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Synthesis of η^2-Phosphonioalkene−Palladium(0) Complexes from Alkenylphosphonium Halides and Palladium(0) Species. Structure and Substitution Reactions of These Complexes

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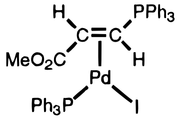
Treatment of $Pd(dba)_2$ (dba = dibenzylideneacetone) with (*trans*-$RCH{=}CHPPh_3)^+Br^-$ in dichloromethane afforded $[Pd($*trans*-$RCH{=}CHPPh_3)_2Br]^+$ (R = CO_2Et (**4**), CO_2Me (**5**), Ph (**6**)). As shown by the results of the X-ray diffraction, **4** adopts a distorted pentagonal geometry with two $EtO_2CCH{=}CH(PPh_3)^+$ moieties and a bromide ligand. The C−C double bond in the $EtO_2CCH{=}CH(PPh_3)^+$ moieties are π-bonded to the palladium(0) center and are coplanar with the bromide ligand and the metal center. Both $(EtO_2CCH{=}CHPPh_3)^+$ moieties are oriented with the two PPh_3 groups trans to each other and the olefin carbon that is attached to PPh_3 occupying the coordination site neighboring to the bromide ligand. Treatment of *trans*-$[R^1CH{=}CR^2(PPh_3)]^+Br^-$ with $Pd(dba)_2$ in the presence of 1 equiv of PPh_3 or $P(OPh)_3$ gave the corresponding palladium complexes Pd[*trans*-$R^1CH{=}CR^2(PPh_3)](L)Br$ (L = PPh_3, R^1 = Ph, R^2 = H (**3**). L = PPh_3, R^1 = Me, R^2 = H (**7**); R^1 = CO_2Et, R^2 = H (**8**); R^1 = CO_2Me, R^2 = H (**9**); R^1 = H, R^2 = Me (**10**). L = $P(OPh)_3$, R^1 = CO_2Me, R^2 = H (**11**)) in 54−92% yields. Substitution studies showed complexes **3** and **9** react with dppe (1,2-bis(diphenylphosphino)ethane) in dichloromethane to give $[Pd(RCH{=}CH(PPh_3)(dppe)]^+Br^-$ (R = Ph (**12**); R = CO_2Me (**13**)), but treatment of **9** and **11** with PPh_3 and $P(OPh)_3$, respectively, afforded only the original complexes on isolation.

Introduction

Coordination of alkenylphosphonium cations to a palladium(0) center via the carbon−carbon double bond in the alkenyl group were recently observed by Rubinskaya *et al.*[1] and by us.[2] The former reported that the palladium(II) complexes $Pd(PPh_3)_2(\sigma\text{-}CH{=}CHCOOR)X$ rearranged in benzene at 75−80 °C to η^2-phosphonioalkene−palladium(0) complexes $Pd((Ph_3PCH{=}CHCOOR)(PPh_3)X$ (**1**). In an attempt to prepare *trans*-$Pd(PPh_3)_2(CH{=}CHPh)Br$ directly from the oxidative addition of bromoalkenes to $Pd(PAr_3)_4$,[3] we isolated η^2-phosphonioalkene−palladium(0) salts [(*trans*-$RCH{=}CHPAr_3)Pd(PAr_3)_2]^+Br^-$ (**2**), with bromide as the counter anion. Moreover, in the reaction of $PhCH{=}CHBr$ with the palladium(II) species $Pd(PPh_3)_2(C_6H_4O\text{-}p\text{-}CH_3)I$, we observed the formation of complex **3**. Complex **2a** (R = Ph, Ar = Ph) was found to be a catalyst intermediate in the preparation of the phosphonium salt $PhCH{=}CH(PPh_3)^+Br^-$ from β-bromostyrene and triphenylphosphine, using $Pd(PPh_3)_4$ as the catalyst precursor. In addition, η^2-phosphonioalkene−palladium(0) complexes were likely involved in the catalysis of cis−trans isomerization of the alkenylphosphonium salt $RCH{=}CH(PAr_3)^+X^-$.

Other than the palladium(0) complexes **1**−**3**, there are only two phosphonioalkene complexes with tungsten[4] and nickel[5] as the metals reported in literature. In view of the limited number of η^2-phosphonioalkene metal complexes known and the lack of a general and convenient synthetic route for the preparation of these complexes, we started to explore the possibility of synthesizing η^2-phosphonioalkene complexes from low oxidation state metal complexes and alkenylphosphonium halides via substitution reactions. The preparation of complexes **2a** and **3** via this route was shown to be simple and effective.[2] This success prompted us to extend this simple substitution method to the synthesis of other phosphonioalkene−palladium complexes. In this paper, we describe the synthesis, structure, scope, and substitution chemistry of these new palladium(0) complexes.



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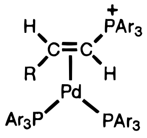

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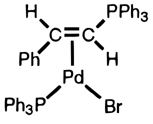

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Results and Discussion

Reaction of $(RO_2CCH{=}CHPPh_3)^+Br^-$ with $Pd(dba)_2$. Treatment of $Pd(dba)_2$ (dba = dibenzylideneacetone) with (*trans*-$EtO_2CCH{=}CHPPh_3)^+Br^-$, prepared from the reaction of PPh_3 with *cis*-$EtO_2CCH{=}CHBr$ using $Pd(PPh_3)_4$ as the catalyst,[2] in dichloromethane led

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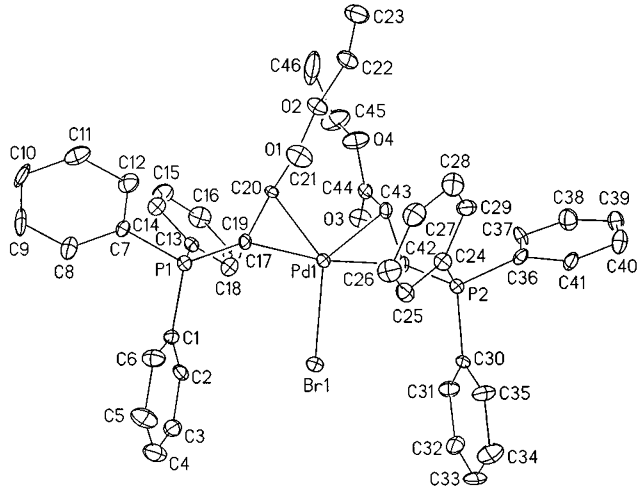
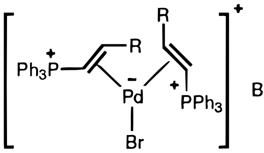


Figure 1. Perspective view and atom-labeling scheme for $[Pd(EtO_2CCH{=}CHPPh_3)_2Br]^+Br^-$ **(4)**.

to a gradual color change of the solution from red-brown to pale yellow. From the solution, a pale yellow complex **4** with the chemical formula $[Pd(EtO_2CCH{=}CHPPh_3)_2Br]^+Br^-$ was isolated. The structure of complex **4** was determined by single-crystal X-ray diffraction. Crystals suitable for X-ray structural analysis were grown from dichloromethane and hexane mixture. A molecular drawing of the complex with atom numbering scheme is shown in Figure 1, while important bond distances and angles are presented in Table 1. As revealed by Figure 1, each carbon−carbon double bond in the $EtO_2CCH{=}CH(PPh_3)^+$ moieties is coordinated to the metal center in an η^2 fashion. The oxidation state of the palladium center is zero, and the complex carries a positive charge with a bromide as the counter anion. Interestingly, in spite of the expected strong steric repulsion between the ligands, the olefin carbons in the $EtO_2CCH{=}CH(PPh_3)^+$ moieties lie essentially in the plane constructed by the ligands and the palladium center. Figure 2 shows the deviation of each coordination site from the least-squares plane. As a result of the conformation of $EtO_2CCH{=}CH(PPh_3)^+$ moieties, the palladium center adopts a distorted pentagonal geometry, although only three ligands are bonded to the metal.

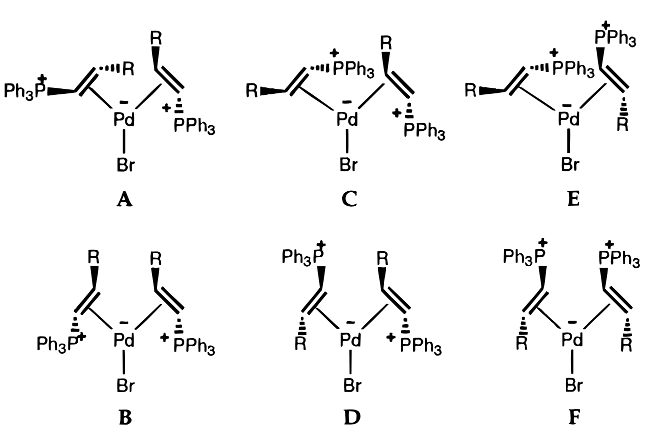


R = COOEt **4**
R = COOMe **5**
R = Ph **6**

The bonding of the two $(EtO_2CCH{=}CHPPh_3)^+$ moieties in complex **4** shows remarkable stereoselectivity. Both $(EtO_2CCH{=}CHPPh_3)^+$ moieties are oriented with the olefin carbon that is attached to PPh_3 occupying the coordination site neighboring to the bromide ligand. Furthermore, both ligands use the same face of the carbon−carbon double bond for coordinating to the palladium center, resulting in a trans arrangement of the two PPh_3 groups and of the two COOEt moieties. It is notable that in total there are ten possible isomers including four enantiomeric pairs (**A**, **C**, **D**, **E** and the corresponding enantiomers) for the chemical formula $[Pd(EtO_2CCH{=}CHPPh_3)_2Br]^+$ with a pentagonal geometry. The results of the X-ray analysis indicate that the structure of the product isolated from the reaction of $Pd(dba)_2$ with $(EtO_2CCH{=}CHPPh_3)^+Br^-$ is isomer **A**.

Table 1. Important Bond Distances (Å) and Angles (deg) for $[(\textit{trans}\text{-}EtO_2CCH{=}CHPPh_3)_2Pd(Br)]^+Br^-$ (4)

	Distances		
Pd(1)−Br(1)	2.494(2)	Pd(1)−C(19)	2.112(11)
Pd(1)−C(20)	2.103(11)	Pd(1)−C(42)	2.122(10)
Pd(1)−C(43)	2.129(10)	Cl(1)−C(47)	1.717(16)
Cl(2)−C(47)	1.746(13)	P(1)−C(1)	1.794(11)
P(1)−C(7)	1.802(13)	P(1)−C(13)	1.790(10)
P(1)−C(19)	1.784(8)	P(2)−C(24)	1.801(13)
P(2)−C(30)	1.795(11)	P(2)−C(36)	1.807(11)
P(2)−C(42)	1.786(9)	O(1)−C(21)	1.164(15)
O(2)−C(21)	1.358(14)	O(2)−C(22)	1.463(11)
O(3)−C(44)	1.209(15)	O(4)−C(44)	1.304(16)
O(4)−C(45)	1.422(16)	C(1)−C(2)	1.384(17)
C(20)−C(21)	1.507(14)	C(19)−C(20)	1.418(12)
C(42)−C(43)	1.398(16)	C(43)−C(44)	1.490(14)
	Angles		
Br(1)−Pd(1)−C(19)	96.9(3)	Br(1)−Pd(1)−C(20)	135.9(2)
C(19)−Pd(1)−C(20)	39.3(4)	Br(1)−Pd(1)−C(42)	92.8(3)
C(19)−Pd(1)−C(42)	169.3(4)	C(20)−Pd(1)−C(42)	131.3(4)
Br(1)−Pd(1)−C(43)	130.7(3)	C(19)−Pd(1)−C(43)	132.4(4)
C(20)−Pd(1)−C(43)	93.1(4)	C(42)−Pd(1)−C(43)	38.4(4)
C(1)−P(1)−C(7)	105.0(5)	C(1)−P(1)−C(13)	112.0(5)
C(7)−P(1)−C(13)	110.3(5)	C(1)−P(1)−C(19)	111.5(5)
C(7)−P(1)−C(19)	108.2(5)	C(13)−P(1)−C(19)	109.7(5)
C(24)−P(2)−C(30)	109.7(5)	C(24)−P(2)−C(36)	109.6(5)
C(30)−P(2)−C(36)	108.6(6)	C(24)−P(2)−C(42)	109.7(5)
C(30)−P(2)−C(42)	110.6(4)	C(36)−P(2)−C(42)	108.7(5)
C(21)−O(2)−C(22)	117.2(8)	C(44)−O(4)−C(45)	117.8(11)
Pd(1)−C(19)−P(1)	120.5(6)	Pd(1)−C(19)−C(20)	70.0(6)
P(1)−C(19)−C(20)	118.8(7)	Pd(1)−C(20)−C(19)	70.7(6)
Pd(1)−C(20)−C(21)	110.9(7)	C(19)−C(20)−C(21)	117.9(9)
O(1)−C(21)−O(2)	124.5(10)	O(1)−C(21)−C(20)	128.1(10)
O(2)−C(21)−C(20)	107.4(9)	Pd(1)−C(42)−P(2)	114.5(5)
Pd(1)−C(42)−C(43)	71.1(6)	P(2)−C(42)−C(43)	121.0(7)
Pd(1)−C(43)−C(42)	70.5(6)	Pd(1)−C(43)−C(44)	108.1(6)
C(42)−C(43)−C(44)	117.7(10)	O(3)−C(44)−O(4)	123.4(10)
O(3)−C(44)−C(43)	124.2(12)	O(4)−C(44)−C(43)	112.4(10)



Moreover, the ^1H NMR spectrum of the reaction solution shows that only isomer **A** was produced from the reaction. While the exact cause is not clear, it appears that minimization of the steric repulsion between the ligands is the driving force for the face and orientation selectivity of $(EtO_2CCH{=}CHPPh_3)^+$ moieties.

The trans geometry of the $(EtO_2CCH{=}CHPPh_3)^+$ moieties in complex **4** is the same as that of the starting $EtO_2CCH{=}CHPPh_3)^+Br^-$ salt. The P−Ph bond distances (1.79 −1.81 Å) are slightly shorter than normal phosphorus−carbon bond in coordinated PPh_3.[4,6] The average distance of 1.784 Å for the phosphorus−alkenyl bonds, P1−C19 and P2−C42, is shorter than that of a normal sp^3 phosphorus−carbon bond, but are longer than an ylide bond.[7] The results indicate the presence of a partial ylide character for these two bonds is due to back-donation from the palladium(0) center to the π^* orbitals of the C−C double bonds. However, the degree of ylide character is significantly less than that in the previously reported phosphonioalkene−palladium complexes $Pd(Ph_3PCH{=}CHCOOMe)(PPh_3)I$,[1] $[(\textit{trans}\text{-}PhCH{=}CHPPh_3)Pd(PPh_3)_2]^+Br^-$ and $(\textit{trans}\text{-}PhCH{=}CHPPh_3)Pd(PPh_3)X$,[2] in which the bond lengths of the phosphorus−alkenyl bonds are in the range 1.74−1.75 Å. The average bond length of the η^2-bonded C−C double bonds, C19−C20 and C42−C43, of 1.408 Å is slightly shorter than the values (∼1.43 Å) for those in the aforementioned three palladium−phosphonioalkene complexes. The observed bond distances for the phosphorus−alkenyl bond and for the η^2-bonded C−C double bonds in complex **4** clearly indicate a lessened degree of back-donation to each $(EtO_2CCH{=}CHPPh_3)^+$ moiety from the palladium center relative to that in the monophosphonioalkene complexes. These results, with little doubt, are due to the fact that $(EtO_2CCH{=}CHPPh_3)^+$ moiety is more π-acidic than PPh_3 and X^-.

Coordination of olefin ligands to d^{10} metals of the nickel family are well-known. Most of these complexes are distorted square planar (or trigonal planar) 16-electron systems consisting of an olefin and two other ligands, with the chemical formula M(olefin)LL′ (M = Pd,[8] Pt,[9,10] and Ni[11]). Complexes of 16-electron systems with the formulas $M(olefin)_2L$ and $M(olefin)_3$ having a distorted pentagonal[12,13] and hexagonal geometry,[14,15] respectively, are much less common. To the best of our knowledge, there is still no pentagonal palladium(0) complex formulated as $Pd(olefin)_2L$ reported in literature. The coplanar structure of the two olefin and bromide ligands in **4** is the result of maximizing overlap of the π^* orbitals in the olefin double bonds with the two d orbitals in the pentagonal plane.[16] For a $M(olefin)_2L$ complex, the two d orbitals in the coordination plane are higher in energy than the three out-of-plane d orbitals, due to repulsion by the ligands. Consequently, the olefin ligands prefer lying in the coordination plane to allow maximum overlap of their π^* orbitals with the in-plane d orbitals.

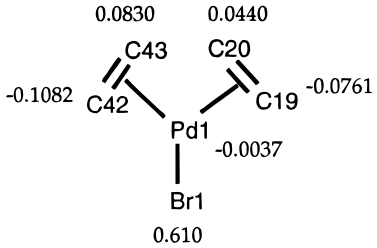


Figure 2. Deviations (Å) from the calculated least-squares plane of atoms Pd1, Br1, C19, C20, C42, and C43. The equation for the least-squares plane is $7.420x - 4.349y + 4.910z = -4.4985$, where x, y, and $\mathbf{z}$ are crystal coordinates.

Similarly, the reaction of $(\textit{trans}\text{-}MeO_2CCH{=}CHPPh_3)^+Br^-$ with $Pd(dba)_2$ in dichloromethane afforded complex **5**, and the reaction of $(\textit{trans}\text{-}PhCH{=}CHPPh_3)^+Br^-$ with $Pd(dba)_2$ in DMSO gave complex **6**. Both **4** and **5** are stable in the solid state, but slowly decompose in chloroform solution to yield palladium metal and the corresponding phosphonium salts. Complex **6** is less stable and cannot be isolated in pure form. For the less electron-withdrawing phosphonium salts, $\textit{trans}\text{-}CH_3CH{=}CH(PPh_3)^+Br^-$ and $CH_2{=}CCH_3(PPh_3)^+Br^-$, no stable product can be isolated on treating with $Pd(dba)_2$.

The ^{1}H NMR spectra in $CDCl_3$ of **4** and **5** exhibit characteristic resonances for η^2-coordinated phosphonioalkene moieties. The resonances at δ 4.92 and 3.88 are assigned to a (near the PPh_3 group) and b olefin protons, respectively, based on the coupling constants between the phosphorus atom and the b olefin proton of 15.8 Hz and the a olefin proton of 12.4 Hz.[17] A *trans*-η^2-coordinated phosphonioalkene ligand was also in agreement with the observed coupling constant of 12.4 Hz between the a and b olefin protons.[18] For complex **4**, the observation of diastereotopic methylene protons at δ 3.76 and 3.89 is due to the presence of the asymmetric center of this complex. The ^{1}H NMR spectrum of complex **6** cannot be obtained in good quality in $CDCl_3$, but in DMSO-d_6, the olefin protons for the coordinated $(PhCH{=}CHPPh_3)^+$ moiety appear at δ 3.91(dd, J = 18.8, 11.2 Hz) and 4.28 (t, J = 11.2 Hz), similar in pattern and coupling constants to complexes **4** and **5**.

Synthesis of $Pd[R^1CH{=}CR^2(PPh_3)](L)Br$ from $Pd(dba)_2$. The reaction of $Pd(dba)_2$ with alkenylphosphonium bromide in the presence of phosphine or phosphite is a convenient way for synthesizing monophosphonioalkene−palladium(0) complexes. In a previous paper,[2] we reported that the reaction of $Pd(dba)_2$ with $PhCH{=}CH(PPh_3)^+Br^-$ and 1 equiv of PPh_3 in

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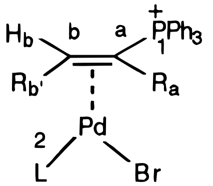
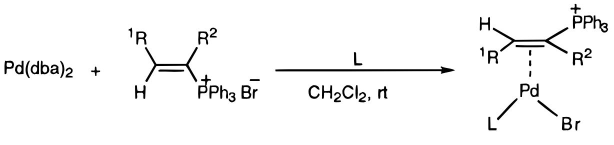
Table 2. Selected NMR Data for Complexes 3, 7, 8, 9, 10, and 11[a]



	H_a		H_b		$H_{b'}$		C_a		C_b	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
3	3.53	$^3J_{ab} = 10.3$ $^2J_{aP_1} = 7.6$ $^3J_{aP_2} = 12.6$	3.24	$^3J_{ab} = 10.3$ $^3J_{bP_1} = 19.0$ $^3J_{bP_2} = 4.4$			27.17	$^1J_{P_1} = 80.6$ $^2J_{P_2} = 37.6$	61.35	$^2J_{P_2} = 6.1$
7	3.03	$^3J_{ab} = 10.5$ $^2J_{aP_1} = 7.7$ $^3J_{aP_2} = 15.9$	2.39	$^3J_{ab} = 10.5$ $^3J_{bP_1} = 13.3$ $^3J_{bP_2} = 0$						
8	3.66	$^3J_{ab} = 10.2$ $^2J_{aP_1} = 9.2$ $^3J_{aP_2} = 13.0$	2.98	$^3J_{ab} = 10.2$ $^3J_{bP_1} = 16.4$ $^3J_{bP_2} = 2.2$			27.06	$^1J_{P_1} = 79.0$ $^2J_{P_2} = 42.2$	48.71	$^2J_{P_2} = 6.8$ $^2J_{P_1} = 1.8$
9	3.66	$^3J_{ab} = 9.9$ $^2J_{aP_1} = 9.6$ $^3J_{aP_2} = 12.8$	2.93	$^3J_{ab} = 9.9$ $^3J_{bP_1} = 16.3$ $^3J_{bP_2} = 2.3$			27.15	$^1J_{P_1} = 79.1$ $^2J_{P_2} = 42.2$	48.50	$^2J_{P_2} = 6.8$
10[b]			2.02	$^2J_{bb'} = 4.0$ $^3J_{bP_1} = 18.8$ $^3J_{bP_2} = 4.0$	2.54	$^2J_{bb'} = 4.0$ $^3J_{b'P_1} = 27.6$ $^3J_{b'P_2} = 4.0$	37.63	$^1J_{P_1} = 66.9$ $^2J_{P_2} = 39.9$	51.36	$^2J_{P_2} = 12.9$
11	3.52	$^3J_{ab} = 11.0$ $^3J_{aP_1} = 11.0$ $^3J_{aP_2} = 13.6$	3.04	$^3J_{ab} = 11.0$ $^3J_{bP_1} = 16.3$ $^3J_{bP_2} = 2.1$			29.71	$^1J_{P_1} = 81.1$ $^2J_{P_2} = 67.4$	49.34	$^2J_{P_2} = 6.7$

[a] In $CDCl_3$ except otherwise mentioned. [b] The solvent used for **10** is CD_2Cl_2.

dichloromethane led to the isolation of **3**. This method may be extended to the synthesis of other monophosphonioalkene−palladium(0) complexes. Thus, *trans*-$CH_3CH{=}CH(PPh_3)^+Br^-$, *trans*-$RO_2CCH{=}CH(PPh_3)^+Br^-$, where R = Et and Me, and $CH_2{=}CCH_3(PPh_3)^+Br^-$ react with $Pd(dba)_2$ in the presence of 1 equiv of PPh_3 to give the palladium complexes **7**−**10**, respectively, with the general formula $Pd[R^1CH{=}CR^2(PPh_3)](PPh_3)Br$ in 54−92% yields (eq 1). Similarly, treatment of $Pd(dba)_2$ with 1 equiv of *trans*-$MeO_2CCH{=}CH(PPh_3)^+Br^-$ and 1 equiv of $P(OPh)_3$ led to the formation of Pd(*trans*-$MeO_2CCH{=}CH(PPh_3)^+$)[$P(OPh)_3$]Br (**11**). It is surprising that even the *trans*-$CH_3CH{=}CH(PPh_3)^+Br^-$ and $CH_2{=}CCH_3(PPh_3)^+Br^-$ salts gave stable products **7** and **10**. As shown in the foregoing results, these two salts did not afford isolable products on reacting with $Pd(dba)_2$ alone. While complexes **8** and **9** have been obtained from the rearrangement of the corresponding oxidative-addition products, $Pd(PPh_3)(CH{=}CHCO_2R)Br$,[1] the present substitution method offers a simple yet efficient alternative for the preparation of these compounds. From these synthetic studies, it is clear that all disubstituted alkenylphosphonium cations interact strongly with palladium(0) to afford stable products. However, the trisubstituted alkenylphosphonium salt *trans*-$(CH_3)CH{=}C(CH_3)(PPh_3)^+Br^-$ did not give the expected product on reacting with $Pd(dba)_2$ and 1 equiv of PPh_3.

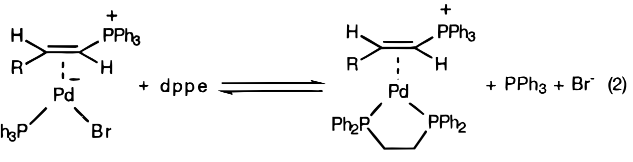


(1)

R^1 = Ph, R^2 = H, L = PPh_3	3	81 %
R^1 = CH_3, R^2 = H, L = PPh_3	7	76 %
R^1 = COOEt, R^2 = H, L = PPh_3	8	54 %
R^1 = COOMe, R^2 = H, L = PPh_3	9	92 %
R^1 = H, R^2 = CH_3, L = PPh_3	10	67 %
R^1 = COOMe, R^2 = H, L = $P(OPh)_3$	11	80 %

The chemical formulation and the structure of complexes **7**−**11** are supported by microanalysis IR and NMR data of these species (see Experimental Section). Similar to **3**, each of these complexes exhibits two ^{31}P NMR resonances at δ 21−28 ppm with coupling constants of 4−8 Hz, in agreement with the formulation that only two types of phosphorus atoms are in each complex. The presence of an η^2-coordinated phosphonioalkene moiety is evidenced by the upfield shift of the olefin proton resonances to the range 2.0−3.7 ppm in the ^1H NMR spectra and the two olefin carbon resonances to the sp^3 region in the ^{13}C NMR spectra. The chemical shifts and coupling constants for the olefin protons and carbons in the coordinated $R^1CH{=}CR^2(PPh_3)^+$ moieties of complexes **7**−**11** are summarized in Table 2. Comparison of the coupling constants of **7**−**11** with the corresponding values of **3** leads us to conclude that **7**−**11** are similar in structure to **3**, i.e., the $R^1CH{=}CR^2(PPh_3)^+$ moieties in these complexes are all trans in geometry and the PPh_3 or $P(OPh)_3$ ligand is trans to C_a in the $R^1CH{=}CR^2(PPh_3)^+$ moiety.

Substitution Reactions. Complex **3** was shown to undergo a substitution reaction with PPh_3 to yield the bis(triphenylphosphine) complex **2**. In the present studies, the facile substitution reaction is further demonstrated by the formation of a cationic dppe complex **12** by treating **3** with 1 equiv of dppe (eq 2). However, **3** does not undergo substitution with nitrogen ligands such as bipyridine and pyridine. The degree of substitution of $Pd[R^1CH{=}CR^2(PPh_3)](PPh_3)Br$ depends greatly on the alkenyl group in $R^1CH{=}CR^2(PPh_3)^+$ and on the phosphine. For complexes **8** and **9**, attempts to isolate the bis(triphenylphosphine) cationic species by addition of 1 equiv of PPh_3 followed by precipitation with ether led only to the isolation of starting complexes **8** and **9**.



3 R = Ph **12**

9 R = COOMe **13**

Similarly, treatment of complex **11** with 1 equiv of $P(OPh)_3$ followed by addition of ether also results in the isolation of the starting complex **11**. However, treatment of **9** with the chelating ligand dppe led to the isolation of **13** in excellent yield (eq 2). The substitution reactions of complexes **7** and **10** appear to behave differently from the other $Pd[R^1CH{=}CR^2(PPh_3)](PPh_3)Br$ complexes, **3**, **8**, and **9**. Treatment of **7** with PPh_3 led to, in part, the formation of the corresponding cationic bisphosphine complex and, in part, the substitution of the $CH_3CH{=}CH(PPh_3)^+$ moiety by PPh_3. Complex **10** behaves similar to **7** on reacting with PPh_3. All of the substitution cationic products were characterized by microanalysis and comparison of the spectral data with those of complex **2**.

In conclusion, we have isolated three classes of phosphonioalkene–palladium(0) complexes, including $[Pd(R^1CH{=}CR^2PPh_3)(L)_2]^+$, $Pd(R^1CH{=}CR^2PPh_3)(L)Br$, and $Pd(R^1CH{=}CR^2PPh_3)_2Br$. In all of these complexes, the olefin carbons of the $R^1CH{=}CR^2(PPh_3)^+$ moiety are coplanar with the other ligands and the palladium center. The stability of these three classes of complexes depends greatly on the phosphonioalkene moiety. Of the alkenylphosphonium bromides tested, only the electron-withdrawing *trans*-$RO_2CCH{=}CH(PPh_3)^+Br^-$ reacts with $Pd(dba)_2$ to give stable bis(phosphonioalkene) complex. On the other hand, most disubstituted alkenylphosphonium bromides react with $Pd(dba)_2$ in the presence of 1 equiv of L to give stable neutral monophosphonioalkene complexes $Pd[R^1CH{=}CH(PPh_3)](L)Br$ (L = PPh_3, $P(OPh)_3$). The stability of the $Pd[R^1CH{=}CH(PPh_3)](L)_2^+$ cation is influenced both by the $R^1CH{=}CH(PPh_3)^+$ moiety and L. An electron-withdrawing substituent on the $R^1CH{=}CH(PPh_3)^+$ moiety in $Pd[R^1CH{=}CH(PPh_3)](L)Br$ reduces the tendency for the palladium complex to further react with a phosphine ligand (L) to yield the cationic product $Pd[R^1CH{=}CH(PPh_3)](L)_2^+$, while an electron-donating substituent on the $R^1CH{=}CH(PPh_3)^+$ moiety enhances the removal of the alkenylphosphonium group from $Pd[R^1CH{=}CH(PPh_3)](L)Br^-$ on addition of a phosphine ligand.

Experimental Section

All reactions were performed under dry nitrogen, and all solvents were dried by standard methods. ^1H and ^{13}C NMR experiments were performed on a Varian Gemini 300 or a Varian Unity 400 spectrometer, while ^{31}P NMR experiments were carried out on a Brucker MSL-300 spectrometer, using 85% H_3PO_4 as an external standard. Infrared spectra were recorded on a Bomem MB-100 spectrophotometer, while mass spectra were obtained on a Jeol JMS-D100 system. Melting point measurements were carried on a MEL-TEMP apparatus and are uncorrected. Microanalytical data were obtained on a Heraeus CHN-O-RAPID instrument.

1-Bromopropene, α-bromostyrene (Aldrich), 2-bromo-2-butene (mixture of isomers), *cis*-2-ethoxybromoethylene, 2-bromopropene, triphenylphosphine (Janssen), and β-bromostyrene (mixture of isomers, TCI) were used as purchased. $Pd(PPh_3)_4$[19] and $Pd(dba)_2$[20] were prepared according to reported methods. All of the alkenylphosphonium salts, *trans*-$PhCH{=}CHPPh_3^+Br^-$, *trans*-$CH_3CH{=}CHPPh_3^+Br^-$, *trans*-$CH_3CH{=}CCH_3PPh_3^+Br^-$, $CH_2{=}CCH_3PPh_3^+Br^-$, *trans*-$(EtOOC)CH{=}CHPPh_3^+Br^-$, and *trans*-$(MeOOC)CH{=}CHPPh_3^+Br^-$ were prepared from the reactions of triphenylphosphine with $CH_3CH{=}CHBr$, $CH_3CH{=}CCH_3Br$, (mixtures of isomers), $CH_2{=}CCH_3Br$, *cis*-$(EtOOC)CH{=}CHBr$, and *cis*-$(MeOOC)CH{=}CHBr$, respectively, using $Pd(PPh_3)_4$ or $Pd(OAc)_2$ as the catalyst.[2] $Pd(dba)_2$ was prepared according to reported methods.[20]

Synthesis of [(*trans*-(EtOOC)CH=CHPPh$_3^+$)$_2$Pd(Br)]-Br$^-$ (4). A round-bottom flask containing $Pd(dba)_2$ (0.144 g, 0.250 mmol) and *trans*-$(EtOOC)CH{=}CHPPh_3^+Br^-$ (0.221 g, 0.500 mmol) was purged by nitrogen gas three times. To the flask was then added dichloromethane (5 mL) by syringe, and the solution was stirred at room temperature for 2 h. The solid formed during the reaction was filtered off, and to the filtrate was added ether to afford a white precipitate, which was collected on a glass filter and was washed with ether (20 mL) to afford the desired pure product (0.136 g, 55%). This material was recrystallized from dichloromethane and hexane. Spectral data and microanalysis data are as follows. ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, CH_3, $J = 7.0$ Hz, 6 H), 3.76 (dq, $J = 11.0$ Hz, $J = 7.1$ Hz, 2 H), 3.88 (dd, $J = 15.8$ Hz, $J = 12.2$ Hz, 2 H), 3.89 (dq, $J = 11.0$ Hz, $J = 7.0$ Hz, 2 H), 4.92 (t, $J = 12.4$ Hz, 2 H), 7.55–7.81 (m, 30 H). IR (KBr): 3012, 1696 (υ(C=O)), 1438, 1246, 1106, 725, 889 cm^{-1}. MS (FAB): *m/z* 907, 909 $[M]^+$. Anal. Calcd for $PdBr_2P_2C_{46}H_{44}O_4{\cdot}CH_2Cl_2{\cdot}H_2O$: C, 52.57; H, 4.32. Found: C, 52.90; H, 4.57. Mp: 120–122 °C dec.

Synthesis of [(*trans*-(MeOOC)CH=CHPPh$_3^+$)$_2$Pd(Br)]-Br$^-$ (5). To $Pd(dba)_2$ (0.144 g, 0.250 mmol) and *trans*-$(MeOOC)CH{=}CHPPh_3^+Br^-$ (0.214 g, 0.500 mmol) in a round-bottom flask under nitrogen was added CH_2Cl_2 (5 mL). The solution was then stirred at room temperature for 4 h. During this period, the color of the solution changed gradually from red-brown to pale yellow. The solid was filtered off, the solvent was removed in vacuo, and the residue was then washed by ether (*ca.* 10 mL) three times to give the desired pale yellow product (0.214 g, 89%). This material was recrystallized from dichloromethane and ether. Spectral data and microanalysis data are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 3.30 (s, OCH_3, 6 H), 3.95 (dd, $J = 15.5$ Hz, $J = 12.1$ Hz, 2 H), 4.91 (t, $J = 12.4$ Hz, 2 H), 7.54–7.80 (m, 30 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 52.36 (OCH_3), 55.30 (d, $^1J_{PC} = 83.0$ Hz), 67.02 (d, $^2J_{PC} = 6.6$ Hz), 118.76 (d, $^1J_{PC} = 90.0$ Hz), 129.80 (d, $^2J_{PC} = 12.7$ Hz), 133.62 (d, $^3J_{PC} = 10.1$ Hz), 134.60, 166.73 (d, CO, $^3J_{PC} = 14.7$ Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 25.77 (s). IR (KBr): 1702 (υ(C=O)), 1559, 1438, 1249, 1157, 1105, 996, 820, 724, 688 cm^{-1}. MS (FAB): *m/z* 879, 881 $[M]^+$. Anal. Calcd for $PdBr_2P_2C_{44}H_{40}O_4{\cdot}{}^1/_2CH_2Cl_2{\cdot}H_2O$: C, 52.33; H, 4.24. Found: C, 52.50; H, 4.54. Mp: 120–122 °C dec.

X-ray Structure Determination of [(*trans*-(EtOOC)-CH=CHPPh$_3$)$_2$PdBr]$^+$Br$^-$ (4). A colorless and bladed crystal with dimensions of 0.22 × 0.12 × 0.04 mm of the title compound was selected for indexing and intensity data collection on a Siemens R3m/V diffractometer using Mo Kα radiation (0.7107 Å). Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit-cell parameters. The parameters of this data collection are presented in Table 3. Of the 7488 reflections collected, 3177 unique reflections were considered observed ($I \geq 3.0\ \sigma(I)$) after Lorentz polarization and empirical absorption corrections. Correction for absorption effects was based on ψ scans of a few suitable reflections with χ values close to 90° using the program XEMP of the SHELXTL-Plus program package. On the basis of the systematic absences, the space

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[19] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

[20] Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *Chem. Commun.* **1970**, 1065.

Table 3. Crystal Data and Structure Refinement Parameters for [(*trans*-$EtO_2CCH{=}CHPPh_3^+)_2Pd(Br)]Br^-$ (4)

chem formula	$C_{46}H_{44}Br_2O_4P_2Pd\cdot(CH_2Cl_2)\cdot(H_2O)$	γ (deg) V (Å^3)	75.36(2) 2373.8(11)
fw	1089.9	Z	2
space group	$P\bar{1}$; triclinic	ρ(calcd Mg m^{-3})	1.525
a (Å)	9.610(2)	μ (mm^{-1})	2.297
b (Å)	15.542(4)	T (K)	295
c (Å)	17.559(5)	R	0.0457
α (deg)	89.32(2)	R_w	0.0389
β (deg)	84.82(2)		

group was determined to be $P\bar{1}$. Direct methods were used to locate most of the non-hydrogen atoms in the structure, with the remaining atoms being found from a difference Fourier map calculated at the final stage of structure analysis. The final cycles of refinement, including the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms and atomic coordinates and fixed isotropic thermal parameters for the H atoms, converged at $R = 0.0457$ and $R_w = 0.0389$. In the final difference map, the deepest hole was 0.52 e Å^{-3} and the highest peak 0.48 e Å^{-3}. Corrections for secondary extinction and anomalous dispersion were applied. Neutral-atom scattering factors were used. Structure solution and least-squares refinements were performed on a DEC VAX 4000/VLC workstation using the SHELXTL-Plus programs.[21]

Synthesis of Pd(*trans*-$R^1CH{=}CR^2PPh_3)(PPh_3)Br$ from $Pd(dba)_2$ and *E*-$R^1CH{=}CR^2PPh_3^+Br^-$. A general procedure for the preparation of Pd(*trans*-$R^1CH{=}CR^2PPh_3)(PPh_3)Br$ is as follows. A round-bottom flask containing $Pd(dba)_2$ (0.287 g, 0.500 mmol), triphenylphosphine (0.131 g, 0.500 mmol), and *trans*-$R^1CH{=}CR^2PPh_3^+Br$ (0.50 mmol) was purged by nitrogen gas three times. To the system was added dichloromethane (5 mL). The solution was then stirred at room temperature for 3−4 h. The color of the solution changed gradually from red-brown to deep yellow, and a small amount of black precipitate was also produced during the reaction. The solid was filtered off, and the solvent was removed in vacuo. The residue was collected on a glass filter and was then washed by ether (*ca.* 10 mL) three times to give the crude product. Recrystallization from dichloromethane and ether afforded the desired pure product. Product yields and spectral data for these compounds are shown below.

[(*trans*-$CH_3CH{=}CHPPh_3^+$)Pd(PPh_3)(Br)] (7): product yield, 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (dd, CH_3, J = 6.1 Hz, J = 3.8 Hz, 3 H), 2.39 (ddq, J = 13.3 Hz, J = 10.5 Hz, J = 6.1 Hz, 1 H), 3.03 (ddd, J = 15.9 Hz, J = 10.5 Hz, J = 7.7 Hz, 1 H), 7.21−7.44 (m, 15 H), 7.54 (td, J = 8.0 Hz, J = 2.4 Hz, 3 H), 7.69−7.73 (m, 6 H), 7.89 (dd, J = 12.2 Hz, J = 7.4 Hz, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 20.65 (d, CH_3, $^3J_{PC}$ = 12.2 Hz), 30.97 (dd, $^1J_{PC}$ = 80.4 Hz, $^2J_{PC}$ = 34.9 Hz), 57.73, 124.24 (d, $^1J_{PC}$ = 88.0 Hz), 127.63 (d, $^3J_{PC}$ = 9.1 Hz), 128.50, 128.65 (d, $^2J_{PC}$ = 12.2 Hz), 132.69, 133.73 (d, $^2J_{PC}$ = 9.2 Hz), 133.83 (d, $^3J_{PC}$ = 9.1 Hz), 136.16 (d, $^1J_{PC}$ = 27.3 Hz). IR (KBr): 3046, 1582, 1434, 1176, 1103, 932, 750, 720, 693 cm^{-1}. MS (FAB): *m/z* 671 [M − Br − 1]$^+$. Mp: 130−132 °C dec.

[(*trans*-$EtO_2CCH{=}CHPPh_3^+$)Pd(PPh_3)(Br)] (8): product yield, 54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (t, CH_3, J = 7.2 Hz, 3 H), 2.98 (ddd, J = 16.4 Hz, J = 10.2 Hz, J = 2.2 Hz, 1 H), 3.38 (dq, J = 10.7 Hz, J = 7.1 Hz, 1 H), 3.66 (ddd, J = 13.0 Hz, J = 10.2 Hz, J = 9.2 Hz, 1 H), 3.74 (dq, J = 10.7 Hz, J = 7.1 Hz, 1 H), 7.22−7.39 (m, 15 H), 7.46 (td, J = 7.8 Hz, J = 3.2 Hz, 6 H), 7.59 (td, J = 7.2 Hz, J = 2.0 Hz, 3 H), 7.89 (dd, J = 12.8 Hz, J = 7.6 Hz, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 14.03 (CH_3), 27.06 (dd, $^1J_{PC}$ = 79.0 Hz, $^2J_{PC}$ = 42.2 Hz), 48.71 (dd, $^2J_{PC}$ = 6.8 Hz, $^2J_{PC}$ = 1.8 Hz), 59.84 (CH_2), 123.45 (dd, $^1J_{PC}$ = 88.2 Hz, $^4J_{PC}$ = 4.0 Hz), 128.09 (d, $^3J_{PC}$ = 9.3 Hz), 129.30 (d, $^2J_{PC}$ = 12.2 Hz), 129.39, 133.63, 134.27 (d, $^3J_{PC}$ = 10.0 Hz), 134.31 (d, $^2J_{PC}$ = 13.6 Hz), 135.45 (d, $^1J_{PC}$ = 32.5 Hz), 171.87 (dd, CO, $^3J_{PC}$ = 14.3 Hz, $^3J_{PC}$ = 1.7 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 22.99 (d, $^3J_{PP}$ = 8.1 Hz), 26.75 (d, $^3J_{PP}$ = 8.1 Hz). IR (KBr): 3047, 1697 (υ(C=O)), 1479, 1434, 1245, 1159, 1101, 750, 725, 693 cm^{-1}. MS (FAB): *m/z* 729 [M − Br − 1]$^+$. Anal. Calcd for $PdBrP_2C_{41}H_{37}O_2$: C, 60.80; H, 4.60. Found: C, 60.11; H, 4.59. Mp: 150−152 °C dec.

[(*trans*-$MeO_2CCH{=}CHPPh_3^+$)Pd(PPh_3)(Br)] (9): product yield, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.93 (ddd, J = 16.3 Hz, J = 9.9 Hz, J = 2.3 Hz, 1 H), 3.05 (s, OCH_3, 3 H), 3.66 (ddd, J = 12.8 Hz, J = 9.9 Hz, J = 9.6 Hz, 1 H), 7.22−7.40 (m, 15 H), 7.47 (td, J = 7.7Hz, J = 3.2 Hz, 6 H), 7.60 (td, J = 7.6 Hz, J = 1.6 Hz, 3 H), 7.89 (dd, J = 12.4 Hz, J = 7.2 Hz, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 27.15 (dd, $^1J_{PC}$ = 79.1 Hz, $^2J_{PC}$ = 42.2 Hz), 48.50 (d, $^2J_{PC}$ = 6.8 Hz), 50.96 (CH_3), 123.49 (dd, $^1J_{PC}$ = 88.5 Hz, $^4J_{PC}$ = 3.6 Hz), 128.19 (d, $^3J_{PC}$ = 9.2 Hz), 129.39 (d, $^2J_{PC}$ = 11.6 Hz), 129.46, 133.68 (d, $^4J_{PC}$ = 1.4 Hz), 134.33 (d, $^3J_{PC}$ = 10.4 Hz), 134.35 (d, $^2J_{PC}$ = 13.4 Hz), 135.48 (d, $^1J_{PC}$ = 31.9 Hz), 172.13 (d, CO, $^3J_{PC}$ = 14.1 Hz). IR (KBr): 1689 (υ(C=O)), 1434, 1217, 1145, 1100, 745, 691, 512 cm^{-1}. MS (FAB): *m/z* 715 [M − Br − 1]$^+$. Anal. Calcd for $PdBrP_2C_{40}H_{35}O_2$: C, 60.36; H, 4.43. Found: C, 59.98; H, 4.51. Mp: 173−175 °C dec.

[($CH_2{=}C(CH_3)PPh_3^+$)Pd(PPh_3)(Br)] (10): product yield, 67%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.79 (dd, CH_3, J = 15.4 Hz, J = 6.6 Hz, 3 H), 2.09 (dt, J = 18.8 Hz, J = 4.0 Hz, 1 H), 2.60 (dt, J = 27.6 Hz, J = 4.0 Hz, 1 H), 7.26−7.44 (m, 15 H), 7.48 (td, J = 7.8 Hz, J = 3.1 Hz, 6 H), 7.60−7.64 (m, 3 H), 7.98 (dd, J = 12.4 Hz, J = 7.6 Hz, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 21.87 (dd, CH_3, $^2J_{PC}$ = 9.0 Hz, $^3J_{PC}$ = 4.5 Hz), 37.63 (dd, $^1J_{PC}$ = 66.9 Hz, $^2J_{PC}$ = 39.9 Hz), 51.36 (d, CH_2, $^2J_{PC}$ = 12.9 Hz), 122.83 (dd, $^1J_{PC}$ = 85.7 Hz, $^4J_{PC}$ = 4.2 Hz), 128.18 (d, $^3J_{PC}$ = 9.0 Hz), 129.11, 129.18 (d, $^2J_{PC}$ = 11.0 Hz), 133.29, 134.31 (d, $^2J_{PC}$ = 14.4 Hz), 135.10 (d, $^3J_{PC}$ = 9.3 Hz), 137.27 (d, $^1J_{PC}$ = 29.0 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 26.05 (d, $^3J_{PP}$ = 4.4 Hz), 27.13 (d, $^3J_{PP}$ = 4.4 Hz). IR (KBr): 3047, 1584, 1478, 1431, 1247, 1099, 896, 748, 704 cm^{-1}. MS (FAB): *m/z* 671 [M − Br − 1]$^+$. Anal. Calcd for $PdBrP_2C_{39}H_{35}\cdot0.5CH_2Cl_2$: C, 59.72; H, 4.57. Found: C, 58.55; H, 4.55. Mp: 115−117 °C dec.

[(*trans*-$MeO_2CCH{=}CHPPh_3^+$)Pd(P(OPh)$_3$)(Br)] (11): product yield, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (ddd, J = 16.3 Hz, J = 10.9 Hz, J = 2.1 Hz, 1 H), 3.26 (s, OCH_3, 3 H), 3.52 (dt, J = 13.6 Hz, J = 11.0 Hz, 1 H), 7.05−7.21 (m, 15 H), 7.48 (td, J = 7.9 Hz, J = 3.3 Hz, 6 H), 7.64 (td, J = 7.4 Hz, J = 1.2 Hz, 3 H), 7.73 (dd, J = 12.4 Hz, J = 7.2 Hz, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 29.71 (dd, $^1J_{PC}$ = 81.1 Hz, $^2J_{PC}$ = 67.4 Hz), 49.34 (d, $^2J_{PC}$ = 6.7 Hz), 51.38 (OCH_3), 121.39 (d, $^3J_{PC}$ = 5.5 Hz), 122.78 (dd, $^1J_{PC}$ = 88.9 Hz, $^4J_{PC}$ = 6.3 Hz), 124.41, 129.56 (d, $^2J_{PC}$ = 12.3 Hz), 129.58, 133.90, 134.24 (d, $^3J_{PC}$ = 10.0 Hz), 151.73, 171.72 (dd, CO, $^3J_{PC}$ = 12.9 Hz, $^3J_{PC}$ = 3.4 Hz). IR (KBr): 1701 (υ(C=O)), 1538, 1485, 1435, 1175, 888, 707, 697, 599, 524, 425 cm^{-1}. MS (FAB): *m/z* 763 [M − Br − 1]$^+$. Anal. Calcd for $PdBrP_2C_{40}H_{35}O_5$: C, 56.93; H, 4.18. Found: C, 56.71; H, 4.26. Mp: 150−152 °C dec.

Synthesis of [Pd(*trans*-$R^1CH{=}CR^2PPh_3$)(dppe)]$^+Br^-$. To $Pd(dba)_2$ (0.287 g, 0.50 mmol) and dppe (0.50 mmol) in a round-bottom flask under nitrogen was added CH_2Cl_2 (5 mL). The solution was then stirred at room temperature for 10 min. During this period, the color of the solution changed gradually from red-brown to orange. Addition of (*E*-$R^1CH{=}CR^2PPh_3)^+$-Br^- (0.50 mmol) was followed by stirring at the same temperature for 4 h. The solid was filtered, and to the filtrate was added ether to precipitate out the product. The solvent was filtered off, and the solid was washed with ether (*ca.* 10 mL) three times to afford the pure material. The complexes prepared according to this method and their spectral data are as follows.

[(*trans*-$PhCH{=}CHPPh_3$)Pd(dppe)]$^+Br^-$ (12): product yield, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05−2.44 (m, 4 H), 4.01−4.08 (m, 1 H), 4.30−4.40 (m, 1 H), 6.56 (ddd, J =

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(21) Sheldrick, G. M. *SHELXTL-Plus Crystallographic System*, release 4.21; Siemens Analytical X-ray Instruments: Madison, WI, 1991.

11.1 Hz, $J = 8.5$ Hz, $J = 1.1$ Hz, 2 H), 6.63 (ddd, $J = 9.9$ Hz, $J = 8.3$ Hz, $J = 1.5$ Hz, 2 H), 6.91 (td, $J = 7.9$ Hz, $J = 2.0$ Hz, 2 H), 6.99−7.74 (m, 34 H). IR (KBr): 1568, 1480, 1433, 1160, 840, 746, 691, 510 cm^{-1}. MS (FAB): *m/z* 869 [M − 1]$^+$. Anal. Calcd for $PdBrP_3C_{52}H_{46}\cdot H_2O$: C, 64.51; H, 5.00. Found: C, 64.22; H, 5.13. Mp: 160−162 °C dec.

[(*trans*-MeO$_2$CCH=CHPPh$_3$)Pd(dppe)]$^+$Br$^-$ (13): product yield, 84%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.03−2.17 (m, 1 H), 2.30−2.42 (m, 2 H), 2.56−2.72 (m, 1 H), 3.03 (s, OCH$_3$, 3 H), 3.56 (dt, $J = 16.0$ Hz, $J = 10.6$ Hz, 1 H), 4.08−4.14 (m, 1 H), 6.63 (dd, $J = 10.6$ Hz, $J = 7.4$ Hz, 2 H), 7.10−7.17 (m, 4 H), 7.29−7.45 (m, 20 H), 7.54−7.71 (m, 9 H). $^{31}P\{^1H\}$ NMR (121 MHz, CDCl$_3$): δ 24.29 (dd, $^3J_{PP} = 12.7$ Hz, $^3J_{PP} = 0.9$ Hz), 43.86 (dd, $^3J_{PP} = 12.7$ Hz, $^3J_{PP} = 7.0$ Hz), 45.31 (dd, $^3J_{PP} = 7.0$ Hz, $^3J_{PP} = 0.9$ Hz). IR (KBr): 1678 (υ(C=O)), 1479, 1434, 1212, 1150, 1100, 996, 748, 693 cm^{-1}. MS (FAB): *m/z* 851 [M − 1]$^+$. Anal. Calcd for $PdBrP_3C_{48}H_{44}O_2\cdot H_2O$: C, 60.68; H, 4.88. Found: C, 60.26; H, 5.10. Mp: 170−172 °C dec.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic positional parameters, complete bond distances and angles, thermal parameters, and hydrogen positions for **4** (8 pages). Ordering information is given on any current masthead page.

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