Insertion Reactions of Allenes with Palladium Aryl Complexes $[PdI(Ph)(PPh_3)]_2$ and PdI(Ph)(dppe)

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Treatment of $[PdI(Ph)(PPh_3)]_2$ with allenes $CH_2{=}C{=}CHR$ (R = CMe_3, CO_2Et, $P(O)(OEt)_2$, and SO_2Ph) in dichloromethane at room temperature produces a mixture of cis and trans isomers of the π-allyl palladium complexes $PdI(\eta^3\text{-}CH_2C(Ph)CHR)(PPh_3)$ in which the R group is anti to the Ph group. The disubstituted allenes $MeCH{=}C{=}CHR$ (R = $P(O)(OEt)_2$ and SO_2Ph) similarly react with $[PdI(Ph)(PPh_3)]_2$ to give the π-allyl palladium complexes $PdI(\eta^3\text{-}MeCHC(Ph)CHR)(PPh_3)$ in which the R group is anti and the Me group is syn to the Ph group. PdI(Ph)(dppe) alone was found to be unreactive toward allenes such as $CH_2{=}C{=}CHSO_2Ph$ and $MeCH{=}C{=}CHSO_2Ph$ at room temperature. In contrast, in the presence of $TlPF_6$, PdI(Ph)(dppe) readily reacts with allenes $CH_2{=}C{=}CHR$ (R = CMe_3, CO_2Et, COPh, and SO_2Ph) and $MeCH{=}C{=}CHSO_2Ph$ to give the π-allyl palladium complexes $[Pd(\eta^3\text{-}CH_2C(Ph)CHR)(dppe)]PF_6$ and $[Pd(\eta^3\text{-}MeCHC(Ph)CHR)(dppe)]PF_6$, respectively. Although mechanistically possible, vinyl complexes were not observed as the insertion products in all cases. The substituents of allenes appear to have no effect on the reaction pathways, at least for the allenes used in this study. The insertion reactions involving $PdI(Ph)(PR_3)$(allene) have been studied by computational chemistry using the model complex $PdI(Ph)(MeCH{=}C{=}CHSO_2H)(PH_3)$.

Introduction

Allenes are an interesting class of organic compounds with unusual chemical properties due to their two cumulated double bonds. There have been much interest in using them as starting materials for the synthesis of various target molecules of industrial and biological significance.[1,2] Among their various reactions, palladium-catalyzed coupling reactions of allenes with aryl halides and related substrates have received much attention. These reactions are usually initiated by palladium phosphine complexes such as $Pd(PPh_3)_4$, $Pd(dba)_2/PPh_3$, and $Pd(OAc)_2/PPh_3$. A variety of products can be obtained from the coupling reactions, for example, 1,3-dienes,[3] 2-arylamines,[4] butenolides,[5] furans,[6] dihydrofuran,[7] benzofuran,[8] pyrrolidines,[9] tetrasubstituted allenes,[10] cyclopropane or cyclopentene derivatives,[11] iminolactones and γ-hydroxy-γ-lactams,[12] 4-substituted-2,5-dihydrofurans or vinylic epoxides,[13] oxazolines,[14] epoxyoxindoles,[15] and other interesting polycyclic compounds,[16] to name a few.

In most of the catalytic reactions mediated by these phosphine complexes, the aryl group is transferred to the central carbon of allenes. Occasionally attachment of aryl to the terminal carbons of allenes was also observed.[17,18] The substituents of

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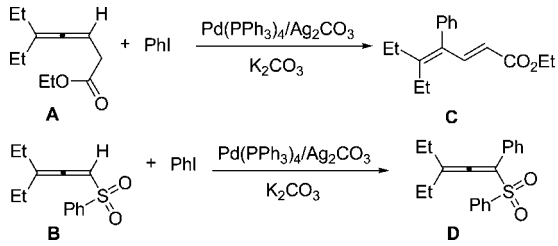
Scheme 1



allenes as well as reaction conditions could have a drastic effect on the regiochemistry of the coupling reactions, as illustrated in Scheme 1 by the reactions of **A**[3] and **B**[10] with PhI catalyzed by $Pd(PPh_3)_4$ to give **C** and **D**, respectively.

It is generally believed that the catalytic reactions proceed by initial oxidative addition of aryl halides to Pd(0) species to give aryl palladium complexes. For reactions giving products with the aryl group attached to the central carbon of allenes, insertion of allenes into Pd−Ar bonds to give π-allyl intermediates has often been proposed as one of the most important fundamental steps. For reactions giving products with the aryl group attached to the terminal carbon of allenes, insertion of allenes into Pd−Ar bonds to give vinyl intermediates has been proposed or implied as one of the most important fundamental steps in some of the catalytic reactions.

In supporting the proposed mechanism, oxidative addition of aryl halide to palladium(0) phosphine complexes has been established; for example, $Pd(PPh_3)_4$ readily undergoes oxidative addition to ArI to give aryl complexes $Pd(Ar)I(PPh_3)_2$.[19] However, experimental evidence for the insertion of allenes into Pd−Ar bonds is still weak since reported examples of insertion reactions of Pd−aryl complexes containing phosphine ligands are surprisingly still very rare, despite their importance in catalytic reactions and a substantial amount of reported work on allene insertion reactions of palladium complexes.[20–27] In fact, only a few examples of insertion of allenes into Pd−aryl bonds have been reported. Allyl complexes were obtained from the reactions of $CH_2{=}C{=}CMe_2$ with cyclometalated palladium complexes such as $[PdCl(C_6H_4C_5H_4N)]_2$[20] and from the reaction of $CH_2{=}C{=}CHPh$ with $PdI(C_6H_3\text{-}3,5\text{-}Me_2)(bipy)/AgBF_4$.[21] The reaction of $PdX(Ph)(PEt_3)_2$ with 1,2-propadiene in the presence of silver tetrafluoroborate to give the cationic η^3-allylic complex $[Pd(PEt_3)_2(\eta^3\text{-}CH_2CPhCH_2)]BF_4$ was briefly mentioned by Stevens et al.[22] We noted that insertion of simple allenes such as $CH_2{=}C{=}CH_2$ and $CH_2{=}C{=}CMe_2$ into Pd−H, Pd−Me, Pd−vinyl, Pd−acyl, and Pd−allyl complexes containing phosphine ligands to give allyl complexes has been reported for complexes such as $PdH(PCy_3)_2(P(O)(OCMe_2CMe_2O))$,[23] $PdClMe(PPh_3)_2$,[24] $[PdMe(MeCN)(dppp)]BF_4$,[24] $Pd(O_2CCF_3)(C(Ph){=}CH_2)(PPh_2Py)$,[25] $[Pd(C(O)C_6H_4\text{-}p\text{-}Me)(MeCN)(PPh_3)_2]BF_4$,[24] and $PdCl(\eta^3\text{-}C_3H_5)(PPh_3)$.[26]

To better understand the mechanisms of coupling reactions of aryl halide and allenes catalyzed by Pd/PPh_3 systems, it is obviously of interest to further study the insertion reactions of allenes with complexes containing phosphine ligands. In reported coupling reactions of aryl halides with allenes catalyzed by Pd/PPh_3 systems, the Pd/PPh_3 ratio varies from 1:1 to 1:4. Insertion reactions of Pd(II) complexes with unsaturated substrates usually proceed through four-coordinate species,[28] while the possibility involving five-coordinate species has also been occasionally proposed.[29] Thus it is reasonable to imagine that the insertion reactions involved in catalytic coupling reactions of aryl halide (ArX) with allenes catalyzed by Pd/PPh_3 systems could proceed through neutral four-coordinate monophosphine intermediates $PdX(Ar)(PR_3)$(allene), five-coordinate bisphosphine intermediates $PdX(Ar)(PR_3)_2$(allene), or cationic four-coordinate bisphosphine intermediates $[Pd(Ar)(PR_3)_2(allene)]^+$. For this purpose, we have studied the reactions of a series of allenes with $[PdI(Ph)(PPh_3)]_2$ and PdI(Ph)(dppe) in either the absence or presence of an iodide abstractor. Through the study, we hope (i) to provide supporting evidence for the insertion reactions of allenes into Pd−Ar bonds proposed in the mechanisms of coupling reactions of aryl halides with allenes and (ii) to find out if substituents on allenes affect the pathways of allene insertions, thereby causing the different regiochemistry observed in the coupling reactions of allenes with aryl halides.

Results and Discussion

Reactions of Allenes with $[PdI(Ph)(PPh_3)]_2$. To study allene insertion reactions involving neutral four-coordinate monophosphine intermediates $PdX(Ar)(PR_3)$(allene), we have studied the reactions of $[PdI(Ph)(PPh_3)]_2$ (**1**) with allenes containing either electron-donating or electron-withdrawing groups. The chloro-bridged dinuclear complexes $[PdCl(Ph)L]_2$ (L = PPh_3, PMePh, or PBu_3) readily undergo bridge cleavage reactions with L to give *trans*-$PdCl(Ph)L_2$.[30] Thus we expected that the iodo-bridged dinuclear complex $[PdI(Ph)(PPh_3)]_2$ (**1**)[31] will react with allenes to give intermediates $PdI(Ph)(PPh_3)$(allene), which may undergo allene insertion reactions.

When a mixture of $[PdI(Ph)(PPh_3)]_2$ (**1**) and 1,2-cyclononadiene (**2**) in dichloromethane was stirred at room temperature

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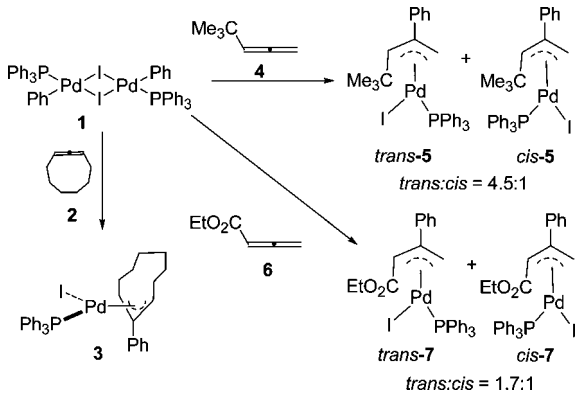
Scheme 2



for 30 min, the allyl complex PdI(η^3-*cyclo*-CHC(Ph)CH-$(CH_2)_6$)(PPh_3) (**3**) was produced (Scheme 2). Complex **3** was isolated as a pale yellow solid. Its structure has been confirmed by an X-ray diffraction study. The molecular structure of **3** is shown in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. The X-ray structure shown in Figure 1 clearly reveals that the complex contains an allyl, a PPh_3, and an iodide ligand. In complex **3**, the two terminal Pd−C(allyl) bond distances (2.197(4) Å for Pd−C(1) and 2.182(4) Å for Pd−C(3)) are noticeably longer than that of the central Pd−C(2) bond (2.147(4) Å). The Pd−C(1) bond is slightly longer than the Pd−C(3) bond. Similar to what has been observed in complexes such as PdI(CH_2CHCH_2)(PPh(*t*-Bu)(*O*-menthyl),[32] PdBr(allyl)(PR_3),[33] PdCl(CH_2CHCH_2)(PR_3),[34] and PdCl(CH_2CMeCH_2)(PR_3),[35] the Pd−C(allyl) bond trans to PR_3 is usually longer than the Pd−C(allyl) bond trans to halide, due to the difference in trans influence.

Consistent with the solid state structure, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 24.5 ppm. The ^1H NMR spectrum shows two ^1H signals of the allylic protons at ca. 4.7 and 5.9 ppm.

Treatment of **1** with *tert*-butylallene (**4**) produces the allyl complex PdI(η^3-$CH_2CPhC(Ph)CHCMe_3$)(PPh_3) (**5**), which was isolated as a bright yellow solid in 84% yield. There are four possible isomers for **5** because the CMe_3 group can be in anti or syn positions relative to the Ph group of the allyl ligand, and the PPh_3 ligand can be trans or cis to the allylic carbon having the CMe_3 group. The NMR data suggest that the isolated solid contains two isomers in a ratio of 4.5:1. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 22.5 (major) and 23.1 (minor) ppm. In the ^1H NMR spectrum, the major isomer shows the allylic proton signals at 3.63 (br s, 1 H, CH_2), 3.70 (br m, 1 H, CH_2), and 5.68 (dd, J(PH) = 6.6 Hz, J(HH) = 1.8 Hz, C*H*CMe_3) ppm. The minor isomer shows the allylic proton signals at 4.06 (dd, J(PH) = 11.0 Hz, J(HH) = 2.4 Hz, 1 H, CH_2), 4.68 (br dt, J(PH) = 7.2 Hz, J(HH) = 2.1 Hz, CH_2), and 4.87 (br m, 1 H, $CHCMe_3$) ppm.

The structures of the isomers can be assigned on the basis of the magnitude of the P−H coupling constants. It has been noted that palladium complexes of the type PdCl(η^3-allyl)(PR_3)[36] and Pd[(η^3-allyl)$(PR_3)_2$]$^+$ [37] have a $J(H_{anti}-P_{trans})$ coupling constant of 11–13 Hz, a $J(H_{syn}-P_{trans})$ coupling constant of 6–8 Hz, and a $J(H_{anti\ or\ syn}-P_{cis})$ coupling constant of ca. 0 Hz. Thus the ^1H NMR data suggest that the major isomer of **5** can be assigned to ***trans*-5**, in which the PPh_3 ligand is trans to $CHCMe_3$ and CMe_3 is anti to Ph, while the minor isomer can be assigned to ***cis*-5**, in which the PPh_3 ligand is cis to $CHCMe_3$ and CMe_3 is also anti to Ph, as shown in Scheme 2.

The structure of ***trans*-5** has been confirmed by X-ray diffraction. As shown in Figure 2, the allylic ligand is bound to Pd unsymmetrically with the more substituted terminal allylic carbon (C(3)) trans to PPh_3 and the CH_2 group (C(1)) trans to iodide. The Pd−C(1) and Pd−C(3) bond distances are 2.143(2) and 2.2363(19) Å, respectively. The longer Pd−C(3) bond compared with Pd−C(1) is expected because of the greater trans influence of PPh_3 compared with I.

The fact that ***trans*-5** is more abundant than ***cis*-5** in solution is probably not surprising when the steric effect of PPh_3 is considered. It has been reported that solutions of

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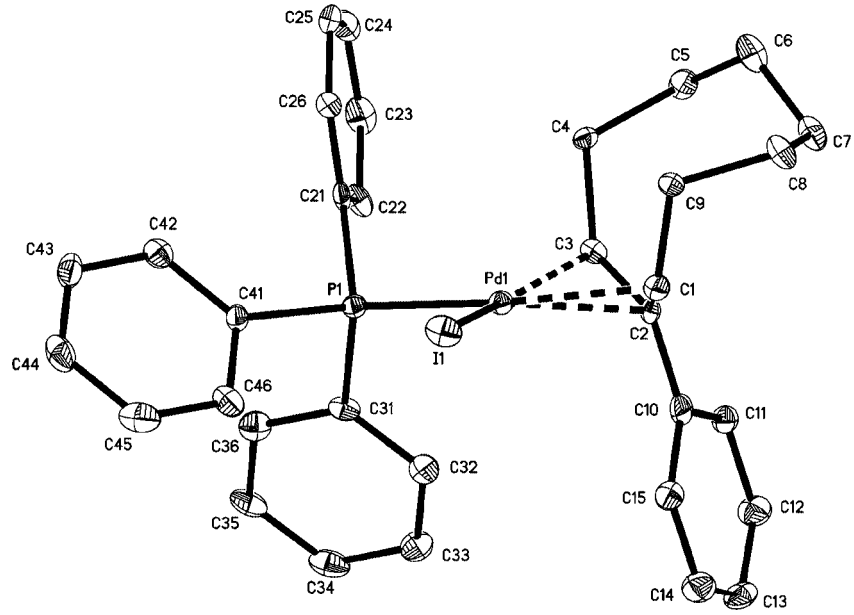

Figure 1. X-ray structure of compound **3** with thermal ellipsoids shown at the 40% probability level.

Table 1. Crystallographic Data and Structure Refinement Details for PdI(η^3-*cyclo*-CHC(Ph)CH(CH$_2$)$_6$)(PPh$_3$) (3), PdI(η^3-(CH$_2$CHC(Ph)CHCMe$_3$)(PPh$_3$) (trans-5), PdI(η^3-CH$_2$C(Ph)CH(SO$_2$Ph))(PPh$_3$) (*cis*-13), PdI(η^3-MeCHC(Ph)CH(SO$_2$Ph))PPh$_3$ (*cis*-15), PdI(η^3-(CH$_2$C(Ph)CH(P(O)(OEt)$_2$))(PPh$_3$) (*trans*-9), and PdI(η^3-MeCHC(Ph)CH(P(O)(OEt)$_2$))(PPh$_3$) (*cis*-11)

	3	***trans*-5**	***cis*-13**	***cis*-15**	***trans*-9**	***cis*-11**
empirical formula	$C_{33}H_{34}IPPd$	$C_{31}H_{32}IPPd$	$C_{33}H_{28}IO_2PPdS$	$C_{34}H_{30}IO_2PPdS$	$C_{31}H_{33}IO_3P_2Pd$	$C_{32}H_{35}IO_3P_2Pd$
fw	694.87	668.84	752.88	766.91	748.81	762.84
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*2(1)	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*n*
a, Å	8.6509(17)	14.8326(11)	9.8674(8)	15.5188(11)	17.7153(12)	12.2084(13)
b, Å	19.449)4)	10.1125(7)	17.5903(14)	17.4313(13)	9.8948(6)	14.0521(15)
c, Å	9.4379(19)	18.9106(14)	17.8699(14)	23.4898(16)	19.5425(13)	19.558(2)
α, deg	90	90	90	90	90	90
β, deg	116.13(3)	95.5750(10)	98.8060	91.454(2)	115.7450(10)	105.207(2)
γ, deg	90	90	90	90	90	90
V, Å^3	1425.6(5)	2823.1(4)	3065.1(4)	6452.2(8)	3085.6(3)	3237.7(6)
Z	2	4	4	8	4	4
D_{calcd}, g cm^{-3}	1.619	1.574	1.632	1.604	1.612	1.565
μ, mm^{-1}	1.810	1.824	1.761	1.701	1.735	1.655
2θ range, deg	2.62–25.00	2.29–26.00	2.23–27.00	1.31–27.50	1.28–27.00	1.78–27.00
no. of data collected	12765	15844	17634	37681	17661	18703
no. of unique data	4795	5514	6653	14 342	6669	7057
no. of params/restraints	325/1	307/0	364/0	723/0	349/0	353/5
goodness of fit on F^2	1.009	1.046	1.006	1.001	1.029	0.914
R1 ($I > 2\sigma(I)$)	0.0243	0.0197	0.0432	0.0444	0.0440	0.0492
wR2 ($I > 2\sigma(I)$)	0.0422	0.0484	0.0939	0.0855	0.1254	0.1173
peak/hole, e Å^{-3}	0.740/−0.407	0.689/−0.371	1.049/−0.482	0.838/−0.624	1.155/−0.838	0.955/−0.640

complexes such as PdCl(CH$_2$C(Fc)CHCOFc)(PPh$_3$),[38] PdX(CH$_2$-CHCHPh)(PPh$_3$) (X = Cl, I),[39] PdCl(CH$_2$CHCHMe)(PCy$_2$R) (R = Cy, 2-biphenyl),[40] PdCl(CH$_2$CHCMe(SiMe$_3$)(PPh$_3$),[41] and PdCl(CH$_2$CHCHMe)(MOP)[42] contain only the trans isomer in which the PR$_3$ is trans to the more substituted alyllic carbon. Both trans and cis isomers were previously observed in complexes PdCl(CH$_2$CHCHPh)(PPh(1-naphthyl)(R)) (R = Me, *i*-Pr).[43]

The substitutents R in allyl complexes PdCl(CH$_2$CHCHR)-(PR′$_3$) are usually at a position syn to the proton of the central allyllic carbon. However, only isomers with the CMe$_3$ group at the anti position were observed for **5**, probably due to the steric effect of the Ph and CMe$_3$ groups. We noted that CH$_2$=C=CHPh undergoes an insertion reaction with PdI(C$_6$H$_3$-3,5-Me$_2$)(bipy) in the presence of AgBF$_4$ to give the allyl complex [Pd(CH$_2$C(C$_6$H$_3$-3,5-Me$_2$)CHPh)(bipy)]BF$_4$ as a 2:1 mixture of syn and anti isomers.[21] Like complex **5**, the C(O)Fc group in complex PdCl(CH$_2$C(Fc)CHC(O)Fc)(PPh$_3$) is also in the anti position.[38]

Similar reaction occurred between **1** and CH$_2$=C=CHCO$_2$Et (**6**), which has the electron-withdrawing group CO$_2$Et, giving the allyl complex PdI(η^3-CH$_2$CPhC(Ph)CHCO$_2$Et)(PPh$_3$) (**7**) as a mixture of ***trans*-7** and ***cis*-7** in a ratio of 1.7:1 (Scheme 2). The structures of the isomers can be readily assigned on the basis of their NMR data. In the room-temperature ^{31}P{^{1}H} NMR

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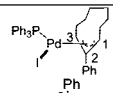
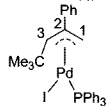
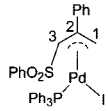
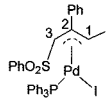
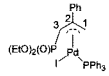
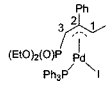
Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 3, *trans*-5, *trans*-9, *cis*-11, *cis*-13, and *cis*-15

compounds	structure	Bond distances (Å)			Bond angles (deg)			
		Pd(1)-C(1)	Pd(1)-C(2)	Pd(1)-C(3)	I-Pd-P	C(1)-Pd(1)-P	C(3)-Pd(1)-P	C(1)-C(2)-C(3)
3		2.197(4)	2.147(4)	2.182(4)	103.71(3)	165.39(10)	96.30(10)	121.6(4)
trans-**5**		2.143(2)	2.1634(19)	2.2363(19)	104.640(13)	92.23(6)	160.00(5)	119.44(18)
cis-**13**		2.218(5)	2.182(4)	2.085(5)	99.80(3)	164.85(16)	97.95(13)	117.0(5)
cis-**15**		2.314(5)	2.189(5)	2.073(5)	100.89(4)	165.21(13)	98.81(14)	119.9(5)
trans-**9**		2.162(4)	2.157(3)	2.183(4)	102.65(2)	92.73(10)	160.76(10)	117.6(3)
cis-**11**		2.263(5)	2.184(4)	2.085(5)	99.64(3)	166.97(14)	100.19(14)	117.4(5)

spectrum, the signals of the major isomer ***trans*-7** and the minor isomer ***cis*-7** were observed at 26.9 and 24.0 ppm, respectively. In the room-temperature ^{1}H NMR spectrum, the minor isomer ***cis*-7** exhibits sharp allylic signals at 4.91 ppm with a J(PH) of 9.9 Hz for anti-CH_2, 5.08 ppm with a J(PH) of 6.0 Hz for syn-CH_2, and 4.68 ppm for CHCO$_2$Et with unresolvable P−H coupling, confirming that PPh_3 is trans to CH_2 and that CO_2Et is anti to Ph. The major isomer ***trans*-7** is fluxional above 258 K, as indicated by the ^{1}H NMR spectrum. Thus, in the room-temperature ^{1}H NMR spectrum, the allylic CHCO$_2$Et proton signal of ***trans*-7** was observed at 5.39 ppm with a J(PH) coupling constant of 8.5 Hz, while the ^{1}H signals of the allylic CH_2 are too broad to be observed due to fast exchange of the two protons. When the temperature is lowered below 258 K, the signals of the CH_2 group appeared. At 218 K, the ^{1}H NMR spectrum showed the allylic signals at 5.35 ppm with a J(PH) coupling constant of 8.5 Hz for CHCO$_2$Et and at 4.90 and 3.88 pm for CH_2. It should be noted that two sharp ^{1}H NMR signals were observed for the allylic CH_2 of ***cis*-7** at room temperature, indicating that the two protons are not exchanging with each other. The observation that ***trans*-7** is fluxional but ***cis*-7** is not at room temperature can be related to the trans effect of PPh_3. Exchange of CH_2 in PdI(η^3-$CH_2C(Ph)CHCO_2Et$)(PPh_3) presumably proceeds through a PdI(η^1-$CH_2C(Ph)$=$CHCO_2Et$)(PPh_3) intermediate (eq 1). Due to the stronger trans influence of PPh_3, the opening of the substituted end of the allyl group in PdI(η^3-$CH_2C(Ph)CHCO_2Et$)(PPh_3) to give PdI(η^1-$CH_2C(Ph)$=$CHCO_2Et$)(PPh_3) is more favorable for the trans isomer. It is noted that the analogous allyl complex *trans*-PdCl(η^3-$CH_2C(Ph)CHCMe_3$)(PPh_3) (***trans*-5**) is not fluxional at room temperature. Probably, the CO_2Et group of ***trans*-7** can help to stabilize the η^1-allyl intermediate through π-conjugation, thus making the fluxional process easier.

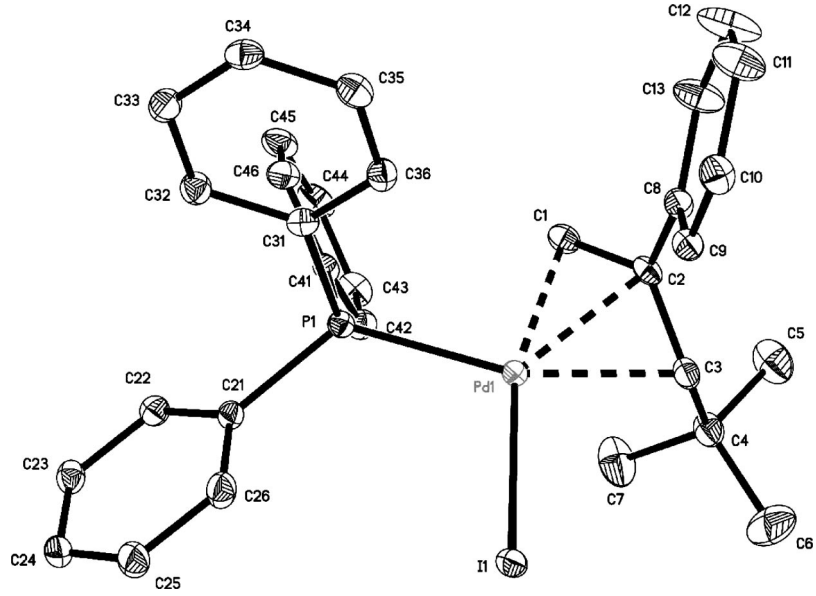
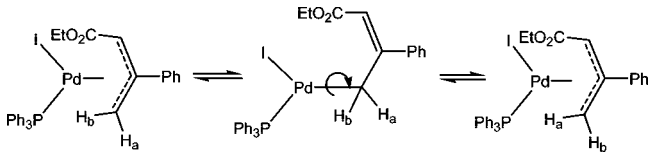


Figure 2. X-ray structure of compound ***trans*-5** with thermal ellipsoids shown at the 40% probability level.



(1)

1,2-Allenyl diethylphosphonate **8** reacts with **1** to give the allyl complex PdI(η^3-$CH_2CPhC(Ph)CHP(O)(OEt)_2$)($PPh_3$) (**9**) as a mixture of ***trans*-9** and ***cis*-9** in a ratio of 3.5:1 (Scheme 3). The presence of these isomers can be readily identified by the $^{31}P\{^1H\}$ NMR spectrum, in which ***trans*-9** shows two doublets at 17.4 ($P(O)(OEt)_2$) and 25.8 (PPh_3) ppm with a J(PP) coupling constant of 19.0 Hz. ***cis*-9** shows two singlets at 19.0 ($P(O)(OEt)_2$) and 25.3 (PPh_3) ppm. The chemical shifts of the palladium-bound PPh_3 are similar to those of complexes **5** and **7**, indicating that they have similar coordination spheres. In the ^1H NMR spectrum, the allylic C*H*P signal of ***trans*-9** was observed at 4.96 ppm with a $J(H-P(PPh_3))$ coupling constant of 7.0 Hz, and that of ***cis*-9** was observed at 4.16 ppm without $J(H-P(PPh_3))$ coupling. The ^1H NMR data are consistent with the structures in which the $P(O)(OEt)_2$ substituent in **9** is anti to the Ph group.

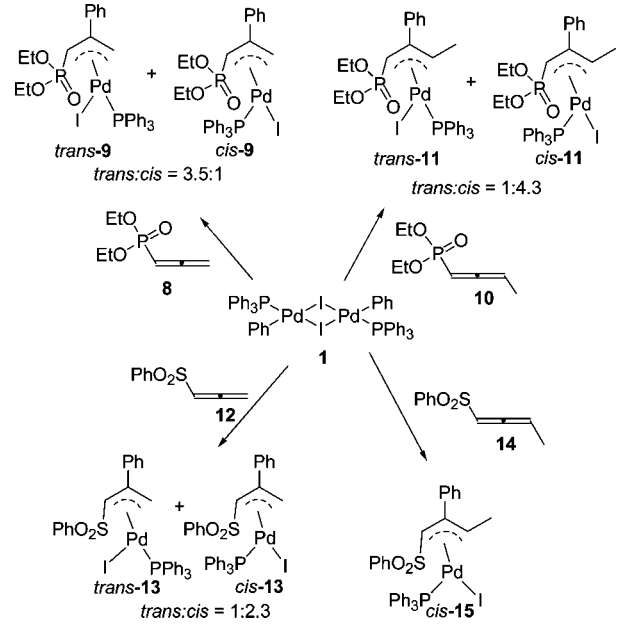
An X-ray diffraction study of ***trans*-9** confirms that $P(O)(OEt)_2$ is indeed anti to the Ph group in the complex (Figure 3). ***trans*-9** is structurally closely related to ***trans*-5**. Some differences in the structural features associated with Pd(η^3-allyl) were noted for ***trans*-9** and ***trans*-5** (Table 2). In particular, the Pd−C(1) bond (2.162(4) Å) in ***trans*-9** is slightly longer than that in ***trans*-5** (2.143(2) Å), while the Pd−C(3) bond (2.183(4) Å) in ***trans*-9** is appreciable shorter than that in ***trans*-5** (2.2363(19) Å). As expected, the Pd−C(1) bond (2.162(4) Å) is shorter than the Pd−C(3) bond (2.183(4) Å) in ***trans*-9** due to stronger trans influence of PPh_3 compared with iodide. However the difference is not as significant as that observed for ***trans*-5**. The structural data may suggest that *C*H($P(O)(OEt)_2$ in ***trans*-9** is bound to Pd more strongly than *C*HCMe_3 in ***trans*-5**. Apparently, the electron-withdrawing nature of $P(O)(OEt)_2$ strengthens the bonding interaction between Pd and the allylic carbon.

When the methyl-substituted allene MeCH=C=CHP(O)-$(OEt)_2$ (**10**) was allowed to react with **1**, a mixture of two isomers of the palladium allyl complex PdI(η^3-MeCHC(Ph)-$CHP(O)(OEt)_2$)(PPh_3) (**11**) was obtained as one might expect (Scheme 3). However, different from the previous cases, the major isomer is the cis isomer ***cis*-11** rather than the trans isomer ***trans*-11** (***trans*-11**/***cis*-11** = 1:4.3). It appears that the Me group decreases the stability of the trans isomer. The presence of the methyl substituent introduces a strong repulsive interaction with the PPh_3 ligand in the trans isomer (not in the cis isomer), weakens the Pd−C(H)(Me) bonding interaction, and therefore decreases the stability.

The structure of ***cis*-11** has been determined by X-ray diffraction. As revealed by the structure shown in Figure 4, the $P(O)(OEt)_2$ substituent is anti to the Ph, while Me is syn to Ph. The allyl ligand is unsymmetrically bound to Pd with the Pd−C(1) bond (2.263(5) Å) being significantly longer than the Pd−C(3) bond (2.085(5) Å). A large difference in the Pd−C bond distances can be related to the fact that PPh_3 is a stronger trans influence ligand than iodide and that $P(O)(OEt)_2$ is electron-withdrawing, while Me is electron-donating.

In the insertion reactions of **1** with $CH_2=C=CHR$ (R = CMe_3, CO_2Et, $P(O)(OEt)_2$), the reaction products are a mixture of two isomeric allyl complexes, with the trans isomer being

Scheme 3



the major one. Thus one might expect that reaction of $CH_2=C=CHSO_2Ph$ (**12**) with **1** would give similar results. Indeed, **12** readily reacts with **1** to produce a mixture of two isomers of PdI(η^3-$CH_2C(Ph)CHSO_2Ph$)(PPh_3) (**13**). However, the cis isomer ***cis*-13** was found to be the major isomer (***trans*-13**:***cis*-13** = 1:2.3). The isomer ratio remained unchanged after standing the reaction mixture for more than 2 days. Therefore the ratio must be related to relative thermodynamic stability. The result implies that the $-SO_2Ph$-substituted carbon ligand could exert the largest trans influence among the carbon ligands studied here with various substituents such as CO_2Et and $P(O)(OEt)_2$) and destabilize the trans isomer that has a PPh_3 ligand trans to it. Among the several X-ray structures of the allyl complexes reported here, we indeed found that the Pd−C(H)(SO_2Ph) bonds are the shortest (Table 2).

The structures of the two isomers can be assigned on the basis of their NMR data, as described previously for analogous

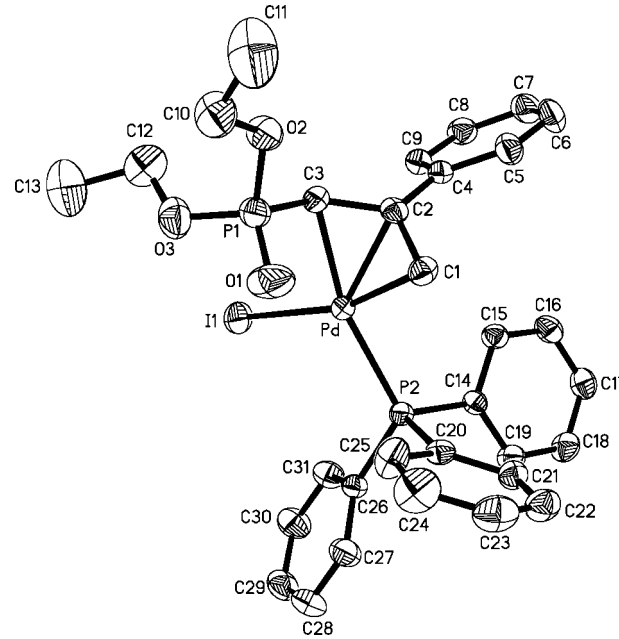


Figure 3. X-ray structure of compound ***trans*-9** with thermal ellipsoids shown at the 30% probability level.

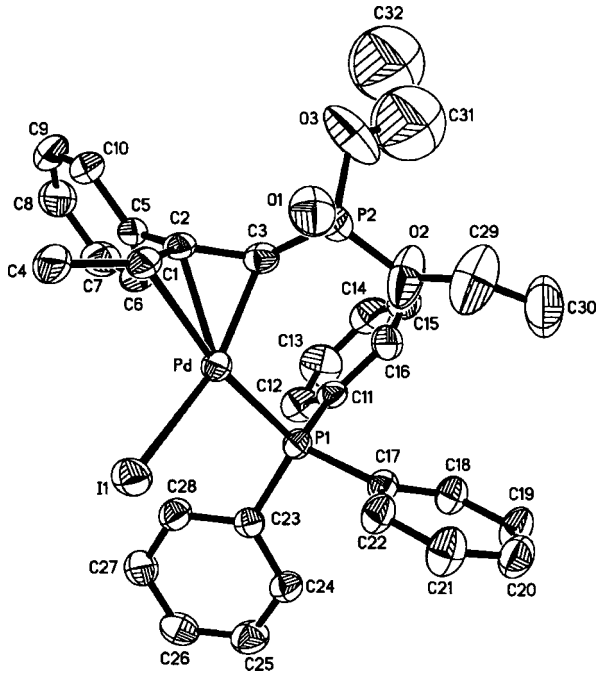


Figure 4. X-ray structure of compound ***cis*-11** with thermal ellipsoids shown at the 30% probability level.

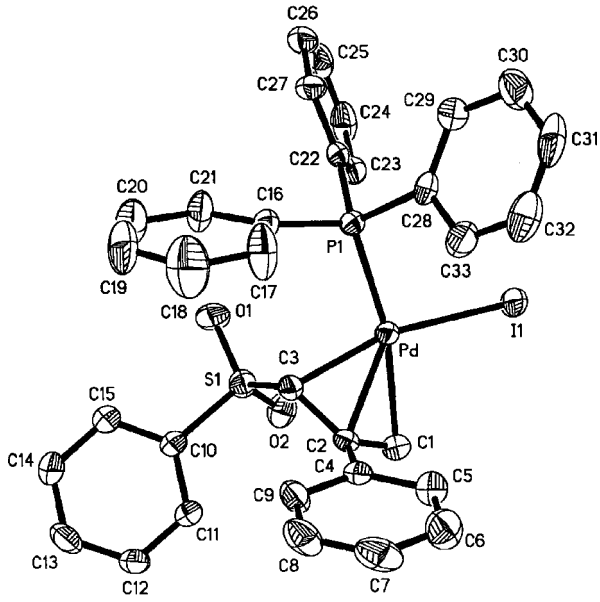


Figure 5. X-ray structure of compound ***cis*-13** with thermal ellipsoids shown at the 30% probability level.

complexes. In addition, the structure of ***cis*-13** has also been confirmed by an X-ray diffraction study (Figure 5). Overall, the structural features associated with the Pd(η^3-allyl) moiety in ***cis*-13** are very similar to those of the analogous complex ***cis*-11**, except that the Pd−C(1) bond (2.218(5) Å) in ***cis*-13** is slightly shorter than that (2.263(5) Å) in ***cis*-11**.

The methyl-substituted allene $MeCH_2$═C═$CHSO_2Ph$ (**14**) undergoes insertion with **1** to give only the cis isomer (***cis*-15**) of the allyl complex PdI(η^3-MeCHC(Ph)$CHSO_2Ph$)(PPh_3). As mentioned previously, a mixture of cis and trans isomers (in a ratio of 2.3:1) was observed for the analogous complex PdI(η^3-CH_2CPhC(Ph)$CHSO_2Ph$)(PPh_3) (**13**). The result is consistent with the stabilizing effect of a methyl group for the cis isomer noted for allyl complexes with a $P(O)(OEt)_2$ substituent (see discussion above).

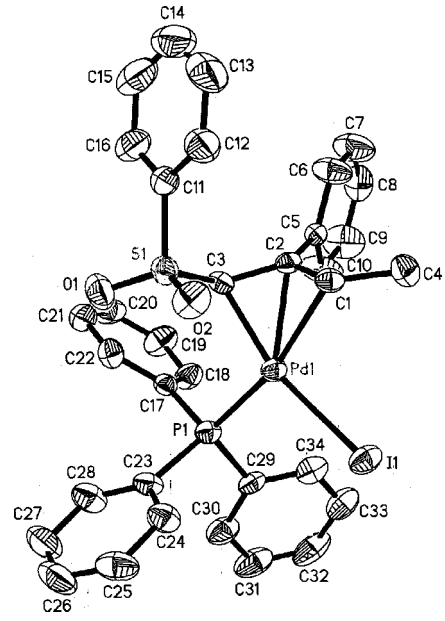


Figure 6. X-ray structure of compound ***cis*-15** with thermal ellipsoids shown at the 30% probability level.

The structure of ***cis*-15** has also been determined by an X-ray diffraction study, which indicates that the SO_2Ph group is anti while Me is syn to the Ph group (Figure 6). The structural features associated with the Pd(η^3-allyl) moiety in ***cis*-15** are very similar to those in PdI(η^3-MeCHC(Ph)CHP(O)$(OEt)_2$)(PPh_3) (***cis*-11**). The only noticeable differences are that the Pd−C(1) bond distance of ***cis*-15** (2.314(5) Å) is appreciably longer than that of ***cis*-11** (2.263(5) Å), while the Pd−C(3) bond distance of ***cis*-15** (2.073(5) Å) is slightly shorter than that of ***cis*-11** (2.085(5) Å), suggesting that SO_2Ph is more electron-withdrawing than $P(O)(OEt)_2$. The solid state structure is fully supported by the solution NMR data.

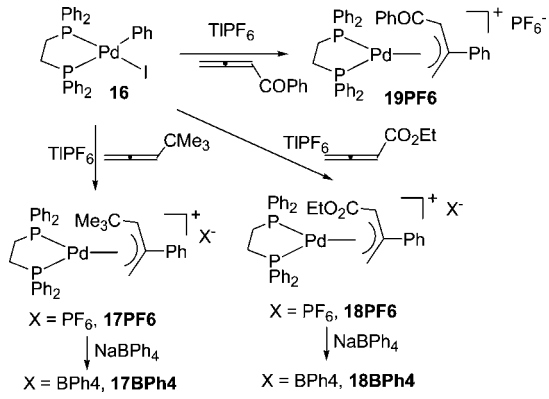
Reactions of Allenes with [PdPhI(dppe)] in the Presence of $TlPF_6$. To model insertion reactions involving Pd species containing two phosphine ligands, we have carried out reactions of allenes with PdI(Ph)(dppe) (**16**). In catalytic reactions using Pd/PPh_3 as the catalyst, PdI(Ph)$(PPh_3)_2$ could be generated. However, PdI(Ph)(dppe) instead of PdI(Ph)$(PPh_3)_2$ was used in our study, because we want to minimize the chance of phosphine dissociation to give monophosphine species. The starting material PdI(Ph)(dppe) was prepared by reaction of $Pd(PPh_3)_4$ with dppe followed by PhI.[44]

It is generally believed that insertion reactions of Pd(II) complexes with unsaturated substrates usually proceed through four-coordinate species, although reactions involving five-coordinated species have also been proposed occasionally in the literature. Thus, without dissociation of phosphine, PdI(Ph)(dppe) may undergo insertion reactions with allenes through four-coordinate intermediates $[PdPh(dppe)(allene)]^+$ or five-coordinate intermediates PdI(Ph)(dppe)(allene).

To test if facile insertion reactions can occur through five-coordinate intermediates PdI(Ph)(dppe)(allene), we have monitored by NMR the reactions of PdI(Ph)(dppe) with allenes CH_2═C═$CHSO_2Ph$ and MeCH═C═$CHSO_2Ph$. As indicated by in situ $^{31}P\{^1H\}$ NMR, no appreciable reactions occurred after a 1:2 (molar ratio) mixture of PdI(Ph)(dppe) and an allene (CH_2═C═$CHSO_2Ph$ or $MeCH_2$═C═$CHSO_2Ph$) in benzene or

(44) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4511.

Scheme 4



dichloromethane was stood at room temperature for 12 h. The observation suggests that insertion reactions through five-coordinate intermediates PdI(Ph)(dppe)(allene) cannot occur readily.

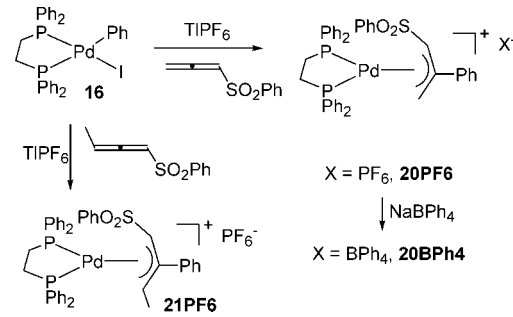
In contrast, facile insertion reactions were observed when the reactions were carried out in the presence of $TlPF_6$, which can help to remove the iodide to generate $[Pd(Ph)(dppe)]^+$ and $[PdPh(dppe)(allene)]^+$ subsequently in situ. Treatment of PdI(Ph)(dppe) (**16**) with $CH_2{=}C{=}CHR$ (R = CMe_3, CO_2Et, COPh, SO_2Ph) in dichloromethane in the presence of $TlPF_6$ rapidly produced the cationic allyl complexes $[Pd(\eta^3\text{-}CH_2C(Ph)CHR)(dppe)]PF_6$ (**17PF6**, R = CMe_3; **18PF6**, R = CO_2Et; **19PF6**, R = COPh; **20PF6**, R = SO_2Ph). Reaction of **16** with $MeCH{=}C{=}CHSO_2Ph$ in the presence of $TlPF_6$ produced the analogous allyl complex $[Pd(\eta^3\text{-}MeCHC(Ph)CHSO_2Ph)(dppe)]PF_6$ (**21PF6**) (Schemes 4 and 5). The complexes can be converted to the corresponding BPh_4 salts on treatment with $NaBPh_4$.

The structures of these allyl complexes can be deduced on the basis of their NMR data. Consistent with the unsymmetrical nature of the structures shown in Schemes 4 and 5, the $^{31}P\{^1H\}$ NMR spectrum of each of the allyl complexes exhibits two doublet signals. The presence of an η^3-allyl ligand and the stereochemistry of the allyl ligand are clearly indicated by the ^1H NMR data. For example, the ^1H NMR spectrum of **17BPh4** displayed two allylic proton signals of CH_2 at 4.15 and 4.49 ppm and that of C*H*CMe_3 at 5.58 ppm with a *J*(PH) coupling constant of 5.8 Hz. The magnitude of the *J*(PH) coupling constant suggests that the CMe_3 group is anti to the Ph group.

The room-temperature ^1H NMR spectrum of $[Pd(\eta^3\text{-}CH_2C(Ph)CHCO_2Et)(dppe)]BPh_4$ (**18BPh4**) shows the signal of the allylic proton of C*H*CO_2Et at 5.41 ppm with a *J*(PH) coupling constant of 6.8 Hz, again suggesting that the allylic proton is syn to the Ph group and that the CO_2Et group is anti to the Ph group. At room temperature, only one signal at 5.01 ppm was observed for the two CH_2 protons of **18BPh4**, suggesting that the two protons are exchanging rapidly. Similarly, the analogous allyl complex $[Pd(\eta^3\text{-}CH_2C(Ph)CHCO_2Et)(dppe)]BPh_4$ (**19BPh4**) displayed the C*H*COPh proton signal at 6.32 ppm and the CH_2 signal at 5.19 ppm. The NMR data of **20** and **21** are in agreement with the structures shown in Scheme 5.

Theoretical Study. In the discussion above, we have presented our experimental results of insertion reactions of $[PdIPh(PR_3)]_2$ and PdI(Ph)(dppe) with a series of allenes containing either an electron-withdrawing or an electron-donating group. The results clearly show that insertion reactions of allenes involving both neutral species $PdI(Ph)(PR_3)$(allene) and the cationic species $[Pd(Ph)(dppe)(allene)]^+$ always give allyl complexes. The possible insertion products of vinyl

Scheme 5



complexes were not observed in our experiments in this study for all the allenes used in this study.

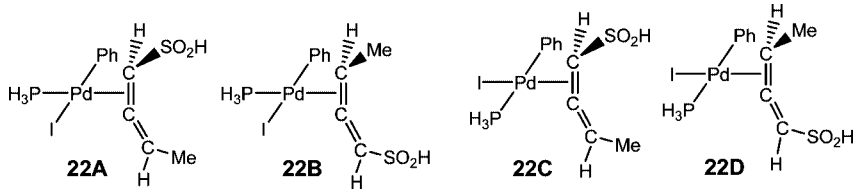
In order to examine the relative barriers for the formation of allyl complexes, which were observed in the present systems, and vinyl complexes, a computational study was carried out. In the computational study, we used the model complex $PdI(Ph)(\eta^2\text{-}MeCH{=}C{=}CHSO_2H)(PH_3)$ (**22**), which is related to the reaction intermediate in the reaction of $[PdI(Ph)(PPh_3)]_2$ with $MeCH{=}C{=}CHSO_2Ph$. Scheme 6 shows four structural isomers of $PdI(Ph)(\eta^2\text{-}MeCH{=}C{=}CHSO_2H)(PH_3)$ (**22**) that are possible precursor complexes for allene insertion. In both the precursor complexes **22A** and **22B**, the Ph ligand is trans to I and the allene ligand is trans to PH_3. In **22A**, the allene is bound to Pd via the C=C double bond having an $-SO_2H$ substituent. In **22B**, the allene is bound to Pd via the C=C double bond having a methyl substitutent. In both the precursor complexes **22C** and **22D**, the Ph ligand is trans to PH_3 and the allene ligand is trans to I. In **22C**, the allene is bound to Pd via the C=C double bond having an $-SO_2H$ substituent. In **22D**, the allene is bound to Pd via the C=C double bond having a methyl substituent.

The four precursor complexes have comparable stabilities, with **22A** being the most stable one. Since a coordinated allene can switch the coordinated C=C double bond rapidly, it is reasonable to assume that the four precursor complexes can all participate in the insertion reaction. Figure 7 shows the relevant energy profiles for the eight possible reaction pathways of the insertion reactions from the four precursor complexes. Each precursor complex gives rise to two possible pathways, one leading to the formation of an allyl complex and the other leading to the formation of a vinyl complex.

The calculation results show that the reaction pathway from **22A** to give first the intermediate **23A**, then ***trans*-24**, and finally the allyl complex ***cis*-24** is both thermodynamically and kinetically the most favorable among all the reaction pathways studied. The allyl complex ***cis*-24** is a model complex for the product ***cis*-15** observed in the reaction of $[PdI(Ph)(PPh_3)]_2$ with $MeCH{=}C{=}CHSO_2Ph$ (see Scheme 3). The calculation results are clearly consistent with the experimental observation discussed above.

The insertion reactions from the precursor complexes **22A** and **22C**, whose coordinated C=C double bond has an $-SO_2H$ substituent, give the allyl complexes favorably. However, the insertion reactions from the precursor complexes **22B** and **22D**, whose coordinated C=C double bond has a methyl substituent, give the vinyl complexes kinetically favorably. In an early study on allene insertion into a metal−hydride bond, we have established that the migratory hydride acts as a nucleophile, attacking one of the two carbons in the η^2-coordinated C=C

Scheme 6



bond.[45] The preferred reaction pathways observed here can also be understood when we also consider the migratory phenyl ligand acting as a nucleophile. It is known that the central carbon of allene is electron-deficient. The $-SO_2H$ substituent is an electron-withdrawing group, while methyl is an electron-donating group. Therefore, the inductive effect of the SO_2H at the coordinated C═C π bond and the methyl group at the noncoordinated C═C π bond will make the central carbon of the allene ligand in **22A** and **22C** even more electron-deficient than the $-SO_2H$-substituted carbon when the π-electron density of the coordinated C═C π bond is considered. As a result, the phenyl ligand migrates preferentially to the central carbon, leading to the formation of an allyl complex. In **22B** and **22D**, in contrast, the central carbon of the allene ligand may become more electron-rich than the methyl-substituted carbon when the π electron density of the coordinated C═C π bond is considered, due to the inductive effect of the methyl at the coordinated C═C π bond and the SO_2H group at the noncoordinated C═C π bond. Therefore, the phenyl ligand migrates preferentially to the methyl-substituted carbon to give a vinyl complex if the insertion reaction occurs in the precursor complex **22B** or **22D**.

It is noted that reaction pathways involving **22C** and **22D** have a higher barrier than the corresponding pathways involving **22A** and **22B**; that is, **TSC** and **TSC′** are higher in energy than **TSA** and **TSA′**, respectively, and **TSD** and **TSD′** are higher in energy than **TSB** and **TSB′**, respectively. It is likely that the trans arrangement of the iodide ligand with respect to the allene ligand in **22C** and **22D** constitutes a push–pull scenario that enhances the metal(d)-to-allene(π*) back-bonding interactions, increases the π electron density of the two carbons in the coordinated C═C bond, and thus increases the phenyl migration energy barriers. Earlier theoretical studies have already shown that olefin insertion into an M−R bond is kinetically and thermodynamically less favorable when a metal(d)-to-olefin(π*) back-bonding interaction is present.[46]

Clearly, the regioselectivity uncovered from the calculation results is a result of both the $-SO_2H$ and −Me substituents being capable of polarizing the π electron density in the coordinated C═C π bond of the allene ligand, making one carbon of the coordinated C═C bond more π-electron-deficient and the other more π-electron-rich, and thus giving rise to the discrimination against the π-electron-rich carbon to which the phenyl ligand migrates. **TSA′** is higher in energy than **TSB′**, but **TSA** is lower than **TSB** (Figure 7a). **TSC′** is higher in energy than **TSD′**, but **TSC** and **TSD** are comparable in stability (Figure 7b). These results indicate that the $-SO_2H$ substituent of the coordinated C═C π bond has a greater polarizing power than the −Me substituent. The lower barrier for the formation of an allyl complex from **22A** via **TSA** compared with that for the formation of a vinyl complex from **22B** via **TSB** is apparently related to the difference in the π electron density of the cabron atom to which the Ph migrates.

In the calculations, we used PH_3 as a model phosphine for PPh_3 employed in the experiments. It is necessary to examine whether the simple model is sufficient. Employing PPh_3 as the phosphine ligand, we optimized the species corresponding to **22A**, **TSA′**, **TSA**, ***trans*-24**, and ***cis*-24** in Figure 7. In the PH_3-based models, the relative electronic energies of **22A**, **TSA′**, **TSA**, ***trans*-24**, and ***cis*-24** are 0.0, 14.7, 6.7, −39.7, and −45.4 kcal/mol, respectively. With PPh_3 used as the phosphine ligand, the relative electronic energies are, 0.0, 17.8, 9.8, −40.3, and −45.3 kcal/mol, respectively. The barriers increase slightly from the simple models to the realistic models. The additional calculations based on the realistic PPh_3 ligand indicate that the conclusions derived from the simple model calculations are valid. The results are understandable because the steric and electronic effects of the PPh_3 ligands are similar for the reactants and the transition states.

Conclusion

We have studied the insertion reactions of $[PdI(Ph)(PPh_3)]_2$ and PhI(Pd)(dppe) with allenes containing various substituents. While PdI(Ph)(dppe) was found to be unreactive toward allenes such as CH_2═C═$CHSO_2Ph$ and MeCH═C═$CHSO_2Ph$ at room temperature, $[PdI(Ph)(PPh_3)]_2$ and PhI(Pd)(dppe)/$TlPF_6$ readily react with allenes to give η^3-allyl complexes, presumably through the intermediates PdI(Ph)(PPh_3)(allene) and $[PdI(Ph)(dppe)(allene)]^+$, respectively. The mechanistically possible insertion products of vinyl complexes were never observed in our experiments in this study. The substituents of allenes appear to have no effect on the reaction pathways, at least for the allenes used in this study. A computational study shows that formation of allyl complex PdI(η^3-MeCHC(Ph)$CHSO_2H$)(PH_3) from PdI(Ph)(MeCH═C═$CHSO_2H$)(PH_3) is both thermodynamically and kinetically favored.

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether, THF) or calcium hydride (CH_2Cl_2). The starting materials $[PdI(Ph)(PPh_3)]_2$,[31] PdI(Ph)(dppe),[44] CH_2═C═CHR (R = CMe_3, CO_2Et, $P(O)(OEt)_2$, and SO_2Ph), and MeCH═C═CHR (R = $P(O)(OEt)_2$ and SO_2Ph)[47] were prepared following the procedures described in the literature. Microanalyses were performed by MHW Laboratory (Phoenix, AZ) or collected on a Vario EL III analyzer at Shanghai Institute of Organic Chemistry. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were collected on a Varian Mercury spectrometer (300 MHz) or a Bruker spectrometer (300, 500 MHz). ^1H and ^{13}C chemical shifts are relative to TMS, and ^{31}P chemical shifts are relative to 85% H_3PO_4.

PdI(η^3-*cyclo*-CHC(Ph)CH$(CH_2)_6$)(PPh_3) (3). A solution of $[PdI(Ph)(PPh_3)]_2$ (151 mg, 0.130 mmol) and 1,2-cyclononadiene

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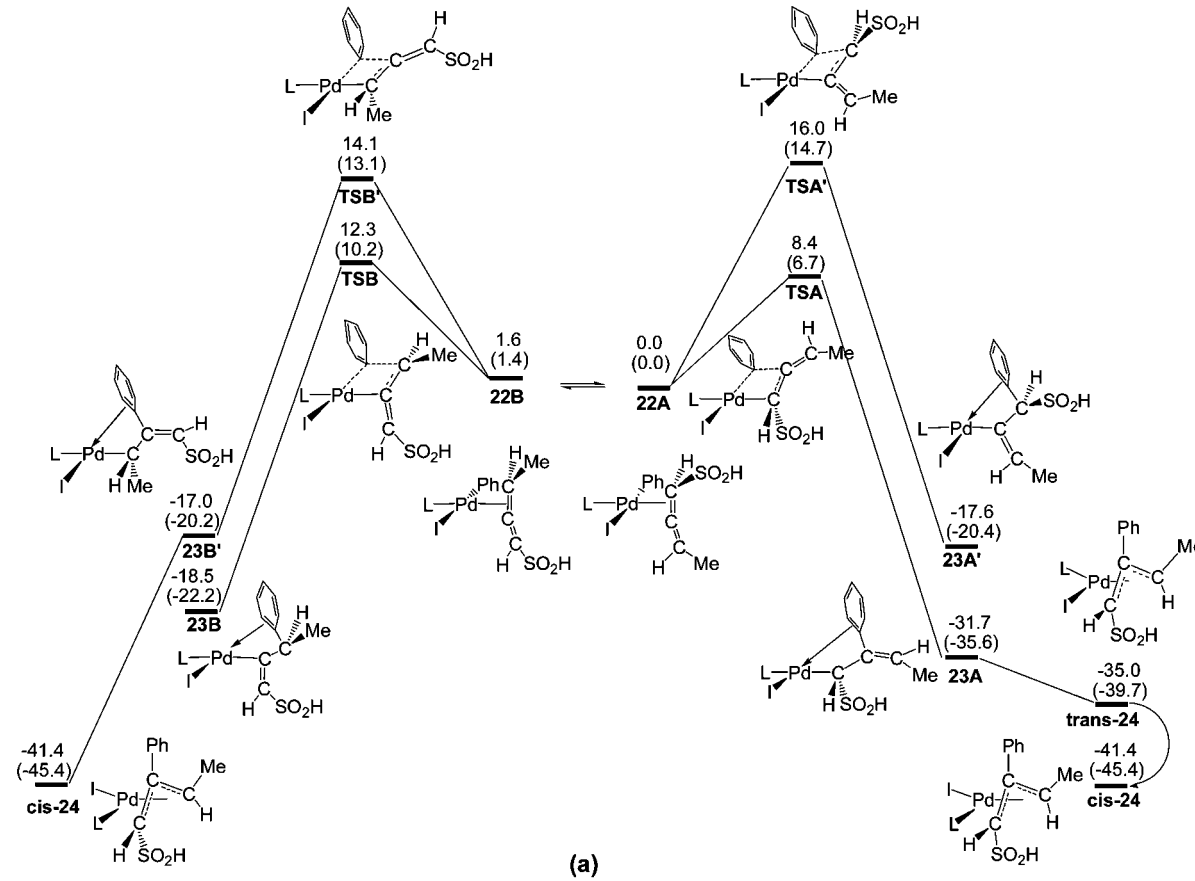
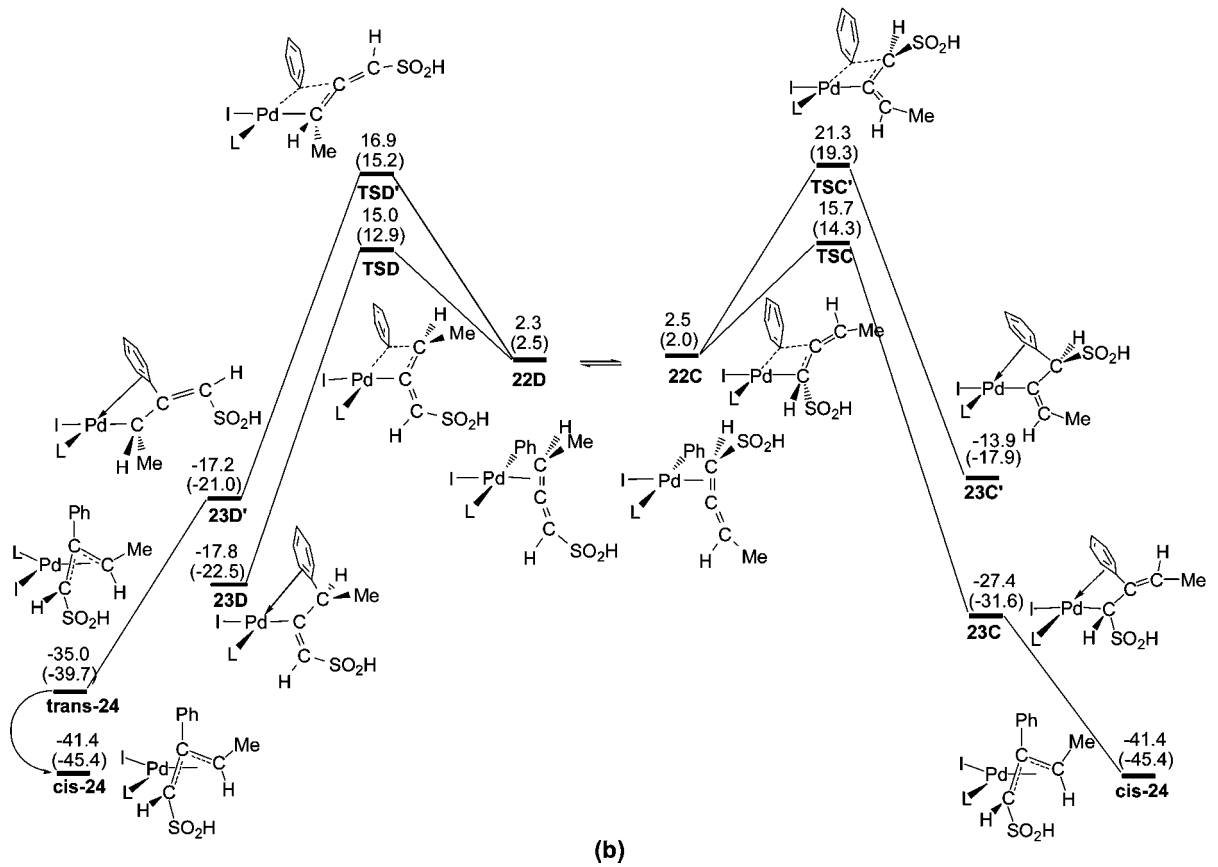


(a)



(b)

Figure 7. Energy profiles calculated for the insertion reactions of PdI(Ph)(PH_3)(η^2-MeCH═C═CHSO$_2$H). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

(0.040 mL, 0.32 mmol) in CH_2Cl_2 (8 mL) was stirred at room temperature for 30 min. The reaction mixture was concentrated to dryness. The residue was washed with diethyl ether (3 mL × 3) and dried under vacuum to afford a pale yellow solid. Yield: 0.14 g, 76%. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.08–1.36 (m, 5 H, CH_2), 1.38–1.54 (m, 1 H, CH_2), 1.54–1.80 (m, 3 H, CH_2), 1.82–2.04 (m, 1 H, CH_2), 2.22–2.46 (m, 1 H, CH_2), 3.18–3.38 (m, 1 H, CH_2), 4.58–4.78 (m, 1 H, CH), 5.78–5.98 (m, 1 H, CH), 7.00–7.26 (m, 14 H, *m,p*-PhP, Ph), 7.78–8.02 (m, 6 H, *o*-PhP). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ 24.5 (s). Anal. Calcd for $C_{33}H_{34}IPPd \cdot 0.25CH_2Cl_2$: C, 55.76; H, 4.86. Found: C, 55.92; H, 5.06.

PdI(η^3-CH$_2$C(Ph)CHCMe$_3$)(PPh$_3$) (5). A suspension of [PdI(Ph)(PPh$_3$)]$_2$ (233 mg, 0.20 mmol) and *tert*-butylallene (0.040 g, 0.42 mmol) in benzene (10 mL) and CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h to give a clear solution. The mixture was concentrated to dryness under vacuum to give a yellow oil, to which was added diethyl ether (4 mL) to give a precipitate. This precipitate was collected by filtration and washed with ether (2 mL × 2) and dried under vacuum to give a bright yellow solid. Yield: 0.23 g, 84%. NMR data show that the product is a mixture of ***trans*-5** and ***cis*-5** in a ratio of 4.5:1. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) of ***trans*-5** (major isomer): δ 1.26 (s, 9 H, CH_3), 3.63 (br s, 1 H, CH_2), 3.70 (br m, 1 H, CH_2), 5.68 (dd, J(PH) = 6.6 Hz, J(HH) = 1.8 Hz, 1 H, CH), 7.12–7.58 (m, 20 H, PPh, Ph, mixed with those of ***cis*-5**). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) of ***cis*-5** (minor isomer): δ 0.82 (s, 9 H, CH_3), 4.06 (dd, J(PH) = 11.0 Hz, J(HH) = 2.4 Hz, CH_2), 4.68 (br d t, J(PH) = 7.2 Hz, J(HH) = 2.1 Hz, CH_2)), 4.87 (br s, 1 H, CH), 7.12–7.58 (m, 20 H, PPh, Ph, mixed with those of ***trans*-5**). ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2, 298 K) of ***trans*-5**: δ 1.26 (s, 9 H, CH_3), 3.62 (d, J(HH) = 1.9 Hz, 1 H, CH_2), 3.70 (t, J(HH) = 1.9 Hz, 1 H, CH_2), 5.68 (d, J(HH) = 1.9 Hz, 1 H, CH), 7.12–7.58 (m, 20 H, PPh, Ph, mixed with those of ***cis*-5**). ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2, 298 K) of ***cis*-5**: δ 0.83 (s, 9 H, CH_3), 4.07 (d, J(HH) = 2.3 Hz, 1 H, CH_2), 4.67 (t, J(HH) = 2.3,1.9 Hz, 1 H, CH_2), 4.87 (d, J(HH) = 1.9 Hz, 1 H, CH), 7.12–7.58 (m, 20 H, PPh, 2-Ph, mixed with those of ***trans*-5**). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 22.5 (s, ***trans*-5**), 23.1 (s, ***cis*-5**). Anal. Calcd for $C_{31}H_{32}IPPd$: C, 55.66; H, 4.82. Found: C, 55.71; H, 5.07.

PdI(η^3-CH$_2$C(Ph)CHCO$_2$Et)(PPh$_3$) (7). A suspension of [PdI(Ph)(PPh$_3$)]$_2$ (225 mg, 0.200 mmol) and ethyl 2,3-butadienoate (0.050 g, 0.44 mmol) in benzene (10 mL) was stirred at room temperature for 2 h to give a clear orange solution. The mixture was concentrated to dryness, and diethyl ether (2 mL) was added to give a yellow solid. The solid was collected by filtration, washed with hexane (2 mL × 3), and dried under vacuum. Yield: 0.22 g, 80%. The NMR data show that the product is an isomeric mixture of ***trans*-7** and ***cis*-7** in a ratio of 1.7:1. ^{1}H NMR (300 MHz, CD_2Cl_2, 218 K) of ***trans*-7** (major isomer): δ 1.20 (t, J(HH) = 7.1 Hz, 3 H, CH_2CH_3), 3.88 (br s, 1 H, CH_2), 3.94–4.22 (m, 2 H, CH_2CH_3), 4.90 (br s, 1 H, CH_2), 5.35 (d, J(PH) = 8.5 Hz, 1 H, CH), 7.04–7.50 (m, 20 H, PPh, Ph, mixed with those of ***cis*-7**). ^{1}H NMR (300 MHz, CD_2Cl_2, 218 K) of ***cis*-7** (minor isomer): δ 0.64 (t, J(HH) = 7.1 Hz, 3 H, CH_2CH_3), 3.20–3.38 (m, 1 H, CH_2CH_3), 3.58–3.76 (m, 1 H, CH_2CH_3), 4.63 (br s, 1 H, $CHCO_2Et$), 4.85 (d, J(PH) = 9.9 Hz, 1 H, CH_2), 5.07 (br d, J(PH) = 5.7 Hz, 1 H, CH_2), 7.04–7.50 (m, 20 H, PPh, Ph, mixed with those of ***cis*-7**). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 218 K): δ 26.6 (s, ***trans*-7**), 24.0 (s, ***cis*-7**). Anal. Calcd for $C_{30}H_{28}IO_2PPd$: C, 52.61; H, 4.12. Found: C, 52.74; H, 4.30.

PdI(η^3-CH$_2$C(Ph)CHP(O)(OEt)$_2$)(PPh$_3$) (9). A mixture of [PdI(Ph)(PPh$_3$)]$_2$ (50 mg, 0.0435 mmol) and 1,2-propadiethyl dienylphosphonate (19 mg, 0.107 mmol) in dichloromethane (2 mL) was stirred at room temperature for 8 h to give a clear yellow solution. The resulting solution was concentrated to dryness under vacuum to give an oily residue, which was treated with ether (3 mL × 2) to give a yellow precipitate. The solid was collected by filtration, washed with ether (3 mL), and dried under vacuum. Yield: 41 mg, 63%. NMR data show that the product is an isomeric mixture of ***trans*-9** and ***cis*-9** in a ratio of 3.5:1. ^{1}H NMR (500 MHz, $CDCl_3$) of ***trans*-9** (major isomer): δ 1.22 (br s, 3 H, CH_2CH_3), 1.32 (br s, 1.32, 3 H, CH_2CH_3), 4.16 (br s, 2 H, CH_2CH_3), 3.88 (br s, 1 H, CH_2), 4.26 (br s, 1 H, CH_2CH_3), 4.35 (br, 1 H, CH_2CH_3), 4.52 (br s, 1 H, CH_2), 4.96 (dd, J(PH) = 7.0, 5.5 Hz, CHP), 7.22–7.54 (m, 20 H, PPh, Ph, mixed with those of ***cis*-9**). ^{1}H NMR (500 MHz, $CDCl_3$) of ***cis*-9** (minor isomer): δ 0.91 (t, J(HH) = 7.1 Hz, 3 H, CH_2CH_3), 1.13 (t, J(HH) = 7.1 Hz, 3 H, CH_2CH_3), 3.62 (m, 1 H, CH_2CH_3), 3.76 (m, 1 H, CH_2CH_3), 3.86 (m, 2 H, CH_2CH_3), 4.16 (dd, J(PH) = 5.2 Hz, J(HH) = 2.5 Hz, CHP), 4.59 (d, J(PH) = 10.0 Hz, 1 H, =CH_2), 5.05 (dd, J(PH) = 6.2, J(HH) = 2.5 Hz, 1 H, CH_2), 7.12–7.53 (m, 20 H, PPh, Ph, mixed with those of ***trans*-9**). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 17.4 (d, J(PP) = 19.0 Hz (***trans*-9**)), 19.0 (s, (**cis-9**)), 25.3 (s, (**cis-9**)), 25.8 (d, J(PP) = 19.0 Hz (***trans*-9**)). Anal. Calcd for $C_{31}H_{33}IO_3P_2Pd$: C, 49.72; H, 4.44. Found: C, 49.78; H, 4.72.

PdI(η^3-MeCHC(Ph)CHP(O)(OEt)$_2$)(PPh$_3$) (11). A mixture of [PdI(Ph)(PPh$_3$)]$_2$ (203 mg, 0.177 mmol) and 1,2-butadiethyl dienylphosphonate (81 mg, 0.426 mmol) in dichloromethane (10 mL) was stirred at room temperature for 10 h to give a clear yellow solution. The resulting solution was concentrated to dryness under vacuum to give an oily residue, which was treated with *n*-hexane (6 mL × 2) to give a yellow precipitate. The solid was collected by filtration, washed with *n*-hexane (6 mL), and dried under vacuum. The NMR data show that the product is an isomeric mixture of ***trans*-11** and ***cis*-11** in a ratio of 1:4, Total yield: 186 mg, 70%. ^{1}H NMR (500 MHz, $CDCl_3$) of ***trans*-9** (minor isomer): δ 1.22 (t, J(HH) = 7.0 Hz, 3 H, CH_2CH_3), 1.29 (t, J(HH) = 7.0 Hz, 3 H, CH_2CH_3), 1.67 (m, 3 H, $CHCH_3$), 3.5–4.08 (m, 3 H, $CHCH_3$ and 2 H of CH_2CH_3), 4.62 (dd, J(PH) = 7.8, 5.3 Hz, 1 H, CHP), 7.20–7.82 (m, 20 H, PPh, Ph, mixed with those of ***cis*-11**). ^{1}H NMR (500 MHz, $CDCl_3$) of ***cis*-9** (major isomer): δ 0.88 (t, J(HH) = 7.1 Hz, 3 H, CH_2CH_3), 1.14 (t, J(HH) = 7.1 Hz, 3 H, CH_2CH_3), 2.16 (dd, J(PH) = 7.9 Hz, J(HH) = 6.8 Hz, $CHCH_3$), 3.54 (m, 1 H, CH_2CH_3), 3.67 (d, J(PH) = 4.9 Hz, 1 H, CHP), 3.84 (m, 2 H, CH_2CH_3), 5.42–5.48 (m, 2 H, $CHCH_3$), 7.20–7.82 (m, 20 H, PPh, Ph, mixed with those of ***trans*-11**). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 17.0 (d, J(PP) = 18.4 Hz, **trans-11**), 19.5 (s, **cis-11**), 27.9 (s, **cis-11**), 30.0 (d, J(PP) = 18.4 Hz, **trans-11**). Anal. Calcd for $C_{32}H_{35}IO_3P_2Pd$: C, 50.38; H, 4.62. Found: C, 50.12; H, 4.61.

PdI(η^3-CH$_2$C(Ph)CHSO$_2$Ph)(PPh$_3$) (13). A mixture of [PdI(Ph)(PPh$_3$)]$_2$ (500 mg, 0.435 mmol) and 1,2-propadienylsulfonylbenzene (200 mg, 1.11 mmol) in dichloromethane (30 mL) was stirred at room temperature for 3 h to give a clear yellow solution. The resulting solution was concentrated to dryness under vacuum to give an oily residue, which was treated with ether (25 mL × 2) to give a yellow precipitate. The solid was collected by filtration, washed with *n*-hexane (25 mL), and dried under vacuum. Yield: 590 mg, 90%. The NMR data show that the product is an isomeric mixture of ***trans*-13** and ***cis*-13** in a ratio of 1:2.3. ^{1}H NMR (300 MHz, $CDCl_3$) of ***trans*-13** (minor isomer): δ 3.97 (s, 1 H, CH_2), 5.03 (s, 1 H, CH_2), 5.93 (dd, 1 H, J(PH) = 7.2 Hz, J(HH) = 1.8 Hz, 1 H, CH), 7.92–6.92 (m, 25 H, Ph and PPh, mixed with those ***cis*-13**). ^{1}H NMR (300 MHz, $CDCl_3$) of ***cis*-13** (major isomer): δ 4.96 (d, J(HH) = 1.5 Hz, 1 H, CH), 5.16 (dt, 1 H, J(PH) = 9.3 Hz, J(HH) = 1.8 Hz, 1 H, CH_2), 5.30 (dd, J(PH) = 8.4 Hz, J(HH) = 1.8 Hz, 1 H, CH_2), 7.92–6.92 (m, 25 H, Ph and PPh_3, mixed with those of ***trans*-13**). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): 24.7 (s, ***trans*-4a**), 27.0 (s, ***cis*-4a**). Anal. Calcd for $C_{33}H_{28}IO_2PPdS$: C, 52.64; H, 3.75. Found: C, 52.53; H, 3.82.

PdI(η^3-MeCHC(Ph)CHSO$_2$Ph)(PPh$_3$) (*cis*-15). A mixture of [PdI(Ph)(PPh$_3$)]$_2$ (2.00 g, 1.746 mmol) and 1,2-butadienylsulfonylbenzene (712 mg, 3.67 mmol) in dichloromethane (60 mL) was stirred at room temperature for 8 h to give a clear yellow solution.

The resulting solution was concentrated to dryness under vacuum. The oily residue was treated with *n*-hexane (35 mL × 2) to give a yellow precipitate. The solid was collected by filtration, washed with *n*-hexane (35 mL), and dried under vacuum. Yield: 2.628 g, 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (dd, 3 H, J(PH) = 7.8 Hz, J(HH) = 6.7 Hz, CH-CH_3), 4.59 (s, 1 H, CHSO_2Ph), 6.19 (dt, J(PH) = 8.4 Hz, J(HH) = 6.7 Hz, 1 H, CH-CH_3), 7.74–6.87 (m, 25 H, Ph and PPh_3). ^{13}C{^{1}H}NMR (75.47 MHz, $CDCl_3$): δ 17.1 (d, J(PC) = 4.0 Hz, CH_3), 53.4 (s, allylic-C), 98.3 (d, J(PC) = 25.9 Hz, allylic-C), 83.1 (d, J(PC) = 4.6 Hz, allylic-C), 126.9–142.53 (m, Ph and PPh_3). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 29.8 (s). Anal. Calcd for $C_{34}H_{30}IO_2PPdS$: C, 53.24; H, 3.94. Found: C, 50.16; H, 4.08. As indicated by ^{1}H NMR, the sample contains dichloromethane. Anal. Calcd for $C_{34}H_{30}IO_2PPdS \cdot 0.75CH_2Cl_2$: C, 50.23; H, 3.82.

PdI(Ph)(dppe) (16). A mixture of $Pd(PPh_3)_4$ (0.500 g, 0.433 mmol) and $Ph_2PCH_2CH_2PPh_2$ (175 mg, 0.44 mmol) in benzene (12 mL) was stirred for 1 h, then PhI (0.056 mL, 0.50 mmol) was added to the mixture at room temperature. The mixture was stirred for further 10 min. The resulting solution was allowed to stand overnight without agitation, during which time yellow crystallites were formed. They were collected by filtration, washed with diethyl ether (2 mL × 3), and dried under vacuum. Yield: 0.22 g, 71%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.00–2.48 (m, 4 H, PCH_2), 6.50–6.72 (m, 3 H, *m*, *p*- Pd-Ph), 6.97(t, J(HH) = 7.6 Hz, 2 H, *o*-Pd-Ph), 7.14–7.62 (m, 16 H, PPh), 7.72–7.96 (m, 4 H, PPh). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 34.7 (d, J(PP) = 27.1 Hz), 49.5 (d, J(PP) = 27.1 Hz). The NMR data are identical to the reported ones.[44]

[Pd(η^3-CH_2C(Ph)CHCMe$_3$)(dppe)]PF_6 (17PF6). To a solution of PdI(Ph)(dppe) (190 mg, 0.268 mmol) and *tert*-butylallene (27 mg, 0.28 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of $TlPF_6$ (96 mg, 0.28 mmol) in acetone (2 mL). The resulting yellow suspension was stirred for 30 min. The mixture was concentrated to dryness, and CH_2Cl_2 (5 mL) was added. The resulting mixture was filtered through a pad of Celite, and the Celite was washed with CH_2Cl_2 (1 mL). The combined filtrates were concentrated to dryness. The residue was washed with diethyl ether (2 mL × 3) and dried under vacuum to give a yellow solid. Yield: 0.18 g, 82%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 0.85 (s, 9 H, CH_3), 1.94–2.18 (m, 1 H, PCH_2), 2.26–2.48 (m, 1 H, PCH_2), 2.54–2.88 (m, 2 H, PCH_2), 4.15 (br d, J(PH) = 9.4 Hz, 1 H, CH_2), 4.49 (br m, 1 H, CH_2), 5.59 (br d, J(PH) = 5.7 Hz, CH), 6.82–7.78 (m, 25 H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ –143.2 (septet, J(PF) = 713 Hz, PF_6), 49.0 (d, J(PP) = 34.3 Hz), 49.7 (d, J(PP) = 34.3 Hz).

[Pd(η^3-CH_2C(Ph)CHCMe$_3$)(dppe)]BPh_4 (17BPh4). To a solution of [Pd(η^3-CH_2C(Ph)CHCMe$_3$)(dppe)]PF_6 (174 mg, 0.21 mmol) in MeOH (4 mL) was added dropwise a solution of $NaBPh_4$ (87 mg, 0.25 mmol) in MeOH (3 mL). After the addition was completed, the resulting mixture was stirred for 2 h. The resulting precipitate was collected by filtration, washed with MeOH (2 mL × 3), and dried under vacuum. Column chromatography on silica with CH_2Cl_2 as the eluent gave a white solid after removal of the solvents. Yield: 145 mg, 69%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 0.85 (s, 9 H, CH_3), 1.80–2.02 (m, 1 H, PCH_2), 2.08–2.34 (m, 1 H, PCH_2), 2.34–2.72 (m, 2 H, PCH_2), 4.14 (br dt, J(PH) = 9.5 Hz, J(HH) = 1.7 Hz, 1 H, CH_2), 4.47 (br m, 1 H, CH_2), 5.58 (br dd, J(PH) = 5.7 Hz, J(HH) = 1.7 Hz, CH), 6.74–7.78 (m, 45 H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 49.0 (d, J(PP) = 34.3 Hz), 49.7 (d, J(PP) = 34.3 Hz). Anal. Calcd for $C_{63}H_{61}BP_2Pd$: C, 75.87; H, 6.16. Found: C, 75.76; H, 6.41.

[Pd(η^3-CH_2C(Ph)CHCO$_2$Et)(dppe)]PF_6 (18PF6). To a solution of PdI(Ph)(dppe) (190 mg, 0.268 mmol) and ethyl 2,3-butadienoate (31 mg, 0.28 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of $TlPF_6$ (96 mg, 0.28 mmol) in acetone (1.5 mL). The resulting suspension was stirred for 30 min. After removal of the solvents, CH_2Cl_2 (5 mL) was added. The mixture was filtered through a pad of Celite, and the Celite was washed with CH_2Cl_2 (1 mL) and filtered. The combined filtrates were concentrated to dryness. The residue was washed with hexane (2 mL × 2) and a mixture of hexane/ether (5 mL, 2/3, v/v) and then dried under vacuum to give an orange solid. Yield: 0.22 g, 96%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 0.85 (t, J(HH) = 7.1 Hz, CH_2CH_3, OEt), 2.42–2.68 (m, 4 H, PCH_2), 3.50–3.78 (br, 2 H, CH_2CH$_3$), 4.98 (d, J(PH) = 6.6 Hz, 2 H, CH_2), 5.37 (d, J(PH) = 6.8 Hz, 1 H, CH), 6.93 (d, J(HH) = 7.6 Hz, 2 H, 2-Ph), 7.21 (dd, J(HH) = 7.6, 7.7 Hz, Ph), 7.24–7.66 (m, 20 H, PPh). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ –143.2 (septet, J(PF) = 713 Hz, PF_6), 53.9 (d, J(PP) = 37.9 Hz), 57.8 (d, J(PP) = 37.9 Hz).

[Pd(η^3-CH_2C(Ph)CHCO$_2$Et)(dppe)]BPh_4 (18BPh4). To a solution of [Pd(η^3-CH_2C(Ph)CHCOOEt)(dppe)]PF_6 (217 mg, 0.26 mmol) in MeOH (5 mL) was added dropwise a solution of $NaBPh_4$ (107 mg, 0.31 mmol) in MeOH (4 mL). After the addition was completed, the resulting mixture was stirred for 30 min. The formed orange precipitate was collected by filtration, washed with MeOH (2 mL × 3), then redissolved in CH_2Cl_2 (5 mL). The solution was filtered through a pad of Celite. The solvent of the filtrate was removed under vacuum to give an orange solid. Yield: 0.15 g, 57%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 0.92 (t, J(HH) = 7.1 Hz, CH_2CH_3), 2.14–2.44 (m, 4 H, PCH_2), 3.46–3.90 (br, 2 H, CH_2CH$_3$), 5.01 (d, J(PH) = 6.5 Hz, 2 H, CH_2), 5.41 (d, J(PH) = 6.8 Hz, 1 H, CH), 6.72–7.68 (m, 45 H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 54.0 (d, J(PP) = 37.8 Hz), 57.9 (d, J(PP) = 37.8 Hz). Anal. Calcd for $C_{62}H_{57}BO_2P_2Pd$: C, 73.49; H, 5.67. Found: C, 73.63; H, 5.82.

[Pd(η^3-CH_2C(Ph)CHC(O)Ph)(dppe)]PF_6 (19PF6). To a solution of PdI(Ph)(dppe) (190 mg, 0.268 mmol) and 1-phenylbuta-2,3-dien-1-one (43 mg, 0.29 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of $TlPF_6$ (96 mg, 0.28 mmol) in acetone (2 mL). The resulting yellow suspension was stirred for 2 h. The mixture was concentrated to dryness, and CH_2Cl_2 (5 mL) was added. The resulting mixture was filtered through a pad of Celite, and the Celite was washed with CH_2Cl_2 (5 mL). The combined filtrates were concentrated to dryness. The residue was washed with diethyl ether (5 mL × 3) and dried under vacuum to give a yellow solid. Yield: 0.15 g, 64%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.44–2.71 (m, 4 H, PCH_2), 5.19 (d, 2 H, J(PH) = 5.4 Hz, CH_2), 6.32 (d, 1 H, J(PH) = 6.9 Hz, CH), 6.96–7.66 (m, 30 H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ –143.2 (septet, J(PF) = 712.8 Hz, PF_6), 55.5 (d, J(PP) = 38.2 Hz), 62.3 (d, J(PP) = 38.2 Hz). Anal. Calcd for $C_{45}H_{44}F_6OP_3Pd$: C, 57.91; H, 4.28. Found: C, 58.38; H, 4.63.

[Pd(η^3-CH_2C(Ph)CH(SO$_2$Ph))(dppe)]BPh_4 (20BPh4). To a solution of PdI(Ph)(dppe) (190 mg, 0.268 mmol) and (propa-1,2-dienylsulfonyl)benzene (60 mg, 0.33 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of $TlPF_6$ (110.2 mg, 0.32 mmol) in acetone (2 mL). The resulting yellow suspension was stirred for 2 h. The mixture was concentrated to dryness, and CH_2Cl_2 (6 mL) was added. The resulting mixture was filtered through a pad of Celite, and the Celite was washed with CH_2Cl_2 (5 mL × 2). The combined filtrates were concentrated to dryness. The residue was washed with diethyl ether (2 mL × 3) and dried under vacuum to give 177 mg of a yellow solid. The ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K) shows major peaks at δ 58.1 (d, J(PP) = 35.4 Hz) and 57.4 (d, J(PP) = 35.4 Hz), −143.2 (septet, J(PF) = 713 Hz, PF_6) ppm assignable to mainly [Pdη^3-CH_2C(Ph)CH(SO$_2$Ph))-(dppe)]PF_6 and other minor peaks of unknown species at δ 56.9, 56.6, 56.3, 55.6, and 55.3 ppm. To further purify the product, the solid was redissolved in methanol (4 mL). To the methanol solution of [Pdη^3-CH_2C(Ph)CH(SO$_2$Ph))(dppe)]PF_6 (177 mg, ca. 0.20 mmol) was added dropwise a solution of $NaBPh_4$ (83 mg, 0.24 mmol) in MeOH (3 mL). After the addition was completed, the resulting mixture was stirred for 2 h. The resulting precipitate was collected

by filtration, washed with MeOH (2 mL × 3), and dried under vacuum. Column chromatography on silica gel with CH_2Cl_2 as the eluent gave a yellow solid after removal of the solvents. Yield: 137 mg, overall yield, 47%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.65–2.30 (m, br, 4 H, PCH_2), 4.78–4.85 (br m 1 H, CH_2), 5.08–5.17 (br m, 1 H, CH_2), 5.36–5.44 (m, br, 1 H, CH), 6.51 (d, 2 H, J(HH) = 6.9 Hz, Ph), 6.72–7.85 (m, 48 H, PPh, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ 58.2 (d, J(PP) = 35.0 Hz), 57.7 (d, J(PP) = 35.0 Hz). Anal. Calcd for $C_{65}H_{57}BO_2P_2PdS$: C, 72.19; H, 5.31. Found: C, 71.70; H, 5.58.

[Pd(η^3-CH(Me)C(Ph)CH(SO_2Ph))(dppe)]PF_6 (21PF6). To a solution of PdI(Ph)(dppe) (190 mg, 0.268 mmol) and (buta-1,2-dienylsulfonyl)benzene (56 mg, 0.29 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of $TlPF_6$ (96 mg, 0.28 mmol) in acetone (2 mL). The resulting green suspension was stirred for 2 h. The mixture was concentrated to dryness, and CH_2Cl_2 (6 mL) was added. The resulting mixture was filtered through a pad of Celite, and the Celite was washed with CH_2Cl_2 (6 mL). The combined filtrates were concentrated to dryness. Column chromatography on silica with CH_2Cl_2 as the eluent gave a yellow solid after removal of the solvents. Yield: 157 mg, 64%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.36 (dd, 3 H, J(PH) = 12.9 Hz, J(HH) = 6.6 Hz, CH_3), 2.45–2.74 (m, 2 H, PCH_2), 2.95–3.10 (m, 2 H, PCH_2), 4.84 (d, 1 H, J(PH) = 6.3 Hz, CH=CPh), 6.24–6.34 (m, 1 H, CHMe), 6.39 (d, J(HH) = 7.2 Hz, Ph), 7.00–7.91 (m, 28 H, PPh_2, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ –143.2 (septet, J(PF) = 713 Hz, PF_6), 56.5 (d, J(PP) = 33.4 Hz), 56.8 (d, J(PP) = 33.4 Hz). Anal. Calcd for $C_{42}H_{39}F_6O_2P_3PdS$: C, 54.76; H, 4.27. Found: C, 54.32; H, 4.75.

Crystal Structure Analyses of 3, *trans*-5, *trans*-9, *cis*-11, *cis*-13, and *cis*-15. Single crystals of **3** suitable for X-ray diffraction were obtained by slow evaporation of solvent from a CH_3CN solution. Single crystals of ***trans*-5**, ***trans*-9**, ***cis*-11**, ***cis*-13**, and ***cis*-15** suitable for X-ray diffraction were obtained by layering ether (***cis*-13**, ***trans*-9**) or *n*-hexane (***trans*-5**, ***cis*-11, *cis*-15**) on top of their CH_2Cl_2 solutions. The compounds are sufficiently air stable to be mounted on glass fibers with epoxy adhesive. The diffraction intensity data were collected with a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K for **3** and ***trans*-5** and 298 K for the rest. Lattice determination and data collection were carried out using SMART v.5.625 software. Data reduction and absorption correction by empirical methods were performed using SAINT v 6.26 and SADABS v 2.03, respectively. Structure solution and refinement were performed using the SHELXTL v.6.10 software package. The structures were all solved by direct methods. All of the structures were refined smoothly. Otherwise, all non-hydrogen atoms were refined anisotropically by full-matrix least-squares, with a riding model for the hydrogen atoms.

Computational Details. Molecular geometries were optimized at the Becke3LYP (B3LYP) level of density functional theory. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency). The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe Pd, P, S, and I atoms,[48] while the standard 6-31G basis set was used for C, O, and H atoms. Polarization functions were added for P (ζ(d) = 0.34), S (ζ(d) = 0.421), I (ζ(d) = 0.266), the three allene carbon atoms, and the metal-bonded carbon atom of the phenyl ligand (C ζ(d) = 0.8).[49] Calculations of intrinsic reaction coordinates (IRC)[50] were also performed on transition states to confirm that such structures are indeed connecting two minima. All the calculations were performed with the Gaussian 03 software package.[51] The natural bond orbital (NBO) program,[52] as implemented in Gaussian 03, was also used to obtain natural populations of atoms.[53]

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Supporting Information Available: Complete ref 51, tables giving Cartesian coordinates and electronic energies for all of the calculated structures, and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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