Mercury in Organic Chemistry. 36.[1] Synthesis of (π-Allyl)palladium Compounds and 1,4-Dienes via Vinylpalladation of Monocyclic Alkenes

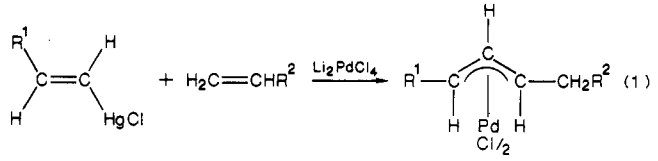
Richard C. Larock* and Kentaro Takagi[2]

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received July 24, 1987

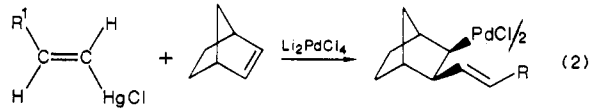
The reaction of vinylmercuric chlorides, cyclic alkenes, and Li_2PdCl_4 in tetrahydrofuran affords (π-allyl)palladium compounds **1**. When the reaction is run in the presence of triethylamine, the corresponding 1,4-dienes **2** are obtained instead. These reactions appear to involve vinylpalladium formation and addition to the cyclic alkene, followed by either palladium hydride migration to form the (π-allyl)palladium compounds or elimination to form the 1,4-dienes.

(π-Allyl)palladium compounds are formed in high yield by the reaction of vinylmercuric chlorides, acyclic alkenes, and Li_2PdCl_4 (eq 1).[3,4] The analogous reaction of bicyclic



(1)

alkenes, such as norbornene, affords stable (σ-alkyl)palladium compounds (eq 2).[5,6] During the course of the

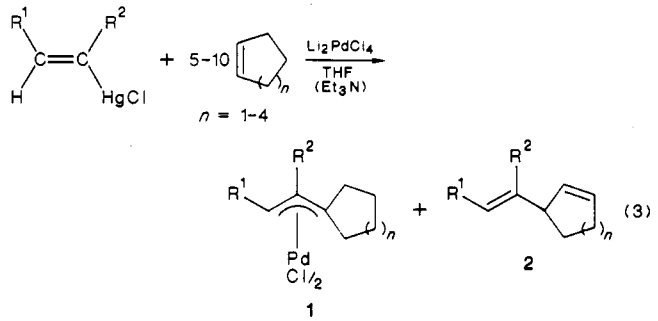


(2)

latter study,[5] we observed that the reaction of vinylmercuric chlorides, monocyclic alkenes, and Li_2PdCl_4 generates either (π-allyl)palladium compounds or 1,4-dienes, depending on the reaction conditions employed. We wish at this time to report the full details of that investigation.

Results and Discussion

Synthesis of (π-Allyl)palladium Compounds. Using conditions essentially identical with those reported earlier for the reactions of vinylmercuric chlorides, Li_2PdCl_4, and acyclic[3,4] or bicyclic[5,6] alkenes, we have been able to obtain a number of new (π-allyl)palladium compounds **1** in modest to good yields accompanied by small amounts of the corresponding 1,4-dienes **2** (eq 3). The results of these reactions are summarized in Table I, entries 1–10.



(3)

Table I. Synthesis of (π-Allyl)palladium Compounds and 1,4-Dienes (Eq 3)

					yield,[a] %	
entry	R^1	R^2	n	Et_3N	**1**	**2**
1	H	H	1	–	–	–
2	Ph	H	1	–	–	–
3	n-C_8H_{17}	H	1	–	35 (13)	20
4	c-C_6H_{11}	H	1	–	34 (12)	23
5	t-Bu	H	1	–	61 (26)	–
6	t-Bu	Me	1	–	62 (43)	10
7	t-Bu	H	2	–	–	–
8	t-Bu	H	3	–	71 (44)	26
9	t-Bu	H	4	–	20[b]	–
10	t-Bu	H	c	–	–	–
11	t-Bu	H	1	+	–	66 (96)
12	n-C_8H_{17}	H	1	+	–	77
13	c-C_6H_{11}	H	1	+	–	(84)
14	t-Bu	H	2	+	–	3
15	t-Bu	H	3	+	–	67
16	t-Bu	H	4	+	–	18

[a] Percent (π-allyl)palladium compound **1** (recrystallized yield) or 1,4-diene **2** (gas chromatographic yield) isolated by column chromatography. [b] Material pure without recrystallization. [c] Alkene was 3,4-dihydropyran.

Relatively few variations in the reaction conditions were examined in view of our earlier success with similar reactions.[3-6] Tetrahydrofuran (THF) is useful as a solvent since most vinylmercuric chlorides are readily soluble in it. Reactions run in benzene or methylene chloride appeared to be very slow and appeared to afford only diene products. While the diene products were not carefully examined, it is likely that both 1,4-dienes **2** and symmetrical[7] and unsymmetrical[8] 1,3-dienes from dimerization of the vinylmercurial are formed. Reactions run in acetonitrile or *N*,*N*-dimethylformamide also afforded dienes. No (π-allyl)palladium compounds could be observed in the crude ^1H NMR spectra of any of these reactions.

While neither vinylmercuric chloride (entry 1) nor styrylmercuric chloride (entry 2) gave any significant amount of (π-allyl)palladium product, alkyl-substituted vinylmercurials gave modest to good yields. The more hindered the vinylmercurial is, the higher the yield of palladium compound isolated. With the alkyl-substituted vinylmercurials, the major side product was usually the corresponding 1,4-diene **2**. The yield of diene **2** increased as the steric bulk of the vinylmercurial decreased.

A substantial difference in yield of (π-allyl)palladium compound was observed as the cyclic alkene was varied from cyclopentene through cyclooctene. While cyclopentene and cycloheptene gave good yields of (π-allyl)palladium products, the yield from cyclooctene was low and none of the anticipated product was obtained from

(1) For "Mercury in Organic Chemistry. 35. Synthesis of Vinylic Lactones from Vinylmercurials and Alkenoic Acids via Intramolecular (π-Allyl)palladium Displacement", see: Larock, R. C.; Leuck, D. J.; Harrison, L. W. *Tetrahedron Lett.* **1987**, *28*, 4977.

(2) Present address: College of Liberal Arts and Sciences, Okayama University, Tsushima, Okayama 700, Japan.

(3) Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 6718.

(4) Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 180.

(5) Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, *22*, 5231.

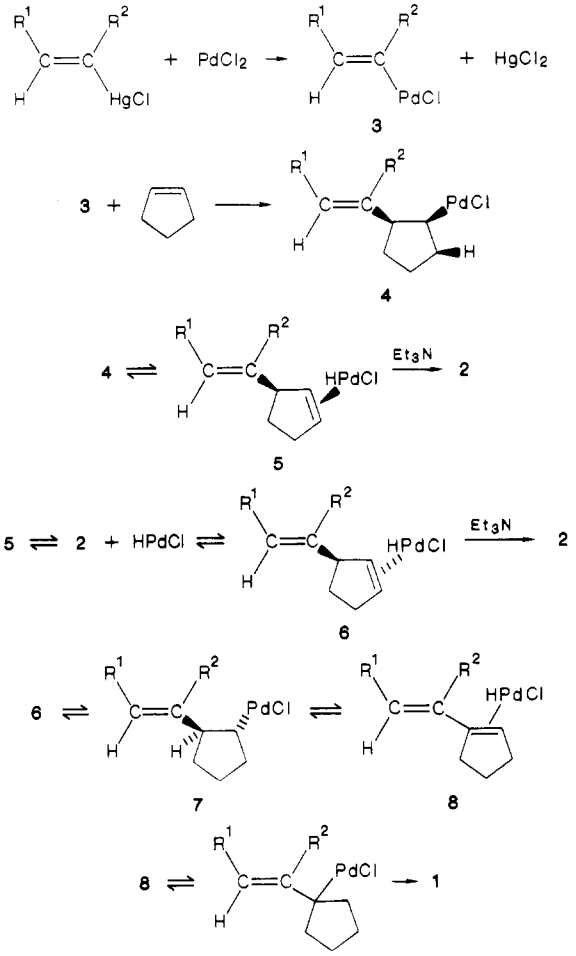
(6) Larock, R. C.; Hershberger, S. S.; Takagi, K.; Mitchell, M. A. *J. Org. Chem.* **1986**, *51*, 2450.

(7) Larock, R. C. *J. Org. Chem.* **1976**, *41*, 2241.

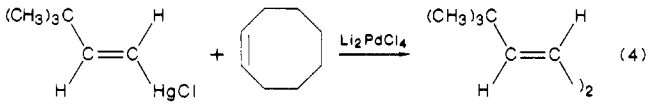
(8) Larock, R. C.; Riefling, B. *J. Org. Chem.* **1978**, *43*, 1468.

0022-3263/88/1953-4329$01.50/0

Scheme I

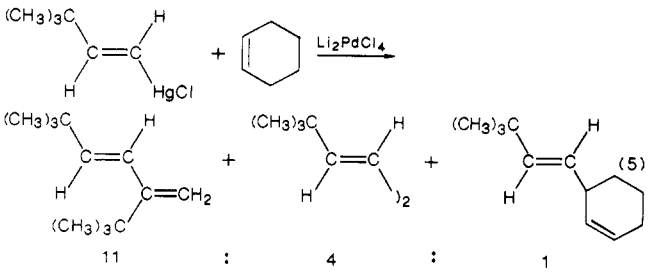


cyclohexene or 3,4-dihydropyran. The low yields are not due to competing formation of the corresponding 1,4-dienes, but result from the low reactivity of these cyclic alkenes toward the vinylpalladium intermediate. The major products from these reactions are symmetrical[7] and unsymmetrical[8] 1,3-dienes formed by dimerization of the vinylmercurials. For example, the reaction of ((*E*)-3,3-dimethyl-1-butenyl)mercuric chloride, Li_2PdCl_4, and cyclooctene afforded (*E*,*E*)-2,2,7,7-tetramethyl-3,5-octadiene in 65% yield (eq 4). The analogous reaction with cyclo-



(4)

hexene gave the unsymmetrical, the symmetrical, and the cross-coupled dienes in a ratio of 11:4:1 (eq 5). With

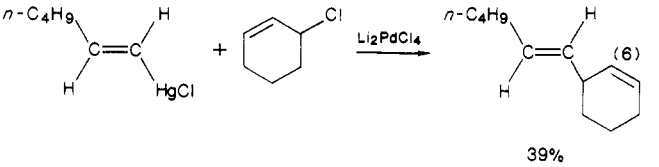


(5)

3,4-dihydropyran, the same unsymmetrical and symmetrical 1,3-dienes were formed in a 5:4 ratio. We have noted a similar reactivity pattern of these alkenes toward other organopalladium species.

Synthesis of 1,4-Dienes. Since the 1,4-diene side product in these reactions appeared to be arising via palladium hydride elimination from a vinylpalladium alkene addition compound (see the mechanistic discussion that follows), we postulated that the addition of ligands that might complex the palladium hydride or perhaps result in its destruction ought to increase the yield of 1,4-diene. Indeed, the addition of triethylamine, which should strongly complex the palladium hydride intermediate or remove the hydrogen chloride resulting from its decomposition, resulted in greatly increased yields of diene **2** (entries 11–16, Table I).

The yields parallel those of the corresponding (π-allyl)palladium reactions. Alkyl-substituted vinylmercurials give high yields of a single isomeric diene. The yields from cyclopentene and cycloheptene are high, but cyclooctene afforded only a very low yield of 1,4-diene, and cyclohexene proved almost unreactive. Once again the major side reaction is dimerization of the vinylmercurial. For example, the reaction of 10 or 50 equiv of cyclohexene and ((*E*)-3,3-dimethyl-1-butenyl)mercuric chloride afforded 55% or 61% of the unsymmetrical diene (*E*)-2-*tert*-butyl-5,5-dimethyl-1,3-hexadiene and 27% or 14% of the symmetrical diene (*E*,*E*)-2,2,7,7-tetramethyl-3,5-octadiene, respectively. With cyclooctene this same symmetrical diene was the predominant product (29% or 74%), while the above unsymmetrical diene (18% or 1%) and the cross-coupled 1,3-diene 1-((*E*)-3,3-dimethyl-1-butenyl)cyclooctene (8% in both cases) were formed in small amounts (using 5 or 50 equiv of cyclooctene, respectively). Overall, this approach appears to afford an attractive route to certain of these cyclic 1,4-dienes and appears to complement our earlier palladium-promoted allylation procedure (eq 6).[9]



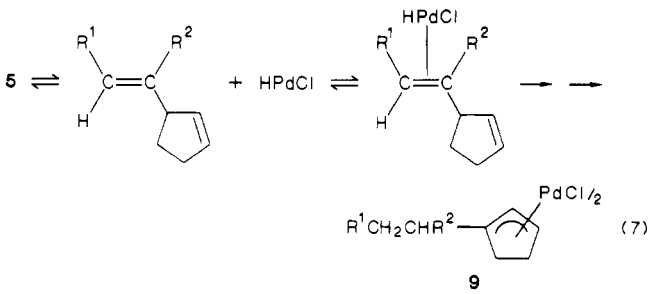
(6)

39%

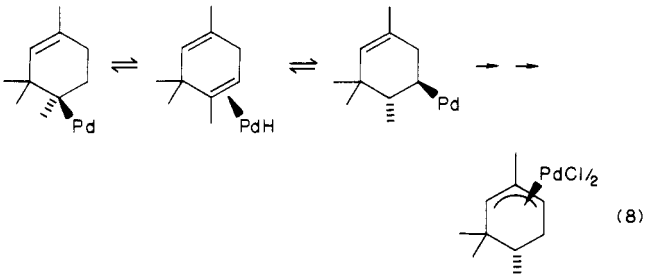
Mechanism. The mechanism of these reactions is intriguing. (π-Allyl)palladium formation appears to proceed as shown in Scheme I. (Additional chloride ligands have been omitted to simplify the scheme.) The majority of steps have ample precedence in our own earlier work on the vinylpalladation of acyclic and bicyclic alkenes,[3-6] as well as in the work of others. Clearly, vinylpalladium species **3** are generated, which no doubt add in a syn fashion to the cyclic alkene to generate a homoallylic palladium species **4**. Palladium hydride elimination is generally assumed to be a syn elimination. A syn π-complex **5** is, therefore, anticipated. To eventually eliminate the allylic hydrogen which undergoes migration, it is necessary for this complex **5** to rearrange to the corresponding anti complex **6**.

While palladium migrations are now well precedented, we believe this may be the first time a palladium hydride has been observed to migrate from one face of a cyclic alkene to the other face. It seems surprising that the palladium hydride, if indeed it comes completely free of the alkene as shown, does not seem to recomplex to the other end of the diene system, eventually resulting in the formation of an isomeric (π-allyl)palladium compound **9** (eq 7). Palladium hydride additions to nonconjugated dienes and subsequent palladium migration have been reported previously by us to afford (π-allyl)palladium

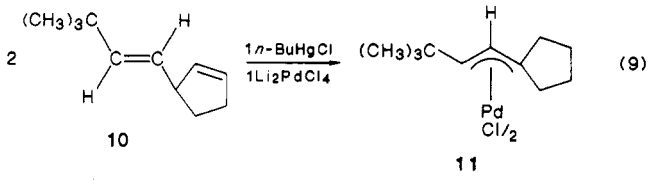
(9) Larock, R. C.; Bernhardt, J. C.; Driggs, R. J. *J. Organomet. Chem.* 1978, *156*, 45.



products in good yields.[10] Our own recent work with optically active bicyclic alkenes has shown that palladium hydride migrations usually proceed without migration to the opposite face of the ring (eq 8).[11]

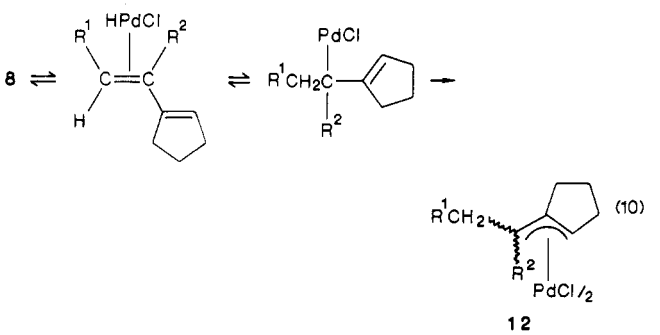


To examine the validity of the steps in our mechanism leading from diene **2** to (π-allyl)palladium compound **1**, we have examined the addition of a palladium hydride to diene **10** (eq 9). The sole (π-allyl)palladium product



formed in 22% isolated yield was compound **11**. There is apparently a clear preference for palladium hydride addition to occur on the carbon–carbon double bond of the ring.

Once the anti complex **6** is formed, addition of the palladium hydride to the carbon–carbon double bond generates an intermediate **7**, which can finally eliminate in a syn manner the hydrogen, which must migrate in order to form the observed (π-allyl)palladium product **1**. As in our previous work,[3,4] there is no evidence that the palladium hydride moiety in intermediate **8** adds to the other end of the diene to generate an isomeric (π-allyl)palladium complex such as **12** (eq 10).



Presumably, the 1,4-dienes **2** that arise in these reactions and predominate in the presence of triethylamine arise by breakdown of the π-complexes **5** and/or **6**. At present we are examining ways in which these same 1,4-dienes can be prepared with vinylic halides, cyclic alkenes, and only catalytic amounts of palladium.

Conclusion

A convenient new approach to (π-allyl)palladium compounds **1** or 1,4-dienes **2** from vinylmercurials, Li_2PdCl_4, and cyclic alkenes has been developed. The reactions are, however, quite sensitive to the substitution pattern of the vinylmercurial and the alkene employed. (π-Allyl)palladium formation appears to proceed via an unusual, highly stereo- and regioselective series of palladium hydride migrations.

Experimental Section

Equipment. Infrared spectra were recorded on a Beckman 4250 or Hitachi 260-10 infrared spectrometer, and proton NMR spectra were obtained in $DCCl_3$ solvent by using either a JEOL PMX 60 or Hitachi Perkin-Elmer R20B NMR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

Reagents. All cyclic alkenes, triethylamine, and tetrahydrofuran (THF) were obtained commercially and distilled prior to use. All mercurials were prepared from the appropriate alkyne by a standard hydroboration–mercuration procedure[12-14] and have been reported previously. Palladium chloride was generously provided by Johnson Matthey, Inc.

Synthesis of (π-Allyl)palladium Compounds. The following procedure was used to prepare all (π-allyl)palladium compounds reported below. To a 60-mL THF solution containing 0.509 g (12 mmol) of lithium chloride, 0.887 g (5 mmol) of palladium chloride, and 25–50 mmol of cycloalkene, 5 mmol of vinylmercuric chloride was added while backflushing with nitrogen at −78 °C. The solution was allowed to slowly warm to room temperature and stirred overnight. Ether and activated carbon were added to the mixture, which was then filtered, washed with aqueous NH_4Cl and aqueous NaCl, and dried over Na_2SO_4. After removal of the solvent, the resultant oil (sometimes solid) was chromatographed on a Florisil or silica gel column, using hexane–ethyl acetate as the elutant. After removal of the solvent from the collected yellow fractions, the yellow residue was recrystallized from CH_2Cl_2 and/or hexane.

Bis[chloro(1,1′,2′-η³-1′-decenylcyclopentane)palladium(II)] [1: $R^1 = n\text{-}C_8H_{17}$, R^2 = H, n = 1; entry 3]: recrystallized from hexane; R_f 0.51 (silica gel, 9:1 hexane/ethyl acetate); mp 54–57 °C; ^1H NMR ($DCCl_3$) δ 0.7–2.2 (m, 25 H), 3.9 (m, 1 H, C_2H), 5.15 (d, J = 11.3 Hz, 1 H, C_1H); IR ($HCCl_3$) 2970, 2940, 2870, 1510, 1470, 1430, 1380, 950, 640 cm^{-1}. Anal. Calcd for $C_{30}H_{54}Cl_2Pd_2$: C, 51.6; H, 7.8. Found: C, 53.23; H, 8.00. (This product appears to contain an inseparable (π-allyl)palladium side product.)

Bis[chloro(1,1′,2′-η³-(2′-cyclohexylethenyl)cyclopentane)palladium(II)] [1: R^1 = cyclohexyl, R^2 = H, n = 1; entry 4]: recrystallized from CH_2Cl_2; R_f 0.40 (silica gel, 9:1 hexane/ethyl acetate); mp 155–165 °C dec; ^1H NMR ($DCCl_3$) δ 0.8–2.2 (m, 19 H), 3.7 (dd, J = 12 and 4.7 Hz, 1 H, C_2H), 5.0 (d, J = 12 Hz, 1 H, C_1H); IR ($HCCl_3$) 3030, 2940, 1510, 1450, 1420, 1130, 920 cm^{-1}. Anal. Calcd for $C_{26}H_{42}Cl_2Pd_2$: C, 48.9; H, 6.6. Found: 48.77; H, 6.54.

Bis[chloro(1,1′,2′-η³-(3′,3′-dimethyl-1′-butenyl)cyclopentane)palladium(II)] (1: R^1 = *tert*-butyl, R^2 = H, n = 1; entry 5; compound 11]: recrystallized from CH_2Cl_2; R_f 0.46 (silica gel, 9:1 hexane/ethyl acetate); mp 161–166 °C dec; ^1H NMR ($DCCl_3$) δ 0.8–2.0 (m, 8 H, cyclopentyl), 1.1 (s, 9 H, *t*-Bu), 3.75 (d, J = 12 Hz, 1 H, C_2H), 5.0 (d, J = 12 Hz, 1 H, C_1H); ^{13}C NMR ($DCCl_3$) δ 99.89, 91.66, 35.49, 34.33, 33.52, 29.91, 26.10, 25.56 (quaternary carbon apparently missing); IR ($HCCl_3$) 3030, 2980, 2880, 1510, 1470, 1430, 1370, 1130, 910 cm^{-1}. Anal. Calcd for

(10) Larock, R. C.; Takagi, K. *J. Org. Chem.* **1984**, *49*, 2701.
(11) Larock, R. C.; Song, H.; Kim, S.; Jacobson, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 834.
(12) Larock, R. C.; Brown, H. C. *J. Organomet. Chem.* **1972**, *36*, 1.
(13) Larock, R. C.; Gupta, S. K.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 4371.
(14) Larock, R. C.; Narayanan, K. *J. Org. Chem.* **1984**, *49*, 3411.

$C_{22}H_{38}Cl_2Pd_2$: C, 45.1; H, 6.5. Found: C, 45.09; H, 6.52.

This compound has also been prepared by the following procedure. In a 100-mL round-bottom flask containing a stirring bar were placed LiCl (0.237 g, 5.59 mmol), $PdCl_2$ (0.413 g, 2.33 mmol), and the 1,4-diene **10** (0.698 g, 4.66 mmol). The contents were flushed with nitrogen, and a nitrogen atmosphere was maintained while THF (28 mL) was injected. The solution was then cooled to −78 °C and (*n*-butyl)mercuric chloride (0.684 g, 2.33 mmol) was added to the solution while backflushing with nitrogen. The solution was allowed to warm to room temperature (~3 h) and stirred for 3 days. Ether (30 mL) and activated charcoal were added to the mixture, and after stirring for 20 min, the mixture was filtered through a small plug of Celite. The filtrate was successively washed with saturated NH_4Cl and NaCl solutions and water, and then dried over $MgSO_4$. After the solvent was removed in vacuo, the solid was chromatographed on a silica gel column (15:1 hexanes/ethyl acetate) to yield 0.150 g (22% yield) of the (π-allyl)palladium complex **11**. The ^1H and ^{13}C NMR data were identical with those reported above.

Bis[chloro(1,1′,2′-η^3-(1′,3′,3′-trimethyl-1′-butenyl)cyclopentane)palladium(II)] [1: R^1 = *tert*-butyl, R^2 = methyl, *n* = 1; entry 6]: recrystallized from hexane/CH_2Cl_2; R_f 0.46 (silica gel, 9:1 hexane/ethyl acetate); mp 158–168 °C dec; ^1H NMR ($DCCl_3$) δ 0.8–2.3 (m, 8 H, cyclopentyl), 1.2 (s, 9 H, *t*-Bu), 1.95 (s, 3 H, Me), 3.55 (s, 1 H, C_2H); IR ($HCCl_3$) 2970, 2880, 1480, 1425, 1365, 1130, 905, 850 cm^{-1}. Anal. Calcd for $C_{24}H_{42}Cl_2Pd_2$: C, 46.9; H, 6.9. Found: C, 47.19; H, 6.97.

Bis[chloro(1,1′,2′-η^3-(3′,3′-dimethyl-1′-butenyl)cycloheptane)palladium(II)] [1: R^1 = *tert*-butyl, R^2 = H, *n* = 3; entry 8]: recrystallized from CH_2Cl_2; R_f 0.37 (silica gel, 9:1 hexane/ethyl acetate); mp 155–160 °C; ^1H NMR ($DCCl_3$) δ 1.2 (s, 9 H, *t*-Bu), 1.3–2.1 (m, 12 H), 3.95 (d, *J* = 12 Hz, 1 H, C_2H), 4.95 (d, *J* = 12 Hz, 1 H, C_1H); IR ($HCCl_3$) 3030, 2940, 2870, 1500, 1365, 920 cm^{-1}. Anal. Calcd for $C_{26}H_{46}Cl_2Pd_2$: C, 48.6; H, 7.2. Found: C, 48.82; H, 7.20.

Bis[chloro(1,1′,2′-η^3-(3′,3′-dimethyl-1′-butenyl)cyclooctane)palladium(II)] [1: R^1 = *tert*-butyl, R^2 = H, *n* = 4; entry 9]: R_f 0.47 (silica gel, 9:1 hexane/ethyl acetate); mp 135–140 °C; ^1H NMR ($DCCl_3$) δ 1.2 (s, 9 H, *t*-Bu), 1.3–2.1 (m, 14 H, cyclooctyl), 4.0 (d, *J* = 12 Hz, 1 H, C_2H), 5.05 (d, 1 H, *J* = 12 Hz, C_1H); IR ($HCCl_3$) 3000, 2960, 2930, 2860, 1500, 1470, 1445, 1365, 1010, 910, 870 cm^{-1}. Anal. Calcd for $C_{28}H_{50}Cl_2Pd_2$: C, 50.2; H, 7.5. Found: C, 50.48; H, 7.68.

Synthesis of 1,4-Dienes. The following procedure was used to prepare all 1,4-dienes reported below. To a 30-mL THF solution containing 204 mg (4.8 mmol) of lithium chloride, 355 mg (2.0 mmol) of palladium chloride, and 10–100 mmol of cycloalkene, 0.56 mL (4.0 mmol) of triethylamine was added by syringe at −78 °C. After 10 min, 2.0 mmol of vinylmercuric chloride was added while backflushing with nitrogen. The solution was allowed to slowly warm to room temperature and stirred overnight. Ether and activated carbon were added to the mixture, which was then filtered, washed with 2 N HCl, aqueous NH_4Cl, and aqueous NaCl, and dried over Na_2SO_4. After removal of the solvent, the resultant oil was chromatographed on a silica gel column, using hexane as the elutant unless otherwise stated.

3-((*E*)-3,3-Dimethyl-1-butenyl)cyclopentene [2: R^1 = *tert*-butyl, R^2 = H, *n* = 1; entry 11]: R_f 0.49 (silica gel, hexane); ^1H NMR ($DCCl_3$) δ 1.0 (s, 9 H, *t*-Bu), 1.3–2.5 (m, 4 H, cyclopentyl), 3.2 (m, 1 H, C=CCHC=C), 5.0–5.4 (m, 2 H, (*E*)-CH=CH), 5.5–5.8 (m, 2 H, (*Z*)-CH=CH); ^{13}C NMR ($DCCl_3$) δ 140.2, 134.7, 130.7, 128.6, 48.5, 32.6, 32.2, 31.0, 29.8; IR (neat) 3060, 3010, 970, 720 cm^{-1}; mass spectrum, *m/z* 150.14082 (calcd for $C_{11}H_{18}$, 150.14085).

3-((*E*)-1-Decenyl)cyclopentene [2: R^1 = *n*-octyl, R^2 = H, *n* = 1; entry 12]: R_f 0.71 (silica gel, benzene); ^1H NMR ($DCCl_3$) δ 0.9 (t, *J* = 8 Hz, 3 H, Me), 1.0–2.5 (m, 18 H), 3.2 (m, 1 H, C=CCHC=C), 5.2–5.9 (m, 4 H, vinylic); IR (CCl_4) 3060, 2930, 2860, 1470, 1380, 960 cm^{-1}; mass spectrum, *m/z* 206.2043 (calcd for $C_{15}H_{24}$, 206.2035).

3-((*E*)-2-Cyclohexylethenyl)cyclopentene [2: R^1 = cyclohexyl, R^2 = H, *n* = 1; entry 13]: ^1H NMR ($DCCl_3$) δ 0.8–2.6 (m, 15 H), 3.3 (m, 1 H, C=CCHC=C), 5.2–5.6 (m, 2 H, (*E*)-CH=CH), 5.6–5.9 (m, 2 H, (*Z*)-CH=CH); IR (neat) 3060, 2930, 2860, 1450, 1350, 965, 910, 890 cm^{-1}; mass spectrum, *m/z* 176.15679 (calcd for $C_{13}H_{20}$, 176.15650).

3-((*E*)-3,3-Dimethyl-1-butenyl)cyclohexene [2: R^1 = *tert*-butyl, R^2 = H, *n* = 2; entry 14]: ^1H NMR ($DCCl_3$) δ 1.0 (s, 9 H, *t*-Bu), 1.2–2.3 (m, 7 H, cyclohexyl), 5.35 (m, 2 H, (*E*)-CH=CH), 5.6 (br s, 2 H, (*Z*)-CH=CH); IR (neat) 3030, 2980, 2840, 1650, 1475, 1440, 1390, 1360, 970, 650 cm^{-1}; mass spectrum, *m/z* 164.15628 (calcd for $C_{12}H_{20}$, 164.15650).

3-((*E*)-3,3-Dimethyl-1-butenyl)cycloheptene [2: R^1 = *tert*-butyl, R^2 = H, *n* = 3; entry 15]: R_f 0.51 (silica gel, hexane); 300-MHz ^1H NMR ($DCCl_3$) δ 1.34–1.42 (m, 2 H), 1.70–1.74 (m, 1 H), 1.88–1.91 (m, 1 H), 2.03–2.17 (m, 5 H), 5.30 (dd, *J* = 6.4 and 15.6 Hz, vinylic), 5.40 (d, *J* = 15.6 Hz, 1 H, C=CHCMe$_3$), 5.73–5.81 (m, 2 H, cycloheptenyl); ^{13}C NMR ($DCCl_3$) δ 138.9, 132.7, 130.8, 130.6, 40.8, 39.1, 35.3, 32.6, 28.8, 27.8, 26.1; IR (CCl_4) 3030, 1655, 1480, 1470, 1450, 1400, 1370, 1275, 960, 690 cm^{-1}; mass spectrum, *m/z* 178.17166 (calcd for $C_{13}H_{22}$, 178.17215).

3-((*E*)-3,3-Dimethyl-1-butenyl)cyclooctene [2: R^1 = *tert*-butyl, R^2 = H, *n* = 4; entry 16]: ^1H NMR ($DCCl_3$) δ 1.0 (s, 9 H, *t*-Bu), 1.3–2.5 (m, 11 H, cyclooctyl), 5.4–5.6 (m, 2 H, (*E*)-CH=CH), 5.65–5.9 (br s, 2 H, ((*Z*)-CH=CH); IR (neat) 3030, 2970, 2870, 1465, 1365, 970, 700 cm^{-1}; mass spectrum, *m/z* 192.18716 (calcd for $C_{14}H_{24}$, 192.18781).

Side Products. The following side products were also isolated and characterized.

3-((*E*)-4,4-Dimethyl-2-pentenyl)cyclopentene: ^1H NMR ($DCCl_3$) δ 1.1 (s, 9 H, *t*-Bu), 1.4–2.5 (m, 4 H, cyclopentyl), 1.6 (d, *J* = 1.5 Hz, 3 H, Me), 3.2 (m, 1 H, C=CCHC=C), 5.2 (s, 1 H, C=CH-*t*-Bu), 5.4–5.8 (m, 2 H, CH=CH); IR (neat) 3060, 2980, 2870, 1460, 1360, 710 cm^{-1}; mass spectrum, *m/z* 164.15635 (calcd for $C_{12}H_{20}$, 164.15650).

1-((*E*)-3,3-Dimethyl-1-butenyl)cyclooctene: ^1H NMR ($DCCl_3$) δ 1.05 (s, 9 H, *t*-Bu), 1.2–1.7 (m, 8 H, cyclooctyl), 1.9–2.6 (m, 4 H, allylic), 5.5–6.2 (m, 3 H, vinylic); IR (neat) 3020, 2920, 2850, 1465, 1440, 1255, 960, 810 cm^{-1}; mass spectrum, *m/z* 192.18826 (calcd for $C_{14}H_{24}$, 192.18781).

Acknowledgment. We gratefully acknowledge the National Institutes of Health (Grant GM 24254) for financial support of this research and Johnson Matthey, Inc., for generous gifts of palladium chloride. We also thank Mr. William Gong for running the experiment described in eq 9.

Registry No. **1** (R^1 = *n*-C_8H_{17}, R^2 = H, *n* = 1), 82328-12-9; **1** (R^1 = *c*-C_6H_{11}, R^2 = H, *n* = 1), 82328-11-8; **1** (R^1 = *t*-Bu, R^2 = Me, *n* = 1), 115590-77-7; **1** (R^1 = *t*-Bu, R^2 = H, *n* = 3), 82328-09-4; **1** (R^1 = *t*-Bu, R^2 = H, *n* = 4), 82328-10-7; **2** (R^1 = *n*-C_8H_{17}, R^2 = H, *n* = 1), 82316-12-9; **2** (R^1 = *c*-C_6H_{11}, R^2 = H, *n* = 1), 82316-11-8; **2** (R^1 = *t*-Bu, R^2 = Me, *n* = 1), 115562-31-7; **2** (R^1 = *t*-Bu, R^2 = H, *n* = 3), 82316-10-7; **2** (R^1 = *t*-Bu, R^2 = H, *n* = 2), 115562-32-8; **2** (R^1 = *t*-Bu, R^2 = H, *n* = 4), 115562-33-9; **10**, 82316-09-4; **11**, 82328-08-3; CH_2=CHHgCl, 762-55-0; (*E*)-PhCH=CHHgCl, 36525-03-8; (*E*)-*n*-C_8H_{17}CH=CHHgCl, 56453-77-1; (*E*)-*c*-C_6H_{11}CH=CHHgCl, 36525-01-6; (*E*)-*t*-BuCH=CHHgCl, 36525-02-7; (*E*)-*t*-BuCH=C(Me)HgCl, 38010-69-4; Li_2PdCl_4, 15525-45-8; *n*-BuHgCl, 543-63-5; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; 3,4-dihydropyran, 110-87-2; 1-((*E*)-3,3-dimethyl-1-butenyl)cyclooctene, 115562-34-0; 3-((*E*)-4,4-dimethyl-2-pentenyl)cyclopentene, 115562-35-1.