MoFe protein from 600 to 350 nm is slightly positive and monotonically increasing—unpublished results of the authors with Dr. John Dawson.
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(6) B. E. Smith, D. J. Lowe, and R. C. Bray, *Biochem. J.*, **135**, 331 (1973).
(7) W. H. Orme-Johnson and L. C. Davis in "Iron-Sulfur Proteins", Vol. 3, W. Lovenberg, Ed., Academic Press, New York, N.Y., 1977, p 31.
(8) As the authors of ref 7 have noted, the Mo might be present in an EPR-active structure with insufficient spin density localized on the metal for observation of the electron–nucleus interaction.
(9) Even the number of Mo atoms necessary for a functional MoFe molecule is still in some doubt (ref 7, p 25). The nutritional requirement is clearly necessary but not sufficient evidence for the involvement of Mo in nitrogenase.
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(13) Throughout this paper, we refer to oxo groups tightly bound to molybdenum, whose short (1.6–1.8 Å) Mo–O bond lengths are indicative of multiple bonding, as "doubly bound" oxygens.
(14) W. G. Zumft and L. E. Mortenson, *Eur. J. Biochem.*, **35**, 401 (1973).
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(26) For lack of suitable all-N complex data, we present data on Mo chlorides. Since the electronegativity of nitrogen is between that of chlorine and oxygen, Mo–N complexes should exhibit edges intermediate to the chloride and oxide edges, for a given metal oxidation state.
(27) Appellations such as 1s–3d and 1s–4s are to some extent misleading, since it is the very fact that the final state is a mixed state with some p character which makes these transitions allowed. The terms are useful in designating the predominant character of the final state, however.
(28) Measurement of the Mo edge inflection point of a dilute sample is subject to an extra source of error because of the protein background absorption, which was almost 99% of the total absorption (A) for the solution experiments. The inflection point E_{inf} is defined as the energy at which the second derivative $d^2A/dE^2 = 0$. If the protein background were a linear function of energy, $A_{back} = a + bE$, its second derivative would be zero and it would not affect the measured inflection point. However, in practice the protein background is a decreasing signal with positive curvature: $A_{back} = a + bE + cE^2$, $b < 0$, $c > 0$. The positive background curvature will shift the observed inflection poit to higher energies as the sample becomes more dilute. It would thus be desirable to repeat these edges with protein samples of exactly the same Mo concentration.
(29) It should be noted here that the air-oxidized edges reported here are essentially the same as the edge previously reported for "resting-state" nitrogenase (ref 12). It now appears that so-called "resting-state" nitrogenase was permanently at rest, that is, irreversibly air oxidized.
(30) E. A. Stern, D. E. Sayers, and F. W. Lytle, *Phys. Rev. Sect. B*, 11, 4836 (1975).
(31) We note here that the EXAFS Fourier transform abscissa, labeled "R", is 0.5× the mathematical transform dimension; thus the frequency difference observed in the transform is one-half the difference observed by direct analysis of the EXAFS in k space.
(32) In structures such as metalloporphyrins and pure metals, which contain highly symmetric shells of atoms around the absorbing atom, EXAFS components for atoms as far as 5 Å are easily observed. However, for most of the Mo compounds studied in ref 21, atoms without a bonding interaction with Mo were not easily seen.
(33) The Mo–Fe phase shift, α_{Mo-Fe}, was calculated as the sum of (1) the theoretical Fe scatterer phase shift and (2) the average difference between empirical Mo–C, Mo–O, and Mo–S and theoretical C, O, and S phase shifts. We are, therefore, using the fact that $\alpha_{Mo-Fe} = \alpha_{Fe}(calcd) + [\alpha_{Mo-X}(empirical) - \alpha_X(calcd)]$, where the quantity in brackets is the average difference between empirical pairwise phase shifts and calculated scatterer phase shifts. The theoretical phase shifts were taken from ref 34, while the procedure for using relationships between phase shifts is a modification of that in ref 35. Since we do not know the shape or magnitude of the MoFe amplitude function, we have assumed that it will be similar to the Mo–S amplitude, only larger by a factor of Z_{Fe}/Z_S or 26/16. The approximately linear Z dependence of EXAFS amplitudes is discussed in ref 21.
(34) P. A. Lee, B. K. Teo, and A. L. Simons, *J. Am. Chem. Soc.*, **99**, 3856 (1977).
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Allylic Alkylation: Preparation of π-Allylpalladium Complexes from Olefins

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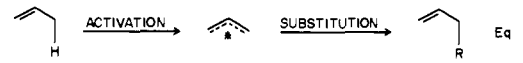
Abstract: Allylic alkylation requires activation of the allylic C–H bond and formation of a C–C bond. A mild way for achieving this activation is developed. A general procedure to obtain π-allylpalladium complexes from simple and complex olefins in good yields is described. The regio- and chemoselectivity is examined. A mechanistic rationale is put forth.

The advent of the Wacker process initiated a flood of activity in organopalladium chemistry.[1] In studying the mechanism of this reaction, the possibility that π-allylpalladium complexes could be formed as by-products leading to allylic oxidation was noted. The possibility that organometallic reagents could be directly available from olefins under mild conditions attracted our attention as a route to allylic alkylation. Specifically, we became concerned with the problem outlined in eq 1, the ability to replace an allylic C–H bond with



Eq 1

an allylic C–C bond. Such a process can be envisioned to involve two stages, activation followed by substitution. Indeed, allylic halogenation followed by coupling with an organometallic such as a cuprate constitutes such a process. Lithiation followed by coupling with an alkylating agent or a carbonyl compound also constitutes a reasonable approach. These ap-

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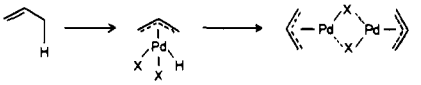
proaches as well as others suffer from a poor chemoselectivity.

The ability to directly palladate an olefin[2-11] seemed particularly promising since we could envision it possessing the desired chemoselectivity. The most extensive work in this area is that of Hüttel[3] and Volger.[4] The problems revolved around the variable yield exhibited in this reaction especially for cyclic olefins. For example, cyclohexene was converted to its π-allylpalladium complex in only 1.4% yield.[3c] Volger noted that his conditions failed for the preparation of complexes without a 2-alkyl or aryl substituent. In examining this reaction, it became clear that the deposition of metallic palladium accompanied the transformation. Such a possibility could be envisioned to arise by invoking a redox process in which, for example, a hydridopalladium species such as **1** was involved. To prevent undesirable decomposition of **1**, it was envisioned

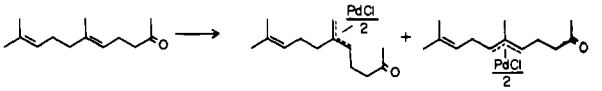


1 2

that addition of an oxidizing agent would rapidly convert **1** to its halo-bridged dimer **2**. Indeed, a general set of reaction conditions has evolved from such considerations. We wish to report that π-allylpalladium complexes are now available from virtually every type of olefin. Furthermore, we have examined the chemo-, regio-, and stereoselectivity exhibited in this reaction.

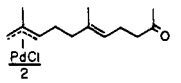
Results

Initially, we focused on the conversion of geranylacetone to its π-allyl complex(es) since we were interested in the application of the method to acyclic terpenoid synthesis such as juvenile hormones. Treatment of geranylacetone with disodium tetrachloropalladate, prepared in situ from sodium chloride and palladium chloride, in the presence of sodium acetate in acetic acid led to the two complexes **3** and **4** in 85% yield. The



3 4

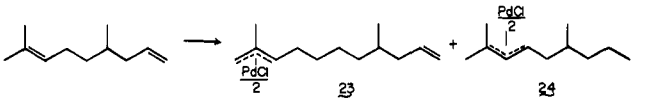
assignment of structure is based upon elemental analysis and spectroscopic data (vide infra). It startled us that only complexes from attack on the C(5)–C(6) double bond appeared. Unfortunately, this reaction proved to be irreproducible. In examining the reaction in detail, it was discovered that reproducibly high yields of π-allyl complex were available by addition of an oxidizing agent such as cupric chloride. However, while **3** was now obtained in 28% isolated yield, the product of attack at the terminal double bond **5** was formed in 41% isolated yield.



5

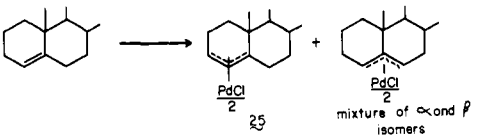
These conditions proved general for acyclic and cyclic olefins as outlined in Table I. Normally, the olefin is used in excess. A ratio of 2:1 olefin:Pd is quite successful. The excess olefin is normally easily recovered although that was not done for most cases. In the cases of geranylacetone and methyl farnesoate, it is important to note that recovered olefin was unchanged (i.e., no cis–trans isomerization occurred). Comparison to Ketley and Braatz[9] who employed palladium chloride and sodium carbonate in methylene chloride revealed the greater generality of the above conditions. For example, *cis*-2-pentene gave a mixture of **6** and **7**, which varied with reaction time, but only in 18% yield after 7 days. Geranylacetone and cyclohexene failed to react under their conditions. Regiochemistry also varies depending upon choice of conditions. Thus, the ratio of **6** to **7** was 1:2 after 2 days and 2:1 after 7 days under Ketley and Braatz's conditions, whereas it is 8:1 under our standard conditions. Use of lithium tetrachloropalladate in methanol appears to be inferior.[13] Conversion of methylenecyclohexane to its complex proceeded only in 21% yield under such conditions, whereas, in the present case, the yield was 92%. As noted before, Volger pointed out the restrictions of his method to noncyclic olefins and to those bearing a substituent in the 2 position of the resultant complex.

The role of cupric chloride is manifold. Not only does it increase the reproducibility of the reaction, it also affects the regioselectivity. The reaction follows a Markownikoff-like orientation—that is the hydrogen abstracted is normally allylic to the more substituted end of the olefin. No exceptions to this have been observed among the examples listed in Table I where this question arises. One exception was the case of 4,8-dimethylnona-1,7-diene which gave an ~1:1 mixture of the expected **23** and an unexpected complex **24**. The latter is the sole



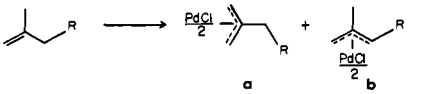
23 24

product with lithium tetrachloropalladate in methanol containing lithium carbonate. Not only did the anti-Markownikoff-like product form but the remote double bond was reduced. It has been reported that conversion of cholest-4-ene to its π-allylpalladium complex in the absence of cupric chloride did give a small amount of anti-Markownikoff-like product **25** (5%) in addition to the expected Markownikoff-like products (34%).[6]



25

The presence of cupric chloride makes a difference in the product ratio among the Markownikoff-like products. For example, with 2-methyl-1-butene, abstraction of hydrogen from the methyl group is preferred over abstraction from the methylene group in the presence of cupric chloride, whereas, in the absence of cupric chloride, the reverse is true.[14] In the case of trisubstituted olefins, in the absence of cupric chloride, 4-methyl-3-heptene gave almost a 1:1 mixture of regioisomers (Table I, entry 7), whereas, in the presence of cupric chloride, methyl farnesoate (Table I, entry 15) and geranylacetone only gave the product from abstraction from the methyl groups to give **21** (in addition to some product from reaction at the internal double bond, **22**, which also shows clean regioselectivity) and **3**, respectively. The general order of reactivity of the position allylic to the more substituted olefinic carbon appears to be $CH_3 > CH_2 \gg CH$ in the absence of conformational effects.

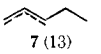
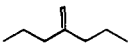
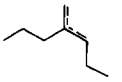
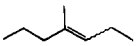
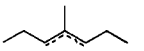
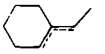
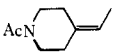
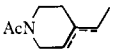
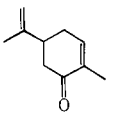
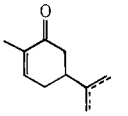
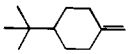
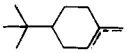
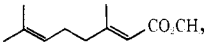
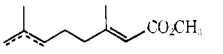
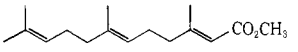
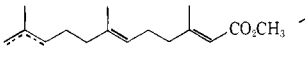
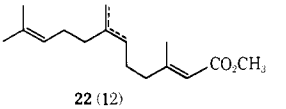


a b

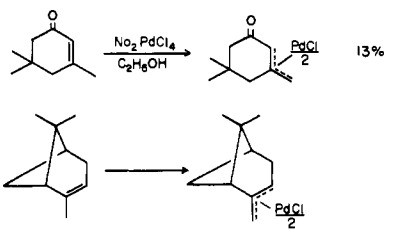
	R	a	b
No additive	CH_3	29	71
	C_4H_9	38	62
$CuCl_2$	CH_3	74	26

The most notable exception is the case of 1-methylcyclohexene (Table I, entry 5) which gave exclusively the endocyclic π complex. In the corresponding five-, seven-,[3c] eight-,[3c] ten-,[11a] and twelve-membered[3e] rings, only the exocyclic

Table I. Preparation of π-Allyl Complexes

Entry	Olefin	Method[a]	Complex(es)[b]	(Relative amounts)	% yields[c]
1		B	 **6** (87)	 **7** (13)	83
2		B		 **8**	66
3		B		 **9**	100
4		B		 **10**	92
5		B		 **11**	86
6		A		 **12**	95
7				 **12**, (50); **13**, (50) **12**, (50); **13**, (50)	91
		A C			96
8		B		 **14**	68
9		B		 **15**	71
10		B		 **16**	52
11		B		 **17**	60
12		B		 **18**	
13		B		 **19**	90
14		B		 **20**	68
15		B	 **21** (88)	 **22** (12)	40

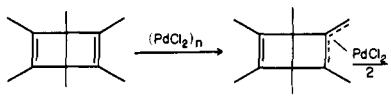
[a] Method A refers to use of sodium chloride, palladium chloride, sodium acetate in acetic acid. Method B refers to the same conditions as method A but with the addition of cupric chloride. Method C refers to palladium chloride and sodium carbonate in methylene chloride. [b] For simplicity, the palladium chloride is omitted from the drawings. The points of bonding are indicated by a dotted line. All complexes are presumably the normal chloride bridged dimers. [c] All yields are for isolated product.



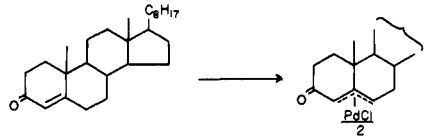
complexes (i.e., abstraction from methyl rather than methylene) are observed. It should also be noted that isophorone is reported to give only the exocyclic adduct, albeit in low yield and not under our conditions.[15] α-Pinene also led only to the exocyclic complex.[16] This result is expected since an endocyclic complex via a Markownikoff-like orientation is not possible.

The chemoselectivity of the reaction is high. Most importantly, carbonyl groups of ketones, esters, and amides are inert

under the reaction conditions. While three-membered rings generally suffer ring cleavage with palladium chloride,[11,17] four-membered rings can survive (see Table I, entries 11 and 12). Methylenecyclobutane has been converted to its π-allyl complex but in low yields.[18a] Even hexamethylbicyclo[2.2.0]-hexadiene forms a complex.[18b] There is a high selectivity

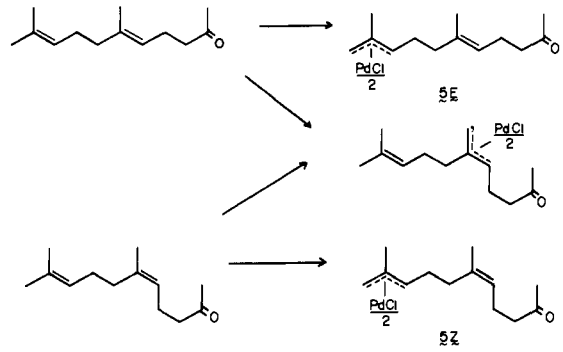


among olefins. Electron-withdrawing groups deactivate the olefin as illustrated by carvone (entry 10), methyl geraniate (entry 14), and methyl farnesoate (entry 15). Double bonds conjugated to a carbonyl group do participate in such reactions as was shown for isophorone (vide supra) and cholestenone.[6,8,19] Among unconjugated double bonds, the cases of li-

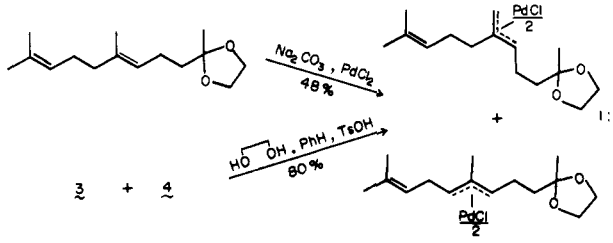


monene[16] and 4,8-dimethylnona-1,7-diene illustrate the higher reactivity of a trisubstituted double bond over a mono- or disubstituted double bond. It appears that the order of olefin reactivity will be tri- > di- > monosubstitution.

The stereochemistry of the olefin does not determine the stereochemistry of the product. Thus, in the cases of ethylidenenorpinane (Table I, entry 12) and 4-methyl-3-heptene (Table I, entry 7), mixtures of olefin isomers gave only a single π-allylcomplex assigned the syn configuration as depicted. Similarly, *cis*-2-pentene (Table I, entry 1) only gives the syn complex. Thus, it appears that olefin isomerization and/or equilibration of the π-allyl complexes occurs. That the latter is the case is demonstrated by the absence of olefin isomerization accompanying formation of the π-allyl complexes. Thus, *cis*- or *trans*-geranylacetone, when converted to their corresponding complexes, allowed recovery of starting olefin in which no isomerization was observed. Furthermore, in the formation of the complex by reaction at the terminal double bond in these cases, the internal double bond retained its stereochemical integrity as illustrated in the accompanying equations.



Ketals do not survive our standard conditions. They do survive the conditions of Ketley and Braatz; unfortunately, the low yields and limited scope of this reaction do not make it

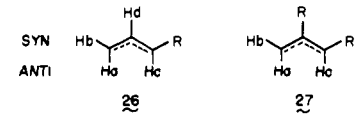


attractive. On the other hand, it is possible to ketalize a carbonyl group in the presence of a π-allylpalladium group under standard conditions. Thus, a better approach appears to be the use of our reaction conditions on the ketone followed by ketalization.

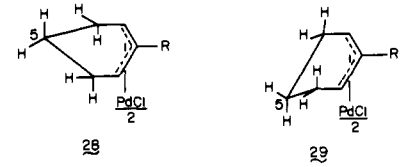
NMR Data. The structures of the complexes are revealed most informatively through their NMR spectra.[3,4,20-22] Table II summarizes the pertinent data. The regiochemistry was easily discerned. For example, the endocyclic complex **11** shows a methyl singlet and a single absorption for the methine protons on the π-allyl unit. The exocyclic complex shows the typical absorptions for a 1,2-disubstituted π-allyl complex. This complex was also characterized by seven clean signals in the ^{13}C NMR spectrum.

The chemoselectivity in the case of carvone was easily discerned by the loss of the absorptions for the terminal methylene group and the retention of the absorptions for the enone. Similarly the complex from methyl geraniate showed absorptions for the enoate but loss of the absorptions for the isopropylidene system. In the case of geranylacetones, the patterns for the methyl groups were very diagnostic. These signals appear between 1.6 and 1.8 in the starting material. Reaction at the terminal double bond removes two signals from this region since the methyl group on the central carbon appears around δ 2.0-2.1. Reaction at the internal double bond removes only one such signal. Similar arguments apply to the complexes from methyl farnesoate.

The question of stereochemistry is also approachable by NMR spectroscopy. A monosubstituted complex such as **26** shows absorptions for the protons normally in the order $H_d < H_b < H_c < H_a$ and a disubstituted complex like **27** in the order

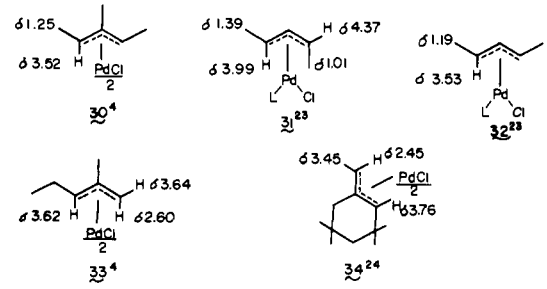


$H_b < H_c < H_a$ except in cyclic cases like **8, 10, 17,** and **19** for which the order is $H_c < H_b < H_a$ (from lowest to highest field). Thus, in general, the palladium strongly shields the protons. Since the anti protons are nearest the palladium, they are most strongly shielded. Complexes **9** and **11** show a 1 H multiplet at extraordinarily high field. In the conformer **28** in which C(5) is bowed away from palladium the axial hydrogens at C(4) and



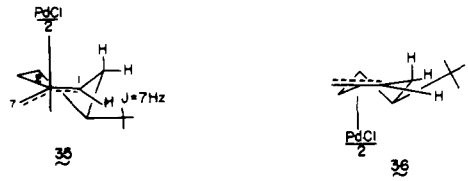
C(6) project directly toward the palladium. The eclipsing of these protons and palladium is relieved in conformer **29**. In such a conformer, the hydrogen at C(5) proximal to palladium would be expected to feel its shielding effect. Thus, we assign conformation **29** as the preferred one in these complexes.

The unsymmetrical substitution also has a notable effect on the charge distribution and thus proton NMR shifts. In par-



ticular, the protons on the more substituted end are deshielded and those on the less substituted end are shielded relative to the symmetrically substituted ones. Compare the literature assignments for **30–34.** Thus, all the complexes can be assigned as the syn isomers as depicted.

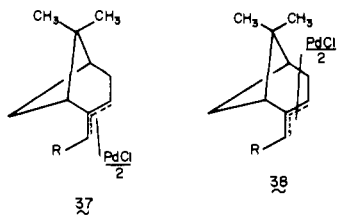
In the case of complexes **17, 18,** and **19,** the question of stereochemistry also arises. Complex **19** is clearly a mixture of two complexes as noted by two absorptions for H_a and H_c. At 270 MHz, the absorptions for H_c appear as a broad singlet at δ 4.26 and a broad doublet (J = 7 Hz) at 4.18. Coordination of the allyl unit to palladium tilts the proton at C(1) away from palladium. In **35** this tilt makes the dihedral angle with the adjacent methylene group approach 0° and the other approach 90°. In **36** both dihedral angles became more nearly equal and



35 36

60°. Thus, the signal at δ 4.18 is tentatively assigned to **35** and that at 4.26 to **36**.

In the case of pinene[25] and ethylidenenorpinane, only a single complex is seen. On steric grounds **37** would be preferred over **38**. Support for this assignment comes from the chemical

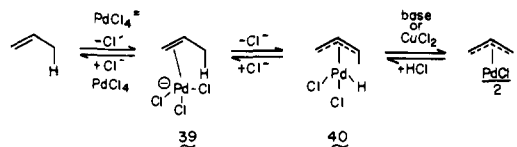


37 38

shifts for the *gem*-dimethyl group. In α-pinene, these absorptions appear at δ 0.84 and 1.27 ($\Delta\delta$ = 0.43). If **38** represents the complex, the relative shifts of these two methyl groups would be greatly affected by the shielding of the proximal methyl group by palladium. In both **17** and **18,** the relative shifts for these methyl groups (see Table II: **17,** $\Delta\delta$ = 0.40; **18,** $\Delta\delta$ = 0.43) indicate almost no difference relative to α-pinene. For this reason, we assign the configuration shown in **37**. It has been confirmed with respect to **18** by a single-crystal x-ray structural determination.

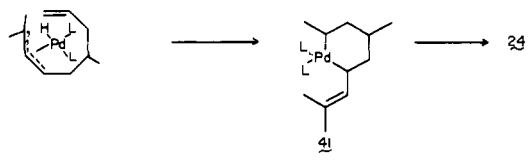
Discussion

We wish to propose the mechanistic scheme shown for the formation of π-allyl complexes from olefins.[4] The key point is invoking the palladium hydride **40** as an intermediate. Such



39 40

intermediates have been invoked in palladium catalyzed isomerizations of olefins and allylic oxidations.[26] The rate of decomposition of **40** determines the success of the reaction. While base can effect a deprotonation, a more efficient conversion of **40** to the desired complex involved oxidative de-



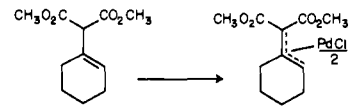
41

composition utilizing cupric chloride. The intermediacy of a palladium hydride such as **40** seems to be supported by the double-bond reaction accompanying complex formation in the case of 4,8-dimethylnona-1,7-diene in which a cyclic intermediate such as **41** can be envisioned.

The chemoselectivity observed suggests it depends upon the ability to form the olefin-Pd^{2+} complex. Double bonds conjugated to electron-withdrawing groups are poorer donors and thus are less reactive than alkyl substituted olefins. Apparently as the degree of alkyl substitution increases, the ability to form the olefin complex increases. Of course, steric factors will hamper complex formation.

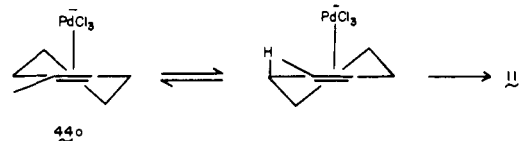
The effect of cupric chloride on the regiochemistry is understandable on the basis of a more rapid decomposition of **40**. The regiochemistry can be kinetically or thermodynamically controlled. If **40** is converted to its π-allyl complex essentially irreversibly, as fast as it is formed it reacts and the ratio of the complexes reflects the intrinsic reactivity of the allylic C–H bonds for insertion (i.e., a kinetic process). In the presence of an acetate buffer, the formation of the complexes is known to be essentially irreversible. On the other hand, if **40** is in rapid equilibrium with **39,** the thermodynamically more stable π-allyl complex will result. The cupric chloride conditions begin to approach the kinetic situation.

The relative reactivity of the various hydrogens appears to be in the order of $CH_3 > CH_2 > CH$ in accord with the C–H insertion mechanism. The acidity of the hydrogen can determine this selectivity–preferential insertion into the more acidic hydrogen. With β,γ-unsaturated esters, only the complex conjugated to the ester is produced. Such is the case even for **42** which gives the exocyclic complex **43** in stark contrast to



42 43

1-methylcyclohexene in which only the endocyclic complex **11** is observed. The formation of the endocyclic complex for 1-methylcyclohexene is also apart from any other ring size in which cases only exocyclic complexes are seen. Attempts to isomerize **11** to **10** failed, although formation of the π-allyl complex from 1-methylcyclohexene at higher temperatures (~100 °C) does give **10,** albeit in low yields (5–10%). Such a result can be taken to suggest that the exocyclic complex **10** is more stable than its endocyclic isomer **11**. Combined with the fact that 1-methylcycloalkenes invariably produce the exocyclic complexes, we believe that **11** represents the kinetic (and probably not the thermodynamic) product. In the olefin–palladium complex **44,** it can been seen that the ring hy-



44o 11

drogen is perfectly aligned for insertion, whereas insertion into the methyl group requires freezing of its rotation. Since no other ring system has as favorable an alignment as the six-membered ring case, it is unique.

It might also be pointed out that the high concentration of chloride ion is also fairly significant. If exchange of the chloride for acetate occurs in the π-allyl complex, the resultant π-allylpalladium acetates would be expected to be much more prone to collapse to allylically substituted systems, i.e., a net allylic oxidation.[27] By maintaining high chloride ion concentration this undesirable exchange is minimized.

In summary, this method has proved to be a mild, regioselective, and chemoselective way of activating an allylic C–H

Table II. NMR Shifts of π-Allyl Complexes

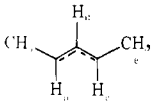
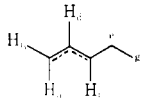
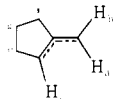
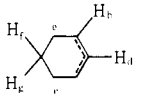
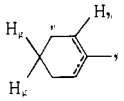
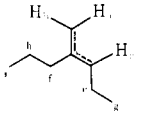
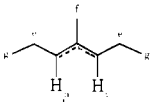
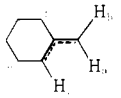
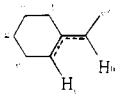
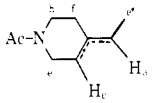
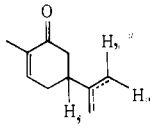
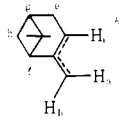
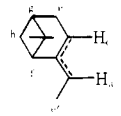
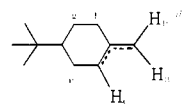
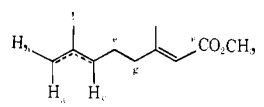
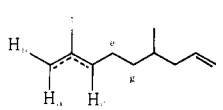
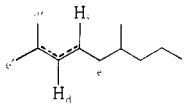
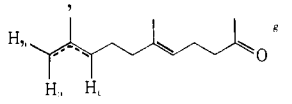
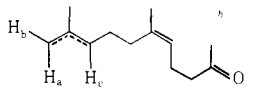
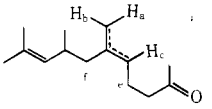
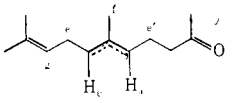
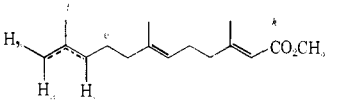
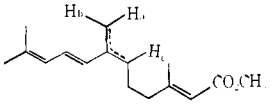
Compd	a	b	c	d	e	e′	f	g	J_{ad}	J_{cd}	J_{ce}	J_{bd}	J_{be}
	3.73		3.73	5.22	1.28				10.8		6.4		
	2.82	2.83	NA[m]	5.27	1.60			1.02	12	12	NA	6.2	
	3.02	3.89	4.10		2.06		2.52	2.06			2.0		
		5.24		5.52	1.80		1.80	1.12					6.0
		4.80			NA		2.20	1.10					4.0
	2.61	3.68	3.52		1.60		2.23	1.14			6.0		
	3.25		3.25		1.61		2.01	1.14			7.0		
	2.65	3.64	4.20		NA		2.53	NA			NA		
	3.42		3.88	NA	NA	1.16	2.75	NA			NA		
	3.72		3.68		NA	1.21	NA	NA			NA		
	2.87	3.88					NA						
	3.00	3.72	4.14		2.36 2.65		2.48	2.10			NA		
	3.72		3.82		2.44 2.62	1.15	2.56	2.07			NA		
	2.51 2.61	3.54	4.15 4.05		NA		2.75 2.41	NA			NA		
	2.73	3.75	3.51		1.82	2.10	2.48				7.0		
	2.68	3.68	3.55		NA		2.06	NA			6.0		

Table II (*Continued*)

Compd	a	b	c	d	e	e′	f	g	J_{ad}	J_{cd}	J_{ce}	J_{bd}	J_{be}
			3.92	4.82	NA	1.22 1.40		NA	11.0				
	2.65	3.65	3.50		NA		2.08	NA			7.0		
	2.63	3.64	3.51		NA		2.08	NA			6.5		
	2.60	3.64	3.48		NA		2.82	NA					
	3.33	3.25		2.7	NA	2.02	5.16			6.0			
	2.67	3.76	3.56		NA		2.09	NA			6.0		
	2.65	3.72	3.50				NA	NA			6.0		

[a] δ 6.75 (1 H, m), 1.81 (3 H, s). [b] δ 1.82 (2 H, pt), 1.37 (3 H, s), 0.97 (3 H, s). [c] δ1.79 (2 H, pt), 1.36 (3 H s, 0.93 3 H s). [d] δ 0.89 (2 H, s). [e] δ 5.75 (1 H, br s), 3.69 (3 H, s), 2.20 (3 H, s). [f] δ 5.68 (1 H, m), 4.94 Br d, J = 14 Hz), 4.92 (b d, J = 12 Hz), 0.90 (d, J = 6 Hz). [g] δ 5.14 (1 H, t, J = 6.5 Hz), 2.12 (3 H, s), 1.65 (3 H, s). [h] δ 5.10 (1 H, br t, J = 6.7 Hz), 2.14 (3 H, s), 1.70 (3 H, s). [i] δ 5.20 (1 H, br t, J = 7 Hz), 2.14 (3 H, s), 1.72 (3H, s), 1.64 (3 H, s). [j] δ 5.16 (1 H, m), 2.14 (3 H, s), 1.70 (3 H, s). [k] δ 5.63 (1 H, br s), 5.12 (1 H, br t, J = 6 Hz), 3.71 (3 H, s), 2.17 (3 H, s), 1.63 (3 H, s). [l] δ 5.63 (1 H, br s), 5.10 (1 H, m), 3.72 (3 H, s), 2.14 (3 H, s), 1.70 (3 H, s), 1.61 (3 H, s). [m] NA, not ascertainable.

bond in an olefinic substrate. To complete the sequence, it is now necessary to achieve C–C bond formation which is the subject of the accompanying manuscript.

Experimental Section

General. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were determined on a Beckman IR-8 or Perkin-Elmer 267 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were determined on a Varian A-60A, Jeolco MH-100, or Brucker 270-MHz spectrometer. Chemical shifts are given in δ units (in parts per million relative to tetramethylsilane as internal standard). Splitting patterns are designated s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants are give in hertz. Mass spectra were taken on an AEI-MS-902 mass spectrometer at an ionizing current of 98 ms and an ionization energy of 70 eV.

Column chromatography was performed on Grace silica gel, grade 62, mesh size 60–200 (Davidson Chemical). Thick layer chromatography was performed on 200 × 400 × 1.5 mm layers of Merck silica gel PF-254 (E. Merck AG Darmstadt). Compounds were removed by repeated washings with ethyl ether. The solvent mixture of chloroform, ether, and 2-propanol was 400:320:8.

Temperatures recorded are external oil-bath temperatures. Copper chloride was dried by heating at 125 °C for 2 h in vacuo. The reagents were added in the following order: sodium acetate, sodium chloride, copper chloride, then palladium chloride. All reactions were performed under a nitrogen atmosphere. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Availability of Olefins. *cis*-2-Pentene, 1-methylcyclopentene, cyclohexene, 1-methylcyclohexene, β-pinene, carvone, and geranylacetone were commercial samples. Pure (*E*)- and (*Z*)-geranylacetone was obtained from Professor W. G. Dauben. Methylenecyclohexane, 2-*n*-propyl-1-pentene, 4-*tert*-butylmethylenecyclohexane, and ethylidenecyclohexane were available by standard Wittig olefinations[28] utilizing triphenylphosphonium methylene and triphenylphosphonium ethylene. Methyl geraniate and methyl farnesoate were prepared from commercial samples of *all-trans* geraniol and farnesol by the procedure of Corey et al.[29] 4-Methyl-3-heptene was prepared by addition of methylmagnesium iodide to 4-heptanone followed by dehydration with iodine at 100 °C which gave a mixture of 34% (*Z*)- and 56% (*E*)-4-methyl-3-heptene and 10% 2-*n*-propyl-1-pentene. *N*-Acetyl-4-ethylidenepiperidine was prepared by the following modified Wittig procedure. Ethyltriphenylphosphonium bromide (51.9 g, 135 mmol) and potassium *tert*-butoxide (14.6 g, 130 mmol) were stirred at ambient temperature for 15 min in tetrahydrofuran (250 mL) forming a dark red slurry. *N*-Acetyl-4-piperidone (14.5 g, 104 mmol) was added over a 15-min period; then the solution refluxed for 16 h, turning light brown. The solution was allowed to cool and filtered, and the solvent removed in vacuo. The oil was dissolved in ether; then the ether solution washed with water, saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. After filtration and removal of solvent in vacuo, the oil was distilled at 96–98 °C (0.2 mm), to give 14.2 g (90%) of *N*-acetyl-4-ethylidenepiperidine: NMR (CCl_4) δ 5.22 (q, J = 7 Hz, 1 H), 3.42 (m, 4 H), 2.18 (m, 4 H), 2.01 (s, 3 H), 1.59 (d, J = 7 Hz, 3 H); IR ($CHCl_3$) 2960, 1650, 1430, 1355, 1275, 1225, 1100, 1032, 1014, 648 cm^{-1}; mass spectrum *m/e* (rel %) 153 (95), 138 (30), 110 (35), 91 (65), 82 (15), 72 (30), 67 (15), 43 (70), 42 (100) (calcd for $C_9H_{15}NO$, 153.1154; found, 153.1153).

Ethylidenenorpinane was prepared from β-pinene.[30] β-Pinene (10.0 g, 73.4 mmol) was dissolved in 100 mL of THF and 30 mL of water containing 100 mg (0.394 mmol) of osmium tetroxide. Sodium metaperiodate (32.8 g, 153 mmol) was added in small portions over a period of 1 h. The resulting slurry was stirred for 65 h at room temperature, then diluted with 100 mL of water, and extracted with ether. After drying ($MgSO_4$) and removal of solvents in vacuo, distillation

Table III. Experimental Details

Olefin (g, mmol)	$PdCl_2$ (g, mmol)	NaOAc (g, mmol)	NaCl (g, mmol)	$CuCl_2$ (g, mmol)	HOAc, mL	Ac_2O, mL	Time at 60 °C, h	Complex (g, % yield)	Mp (dec), °C
cis-2-Pentene (13.3, 190)	4.0, 20	24, 290	16.8, 290	18.4, 140	600	10	48[a]	**6**[c] (3.52, 83)	Oil
1-Methylcyclopentene (2.5, 30.4)	2.0, 11.3	12, 146	8.4, 146	9.6, 77.8	200	5	20	**8**[d] (1.5, 66	129-130[e]
Cyclohexene (1.0, 12.2)	200 mg, 1.13	1.20, 14.6	840 mg, 14.6	1.16, 6.78	50	1	12	**9**[f] (251 mg, 100)	92-95[g]
1-Methylcyclohexene (2.5, 26)	1.0, 5.65	6.0, 73.2	4.2, 73.2	4.6, 33.9	150	5	24	**11**[h] (1.15, 86)	88-90[i]
Ethylidenecyclohexane (2.5, 22.7)	2.0, 11.3	12.0, 146.4	8.4, 146.4	9.2, 67.8	200	5	20	**14**[j] (1.9, 68)	123-129
Carvone (600 mg, 4.0)	200 mg, 1.13	1.20, 14.6	210 mg, 3.6	920 mg, 6.8	50	2	16	**16** (170 mg, 52)	152-156
β-Pinene (2.0, 14.6)	200 mg, 1.13	1.20, 14.6	840 mg, 14.6	920 mg, 6.9	50	2	20	**17** (186 mg, 60)	161-168[k]
2-Ethylidenenorpinane (2.55, 17)	1.02, 5.77	6.0, 73.2	4.2, 73.2	4.6, 33.9	100	3	1.25	**18**[l] (925 mg, 55)	155-165
4-*tert*-Butylmethylene-cyclohexane (2.0, 13)	500 mg, 2.8	2.0, 37	2.1, 36	2.1, 36	125	5	20	**19**[m] (740 mg, 90)	165-170
1-Acetyl-4-ethylidene-piperidine (2.72, 17.8)	1.00, 5.65	6.0, 73.2	4.2, 73.2	6.6, 33.9	125	2	48	**15**[n] (1.17, 71)	142-152
(*Z*)-Geranylacetone (5.9, 30.4)	2.0, 11.6	1.86, 22.6	1.32, 22.6	None	150[o]	None	72	**3**[p] (863 mg, 23) (*Z*)-**5**[q] 568 mg, 15)	
(*E*)-Geranylacetone (5.9, 30.4)	2.0, 11.6	1.86, 22.6	1.32, 22.6	None	150	None	72	**3**[p] 576 mg, 16) (*E*)-**5**[q,r] 804 mg, 22)	
(*E*)-Geranylacetone (3.4, 17.5)	1.00, 5.65	6.00, 73.2	4.2, 73.2	4.6, 33.9	150	2	16[b]	**3**[p] (519 mg, 28) (*E*)-**5**[q] (770 mg, 41)	
Methyl geraniate (800 mg, 4.4[s])	503 mg, 2.83	3.00, 36.6	2.12, 36.5	2.30, 17.0	50	5	2.3[b]	**20** (617 mg, 68)	117-118
Methyl farnesoate (280 mg, 1.12)	100 mg, 0.565	600 mg, 32	420 mg, 7.32	460 mg, 3.39	10	1	2	**21**[t] (74.8 mg, 35) Oil[u] **22**[v] (10 mg, 5)	114-121
4,8-Dimethyl-1,7-nona-diene (560 mg, 3.69)	151 mg, 0.853	900 mg, 11.0	630 mg, 11.2	690 mg, 5.10	10	2	2[b]	**23** (26.7 mg, 10) **24**[w] (29.8 mg, 12)	95-98 108-115

[a] This reaction was performed at 90 instead of 60 °C. [b] This reaction was performed at 95 instead of 60 °C. [c] Reference 23. [d] Anal. Calcd for $C_{12}H_{18}Cl_2Pd_2$: C, 32.30; H, 4.08; Cl. 15.90. Found: C, 32.47; H, 4.09, Cl, 15.86. [e] Lit.[13] mp 151-152.5 °C. [f] Anal. Calcd for $C_{12}H_{18}Cl_2Pd_2$: C, 32.30; H, 4.08; Cl, 15.90. Found: C, 32.44; H, 4.11; Cl, 15.70. [g] Lit.[3c] mp 90-95 °C. [h] Anal. Calcd for $C_{14}H_{22}Cl_2Pd_2$: C, 35.45; H, 4.69; Cl, 14.76. Found: C, 35.73; H, 4.54; Cl, 14.69. [i] Lit.[3c] mp 87-89 °C. [j] Anal. Calcd for $C_{16}H_{26}Cl_2Pd_2$: C, 38.25; H, 5.23; Cl, 14.12. Found: C, 38.28; H, 5.15; Cl, 14.01. [k] Reference 25. [l] Anal. Calcd for $C_{22}H_{34}Cl_2Pd_2$: C, 45.36; H, 5.90; Cl, 12.18. Found: C, 45.33, H, 5.94; Cl, 12.22. [m] Anal. Calcd for $C_{22}H_{38}Cl_2Pd_2$: C, 45.05; H, 6.55; Cl, 12.10. Found: C, 45.21; H, 6.55; Cl, 11.94. [n] Anal. Calcd for $C_{18}H_{28}Cl_2N_2O_2Pd_2$: C, 36.73; H, 4.81; Cl, 12.06; N, 4.76. Found: C, 36.52; H, 4.70; Cl, 12.06; N, 4.65. [o] 10 mL of water was added for this reaction. [p] Faster moving compound upon chromatography on silica gel. [q] Slower moving compound upon chromatography on silica gel. [r] Anal. Calcd for $C_{26}H_{42}Cl_2O_2Pd_2$: C, 46.56; H, 6.33; Cl, 10.58. Found: C, 46.72; H, 6.17; Cl, 10.48. [s] Anal. Calcd for $C_{22}H_{34}Cl_2O_4Pd_2$: C, 40.86; H, 5.31; Cl, 10.97. Found: C, 40.97; H, 5.18; Cl, 11.12. [t] Anal. Calcd for $C_{32}H_{50}Cl_2O_4Pd_2$: C, 49.09; H, 6.46; Cl, 9.06. Found: C, 49.09; H, 6.36; Cl, 9.14. [u] While an oil at room temperature, it crystallizes from hexane at −78 °C. Purification by recrystallization at −78 °C was highly successful. [v] Anal. Calcd for $C_{32}H_{50}Cl_2O_4Pd_2$: C, 49.09; H, 6.46; Cl, 9.06. Found: C, 49.18; H, 6.35; Cl, 9.13. [w] Anal. Calcd for $C_{22}H_{42}Cl_2Pd_2$: C, 44.74; H, 7.11, Cl, 12.01; C, 45.00; H, 6.48; Cl, 12.07.

at 51-53 °C (2 mm) (lit.[31] bp 83-86 °C (12 mm)) gave 4.93 g (49%) of nopinone. As reported above, 55.6 g (150 mmol) of ethyltriphenylphosphonium bromide, 14.2 g (127 mmol) of potassium *tert*-butoxide, and 14.0 g (101 mmol) of nopinone in 120 mL of dry THF gave, after 22-h reflux and workup as before, 10.82 g (72%) of α-ethylidenenorpinane as a ~1:1 stereoisomeric mixture of olefins: NMR (CCl_4) δ 5.11 and 4.95 (2 br q, J = 7 Hz, 1 H), 2.1-2.4 (m, 3 H), 1.6-2.1 (m, 3 H), 1.2-1.5 (m, 5 H), 1.28 and 1.22 (2 s, 3 H), 0.72 (s, 3 H); IR ($CHCl_3$) 1671 cm^{-1}; mass spectrum *m/e* (rel %) 150 (17), 107 (100), 91 (13), 79 (25), 69 (60), 41 (48) (calcd for $C_{11}H_{18}$, 150.1408; found, 150.1409).

4,8-Dimethylnona-1,7-diene was prepared by a standard Wittig olefination of citronellal which in turn was prepared by a Collins oxidation of commercially available citronellol: NMR ($CDCl_3$) δ 5.79 (ddt, J = 17, 12, 7 Hz), 5.11 (m, 11 H), 5.00 (d, J = 17 Hz, 1 H), 4.97 (d, J = 12 Hz, 1 H), 1.8-2.2 (m, 4 H), 1.68 (s, 3 H), 1.51 (s, 3 H), 1.0-1.8 (m), 0.89 (d, J = 7 Hz); IR (CCl_4) 1637, 993, 912 cm^{-1}; mass spectrum *m/e* (rel %) 152 (1), 105 (14), 81 (22), 69 (60), 55 (36), 41 (100) (calcd for $C_{11}H_{20}$, 152.1565; found, 152.1569).

General Procedure for Preparation of π-Allylpalladium Complexes. Preparation of Di-μ-chlorobis(1,2-tetramethylene-π-allyl)dipalladium. To 250 mL of glacial acetic acid and 5 mL of acetic anhydride were added 24.0 g (293 mmol) of sodium acetate, 16.8 g (288 mmol) of sodium chloride, 18.4 g (137 mmol) of anhydrous cupric chloride (dried in vacuo at 125 °C for 2 h), and then 4.0 g (22.6 mmol) of palladium chloride in that order. This mixture was heated to 95 °C for 2 h. After the mixture cooled to 60 °C, methylenecyclohexane (5.0 g, 52 mmol) in 15 mL of glacial acetic was added in one portion and the solution maintained at 60 °C for 2.4 h. The solution was cooled, filtered, poured into 500 mL of water, and extracted with benzene (3 × 10 mL). The combined organic layers were washed with water, saturated aqueous sodium bicarbonate solution, and saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. After filtration and removal of solvent in vacuo, the crude yllow oil was purified by column chromatography on silica gel (120 g, 50 cm) with chloroform as the eluting solvent. Addition of hexane to the purified yellow oil induces crystallization to give di-μ-chlorobis(1,2-tetramethylene-π-allyl)dipalladium (4.94 g, 92%) as yellow crystals:

mp 131–138 °C dec; NMR (CCl_4) δ 4.14 (s, 1 H), 3.60 (s, 1 H), 2.60 Br s, 3 H), 1.5–2.2 (m, 6 H); IR (CCl_4) 2959, 3882, 2841, 1876, 1745, 1721, 1479, 1453, 1433, 1370, 1351, 1350, 1290, 1142 cm^{-1}. Anal. Calcd for $C_{14}H_{22}Cl_2Pd_2$: C, 35.42; H, 4.69; Cl, 14.79. Found: C, 35.82; H, 4.52; Cl, 14.21. Table III outlines the details for other cases. Table II outlines the NMR data.

Reaction of Dilithium Tetrachloropalladate with 4,8-Dimethylnona-1,7-diene. A mixture of 114.6 mg (0.645 mmol) of palladium chloride and 536.0 mg (12.62 mmol) of lithium chloride was stirred in 10 mL of methanol until solution was effected. To the red-orange solution was added 210 mg (1.38 mmol) of olefin and 500 mg (0.76 mmol) of lithium carbonate. After stirring 8 h at room temperature, the solution was poured into 20 mL of water and extracted with chloroform. After drying ($MgSO_4$) and removal of solvent in vacuo, TLC purification, eluting with chloroform, gave 65.1 mg (34%) of **24** as yellow crystals: mp 108–115 °C dec; mass spectrum *m/e* (rel %) 152 (35), 110 (10), 109 (100), 96 (20), 95 (22), 82 (55), 81 (58), 79 (22), 71 (24), 69 (53), 68 (55), 67 (75), 56 (33), 55 (58). It is identical with the sample obtained under our standard conditions. See Tables II and III for pertinent data.

Preparation of Di-μ-chlorobis(*syn*-1-ethyl-2-propyl-π-allyl)dipalladium (12). Method 1 (from 4-Methyl-3-heptene). A mixture of 112 mg (0.63 mmol) of palladium chloride, 40 mg (0.38 mmol) of sodium carbonate, and 154 mg (1.37 mmol) of 4-methyl-3-heptene in 10 mL of methylene chloride was stirred under nitrogen at room temperature for 68 h. The solution was then filtered and the filtrate washed with chloroform. The combined organic portions were evaporated in vacuo to 154 mg (96%) of a yellow oil. NMR examination (see Table II) indicated a 1:1 mixture of **12** and **13**. Selective crystallization of **12** from hexane gave a yellow crystalline solid: mp 130–131 °C; mass spectrum *m/e* (rel %) at 14 eV 112 (50), 111 (20), 110 (100), 95 (52). Anal. Calcd for $C_{16}H_{30}Cl_2Pd_2$: C, 37.92; H, 5.98. Found: C, 37.89; H, 5.85. From the mother liquors, complex **13** was isolated as a yellow oil. It was characterized by its spectroscopic properties (see Table II): mass spectrum *m/e* (rel %) at 14 eV 112 (50), 111 (20), 110 (100), 95 (52).

Method 2 (from 4-Methyl-3-heptene). A mixture of 1.043 g (5.9 mmol) of palladium chloride, 0.92 g (11.2 mmol) of sodium acetate, and 0.68 g (11.7 mmol) of sodium chloride in 20 mL of acetic acid was warmed at 80 °C for 14 min. After the mixture cooled to 50 °C, 2.50 g (24.3 mmol) of 4-methyl-3-heptene dissolved in 3 mL of acetic acid was injected and the temperature maintained at 50 °C for 48 h. The reaction mixture was filtered and the resultant solution poured into water and extracted with ether. The yellow ether layer was washed with water, aqueous sodium bicarbonate solution, and then water. After drying ($MgSO_4$) and evaporation of solvent in vacuo, 1.40 g (91%) of yellow oil which was a 1:1 mixture of the two complexes was isolated.

Method 3 (from 2-Propyl-1-pentene). The reaction was performed as outlined in method 2 utilizing 630 mg (3.55 mmol) of palladium chloride, 584 mg (7.1 mmol) of sodium acetate, 416 mg (7.1 mmol) of sodium chloride, and 1.09 g (9.7 mmol) of 2-propyl-1-pentene in 20 mL of acetic acid. Upon workup as above, 0.85 g (95%) of crystalline yellow complexes **12** was obtained. It was identical with the previous sample.

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