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# Synthesis and Structure of $\eta^2$-Phosphonioalkene−Palladium(0) Complexes. A Catalyst Intermediate in the Palladium-Mediated Synthesis of Alkenylphosphonium Halides

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Treatment of $Pd(PPh_3)_4$ with $PhCH=CHBr$ in THF at 45 °C gave $[(trans\text{-}PhCH=CHPPh_3)Pd(PPh_3)_2]^+Br^-$ (**1**), which was found to be converted from $Pd(PPh_3)_2(CH=CHPh)Br$. X-ray structural analysis shows that **1** adopts a distorted-square-planar geometry with two $PPh_3$ ligands and a $(PhCH=CHPPh_3)^+$ moiety. The C−C double bond in the latter is $\pi$-bonded to the palladium(0) center and occupies two of the four square-planar coordination sites. Under similar reaction conditions, $\{Pd[trans\text{-}PhCH=CHP(p\text{-}tolyl)_3][P(p\text{-}tolyl)_3]_2\}^+Br^-$ (**2**) was formed from $Pd[P(p\text{-}tolyl)_3]_4$ and $PhCH=CHBr$, while $[(trans\text{-}MeCH=CHPPh_3)Pd(PPh_3)_2]^+Br^-$ (**3**) was isolated from the reactions of $Pd(PPh_3)_4$ with $MeCH=CHBr$. Treating $PhCH=CHBr$ with $trans\text{-}Pd(PPh_3)_2(C_6H_4O\text{-}p\text{-}CH_3)I$ in THF at ambient temperature led to the formation of $(trans\text{-}PhCH=CHPPh_3)Pd(PPh_3)X$ (**5**) and $(p\text{-}CH_3OC_6H_4PPh_3)^+X^-$ (X, mixture of Br and I). Complex **5** (X = Br) can be prepared by treating $trans\text{-}PhCH=CH(PPh_3)^+Br^-$ with $Pd(dba)_2$ and 1 equiv of $PPh_3$ in $CH_2Cl_2$. X-ray analysis shows **5** adopts a distorted-square-planar structure consisting of $PPh_3$, X, and $PhCH=CH(PPh_3)^+$ as ligands. The $PPh_3$ ligand is trans to the olefin carbon that is connected to the $PPh_3$ group in $PhCH=CH(PPh_3)^+$, while the halide ligand is trans to the olefin carbon bonded to a phenyl moiety. Reaction of **5** (X = Br) with 1 equiv of $PPh_3$ at ambient temperature afforded **1** in high yield. $Pd(PPh_3)_4$ or $Pd(OAc)_2$ catalyzes the reactions of $PPh_3$ with $PhCH=CHBr$, $MeCH=CHBr$, $MeCH=C(Me)Br$ (mixtures of isomers), $CH_2=C(Me)Br$, $cis\text{-}(EtO_2C)CH=CHBr$, and $cis\text{-}(MeO_2C)CH=CHBr$ to give the corresponding $trans\text{-}RCH=CR'(PPh_3)^+Br^-$. During the reaction of $PPh_3$ with $PhCH=CHBr$, **1** was found to be a catalyst intermediate in the reaction solution. All the phosphonioalkene−palladium(0) complexes and alkenylphosphonium halides isolated are trans in the $(RCH=CR'PPh_3)^+$ moiety.

## Introduction

Oxidative addition of a haloalkene to a palladium(0) species is a key step in the palladium-mediated coupling reactions of haloalkenes with alkenes[1] and nucleophiles, including tin,[2] boron,[3] zinc,[4] magnesium,[5] and lithium reagents[6] and acetylides.[7] Although a vast number of haloalkenes were employed in these coupling reactions, most of the oxidative addition products of palladium(0) complexes with haloalkenes isolated were limited to those in which the alkenyl groups bear electon-withdrawing substituents.[8,9] One pathway accounting for the instability of palladium(II)−alkenyl complexes was demonstrated by Rubinskaya and co-workers.[9] They

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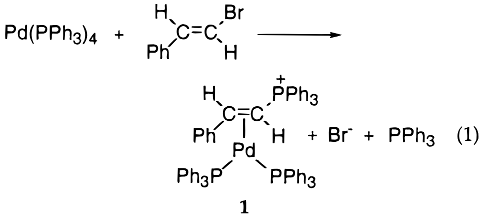
reported that $\sigma$-vinyl–palladium complexes $Pd(PPh_3)_2(\sigma\text{-}CH{=}CHCOOR)X$ (R = Me, Et; X = Cl, I) underwent interesting reductive coupling in benzene at 75–80 °C to give the corresponding $\eta^2$-phosphonioalkene–palladium(0) complexes $Pd((Ph_3PCH{=}CHCOOR)(PPh_3)X$. The observation raises the question whether this rearrangement occurs for other alkenyl–palladium(II) phosphine complexes.

Recently, we and others observed facile Ar′/Ar exchange for $Pd(PAr'_3)_2(Ar)X$.[10] In an attempt to synthesize pure alkenylpalladium(II) phosphine complexes from bromoalkenes and $Pd(PPh_3)_4$ to see whether $Pd(PAr'_3)_2(R)X$, where R = alkenyl, also experiences Ar′/R exchange, we found that alkenyl–palladium(II) phosphine complexes were unstable and isomerized to $\eta^2$-phosphonioalkene–palladium(0) complexes. Moreover, in the synthesis of alkenylphosphonium halides from haloalkenes and phosphines catalyzed by palladium complexes, $\eta^2$-phosphonioalkene–palladium(0) complexes were found to be catalyst species existing in the solutions. Herein, we report the isolation and characterization of these complexes and their role in the catalytic formation of alkenylphosphonium halides.

## Results and Discussion

**Reaction of Styryl Bromide with $Pd(PPh_3)_4$.** In an attempt to prepare *trans*-$Pd(PPh_3)_2(CH{=}CHPh)Br$[11] directly from the oxidative addition of $\beta$-bromostyrene (mixture of trans and cis forms) to $Pd(PPh_3)_4$ at ambient temperature in THF, we observed surprisingly a mixture of $Pd(PPh_3)_2(CH{=}CHPh)Br$ and the $\eta^2$-phosphonioalkene complex **1**. Monitoring the reaction mixture by $^1H$ NMR spectroscopy showed that $Pd(PPh_3)_2(CH{=}CHPh)Br$ reacts slowly with $PPh_3$ in the solution at ambient temperature to give **1**, which is only slightly soluble in THF and was mostly precipitated out of the solution. If $\beta$-bromostyrene was allowed to react with $Pd(PPh_3)_4$ in THF at 45 °C for 18 h, complex **1** was isolated in 88% yield (eq 1).



The structure of complex **1** was determined by single-crystal X-ray crystallographic analysis. Crystals suitable for X-ray diffraction were grown from a mixture of acetonitrile and ether. An ORTEP drawing of the complex with atom-numbering scheme is presented in Figure 1, while important bond distances and angles are listed in Table 1. The results show that **1** is a salt containing a cationic palladium complex and a bromide as the counteranion. The palladium center adopts a distorted-square-planar geometry with two $PPh_3$ ligands and a $PhCH{=}CH(PPh_3)^+$ moiety in which the olefin double bond is $\pi$-bonded to the palladium(0) center and occupies two of the four square-planar coordination sites. The two olefin carbons, two phosphorus atoms, and palladium center are nearly coplanar with a dihedral angle for the P(1)–Pd(1)–(P2) and C(61)–Pd(1)–C(62) planes of 5.7°.

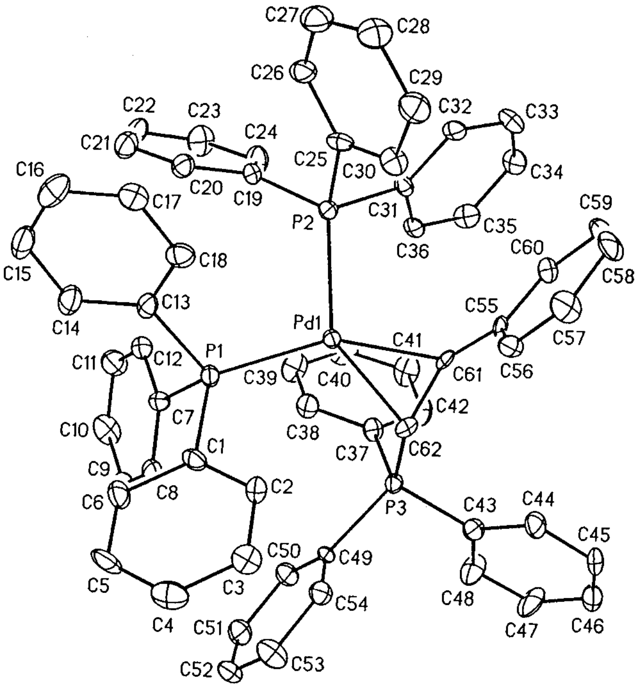


**Figure 1.** Perspective view and atom-labeling scheme for $[Pd(PhCH{=}CHPPh_3)(PPh_3)_2]^+Br^-$ (**1**).

**Table 1. Important Bond Distances (Å) and Angles (deg) for $[(\textit{trans}\text{-}PhCH{=}CHPPh_3)Pd(PPh_3)_2]^+Br^-$ (1)**

| | | | |
|---|---|---|---|
| Distances | | | |
| Pd(1)–P(1) | 2.345(3) | Pd(1)–P(2) | 2.369(3) |
| Pd(1)–C(61) | 2.148(11) | Pd(1)–C(62) | 2.123(12) |
| P(1)–C(1) | 1.836(12) | P(1)–C(7) | 1.867(13) |
| P(1)–C(13) | 1.838(14) | P(2)–C(19) | 1.847(11) |
| P(2)–C(25) | 1.847(17) | P(2)–C(31) | 1.813(12) |
| P(3)–C(37) | 1.814(11) | P(3)–C(43) | 1.815(14) |
| P(3)–C(49) | 1.825(11) | P(3)–C(62) | 1.749(13) |
| C(61)–C(62) | 1.433(17) | | |
| Angles | | | |
| P(1)–Pd(1)–P(2) | 106.6(1) | P(1)–Pd(1)–C(61) | 152.7(3) |
| P(2)–Pd(1)–C(61) | 100.7(3) | P(1)–Pd(1)–C(62) | 113.6(4) |
| P(2)–Pd(1)–C(62) | 139.6(4) | C(61)–Pd(1)–C(62) | 39.2(5) |
| Pd(1)–P(1)–C(1) | 118.5(4) | Pd(1)–P(1)–C(7) | 110.9(4) |
| C(1)–P(1)–C(7) | 104.2(6) | Pd(1)–P(1)–C(13) | 117.4(4) |
| C(1)–P(1)–C(13) | 100.0(6) | C(7)–P(1)–C(13) | 104.0(5) |
| Pd(1)–P(2)–C(19) | 120.4(4) | Pd(1)–P(2)–C(25) | 116.1(4) |
| C(19)–P(2)–C(25) | 104.0(6) | Pd(1)–P(2)–C(31) | 109.9(4) |
| C(19)–P(2)–C(31) | 102.3(5) | C(25)–P(2)–C(31) | 101.9(6) |
| C(37)–P(3)–C(43) | 105.7(6) | C(37)–P(3)–C(49) | 110.2(5) |
| C(43)–P(3)–C(49) | 105.1(6) | C(37)–P(3)–C(62) | 110.3(6) |
| C(43)–P(3)–C(62) | 112.1(6) | C(49)–P(3)–C(62) | 113.1(6) |
| Pd(1)–C(61)–C(55) | 113.8(8) | Pd(1)–C(61)–C(62) | 69.5(7) |
| Pd(1)–C(62)–C(61) | 71.3(6) | Pd(1)–C(62)–P(3) | 117.7(6) |
| P(3)–C(62)–C(61) | 116.5(9) | | |

The olefin complexes of the nickel family with the formula $M(olefin)L_2$ (M = Pd,[12] Pt,[13] and Ni;[14] L = phosphine and phosphite) are well-known, but prior to this report only one palladium complex, $Pd(Ph_3PCH{=}CHCOOMe)(PPh_3)I$,[9] had been structurally characterized by X-ray diffraction. Both complex **1** and $Pd(Ph_3PCH{=}CHCOOMe)(PPh_3)I$ are distorted square pla-

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nar with the two olefin carbons coplanar with the palladium metal and the other two coordination sites. This coplanar geometry of the olefin ligand in $d^{10}$ systems with the chemical formula M(olefin)$L_2$ may be explained on the basis of the energy levels of the five d orbitals in the metal and the interactions of these d orbitals with the $\pi^*$ orbital of the olefin double bond.[15]

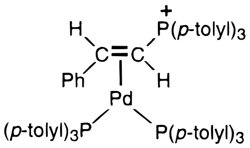
The structure of the $(PhCH{=}CHPPh_3)^+$ moiety is interesting. The phenyl and $PPh_3$ groups in this ligand are trans to each other. The P−Ph bond distances (1.81−1.83 Å) are in the range for $sp^3$-phosphorus−carbon bonds, but the P(3)−C(62) bond distance of 1.749(13) Å is significantly shorter than a normal $sp^3$-phosphorus−carbon bond[16] and is longer than an ylide $(R)HC^-{-}^+PPh_3$ bond (∼1.64 Å).[17] The bond length for the C(61)−C(62) bond of 1.433(17) Å is close to the value (1.434(7) Å) reported for the $\eta^2$-bound carbon−carbon double bond in $Pd(Ph_3PCH{=}CHCOOMe)(PPh_3)I$[9] but is significantly shorter than the distance (1.488(4) Å) in the $[(Ph_3P)(NC)C{=}CHCN]^+$ moiety of $(\eta^5\text{-}C_5H_5)(CO)_2$-Mo[$\eta^2$-C(CN)$PPh_3$CHCN].[16] The observed bond distance for P(3)−C(62) clearly suggests the existence of partial ylide character of this bond. The back-donation from the palladium(0) center to the C−C double bond in $(PhCH{=}CHPPh_3)^+$ producing a partial negative charge on C(61) and C(62) accounts for both the ylide character of the P−C(62) bond and the elongation of the C(61)−C(62) bond.

As shown in Table 1, the bond distance for Pd−C(62) (2.12 (1) Å) is slightly shorter than that for Pd−C(61) (2.15(1) Å). This unsymmetric bonding nature likely reflects the degree of back-bonding from the metal center to the two olefin carbons in the $(PhCH{=}CHPPh_3)^+$ moiety. Stronger back-donation to C(62) than to C(61) from palladium is expected, due to the fact that the negative charge on C(62) can be stabilized through formation of an ylide bond. As a result of the unsymmetrical bonding nature, the Pd−P(2) bond, which is trans to C(62), is slightly longer than the Pd−P(1) bond. The unsymmetrical bonding of the $(PhCH{=}CHPPh_3)^+$ moiety to the palladium was also observed in the bond angles surrounding the metal. The P(1)−Pd−C(62) angle of 113.6° is larger than the P(2)−Pd−C(61) angle by 13°. The large value for P(1)−Pd−C(62) may be rationalized on the basis of the steric repulsion between the bulky phosphine ligand P(1)$Ph_3$ and the $PPh_3$ group in the $PhCH{=}CH(PPh_3)^+$ moiety.

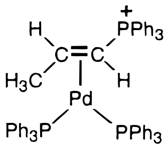
The NMR spectra of **1** exhibit characteristic resonances for an olefin $\pi$-coordinated to a low-oxidation-state metal center.[18] In the $^1H$ NMR spectrum, the absorptions at $\delta$ 3.62 (m) and 4.27 (m) for the two olefin protons are shifted upfield by ca. 4 ppm relative to the corresponding resonances of the free salt $(PhCH{=}CHPPh_3)^+Br^-$. In like manner, the $^{13}C$ NMR resonances for the α- and $\beta$-olefin carbons (relative to the $PPh_3$ group) in the $PhCH{=}CH(PPh_3)^+$ moiety appear at $\delta$ 33.72 (m, $^1J_{C-P} = 78$ Hz, $^2J_{C-P} = 33$ Hz, $^2J_{C-P} = 3$ Hz) and 69.99 (q, $^2J_{C-P} = 35$ Hz, $^2J_{C-P} = 7$ Hz), respectively, showing an upfield shift of the resonances by ca. 90 and 70 ppm, respectively, relative to those of the free salt. These observations indicate that the two olefin carbons in the coordinated $(PhCH{=}CHPPh_3)^+$ moiety are close to $sp^3$ hybridization due to strong back-donation from the palladium(0) center to the carbon−carbon double bond.

The $(PhCH{=}CHPPh_3)^+$ ligand appears to be strongly bonded to **1**. Addition of 5 equiv of $PPh_3$ to the chloroform solution of **1** did not replace this ligand. Indeed, **1** may also be prepared in essentially quantitative yield by treating 1 equiv of $(PhCH{=}CHPPh_3)^+Br^-$ with $Pd(PPh_3)_4$. Complex **1** is also stable toward $(PhCH{=}CHPPh_3)^+$ and bromide ions. Treatment of **1** with 1 equiv of $(PhCH{=}CHPPh_3)^+Br^-$ or with 10 equiv of LiBr in $CD_3OD$ did not lead to substitution of the $PPh_3$ ligand by $(PhCH{=}CHPPh_3)^+$ or by $Br^-$.

Under similar reaction conditions for the formation of **1**, Pd[P($p$-tolyl)$_3$]$_4$ reacts with styryl bromide to afford complex **2**, while $Pd(PPh_3)_4$ reacts with $CH_3HC{=}CHBr$ at 60 °C to yield complex **3**. Both **2** and **3** show characteristic $^1H$ and $^{13}C$ NMR resonances for the two olefin protons and carbons which are $\pi$-coordinated to the palladium center. In addition, the mass data of these salts, which clearly shows the presence of the molecular ion ($m/e$ 1121 for **2**; 933 for **3**) support the proposed molecular formula $PdL_2[trans\text{-}RCH{=}CHPPh_3]^+$. However, both **2** and **3** are relatively unstable in solution and in the solid state and decompose gradually to give the corresponding phosphonium salts and unknown products. Further characterization of these species is difficult.



**2**



**3**

The formation of complexes **1**−**3** from the reaction of $PdL_4$ with the corresponding bromoalkenes may be understood on the basis of the established palladium chemistry. There is little doubt that the first step for the reaction is oxidative addition of bromoalkene (RBr) to $PdL_4$ to yield $PdL_2RBr$. Reductive coupling of the

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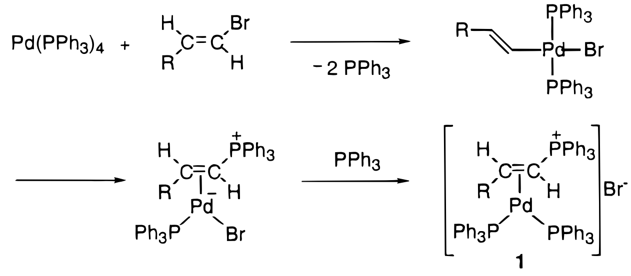
## Scheme 1



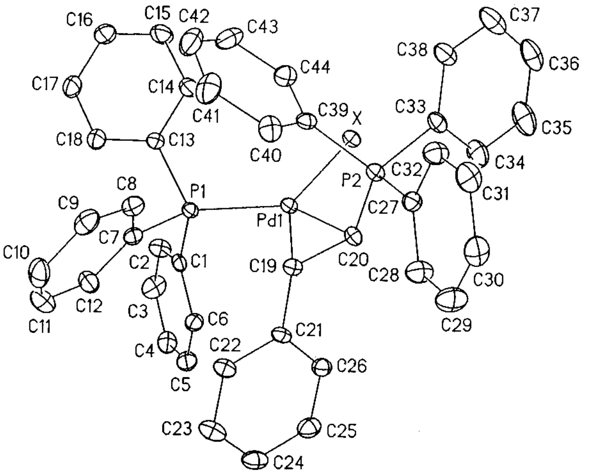
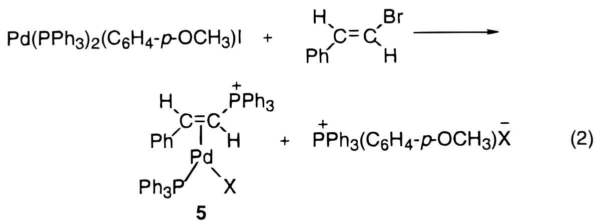


**Figure 2.** Perspective view and atom-labeling scheme for Pd(PhCH=CHPPh$_3$)(PPh$_3$)(X) (**5**).

alkenyl group with phosphine affords a $\eta^2$-phosphonioalkene−palladium(0) species. Substitution of the bromide ligand in the latter complex by a phosphine ligand gives the final product. Scheme 1 summarizes the pathways for the formation of complex **1**. The oxidative addition and reductive coupling in the mechanism gain support from the observation that Pd(PPh$_3$)$_2$(CH=CHCOOMe)I rearranges readily to Pd(Ph$_3$PCH=CHCOOMe)(PPh$_3$)I.[9]

**Reaction of PhCH=CHBr with Pd(PPh$_3$)$_2$(C$_6$H$_4$O-*p*-CH$_3$)I (4).** An $\eta^2$-phosphonioalkene−palladium(0) species was produced even from the reaction of haloalkene with a palladium(II) complex. Treating PhCH=CHBr with *trans*-Pd(PPh$_3$)$_2$(C$_6$H$_4$O-*p*-CH$_3$)I (**4**) in THF at ambient temperature resulted in the isolation of the $\eta^2$-phosphoniostyrene complex **5** in ~25% yield and (PPh$_3$C$_6$H$_4$O-*p*-CH$_3$)$^+$X$^-$.



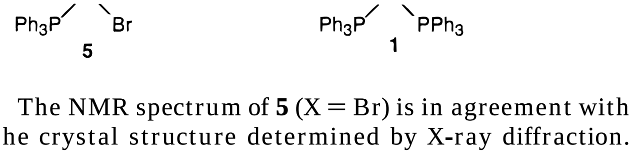
The structure of **5** was also determined by the X-ray diffraction method. The product from reaction 2 was recrystallized from dichloromethane/hexane to afford crystals suitable for X-ray analysis. An ORTEP diagram of **5** with atomic numbering is presented in Figure 2, while important bond distances and angles are shown in Table 2. Because both I$^-$ and Br$^-$ were present in reaction 2, the halide ligand in **5** is a mixture of I$^-$ and Br$^-$ with an I/Br ratio of 3.34/1. This value was determined by elemental analysis and is in agreement with the result obtained from crystallographic data analysis. Similar to **1**, complex **5** is distorted square-planar consisting of PPh$_3$, a halide, and PhCH=CH(PPh$_3$)$^+$ as ligands. The carbon−carbon double bond in the latter is $\pi$-coordinated to the metal and is nearly coplanar with the halide and PPh$_3$ ligands with a dihedral angle of 6.8° for the two planes, P(1)−Pd(1)−X and C(19)−Pd(1)−C(20). The PPh$_3$ ligand is trans to the olefin carbon that is connected to a PPh$_3$ group, while the halide ligand is trans to the olefin carbon bonded to a phenyl moiety. The bond length for C(19)−C(20) of 1.435 Å is nearly the same as the corresponding value in complex **1** and in Pd(Ph$_3$PCH=CHCOOMe)(PPh$_3$)I[9] within experimental error. The data in Table 2 clearly show that the PhCH=CH(PPh$_3$)$^+$ moiety is unsymmetrically bonded to the palladium center with bond distances for Pd(1)−C(19) of 2.084(8) Å and for Pd(1)−C(20) of 2.136(7) Å. It is noteworthy that a reverse trend was observed for the bis(phosphine) complex **1**, i.e., the bond distance for Pd−C(62) is slightly shorter than that for Pd−C(61) in **1**. The greater trans influence of PPh$_3$ relative to bromide likely accounts for the longer bond distance of the Pd(1)−C(20) bond, which is trans to the PPh$_3$ ligand.

**Table 2. Important Bond Distances (Å) and Angles (deg) for Pd(*trans*-PhCH=CHPPh$_3$)(PPh$_3$)(X) (5)**

| Distances | | | |
|---|---|---|---|
| X−Pd(1) | 2.691(1) | Pd(1)−P(1) | 2.291(2) |
| Pd(1)−C(19) | 2.084(8) | Pd(1)−C(20) | 2.136(7) |
| P(1)−C(1) | 1.828(6) | P(1)−C(7) | 1.832(8) |
| P(1)−C(13) | 1.829(8) | P(2)−C(20) | 1.749(6) |
| P(2)−C(27) | 1.819(8) | P(2)−C(33) | 1.806(8) |
| P(2)−C(39) | 1.795(7) | C(19)−C(20) | 1.435(10) |
| C(19)−C(21) | 1.481(10) | | |

| Angles | | | |
|---|---|---|---|
| X−Pd(1)−P(1) | 108.8(1) | X−Pd(1)−C(19) | 145.5(2) |
| P(1)−Pd(1)−C(19) | 105.4(2) | X−Pd(1)−C(20) | 106.2(2) |
| P(1)−Pd(1)−C(20) | 145.0(2) | C(19)−Pd(1)−C(20) | 39.7(3) |
| Pd(1)−P(1)−C(1) | 115.3(2) | Pd(1)−P(1)−C(7) | 113.0(2) |
| C(1)−P(1)−C(7) | 102.3(3) | Pd(1)−P(1)−C(13) | 119.3(2) |
| C(1)−P(1)−C(13) | 105.3(3) | C(7)−P(1)−C(!3) | 99.4(3) |
| C(20)−P(2)−C(27) | 112.3(4) | C(20)−P(2)−C(33) | 110.0(3) |
| C(27)−P(2)−C(33) | 106.7(3) | C(20)−P(2)−C(39) | 111.6(3) |
| C(27)−P(2)−C(39) | 106.4(3) | C(33)−P(2)−C(39) | 109.7(4) |
| Pd(1)−C(19)−C(20) | 72.1(4) | Pd(1)−C(19)−C(21) | 113.4(4) |
| Pd(1)−C(20)−C(19) | 68.2(4) | Pd(1)−C(20)−P(2) | 111.2(4) |
| P(2)−C(20)−C(19) | 117.8(4) | | |

Complex **5** (X = Br) can be prepared in much higher yield by treating PhCH=CH(PPh$_3$)$^+$Br$^-$ with Pd(dba)$_2$ and 1 equiv of PPh$_3$ in dichloromethane. Addition of 1 equiv of PPh$_3$ to this complex in dichloromethane at ambient temperature led immediately to replacement of the bromide ligand by the phosphine and the formation of complex **1** (eq 3).



The NMR spectrum of **5** (X = Br) is in agreement with the crystal structure determined by X-ray diffraction. Unlike **1**, complex **5** displays only two $^{31}$P NMR resonances with equal intensity at $\delta$ 21.20 (d) and 21.68 (d),

**Table 3. Results and Reaction Conditions for the Reactions of Bromoalkenes with Triphenylphosphine**[a]

| entry no. | alkenyl bromide (amt, M)[b] | amt of $PPh_3$ (M)[b] | amt of catalyst (M)[b] | temp (°C) | time (h) | product (yield, %)[c] |
|---|---|---|---|---|---|---|
| 1 | PhCHCHBr (0.4) | 0.4 | $Pd(OAc)_2$ (0.02) | 100 | 14 | $[PhCH{=}CH(PPh_3)]^+Br^-$ (99)[d] |
| 2 | $CH_3CHCHBr$ (0.67) | 0.33 | $Pd(PPh_3)_4$ (0.0083) | 100 | 11.5 | $[CH_3CH{=}CH(PPh_3)]^+Br^-$ (91)[d] |
| 3 | $CH_3CHCBrCH_3$ (0.67) | 0.33 | $Pd(PPh_3)_4$ (0.0083) | 100 | 11.5 | $[CH_3CH{=}CCH_3(PPh_3)]^+Br^-$ (74)[d] |
| 4 | $CH_3CBrCH_2$ (1.5) | 0.5 | $Pd(PPh_{3)4}$ (0.025) | 80 | 12 | $[CH_2{=}CCH_3(PPh_3)]^+Br^-$ (88) |
| 5[e] | $PhCBrCH_2$ (3.0) | 3.3 | $Pd(OAc)_2$ (0.3) | 125 | 24 | 0 |
| 6 | *cis*-CHBrCHCOOEt (0.4) | 0.4 | $Pd(OAc)_2$ (0.02) | 80 | 12 | $[EtO_2CCH{=}CH(PPh_3)]^+Br^-$(83)[d] |
| 7 | *cis*-CHBrCHOEt (0.4) | 0.4 | $Pd(OAc)_2$ (0.02) | 100 | 6 | ∼0 |
| 8 | *cis*-CHBrCHCOOMe (0.4) | 0.4 | $Pd(PPh_3)_4$ (0.02) | 80 | 12 | $[MeO_2CCH{=}CH(PPh_3)]^+Br^-$ (86)[d] |
| 9[f] | $CH_2CHBr$ (0.6) | 0.3 | $Pd(PPh_3)_4$ (0.05) | 110 | 12 | $[CH_2{=}CH(PPh_3)]^+Br^-$ (78) |

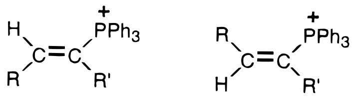
[a] All reactions were carried out in toluene unless otherwise noted. [b] M = mol/L. [c] Isolated yield. [d] Only trans isomer was isolated. [e] Solvent is xylene. [f] A pressure reactor was used for the reaction.

indicating that only two phosphorus atoms are in the complex. In the $^1H$ NMR spectrum, the resonances of the olefin protons $H_\alpha$ and $H_\beta$ in the $PhCH{=}CH(PPh_3)^+$ moiety shift upfield dramatically to 3.53 and 3.24 ppm, respectively, suggesting the presence of $\eta^2$-coordination of the carbon−carbon double bond to the palladium center. On the basis of the observed coupling constants 7.6 and 19.0 Hz for the resonances at 3.53 and 3.24 ppm, respectively, we assign the former resonance to $H_\alpha$ and the latter to $H_\beta$. These coupling constants fall in the range for $^2J_{HP}$ and $^3J_{HP}$.[19] In accordance with the results from X-ray analysis, the observed coupling constants between $P_1$ (in the $PPh_3$ ligand) and $H_\alpha$ of 12.6 Hz and between $P_1$ and $H_\beta$ of 4.4 Hz suggest that the $PPh_3$ ligand is trans to $H_\alpha$ and cis to $H_\beta$. Similarly, the $^{13}C$ NMR data for the two olefin carbons in the $PhCH{=}CH(PPh_3)^+$ moiety provide substantial information for the structure of the complex. The chemical shifts for $C_\alpha$ and $C_\beta$ move upfield drastically to 27.17 and 61.35 ppm, strongly supporting $\eta^2$-coordination of the two olefin carbons to the palladium metal. A stronger coupling (37.6 Hz) of the phosphorus atom in the $PPh_3$ ligand to $C_\alpha$ and a weaker coupling (6.1 Hz) to $C_\beta$ indicates that the $PPh_3$ ligand is trans to $C_\alpha$ and cis to $C_\beta$.

The reaction of the palladium(II) complex **4** with $PhCH{=}CHBr$ to yield the palladium(0) complex **5** is surprising. A reasonable pathway for this reaction is that **4** first undergoes reductive coupling to give a palladium(0) intermediate and a phosphonium salt. Oxidative addition of $PhCH{=}CHBr$ to the intermediate followed by another reductive elimination and phosphine coordination gives product **5**. The reductive coupling step is evidenced by the observation of the phosphonium salt $(PPh_3C_6H_4O\text{-}p\text{-}CH_3)^+X^-$.

**Catalytic Synthesis of (*trans*-RCH═CR′PPh$_3$)$^+$Br$^-$.** In the reaction of $Pd(PPh_3)_4$ with excess $\beta$-bromostyrene at 45 °C in THF, prolonged heating resulted in the production of the phosphonium salt *trans*-$PhCH{=}CH(PPh_{3)})^+Br^-$, albeit slowly, in addition to complex **1**. If the reaction temperature was raised to 80 °C (THF was replaced by toluene), the production of phosphonium salt became catalytic (see Table 3). During the course of the catalytic reaction, complex **1** was found to be a major palladium species in addition to the oxidative-addition product $Pd(PPh_3)_2(CH{=}CHPh)Br$[20] and other unidentified species.

Under similar reaction conditions, $Pd(PPh_3)_4$ or $Pd(OAc)_2$ catalyzes the formation of $(trans\text{-}RCH{=}CR'PPh_3)^+Br^-$ from $RCH{=}CR'Br$ and $PPh_3$. Results and detailed reaction conditions are presented in Table 3. Mixtures of trans and cis isomers of $PhCH{=}CHBr$ and $CH_3CH{=}CHBr$ and cis isomers of $EtOOCCH{=}CHBr$ and $MeOOCCH{=}CHBr$ were used for the catalytic reactions. However, only the corresponding *trans*-alkenylphosphonium salts were produced, indicating that facile cis to trans rearrangement for the alkenyl group occurred during these reactions. For all these phosphonium salts, coupling constants of ∼17 Hz between the two olefinic protons characteristic of trans geometry were observed. Under similar reaction conditions, the trisubstituted bromoalkene $CH_3CH{=}CCH_3Br$ also reacts with $PPh_3$ to yield the phosphonium product $CH_3CH{=}C(CH_3)(PPh_3)^+Br^-$. The determination of correct geometry of this product is less obvious, due to the absence of the characteristic coupling constant for trans olefinic protons. By comparison of the coupling constants of the phosphorus and a $\beta$-olefin proton in an alkenylphosphonium product, we discovered that the coupling constant for a proton trans to the phosphorus is ∼48 Hz more than twice as large as the value of *ca.* 23 Hz for a cis $\beta$-proton.[21] Consequently, the observed coupling constant $^3J_{PH}$ = 23.4 Hz for $CH_3CH{=}C(CH_3)(PPh_3)^+Br^-$ strongly suggests a trans geometry for this phosphonium salt.



$^3J_{PH}$ ∼ 23 Hz $^3J_{PH}$ ∼ 48 Hz

It should be noted that catalytic synthesis of tetraarylphosphonium halides from triphenylphosphine and aryl halides in the presence of palladium complexes are known previously.[22] However, no report about the catalytic preparation of akenylphosphonium halides appeared in the literature.[21] Alkenylphosphonium halides, particularly $CH_2{=}CHPPh_3X$, are useful in organic

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(19) (a) Verkade, J. G.; Quin, L. D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; VCH: Deerfield Beach, FL, 1987. (b) Gorenstein, D. G. *Phosphorus-31 NMR: Principles and Applications*; Academic Press: Orlando, FL, 1984.

(20) $^1H$ NMR monitoring of the reaction solution indicated the presence of characteristic signals at $\delta$ 3.62 (m) and 4.27 (m) for the two olefin protons of complex **1** and at $\delta$ 5.43 (d, $^3J$ = 16 Hz) for the $\beta$-proton of the oxidative-addition product $Pd(PPh_3)_2(CH{=}CHPh)Br$ identified by comparison with an authentic sample. The other signals for the latter were buried in the aromatic region. The ratio of **1** to $Pd(PPh_3)_2(CH{=}CHPh)Br$ changed with reaction time with the former increased in relative concentration as the reaction proceeded.

(21) Seyferth, D.; Fogel, J. *J. Organomet. Chem.* **1966**, *6*, 205.

(22) Migita, T.; Nagai, T.; Kiughi, K.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2869.

synthesis;[21] the present catalysis is a general and convenient method for the preparation of these salts.

In conclusion, we have shown that $\eta^2$-phosphonioalkene−palladium(0) complexes were readily produced from oxidative addition of haloalkenes to palladium(0)−phosphine complexes, from the interaction of haloalkenes with palladium(II) species, and from direct reactions of alkenylphosphonium halides with palladium(0) species. In the catalytic synthesis of alkenylphosphonium halides from alkenyl halides and triphenylphosphine, $\eta^2$-phosphonioalkene−palladium(0) complexes and the corresponding oxidative-addition products appear to be the main intermediates in solutions. In view of the large number of palladium−phosphine-mediated coupling reactions involving haloalkenes, it is important to see the effect of the formation of $\eta^2$-phosphonioalkene-palladium(0) complexes on the catalytic activity of these reactions. Investigations in this direction are underway.

## Experimental Section

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

1-Bromopropene and α-bromostyrene (Aldrich), 2-bromo-2-butene (mixture of isomers), *cis*-2-ethoxybromoethylene, 2-bromopropene, and triphenylphosphine (Janssen), and $\beta$-bromostyrene (mixture of isomers) (TCI) were used as purchased. $Pd(PPh_3)_4$,[23] $Pd(dba)_2$,[24] and $PdI(p\text{-}CH_3OC_6H_4)(PPh_3)_2$ were prepared according to reported methods.[25]

**Synthesis of $[(trans\text{-}PhCH{=}CHPPh_3)Pd(PPh_3)_2]^+Br^-$ (1) from $Pd(PPh_3)_4$ and PhCH═CHBr.** To a round-bottom flask containing $Pd(PPh_3)_4$ (0.55 g, 0.48 mmol) and $\beta$-bromostyrene (mixture of trans and cis isomers, 0.13 g, 0.71 mmol) under nitrogen was added THF (5 mL) via a syringe. The system was further purged by nitrogen gas three times and was heated at 43 °C for 18 h. The precipitate was filtered and was washed by ether to afford an air-sensitive pale yellow product (0.45 g) in 88% yield. Crystals suitable for X-ray analysis were grown from an acetonitrile/ether mixture. Selected spectral data and microanalysis data for this complex are as follows. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.62 (m, 1 H), 4.27 (m, 1 H), 6.4 (m, 5 H), 6.86−7.65 (m, 45 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 33.72 (m, $^1J_{CP} = 78.0$ Hz, $^2J_{CP} = 33.1$ Hz, $^2J_{CP} = 2.7$ Hz), 69.99 (q, $^2J_{CP} = 34.8$ Hz, $^2J_{CP} = 6.6$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ 22.24 (dd, $^3J_{PP} = 5.5$ Hz, $^3J_{PP} = 1.7$ Hz), 26.25 (dd, $^3J_{PP} = 15.2$ Hz, $^3J_{PP} = 1.7$ Hz), 27.33 (dd, $^3J_{PP} = 15.2$ Hz, $^3J_{PP} = 5.5$ Hz). IR (KBr): 1618, 1586, 1478, 1427 cm$^{-1}$. MS (FAB): *m/e* 996 ($M^+ - Br + 1$), 365. Anal. Calcd for $C_{62}H_{52}BrP_3Pd$: C, 69.18; H, 4.87. Found: C, 68.47; H, 4.98.

The complexes $\{Pd[trans\text{-}PhCH{=}CHP(p\text{-}tolyl)_3][P(p\text{-}tolyl)_3]_2\}^+Br^-$ (**2**) and $[Pd(CH_3CH{=}CHPPh_3)(PPh_3)_2]^+Br^-$ (**3**) were prepared in a manner similar to the above procedure. Both **2** and **3** are thermally unstable and decompose even in the solid state. Complete characterization of these species is difficult. Important spectral data for **2** are as follows: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.35 (m, 9 H), 3.69 (m, 1 H), 3.96 (m, 1 H), 6.29 (m, 5 H), 6.05−7.17 (m, 36 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 21.22 (m), 34.54 (m, $^1J_{CP} = 78.0$ Hz, $^2J_{CP} = 33.2$ Hz, $^2J_{CP} = 6.7$ Hz), 69.83 (q, $^2J_{CP} = 29.0$ Hz, $^2J_{CP} = 2.9$ Hz). IR (KBr): 1596, 1495, 1449, 1397 cm$^{-1}$. MS (FAB): *m/e* 1121 ($M^+$), 817, 407.

Important spectral data for $[Pd(CH_3CH{=}CHPPh_3)(PPh_3)_2]^+Br^-$ (**3**) are as follows. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.37 (q, $^1J_{HP} = 7.1$ Hz, $^4J_{HP} = 5.9$ Hz, 3 H), 2.55 (m, 1 H), 3.62 (m, 1 H), 7.03−7.3 (m, 45 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 21.48 (dt, $^3J_{CP} = 13.5$ Hz, $^3J_{CP} = 4.5$ Hz), 39.62 (m, $^1J_{CP} = 76.7$ Hz, $^2J_{CP} = 31.4$ Hz, $^2J_{CP} = 6.7$ Hz), 68.82 (d, $^2J_{CP} = 28.0$ Hz). IR (KBr): 1637, 1588, 1481, 1435 cm$^{-1}$. MS (FAB): *m/e* 933 ($M^+$), 630, 303.

**Synthesis of $(trans\text{-}PhCH{=}CHPPh_3)Pd(PPh_3)(X)$ (5).** A round-bottom flask containing $Pd(PPh_3)_2(p\text{-}CH_3OC_6H_4)I$ (0.432 g, 0.50 mmol) and $\beta$-bromostyrene (0.182 g, 1.00 mmol) was purged by nitrogen gas three times. THF (5 mL) was then syringed into the flask, and the solution was stirred at room temperature for 105 h. During the reaction period, the color of the solution changed gradually from pale yellow to orange red and a precipitate was formed. The precipitate was filtered off, and the filtrate was concentrated. Addition of hexane led to the formation of orange precipitate, which was collected on a glass filter and was washed with ether (20 mL). Recrystallization from a mixture of dichloromethane and hexane gave deep orange-red and yellow crystals. A yellow crystal was selected for X-ray analysis. The yield of the yellow crystals $[(E)\text{-}PhCH{=}CHPPh_3{}^+]Pd(PPh_3)(X)$ (0.095 g), where X is a mixture of Br and I, is 24% assuming that X = I.

**Synthesis of $Pd(trans\text{-}PhCH{=}CHPPh_3)(PPh_3)Br$ (5) from $Pd(dba)_2$ and $trans\text{-}PhCH{=}CHPPh_3{}^+Br^-$.** To a round-bottom flask containing $Pd(dba)_2$ (0.287 g, 0.50 mmol), triphenylphosphine (0.131 g, 0.50 mmol), and $trans\text{-}PhCH{=}CHPPh_3{}^+Br^-$ (0.50 mmol) under nitrogen was added $CH_2Cl_2$ (5 mL). The solution was then stirred at room temperature for 3 h. During the reaction period, the color of the solution changed gradually from red-brown to deep yellow and a small amount of black precipitate was also produced. 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 in 81% yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.24 (ddd, $J = 19.0$ Hz, $J = 10.3$ Hz, $J = 4.4$ Hz, 1 H), 3.53 (ddd, $J = 12.6$ Hz, $J = 10.3$ Hz, $J = 7.6$ Hz, 1 H), 5.31 (s, 2 H), 6.57 (d, $J = 7.6$ Hz, 2 H), 6.88 (t, $J = 7.4$ Hz, 2 H), 6.96 (t, $J = 7.2$ Hz, 1 H), 7.00 (dd, $J = 10.0$ Hz, $J = 7.6$ Hz, 6 H), 7.12 (t, $J = 6.8$ Hz, 6 H), 7.21 (t, $J = 6.8$ Hz, 3 H), 7.46 (td, $J = 7.8$ Hz, $J = 2.9$ Hz, 6 H), 7.59 (td, $J = 7.4$ Hz, $J = 1.2$ Hz, 3 H), 7.97 (dd, $J = 12.4$ Hz, $J = 8.0$ Hz, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CD_2Cl_2$): $\delta$ 27.17 (dd, $^1J_{PC} = 80.6$ Hz, $^2J_{PC} = 37.6$ Hz), 53.44 (s), 61.35 (d, $^2J_{PC} = 6.1$ Hz), 124.57 (dd, $^1J_{PC} = 88.5$ Hz, $^4J_{PC} = 3.5$ Hz), 124.85, 125.23, 128.01 (d, $^3J_{PC} = 9.2$ Hz), 128.33, 129.02, 129.26 (d, $^2J_{PC} = 12.1$ Hz), 133.43 (d, $^4J_{PC} = 2.8$ Hz), 134.20 (d, $^2J_{PC} = 14.0$ Hz), 134.49 (d, $^3J_{PC} = 9.8$ Hz), 135.89 (d, $^1J_{PC} = 29.6$ Hz), 143.88 (d, $^3J_{PC} = 12.2$ Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$): $\delta$ 21.20 (d, $^3J_{PP} = 7.0$ Hz), 21.68 (d, $^3J_{PP} = 7.0$ Hz). IR (KBr): 3039, 1586, 1480, 1434, 1181, 1099, 849, 746, 720, 691 cm$^{-1}$. MS (FAB): *m/z* 733 $[M - Br]^+$. Anal. Calcd for $PdBrP_2C_{44}H_{37}{\cdot}CH_2Cl_2$: C, 60.12; H, 4.37. Found: C, 60.34; H, 4.40. Mp: 120−122 °C dec.

**Synthesis of $trans\text{-}PhCH{=}CHPPh_3{}^+Br^-$.** A round-bottom flask containing $Pd(PPh_3)_4$ (0.0577 g, 0.050 mmol), $\beta$-bromostyrene (0.183 g, 1.00 mmol), and triphenylphosphine (0.262 g, 1.00 mmol) was purged with nitrogen gas three times. Toluene (5 mL) was then syringed into the flask, and the solution was heated to 100 °C with stirring for 15 h. The solvent was removed in vacuo, and the residue was then washed with ether (ca. 10 mL) three times to give the desired pure product (0.278 g, 63% yield). Spectral data for *trans*-

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(23) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(24) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc. D* **1970**, 1065.

(25) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

$PhCH{=}CHPPh_3^+Br^-$ are as follows. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.04 (dd, $J = 23.2$ Hz, $J = 17.1$ Hz, 1 H), 7.46−8.03 (m, 20 H), 8.58 (dd, $J = 19.9$ Hz, $J = 17.1$ Hz, 1 H). IR (neat): 3651, 1601, 1572, 1439, 1109, 996, 857, 825, 749, 690, 598 $cm^{-1}$.

Under similar reaction conditions, the alkenylphosphonium salts *trans*-$CH_3CH{=}CHPPh_3^+Br^-$, *trans*-$CH_3CH{=}CCH_3PPh_3^+$-$Br^-$, $CH_2{=}CCH_3PPh_3^+Br^-$, *trans*-$(EtOOCCH{=}CHPPh_3)^+Br^-$, and *trans*-$(MeOOC)CH{=}CHPPh_3^+Br^-$ were also prepared from the reactions of triphenylphosphine with $CH_3CH{=}CHBr$, $CH_3$-$CH{=}CCH_3Br$ (mixtures of isomers), $CH_2{=}CCH_3Br$, *cis*-(EtOOC)-CH=CHBr, and *cis*-(MeOOC)CH=CHBr, respectively, in 74−91% yields and $[PhCH{=}CHP(p\text{-tolyl})_3]^+Br^-$ was prepared from tri-*p*-tolylphosphine with PhCH=CHBr in 85% yield in the presence of $Pd(PPh_3)_4$ or $Pd(OAc)_2$. These products were characterized by comparing the observed spectral data with those reported in the literature.[9,21] The vinylphosphonium salt $(CH_2{=}CHPPh_3)^+Br^-$ was obtained in 78% yield from triphenylphosphine and vinyl bromide at 110 °C in the presence of 5% $Pd(PPh_3)_4$.[21]

**X-ray Structure Determination of [(*trans*-PhCH=CHPPh$_3$)Pd(PPh$_3$)$_2$]$^+$Br$^-$ (1).** A pale yellow crystal of dimensions 0.54 × 0.10 × 0.14 $mm^3$ was selected for X-ray diffraction. Data were collected on a Siemens R3m/V diffractometer equipped with a graphite-monochromated Mo source (K$\alpha$ radiation, 0.7107 Å). Cell parameters as listed in Table 4 were determined from the fit of 11 reflections ($9.73 \leq 2\theta \leq 22.50°$). The other parameters of this data collection are presented in Table 4. No significant variation in intensities of 3 standards monitored every 50 reflections occurred. A total of 5269 reflections were collected, but only 3287 unique reflections with $I \geq 3\sigma(I)$ were used for structure solution and refinement. These data were corrected for absorption, Lorentz, and polarization effects. The structure was solved using the Patterson-superposition technique and refined by a full-matrix least-squares method based on $F$ values. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms included in the refinement were calculated with C−H = 0.96 Å and C−H−C = 109.4° and fixed at a $U$ value of 0.08 Å.[2] The final residuals for variables and independent reflections with $I \geq 3\sigma(I)$ were $R = 0.0473$ and $R_w = 0.0513$. The final difference Fourier map had no peak greater than 1.54 e Å$^{-3}$. The final positional parameters were determined with final refinements of the structure with Rogers' $\eta$ value.[26] Scattering factors were taken from ref 27. All calculations were performed on a Micro VAX II computer system using SHELXTL-Plus programs.

**Table 4. Crystal Data and Structure Refinement Parameters for [(PhCH=CHPPh$_3$)Pd(PPh$_3$)$_2$]$^+$Br$^-$ (1) and Pd(PhCH=CHPPh$_3$)(PPh$_3$)(X) (5)**

| | | |
|---|---|---|
| chem formula | $C_{62}H_{52}BrP_3Pd$ (**1**) | $C_{46}H_{41}I_{0.769}Br_{0.231}OP_2Pd$ (**5**) |
| fw | 1076.3 | 901.0 |
| space group | *Cc*; monoclinic | *C*2/*c*; monoclinic |
| *a*, Å | 12.772(3) | 21.333(4) |
| *b*, Å | 23.103(6) | 17.342(4) |
| *c*, Å | 18.231(4) | 23.738(4) |
| $\beta$, deg | 104.07(2) | 111.95(2) |
| *V*, Å$^3$ | 5198(2) | 8145(3) |
| Z | 4 | 8 |
| $\rho$(calc), Mg m$^{-3}$ | 1.375 | 1.469 |
| $\mu$, mm$^{-1}$ | 1.257 | 1.325 |
| *T*, K | 297 | 296 |
| *R* | 0.0437 | 0.0594 |
| $R_w$ | 0.0513 | 0.0563 |

**X-ray Structure Determination of (*trans*-PhCH=CHPPh$_3$)Pd(PPh$_3$)Br (5).** A pale yellow crystal of dimensions 0.42 × 0.34 × 0.16 $mm^3$ was selected for X-ray diffraction. Procedures similar to those for complex **1** were employed for data collection and structural refinement of **5**. Important crystallographic data are presented in Table 4.

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**Supporting Information Available:** Tables of atomic positional parameters, all bond distances and angles, thermal parameters, hydrogen positions and crystal data and structure refinement details for **1** and **5** (15 pages). Ordering information is given on any current masthead page.

OM970709N

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(26) Roger, D. *Acta Crystallogr.* **1981**, *A37*, 734.

(27) Atomic scattering factors were obtained from the following: *International Tables for X-Ray Crystallography;* Kynoch Press: Birmingham, U.K., 1974; Vol. IV.