Intermediates in the Palladium-Catalyzed Reactions of 1,3-Dienes. 2.[1] Preparation and Structure of (η^1,η^3-Octadienediyl)palladium Complexes

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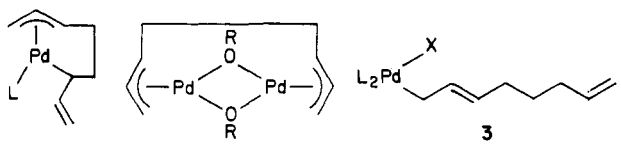
A series of (η^1,η^3-octadienediyl)palladium complexes, [Pd(L)(η^1,η^3-C_8H_{12})] and [Pd(L)(η^1,η^3-$Me_2C_8H_{10}$)], has been prepared by reacting bis(η^3-2-methylallyl)palladium with donor ligands and butadiene or isoprene. The reactions occur in a stepwise manner through the intermediacy of [Pd(L)(η^1,η^3-allyl)$_2$] and [{Pd(L)(μ-η^3-allyl)}$_2$] complexes. The η^1,η^3-octadienediyl systems react with olefins such as methyl acrylate to give (η^2-olefin)$_2$Pd–L complexes and with acids to give (η^2,η^3-octadienyl)- and/or (η^3-octadienyl)palladium complexes.

Introduction

It has been known for almost 20 years that palladium complexes catalyze the oligomerization, cooligomerization, and telomerization of 1,3-dienes to give linear products. The course of these reactions can be influenced to some extent by the addition of donor ligands such as tertiary phosphines. For example, ligand-free palladium catalysts generally convert butadiene into a mixture of isomers of the linear trimer dodecatetraene, while catalysts with a Pd:L ratio of 1:1 produce linear dimers or 2:1 telomers and catalysts having a Pd:L ratio of 1:2 (or larger) lead to the formation of 1:1 telomers as well as catalyzing the cyclocooligomerization of butadiene with heteroolefins (Scheme I).[2]

Traditionally, the description of these reactions has included a discussion of the mechanisms involved. In general these have, however, leaned heavily on those postulated for the related nickel-catalyzed reactions, from which a number of plausible intermediates have been isolated. In a short series of papers we intend to report the preparation and reactions of some organopalladium complexes which allow a more detailed insight into the mechanisms involved. Some aspects of this work have been published as a short communication[3] and an overview[4] while full details are contained in four doctoral theses.[5]

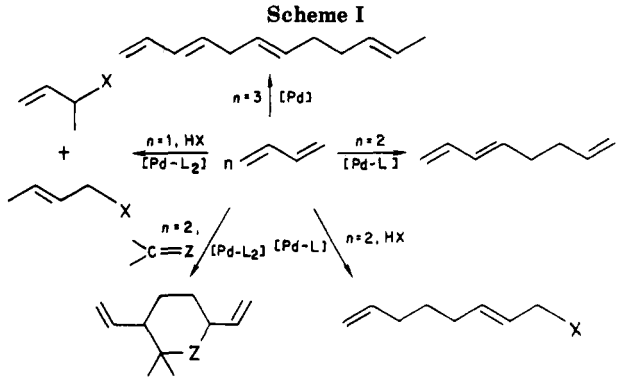
Three C_8–Pd species have been discussed as intermediates in the palladium-catalyzed reactions of butadiene **1**–**3**. **1** was first proposed by G. Wilke and co-workers to



1 **2**, R = Ph, OAc **3**

account for the formation of vinylcyclohexene in the [Pd(η^3-C_3H_5)$_2$]/PCl_3-catalyzed cyclodimerization of butadiene[6] and was subsequently suggested to be also involved in the reactions leading to linear products.[2a] Complexes of type **2** have been isolated by reacting the appropriate (η^3-allyl)palladium derivative with butadiene and have been implicated as intermediates in the linear dimerization and telomerization of butadiene.[2c,7] However, the observation that polymer-anchored palladium catalysts give the same product distribution in the telomerization of butadiene with acetic acid as that obtained by using a homogeneous system has been cited as evidence against the involvement of binuclear species.[8] Complex **3** is the penultimate step in a mechanism proposed by Maitlis and is formed by addition of a Pd–H species to butadiene followed by insertion of a second diene molecule and does at least provide a simple explanation for the preferred formation of linear as opposed to cyclic products.[9]

Scheme I



We report here details of the preparation and characterization of a series of (η^1,η^3-octadienediyl)palladium ligand complexes from reactions involving butadiene and isoprene. A discussion of the relevance of these species to the palladium-catalyzed transformation of 1,3-dienes is the subject of a subsequent publication. It is surprising that the isolation of a mononuclear [Pd(L)(η^1,η^3-C_8H_{12})] complex should have been so evasive, particulary since the analogous complexes of nickel[10] and platinum[11] have been

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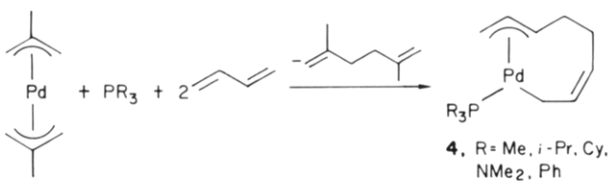
known for many years. One reason for this was presumably the lack of an obvious palladium(0) complex to react with the butadiene. In the case of nickel and platinum, [Ni(cod)$_2$], [Ni(cdt)], and [Pt(cod)$_2$] are stable, relatively easily prepared starting materials, whereas [Pd(cod)$_2$][12] is thermally labile and its preparation is tedious. However, it is known that the reaction of bis(η^3-allyl)nickel with various donor molecules is accompanied by a formal reduction of the nickel from +2 to zero (eq 1).[13] An indication that bis(η^3-allyl)palladium behaves similarly is to be found in the reaction with triphenylphosphine: [Pd(PPh$_3$)$_4$] is formed in good yield.[14]

$$[Ni(\eta^3\text{-}C_3H_5)_2] + PCy_3 \rightarrow Cy_3P\text{—}Ni \qquad (1)$$

Results and Discussion

Bis(η^3-allyl)palladium complexes react with butadiene in the presence of monodentate P-donor ligands to give the [Pd(PR$_3$)(η^1,η^3-C$_8$H$_{12}$)] complexes (**4**) in good yield (eq 2). The preferred starting material is [Pd(η^3-2-MeC$_3$H$_4$)$_2$],

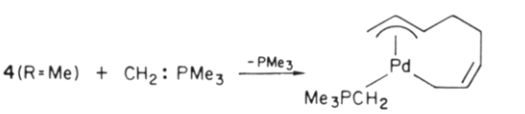


(2)

4, R = Me, *i*-Pr, Cy, NMe_2, Ph

and the reaction is best carried out in THF at room temperature. It was subsequently discovered that the same complexes could also be prepared in respectable yields by reducing palladium salts with magnesium anthracene[15] in the presence of a ligand and butadiene (eq 3) but neither this method nor that involving [Pd(η^3-C$_3$H$_5$)(η^5-C$_5$H$_5$)] offers any synthetic advantage. The trimethylmethylenephosphorane derivative was prepared by ligand exchange (eq 4) and proved to be stable at room temperature—the other examples decompose in solution at −25 to −10 °C.

$$[Pd(acac)_2] + Mg(anthr) + PPh_3 + 2 \xrightarrow{-anthr} \mathbf{4}\,(R = Ph) + Mg(acac)_2 \qquad (3)$$



(4)

The reaction between the bis(η^3-allyl)palladium complex and the tertiary phosphine proceeds in a stepwise manner, and the intermediacy of **5** and **6** have been demonstrated either spectroscopically (^{31}P NMR) or by their isolation (eq 5; see Experimental Section and ref 13a and 16). The structure of **6** (R′ = H, R = Ph) has been confirmed by

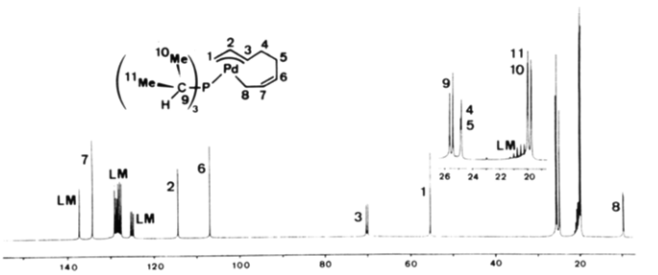


Figure 1. The $^{13}C\{^1H\}$ NMR spectrum of [Pd(P-*i*-Pr$_3$)(η^1,η^3-C$_8$H$_{12}$)] (**4**, R = *i*-Pr) (75 mHz, toluene-d_8, −30 °C).

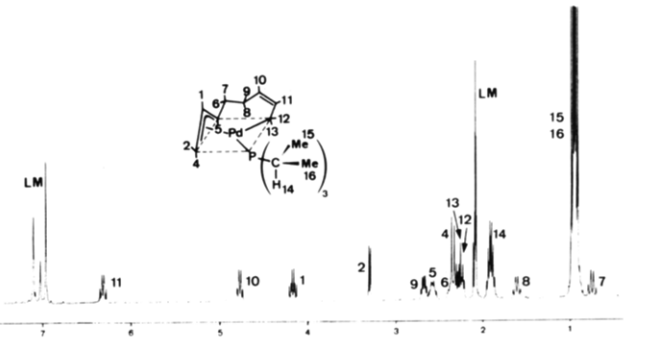
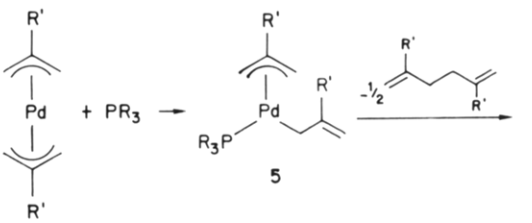


Figure 2. The ^{1}H NMR spectrum of [Pd(P-*i*-Pr$_3$)(η^1,η^3-C$_8$H$_{12}$) (**4**, R = *i*-Pr) (400 MHz, toluene-d_8, −30 °C).

X-ray diffraction.[17] The further reaction of **6** (R′ = Me, R = *i*-Pr; R′ = H, R = Cy) with butadiene to give **4** has been confirmed directly.



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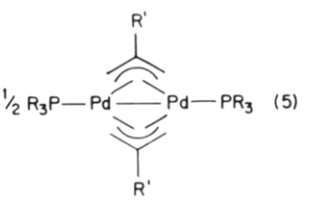
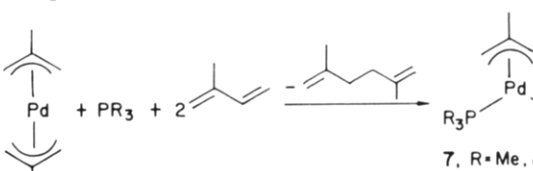


(5)

6, R′ = H, Me

Reactions analogous to those described above have been used to prepare (η^1,η^3-dimethyloctadienediyl)palladium complexes (**7**) from isoprene (eq 6). Here also, selected examples have been prepared by alternative procedures: the P-*i*-Pr$_3$- and PPh$_3$-stabilized complexes by reacting PdCl$_2$ with Mg(anthracene) in the presence of isoprene, the P(NMe$_2$)$_3$-stabilized complex from [Pd(dba)$_2$], and the PCy$_3$-stabilized complex by displacing the diolefin in [Pd(PCy$_3$)(η^2,η^2-1,6-C$_8$H$_{13}$OMe)][3] with isoprene (see Experimental Section).



(6)

7, R = Me, *i*-Pr, Cy, NMe_2, Ph

Preliminary experiments have shown that 2-butyl-1,3-butadiene reacts in a manner similar to isoprene while a related complex has been prepared by reacting allylidenecyclopropane with [Pd(η^3-C$_3$H$_5$)(η^5-C$_5$H$_5$)] and trimethylphosphine.[18]

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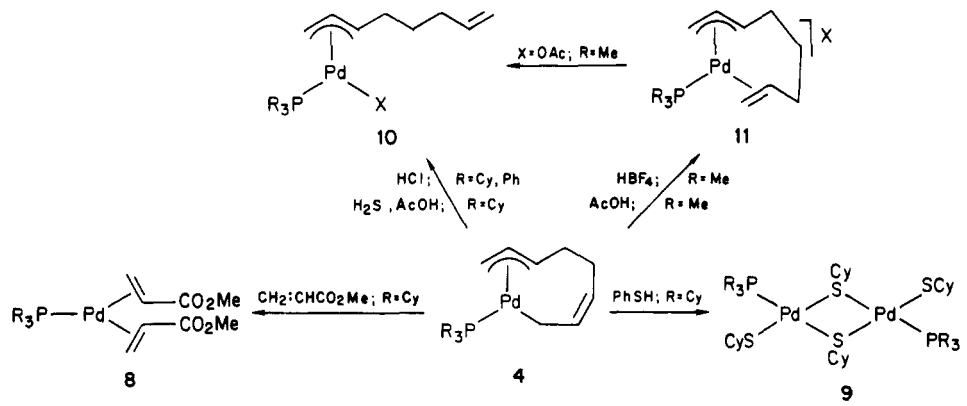
Scheme II



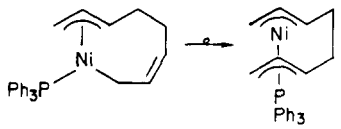
The structures assigned to the various $(\eta^1,\eta^3\text{-}C_8H_{12})$Pd complexes are based upon analysis of their NMR spectra, comparison with data for the analogous nickel complexes,[10] and the crystal structure determination of $[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$.

We will limit ourselves here to discussing the results for $[Pd(P\text{-}i\text{-}Pr_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$. The ^{13}C and ^1H NMR spectra are shown as Figures 1 and 2; complete data for the remaining complexes has been brought together in Tables IV and V. The IR (KBr) spectrum shows absorptions characteristic of an η^3-allyl group at 1521 cm^{-1} and of a cis double bond at 1604 and 703 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum (Figure 1) consists of eight signals for the eight different carbon atoms of the C_8 chain. Diagnostically relevant are, in addition to the multiplicities of the signals in the gated-decoupled spectrum and the ^{13}C–^1H coupling constants, the signals at 55.3, 114.4, and 70.1 ppm, which are typical for the carbon atoms C-1, C-2, and C-3 of an η^3-allyl group, the signals at 106.9 and 134.3 ppm which can be assigned to the double bond (C-6, C-7), and the signal at 9.6 ppm which is characteristic of a metal-bonded carbon atom (C-8). The difference in the P–C coupling constants for the terminal η^3-allylic carbon atoms (C-1, C-3), i.e., $J_{1,P} < 1$ and $J_{3,P} = 27.7$ Hz, are consistent with a square-planar arrangement of the groups about a central metal atom whereby C-1 occupies a position cis and C-3 a position trans to the P atom. The molecule is chiral and as expected two signals are observed for the isopropyl methyl groups.

The 400-MHz ^1H NMR spectrum (Figure 2) has been completely analyzed. The signals at δ 4.17, 3.30, and 2.34 are assigned to the protons of the η^3-allyl group (H-1, H-2, H-4) and its syn substitution follows from the value of 12.3 Hz for $J_{1,5}$. The two quartets at 4.78 and 6.33 ppm are assigned to the olefinic protons H-10 and H-11, and the value of 9.9 Hz for $J_{10,11}$ suggests cis substitition. The antiperiplanar arrangement of H-5 and H-7 as well as H-7 and H-8 follows from the coupling constants $J_{5,7}$ (10.3 Hz) and $J_{7,8}$ (11.7 Hz). The coupling constants $J_{5,6}$, $J_{6,8}$, and $J_{7,9}$ are much smaller (4.9, 2.3, and 1.5 Hz, respectively), indicating that the angles of torsion between these protons lie in the range 60–120 °C and thereby establish the conformation of the chain to be that shown in the figure.

The same conformation of the C_8 chain as in solution has also been verified by X-ray diffraction to be present in the crystal for $[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$.[4,5a] A detailed discussion of this structure is not warranted since a satisfactory refinement of the data was hindered by enantiomeric disorder. However, the basic geometry is identical with that found by X-ray diffraction in $[Pd(PMe_3)(\eta^1,\eta^3\text{-}(c\text{-}C_2H_4)_2C_8H_{10})]$,[18] $[Pt(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$,[11] $[Ni(PCy_3)(\eta^1,\eta^3\text{-}2,6\text{-}Me_2C_8H_{10})]$.[19] The platinum and palladium complexes are moreover isomorphous.

It is of interest that the PPh_3-stabilized complex shows no tendency to rearrange below its decomposition temperature (>–25 °C). This is in contrast to the analogous nickel system which has been shown to rearrange at room temperature to give an η^3,η^3-octadienediyl isomer (eq 7).[10]



(7)

A number of reactions which help to characterize the $(\eta^1,\eta^3$-octadienediyl)palladium complexes are described (Scheme II). Others, relevant as models for palladium-catalyzed telomerization reactions, will be discussed in subsequent publications.

The reaction of $[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ (4, R = Me) and $[Pd(PCy_3)(\eta^1,\eta^3\text{-}Me_2C_8H_{10})]$ (7, R = Cy) with CO or excess PPh_3 results in cleavage of the C_8 chain and elimination of butadiene or isoprene. The reaction of the PMe_3-stabilized complex with CO has been shown to be accompanied by the formation of a 7-metal atom cluster compound, $[\{Pd(PMe_3)(CO)\}_7]$, in which the presence of a face-capped-octahedral arrangement of the palladium atoms has been demonstrated by X-ray methods.[20]

The organic ligand is also displaced in reactions with activated olefins such as methyl acrylate and acrylonitrile to give bis(olefin)palladium ligand complexes, e.g., 8. Preliminary NMR investigations, which have not been pursued further, indicate that these complexes exist in solution as rotamers. Reaction with mercaptans is also accompanied by displacement of the organic ligand to give a complex which is provisionally assigned a binuclear structure with sulfide bridges (9) on the basis of the analytical data. A similar compound is formed in the reactions with diphenyl disulfide.

The reaction with acids deserves to be discussed in more detail since the results are relevant to the mechanism of the palladium-catalyzed telomerization of butadiene with nucleophiles which is the subject of a following paper. A variable-temperature ^{31}P NMR study of the reaction of $[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ (4, R = Me) with acetic acid is shown in Figure 3. The reaction occurs in two steps: at –80 °C an intermediate is formed which reacts further at –30 °C. The first intermediate was not isolable, but its

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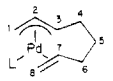
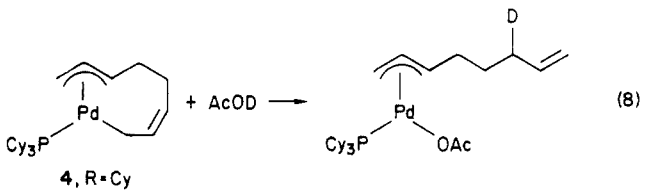
Table I. Selected $^{13}C\{^1H\}$ NMR Data for the $[Pd(PMe_3)(\eta^2,\eta^3\text{-}C_8H_{13})]X$ Complex (11)



	^{13}C NMR δ ($J_{P,C}$ Hz)		
	X = BF_4	X = OAc	X = OMe^3
1	71.0	72.6	71.0
2	116.0 (5.3)	117.2 (4.1)	116.2 (5.8)
3	97.8 (22.2)	97.6 (22.4)	97.1 (22.7)
7	108.8	107.7	107.3
8	75.2	75.8	74.9

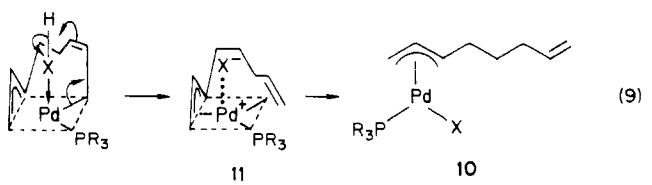
^{13}C NMR spectrum was recorded by following the reaction in an NMR tube and was assigned the (η^2,η^3-octadienyl)-palladium structure **11** by comparing the spectrum with that of the product formed, for example, by treating **4** (R = Me) with HBF_4. The second intermediate was isolated and fully characterized as the η^3-octadienyl derivative **10** (X = OAc).

In other cases (e.g., reaction with HCl or H_2S) only (η^3-octadienyl)palladium complexes were isolated. Of mechanistic importance is the observation that that final product of the reaction of the PCy_3-stabilized complexes (**4**, R = Cy) with AcOD is deuterated exclusively at C-6 (^{13}C NMR δ 34.4 (C-6, $J_{C,D}$ = 19.5 Hz)) (eq 8).



4, R = Cy (8)

Any mechanism which describes the formation of **10** and **11** must explain why the generation of a terminal double bond (which, depending upon the nature of the group X, may or may not interact with the metal) is accompanied by retention of a syn-substituted η^3-allyl group. Various mechanisms can be considered, and for none have we direct evidence. The original suggestion was that of an initial acid (nucleophile) instigated rearrangement of the η^1,η^3-octadienediyl chain to give a configuration having a vinyl substituent (similar to that suggested for **1** followed by addition across the Pd–C bond. However, inspection of models indicates that complexation of the acid to the fifth coordination position at palladium leads to a juxtaposition of the double bond and the proton (one possibility is shown in eq 9; the opposite side of the molecular plane is equally



11 **10** (9)

accessible) and direct attack is perhaps less devious. Conceivable are also mechanisms involving attack of the η^3-allyl fragment, either directly or via the metal, accompanied by rearrangement of the η^1-allyl fragment. Similar behavior has been observed on treatment $[PdL_2(\eta^1,\eta^1\text{-}C_{12}H_{18})]$ with acids.[1]

The nature of the Pd–X bond in **11** will depend upon X. The similarity in the $^{13}C\{^1H\}$ NMR data for the trimethylphosphine-stabilized complexes where X is BF_4, PF_6, OAc, or OMe^3 (Table I) indicates that the bonding of the organic fragment to the metal is very similar in all cases. The BF_4 and PF_6 complexes are certainly ionic as

Table II. The Effect of the Ligand on the Composition of 7 at −30 °C

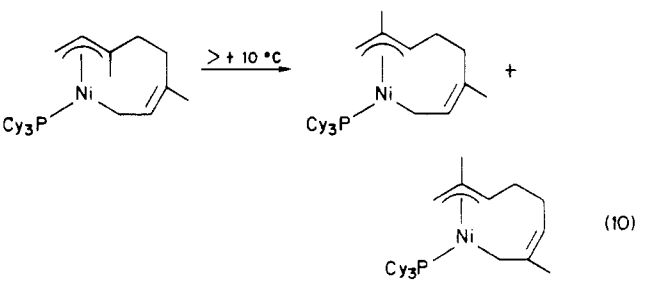
L	2,6-Me_2 subst, %	2,7-Me_2 subst, %
$P(NMe_2)_3$	74	26
P-*i*-Pr_3	65	35
PCy_3	64	36
PPh_3	55	45
PMe_3	28	72

shown by the typical value of 81 $cm^2/(\Omega\cdot mol)$ for the molar conductivity of the PF_6 complex in nitromethane,[5d] and it may be supposed that the acetate and methoxy groups, while occupying the fifth coordination position at palladium, form a strongly polarized bond to the metal.

The $[Pd(PR_3)(\eta^1,\eta^3\text{-}Me_2C_8H_{10})]$ complexes (**7**) prepared by reaction of isoprene are formed as a mixture of two isomers having methyl groups in 2,6- or 2,7-positions. In other words, of the four possible directions of addition of two isoprene molecules only those resulting from tail–tail and tail–head coupling are observed. The relative concentrations of the two isomers were most easily determined from the ^{31}P NMR spectra while the detailed structures followed from an analysis of the ^{13}C and ^1H NMR spectra (Tables VI and VII). This analysis was assisted by comparison with the spectra of the corresponding nickel complexes[10] for one of which, viz., $[Ni(PCy_3)(\eta^1,\eta^3\text{-}2,6\text{-}Me_2C_8H_{10})]$,[19] the structure had been confirmed by X-ray methods. The ratio of the two isomers is ligand dependent (Table II). The values shown are reproducible and correlate with the basicity of the ligand (PMe_3 is an exception).

That the 2,6-substituted isomer is the product of kinetic control and that the 2,7-substituted isomer is thermodynamically more stable are suggested by the results of the reduction of $PdCl_2$ with magnesium anthracene in the presence of P-*i*-Pr_3 or PCy_3 and isoprene at different temperatures which was followed by ^{31}P NMR spectroscopy: at −30 °C the 2,6-substituted isomer is formed exclusively while at +20 °C a 2:1 mixture of the 2,6- and 2,7-substituted isomers is observed.

A comparison of these results with those obtained for the analogous nickel system is of interest. In the case of nickel, the initial product was shown to have 3,6-substitution and to rearrange above +10 °C to the 2,6- and 2,7-substituted isomers (eq 10).[10] No evidence for the



(10)

initial formation of a 3,6-substituted isomer was found in the case of the palladium system; however, this could be the result of the somewhat higher temperature needed to carry out the reaction in the case of palladium.

Experimental Section

Most of the complexes described below are air sensitive and decompose well below room temperature. All reactions were carried out under argon using standard cryomat systems. Solvents were dried and freed from dissolved oxygen by distillation from sodium–potassium alloy and were generally precooled before being used. Butadiene was passed through a tower filled with molecular sieve (4 Å) and then bubbled through monoethoxydiethylaluminum before being distilled.

Table III. Analytical Data for the [Pd(L)(η^1,η^3-$R_2C_8H_{10}$)] Complexes 4 (R = H) and 7 (R = Me)

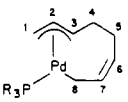
complex	yield, %	color (dec/°C)[c]	anal. (calcd) Pd	P	C	H
L = PMe_3, R = H	75	yellow (>−25)	37.04 (36.60)	10.73 (10.65)	45.91 (45.45)	6.23 (7.30)
L = P-*i*-Pr_3, R = H	87	yellow (>−10)	28.16 (28.39)	8.16 (8.26)	54.56 (54.48)	8.79 (8.87)
L = PCy_3, R = H	80	yellow (>−10)	21.52 (21.49)	6.23 (6.26)	63.14 (63.07)	9.09 (9.18)
L = $P(NMe_2)_3$, R = H	94	yellow (>−20)	28.09[a] =28.16)	8.36 (8.21)	44.66 (44.51)	7.98 (8.00)
L = CH_2PMe_3, R = H	69	palle yellow (stable room temp)	34.73 (34.93)	10.31 (10.17)	47.40 (47.30)	7.40 (7.61)
L = PPh_3, R = H	60	yellow (>−25)	22.12 (22.31)	6.38 (6.50)	65.40 (65.49)	5.85 (5.71)
L = PMe_3, R = Me	72	yellow (>−25)	33.31 (33.38)	9.66 (9.72)	49.09 (48.99)	7.87 (7.91)
L = *i*-Pr_3, R = Me	85	yellow (>−10)	26.49 (26.41)	7.59 (7.69)	56.69 (56.65)	9.19 (9.26)
L = Cy_3, R = Me	91	gray-green (>−10)	20.31 (20.34)	5.89 (5.92)	64.17 (64.30)	9.36 (9.44)
L = $P(NMe_2)_3$, R = Me	88	yellow (>−10)	26.28[b] (26.22)	7.48 (7.63)	47.55 (47.35)	8.51 (8.44)
L = PPh_3, R = Me	59	yellow (>−25)	21.19 (21.07)	6.19 (6.13)	66.49 (66.61)	6.16 (6.19)

[a] % N: 11.16 (calcd 11.12). [b] % N: 10.28 (calcd 10.35). [c] In solution.

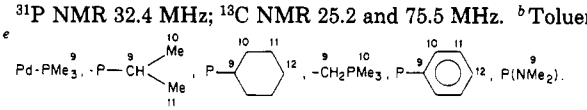
Table IV. ^{31}P and $^{13}C\{^1H\}$ NMR Spectral Data for the [Pd(L)(η^1,η^3-C_8H_{12})] Complexes[a] (4)

	L = PMe_3	P-*i*-Pr_3	PCy_3	$P(NMe_2)_3$	CH_2PMe_3	PPh_3
$\delta(^{31}P)$[b]	−14.1	56.8	43.9	134.0	22.0[c]	36.0
δ(C-1)[b] ($J_{P,C}$, Hz)	56.3 (1.4)	55.34	56.03	51.13 (1.5)	52.6[c]	63.96
δ(C-2) ($J_{P,C}$, Hz)	115.8 (3.4)	114.40 (3.1)	114.85 (3.0)	114.02 (4.0)	110.6	116.64 (3.1)
δ(C-3) ($J_{P,C}$, Hz)	68.0 (30.8)	70.13 (27.7)	69.79 (27.5)	70.90 (35.8)	59.3	68.28 (29.5)
δ(C-4)[d] ($J_{P,C}$, Hz)	25.3 (5.2)	24.84 (1.0)	24.86	24.97 (6.1)	25.9	25.16 (5.1)
δ(C-5)[d] ($J_{P,C}$, Hz)	25.9 (3.6)	24.79	24.93 (3.7)	24.63 (3.8)	25.6	24.42 (3.1)
δ(C-6) ($J_{P,C}$, Hz)	106.2 (1.0)	106.94	107.29	108.05	104.7	107.54
δ(C-7) ($J_{P,C}$, Hz)	133.2	134.28	134.51	135.20	135.8	133.38
δ(C-8) ($J_{P,C}$, Hz)	11.6 (10.5)	9.61 (10.4)	10.07 (10.3)	10.56 (11.2)	16.3	13.66 (9.2)
δ(C-9)[e] ($J_{P,C}$, Hz)	17.1 (25.1)	25.53 (17.8)	35.71 (17.7)	38.13 (9.5)	−5.6 (34.6)	135.33 (38.7)
δ(C-10)[e] ($J_{P,C}$, Hz)		19.99 (3.0)	30.41		15.0 (56.0)	134.18 (13.2)
δ(C-11)[e] ($J_{P,C}$, Hz)		19.73 (2.2)	27.83 (10.4)			128.5 (10.2)
δ(C-12)[e] n$J_{P,C}$, Hz)			26.91			129.95

[a] Structure 4:



[b] ^{31}P NMR 32.4 MHz; ^{13}C NMR 25.2 and 75.5 MHz. [c] Toluene-d_8, −30 °C. [d] THF-d_8, −30 °C. [e] δ(C-4), δ(C-5) assignment could be reversed.



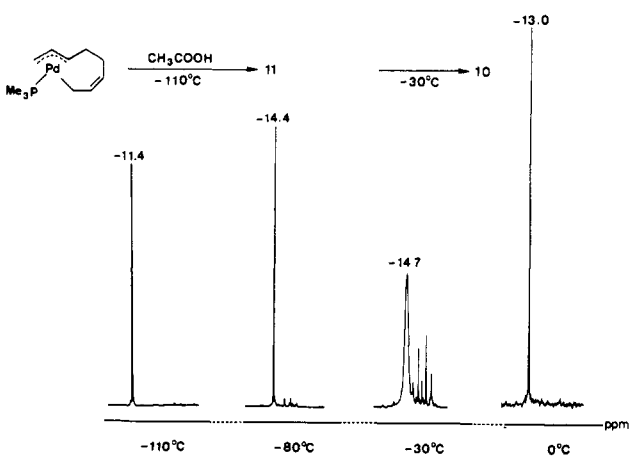


Figure 3. Variable-temperature ^{31}P NMR study of the reaction of [Pd(PMe_3)(η^1,η^3-C_8H_{12})] (4, R = Me) with acetic acid (32.4 MHz, THF-d_8).

The ^{13}C NMR spectra were measured at 75.5 MHz with a Bruker WM 300 and the ^1H NMR spectra at 80 MHz and 400 MHz with Bruker WP 80 and WH 400 instruments. The ^{31}P NMR spectra were measured at 32.4 MHz with a Bruker WP 80 instrument, and the chemical shifts are quoted relative to external aqueous 85% phosphoric acid. The infrared spectra were measured by using a FT-IR spectrometer 7199 from Nicolet Instrument Corp.

Published procedures were used to prepare [Pd(η^3-2-$MeC_3H_4)_2$],[21] [Pd(dba)$_2$],[22] and Mg(anthracene).[15]

Elemental analysis were performed by the firm Dornis & Kolbe, Mülheim a.d. Ruhr.

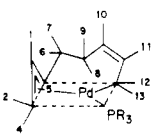
[Pd(P-*i*-Pr_3)(η^1,η^3-C_8H_{12})] (4, R = *i*-Pr). Triisopropylphosphine (3.70 mL, 3.07 g, 19.2 mmol) was added to a solution of [Pd(η^3-2-$MeC_3H_4)_2$] (4.16 g, 19.2 mmol) in THF (80 mL) at −10 °C and cooled to −40 °C. Liquid butadiene (80 mL) was added and the resulting yellow solution stirred at room temperature for 8 days. The butadiene-THF was removed by vacuum distillation at −35 °C, and the raw product treated with THF/pentane (25 mL/100 mL) at −70 °C and cooled to −78 °C. After 2 days the yellow solution was separated from a small amount of gray precipitate, concentrated at −35 °C to $^2/_3$ of the original volume, and then held at −78 °C for 3 days. Yellow crystals precipitated and were isolated at −78 °C, washed with precooled pentane (3 × 50 mL) and dried under high vacuum at −35 °C. Further product was obtained by concentrating the combined mother liquor to give a total of 6.25 g of (4, R = *i*-Pr) (87% theory) as a yellow solid which decomposes above −10 °C. The analytical and spectral data are summarized in Tables III–V: IR (KBr, −35 °C) ν_{allyl} 1521, $\nu_{=CH}$ 3051, $\nu_{C=C}$ 1604, $\nu_{C=CH}$ 3012, $\nu_{cis\text{-}HC=CH}$ 730 cm^{-1}. The complexes 4, stabilized by PMe_3, PCy_3, $P(NMe_2)_3$ and PPh_3, were

(21) Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 425.
(22) Takahasi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

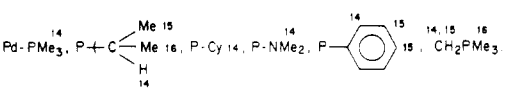
Table V. ^{1}H NMR Spectral Data for the [Pd(L)(η^1,η^3-C_8H_{12})] Complexes[a] (4)

δ(H-*n*) m, *J*, Hz)	PMe_3[b]	P-*i*-Pr_3[b]	PCy_3[c,f]	$P(NMe_2)_3$[b,f]	CH_2PMe_3[d]	PPh_3[b]
H-1	4.18 (dt, $J_{1,4}$ = 12.9, $J_{1,5}$ = 12.1)	4.17 (dt, $J_{1,2}$ = 7.5, $J_{1,4}$ = 12.7, $J_{1,5}$ = 12.3)	4.18 (m)	4.15 (dt, $J_{1,2}$ 7.5)	3.81 (m, $J_{1,2}$ = 7.4, $J_{1,4}$ = 12.6, $J_{1,5}$ = 11.3)	4.29 (dt, $J_{1,2}$ = 7.5, $J_{1,4}$ = 13.0, $J_{1,5}$ = 12.2)
H-2	3.30 (d)	3.30 (d, $J_{2,P}$ = 1.3)	3.36 (d)	3.61 (dd)	2.83 (d)	3.30 (d)
H-4	2.42 (d)	2.34 (d)	2.47 (m)		1.92 (d)	2.79 (d)
H-5	2.61 (m, $J_{5,7}$ = 10.3)	2.58 (m, $J_{5,6}$ = 4.9, $J_{5,7}$ = 10.3, $J_{5,P}$ = 8.1)			1.95 (m, $J_{5,6}$ = 5.0, $J_{5,7}$ = 10.5)	2.74 (m, $J_{5,6}$ = 5.0, $J_{5,7}$ = 11.0, $J_{5,P}$ = 4.0)
H_6	2.33 (m)	2.36 (m, $J_{6,7}$ = −13.1, $J_{6,8}$ = 2.3, $J_{6,9}$ = 7.2)			2.05 (m, $J_{6,7}$ = −12.7, $J_{6,8}$ = 1.9, $J_{6,9}$ = 7.3)	under solv ($J_{6,9}$ = −7.2)
H-7	0.68 (q, $J_{7,8}$ = 12.2)	0.74 (q, $J_{7,8}$ = 11.7, $J_{7,9}$ = 1.5)		0.74 (m)	0.33 (m, $J_{7,8}$ = 12.0, $J_{7,9}$ = 1.4)	0.68 (q, $J_{7,6}$ = −12.0, $J_{7,8}$ = 13.0, $J_{7,9}$ = 1.8)
H-8	1.56 (q)	1.61 (q, $J_{8,9}$ = −12.7, $J_{8,11}$ = −1.1)		1.57 (m)	1.19 (m, $J_{8,9}$ = −12.5, $J_{8,10}$ = 9.0, $J_{8,11}$ = −1.3)	1.58 (q, $J_{8,9}$ = −12.8, $J_{8,10}$ = 9.0, $J_{8,11}$ = −1.2)
H-9	2.65 (m)	2.68 (m, $J_{9,10}$ = 7.4)			2.19 (m, $J_{9,10}$ = 7.3)	2.69 (m, $J_{9,10}$ = 7.3)
H-10	4.68 (q)	4.78 (q, $J_{10,11}$ = 9.9, $J_{10,12}$ = −1.3)	4.82 (m)	4.87 (q)	4.03 (m, $J_{10,11}$ = 10.0, $J_{10,12}$ = −1.7)	4.77 (q, $J_{10,11}$ = 10.2, $J_{10,12}$ = −1.4)
H-11	6.34 (q)	6.33 (q, $J_{11,12}$ = 11.1, $J_{11,13}$ = 7.5)	6.40 (m)	6.40 (q)	5.81 (m, $J_{11,12}$ = 10.5, $J_{11,13}$ = 7.9)	6.20 (q, $J_{11,12}$ = 10.9, $J_{11,13}$ = 7.4)
H-12	2.37 (m)	2.23 (m, $J_{12,13}$ = −6.5)			2.04 (m, $J_{12,13}$ = −5.9)	2.40 (m, $J_{12,13}$ = −6.0)
H-13	2.14 (m)	2.28 (m, $J_{13,P}$ = 12.3)			(1.40) (m)	2.32 (m, $J_{13,P}$ = 13.4)
H-14[e]	0.94 (d)	1.90 (m, $J_{14,15}$ = 7.2, $J_{14,16}$ = 7.1, $J_{14,P}$ = 9.1)		2.39 (d)	(1.37) (m, $J_{14,15}$ −11.4, $J_{14,P}$ 12.9)	7.52 (m)
H-15		0.96[c] (m, $J_{15,P}$ = 13.9)	1.0 − 2.1 (m)		0.78 ($J_{15,P}$ = 12.2)	6.9 (m)
H-16		0.93[c] (m, $J_{16,P}$ = 13.7)			1.60 (d, $J_{16,P}$ = 13.4)	

[a] Structure **4** (400 MHz):



[b] Toluene-d_8, −30 °C. [c] Toluene-d_8, room temperature. [d] THF-d_8 −40 °C. [e]



[f] 80 MHz.

prepared in an analogous manner. The time needed for the reaction to proceed to completion was dependent upon the ligand and increased in the order $P(NMe_2)_3$ (3 days) ≈ PPh_3 > P-*i*-Pr_3 ≈ PCy_3 > PMe_3 (10 days).

[Pd(CH_2PMe_3)(η^1,η^3-C_8H_{12})]. Trimethylmethylenephosphorane (0.14 g, 1.58 mmol) was added to an ether (30 mL) suspension of [Pd(PCy_3)(η^1,η^3-C_8H_{12})] (**4**, R = Cy) (0.783 g, 1.58 mmol) cooled to −78 °C. A pale yellow suspension was formed immediately. The reaction mixture was stirred at −50 °C for a further 4 h, and the precipitate was collected, washed with precooled pentane, and dried under high vacuum at 0 °C; yield 0.33 g (69% theory). The analytical and NMR spectral data are summarized in Tables III–V: IR (KBr) ν_{allyl} 1514, $\nu_{C=C}$ 1595 cm^{-1}.

Alternative Preparative Procedures. The P-*i*-Pr_3-stabilized complex could also be prepared by reacting [{Pd(P-*i*-Pr_3)(μ-η^3-2-MeC_3H_4)}$_2$] (**6**) (1.2 g) with liquid butadiene (30 mL) in THF (30 mL) for 10 days at room temperature. The pale yellow solution was evaporated to dryness at −30 °C and the formation of (**4**, R = *i*-Pr) in 87% yield was demonstrated by ^{31}P NMR spectroscopy. The PPh_3-stabilized complex was also prepared by adding [Pd(acac)$_2$] (1.74 g, 5.7 mmol) to Mg(anthracene)·4.76THF (3.1 g, 5.7 mmol), liquid butadiene (70 mL), and triphenylphosphine (1.50 g, 5.7 mmol) in THF (70 mL) at −30 °C. The suspension was stirred for 20 h at −30 °C, filtered, and evaporated to dryness under high vacuum and dried at −30 °C for 2 days. **4** (R = Ph) was shown by ^{13}C and ^{31}P NMR spectroscopy to have been formed in 77% yield. Mg(anthracene) was also used to convert $PdCl_2$ into the PCy_3-stabilized complex **4** (R = Cy) in a yield of 57%.

The PCy_3-stabilized complex was also prepared by reacting [Pd(η^3-C_3H_5)(η^5-C_5H_5)][23] (0.934 g, 4.12 mmol) with PCy_3 (1.209 g, 4.31 mmol) in ether (40 mL) at −50 °C. After 1 h an orange-red precipitate had formed, and butadiene (40 mL) was added. The reaction mixture was transferred to an autoclave and stirred for 7 days at 50 °C. The reaction mixture was then filtered, cooled to −30 °C, and concentrated to give a yellow precipitate which was collected at −78 °C, washed with pentane, and dried under high vacuum at −30 °C; yield 1.350 g (66% theory).

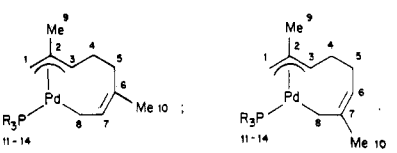
[Pd(P-*i*-Pr_3)(η^1,η^3-$Me_2C_8H_{10}$)] (7, R = *i*-Pr). Triisopropylphosphine (2.64 mL, 2.19 g, 13.7 mmol) was added to a solution of [Pd(η^3-2-MeC_3H_4)$_2$] (2.97 g, 13.7 mmol) in THF (40 mL). Isoprene (40 mL) was added at 0 °C and the reaction mixture

(23) Tatsumo, Y.; Yoshida, T. *Inorg. Synth.* **1979**, *19*, 220.

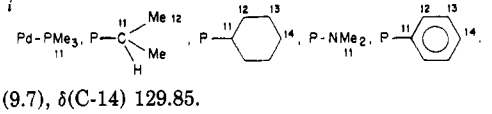
Table VI. ^{31}P and $^{13}C\{^1H\}$ NMR Data for the $[Pd(L)(\eta^1,\eta^3\text{-}Me_2C_8H_{10})]$ Complexes[a] (7)

	PMe_3[c]		P-*i*-Pr_3[c]		PCy_3[d]	$P(NMe_2)_3$[e]		PPh_3[d]	
L	2,6-Me_2	2,7-Me_2	2,6-Me_2	2,7-Me_2	2,6-Me_2	2,6-Me_2	2,7-Me_2	2,6-Me_2	2,7-Me_2
$\delta(^{31}P)$[b]	−13.9	−13.8	58.2	57.1	45.5[f]	136.3	135.6	36.8[g]	36.7[g]
δ(C-1) ($J_{P,C}$, Hz)	57.34	57.10	57.3	57.3	57.41	53.41	55.0	64.1	63.3
δ(C-2) ($J_{P,C}$, Hz)	126.03 (3.0)	126.35 (4.0)	124.11 (2.0)	124.70 (2.0)	124.62	126.96 (4.1)	ca. 124	127.0	ca. 128
δ(C-3) ($J_{P,C}$, Hz)	70.05 (32.8)	66.35 (33.5)	69.61 (29.5)	72.15 (30.5)	72.47	73.23 (38.7)	70.92 (38.7)	71.7	70
δ(C-4) ($J_{P,C}$, Hz)	18.20 (3.1)	20.50 (3.6)	nd	18.3		18.06	ca. 20	17.70 (1.8)	19.84 (4.1)
δ(C-5) ($J_{P,C}$, Hz)	30.82 (5.8)	26.66 (5.5)	26.51 (5.1)	30.38 (5.1)		30.36 (6.1)	26.71 (4.1)	30.72 (5.2)	26.43 (6.1)
δ(C-6) ($J_{P,C}$, Hz)	109.73 (1.6)	103.92	105.82	110.67	111.68	112.50	107.21	112.1	105.9
δ(C-7) ($J_{P,C}$, Hz)	130.16	143.85	144.17	130.94		131.36	143.87	ca. 127.5	144.2
δ(C-8) ($J_{P,C}$, Hz)	12.29 (10.6)	14.66 (10.6)	14.3	11.0 (~7)		12.12 (11.2)	13.59 (9.2)	15.15 (9.7)	18.59 (9.3)
δ(C-9) ($J_{P,C}$, Hz)	21.25	21.10	20.45	21.01	24.27[h]	21.01	ca. 21	20.80	20.59
δ(C-10) ($J_{P,C}$, Hz)	23.98	26.99	27.40	24.15	20.80[h]	24.55	28.11	24.17	26.00
δ(C-11)[i] ($J_{P,C}$, Hz)	17.31 (25.0)	17.60 (24.7)	nd	nd	35.46	38.09 (9.2)	38.32 (10.2)	135.59 (38.4)	135.36 (37.7)
δ(C-12)[i] ($J_{P,C}$, Hz)			20.3	20.3	30.48[i]			134.22[k] (9.1)	134.28[l] (13.8)

[a] Structure 7:



[b] ^{31}P spectra, 32.4 MHz, toluene-d_8, −30 °C. [c] $^{13}C\{^1H\}$ spectra, 75.5 MHz, THF-d_8, −80 °C. [d] $^{13}C\{^1H\}$ spectra, 75.5 MHz, toluene-d_8, −30 °C. [e] $^{13}C\{^1H\}$ spectra, 75.5 MHz, toluene-d_8 −80 °C. [f] 2,7-Me_2 isomer, $\delta(^{31}P)$ 44.1. [g] At −80 °C; at −30 °C both signals fall at 37.0 ppm. [h] Assignment could be reversed. [i]



[j] δ(C-13) 27.88, δ(C-14) 26.89. [k] δ(C-13) 128.48 (9.7), δ(C-14) 129.85. [l] δ(C-13) 128.48 (9.7), δ(C-14) 129.85.

stirred at room temperature for 13 days. The reaction mixture was filtered and evaporated to dryness at −30 °C. The resulting yellow solid was washed with pentane (3 × 30 mL) at −70 °C and dried at −40 °C under high vacuum for 2 days; yield 4.69 g (85% theory). The analytical and NMR spectral data are summarized in Tables III, VI, and VII.

The complexes **7** stabilized by PMe_3, PCy_3, $P(NMe_2)_3$, and PPh_3 were prepared similarly except that the solvent, reaction time, and temperature were varied: **7** (R = Me), ether, 10 days, reflux; **7** (R = Cy), ether, 10 days, reflux; **7** (R = NMe_2), THF, 4 days, room temperature; **7** (R = Ph), THF, 10 days, room temperature.

Alternative Preparative Procedures. **7** (R = NMe_2) was also prepared in a spectroscopic (^{31}P NMR) yield of 56% by reacting $[Pd(dba)_2]$ (160 mg, 0.28 mmol) with isoprene (4 mL) and $P(NMe_2)_3$ (45 mg, 0.28 mmol) at 0 °C. The reaction mixture was stirred overnight and filtered and the yellow solution evaporated to dryness at −30 °C.

7 (R = Cy) was prepared in a spectroscopic (^{31}P NMR) yield of 94% by reacting $[Pd(PCy_3)(\eta^2,\eta^2\text{-}C_8H_{13}OMe)]$[3,5a] (200 mg) with isoprene (40 mL) in ether (200 mL) at −10 °C for 27 h. The solvent was evaporated off at −30 °C and the product dried overnight.

7 (R = *i*-Pr) was prepared in a spectroscopic (^{31}P NMR) yield of 60% by adding $PdCl_2$ (1.22 g, 6.9 mmol) to a mixture of Mg(anthracene)·4.76 THF (3.77 g, 6.9 mmol), isoprene (50 mL), and triisopropylphosphine (1.33 mL, 1.10 g, 6.9 mmol) in THF (50 mL) at −30 °C. The reaction mixture was stirred at −30 °C for 20 h, filtered through a 5 cm Avicel pad, evaporated to dryness, and dried at −35 °C overnight.

A similar procedure was used to prepare **7** (R = Cy) in 48% yield.

$[Pd(PR_3)(\eta^1,\eta^3\text{-allyl})_2]$ Complexes (5). **$[Pd\{P(NMe_2)_3\}(\eta^1,\eta^3\text{-2-}MeC_3H_4)_2]$.** $[Pd(\eta^3\text{-2-}MeC_3H_4)_2]$ (4.51 g, 20.82 mmol) was dissolved in pentane (50 mL) at −78 °C. $P(NMe_2)_3$ (3.8 mL, 20.82 mmol) was added dropwise and the solution stirred for 60 h at −78 °C. A yellow precipitate formed which was collected at −78 °C, washed with pentane (50 mL), and dried under high vacuum at −40 °C yield 7.28 g (92% theory); ^{31}P NMR (32.4 MHz, toluene-d_8, −50 °C) δ 133.2. Anal. Calcd for $C_{14}H_{32}N_3PPd$: C, 44.27; H, 8.49; N, 11.06; P, 8.16; Pd, 28.01. Found: C, 44.30; H, 8.42; N, 11.20; P, 8.22; Pd, 27.93.

$[Pd\{P(OC_6H_4\text{-}o\text{-}Ph)_3\}(\eta^1,\eta^3\text{-2-}MeC_3H_4)_2]$ was prepared similarly: ^{31}P NMR (32.4 MHz, THF-d_8, −50 °C) δ 136.6. Anal. Calcd for $C_{44}H_{41}PPd$: C, 69.98; H, 5.47; P, 4.10; Pd, 14.09. Found: C, 70.10; H, 5.45; P, 3.96; Pd, 13.92.

$[\{Pd(PR_3)(\mu\text{-}\eta^3\text{-allyl})\}_2]$ Complexes (6). **$[\{Pd(PCy_3)(\mu\text{-}\eta^3\text{-}C_3H_5)\}_2]$.** $[Pd(\eta^3\text{-}C_3H_5)_2]$ (1.002 g, 5.3 mmol) and PCy_3 (1.508 g, 5.4 mmol) were dissolved in toluene (50 mL) at −30 °C. The solution was allowed to slowly reach room temperature, and the resulting pale yellow precipitate was filtered off, washed with toluene, and dried under high vacuum: yield 1.766 g (78% theory): ^{31}P NMR (32.4 MHz, toluene-d_8, −30 °C) δ 32.0. Anal. Calcd for $C_{42}H_{76}P_2Pd_2$: C, 58.93; H, 8.97; P, 7.24; Pd, 24.86. Found: C, 59.39; H, 9.00; P, 6.89; Pd, 24.64.

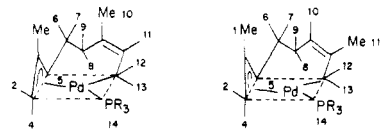
$[\{Pd(PPh_3)(\mu\text{-}\eta^3\text{-}C_3H_5)\}_2]$ was prepared as a pale yellow powder in a similar manner: ^{31}P NMR (32.4 MHz, toluene-d_8, −30 °C) δ 31.1. Anal. Calcd for $C_{42}H_{40}P_2Pd_2$: C, 61.56; H, 4.92; P, 7.56; Pd, 25.97. Found: C, 61.60; H, 4.85; P, 7.50; Pd, 25.95.

$[\{Pd(PMe_3)(\mu\text{-}\eta^3\text{-}C_3H_5)\}_2]$ was prepared similarly as a beige powder: ^{31}P NMR (32.4 MHz, toluene-d_8, −30 °C) δ −22.3; ^1H NMR (80 MHz, toluene-d_8, −30 °C) δ 3.88 (H-1, meso, $J_{1,2}$ = 6.5, $J_{1,3}$ = 12, $J_{1,P}$ = 4 Hz), 2.68 (H-2, syn, J_{2P} = 6 Hz), 1.72 (H-3, anti), 1.01 (PMe); ^{13}C NMR (25.2 MHz, toluene-d_8, −30 °C) δ 27.56

Table VII. ^{1}H NMR Spectral Data for the [Pd(L)(η^1,η^3-$Me_2C_8H_{10}$)] Complexes[a] (7)

δ(H-*n*) (m, *J*, Hz)	PMe_3[b]		P-*i*-Pr_3[c]		PCy_3[c,e]	$P(NMe_2)_3$[c]		PPh_3[c]	
	2,6-Me_2	2,7-Me_2	2,6-Me_2	2,7-Me_2	2,6-Me_2	2,6-Me_2	2,7-Me_2	2,6-Me_2	2,7-Me_2
H-1	1.15 (s)	1.18 (s)	1.27 (s)	1.31 (s)	1.33 (s)	1.28 (s)	1.33 (s)	1.26 (s)	1.31 (s)
H-2	3.16 (s)	3.15 (s)	3.18 (br)	3.18 (br)	3.14	3.48 (d)	3.30 (d)	3.29 (br)	3.25 (br)
H-4	2.05 (s)	2.04 (s)						2.61 (br)	2.51 (br)
H-5	2.78 (dt, $J_{5,6}$ = 6.1, $J_{5,7}$ = 10.4, $J_{5,P}$ = 9.0)	2.49 (dt, $J_{5,6}$ = 5.7, $J_{5,7}$ = 10.8, $J_{5,P}$ = 9.4)			3.05 (t)				
H-6	nd ($J_{6,9}$ = 6.8)	1.95 (m, $J_{6,7}$ = −12.9,. $J_{6,9}$ = 5.5)							
H-7	nd ($J_{7,9}$ = 1.4)	0.94 (m, $J_{7,8}$ = 12.9, $J_{7,9}$ = 1.3)							
H-8	nd ($J_{8,9}$ = −12.4)	1.21 (m, $J_{8,9}$ = −12.6, $J_{8,10}$ = 9.1)							
H-9	2.22 (m)	2.38 (m, $J_{9,10}$ = 7.5)							
H-10	1.41 (s)	3.84 (t)	1.81 (s)	4.70 (t)	1.82 (s)	1.83 (s)	4.71 (t)	1.76 (s)	4.49 (t)
H-11	5.52 (t, $J_{11,12}$ = 10.5, $J_{11,13}$ = 8.0)	1.68 (s)	6.09 (t)		6.12 (t)	6.12 (t)		5.94 (t)	1.64 (s)
H-12		1.90 (d, $J_{12,13}$ = −6.5)							
H-13		1.63 (d, $J_{13,P}$ = 16.5)							
H-14[d]	1.47 (d, $J_{14,P}$ = 8.7)	1.51 (d, $J_{14,P}$ = 8.7)	0.99 (m)	1.01 (m)		2.30 (d)	2.32 (d)	7.63/7.1 (m/m)	7.63/7.1 (m/m)

[a] Structure 7:



[b] 400 MHz, THF-d_8 −80 °C. [c] 80 MHz, toluene-d_8, −30 °C. [d] Pd-PMe_3, P-$CHMe_2$, P-NMe_2, P-C_6H_5 ^{14} ^{14} ^{14} ^{14} [e] 2,7-Isomer, δ(H-2) 3.11, δ(H-10) 4.75 (t).

(CH_2), 87.08 (CH), 16.56 (CH_3). Anal. Calcd for $C_{12}H_{28}P_2Pd_2$: C, 32.23; H, 6.32; P, 13.85; Pd, 47.59. Found: C, 32.31; H, 6.11; P, 13.96; Pd, 47.71.

[{Pd(P(NMe_2)$_3$)(μ-η^3-2-MeC_3H_4)}$_2$] was prepared similarly as a yellow powder: ^{31}P NMR (32.4 MHz, toluene-d_8, −30 °C) δ 132.3. Anal. Calcd for $C_{20}H_{50}N_6P_2Pd_2$: C, 36.99; H, 7.76, N, 12.94; P, 9.54; Pd, 32.77. Found: C, 37.11; H, 7.80; N, 12.96; P, 9.41; Pd. 32.54.

[{Pd(P-*i*-Pr)(μ-η^3-2-MeC_3H_4)}$_2$] was prepared similarly as a bright yellow powder: ^{31}P NMR (32.4 MHz, THF-d_8, −30 °C) δ 41.3. Anal. Calcd for $C_{26}H_{56}P_2Pd_2$: C, 48.53; H, 8.77; P, 9.63; Pd, 33.07. Found: C, 48.70; H, 8.86; P, 9.55; Pd, 32.81.

[{Pd(P(OC_6H_4-*o*-Ph)$_3$)(μ-η^3-2-MeC_3H_4)}$_2$]. [Pd(P(OC_6H_4-*o*-Ph)$_3$)(η^1,η^3-2-MeC_3H_4)$_2$] (1 g, 1.32 mmol) was dissolved in ether (50 mL) and stirred at room temperature for 21 h. The solvent was removed and the yellow solid dried overnight under high vacuum: yield 0.42 g (quantitative); ^{31}P NMR (32.4 MHz, THF-d_8, −30 °C) δ 132.9. Anal. Calcd for $C_{80}H_{68}O_6P_2Pd_2$: C, 68.63; H, 4.90; P, 4.42; Pd, 15.20. Found: C, 68.71; H, 5.00; P, 4.54; Pd, 15.04.

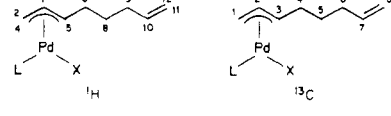
[PdX(PR_3)(η^3-C_8H_{13})] Complexes (10). [PdCl(PCy_3)(η^3-C_8H_{13})]. [Pd(PCy_3)(μ^1,η^3-C_8H_{12})] (4, R = Cy) (1.143 g, 2.31 mmol) was suspended in ether at −70 °C, and 5 mL of a 0.28-mol, cooled solution of HCl in ether was added. A clear, yellow solution resulted which was stirred for a further 4 h. The solution was concentrated, and pentane (10 mL) was added. The resulting white precipitate was collected at −50 °C and dried under high vacuum: yield 0.85 g (69% theory); IR (KBr) $\nu_{C:C}$ 1639, ν_{allyl} 1527 cm^{-1}; ^{31}P NMR (32.4 MHz, toluene-d_8, −50 °C) δ 41.5. ^{13}C NMR (75.5 MHz, toluene-d_8, −30 °C)[24], δ 46.23 (C-1), 113.26 (C-2, $J_{P,C}$ = 3.8 Hz), 102.16 (C-3, $J_{P,C}$ = 26.2 Hz), 31.46 (C-4, $J_{P,C}$ = 3.6 Hz), 28.84 (C-4/5, $J_{P,C}$ = 3.6 Hz), 28.84 (C-5/4, $J_{P,C}$ = 6.1 Hz), 33.93 (C-6), 139.00 (C-7), 114.74 (C-8), 34.46 (Cy, $J_{P,C}$ = 18.9 Hz), 30.34 (Cy), 27.70 (Cy, $J_{P,C}$ = 10.9 Hz), 26.70 (Cy). Anal. Calcd for $C_{26}H_{46}ClPPd$: C, 58.76; H, 8.72; Cl, 6.67; P, 5.83; Pd, 20.02. Found: C, 58.80; H, 8.74; Cl, 6.80; P, 5.87; Pd, 20.06.

[PdCl(PPh_3)(η^3-C_8H_{13})] was prepared similarly as a pale yellow powder in 71% yield: IR (KBr) $\nu_{C:C}$ 1640, ν_{allyl} 1530 cm^{-1}; ^{31}P NMR (32.4 MHz, toluene-d_8, −30 °C) δ 22.5; ^{1}H NMR (80 MHz, THF-d_8, −30 °C)[24] δ 5.46 (H-1, m, $J_{1,2}$ = 6.5 Hz), 2.72 (H-2/4, d, $J_{1,4}$ = 11.5 Hz), 4.35 (H-5, m), 2.16 (H-6/9, m), 5.89 (H-10, m), 4.96 (H-11, d), 5.03 (H-12, d). Anal. Calcd for $C_{26}H_{28}ClPPd$: C, 60.83; H, 5.46; Cl, 6.90; P, 6.04; Pd, 20.74. Found: C, 60.89; H, 5.60; Cl, 6.73; P, 5.97; Pd, 20.66.

[PdSH(PCy_3)(η^3-C_8H_{13})]. [Pd(PCy_3)(η^1,η^3-C_8H_{12})] (4, R = Cy) (0.896 g, 1.81 mmol) was suspended in ether at −70 °C, and 48 mL of a 0.3-mol, cooled solution of H_2S in ether was added. The reaction mixture was stirred overnight to give a clear, orange solution. The solvent was removed, and pentane (10 mL) was added to give a yellow-brown solid = 9.0 was dried at 0 °C under high vacuum: yield 0.56 g (58.5% theory); IR (KBr) ν_{SH} 2550, $\nu_{C:C}$ 1640, ν_{allyl} 1520 cm^{-1}; ^{31}P NMR (32.4 MHz, toluene-d_8 −30 °C) δ 41.5; ^{1}H NMR (400 MHz, toluene-d_8, −30 °C)[24] δ 4.64 (H-1, m, $J_{1,2}$ = 7.0, $J_{1,4}$ = 12.0 Hz), 3.22 (H-2, d, $J_{1,5}$ = 12.5 Hz), 2.21 (H-3, d), 3.53 (H-5, m, $J_{5,7}$ = 3.5, $J_{5,6}$ = 9.0 Hz), 2.36 (H-6, m), 5.72 (H-10, m, $J_{10,9}$ = 6.6, $J_{10,11}$ = 10.0 Hz), 4.98 (H-11, m), 5.01 (H-12, m, $J_{10,12}$ = 17.0 Hz), −0.98 (SH, d, $J_{P,SH}$ = 6.8, $J_{P,5}$ = 9.0 Hz); ^{13}C NMR (75.5 MHz, toluene-d_8, −30 °C) δ 53.37 (C-1), 113.21 (C-2, $J_{P,C}$ = 5.1 Hz), 89.83 (C-3, $J_{P,C}$ = 29.5 Hz), 31.51 (C-4/5, $J_{P,C}$ = 3.6 Hz), 30.20 (C-5/4), 33.89 (C-6), 138.93 (C-7), 114.79 (C-8), 34.96 (Cy, $J_{P,C}$ = 18.3 Hz), 30.45, 30.29 (Cy), 27.75 ($J_{P,C}$ = 11.2 Hz), 27.72 ($J_{P,C}$ = 10.7 Hz, Cy), 26.73 (Cy). Anal. Calcd for $C_{26}H_{47}PPdS$: C, 59.02; H, 8.95; P, 5.85; Pd, 20.11; S, 6.06. Found: C, 59.12; H, 9.02; P, 5.78; Pd, 20.05; S, 5.88.

[PdOAc(PCy_3)(η^3-C_8H_{13})]. [Pd(PCy_3)(η^1,η^3-C_8H_{12})] (4, R = Cy) (0.983 g, 1.99 mmol) was suspended in ether (20 mL) at −30 °C. Acetic acid (0.5 mL, 8.74 mmol) was added, and the yellow solution became almost colorless. The reaction mixture was stirred for 2 h at room temperature and then concentrated. The residue was cooled to −78 °C and reduced with pentane (10 mL). The resulting white precipitate was filtered off, washed with pentane, and dried under high vacuum; yield 0.43 g (39% theory); IR (KBr)

(24) NMR numbering scheme:



ν_{allyl} 1530, $\nu_{C:C}$ 1640, $\nu_{C:O}$ 1600 cm^{-1}; ^{31}P NMR (32.4 MHz, toluene-d_8, −30 °C) δ 40.8. ^{13}C NMR (75.5 MHz, THF-d_8, −30 °C)[24] δ 40.9 (C-1), 113.8 (C-2, $J_{P,C}$ = 3.9 Hz), 101.1 (C-3, $J_{P,C}$ = 25.2 Hz), 32.2 (C-4/5, $J_{P,C}$ = 2.9 Hz), 29.3 (C-5/4, $J_{P,C}$ = 5.6 Hz), 34.5 (C-6), 139.6 (C-7), 114.9 (C-8), 174.5 (C:O), 24.5 (Me), 34.6 (Cy, $J_{P,C}$ = 18.1 Hz), 30.6 (Cy), 28.5 (Cy, $J_{P,C}$ = 10.8 Hz), 27.3 (Cy). Anal. Calcd for $C_{28}H_{48}O_2PPd$: C, 60.59; H, 8.90; P, 5.58; Pd, 19.17. Found: C, 60.43; H, 8.83; P, 5.51; Pd, 19.36.

$[Pd(PR_3)(\eta^2,\eta^3\text{-}C_8H_{13})]^+X^-$ Complexes (11). $[Pd(PMe_3)(\eta^2,\eta^3\text{-}C_8H_{13})]^+BF_4^-$. $[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ (**4**, R = Me) (1.12 g, 3.84 mmol) was stirred in ether (30 mL), and $HBF_4{\cdot}Et_2O$ (0.52 mL, 3.84 mmol) was added at −70 °C. A pale yellow suspension was formed immediately. The reaction was stirred for a further 3 h at −70 °C and the precipitate isolated, washed with pentane at −50 °C, and dried under high vacuum at −30 °C: yield 0.65 g (45% theory); IR (KBr) $\nu_{C:C}$ 1430, 1522, ν_{allyl} 1542 cm^{-1}; ^{31}P NMR (32.4 MHz, acetone-d_8 −30 °C) δ −15.5; ^1H NMR (400 MHz, $CDCl_3$, −30 °C)[25] δ 5.04 (H-1, m, $J_{1,2}$ = 7.2, $J_{1,4}$ = 13.1, $J_{1,5}$ = 12.3 Hz), 4.57 (H-2, d, $J_{2,P}$ = 3.4 Hz), 3.31 (H-4, d), 4.04 (H-5, m, $J_{5,6}$ = 11.5, $J_{5,7}$ = 3.3, $J_{5,P}$ = 9.8 Hz), 1.22 (H-6, m, $J_{6,P} \approx 0.5$ Hz), 2.55 (H-7, m, $J_{7,P}$ = 17.7 Hz), 2.42 (H-8, m), 1.97 (H-9, m), 0.81 (H-10, m), 2.61 (H-11, m), 4.62 (H-12, m), 4.32 (H-13, t, $J_{13,P}$ = 7,9 Hz), 3.52 (H-14, d, $J_{14,P}$ = 1.6 Hz), 1.61 (PMe, d, $J_{P,H}$ = 10.1 Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2, −30 °C) δ 71.0 (C-1), 116.0 (C-2, $J_{P,C}$ = 5.3 Hz), 97.8 (C-3, $J_{P,C}$ = 22.2 Hz), 33.3 (C-4, $J_{P,C}$ = 6.5 Hz), 28.4 (C-5, $J_{P,C}$ = 3.6), 27.7 (C-6), 108.8 (C-7), 75.2 (C-8), 16.4 (PMe, $J_{P,C}$ = 29.4 Hz); molar conductivity (1 °C, CH_2Cl_2, 0.03 mol/L) 22.54 $cm^2/(\Omega{\cdot}mol)$. Anal. Calcd for $C_{11}H_{22}BF_4PPd$: C, 34.91; H, 5.86; B, 2.68; F, 20.08; P, 8.18; Pd, 28.11. Found: C, 34.91; H, 5.83; B, 2.86; F, 20.08; P, 8.26; Pd, 28.08.

$[Pd(PMe_3)(\eta^2,\eta^3\text{-}C_8H_{13})]^+ PF_6^-$.[5d] $[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ (**4**, R = Me) (0.48 g, 1.6 mmol) was suspended in ether (20 mL) at −78 °C, and acetic acid (1 mL) was added. The reaction mixture was held at 0 °C for 5 h and the resulting precipitate collected, washed with water (3 × 10 mL) at 0 °C, and then added to a solution of NH_4PF_6 (1.5 g) in water (10 mL). The resulting yellow solid was washed with water (3 × 5 mL) and dried under high vacuum: yield 0.40 g (58 % theory); IR (KBr, room temperature) ν 1500–1700, ν_{PF_6} 840, 560 cm^{-1}; ^{31}P NMR (32.4 MHz, acetone-d_6, room temperature) δ −16.9 (PMe_3), −145.2 (PF_6, sept, $J_{P,F}$ = 709 Hz); ^1H NMR (400 MHz, acetone-d_6, −30 °C)[25] δ 5.25 (H-1, m, $J_{1,2}$ = 7.4, $J_{1,4}$ = 13.1, $J_{1,5}$ = 12.2 Hz), 4.91 (H-2, m, $J_{2,4}$ = 1.2, $J_{2,5} \approx 0.3$ $J_{2,P}$ = 3.3 Hz), 3.41 (H-4, m, $J_{4,5} = \sim 1.0$, $J_{4,P}$ = 1.5 Hz), 4.20 (H-5, m, $J_{5,6}$ = 3.4, $J_{5,7}$ = 11.4, $J_{5,P}$ = 9.6 Hz), 2.60 (H-6, m, $J_{6,7}$ = −14.6, $J_{6,8} \approx 3.7$, $J_{6,9}$ = 3.9, $J_{6,P}$ = 17.5 Hz), 1.34 (H-7, m, $J_{7,P}$ = 1.4 Hz), 2.41 (H-8, m), 2.05 (H-9, m), 2.65 (H-10, m), 0.86 (H-11, m), 4.70 (H-12, m), 4.57 (H-13, m, $J_{13,P}$ = 7.6 Hz), 3.83 (H-14, d, $J_{14,P}$ = 1.4 Hz), 1.74 (PMe, d, $J_{P,H}$ = 10.6 Hz); molar conductivity (CH_3NO_2) 81 $cm^2/(\Omega{\cdot}mol)$. Anal. Calcd for $C_{11}H_{22}F_6P_3Pd$: C, 30.24; H, 5.08; F, 26.10; P, 14.18; Pd, 24.36. Found: C, 30.26; H, 5.08; F, 26.11; P, 14.19; Pd, 24.37.

$[Pd(PMe_3)(\eta^2,\eta^3\text{-}C_8H_{13})]OAc$ was prepared in solution by reacting $[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ (**4**, R = Me) with acetic acid at −80 °C: ^{31}P NMR (32.4 MHz, THF-d_8 −80 °C) δ −14.4; ^{13}C NMR 75.5 MHz, THF-d_8, −80 °C)[25] δ 72.6 (C-1), 117.2 (C-2, $J_{P,C}$ = 4.1 Hz), 97.6 (C-3, $J_{P,C}$ = 22.4 Hz), 33.9, 29.4, 28.6 (C-4/5/6), 107.7 (C-7), 75.8 (C-8), 15.7 (PMe, $J_{P,C}$ = 29.5 Hz), 174.2 (C:O), 21.7 (Me).

$[Pd(PCy_3)(\eta^2\text{-}CH_2{:}CHCO_2Me)_2]$ (8). $[Pd(PCy_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ (**4**, R = Cy) (1.529 g, 3.09 mmol) was suspended in ether at −40 °C. Methyl acrylate (1.39 mL, 15.46 mmol) was added and the reaction mixture stirred for 24 h at 0 °C. The solution was concentrated and cooled to −40 °C, and cold pentane was added under vigorous stirring. A pale yellow suspension was formed which was filtered off, washed with pentane, and dried under high vacuum at 0 °C: yield 0.73 g (42.3% theory); IR (KBr) $\nu_{C:C}$ 1480, 1510, $\nu_{C:O}$ 1705 (br) cm^{-1}; ^{31}P NMR (32.4 Hz, THF-d_8, +10 °C) δ 35.1, 32.9 (intensity 1:1); ^1H NMR (80 MHz, THF-d_8, −30 °C) δ 3.75 (:CH, br), 2.95 (H_2C:, br), 3.38, 3.40 (Me).

$[\{Pd(SCy)(\mu\text{-}SCy)(PCy_3)\}_2]$ (9). $[Pd(PCy_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ (**4**, R = Cy) (0.72 g, 1.46 mmol) was suspended in ether at −50 °C. The cyclohexylmercaptan (0.17 g, 1.46 mmol) was added and the reaction mixture allowed to reach −20 °C. The suspension changed from red to yellow and a yellow-green precipitate was deposited which was collected and dried under high vacuum at room temperature: yield 0.25 g (28% theory). Anal. Calcd for $C_{30}H_{55}PPdS_2$: C, 58.38; H, 8.98; P, 5.02; Pd, 17.24; S, 10.39. Found: C, 58.33; H, 8.95;, P, 5.10; Pd, 17.37; S, 10.24.

$[\{Pd(SPh)(\mu\text{-}SPh)(PCy_3)\}_2]$. $[Pd(PCy_3)(\eta^1,\eta^3\text{-}C_5H_{12})]$ (**4**, R = Cy) (0.69 g, 1.38 mmol) were suspended in ether (30 mL) at −30 °C. Diphenyl disulfide (0.3 g, 1.38 mmol) was added and the suspension became immediately brown. The reaction mixture was allowed to reach room temperature during which the suspension became red. The reaction mixture was stirred for a further 24 h, and the precipitate was collected and dried under high vacuum at room temperature; yield 0.5 g (71.8% theory). Anal. Calcd for $C_{30}H_{43}PPdS_2$: C, 59.54; H, 7.16; P, 5.12; Pd, 17.58; S, 10.60. Found: C, 59.40; H, 7.15; P, 5.12; Pd, 17.69; S, 10.77.

Registry No. **4** (R = Me), 98391-70-9; **4** (R = Cy), 98391-71-0; **4** ($R = NMe_2$), 98267-92-6; **4** (R = Ph), 98267-93-7; **4** (R = *i*-Pr), 98268-19-0; **5** ($R = NMe_2$, R′ = Me), 98268-06-5; **5** ($R = OC_6H_4$-*o*-Ph, R′ = Me), 98268-07-6; **6** (R = Cy, R′ = H), 98268-08-7; **6** (R = Ph, R′ = H), 75008-90-1; **6** (R = Me, R′ = H), 98268-09-8; **6** ($R = NMe_2$, R′ = Me), 98303-48-1; **6** ($R = OC_6H_4$-*o*-Ph, R′ = Me), 98268-10-1; **6** (R = *i*-Pr, R′ = Me), 62586-39-4; **7** (L = P-$(NMe_2)_3$, 2, 6-Me_2), 98267-95-9; **7** (L = $P(NMe_2)_3$, 2,7-Me_2), 98267-96-0; **7** (L = P(*i*-Pr)$_3$, 2,6-Me_2), 98267-97-1; **7** (L = P(*i*-Pr)$_3$, 2,7-Me_2), 98267-98-2; **7** (L = PCy_3, 2,6-Me_2), 98267-99-3; **7** (L = PCy_3, 2,7-Me_2), 98268-00-9; **7** (L = PPh_3, 2,6-Me_2), 98268-01-0; **7** (L = PPh_3, 2,7-Me_2), 98268-02-1; **7** (L = PMe_3, 2,6-Me_2), 98268-03-2; **7** (L = PMe_3, 2,7-Me_2), 98268-04-3; **8**, 98268-17-8; **9**, 98268-18-9; **10** (R = Cy, X = Cl), 98268-11-2; **10** (R = Ph, X = Cl), 98268-12-3; **10** (R = Cy, X = SH), 98268-13-4; **10** (R = Cy, X = OAc), 98268-14-5; **11** (R = Me, X = BF_4^-), 98268-16-7; **11** (R = Me, X = PF_6^-), 98391-72-1; **11** (R = Me, X = OAc), 98391-73-2; $[Pd(\eta_3\text{-}2\text{-}MeC_3H_4)]$, 41348-25-8; $[Pd(CH_2PMe_3)(\eta^1,\eta^3\text{-}C_8H_{12}]$, 98267-94-8; $Pd(acac)_2$, 14024-61-4; $Pd(dba)_2$, 32005-36-0; $[Pd(PCy_3)(\eta^2,\eta^2\text{-}C_8H_{13}OMe)]$, 98268-05-4; $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$, 1271-03-0; $P(OC_6H_4$-*o*-Ph$)_3$, 2752-19-4; $[Pd(\eta^3\text{-}C_3H_5)_2]$, 12240-87-8; $[\{Pd(PMe_3)(CO)\}_2]$, 83632-51-3; butadiene, 106-99-0; trimethylmethylenephosphorane, 14580-91-7; isoprene, 78-79-5; methyl acrylate, 96-33-3; cyclohexylmercaptan, 1569-69-3; diphenyl disulfide, 882-33-7.

(25) NMR numbering scheme: