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General Route to Halide-Bridged Organopalladium A-Frame Complexes and Studies of Reductive Elimination from These Bimetallic Systems

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Reactions of [Pd$_2$Cl$_2$(μ-dppm)$_2$] with RMgX (R = Me, Et, Bu, Ph, C$_6$H$_4$Me-4) at low temperature, followed by addition of CBr$_4$ and excess NH$_4$PF$_6$ or 1 equiv of TlPF$_6$, provided halide-bridged organopalladium A-frame complexes of the form [Pd$_2$R$_2$(μ-X)(μ-dppm)$_2$]PF$_6$. Mixed metal complexes were obtained similarly starting from [PdPtCl$_2$(μ-dppm)$_2$]. Unsymmetrical A-frames of the type [Pd$_2$(C$_6$H$_2$Me$_3$-2,4,6)R(μ-Cl)(μ-dppm)$_2$]$^+$ were generated by reaction of [Pd(C$_6$H$_2$Me$_3$-2,4,6)(dppm)$_2$]$^+$ (obtained by treatment of [PdCl$_2$(cod)] with mesitylmagnesium bromide at low temperature, followed by 2 equiv of dppm) with [Pd$_2$R$_2$(μ-Cl)$_2$(AsPh$_3$)$_2$]. The organopalladium A-frames did not react readily with CO, but the corresponding acyl derivatives [Pd$_2$(COR)$_2$(μ-Cl)(μ-dppm)$_2$]PF$_6$ were produced by carbonylation of [Pd$_2$R$_2$(μ-Cl)$_2$(AsPh$_3$)$_2$] followed by addition of dppm (R = Me, Et, Bn). Thermal decomposition of [Pd$_2$(CH$_2$Ph)$_2$(μ-Cl)(μ-dppm)$_2$]Cl was found to be first order in A-frame and resulted in quantitative formation of [Pd$_2$Cl$_2$(μ-dppm)$_2$] and 1,2-diphenylethane. The methyl and aryl complexes underwent both reductive elimination and hydrogen abstraction reactions. [Pd$_2$Et$_2$(μ-Br)(μ-dppm)$_2$]PF$_6$ decomposed by β-hydride elimination and subsequent reductive elimination to yield ethene and ethane, whereas the butyl derivative gave both 1- and 2-butene. Acetic acid was formed when [Pd$_2$(COMe)$_2$(μ-Cl)(μ-dppm)$_2$]PF$_6$ was heated in dmso-d_6 solution, but decarbonylation was the predominant process in dioxane. The molecular structures of [Pd$_2$(CH$_2$Ph)$_2$(μ-Br)(μ-dppm)$_2$]PF$_6$·H$_2$O,2C$_6$H$_6$ and [Pd$_2$Cl$_2$(μ-Cl)(μ-dppm)$_2$]OH·0.5(CH$_3$)$_2$CO are also described.

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Introduction

The term A-frame was coined by Kubiak and Eisenberg in 1977 when they prepared [Rh$_2$(μ-S)(CO)$_2$(μ-dppm)$_2$] by reaction of [Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$] with Na$_2$S.[1] Since then, many A-frame complexes bridged by dppm or related ligands, particularly of the group 9 and 10 metals, have been prepared and by a number of different methods. These methods include insertion of a small molecule, such as CO, SO$_2$, or CNR, into the metal−metal bond of a side-by-side dimer,[2−4] oxidative addition to a low-valent dimer,[5] or dimerization of a monomeric precursor.[6,7] Group 10 A-frames containing terminal organic groups, in particular, have been generated by treating [Pt$_2$Cl$_2$(μ-dppm)$_2$] with Hg(C≡CAr)$_2$,[8] by insertion of unsaturated molecules into the Pd−Pd bond of [Pd$_2$X(C$_6$Y$_5$)(μ-dppm)$_2$] (Y = F, Cl),[9] by addition of MeI to [Pd$_2$(μ-dppm)$_3$],[5] or by dimerization of [PtClR(dppm)].[6,7] Organorhodium A-frames have been prepared by reactions of [Rh$_2$Cl$_2$(CO)$_2$(μ-dmpm)$_2$] with PhMgCl[10] or of [Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$] with BnMgCl,[11] and we have shown that reactions of [PdX$_2$(dppm)] with alkyl Grignard reagents yield complexes of the form [Pd$_2$R$_2$(μ-X)(μ-dppm)$_2$]$^+$.[12] An acylrhodium A-frame has been prepared by reaction of [Rh$_2$(CO)$_3$(μ-dppm)$_2$] with MeOSO$_2$CF$_3$, but it undergoes decarbonylation at 70 °C to give [Rh$_2$Me(μ-CO)(CO)(μ-dppm)$_2$]$^+$.[13]

In this paper we describe a general synthetic route to organopalladium halide-bridged A-frame complexes, [Pd$_2$R$_2$(μ-X)(μ-dppm)$_2$]PF$_6$, starting from the readily available palladium(I) dimer, [Pd$_2$Cl$_2$(μ-dppm)$_2$].[14] The

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decomposition reactions of these complexes, as well as the analogous acylpalladium derivatives, are also described.

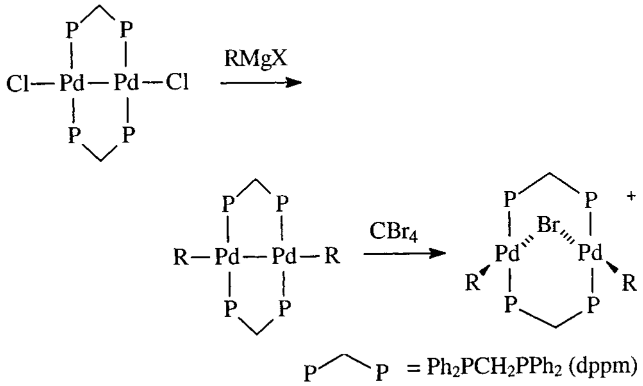
Results and Discussion

Synthesis of Halide-Bridged A-Frame Complexes. We have reported previously that halide-bridged organopalladium A-frame complexes may be prepared by reaction of [PdClR(cod)] (R = Me, Bn) or [$Pd_2R_2(\mu\text{-}Cl)_2(AsPh_3)_2$] (R = Me, Et, Bn, Ph) with dppm[15] or by treatment of [PdX_2(dppm)] with RMgX (R = Me, Et, Bu, Bn),[16] but neither of these approaches is suitable in all cases. The cyclooctadiene precursors are readily available only for the methyl and benzyl cases,[17,18] and the reactions of [PdX_2(dppm)] with aryl Grignard reagents result in reductive elimination of the diaryl from [PdR_2(dppm)] formed in the course of the reaction. With bulky organic groups (R = CH_2SiMe_3, $C_6H_2Me_3$-2,4,6) the diorganopalladium complexes are again formed, but they are resistant to reductive elimination and may be isolated in pure form.[16] In contrast to the above examples, we have found that treatment of the dppm-bridged palladium(I) dimer with a Grignard reagent in CH_2Cl_2 solution at low temperature, followed by addition of CBr_4 and $TlPF_6$, allows complexes of the type [$Pd_2R_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$PF_6$ to be prepared for a wide variety of R groups.

We noticed that when [PdX_2(dppm)] (X = Cl, Br) was treated with 1 equiv of ArMgX, reductive elimination of diaryl occurred and the palladium(I) complex [$Pd_2X_2(\mu\text{-}dppm)_2$] was formed. When excess Grignard reagent was used, however, a species consistent with the formulation [$Pd_2Ar_2(\mu\text{-}dppm)_2$] was generated,[16] and we surmised that addition to the Pd−Pd bond to produce an A-frame complex might take place with suitable substrates, such as a halogen source or H^+. Thus, when a solution of [$Pd_2Cl_2(\mu\text{-}dppm)_2$] ($\delta(P)$ −2.5) in CH_2Cl_2 solution at −78 °C was treated with MeMgBr, the original resonance was replaced by one at 19.1 ppm, which we assign to [$Pd_2Me_2(\mu\text{-}dppm)_2$].[19] When the solution was allowed to warm to ambient temperature, the complex decomposed rapidly. If it was maintained at −78 °C, however, it was stable for several hours. Addition of 1 equiv of Br_2 resulted in a 1:4 ratio of [$Pd_2Me_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$^+$ and [$PdBr_2$(dppm)] (−52.4 ppm). When excess Br_2 was employed, [$PdBr_2$(dppm)] was the sole product. With 1 equiv of *N*-bromosuccinimide a 1:1 mixture of the two products was formed, and [$PdBr_2$(dppm)] was again the only product when excess NBS was added.

Use of CBr_4 proved more successful. Addition of 3−4 equiv of CBr_4 to a solution of [$Pd_2Me_2(\mu\text{-}dppm)_2$] resulted in formation of the A-frame complex [$Pd_2Me_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$^+$ as the sole palladium-containing product (Scheme 1). When CCl_4 was used, a mixture of chloride- and bromide-bridged A-frames was formed because the methyl groups were introduced using MeMgBr. The mechanism of halogenation of the metal−metal bond is unclear, but the reaction with CBr_4 produces [$Pd_2Me_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]Br quantitatively. This method is tolerant of a variety of alkyl and aryl groups, including methyl, ethyl, *n*-butyl, benzyl, phenyl, and 4-tolyl. The exceptions are bulky groups, such as CH_2SiMe_3 and mesityl, where only one organic group is incorporated, giving unsymmetrical complexes of the form [$Pd_2BrR(\mu\text{-}dppm)_2$] and [$Pd_2BrR(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$^+$. Although the A-frame complexes are quite stable as their bromide salts, they are not isolated easily, but metathesis with excess NH_4PF_6 or 1 equiv of $TlPF_6$ allows their isolation as the hexafluorophosphate salts, [$Pd_2R_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$PF_6$.

Scheme 1



This method may be extended to heterobimetallic A-frames of the form [$PdPtAr_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$PF_6$. Treatment of a CH_2Cl_2 solution of [$PdPtCl_2(\mu\text{-}dppm)_2$][20] with PhMgBr or 4-$MeC_6H_4MgBr$ at −78 °C, followed by addition of CBr_4 and 1 equiv of $TlPF_6$, generated [$PdPtAr_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$PF_6$ in high yield. This approach to mixed metal A-frames appears to be limited to aryl substituents, however. When [$PdPtCl_2(\mu\text{-}dppm)_2$] was treated with MeMgBr at −78 °C, followed by CBr_4 and $TlPF_6$, analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed the presence of a number of products that included [$PdPtMe_2(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$^+$, [$PdPtMe_2(\mu\text{-}dppm)_2$], and the unsymmetrically substituted [$PdPtMeBr(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$^+$. A similar mixture of products was obtained if the reaction was performed at ambient temperature. The observation of the side-by-side dimer [$PdPtMe_2(\mu\text{-}dppm)_2$], even at 25 °C, suggests that the Pd−Pt bond is less reactive toward CBr_4. The lower reactivity of the Pt−Cl bond, compared with the Pd−Cl bond, may be responsible for the detection of the unsymmetrical species [$PdPtMeBr(\mu\text{-}Br)(\mu\text{-}dppm)_2$]$^+$.

We have shown that unsymmetrically substituted diplatinum complexes of the type [$Pt_2RR'(\mu\text{-}Cl)(\mu\text{-}dppm)_2$]$PF_6$ (R, R′ = Me, Et, Ph) can be obtained by treatment of [PtClR(cod)] with 2 equiv of dppm to produce [PtR(dppm-*PP*)(dppm-*P*)]$^+$, followed by addition of [PtClR′(cod)].[21] Such an approach to unsymmetrical A-frames is generally unavailable for palladium. We had noted, however, that with sterically demanding organic groups

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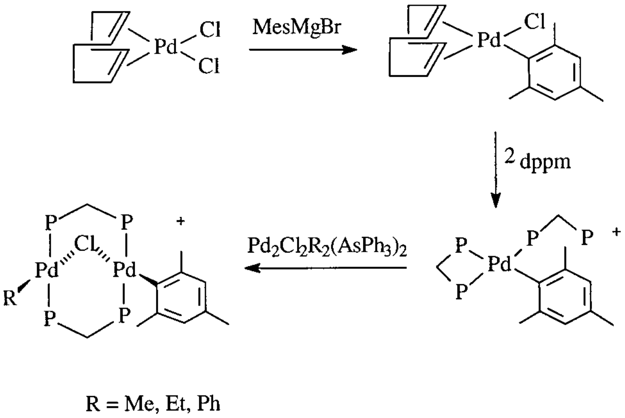
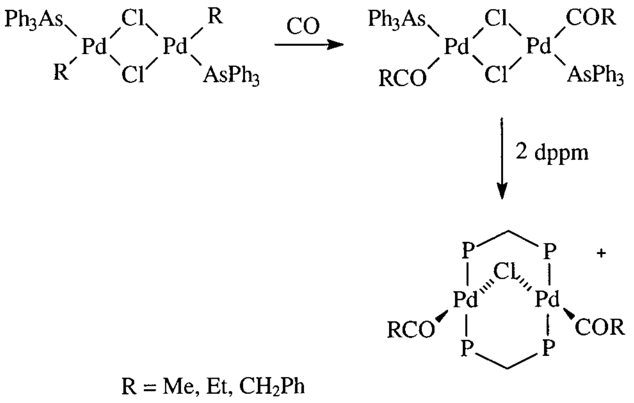
Scheme 2



Scheme 3



the reaction of $[PdCl_2(dppm)]$ with RMgX generated $[PdR_2(dppm)]$, and further treatment with HCl gave the A-frames $[Pd_2R_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$. This presumably proceeds via [PdClR(dppm)], and we thought it might be possible to isolate such species at low temperature. Reaction of $[PdR_2(dppm)]$ (R = CH_2SiMe_3, mesityl) with 1 equiv of HCl at −78 °C, however, gave an intractable mixture of products. We have found, though, that treatment of $[PdCl_2(cod)]$ with 1.5 equiv of mesitylmagnesium bromide in CH_2Cl_2 solution at low temperature gives $[PdCl(C_6H_2Me_3\text{-}2,4,6)(cod)]$ quite cleanly. Addition of 2 equiv of dppm results in formation of the cationic complex $[Pd(C_6H_2Me_3\text{-}2,4,6)(dppm\text{-}PP)(dppm\text{-}P)]^+$. At low temperature, the $^{31}P\{^1H\}$ NMR spectrum of this species exhibits four resonances. The uncoordinated P atom resonates at −28.7 ppm and appears as a broad doublet ($^2J_{PP}$ = 67 Hz). The signal due to the coordinated P atom of the monodentate ligand is observed at 11.9 ppm and shows coupling to all of the other P atoms (ddd, $^2J_{PP}$ = 391, 67, and 29 Hz). The two P atoms of the chelated dppm ligand give rise to resonances at −34.9 and −35.9, each being observed as a doublet of doublets. The coupling between these two P atoms is 45 Hz. Warming the solution to ambient temperature results in formation of $[Pd_2(C_6H_2Me_3\text{-}2,4,6)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]^+$ and free dppm. If the solution is kept at −78 °C, however, and treated with 0.5 equiv of $[Pd_2R_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (R = Me, Et, Ph), subsequent warming to ambient temperature affords the unsymmetrical A-frame $[Pd_2(C_6H_2Me_3\text{-}2,4,6)R(\mu\text{-}X)(\mu\text{-}dppm)_2]^+$ as a mixture of chloride- and bromide-bridged species (about 5% of the symmetrical A-frames were formed also) (Scheme 2). We would later convert these to hydride-bridged derivatives,[22] so it was unnecessary to attempt to separate the chloride- and bromide-containing materials.

Balch has reported that $[Pd_2Me_2(\mu\text{-}X)(\mu\text{-}dppm)_2]X$ reacts with carbon monoxide to produce the corresponding acetylpalladium dimers, but only at elevated CO pressures. The rate of CO insertion was found to depend on the nature of the halide (I > Br > Cl).[23] We found that no reaction occurred when CO was bubbled through solutions of $[Pd_2R_2(\mu\text{-}X)(\mu\text{-}dppm)_2]PF_6$ (R = Me, Ph, C_6H_4Me-4) for extended periods. Addition of free chloride, in the form of $(Ph_3P)_2N^+Cl^-$ or Et_4NCl, had no effect. Since acylpalladium derivatives were not readily available by this method, we sought an alternative approach.

Previously we found that treatment of [PdClMe(cod)] with CO (1 atm) resulted in carbonylation to give [PdCl(COMe)(cod)].[24] Since [PdClMe(cod)] reacts with dppm to produce an A-frame complex, it seemed likely that [PdCl(COMe)(cod)] would be a suitable precursor to $[Pd_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$. Indeed, treatment of [PdClMe(cod)] with CO, followed by 1 equiv of dppm, generated the acetylpalladium A-frame, which was isolated as its PF_6^- salt. Since $[PdCl(CH_2Ph)(cod)]$ is the only other compound of this type that is readily available, we chose to investigate the reactions of $[Pd_2R_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (R = Me, Et, CH_2Ph, Ph) with carbon monoxide (since reactions of $[Pd_2R_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ with dppm also produce A-frames). When CO was bubbled through a CH_2Cl_2 solution of $[Pd_2Me_2(\mu\text{-}Cl)_2(AsPh_3)_2]$, there was no observable color change, but carbonylation did occur. Further treatment with 2 equiv of dppm and 1 equiv of $TlPF_6$ allowed isolation of the A-frame complex $[Pd_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$ in high yield. The corresponding reactions where R = Et or CH_2Ph proceeded similarly (Scheme 3).

Treatment of $[Pd_2Ph_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ with CO and dppm, however, resulted in two species. One of these appeared to be consistent with $[Pd_2(COPh)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$, whereas the other was an unsymmetrical species that seemed to have one benzoyl and one phenyl substituent. These two compounds could not be separated. They were formed in an approximately 1:1 ratio regardless of the length of time for which CO was passed through the solution (5 min, 20 min, or 5 h). There was also no change in the ratio of the two species after standing at ambient temperature for 12 h, i.e., loss of CO did not occur spontaneously. When $[Pd_2Ph_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ was allowed to react with ^{13}CO, two peaks were observed in the $^{13}C\{^1H\}$ NMR spectrum at 213.6 and 214.5 ppm. These chemical shifts are consistent with benzoyl rather than terminal carbonyl groups. These could be due to the cis and trans forms of $[Pd_2(COPh)_2(\mu\text{-}Cl)_2(AsPh_3)_2]$, or perhaps to one isomer of $[Pd_2(COPh)_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (or to both if the cis and trans forms are indistinguishable by ^{13}C NMR spectroscopy) and the partially carbonylated $[Pd_2Ph(COPh)(\mu\text{-}Cl)_2(AsPh_3)_2]$. Addition of dppm caused the ^{13}C reso-

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nances to shift to higher frequency, but two resonances were still observed (217.8 and 218.7 ppm). Both signals were broad, but with Gaussian enhancement the high-frequency resonance could be resolved into a triplet ($^2J_{PC}$ = 4 Hz), consistent with a C atom lying cis to two equivalent P atoms.

If the reaction of $[Pd_2Ph_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ with CO was simply slow, then longer reaction times should result in greater conversion to $[Pd_2(COPh)_2(\mu\text{-}Cl)_2(AsPh_3)_2]$, and hence $[Pd_2(COPh)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$, but the ratio of products did not appear to change with reaction time. If an equilibrium exists between $[Pd_2(COPh)_2(\mu\text{-}Cl)_2(AsPh_3)_2]$, $[Pd_2(COPh)Ph(\mu\text{-}Cl)_2(AsPh_3)_2]$, and free CO, such that the ratio of palladium complexes is approximately 1:1, then dppm addition would generate the symmetrical and unsymmetrical A-frames in the same ratio. Since the reaction with dppm is rapid, this would be consistent with the same ratio of products being formed, irrespective of the carbonylation time.

The halide-bridged A-frame complexes have been characterized by elemental analysis, by ^1H and ^{31}P NMR spectroscopy, and, in the case of $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$, by X-ray crystallography. The symmetrical dipalladium species give rise to a single ^{31}P resonance, whereas the unsymmetrical derivatives $[Pd_2(C_6H_2Me_3\text{-}2,4,6)R(\mu\text{-}X)(\mu\text{-}dppm)_2]^+$ and $[PdPtR_2(\mu\text{-}X)(\mu\text{-}dppm)_2]^+$ exhibit the expected two signals in each case. Their ^1H NMR spectra contain the expected resonances for the organic substituents on the metals. The methylene hydrogens of the dppm ligands are nonequivalent, consistent with a rigid A-frame structure in which one hydrogen is disposed toward the bridging halide and the other is directed toward the opposite face of the dimeric unit. In the presence of free halide ion these two signals coalesce into one broad resonance, indicative of a fluxional process involving halide attack on one metal center and bridge opening to generate the face-to-face species $[Pd_2R_2X_2(\mu\text{-}dppm)_2]$. In the benzyl derivative, $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]^+$, the aromatic signals associated with the benzyl group appear at unexpectedly low frequencies as a doublet at 5.17 ppm due to the *o*-hydrogens, and triplets at 6.35 and 6.65 ppm due to the *m*- and *p*-hydrogens, respectively.

Molecular Structure of $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6.H_2O,2C_6H_6$. Slow evaporation of a CH_2Cl_2/C_6H_6 solution of $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$, obtained from $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ and $PhCH_2MgBr$, dppm, and NH_4PF_6, produced orange cuboids. The compound crystallizes in the monoclinic space group *Pm*. In addition to two cations and two PF_6^- anions, the unit cell contains two water molecules and four molecules of benzene. The molecular structure of the cation is shown in Figure 1, and selected bond distances and angles are given in Table 1.

The cation contains two PdP_2CBr square planes inclined toward each other at an angle of 82.42(2)°. The Pd−Pd distance is 3.356 Å, indicating the lack of any metal−metal bonding. The Pd−P distances are normal, and the P−Pd−P angles are 172.35(5)°. The $Pd_2(\mu\text{-}dppm)_2$ unit forms an elongated boat, with the CH_2 groups lying on the same side as the bridging bromide. The molecule exhibits classic A-frame geometry, with the bromide and benzyl groups located on opposite sides of the Pd_2P_4 plane. The benzyl groups lie trans to the bromide, with C−Pd−Br angles of 165.6(2)°. The P−Pd−Pd−P torsion angles are 21.2°, demonstrating that there is significant twisting of the P−Pd−P units about the Pd···Pd axis.

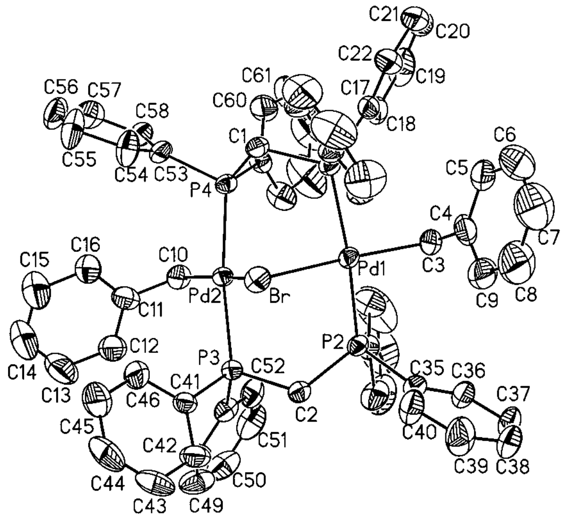

Figure 1. Projection view of the molecular structure of the $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]^+$ cation using 50% probability ellipsoids, showing the atom-labeling scheme.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]^+$ Cation

Pd(1)−Br	2.5461(7)	Pd(2)−Br	2.5480(7)
Pd(1)−P(1)	2.3344(13)	Pd(2)−P(3)	2.3342(13)
Pd(1)−P(2)	2.3180(13)	Pd(2)−P(4)	2.3179(13)
Pd(1)−C(3)	2.095(5)	Pd(2)−C(10)	2.087(5)
Pd(1)−Br−Pd(2)	82.42(2)	P(1)−Pd(1)−P(2)	172.35(5)
P(1)−Pd(1)−Br	84.44(3)	P(1)−Pd(1)−C(3)	94.7(2)
P(2)−Pd(1)−Br	93.27(4)	P(2)−Pd(1)−C(3)	89.3(2)
Br−Pd(1)−C(3)	165.6(2)	P(3)−Pd(2)−P(4)	172.36(5)
P(3)−Pd(2)−Br	84.45(4)	P(3)−Pd(2)−C(10)	94.9(2)
P(4)−Pd(2)−Br	93.28(4)	P(4)−Pd(2)−C(10)	89.1(2)
Br−Pd(2)−C(10)	165.6(2)		

One of the *o*-hydrogens of each benzyl aromatic ring points directly toward the centroid of a dppm phenyl ring. The angle about the hydrogen is 171.6°, with an H−centroid distance of 2.57 Å. This hydrogen should experience an increase in shielding due to the ring current effect. Rotation of the aromatic ring will occur in solution, averaging the environments of the *o*-hydrogens. The ^1H NMR resonance due to these hydrogens is shifted to low frequency (5.17 ppm), however, suggesting that a similar conformation is maintained in solution.[12] The *m*- and *p*-hydrogens experience a ring current also, but the resonances for those hydrogens are affected to a lesser extent (6.35 and 6.65 ppm).

Elimination Reactions. These halide-bridged A-frames represent suitable examples in which to study elimination reactions involving a dinuclear system. When a dmso-d_6 solution of $[Pd_2(CH_2Ph)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ was heated to 97 °C and monitored by ^{31}P NMR spectroscopy, the original resonance at 12.0 ppm gradually decreased in intensity and a new signal appeared at −2.8 ppm. The new signal was identified as being due to $[Pd_2Cl_2(\mu\text{-}dppm)_2]$. Changes were also noted in the ^1H NMR spectrum. The broad signals due to the CH_2 groups of the benzyl moiety (2.89 ppm) and dppm (3.90 ppm) gradually decreased, along with the aromatic signals at 5.20, 6.27, and 6.65 ppm. These were replaced

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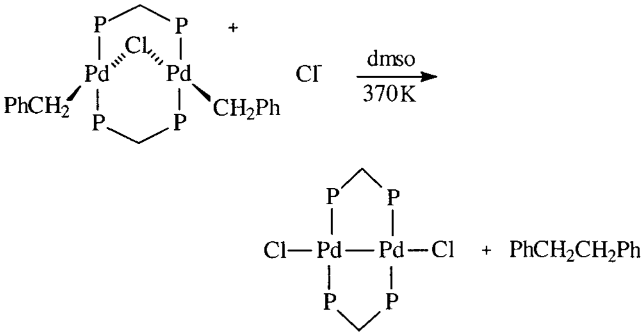
Scheme 4



by a sharp singlet at 1.89 ppm and a quintet at 4.35 ppm ($^2J_{PH}$ = 4.0 Hz). The quintet is due to the dppm CH_2 groups in $[Pd_2Cl_2(\mu\text{-dppm})_2]$, whereas the singlet is assigned to the CH_2 groups of 1,2-diphenylethane (Scheme 4). Subsequent analysis by GC−MS confirmed the presence of the latter. When a solution of $[Pd_2(CH_2Ph)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]PF_6$ was treated similarly, 1,2-diphenylethane was formed, but $[Pd_2Cl_2(\mu\text{-dppm})_2]$ was formed in less than 40% yield (by NMR) and extensive decomposition was observed. This is consistent with there being only one chloride for every two palladium atoms in the starting complex.

The disappearance of $[Pd_2(CH_2Ph)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ was monitored by ^1H and ^{31}P NMR spectroscopy. Plots of log[complex] vs time were found to be linear, and the rate of elimination was unchanged when the reactant concentration was varied by a factor of 4. Both observations are consistent with the elimination being first order in A-frame complex. Rate constants were determined at several temperatures (82−112 °C), and the activation parameters for the process were determined to be $\Delta G^‡ = 47 \pm 1$ kcal/mol, $\Delta H^‡ = 28 \pm 1$ kcal/mol, and $\Delta S^‡ = 50 \pm 5$ cal/mol·K. These parameters are consistent with a significant degree of bond breaking in the transition state. The nature of the transition state is difficult to establish, however, since the exact nature of the starting material is uncertain. The starting material is fluxional, consisting of an unknown ratio of $[Pd_2(CH_2Ph)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ (as its chloride salt) and the bridge-opened form $[Pd_2(CH_2Ph)_2Cl_2(\mu\text{-dppm})_2]$. Even when a $CDCl_3$ solution of $[Pd_2(CH_2Ph)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ was cooled to −60 °C, the signals remained broad. The lack of free chloride in $[Pd_2(CH_2Ph)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]PF_6$ results in spectra that are indicative of a static system in $CDCl_3$ solution, but broad signals are observed in dmso-d_6 solution, where the solvent is apparently sufficiently nucleophilic to reversibly cleave the chloride bridge.

Elimination of 1,2-diphenylethane could take place through a 1,1-elimination where both organic groups must first become bonded to the same palladium center, by means of a 1,2-elimination involving a four-centered intermediate or transition state, or by homolytic cleavage of the two Pd−C bonds. We believe the first is most likely, although a radical process certainly cannot be ruled out.[11] Transfer of one benzyl group to the adjacent metal could occur by elimination of benzyl chloride from one palladium, promoted by Cl^- attack, followed by oxidative addition to the other. Alternatively, direct transfer could take place via a transient bridging benzyl group, with or without the involvement of free Cl^- ions.

To try to distinguish between these two possibilities, we carried out the elimination from $[Pd_2(CH_2Ph)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ in the presence of $4\text{-MeC}_6H_4CH_2Cl$. The reaction was monitored by ^{31}P NMR spectroscopy, and $[Pd_2Cl_2(\mu\text{-dppm})_2]$ was the only Pd-containing product formed. Analysis of the organic products by GC−MS revealed the presence of $4\text{-MeC}_6H_4CH_2Cl$ and $PhCH_2CH_2Ph$ only; that is, no crossover product was formed. If a mechanism involving elimination and readdition of $PhCH_2Cl$ was operative, we would expect incorporation of $4\text{-MeC}_6H_4CH_2Cl$ to form $4\text{-MeC}_6H_4CH_2CH_2Ph$. Thus, if a nonradical process is involved, it appears most likely that the benzyl group is transferred intramolecularly.

When a dmso-d_6 solution of $[Pd_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ was heated to 107 °C for 2 h, a 5:1 ratio of methane and ethane was produced. When such a solution was heated rapidly to 127 °C, a 1:1 ratio was formed. $[Pd_2Cl_2(\mu\text{-dppm})_2]$ was produced in less than 50% yield (by NMR) in either case. Ethane is the expected product of reductive elimination, whereas hydrogen abstraction must take place in order to produce methane. Hydrogen abstraction could occur from an organic fragment within the complex or from dmso or adventitious water. When D_2O was deliberately added to the dmso-d_6 solution, no change in the rate of decomposition of $[Pd_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ at 127 °C was detected. The temperature dependence of the product ratio implies that hydrogen abstraction is a lower energy process, and reductive elimination competes effectively only when the reaction is performed at higher temperatures.

Similar results were obtained for the arylpalladium derivatives $[Pd_2Ar_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6$ (Ar = Ph, 4-MeC_6H_4). When a dmso-d_6 solution of $[Pd_2Ph_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6$ was heated to 127 °C for 1 h, the ^{31}P NMR signal due to the A-frame complex gradually disappeared, and GC−MS analysis confirmed the formation of benzene and diphenyl in an approximately 1:1 ratio. Toluene and 4,4′-dimethyldiphenyl were formed in a 1:1 ratio when $[Pd_2(4\text{-MeC}_6H_4)_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6$ was heated to 97 °C, but at 127 °C the latter was produced almost exclusively. In neither case was the palladium(I) dimer observed. If 1 equiv of $(Ph_3P)_2N^+Cl^-$ was added to a solution of $[Pd_2(4\text{-MeC}_6H_4)_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6$, there was no change in the ratio of organic products formed at 97 °C, but a signal due to $[Pd_2Cl_2(\mu\text{-dppm})_2]$ was observed in the ^{31}P NMR spectrum. Again, the source of hydrogen in forming benzene or toluene is uncertain. Heating a dmso-d_6 solution of $[Pd_2(4\text{-MeC}_6H_4)_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6$, to which excess D_2O had been added, to 97 °C for 1 h produced $C_6H_5CH_3$ and $(4\text{-CH}_3C_6H_4)_2$. GC−MS analysis provided no evidence for deuterium incorporation. This suggests that the hydrogen is abstracted from another aryl group or from dppm.

Elimination from the ethyl derivative $[Pd_2Et_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6$ took place more readily. When a dmso-d_6 solution was heated to 67 °C for 1 h, the ^{31}P NMR signal at 16.0 ppm gradually diminished in intensity and was replaced by several resonances in the range 20−30 ppm. The ^1H signals due to the ethyl groups also disappeared, and they were replaced by two sharp singlets at 0.80 and 4.13 ppm, in an approximately 1:1 ratio, which were assigned to ethane and ethene, respectively. Ethene is likely to be formed by β-hydride elimination, although the palladium hydride thus formed

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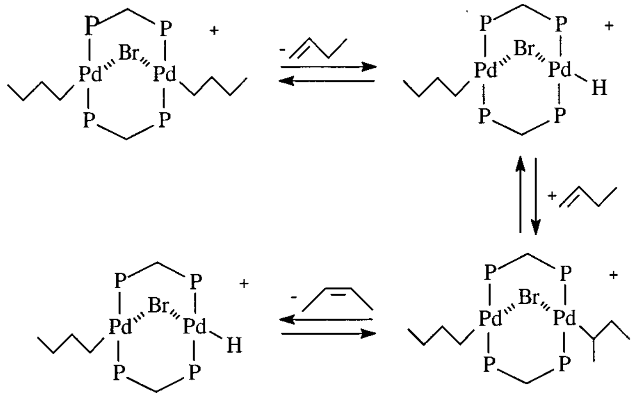
Scheme 5



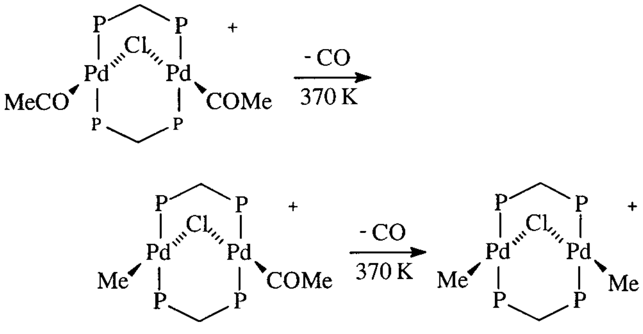
could not be detected by ^{1}H NMR spectroscopy. Ethane would result from reductive elimination of the hydride and the remaining ethyl group.

A dmso-d_6 solution of $[Pd_2Et_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$, to which excess D_2O had been added, was maintained at 67 °C and monitored for several hours by ^{1}H NMR spectroscopy. The resonance due to ethene grew rapidly, but after 30 min it began to decrease in intensity. The signal for ethane grew in more slowly, but its intensity did not diminish with time. This may be explained as follows. Ethene would be formed first by β-elimination, leaving a Pd−H species. If ethane elimination were rapid, then C_2H_6 would be formed. If not, exchange with D_2O could occur to generate a Pd−D species, from which elimination would yield C_2H_5D. Also, β-hydride elimination may well be reversible, and reinsertion of C_2H_4 into the Pd−D bond would give a $Pd-CH_2CH_2D$ fragment. A second β-elimination could produce C_2H_3D and Pd−H. Repeated H−D exchange with D_2O and insertion/β-elimination would generate a series of partially deuterated ethenes, which could account for the decrease in intensity of the signal at 4.13 ppm.

When a sample of $[Pd_2Et_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ in $CDCl_3$/acetone-d_6 solution was kept at −40 °C for a prolonged period, orange crystals deposited on the sides of the NMR tube. These were identified by X-ray crystallography as $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]OH$ (vide infra), apparently formed through a series of bond-breaking and bond-forming reactions, presumably involving the chlorinated solvent and adventitious water.

The butylpalladium A-frame, $[Pd_2Bu_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$, also undergoes β-hydride elimination. This complex is more soluble in common organic solvents, so the elimination could be monitored in toluene solution. When a toluene-d_8 solution of the complex was maintained at 67 °C, the resonances due to the butyl groups gradually diminished in intensity over 1 h. Simultaneously, signals due to 1-butene ($\delta(H)$ 0.89 (t, $^2J_{HH} = 8$ Hz), 1.92 (m), 4.92 (m), 5.75 (m)) gradually appeared. Additional multiplets at 1.45 and 5.35 ppm were also observed, and these were identified as being associated with 2-butene. While 1-butene is the expected β-elimination product, reinsertion into the resulting Pd−H bond could form either an *n*-butyl- or *sec*-butylpalladium complex, and β-elimination from the latter would generate 2-butene (Scheme 5). In contrast to the ethyl case, no alkane was observed on thermolysis of $[Pd_2Bu_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$.

Scheme 6



Reductive elimination from an acyl complex of the type $[Pd_2(COR)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ could generate α,β-diketones. Indeed, treatment of $[Rh_2Me_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ with CO (25 °C, 100 atm) gave 2,3-butanedione as the major organic product.[26] Heating a dmso-d_6 solution of $[Pd_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$ to 97 °C in the absence of free CO, however, resulted in formation of acetic acid and an unidentified palladium-containing complex ($\delta(P)$ −9.2). If dioxane was employed as solvent, acetic acid was not formed. Instead, $[Pd_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ ($\delta(P)$ 7.2) underwent decarbonylation to yield the corresponding methylpalladium derivative ($\delta(P)$ 17.6). When the reaction was monitored by ^{31}P NMR spectroscopy, the partially decarbonylated intermediate $[Pd_2Me(COMe)(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ could be detected ($\delta(P)$ 9.3 and 15.0) (Scheme 6). Similar decarbonylations have been reported by Balch.[23] Formation of acetic acid was unexpected, however. It seemed possible that trace amounts of moisture present in the dmso-d_6 could promote this reaction. When water was added deliberately to a dioxane solution of $[Pd_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$, however, heating to 97 °C produced only a small amount of acetic acid. Formation of acetic acid seemed to depend not only on the presence of water, but also on the use of dmso as the solvent.

Molecular Structure of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]OH\cdot 0.5(CH_3)_2CO$. The complex crystallizes as orange-red plates in the tetragonal space group $P4_12_12_1$. In addition to four molecules of the A-frame cation and associated hydroxide anions, the unit cell contains two acetone molecules. The molecular structure of the cation is shown in Figure 2, and selected bond distances and angles are presented in Table 2. The structure of the cation is similar to that of $[Hg_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$, formed unexpectedly in the reaction of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ with elemental mercury.[26]

The cation consists of two palladium centers linked by two dppm ligands and a chloride. The geometry about each palladium is approximately square planar, and the two planes are inclined toward each other at an angle of 87.5° through the bridging chloride. The Pd−Pd distance is 3.170 Å, too long for the existence of any significant metal−metal interaction. The unique Pd−P distances are 2.340(2) and 2.304(2) Å, and the P−Pd−P angles are 169.91(8)°. The terminal Pd−Cl distances are 2.371(2) Å, and the bridging Pd−Cl bond lengths are shorter at 2.293(2) Å. The Cl−Pd−Cl angles are

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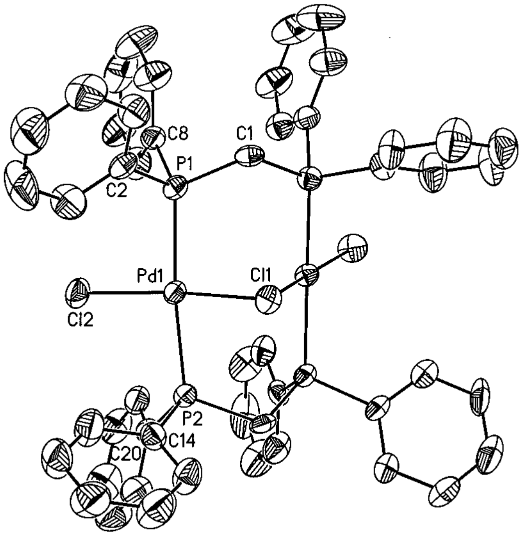

Figure 2. Projection view of the molecular structure of the $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ cation using 50% probability ellipsoids, showing the atom-labeling scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ Cation

Pd(1)−Cl(1)	2.293(2)	Pd(1)−Cl(2)	2.371(2)
Pd(1)−P(1)	2.340(2)	Pd(1)−P(2)	2.304(2)
Pd(1)−Cl(1)−Pd(1)′	87.46(10)	P(1)−Pd(1)−P(2)	169.91(8)
P(1)−Pd(1)−Cl(1)	87.55(5)	P(1)−Pd(1)−Cl(2)	95.48(7)
Cl(1)−Pd(1)−Cl(2)	173.27(8)	P(2)−Pd(1)−Cl(1)	83.29(5)
P(2)−Pd(1)−Cl(2)	93.20(7)		

173.27(8)°. The P−Pd−Pd−P torsion angles are 9.0°, indicating that there is only a slight twisting of the structure. As in the benzyl case, the dppm ligands are oriented to give an elongated boat configuration, with the methylene moieties on the same side as the bridging chloride. This is typical of group 10 A-frames, exceptions being $[Pd_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, which adopts an elongated chair conformation,[27] and $[Pd_2(C_6H_2Me_3\text{-}2,4,6)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]^+$, which was found in a boat conformation but with the CH_2 groups on the opposite face from the bridging bromide.[16]

Experimental Section

All reactions were carried out under an atmosphere of argon. The complexes [PdClMe(cod)],[17] $[Pd_2Cl_2(\mu\text{-}dppm)_2]$,[14] and $[PdPtCl_2(\mu\text{-}dppm)_2]$[20] were prepared by reported methods. Grignard reagents were purchased from Aldrich. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity plus 300 or Bruker ARX-500 spectrometer. Chemical shifts are relative to the residual solvent resonance or external H_3PO_4, respectively, positive shifts representing deshielding. GC−MS data were obtained on a Hewlett-Packard 5988 instrument. Microanalyses were performed by Atlantic Microlab, Inc, Norcross, GA.

$[Pd_2(C_6H_5)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$. To a stirred CH_2Cl_2 solution (30 mL) of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ (0.10 g, 0.095 mmol) at −78 °C was added an ether solution of PhMgBr (0.5 mL of a 3.0 M solution). The solution turned dark red immediately and was allowed to stir for 4 h. Methanol (1.0 mL), CBr_4 (0.10 g, 0.30 mmol), and $TlPF_6$ (0.034 g, 0.097 mmol) were added, and the mixture was allowed to warm to ambient temperature, while the solvents were removed under reduced pressure. After washing with ether and hexane, the solid residue was extracted with CH_2Cl_2 and passed through a short column of neutral alumina, eluting with CH_2Cl_2 (50 mL). The solvent was removed and the crude material was crystallized from CH_2Cl_2/Et_2O. Due to incorporation of ether, which could not be removed by pumping, the crystals were dissolved in CH_2Cl_2 and the solvent was removed rapidly. The residue was dried in vacuo, leaving a pale yellow solid (0.12 g, 92%). Anal. Calcd for $C_{62}H_{54}BrF_6P_5Pd_2$: C, 54.71; H, 3.97. Found: C, 54.24; H, 4.04. ^1H NMR (acetone-d_6): $\delta(H)$ 4.44 (dq, 2H, $^2J_{HH} = 14.2$ Hz, $^2J_{PH} = 3.7$ Hz, PCH_2P); 4.61 (dq, 2H, $^2J_{HH} = 14.2$ Hz, $^2J_{PH} = 5.2$ Hz, PCH_2P); 6.54−6.58 (m, 10H, PdC_6H_5); 7.05−7.9 (m, 40H, PC_6H_5). $^{31}P\{^1H\}$ NMR (acetone-d_6): $\delta(P)$ 11.5 (s).

$[Pd_2(C_6H_4Me\text{-}4)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$ was prepared similarly and isolated as a pale yellow solid in 83% yield. Anal. Calcd for $C_{64}H_{58}BrF_6P_5Pd_2$: C, 55.34; H, 4.18. Found: C, 55.15; H, 4.26. ^1H NMR ($CDCl_3$): $\delta(H)$ 1.97 (s, 6H, CH_3) 3.71 (dq, 2H, $^2J_{HH} = 13.9$ Hz, $^2J_{PH} = 3.4$ Hz, PCH_2P); 4.38 (dq, 2H, $^2J_{HH} = 13.9$ Hz, $^2J_{PH} = 5.5$ Hz, PCH_2P); 6.35−6.40 (m, 8H, C_6H_4-Me); 6.98−7.67 (m, 40H, PC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 10.5 (s).

The methyl, ethyl, *n*-butyl, and benzyl derivatives, prepared previously from $[PdBr_2(dppm)]$ and the appropriate Grignards reagent,[12] were also prepared in good yield by the above method.

$[PdPt(C_6H_4Me\text{-}4)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$. To a stirred CH_2Cl_2 solution (30 mL) of $[PdPtCl_2(\mu\text{-}dppm)_2]$ (0.10 g, 0.088 mmol) at −78 °C was added $4\text{-}MeC_6H_4MgBr$ (1.0 mL of a 1.0 M solution). The solution darkened immediately, and it was allowed to stir for 14 h. Methanol (1.0 mL), CBr_4 (0.10 g, 0.30 mmol), and $TlPF_6$ (0.031 g, 0.089 mmol) were introduced, and the mixture was allowed to warm to ambient temperature while the solvents were removed under reduced pressure. The product was isolated in a manner similar to that described for the dipalladium case. It was obtained as a pale yellow solid in 85% yield. Anal. Calcd for $C_{64}H_{58}BrF_6P_5Pd_2$: C, 52.01; H, 3.93. Found: C, 51.77; H, 3.96. ^1H NMR ($CDCl_3$): $\delta(H)$ 1.91 (s, 3H, $C_6H_4CH_3$); 1.98 (s, 3H, $C_6H_4CH_3$); 4.03 (dq, 2H, $^2J_{HH} = 14.1$ Hz, $^2J_{PH} = 3.8$ Hz, PCH_2P); 4.44 (dq, 2H, $^2J_{HH} = 14.1$ Hz, $^2J_{PH} = 5.9$ Hz, PCH_2P); 6.2−6.6 (m, 8H, C_6H_4Me); 7.0−7.8 (m, 40H, PC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 8.3 (m, PdP_2); 10.7 (m, $^1J_{PtP} = 2955$ Hz, PtP_2).

$[PdPt(C_6H_5)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$ was prepared similarly and isolated as a pale yellow solid in 85% yield. Anal. Calcd for $C_{62}H_{54}BrF_6P_5Pd_2$: C, 51.34; H, 3.72. Found: C, 51.20; H, 3.87.

$[Pd_2(COMe)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$. Method 1. Carbon monoxide was bubbled through a stirred CH_2Cl_2 solution (30 mL) of [PdClMe(cod)] (0.10 g, 0.38 mmol) for 1 h, then dppm (0.15 g, 0.38 mmol), methanol (1.0 mL) and $TlPF_6$ (0.13 g, 0.38 mmol) were added. The reaction mixture was stirred for a further 30 min, then the solvents were removed. The residue was washed with ether and pentane, then extracted with CH_2Cl_2 (30 mL). The resulting dark solution was passed through a short, neutral alumina column (5 cm), eluting with CH_2Cl_2 (30 mL). The solvent was removed, and the crude material was precipitated from CH_2Cl_2/Et_2O as a yellow solid. The solid was dissolved in CH_2Cl_2 and the solvent was removed rapidly. The residue was dried in vacuo, leaving a pale yellow solid (0.21 g, 90%). Anal. Calcd for $C_{54}H_{50}ClF_6O_2P_5Pd_2$: C, 51.94; H, 4.01. Found: C, 51.67; H, 4.04. ^1H NMR ($CDCl_3$): $\delta(H)$ 1.67 (s, 6H, $COCH_3$); 3.39 (dq, 2H, $^2J_{HH} = 13.7$ Hz, $^2J_{PH} = 4.6$ Hz, PCH_2P); 4.18 (dq, 2H, $^2J_{HH} = 13.7$ Hz, $^2J_{PH} = 5.3$ Hz, PCH_2P); 7.20−7.70 (m, 40H, PC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 7.3 (s).

Method 2. To a suspension of $[Pd_2Cl_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (0.10 g, 0.10 mmol) in CH_2Cl_2 (30 mL) was added Me_4Sn (0.042 mL, 0.31 mmol). The reaction mixture was stirred for 3 h to generate $[Pd_2Me_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ in situ. After bubbling CO through the solution for 1 h, dppm (0.079 g, 0.21 mmol), methanol (1.0 mL), and $TlPF_6$ (0.072 g, 0.21 mmol) were added, and the contents of the flask were stirred for an additional 30

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min before the solvents were removed. The resulting solid was purified as in method 1, and the product was obtained in 87% yield.

$[Pd_2(COEt)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$. This complex was prepared by method 2 and isolated in 87% yield. Anal. Calcd for $C_{56}H_{54}ClF_6O_2P_5Pd_2$: C, 52.69; H, 4.23. Found: C, 52.40; H, 4.31. ^{1}H NMR ($CDCl_3$): $\delta(H)$ 0.16 (t, 6H, $^3J_{HH} = 7.0$ Hz, CH_3); 2.00 (q, 4H, $^3J_{HH} = 7.0$ Hz, $COCH_2$); 3.41 (dq, 2H, $^2J_{HH} = 13.5$ Hz, $^2J_{PH} = 4.4$ Hz, PCH_2P); 4.13 (dq, 2H, $^2J_{HH} = 13.7$ Hz, $^2J_{PH} = 5.3$ Hz, PCH_2P); 7.20−7.90 (m, 40H, PC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 7.4 (s).

$[Pd_2(COCH_2Ph)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$. This complex was prepared by method 2 and isolated in 90% yield. Anal. Calcd for $C_{66}H_{58}ClF_6O_2P_5Pd_2$: C, 56.60; H, 4.15. Found: C, 56.15; H, 4.26. ^{1}H NMR ($CDCl_3$): $\delta(H)$ 3.30 (s, 4H, $COCH_2$); 3.47 (dq, 2H, $^2J_{HH} = 13.8$ Hz, $^2J_{PH} = 4.5$ Hz, PCH_2P); 4.24 (dq, 2H, $^2J_{HH} = 13.8$ Hz, $^2J_{PH} = 5.5$ Hz, PCH_2P); 5.87 (d, 4H, $^3J_{HH} = 7.5$ Hz, $CH_2C_6H_5$-2,6); 6.88 (t, 4H, $^3J_{HH} = 7.5$ Hz, $CH_2C_6H_5$-3,5); 6.98 (t, 2H, $^3J_{HH} = 7.5$ Hz, $CH_2C_6H_5$-4); 7.20−7.60 (m, 40H, PC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 7.4 (s).

Elimination Reactions. In a typical experiment, the A-frame complex (0.005 g) was dissolved in dmso-d_6 (0.5 mL) in an NMR tube along with Ph_2BnPO (0.0025 g) as an internal standard. The tube was evacuated and filled with argon. The sample was placed in the NMR probe and heated rapidly to the appropriate temperature. The progress of the reaction was monitored by ^{1}H and $^{31}P\{^1H\}$ (gated decoupling) NMR spectroscopy, the CH_2 and ^{31}P resonances being integrated relative to the corresponding signals from Ph_2BnPO. To ensure that the desired temperature had been reached, data obtained within the first 5 min were not used. The rate of disappearance of the A-frame was determined by plotting ln[A] vs time.

X-ray Crystallography. In each case, a crystal was mounted on a glass fiber in random orientation. Preliminary examination and data collection were performed using a Siemens SMART CCD detector system single-crystal X-ray diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), equipped with a sealed tube X-ray source (50 kV × 40 mA). Preliminary unit cell constants were determined with a set of 45 narrow frame (0.3° in $\bar{\omega}$) scans. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. The SMART software package[28] was used for data collection as well as frame integration. Final cell constants were determined by a global refinement of *xyz* centroids of 8192 reflections ($\theta < 19.0°$). An empirical absorption correction was applied using SADABS.[29] Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package.[30] The structure was solved by Patterson methods and refined successfully. Full matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using appropriate riding models (AFIX m3). Crystal data and structure refinement parameters are given in Table 3.

Table 3. Crystal Data and Structure Refinement Parameters for $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6\cdot H_2O,2C_6H_6$ and $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]OH\cdot 0.5(CH_3)_2CO$

	$[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6\cdot H_2O,2C_6H_6$	$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]\text{-}OH\cdot 0.5(CH_3)_2CO$
cryst syst	monoclinic	tetragonal
space group, Z	Pm, 2	$P4_12_12_1$, 4
a (Å)	12.6462(14)	14.8997(9)
b (Å)	27.937(3)	14.8997(9)
c (Å)	12.662(2)	26.308(2)
α (deg)	90	90
β (deg)	116.544(6)	90
γ (deg)	90	90
V (Å^3)	4001.9(8)	5840.4(7)
density (g/cm^{-3})	1.427	1.389
temp (K)	223(2)	223(2)
θ range (deg)	1.80 to 27.50	1.93 to 24.99
no. of ind reflns (R_{int})	18 773 (0.0000)	5141 (0.2)
$R(F)$, $R_w(F^2)$ ($F^2 > 2.0\sigma(F^2)$)	0.0450, 0.1082	0.0532, 0.1175
$R(F)$, $R_w(F^2)$ (all data)	0.0549, 0.1147	0.0838, 0.1297
goodness of fit on F^2	1.167	1.079

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Supporting Information Available: Tables of crystal data, atomic coordinates, and anisotropic displacement coefficients for the non-hydrogen atoms, positional and isotropic displacement coefficients for the hydrogen atoms, and a complete list of bond distances and angles for $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6\cdot H_2O,2C_6H_6$ and $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]OH\cdot 0.5(CH_3)_2CO$. This material is available free of charge via the Internet at http://pubs.acs.org.

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