Reactions of [PdX_2(dppm)] Complexes with Grignard Reagents

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Reactions of [PdX_2(dppm)] (X = Cl, Br) with a range of Grignard reagents have been investigated. Diorganopalladium complexes of the type [PdR_2(dppm)] were obtained in good yield with the bulky mesityl or trimethylsilylmethyl groups, provided the reactions were performed using high Grignard:Pd ratios in ether solution. With the smaller R groups Me, Et, Bu, and CH_2Ph, only the halide-bridged A-frame complexes [$Pd_2R_2(\mu\text{-}X)(\mu\text{-dppm})_2]^+$ were formed, irrespective of the reaction conditions. Mixtures of chloride- and bromide-bridged complexes were produced when [$PdCl_2$(dppm)] was treated with RMgBr, so [$PdBr_2$(dppm)] was used as the starting material in certain cases. The mesityl derivative [$Pd_2(C_6H_2Me_3)_2(\mu\text{-Br})(\mu\text{-dppm})_2]^+$ could be obtained from the reaction of [$PdBr_2$(dppm)] with 4 mol equiv of $C_6H_2Me_3MgBr$ in CH_2Cl_2 solution, but with Me_3SiCH_2MgCl mixtures of monomeric and dimeric complexes were obtained under these conditions. The A-frame complex [$Pd_2(CH_2SiMe_3)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ was generated, however, by reaction of [$Pd(CH_2SiMe_3)_2$(dppm)] with 1 mol equiv of HCl. The A-frames were isolated as their PF_6^- salts. They were characterized by elemental analysis, NMR spectroscopy, and, in the case of [$Pd_2(C_6H_2Me_3)_2(\mu\text{-Br})(\mu\text{-dppm})_2$]-$PF_6$, X-ray crystallography. The molecular structure of the [$Pd_2(C_6H_2Me_3)_2(\mu\text{-Br})(\mu\text{-dppm})_2]^+$ cation reveals that it adopts an elongated boat conformation, with the dppm CH_2 groups lying on the same side of the Pd_2P_4 framework as the bridging bromide. With the smaller aryl Grignards PhMgBr, *p*-tolylMgBr, or *o*-tolylMgCl, the diarylpalladium species [$PdAr_2$-(dppm)] could be detected in solution at low temperatures but at ambient temperature reductive coupling of the aryl groups occurred and the palladium(I) complexes [Pd_2X_2-$(\mu\text{-dppm})_2$] were formed.

Introduction

We have prepared a number of hydride-bridged palladium or platinum complexes of the type [$M_2R_2(\mu\text{-H})$-$(\mu\text{-dppm})_2]PF_6$, including unsymmetrical diplatinum or platinum−palladium species.[1−4] In each case, the final step was reduction of the corresponding halide-bridged dimer. In the case of platinum, the cyclooctadiene complexes [PtClR(cod)] proved to be convenient sources of the chloride-bridged derivatives[5] and several such precursors are available.[6] For palladium, however, only the corresponding methyl[7,8] and benzyl[9] complexes are known, stable materials. We investigated the use of chloride-bridged arsine complexes of the type [$Pd_2R_2(\mu$-$Cl)_2(AsPh_3)_2$],[4] but these were also of limited stability, and removal of triphenylarsine proved problematic in certain cases. Thus, we decided to investigate the reactions of [$PdCl_2$(dppm)] with organometallic reagents, and we have reported[4] that reactions with Me_4-Sn or MeMgBr, for example, cleanly produced the halide-bridged methylpalladium cation [$Pd_2Me_2(\mu\text{-X})(\mu$-$dppm)_2]^+$. In contrast to this, reaction of the platinum complex [$PtCl_2$(dppm)] with MeLi has been reported to give [$PtMe_2$(dppm)],[10,11] although with MeMgI the iodide-bridged A-frame compound was obtained.[12] Reactions with EtMgBr or $PhCH_2MgBr$ gave the appropriate dialkylplatinum complex, and treatment of [$PtCl_2$-(dppm)] with arylmagnesium bromides also produced species of the type [$PtAr_2$(dppm)].[12] In this paper, we report the reactions of [$PdCl_2$(dppm)] or [$PdBr_2$(dppm)] with a range of Grignard reagents.

Results and Discussion

Reactions of [$PdCl_2$(dppm)] with Excess RMgX (R = CH_2SiMe_3, $C_6H_2Me_3$). Treatment of an ether suspension of [$PdCl_2$(dppm)] with 8 mol equiv of ((trimethylsilyl)methyl)magnesium chloride or mesitylmagnesium bromide resulted in quantitative formation of the diorganopalladium complexes [PdR_2(dppm)] (eq 1). The complexes were isolated as analytically pure, air-stable solids. They are soluble in most common organic solvents but decompose slowly in halogenated solvents, such as chloroform or CH_2Cl_2. Each compound exhibits a single resonance at approximately −30 ppm in its ^{31}P-

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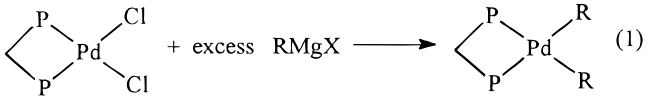


(1)

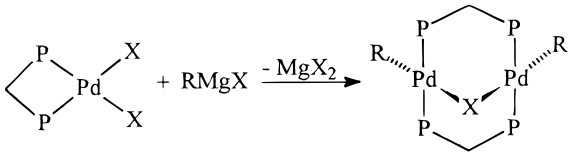
P P = dppm; R = CH_2SiMe_3, $C_6H_2Me_3$

{^{1}H} NMR spectrum, this negative chemical shift being indicative of the presence of a four-membered chelate ring.[13] In each case, a simple triplet for the methylene hydrogens of the dppm ligand is observed in the ^{1}H NMR spectrum, as expected for a symmetrical monomeric species. The ^{1}H NMR spectrum of the (trimethylsilyl)methyl derivative also contains a singlet due to the six equivalent methyl groups, a doublet of doublets for the CH_2 groups attached to palladium, and the expected aromatic signals. The spectrum for [Pd($C_6H_2Me_3$)$_2$(dppm)] shows two singlets in a 2:1 ratio for the methyl groups and a single resonance for the aromatic hydrogens of the mesityl groups, indicating that the *o*-CH_3 as well as the aromatic CH groups are magnetically equivalent. No broadening of these signals occurred as the temperature was lowered to 210 K in $CDCl_3$ solution. This indicates that the molecule is already static at ambient temperature, the two mesityl groups lying perpendicular to the square plane of the molecule such that it represents a plane of symmetry. The related platinum complexes [PtR$_2$(dppm)] (R = *o*-tolyl, 1-naphthyl) were found to exist as mixtures of *syn* and *anti* forms at low temperatures, when rotation about the Pt—C bonds became slow on the NMR time scale.[12]

With smaller alkyl Grignards, the dialkylpalladium complexes were not obtained but rather the A-frame derivatives (*vide infra*). For example, addition of 8 mol equiv of MeMgBr to [PdCl$_2$(dppm)] gave only the bromide-bridged A-frame complex [Pd$_2$Me$_2$(μ-Br)(μ-dppm)$_2$]$^+$. With neopentylmagnesium chloride, mixtures of [Pd(CH_2CMe_3)$_2$(dppm)] (δ(P) −23.8) and [Pd$_2$(CH_2CMe_3)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ (δ(H) 0.01 (s, 18H, C*Me*$_3$), 1.00 (s, 4H, PdC*H*$_2$), 4.31 (dq, 2H, ^2J(H,H) = 14.5 Hz, ^2J(P,H) = 3.5 Hz, PC*H*$_2$P), 4.53 (dq, 2H, ^2J(H,H) = 14.5 Hz, ^2J(P,H) = 5 Hz, PC*H*$_2$P); δ(P) 13.0) were obtained, the former being favored at high Grignard to palladium ratios, but the dialkylpalladium complex could not be isolated in pure form. The diorganopalladium complexes could be converted to the corresponding A-frames by treatment with 1 mol equiv of HCl, generated *in situ* from the reaction of acetyl chloride with methanol.

Evidently it is only with very bulky organic groups that we have been able to isolate complexes of the type [PdR$_2$(dppm)], whereas with smaller R groups the dimeric A-frame species is formed preferentially. Since substitution of the chlorides by R groups must take place in a stepwise manner, an intermediate species of the form [PdClR(dppm)] would be generated. Which product forms subsequently would depend on the relative rates of dimerization or reaction with a second equivalent of the Grignard reagent. Whereas both processes might be expected to be slower with bulky groups, dimerization is apparently slowed to a greater extent, allowing reaction with RMgX to proceed further, at least when excess Grignard reagent is present. With smaller R groups, dimerization is so rapid that even when a large excess of Grignard is employed, the second substitution cannot compete with A-frame formation.

Reactions of [PdCl$_2$(dppm)] with RMgX (R = Et, Bu, CH_2Ph, CH_2SiMe_3, $C_6H_2Me_3$). We have described previously the reaction of [PdCl$_2$(dppm)] with methylmagnesium bromide,[4] although in that instance we did not isolate the known halide-bridged A-frame complex generated *in situ*, but allowed it to react with $NaBH_3CN$ to give the corresponding hydride-bridged cation [Pd$_2$Me$_2$(μ-H)(μ-dppm)$_2$]$^+$. Analogous reactions with *ca.* 3 mol equiv of RMgBr (R = Et, Bu, CH_2Ph) in CH_2Cl_2 solution at −78 °C also gave halide-bridged A-frame complexes of the type [Pd$_2$R$_2$(μ-X)(μ-dppm)$_2$]$^+$, which we isolated as their PF_6^- salts after metathesis with NH_4PF_6 or $TlPF_6$. When [PdCl$_2$(dppm)] was treated with these bromide-containing Grignard reagents, however, mixtures of chloride- and bromide-bridged compounds were obtained, so [PdBr$_2$(dppm)] was used as the starting material in these cases. Under such conditions, reaction with RMgBr cleanly produced the bromide-bridged A-frame species [Pd$_2$R$_2$(μ-Br)(μ-dppm)$_2$]PF$_6$ in excellent yields (eq 2).



(2)

R = Et, Bu, CH_2Ph, $C_6H_2Me_3$

Whereas treatment of [PdCl$_2$(dppm)] with 8 mol equiv of mesitylmagnesium bromide in ether produced [Pd($C_6H_2Me_3$)$_2$(dppm)], reaction with 4 mol equiv of the Grignard reagent in CH_2Cl_2 solution gave the halide-bridged A-frame complex. (The Grignard reagent reacts with the palladium complex more rapidly than with the chlorinated solvent.) Again, a mixture of chloride- and bromide-bridged species was formed, but with [PdBr$_2$(dppm)] as the starting material the reaction produced [Pd$_2$($C_6H_2Me_3$)$_2$(μ-Br)(μ-dppm)$_2$]$^+$ cleanly.

The reaction of [PdCl$_2$(dppm)] with 8 mol equiv of ((trimethylsilyl)methyl)magnesium chloride in ether gave [Pd(CH_2SiMe_3)$_2$(dppm)], whereas when CH_2Cl_2 was used as the solvent mixtures of [Pd$_2$(CH_2SiMe_3)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ and [Pd(CH_2SiMe_3)$_2$(dppm)] were obtained. The chloride-bridged A-frame was obtained, however, by treating [Pd(CH_2SiMe_3)$_2$(dppm)] with HCl (generated *in situ* from acetyl chloride and methanol). The monomeric complex [PdCl(CH_2SiMe_3)(dppm)] (δ(P) −7.0 d, δ(P) −39.5 d, ^2J(P,P) = 70 Hz) was formed initially, but this converted to the A-frame complex on standing. The dimesitylpalladium complex also reacted with HCl to give [PdCl($C_6H_2Me_3$)(dppm)] first (δ(P) −23.3 d, δ(P) −44.7 d, ^2J(P,P) = 63 Hz), which dimerized on standing in solution. As pointed out above, [Pd$_2$(CH_2CMe_3)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ could be observed in solution, but we have been unable to isolate it in pure form.

The halide-bridged A-frame complexes are air-stable, colorless to yellow or orange solids. The cations are stable as their halide salts if kept below 0 °C, but they are more stable as their hexafluorophosphate salts, obtained by metathesis with NH_4PF_6 or $TlPF_6$. They have been characterized by NMR spectroscopy, elemental analysis, and, in the case of the mesityl derivative, X-ray crystallography. The ^{31}P{^{1}H} NMR spectrum of

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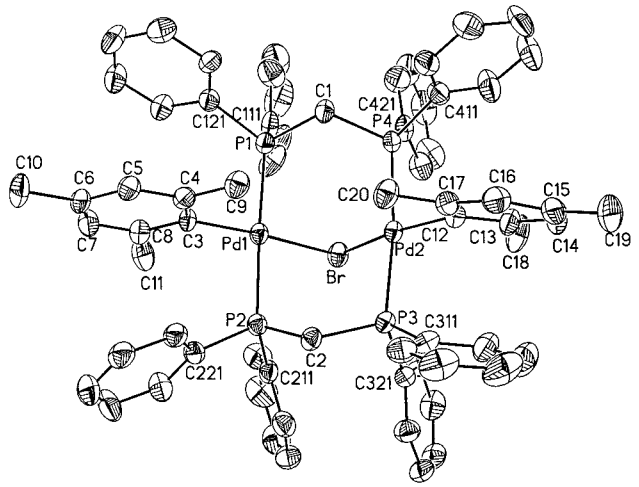

Figure 1. Projection view of the molecular structure of the $[Pd_2(C_6H_2Me_3)_2(\mu\text{-Br})(\mu\text{-dppm})_2]^+$ cation showing the atom-labeling scheme, with non-hydrogen atoms represented by 50% probability ellipsoids.

each complex exhibits a single resonance in the range 8−17 ppm, typical of bridging dppm. The ^{1}H NMR spectrum exhibits two doublets of quintets for the methylene hydrogens of the dppm ligands (although these overlap in the butyl case). This is due to the presence of axial and equatorial environments for these hydrogens, since inversion of the A-frame structure is slow on the NMR time scale.[14] Each hydrogen exhibits coupling to the other of *ca*. 14 Hz and to the four equivalent P atoms.

The ethyl, butyl, and (trimethylsilyl)methyl complexes display the expected resonances due to the alkyl groups. The mesityl derivative exhibits three signals due to the methyl groups and two aromatic CH resonances, indicating that there is hindered rotation about the Pd−C bonds. The benzyl derivative $[Pd_2(CH_2Ph)_2(\mu\text{-Br})(\mu\text{-dppm})_2]^+$ exhibits a broad singlet resonance at 2.89 ppm, due to the benzyl methylene hydrogens. The aromatic signals associated with the benzyl group appear at unexpectedly low frequencies, namely, a doublet at 5.17 ppm due to the *o*-hydrogens, a triplet at 6.35 ppm due to the *m*-hydrogens, and a further triplet of lower intensity at 6.65 ppm due to the *p*-hydrogens. These all appear at lower frequencies than the dppm aromatic signals (7.2−7.8 ppm). Similar chemical shifts are observed for the chloride-bridged complex, obtained from the reaction of $[PdCl(CH_2Ph)(cod)]$[9] with dppm.

X-ray Structure Determination of $[Pd_2(C_6H_2Me_3)_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6\cdot 3CH_2Cl_2$. Crystals of the bromide-bridged mesitylpalladium A-frame complex suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane solution. The crystal structure belongs to the space group $P\bar{1}$. The lattice contains three molecules of CH_2Cl_2 per $[Pd_2(C_6H_2Me_3)_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6$ unit. The molecular structure of the cation is shown in Figure 1, and selected bond distances and angles are presented in Table 1. There are no significant interactions between the cation, the anion, or the solvent molecules.

The molecule exhibits approximate square planar geometry about each of the palladium atoms, with the two planes being inclined toward each other at an angle of 83° through the bridging bromide. The eight-membered $Pd_2P_4C_2$ ring adopts an elongated boat conformation, with the two CH_2 groups and the bridging bromide lying on opposite faces of the Pd_2P_4 plane. The mesityl groups occupy terminal positions *trans* to the bridging bromide, the C−Pd−Br angles being 174.9° and 167.5°. The mesityl rings lie almost perpendicular to the Pd_2P_4 plane, presumably in order to minimize repulsions between these rings and the phenyl rings of the dppm ligands. This conformation is likely to persist in solution also, since the *o*-methyl groups are magnetically nonequivalent in the ^{1}H NMR spectrum, indicating that rotation about the Pd−C bonds is slow on the NMR time scale at ambient temperature (*vide supra*).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Pd_2(C_6H_2Me_3)_2(\mu\text{-Br})(\mu\text{-dppm})_2]PF_6\cdot 3CH_2Cl_2$

Pd(1)−P(1)	2.340(2)	Pd(1)−P(2)	2.330(2)
Pd(1)−C(3)	2.034(6)	Pd(1)−Br	2.5273(8)
Pd(2)−P(3)	2.350(2)	Pd(2)−P(4)	2.329(2)
Pd(2)−C(12)	2.033(7)	Pd(2)−Br	2.5551(8)
P(1)−Pd(1)−P(2)	172.87(6)	P(1)−Pd(1)−C(3)	89.2(2)
P(1)−Pd(1)−Br	93.09(5)	P(2)−Pd(1)−C(3)	89.6(2)
P(2)−Pd(1)−Br	88.67(5)	C(3)−Pd(1)−Br	174.9(2)
P(3)−Pd(2)−P(4)	170.30(6)	P(3)−Pd(2)−C(12)	88.7(2)
P(3)−Pd(2)−Br	92.35(5)	P(4)−Pd(2)−C(12)	90.3(2)
P(4)−Pd(2)−Br	90.73(5)	C(12)−Pd(2)−Br	167.5(2)
Pd(1)−Br−Pd(2)	83.32(2)		

The solid state structures of a number of dipalladium[15−30] and diplatinum[31−41] A-frame complexes

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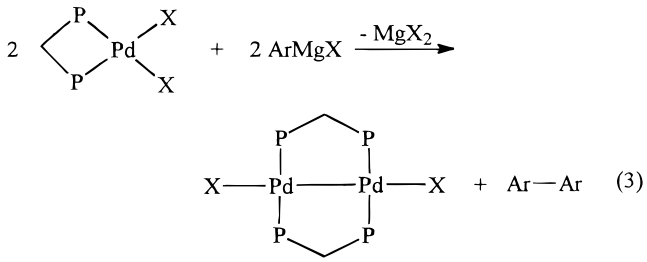
have been reported. A large majority of these adopt elongated boat conformations, the exceptions being the carbonyl-bridged dipalladium species $[Pd_2Cl_2(\mu\text{-CO})(\mu\text{-dmpm})_2]$[19] and $[Pd_2(OCOCF_3)_2(\mu\text{-CO})(\mu\text{-dppm})_2]$[23] and $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$,[38] which exist in chair conformations. In each of the previously reported boat structures, the CH_2 groups of the bridging diphosphine ligands lie on the same side of the M_2P_4 plane as the group occupying the apex of the A-frame structure. Thus, the present study represents the first example of a boat conformation in which the terminal groups (the mesityl groups here) and the dppm CH_2 groups lie on the same face of the dimer. Consideration of the molecular structure reveals that two of the phenyl rings of the dppm ligands and the mesityl ring on each side of the A-frame lie almost parallel to each other, and this π-stacking effect may be responsible for the conformation adopted in this case.

Reactions of [PdCl₂(dppm)] with ArMgX (Ar = Ph, 4-Tolyl, 2-Tolyl). When an ether suspension of $[PdCl_2(dppm)]$ was treated with 1 mol equiv of phenylmagnesium bromide at ambient temperature, the mixture turned dark red rapidly. After filtration of the palladium-containing species and magnesium salts, the ether was evaporated and the resulting solid was identified by ^1H NMR spectroscopy and GC-MS as diphenyl. The palladium species was identified as the palladium(I) complex $[Pd_2Br_2(\mu\text{-dppm})_2]$ (δ(P) −5.2),[42] the terminal ligands being derived from the bromide in the Grignard reagent used. The analogous reaction with 4-tolylmagnesium bromide produced 4,4′-ditolyl and $[Pd_2Br_2(\mu\text{-dppm})_2]$, whereas with *o*-tolylmagnesium chloride the products were 2,2′-ditolyl and $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (δ(P) −2.5),[42] the organic products again being identified by their ^1H NMR and GC-MS data (eq 3).

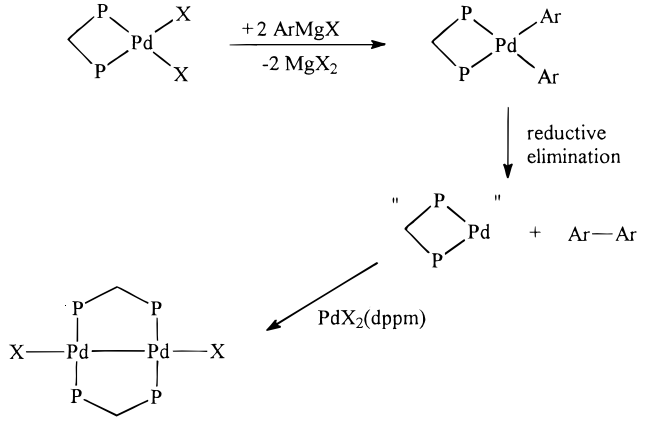


(3)

Ar = Ph, 4-tolyl, 2-tolyl

When the reaction of $[PdCl_2(dppm)]$ with PhMgBr was carried out at −78 °C in CD_2Cl_2 solution ($[PdCl_2(dppm)]$ is only slightly soluble at this temperature), a single resonance was observed in the $^{31}P\{^1H\}$ NMR spectrum at −31.1 ppm. This is shifted to higher frequency than the signal observed for the starting material (δ(P) −53.2) and is very close to that found for $[Pd(C_6H_2Me_3)_2(dppm)]$ (*vide supra*). Thus, we have assigned this resonance to $[PdPh_2(dppm)]$. When the solution was allowed to warm to ambient temperature, a further reaction took place and several phosphorus-containing species were formed. The corresponding low-temperature reaction with 4-MeC_6H_4MgBr in CD_2Cl_2 solution gave $[Pd(C_6H_4Me\text{-}4)_2(dppm)]$ (δ(P) −29.0), and treatment of $[PdCl_2(dppm)]$ with 2-MeC_6H_4MgCl in toluene-d_8 produced $[Pd(C_6H_4\text{-}Me\text{-}2)_2(dppm)]$ (δ(P) −27.8). Again, in each case, a number of species was formed when the solution was allowed to warm to ambient temperature.

Scheme 1



Although allowing the low-temperature reaction mixtures to warm to ambient temperature did not cleanly produce the palladium(I) complexes found when the reactions were performed at 25 °C, the detection of $[PdAr_2(dppm)]$ at −78 °C strongly suggests that such species are involved in the ambient-temperature reactions also. We propose the sequence of events shown in Scheme 1. The first step is reaction of $[PdCl_2(dppm)]$ with the Grignard reagent to produce $[PdAr_2(dppm)]$. Although only 1 mol equiv of the Grignard was added, the low solubility of $[PdCl_2(dppm)]$ in ether (or in CD_2Cl_2 or toluene-d_8 at low temperatures) would ensure that the ArMgX:Pd ratio in solution was high. This would allow rapid replacement of the second halide before dimerization of [PdClAr(dppm)] to give the A-frame complex $[Pd_2Ar_2(\mu\text{-X})(\mu\text{-dppm})_2]^+$ could occur. Reductive elimination of the diaryl would produce the highly reactive palladium(0) species [Pd(dppm)], which would react with another molecule of $[PdCl_2(dppm)]$ to generate the palladium(I) complex $[Pd_2X_2(\mu\text{-dppm})_2]$ (X = Cl or Br, depending on the Grignard reagent employed).

Reductive eliminations from diorganopalladium(II) and -platinum(II) complexes are well-known. With aryl substituents, stable palladium complexes of the type *cis*-$[Pd(C_6X_5)_2L_2]$ (X = F, Cl) have been reported, but the corresponding *cis*-$[PdPh_2L_2]$ species are unknown.[43] The strongly electron-withdrawing nature of the pentafluorophenyl groups enhances the stability of their complexes. In the present instance, we have been unable to distinguish between the rates of reductive elimination for the three different aryl groups, phenyl, 4-tolyl, and 2-tolyl, each reaction being rapid at ambient temperature. When Ar = mesityl, however, the dimesitylpalladium complex could be isolated and reductive elimination did not occur. Reductive elimination from *cis*-diarylplatinum(II) complexes proceeds by a concerted mechanism,[44] and it has been shown that the two aryl groups must lie perpendicular to the square plane in

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order that elimination may occur.[45] When the aryl groups are mesityl groups, they will indeed both lie perpendicular to the plane but they must be oriented at 90° to each other in the product dimesityl,[46] and this will inhibit the reductive elimination process.

Summary

With the bulky organic groups mesityl and (trimethylsilyl)methyl, the reactions of $[PdX_2(dppm)]$ (X = Cl, Br) proceed to give the diorganopalladium species $[PdR_2(dppm)]$. In contrast, with smaller alkyl groups, the halide-bridged A-frame complexes $[Pd_2R_2(\mu\text{-}X)(\mu\text{-}dppm)_2]^+$ (R = Me, Et, Bu, CH_2Ph) are formed. The nature of the products obtained depends on the relative rates of reaction of [PdXR(dppm)] with further Grignard reagent to produce $[PdR_2(dppm)]$ or with a second molecule of [PdXR(dppm)] to produce the dimer. With smaller aryl groups, the diarylpalladium species are formed, but they undergo rapid reductive elimination at ambient temperature to produce the diaryl and the palladium(I) complex $[Pd_2X_2(\mu\text{-}dppm)_2]$.

Experimental Section

All reactions were carried out under an atmosphere of argon. $[PdCl_2(dppm)]$ was prepared by reaction of $[PdCl_2(cod)]$ with dppm, and $[PdBr_2(dppm)]$ (δ(P) −56.3) was generated by stirring an acetone solution of $[PdCl_2(dppm)]$ with excess LiBr for 24 h at ambient temperature. Grignard reagents were purchased from Aldrich. ^{1}H and ^{31}P{^{1}H} 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. The following abbreviations are used: s = singlet, t = triplet, q = quintet, sx = sextet, m = multiplet. GC-MS data were obtained on a Hewlett-Packard 5988 instrument. Microanalyses were performed by Atlantic Microlab, Inc, Norcross, GA.

Preparation of $[Pd(CH_2SiMe_3)_2(dppm)]$. $[PdCl_2(dppm)]$ (0.100 g, 0.178 mmol) was suspended in ether (5 mL) at ambient temperature. Me_3SiCH_2MgCl (1.42 mL of a 1.0 M solution) was added by syringe. The solution was stirred for 20 min. Methanol (0.5 mL) was added to quench the excess Grignard reagent. The solvents were removed, and the solid was dried *in vacuo*. The solid was washed with ether and hexane at −78 °C. The residue was then extracted with CH_2Cl_2 (30 mL) and filtered. The solvent was removed to leave the product as a pale yellow solid (0.108 g, 91%). Anal. Calcd for $C_{33}H_{44}P_2PdSi_2$: C, 59.55; H, 6.61. Found: C, 59.38; H, 6.55. ^{1}H NMR ($CDCl_3$): δ(H) −0.15 (s, 18H, Si*Me*$_3$), 0.70 (dd, 4H, ^3J(P,H) = 12, 10 Hz, C*H*$_2$SiMe$_3$), 3.81 (t, 2H, ^1J(P,H) = 7.5 Hz, PC*H*$_2$P), 7.2−7.6 (m, 20H, P*Ph*$_2$). ^{31}P{H} NMR: δ(P) −27.0 (s).

Preparation of $[Pd(C_6H_2Me_3\text{-}2,4,6)_2(dppm)]$. $[PdCl_2(dppm)]$ (0.200 g, 0.356 mmol) was added to an ether solution of $Me_3C_6H_2MgBr$ (2.85 mL of a 1.0 M solution). The suspension was stirred for 20 min, then methanol (0.4 mL) was added, and the solvent was removed *in vacuo*. The orange residue was extracted with CH_2Cl_2 and filtered, then the CH_2Cl_2 was evaporated, and the residue was washed with ether and hexane. The solid was dissolved in benzene and passed through a Florisil column, eluting with benzene (50 mL). The benzene was removed *in vacuo* to leave the product as a colorless solid (0.217 g, 84%). Anal. Calcd for $C_{43}H_{44}P_2Pd$: C, 70.80; H, 6.04. Found: C, 70.72; H, 6.13. ^{1}H NMR (C_6D_6): δ(H) 2.31 (s, 6H, *p-Me*), 2.79 (s, 12H, *o-Me*), 3.59 (t, 2H, ^2J(P,H) = 8 Hz, PC*H*$_2$P), 6.91 (s, 4H, C$_6$*H*$_2$Me$_3$), 6.95−7.3 (m, 20H, P*Ph*$_2$). ^{31}P{H} NMR: δ(P) −30.6 (s).

Preparation of $[Pd_2(CH_2SiMe_3)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$. $[PdCl_2(dppm)]$ (0.200 g, 0.356 mmol) was suspended in ether (30 mL) at ambient temperature. Me_3SiCH_2MgCl (2.85 mL of a 1.0 M ether solution) was added by syringe. The yellow solution was stirred for 30 min, then methanol (0.5 mL) was added to quench the excess Grignard reagent. Acetyl chloride (0.71 mL of a 0.5 M solution in toluene) was added by syringe, and the solution was stirred for 10 min. The solvents were removed *in vacuo*, and the resulting solid was dried overnight. The solid was extracted with CH_2Cl_2 (30 mL), and this solution was treated with NH_4PF_6 (0.202g, 1.23 mmol) in methanol (2.0 mL). The mixture was stirred at ambient temperature for 30 min, then the solvent was removed *in vacuo*. The resulting solid was dried, then washed with ether and hexane at −78 °C. Finally, it was extracted with CH_2Cl_2 (30 mL). The solution was filtered, then the solvent was evaporated. The solid was recrystallized from CH_2Cl_2/hexane at 0 °C to give the product as a pale yellow solid (0.209 g, 88%). Anal. Calcd for $C_{58}H_{66}ClF_6P_5Pd_2Si_2$: C, 52.09; H, 4.93. Found: C, 51.85; H, 5.00. ^{1}H NMR (acetone-d_6): δ(H) −0.95 (s, 18H, Si*Me*$_3$), 1.04 (m, 4H, C*H*$_2$SiMe$_3$), 3.98 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 4 Hz, PC*H*$_2$P), 4.45 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 5 Hz, PC*H*$_2$P), 7.5−7.9 (m, 40H, P*Ph*$_2$). ^{31}P{^{1}H}NMR: δ(P) 13.5 (s).

Preparation of $[Pd_2(C_6H_2Me_3)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$. To a CH_2Cl_2 solution of $[PdBr_2(dppm)]$ (0.200 g, 0.307 mmol) was added $Me_3C_6H_2MgBr$ (1.23 mL of a 1.0 M solution in ether). The yellow solution was stirred for 30 min, then methanol (2.0 mL) was added by syringe. The mixture was stirred for an additional 1 h, then the solvent was removed *in vacuo*. The resulting solid was dried, then extracted with CH_2Cl_2 and treated with NH_4PF_6 (0.20 g, 1.23 mmol) in methanol (1.0 mL). After 1 h, the solvent was evaporated, and the solid was dried, washed with ether and hexane, and extracted with CH_2Cl_2 (5.0 mL). The resulting solution was passed through a short column of neutral alumina, eluting with CH_2Cl_2 (40 mL). The solvent was removed *in vacuo*, leaving the product as a colorless solid (0.187 g, 84%). Crystals suitable for an X-ray diffraction study were obtained from a CH_2Cl_2/hexane solution at 0 °C. ^{1}H NMR ($CDCl_3$): δ(H) 1.79, 2.42, 2.58 (s, 9H, C$_6$H$_2$*Me*$_3$), 3.83 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 4.5 Hz, PC*H*$_2$P), 4.35 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 4.5 Hz, PC*H*$_2$P), 5.85, 5.97 (s, 2H, C$_6$*H*$_2$Me$_3$), 6.8−7.8 (m, 40H, P*Ph*$_2$). ^{31}P{^{1}H} NMR: δ(P) 8.6 (s).

Preparation of $[Pd_2(CH_2Ph)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$. A CH_2Cl_2 solution (30 mL) of $[PdBr_2(dppm)]$ (0.200 g, 0.307 mmol) was cooled to −78 °C and treated with $PhCH_2MgBr$ (1.0 mL of a 1.0 M ether solution). The solution was stirred for 3 h at −78 °C, then methanol (1.0 mL) was added, and the solution was allowed to warm slowly to 0 °C. The solvents were removed at 0 °C. The resulting solid was dried, then extracted with CH_2Cl_2 and treated with NH_4PF_6 (0.20 g, 1.23 mmol) in methanol (1.0 mL). The mixture was maintained at 0 °C for 1 h, then the solvents were removed, and the solid was dried *in vacuo*. The solid was washed with ether, hexane, and warm benzene, then extracted with CH_2Cl_2 and filtered. The solvent was evaporated, and the residue was crystallized from a CH_2Cl_2/hexane solution at 0 °C, yielding the product as a yellow powder (0.190 g, 89%). Anal. Calcd for $C_{64}H_{58}BrF_6P_5Pd_2$: C, 55.31; H, 4.18. Found: C, 55.87; H, 4.33. ^{1}H NMR ($CDCl_3$): δ(H) 2.89 (br s, 4H, C*H*$_2$C$_6$H$_5$), 3.68 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 3.5 Hz, PC*H*$_2$P), 4.39 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 5 Hz, PC*H*$_2$P), 5.17 (d, 4H, ^3J(H,H) = 7.5 Hz, CH$_2$C$_6$H$_5$ *o*-hydrogens), 6.35 (t, 4H, ^3J(H,H) = 7.5 Hz, CH$_2$C$_6$*H*$_5$, *m*-hydrogens), 6.65 (t, 2H, ^3J(H,H) = 7.5 Hz, CH$_2$C$_6$*H*$_5$, *p*-hydrogens), 7.2−7.8 (m, 40H, P*Ph*$_2$). ^{31}P{^{1}H} NMR: δ(P) 10.2 (s).

Preparation of $[Pd_2Et_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]PF_6$. To a CH_2Cl_2 solution (30 mL) of $[PdBr_2(dppm)]$ (0.200 g, 0.307 mmol) maintained at −78 °C was added EtMgBr (1.0 mL of a 1.0 M

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ether solution) by syringe. The solution was stirred for 4 h, then methanol (1.0 mL) was added, and the solution was allowed to warm slowly to 0 °C. The solvent was removed at 0 °C, and the residue was extracted with CH_2Cl_2. To the CH_2Cl_2 solution was added NH_4PF_6 (0.20 g, 1.23 mmol) in methanol (1.0 mL). The mixture was stirred at 0 °C for 30 min, then the solvent was removed *in vacuo*. The resulting solid was dried, washed with ether and hexane, then extracted with CH_2Cl_2 (5 mL). This solution was passed through a column of neutral alumina, eluting with CH_2Cl_2 (50 mL). The solvent was evaporated, leaving the product as an orange powder (0.146 g, 75%). Anal. Calcd for $C_{54}H_{54}BrF_6P_5Pd_2$: C, 51.29; H, 4.27. Found: C, 51.44; H, 4.30. ^{1}H NMR ($CDCl_3$): δ(H) −0.03 (m, 6H, CH_2CH_3), 1.69 (m, 4H, CH_2CH_3), 3.74 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 4 Hz, PCH_2P), 4.28 (dq, 2H, ^2J(H,H) = 14 Hz, ^2J(P,H) = 5.5 Hz, PCH_2P), 7.1−8.1 (m, 40H, PPh_2). ^{31}P{^{1}H} NMR: δ(P) 16.8 (s).

Preparation of [Pd₂Bu₂(μ-Br)(μ-dppm)₂]PF₆. *n*-BuMgBr (1.0 mL of a 1.0 M ether solution) was added to a CH_2Cl_2 solution (5.0 mL) of [$PdBr_2$(dppm)] (0.200 g, 0.307 mmol) at −78 °C. After 4 h, methanol (1.0 mL) was added and the solution was allowed to warm slowly to 0 °C. The solvent was removed at this temperature, and the residue was extracted with acetone and treated with $TlPF_6$ (0.0645 g, 0.184 mmol). After being stirred for 20 min, the solvent was removed *in vacuo* and the residue was washed with ether and hexane. The residue was extracted with CH_2Cl_2, and the solution was filtered and evaporated to dryness to leave the product as a yellow powder (0.160 g, 79%). Anal. Calcd for $C_{58}H_{62}BrF_6P_5Pd_2$: C, 52.71; H, 4.70. Found: C, 52.47; H, 4.73. ^{1}H NMR (acetone-d_6): δ(H) 0.02 (t, 6H, ^3J(H,H) = 7 Hz, $CH_2CH_2CH_2CH_3$), 0.21 (sx, 4H, ^3J(H,H) = 7 Hz, $CH_2CH_2CH_2CH_3$), 0.37 (q, 4H, ^3J(H,H) = 8 Hz, $CH_2CH_2CH_2CH_3$), 1.65 (m, 4H, $CH_2CH_2CH_2CH_3$), 4.38 (m, 4H, PCH_2P), 7.2−8.1 (m, 40H, PPh_2). ^{31}P{^{1}H} NMR: δ(P) 17.2 (s).

Reactions of [PdCl₂(dppm)] with ArMgX. (a) Reactions at Ambient Temperature. [$PdCl_2$(dppm)] (0.100 g, 0.178 mmol) was suspended in ether (30 mL) at ambient temperature. A solution of ArMgX (0.18 mL of a 1.0 M ether solution; ArMgX = PhMgBr, (4-tolyl)MgBr, (2-tolyl)MgCl) was added by syringe. The yellow mixture turned dark red immediately. After the mixture was stirred for 15 min, the solution was filtered to remove the palladium-containing products and magnesium salts and the solvent was evaporated. Analysis of the filtered material by NMR spectroscopy revealed the presence of [Pd_2Cl_2(μ-dppm)$_2$] (δ(H) 4.17 (q, J(P,H) = 4 Hz, CH_2), 7.1−7.6 (m, PPh_2); δ(P) −2.5) or [Pd_2Br_2(μ-dppm)$_2$] (δ(H) 4.15 (q, J(P,H) = 4 Hz, CH_2), 7.2−7.4 (m, PPh_2); δ(P) −5.2). The organic products obtained by solvent removal were identified as the diaryls by GC-MS (diphenyl, *m*/*z* 154 (p^+, 100); 2,2′-ditolyl, *m*/*z* 182 (p^+, 100); 4,4′-ditolyl, *m*/*z* 182 (p^+, 100)) and ^{1}H NMR spectroscopy (2,2′-ditolyl, 2.04 (s, 6H, CH_3), 7.09 (d, 2H, ^3J(H,H) = 7 Hz, C_6H_4Me), 7.18−7.26 (m, 6H, C_6H_4Me); 4,4′-ditolyl, 2.30 (s, 6H, CH_3), 7.4−7.7 (m, 8H, C_6H_4Me)).

(b) Reactions at Low Temperature. To a CD_2Cl_2 solution (0.5 mL) of [$PdCl_2$(dppm)] (0.010 g, 0.018 mmol) was added 1 mol equiv of PhMgBr (0.017 mL of a 1.0 M ether solution) at −78 °C. The ^{31}P{^{1}H} NMR spectrum at 200 K exhibited a singlet resonance at −31.1 ppm, attributed to [$PdPh_2$(dppm)]. Warming this solution to ambient temperature resulted in formation of a large number of species, many of which remain unidentified.

Analogous reactions with (2-tolyl)MgCl or (4-tolyl)MgBr at −78 °C yielded [Pd(2-tolyl)$_2$(dppm)] (δ(P) −29.0 (CD_2Cl_2)) or [Pd(4-tolyl)$_2$(dppm)] (δ(P) −27.8 (toluene-d_8)).

X-ray Structure Determination of [Pd₂(C₆H₂Me₃)₂(μ-Br)(μ-dppm)₂]PF₆. A crystal of dimensions 0.42 × 0.22 × 0.12 mm 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 (λ = 0.710 73 Å) equipped with a sealed tube X-ray source (50 kV × 40 mA) at 203 K. Preliminary unit cell constants were determined with a set of 45 narrow frame (0.3° in ω) scans. A total of 5554 frames of intensity data were collected, with a counting time of 10 s/frame at a crystal to detector distance of 4.930 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. The SMART software package[47] was used for data collection as well as frame integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of *x*,*y*,*z* centroids of 8192 reflections (θ < 19.0°). An empirical absorption correction was applied using SADABS[48] based on the Laue symmetry using 47 740 equivalent reflections (T_{max}/T_{min} = 0.84/0.61, R_{int} = 8.6% and 5.9% before and after absorption correction).

Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package.[49] The structure was solved by Patterson methods and refined successfully in the space group $P\bar{1}$. 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). The final residual values were $R(F)$ = 11.2% and $R_w(F^2)$ = 21.5%, s =1.03 for all data. Crystal data and structure refinement parameters are given in Table 2.

Table 2. Crystal Data and Structure Refinement for [Pd₂(C₆H₂Me₃)₂(μ-Br)(μ-dppm)₂]PF₆·3CH₂Cl₂

cryst syst	triclinic
space group, *Z*	$P\bar{1}$, 2
a (Å)	15.0482(2)
b (Å)	16.2499(2)
c (Å)	17.7349(2)
α (deg)	84.254(1)
β (deg)	66.663(1)
γ (deg)	64.989(1)
V (Å^3)	3596.72(8)
density (g/cm^{-3})	1.569
temperature (K)	203(2)
θ range (deg)	1.62−27.0
no. of indep reflns (R_{int})	15 636 (0.051)
$R(F)$, $R_w(F^2)$($F^2 > 2.0\ \sigma(F^2)$)	0.0673, 0.1806
$R(F)$, $R_w(F^2)$ (all data)	0.1121, 0.2153
goodness of fit on F^2	1.034

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Supporting Information Available: Tables of 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 (14 pages). Ordering information is given on any current masthead page.

OM970376U

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