of the 2,2-dimethyl analogue.[2] In the former case, no selectivity between the CH_2 and CPh_2 termini is observed, whereas in the latter case, Cl exhibits a kinetic preference of 9:1 for the CMe_2 terminus over the CH_2 terminus. Similarly, 1,3 chloropalladation of 2-phenylmethylenecyclopropane exhibits zero selectivity for Cl migration to the CH_2 vs. the CHPh terminus, paralleling the diphenyl analogue.

Also noteworthy is the facile interconversion of the syn and anti isomers **10** and **11**. Isomer **11**, having the bulky phenyl group anti to the central CH_2Cl substituent, is thermodynamically preferred in $CDCl_3$ solution, whereas the two isomers have equal populations in C_6D_6; similar facile syn–anti isomerizations involving phenyl-substituted allyl ligands have been noted elsewhere.[6a] Clearly, the solvent-dependent ratio of **10**:**11** is not a kinetic consequence of the chloropalladation step itself but is determined by a subsequent $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ transformation of the allylic ligand. Similar fast isomerizations have been observed in some products arising from chloropalladation of alkyl-substituted methylenecyclopropanes.[2]

Finally, the mechanism of isomerization of **4** → **1**, and of **9** to an equilibrium mixture of **10** and **11**, also requires some discussion. The activation parameters obtained for the conversion of **4** → **1** are consistent with a dissociative rate-determining step[7] involving facile dissociation of Cl^- from the dibenzylic carbon center (Scheme I). Such a dissociation would produce the η^3-trimethylenemethane species **19** (R = Ph). Theoretical and experimental studies indicate that such η^3-trimethylenemethane complexes of Pd(II) should not collapse to the corresponding η^4-analogues but that rapid migration of the metal around the periphery of the η^3-ligand should occur.[11,18,19] The activation energy for the conversion of **19** (R = Ph) to **20** (R = Ph) by metal migration should be very low, and irreversible trapping of **20** (R = Ph) by Cl^- would afford the observed thermodynamic product **1**. An identical reaction sequence can be envisioned for the isomerization of **9**, except that more vigorous thermal conditions and a more polar solvent are required to effect Cl^- dissociation from the monobenzylic carbon atom. Similarly, the isomerization of **6** must occur to give equimolar amounts of **7** and **8** by an analogous pathway; since the initially formed **7** undergoes no isomerization, this results in a final 3:1 ratio of **7**:**8**.

The observation that thermolysis of a mixture of **9**, **10**, and **11** in methanol results in quantitative conversion of **9** → **12** but no change in **10** or **11** clearly indicates that the intermediate **19** (R = H) is trapped by solvent in an irreversible step before metal migration can occur to give **20** (R = H). Similarly, the observation that chloropalladation of 2,2-diphenylmethylenecyclopropane in methanol at room temperature leads to formation of an equimolar mixture of **1** and **5** is consistent with formation of **1** and **4** as the kinetic chloropalladation products followed by rapid solvolysis of the dibenzylic chloride in **4**. The facility with which carbonium ion centers are trapped by methanol[18] in these latter reactions clearly speaks against the presence of such intermediates in the chloropalladation step (vide supra). Notably, chloropalladation products that do not contain a phenyl group on the Cl-bearing carbon atom are unreactive toward isomerization or solvolysis.[2]

Experimental Section

All reactions were run under an atmosphere of dry nitrogen. Spectrograde solvents (Fisher) were used without further purification except for Et_2O, which was distilled from Na/benzophenone. ^1H NMR spectra were run at 270 MHz at the Northeast Regional NSF-NMR facility at Yale University or at 60 MHz on a JEOL FX-60Q Fourier transform instrument at Dartmouth. Microanalyses were performed by Spang, Ann Arbor, MI.

2-Phenylmethylenecyclopropane was prepared by the literature method,[14] which was also adapted to the synthesis of 2,2-diphenylmethylenecyclopropane.

2,2-Diphenylmethylenecyclopropane. 1,1-Diphenylethylene (Aldrich, 25.0 g, 0.139 mol) and 1,1-dichloroethane (Aldrich, 13.8 g, 0.139 mol) were dissolved in dry Et_2O (55 mL) and cooled to −40 °C. *n*-Butyllithium (Aldrich, 81.3 mL of a 1.6 M solution in hexane, 0.130 mol) was added dropwise over a period of 2 h while maintaining the reaction mixture between −30 and −40 °C. The mixture was allowed to warm to ambient temperature and was stirred for 12 h. Water (25 mL) was added, and the organic layer was separated, dried ($MgSO_4$), and evaporated to give a viscous oil from which crystallized 1-chloro-1-methyl-2,2-diphenylcyclopropane, mp 68–69 °C (9.31 g, 30%).

A solution of 1-chloro-1-methyl-2,2-diphenylcyclopropane (9.29 g, 0.038 mol) was dissolved in dimethyl sulfoxide (35 mL) and was slowly added (1.5 h) to a solution of potassium *tert*-butoxide (4.30 g, 0.038 mol) in Me_2SO (20 mL) at 95 °C. The mixture was cooled to 65 °C and stirred overnight. The hot mixture was poured onto ice (100 g), and the mixture was extracted with isopentane (3 × 50 mL). The isopentane extract was washed with water (3 × 50 mL), dried ($MgSO_4$), and evaporated to give a noxious brown oil. Dry column chromatography of this oil (36 × 1 in silica gel column, hexane eluant) caused the product to run with the solvent front. Extraction of the lower third of the column packing with dichloromethane followed by removal of the solvent under

(13) Hughes, R. P.; Hunton, D. E.; Schumann, K. *J. Organomet. Chem.* **1979**, *169*, C37–C41.
(14) Arora, S.; Binger, P. *Synthesis* **1974**, 801–803.
(15) Slafer, W. E.; English, A. D.; Harris, D. O.; Shellhamer, D. F.; Meshishnek, M. J.; Aue, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 6638–6646.
(16) Use of longer reaction times or more vigorous thermal conditions leads to appreciable deuterium incorporation at the vinylic positions. It is not clear whether this results from direct base-induced exchange at the vinylic sites or whether the equilibrium shown below is established via the "methylenecyclopropane rearrangement"[17]

$$\overline{CD_2CPh_2C{=}CH_2} \rightleftharpoons \overline{CH_2CD_2C{=}CPh_2} \rightleftharpoons \overline{CH_2CPh_2C{=}CD_2}$$

at higher temperatures; this equilibrium would have to lie well on the side of 2,2-diphenylmethylenecyclopropane since this is the only isomer observed in the reaction.
(17) Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 4450–4458.
(18) Lukas, J.; Kramer, P. A. *J. Organomet. Chem.* **1971**, *31*, 111–118.
(19) Other zwitteronic η^3-trimethylenemethane compounds of Pd(II), $[Pd(\eta^3\text{-trimethylenemethane})(PR_3)_2]$, have been characterized as reactive intermediates in palladium-promoted annulation reactions.[20] These species formally bear a positive charge on Pd and a negative charge on the uncoordinated trimethylenemethane carbon atom and thus can be regarded as *umpolung* analogues of **15** and **16**. In the absence of fast trapping agents, these intermediates also appear to be nonrigid in solution, with the metal-atom scrambling among the possible η^3-forms.
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reduced pressure yielded the product as a colorless oil (3.10 g, 39%) having spectral data identical with those reported in the literature.

2,2-Diphenylmethylenecyclopropane-*3,3*-d_2. This method is a modification of a literature procedure for the synthesis of deuterated methylenecyclopropane.[15] A mixture of 2,2-diphenylmethylenecyclopropane (3.70 g, 0.018 mol) and potassium *tert*-butoxide (1.70 g, 0.015 mol) in Me_2SO-d_6 (10 mL) was stirred at 60 °C for 20 min. The mixture was cooled to room temperature and quenched with D_2O (5 mL). Workup as described above yielded the product (3.05 g, 83%), which was shown by ^1H NMR spectroscopy to contain >95% deuterium at the 3-position of the cyclopropane ring.[16]

Chloropalladation of 2,2-Diphenylmethylenecyclopropane. A sample of $PdCl_2(PhCN)_2$ (0.630 g, 1.6 mmol) was dissolved in $CDCl_3$ (2 mL) in an NMR tube and 2,2-diphenylmethylenecyclopropane (0.330 g, 1.6 mmol) was added by using a syringe. The red-orange solution quickly faded to pale yellow, and a ^1H NMR spectrum of the mixture taken after 1 min indicated a quantitative conversion to a 1.0:1.0 mixture of complexes **1** and **4**. Over a period of ca. 1 h at 25 °C, the resonances of **4** diminished with concomitant increase in the intensity of the resonances of **1**. Evaporation of the solvent under reduced pressure followed by exposure of the residue to high vacuum (10^{-2} torr) for 8 h afforded pure **1** as a yellow solid (0.600 g, 98%). Recrystallization of this solid from CH_2Cl_2/hexanes (−30 °C) afforded an analytical sample as yellow prisms, mp 164–170 °C dec. Anal. Calcd for $[C_{16}H_{14}Cl_2Pd]_2$: C, 50.08; H, 3.68. Found: C, 50.40; H, 3.90.

Similar reactions run in C_6D_6 solution gave similar results.

In contrast, a solution of $PdCl_2(PhCN)_2$ (0.100 g, 0.27 mmol) in CH_3OH (20 mL) was treated with 2,2-diphenylmethylenecyclopropane (0.055 g, 0.27 mmol). The color of the solution turned rapidly from red-orange to yellow. After the mixture was stirred at room temperature for 2 h, the solvent was removed under reduced pressure, and the residue was exposed to high vacuum for 6 h to yield a yellow solid, shown by its ^1H NMR spectrum to consist of a 1.0:1.0 mixture of **1** and **5** (combined yield 0.095 g). Identical results were obtained by using Na_2PdCl_4 in CH_3OH solution.

Chloropalladation of 2,2-Diphenylmethylenecyclopropane-*3,3*-d_2. A solution of $PdCl_2(PhCN)_2$ (0.500 g, 1.3 mmol) in $CDCl_3$ (2 mL) in an NMR tube was treated with 2,2-diphenylmethylenecyclopropane-*3,3*-d_2 (0.270 g, 1.3 mmol), and ^1H NMR spectra were recorded at frequent intervals for ca. 1 h. The initial product mixture (1 min) was shown to consist of a 1.0:1.0 mixture of **6** and **7**. The resonances of **6** diminished with time, and those of **7** and its isomer **8** increased in intensity, giving a final product mixture of **7** (75%) and **8** (25%).

Chloropalladation of 2-Phenylmethylenecyclopropane. A solution of $PdCl_2(PhCN)_2$ (2.00 g, 5.2 mmol) in CH_2Cl_2 (250 mL) was treated with 2-phenylmethylenecyclopropane (0.680 g, 5.2 mmol). The color of the solution changed immediately from red-orange to pale yellow. Removal of the solvent under reduced pressure followed by exposure of the residue to high vacuum for 12 h afforded a yellow solid, shown by its ^1H NMR spectrum ($CDCl_3$ solution) to consist of a 3:1:2 mixture of **9**, **10**, and **11** (1.52 g, 94%). Anal. Calcd for $[C_{10}H_{10}Cl_2Pd]_2$: C, 39.06; H, 3.28. Found: C, 39.10; H, 3.45. The composition of this mixture was not time dependent in $CDCl_3$ solution over a period of 24 h at 25 °C, and the product ratio also remained unchanged after a benzene solution was refluxed for 24 h. However, a sample of the mixture (0.344 g, 1.1 mmol) was refluxed in CH_3CN (100 mL) for 10 h. Removal of the solvent under reduced pressure yielded a yellow solid (0.340 g), shown by its ^1H NMR spectrum ($CDCl_3$ solution) to consist of a 1:2 mixture of **10** and **11**.

Similarly, a sample of the kinetic mixture of isomers **9**, **10**, and **11** (0.200 g) was refluxed in CH_3OH (50 mL) for 12 h. Removal of the solvent under reduced pressure left a yellow solid (0.190 g), shown by its ^1H NMR spectrum ($CDCl_3$ solution) to consist of a 3:1:2 mixture of **12**, **10**, and **11**, respectively.

Kinetic Studies on the Conversion of 4 → 1. Experiments were run in 10-mm tubes on a JEOL FX-60Q FT NMR Spectrometer at various temperatures by integrating the resonances of **4** and **1** as a function of time. A software timing routine was used to accumulate spectra at regular time intervals. For each spectrum, data points (8K) were accumulated by using 8 pulses (10 μs) with a repetition time of 4 s and a 1500-Hz window. Each run consisted of 31 spectra recorded over a period of between four and five half-lives and stored on a magnetic disk. Integration was carried out on Fourier-transformed 16K zero-filled FID curves to maximize signal to noise ratio.

In a typical experiment, a solution of $PdCl_2(PhCN)_2$ (0.186 g, 0.48 mmol) in $CDCl_3$ (3.00 mL) was placed in a thin-walled 10-mm NMR tube. The sample was placed in the spectrometer probe and was allowed to stand for 15 min in order to reach the probe temperature of 30.5 °C. 2,2-Diphenylmethylenecyclopropane (0.100 g, 0.48 mmol) was injected into the tube through a septum cap, and the tube was quickly removed from the probe, inverted twice to mix the contents, and replaced in the probe. A spectral accumulation run was started exactly 1 min after mixing, and spectra were recorded at 32-s intervals thereafter.

Similar experiments were performed at 16.3, 20.3, and 23.8 °C. The kinetic data exhibited a first-order dependence on [Pd] or a half-order dependence on [dimer] over four to five half-lives. Rate constants (temperature in °C in parentheses) were found to be 2.75×10^{-4} (16.3), 4.58×10^{-4} (20.3), 5.95×10^{-4} (23.8), and 8.03×10^{-4} (30.5) s^{-1}. An Arrhenius plot of ln k vs. $1/T$ resulted in a value of E_a of 50 kJ mol^{-1}, $\Delta H^{\ddagger}$ (calculated from $\Delta H^{\ddagger} = E_a - RT$)[7] was found to be 55 kJ mol^{-1} at 25 °C, and $\Delta S^{\ddagger}$ [calculated from $A = (ekT/h)\exp(\Delta S^{\ddagger}/R)$][7] was found to be −55 cal K^{-1} at 25 °C.[21]

Acknowledgment. We are grateful to the National Science Foundation (Grants CHE 7717877 and CHE 8022854), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Alfred P. Sloan Foundation for their generous support of our research. The use of the Northeast Regional NSF-NMR Facility at Yale University (supported by Grant CHE 7916210 from the Chemistry Division) is also acknowledged.

Registry No. **1**, 32715-98-3; **4**, 73730-93-5; **5**, 82740-49-6; **6**, 73731-04-1; **7**, 82732-12-5; **8**, 82732-13-6; **9**, 82732-14-7; **10**, 82740-50-9; **11**, 82795-54-8; **12**, 82732-15-8; 2,2-diphenylmethylenecyclopropane, 25152-47-0; 1,1-diphenylethylene, 530-48-3; 1,1-dichloroethane, 75-34-3; 1-chloro-1-methyl-2,2-diphenylcyclopropane, 74972-62-6; 2,2-diphenylmethylenecyclopropane-*3,3*-d_2, 73706-42-0; 2-phenylmethylenecyclopropane, 29817-69-2.

(21) The relatively small temperature range (14°) over which these studies were made indicates that relatively large error limits may be associated with these numbers, though not sufficiently large as to change their signs.