Organometallics **2000,** *19,* 3447−3454

Synthesis and Structure of Dinuclear Palladium(II) Complexes with Bridging Hydrido and Phosphido Ligands

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Received April 24, 2000

The reaction of Pd(dppf)(Ph)(I) (**1**, dppf = $Ph_2PC_5H_4FeC_5H_4PPh_2$) with 1.5 equiv of PPh_2H leads to the formation of the Pd(II) dinuclear complex $Pd_2I_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-PPh}_2)$ (**2**) and the phosphines PPh_3 and dppf. The reaction of **1** with 1 equiv of PCy_2H (Cy = cyclo-C_6H_{11}) slowly gives $Pd_2I_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-PCy}_2)$ (**3**). Complex **2** reacts further with PPh_2H to give the known $[Pd(\mu\text{-PPh}_2)(I)(PPh_2H)]_2$ (**4**). Reaction of Pd(dcpm)(Ph)(I) (dcpm = $Cy_2PCH_2PCy_2$) with PPh_2H gives $[Pd_2(PPh_2H)_2(\mu\text{-dcpm})(\mu\text{-PPh}_2)][I]$ (**5**). Treatment of Pd(dmpe)(Me)(Cl) (dmpe = $Me_2PCH_2CH_2PMe_2$) with AgOTf and PPh_2H gives $[Pd(dmpe)(\mu\text{-PPh}_2)]_2[OTf]_2$ (**6**, OTf = OSO_2CF_3) as well as a small amount of $[Pd_2(dmpe)_2(\mu\text{-H})(\mu\text{-PPh}_2)][OTf]_2$ (**7**). Slow decomposition of $[Pd(dmpe)(Me)(PCy_2H)]^+$, prepared by the reaction of Pd(dmpe)(Me)(Cl), AgOTf, and PCy_2H, gives $[Pd_2(dmpe)_2(\mu\text{-H})(\mu\text{-PCy}_2)][OTf]_2$ (**8**), which was also prepared from $Pd(dmpe)Cl_2$, AgOTf, Pd(dmpe)(dba) (dba = dibenzylideneacetone), and PCy_2H. Complexes **3**, **4**, **5**, and **8** were structurally characterized by X-ray crystallography.

Introduction

We previously reported that deprotonation of $[Pd(dppe)(Me)(PH_2Mes^*)][BF_4]$ (dppe = $Ph_2PCH_2CH_2PPh_2$, Mes* = 2,4,6-$(t\text{-Bu})_3C_6H_2$) gave Pd(dppe)(Me)(PHMes*), which underwent reductive elimination to give PH(Me)(Mes*) and Pd(0). Since this type of P−C bond-forming step is important in Pd-catalyzed cross-coupling reactions used for synthesis of tertiary phosphines, we have investigated its generality and mechanism. Several complexes $[Pd(diphos)(R)(PR'_2H)]^+$ could be prepared by the reaction of Pd(diphos)(R)(X) (diphos = dppe or dcpe ($Cy_2PCH_2CH_2PCy_2$, Cy = cyclo-C_6H_{11}); R = Me, Ph, Mes (2,4,6-$Me_3C_6H_2$); R′ = Ph, Cy, Mes; X = Cl, Br, I) with Ag^+ and secondary phosphines.[1] However, attempts to extend these syntheses to complexes with diphosphines having different bite angles and/or steric bulk did not give analogous products. We report here that, instead, dinuclear complexes with bridging phosphido, hydrido, and diphosphine ligands were formed via some interesting transformations, such as P−C bond formation, P−H bond activation, and conversion of a chelate diphosphine to one bridging two metal centers.

Results and Discussion

Dppf Complexes An attempt to prepare the cationic complex $[Pd(dppf)(Ph)(PPh_2H)][OTf]$ (dppf = $Ph_2PC_5H_4FeC_5H_4PPh_2$, OTf = OSO_2CF_3) by treatment of Pd(dppf)(Ph)(I) (**1**) with AgOTf and PPh_2H produces an ill-defined mixture of products. However, when ca. 1.5 equiv of PPh_2H is added to a yellow slurry of **1** in THF/MeCN, the starting material dissolves instantly, forming a dark orange solution. Addition of petroleum ether and cooling to −25 °C affords orange crystals in 75% yield, based on palladium. The reaction also produces PPh_3 and dppf, according to ^{31}P NMR and comparison with authentic samples.

The $^{31}P\{^1H\}$ NMR spectrum of the Pd-containing product (CD_2Cl_2) shows a doublet at δ 15.0 and a triplet at δ 266.2 with J_{PP} = 332 Hz. The large coupling constant is indicative of trans location of the P nuclei, while the chemical shift at low field is consistent with the presence of a phosphido bridge and a metal−metal bond.[2] The ^1H NMR spectrum includes three multiplets at δ 8.06−7.40, two broad singlets at δ 4.50 and 3.98, and a broad resonance at δ −8.27 consistent with the presence of 30 phenyl, eight Cp, and one hydride proton. No Pd−H stretch can be seen in the IR spectrum (KBr), suggesting that the hydride is bridging. The FAB-MS spectrum shows a parent ion peak at 1207.8 amu. These spectroscopic data and the observed phosphine products suggest the formation of the neutral dinuclear complex $Pd_2(I)_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-PPh}_2)$ (**2**) according to the stoichiometry shown in Scheme 1.

Treatment of **1** with 1.5 equiv of PCy_2H results in decomposition, but using 1 equiv of PCy_2H gives the dinuclear complex $Pd_2(I)_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-PCy}_2)$ (**3**, eq 1),

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[1] (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040. (b) Zhuravel, M. A.; Grewal, N. S.; Glueck, D. S.; Lam, K.-C.; Rheingold, A. L. *Organometallics*, in press. (c) Zhuravel, M. A. Ph.D. Thesis, Dartmouth College, June 2000. (d) Zhuravel, M. A.; Wicht, D. K.; Moncarz, J. R.; Sweeder, R. D.; Glueck, D. S.; Lam, K.-C.; Liable-Sands, L. M.; Rheingold, A. L. Manuscript in preparation.

[2] (a) Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; pp 559−619. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163−193.

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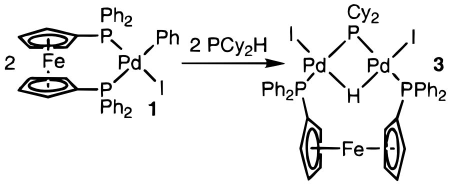
which was characterized spectroscopically as well as by elemental analysis and X-ray crystallography. We were



(1)

not able to identify the other products of the reaction. Unlike **2**, **3** does not form instantly on addition of the phosphine to **1**, probably due to the relatively large size of PCy_2H. Spectroscopic data for **3** are similar to that of **2**. The ^{31}P NMR spectrum (CD_2Cl_2) contains signals due to dppf (d, δ 14.0) and the bridging phosphido group (t, δ 349.6) with $^2J_{PP} = 299$ Hz. In the ^1H NMR spectrum (CD_2Cl_2), the bridging hydride signal appears at δ -8.84.

An X-ray crystallography study of a THF solvate confirmed the proposed structure of **3** (Figure 1). Data collection and structure refinement are summarized in Table 1, selected bond lengths and angles appear in the figure caption, and additional details are given in the Experimental Section and the Supporting Information. The structure of **3** shows slightly distorted square planar geometry at each metal center with both dppf P atoms trans to the bridging phosphido group. The ferrocene backbone is twisted out of the square plane of the molecule and, thus, is able to accommodate the P−P distance of 5.129 Å, which is considerably smaller than the distance of 6.920 Å found in the free ligand.[3] The conformation of the ferrocene is gauche eclipsed[4] with the torsion angle 70.42°.[5] The ferrocene backbone is slightly distorted, with the angle between Cp planes being 2.7(5)°. The ^1H NMR spectrum of **3** shows two signals due to the Cp protons, instead of the eight expected for the solid-state structure, perhaps due to a dynamic process in solution.

Dppf is known to act as a bridging ligand with a variety of transition metals.[4] Recently, for example, the Pd(II) cluster $[Pd_3Cl_2(dppf)(\mu\text{-dppf})(\mu_3\text{-S})_2]$ was characterized crystallographically.[6] There is also precedent for complexes like **2** and **3**, which contain bridging phosphido, hydrido, and diphosphine ligands, such as $[Co_2(CO)_4(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})]$,[7] $[Fe_2(Cp)_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})]$,[8] and $[Fe_2(CO)_4(\mu\text{-H})(\mu\text{-CO})(\mu\text{-PCy}_2)(\mu\text{-dppm})]$[9] (dppm = $Ph_2PCH_2PPh_2$).

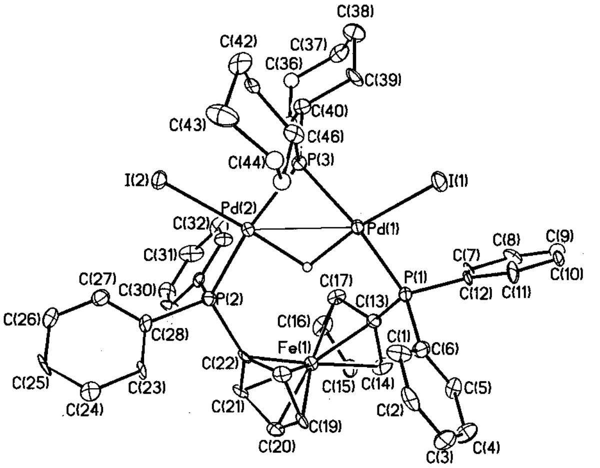
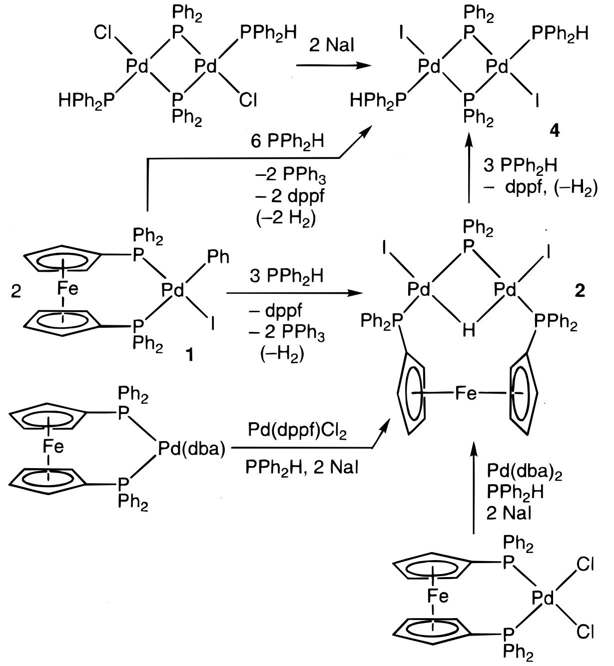


Figure 1. ORTEP diagram of **3**·THF with thermal ellipsoids at 30% probability. For clarity the THF molecule and hydrogen atoms, except the bridging hydrogen, are omitted. Selected bond lengths (Å) and angles (deg): Pd(1)−H(1) 1.77(12), Pd(2)−H(1) 1.85(11), Pd(1)−Pd(2) 2.8008(14), Pd(1)−P(1) 2.386(3), Pd(2)−P(2) 2.375(4), Pd(1)−P(3) 2.264(3), Pd(2)−P(3) 2.257(4); Pd(2)−P(3)−Pd(1) 76.55(11), P(3)−Pd(2)−P(2) 169.64(14), P(3)−Pd(1)−P(1) 168.80(14).

Scheme 1



The proposed dinuclear structure of **2** suggested two other syntheses using sources of Pd(0), Pd(II), iodide, and diphenylphosphine (Scheme 1). When PPh_2H and NaI are added to a mixture of $Pd(dba)_2$ and $Pd(dppf)Cl_2$ in THF, **2** forms rapidly in modest yield. Similarly, the reaction of Pd(dppf)(dba), $Pd(dppf)Cl_2$, PPh_2H, and NaI gives **2** in low yield.

Complex **2** decomposes in the presence of PPh_2H. This reaction was first observed in the original synthesis and during recrystallization of impure samples of **2**; it can be avoided by using a substoichiometric amount of the phosphine. Deliberate addition of 3 equiv of PPh_2H to **2** gives the known phosphido-bridged dimer $[Pd(I)(PPh_2H)(\mu\text{-PPh}_2)]_2$ (**4**) (Scheme 1) over 2 days.[10] Direct reaction of **1** with 3 equiv of PPh_2H in THF with heating at 60 °C for 2 h also gives **4** in good yield; as expected, PPh_3 and dppf are also formed.

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Table 1. Crystallographic Data for $Pd_2I_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-PCy}_2)$ (3)·THF, $[Pd(PPh_2H)(\mu\text{-PPh}_2)I]_2$ (4), $[Pd_2(\mu\text{-dcpm})(\mu\text{-PPh}_2)(PHPh_2)_2][I]$ (5), and $[Pd_2(dmpe)_2(\mu\text{-H})(\mu\text{-PCy}_2)][OTf]_2$ (8)·THF

	(**3**)·THF	(**4**)	(**5**)	(**8**)·THF
formula	$C_{50}H_{59}FeI_2OP_3Pd_2$	$C_{48}H_{42}I_2P_4Pd_2$	$C_{61}H_{78}IP_5Pd_2$	$C_{30}H_{63}F_6O_7P_5Pd_2S_2$
fw	1291.33	1209.30	1305.78	1081.57
space group	$P\bar{1}$	$P2_1/n$	$I2$	$P2_1/n$
a, Å	10.9984(4)	10.4481(2)	21.9383(1)	15.5310(2)
b, Å	12.2340(4)	9.3127(2)	25.3614(3)	17.6718(2)
c, Å	20.2598(6)	23.2617(3)	23.0561(1)	16.6645(2)
α, deg	97.8289(8)			
β, deg	99.4108(9)	90.3660(5)	90.130(1)	92.1200(2)
γ, deg	111.0779(8)			
V, Å^3	2452.5(2)	2263.32(5)	12828.06(17)	4570.64(7)
Z	2	2	8	4
cryst color, habit	orange plate	orange block	orange block	colorless block
D(calc), g/cm^3	1.749	1.774	1.352	1.572
μ(Mo Kα), cm^{-1}	24.09	23.33	12.0	11.16
temp, K	233(2)	173(2)	173(2)	173(2)
diffractometer	Siemens P4/CCD			
radiation	Mo Kα (λ = 0.71073 Å)			
$R(F)$, %[a]	5.31	2.20	10.58	2.83
$R(wF^2)$, %[a]	18.93	9.09	26.43	10.92

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$.

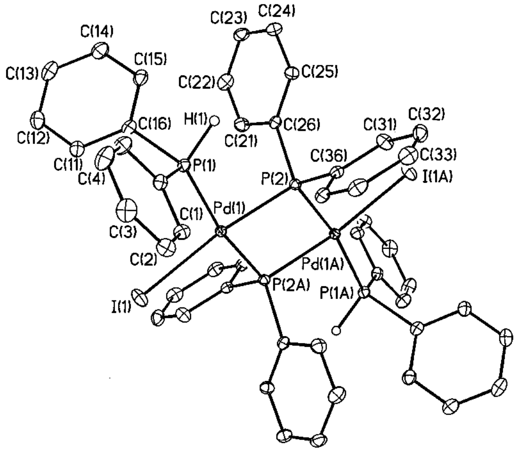
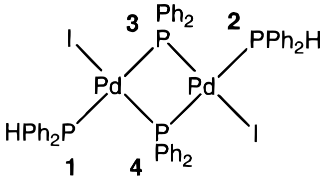


Figure 2. ORTEP diagram of **4** with thermal ellipsoids at 30% probability. All hydrogen atoms, except those of the phosphine ligand, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Pd(1A) 3.6400(7), Pd(1)−P(2) 2.2901(7), Pd(1)−P(1) 2.3289(7), Pd(1)−P(2A) 2.3311(7), Pd(1)−I(1) 2.6630(3); P(2)−Pd(1)−P(2A) 76.08(3), Pd(1)−P(2)−Pd(1A) 103.92(3).

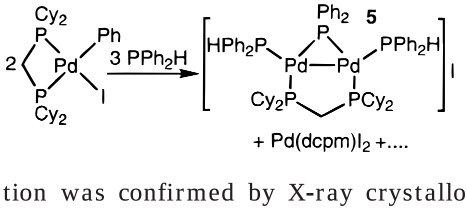
Chart 1. Atom Labeling and Coupling Constants (in Hz) for Complex 4: $^2J_{13}$ = 423.7, $^2J_{14}$ = 23.5, $^2J_{34}$ = −263[a,b]



[a] The results are in good agreement with the coupling constants (in Hz) reported for $[Pd(Cl)(PPh_2H)(\mu\text{-PPh}_2)]_2$: $^2J_{13}$ = 423.1, $^2J_{14}$ = 20.9, $^2J_{34}$ = −261.1. See: Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188−1200. [b]The sign of $^2J_{34}$ was preserved in agreement with the previously reported data, but it did not affect the results of the simulation.

Complex **4** was also prepared independently from the corresponding chloride dimer $[Pd(Cl)(PPh_2H)(\mu\text{-PPh}_2)]_2$ by a modification of the original synthesis of Hayter and was characterized spectroscopically as well as by X-ray crystallography (Table 1). The $^{31}P\{^1H\}$ NMR spectrum of **4** (CD_2Cl_2) shows two multiplets at δ 2.8 and −152.1, consistent with the AA′BB′ spin system (Chart 1). The X-ray crystal structure of **4** (Figure 2) is very similar to that of the chloride complex $[Pd(Cl)(PPh_2H)(\mu\text{-PPh}_2)]_2$.[11] The Pd−I bond (2.6630(3) Å) is longer than the Pd−Cl one (2.369(1) and 2.382(3) Å), and the Pd−P bond length for the phosphorus trans to halide is only slightly larger for **4** (2.2901(7) Å) than in the chloride complex, in which these Pd−P bond lengths are 2.266(1) and 2.275(3) Å. Otherwise, there is no significant difference between the two structures.

Dcpm Complexes Similar chemistry leading to the formation of a dinuclear μ-diphosphine μ-phosphido complex occurs with the small bite angle ligand dcpm ($Cy_2PCH_2PCy_2$), but with some important differences. Treatment of Pd(dcpm)(Ph)(I) with 1.5 equiv of PPh_2H gives a mixture of products. The $^{31}P\{^1H\}$ NMR spectrum of the major product (CD_3CN) shows three peaks: a triplet of triplets at δ 222.5 ($^2J_{PP}$ = 192, 26 Hz), a doublet of multiplets at δ 9.5 ($^2J_{PP}$ = 192 Hz), and a multiplet at δ −14.5. No hydride resonance is visible in the ^1H NMR spectrum. These observations are consistent with the formation of the Pd(I) complex $[Pd_2(\mu\text{-dcpm})(\mu\text{-PPh}_2)(PPh_2H)_2]$ [I] (**5**) (eq 2). This structural formulation was confirmed by X-ray crystallography (Figure 3 and Table 1), which, due to the high R-factor, was used only to establish the connectivity and will not be discussed in detail. Unfortunately, cation **5** is formed along with $Pd(dcpm)I_2$ (identified by independent synthesis) and other unidentified products, from which it is difficult to separate, so it could not be obtained in pure form for elemental analysis. However, the presence of PH groups was confirmed by both the IR spectrum (KBr, 2292 cm^{-1}) and the ^1H NMR spectrum (CD_2Cl_2, m, δ 6.46).



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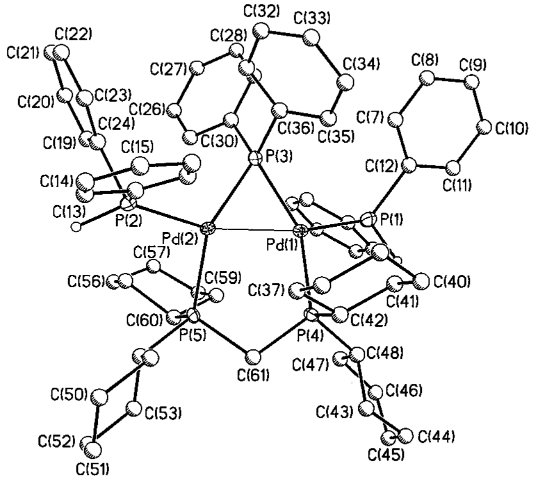
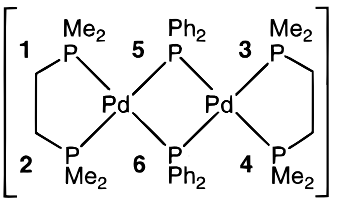


Figure 3. ORTEP diagram of **5** with thermal ellipsoids at 30% probability. The iodide counterion and all hydrogen atoms, except those of the phosphine ligand, are omitted for clarity.

Chart 2. Atom Labeling and Coupling Constants (in Hz) for Complex 6: $^2J_{16} = 312.5$, $^2J_{15} = 8.3$, $^2J_{12} = -3.2$, $^4J_{14} = -12.1$, $^4J_{13} = -3.4$, $^2J_{56} = -234.4$[a]



[a] The results are similar to those reported for $[Pd(dppe)(\mu\text{-}PPh_2)]_2^{2+}$: $^2J_{16} = 311.0$, $^2J_{15} = 28.2$, $^2J_{12} = -17.5$, $^4J_{14} = 0$, $^4J_{14} = 0$, $^4J_{56} = -349.4$. See: Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188−1200.

Complex **5** is structurally similar to several related Pd(I) complexes with *μ*-dppm ligands, such as $[M_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)(PPh_3)_2]^+$ (M = Pd, Pt)[12] and $[Pd(\mu\text{-}dppm)(\mu\text{-}P(t\text{-}Bu)_2)(PR_3)_2]^+$ (R = Me, Et), reported recently by Leoni.[13] However, as far as we know, the only other Pd(I) compound featuring a bridging dcpm ligand is $[PdCl(\mu\text{-}dcpm)]_2$.[14]

Dmpe Complexes The syntheses of the dinuclear dppf and dcpm complexes described above show that changes in bite angle significantly affect the observed chemistry. Similarly, using the smaller dmpe ($Me_2PCH_2CH_2PMe_2$) instead of dppe or dcpe gives dinuclear complexes instead of the expected mononuclear cations.

Treatment of Pd(dmpe)(Me)(Cl)[15] with AgOTf and PPh_2H gives a mixture of the phosphido-bridged dimer $[Pd(dmpe)(\mu\text{-}PPh_2)]_2[OTf]_2$ (**6**) and a trace of $[Pd_2(dmpe)_2(\mu\text{-}H)(\mu\text{-}PPh_2)][OTf]_2$ (**7**) (Scheme 2). Alternatively, **6** can be prepared by reaction of **4** or the analogous chloride complex $[Pd(Cl)(PPh_2H)(\mu\text{-}PPh_2)]_2$ with 2 equiv of dmpe and AgOTf in THF. Dimer **6** was characterized spectroscopically. The ^{31}P NMR (CD_2Cl_2) spectrum shows two multiplets at *δ* 36.2 and −113.3. The coupling constants for this AA′A″A‴XX′ spin system, found by spectral simulation, agree reasonably well with the results for the known $[Pd(dppe)(\mu\text{-}PPh_2)]_2^{2+}$ (Chart 2).[16] Although hydride **7** could not be separated from **6**, it was identified by NMR in comparison to the analogous *μ*-PCy_2 complex **8** (see below). The ^{31}P NMR spectrum of **7** (acetone-d_6) contains an apparent triplet at *δ* 168.3 ($^2J_{PP} = 285$ Hz, PCy_2) and a set of multiplets at *δ* 43.3−40.7 (dmpe). The bridging hydride signal appears in the ^1H NMR spectrum (acetone-d_6) at *δ* −6.04 (t ($^2J_{PH} = 80$ Hz) of d ($^2J_{PH} = 17$ Hz)).

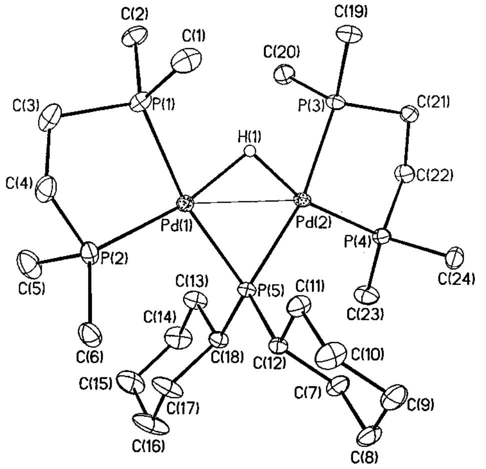


Figure 4. ORTEP diagram of **8**·THF with thermal ellipsoids at 30% probability. The triflate counterion, THF solvent molecule, and all hydrogen atoms, except the bridging hydrogen atom, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−H(1) 1.80(3), Pd(2)−H(1) 1.72(3), Pd(1)−P(1) 2.3216(8), Pd(1)−P(2) 2.2778(7), Pd(1)−P(5) 2.3023(7), Pd(1)−Pd(2) 2.8041(3), Pd(2)−P(3) 2.3311(7), Pd(2)−P(4) 2.2879(7), Pd(2)−P(5) 2.3153(6); P(2)−Pd(1)−P(1) 86.44(3), P(4)−Pd(2)−P(3) 85.86(2), Pd(1)−P(5)−Pd(2) 74.78(2), P(5)−Pd(1)−P(1) 168.71(3), P(5)−Pd(2)−P(3) 167.45(2).

Analogous chemistry with PCy_2H (Scheme 2) is not so clean. Reaction of Pd(dmpe)(Me)(Cl) with AgOTf and PCy_2H gives a clear solution containing mostly the expected cationic complex $[Pd(dmpe)(Me)(PCy_2H)]^+$ (identified by $^{31}P\{^1H\}$ NMR) and a small amount of unidentified impurities. Attempted workup led to substantial decomposition. A single crystal was isolated from such a mixture and shown to be $[Pd_2(dmpe)_2(\mu\text{-}H)(\mu\text{-}PCy_2)][OTf]_2$ (**8**) by X-ray crystallography (Table 1). The crystal structure of **8**·THF (Figure 4) exhibits slightly distorted square planar geometry, with a Pd−Pd distance of 2.8041(3) Å.

As with dppf complex **2**, complex **8** could also be produced from (dmpe)Pd(II) and (dmpe)Pd(0) fragments and PCy_2H. Thus, the reaction of in situ prepared Pd(dmpe)(dba) and $Pd(dmpe)I_2$ with PCy_2H and 2 equiv of AgOTf gives **8** in low yields. Unfortunately this reaction was irreproducible, so amounts of pure **8** sufficient for elemental analysis could not be obtained, and it was characterized spectroscopically. In the ^{31}P NMR (CD_2Cl_2) spectrum, the bridging phosphido group gives rise to an apparent triplet at *δ* 244.2 ($^2J_{PP} = 266$ Hz); no coupling to the cis dmpe P nuclei was observed. The dmpe signals appear as multiplets at *δ* 38.3 and

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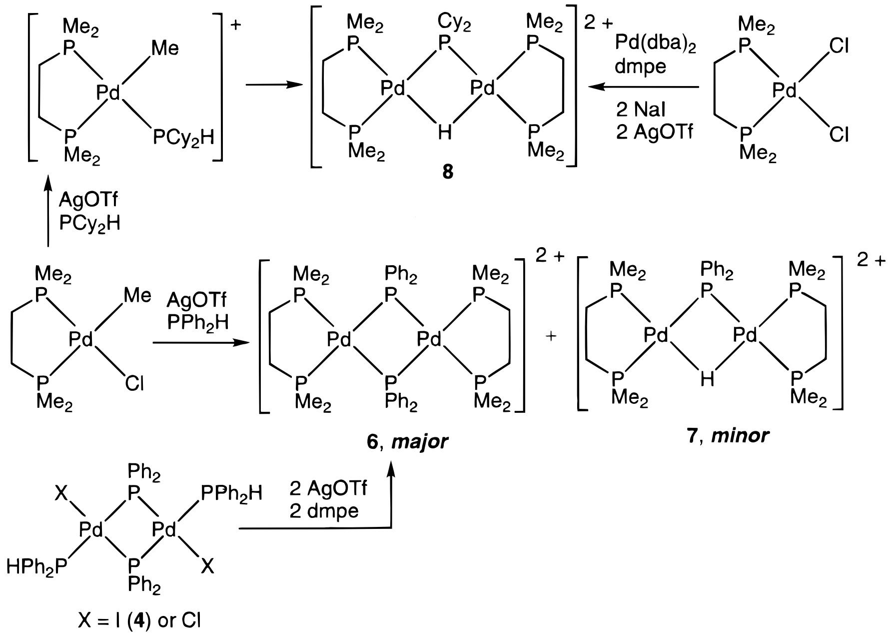
Scheme 2



38.1. In the ^{1}H NMR spectrum (CD_2Cl_2), the bridging hydride signal appears at δ −6.38 as a triplet ($^2J_{PH}$ = 77 Hz) of doublets ($^2J_{PH}$ = 14 Hz).

Pd−Pd Bonding in Dinuclear Complexes. Pd−Pd bonding in dinuclear phosphido-bridged Pd(I) complexes such as **5** has been characterized structurally and by computational studies, as discussed recently by Mealli and co-workers.[17] However, the presence of Pd−Pd bonding in dinuclear Pd(II) complexes has been more controversial. As discussed by Clegg, short Pd−Pd distances observed in X-ray crystal structures of Pd(II) complexes do not require the presence of Pd−Pd interactions.[18] The very long Pd−Pd distance in **4** (3.6400(7) Å) and the upfield ^{31}P NMR chemical shift for the μ-PPh_2 groups (δ −152.1) suggest, as expected for square planar Pd(II), that there is no Pd−Pd bonding in this complex. In contrast, the downfield ^{31}P NMR chemical shifts for the μ-phosphido ligands in **2**, **3**, **7**, and **8** (δ 266.2, 349.6, 168.3, and 244.2, respectively) are usually considered to indicate the presence of a metal−metal bond. The Pd−Pd distances in **3** (2.8008(14) Å) and **8** (2.8041(3) Å) are much shorter than in **4**, consistent with the NMR data. As noted by van Leeuwen et al., however, such low-field ^{31}P NMR chemical shifts are routinely observed in dinuclear complexes containing both μ-phosphido and μ-hydrido ligands. The three-center, two-electron interaction in the MHM unit may also be described as a protonated metal−metal bond.[19]

Conclusion. Small changes in the diphosphine ligand lead to big differences in the reaction of complexes Pd(diphosphine)(R)(X) (R = Ph or Me, X = halide) with secondary phosphines with or without added AgOTf as a halide-abstracting agent. The ligands dppf and dcpm, which have large and small bite angles, respectively, give dinuclear complexes that both have bridging diphosphine and phosphido ligands, but dppf-containing **2** and **3** are Pd(II) complexes with a bridging hydride, and dcpm complex **5** is a Pd(I) cation with no hydride. The dmpe ligand was not observed to bridge, but it gave dinuclear complexes **6**−**8** with bridging phosphido and/or hydrido ligands. Presumably, these results are a consequence of several factors, including the lability of the diphosphine and halide ligands, the acidity of coordinated secondary phosphines, and steric effects at the metal center.

Experimental Section

General Experimental Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, and toluene were dried and distilled before use by employing Na/benzophenone. CH_2Cl_2 was distilled from CaH_2. Acetone and acetonitrile were degassed by purging with N_2 and stored over molecular sieves.

Unless otherwise noted, all NMR spectra were recorded by using a Varian 300 MHz spectrometer. ^{1}H or ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H_3PO_4 (85%) used as an external reference. Coupling constants are reported in hertz as absolute values unless noted otherwise. Unless indicated, peaks in NMR spectra are singlets. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR machine and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. Low-resolution FAB mass spectroscopy was performed on a VG ZAB-SE instrument at the University of Illinois.

Unless otherwise noted, reagents were from commercial suppliers. The following compounds were made by the literature methods: $[Pd(\mu\text{-}PPh_2)(Cl)(PPh_2H)]_2$,[10] Pd(dppf)(Ph)(I),[20] Pd(cod)(Me)(Cl),[21] Pd(dppf)Cl_2,[22] $Pd(dba)_2$,[23] Pd(dppf)(dba),[24] trans-$Pd(PPh_3)_2$(Ph)(I),[25] and Pd(cod)Cl_2.[26]

$Pd_2(I)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppf)$ (2). 1. To a yellow slurry of Pd(dppf)(Ph)(I) (117 mg, 0.14 mmol) in THF/MeCN (2 mL, 5:1

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mixture) was added PPh_2H (38 mg, 0.20 mmol). The remaining solid rapidly dissolved, forming an orange solution. After 15 min of stirring the solution acquired a dark orange/purple color. Petroleum ether was added, and cooling to −25 °C gave the product as 61 mg (75% yield) of orange solid. The other products were isolated together from the mother liquor and identified as PPh_3 and dppf by spiking ($^{31}P\{^1H\}$ NMR). Anal. Calcd for $C_{46}H_{39}P_3I_2FePd_2 \cdot 1.25THF$: C, 47.22; H, 3.81. Found: C, 47.11; H, 3.54. The presence of THF was confirmed quantitatively by ^1H NMR.

2. To a slurry of $Pd(dppf)Cl_2$ (69 mg, 0.09 mmol) and $Pd(dba)_2$ (54 mg, 0.09 mmol) in 3 mL of THF were added PPh_2H (17 mg, 0.09 mmol, via microliter syringe) and NaI (30 mg, 0.20 mmol), and the resulting black slurry was allowed to stand for 5 days. The slurry was filtered, and 11 mg of red crystals was separated. The solid residue was redissolved in CH_2Cl_2 and filtered. Ether was added, and cooling to −30 °C gave an additional 10 mg of the product (21 mg, 19% total yield) as red crystals.

3. To a stirred slurry of Pd(dppf)(dba) (30 mg, 0.03 mmol) and $Pd(dppf)Cl_2$ (25 mg, 0.03 mmol) in 3 mL of THF were added PPh_2H (6 mg, 0.03 mmol) and NaI (10 mg, 0.07 mmol). The initially orange slurry darkened and then slowly turned purple. The mixture was filtered; the ^{31}P NMR spectrum of the filtrate showed that complexes **2** and **4** were formed.

^1H NMR (CD_2Cl_2): δ 8.06−8.00 (m, 4H, Ph), 7.70−7.55 (m, 8H, Ph), 7.55−7.35 (m, 18H, Ph), 4.50 (br, 4H, Cp), 3.98 (broad, 4H, Cp), −8.27 (br, 1H, Pd−H−Pd). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 266.2 (t, $^2J_{PP} = 332$), 15.0 (d, $^2J_{PP} = 332$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 136.3 (m), 136.1−135.8 (m), 131.4 (m), 130.1, 128.2−127.9 (m), 77.0−76.3 (m), 72.9 (broad), 68.0. IR: 3049, 2974, 2858, 1959, 1584, 1479, 1433, 1385, 1307, 1168, 1096, 1066, 1027, 998, 898, 838, 742, 693. Low-resolution FAB-MS (3-NBA): 1207.8 (parent ion), 1078.9 ($Pd_2(dppf)(PPh_2)(I)$), 951.0, 894.8 ($Pd_2(dppf)(I)$), 685.9, 660, 583.0, 500.8, 460.1.

$Pd_2(I)_2(\mu\text{-}H)(\mu\text{-}PCy_2)(\mu\text{-}dppf)$ (3). To a yellow slurry of Pd(dppf)(Ph)(I) (197 mg, 0.23 mmol) in THF/MeCN (2 mL, 5:1 mixture) was added PCy_2H (45 mg, 0.23 mmol). The remaining solid dissolved, forming a yellow solution. The solution was allowed to stand for 3 days; then petroleum ether was added, and cooling to −25 °C gave the product as 81 mg (58% yield) of olive-green solid. Prolonged standing of the original reaction mixture gave crystals of a THF solvate, as shown by X-ray crystallography and elemental analysis. Anal. Calcd for $C_{46}H_{51}P_3I_2FePd_2 \cdot THF$: C, 46.50; H, 4.61. Found: C, 46.58; H, 4.53.

^1H NMR (CD_2Cl_2): δ 7.60−7.36 (m, 20H, Ph), 4.38 (4H, Cp), 3.92 (4H, Cp), 3.30−3.07 (m, 2H, Cy), 2.20−2.05 (m, 3H, Cy), 1.96−1.61 (m, 9H, Cy), 1.45−1.16 (m, 6H, Cy), 0.90−0.83 (m, 2H, Cy), −8.84 (1H, Pd−H−Pd). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 349.6 (t, $^2J_{PP} = 299$), 14.0 (d, $^2J_{PP} = 299$). IR: 3052, 2925, 2849, 1628, 1481, 1434, 1385, 1169, 1099, 1028, 999, 846, 818, 742.

$[Pd(PPh_2H)(I)(\mu\text{-}PPh_2)]_2$ (4). 1. This is a minor modification of Hayter's synthesis.[10] $[Pd(PPh_2H)(Cl)(\mu\text{-}PPh_2)]_2$ (257 mg, 0.25 mmol) was dissolved in 10 mL of CH_2Cl_2. NaI (80 mg, 0.54 mmol) was added as a solid, and the yellow slurry was stirred for 16 h. Over the course of the reaction the color of the slurry changed from yellow to bright orange. The solution was filtered twice, and the solid residue was dried in a vacuum to give 248 mg (82% yield) of orange solid product. Anal. Calcd for $C_{48}H_{42}P_4I_2Pd_2$: C, 47.67; H, 3.50. Found: C, 47.73; H, 3.37.

2. Pd(dppf)(Ph)(I) (66 mg, 0.08 mmol) was suspended in 1 mL of THF. Upon addition of PPh_2H (43 mg, 0.24 mmol) to the slurry the remaining solid dissolved and the solution acquired a dark orange color. The solution was heated at 60 °C for 2 h, causing a color change to light orange. Addition of petroleum ether and cooling to −25 °C afforded the product as 35 mg of orange crystals (76% yield). Additional recrystallization from CH_2Cl_2 gave crystals of X-ray quality.

^1H NMR ($CDCl_3$): δ 8.00−7.00 (m, 40H, Ar), 5.08 (m, $^1J_{PH} = 358$, 2H, P−H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.8 (m), −152.1 (m). IR: 3049, 2923, 2850, 2321 (PH), 1962, 1887, 1811, 1662, 1581, 1476, 1433, 1304, 1261, 1181, 1157, 1093, 1025, 854, 737, 690.

Pd(dcpm)(Ph)(I). To a solution of *trans*-$Pd(PPh_3)_2(Ph)(I)$ (1.20 g, 1.44 mmol) in toluene (6 mL) was transferred a solution of dcpm (589 mg, 1.44 mmol) in toluene (6 mL). The pale yellow suspension was stirred at room temperature for 12 h. The solid was collected on a fine frit and washed with petroleum ether (20 mL) to give 994 mg (96%) of crude product. A sample recrystallized from CH_2Cl_2/ether at −25 °C was found to be a CH_2Cl_2 solvate by elemental analysis. Anal. Calcd for $C_{31}H_{51}P_2IPd \cdot CH_2Cl_2$: C, 47.81; H, 6.65. Found: C, 47.74; H, 6.80.

^1H NMR ($CDCl_3$): δ 7.55−7.33 (m, 2H, Ar), 6.96 (br, 2H, Ar), 6.79−6.75 (m, 1H, Ar), 2.85−2.79 (m, 2H, CH_2), 2.15−1.21 (m, 42H, Cy), 0.98 (br, 2H, Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −15.6 (d, $^2J_{PP} = 69$), −38.8 (d, $^2J_{PP} = 69$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.1 (dd, $^2J_{PC} = 13$, 147, Ar), 137.7 (Ar, CH), 126.8 (d, $^3J_{PC} = 9$, Ar, CH), 122.6 (Ar, CH), 34.8−34.7 (m, Cy, CH), 33.5 (dd, $J_{PC} = 3$, 20, Cy, CH), 29.3 (Cy, CH_2), 29.1 (Cy, CH_2), 27.9 (Cy, CH_2), 27.4 (Cy, CH_2), 27.2 (Cy, CH_2), 27.1 (Cy, CH_2), 27.0 (Cy, CH_2), 26.8 (Cy, CH_2), 26.6 (Cy, CH_2), 26.4 (Cy, CH_2), 26.0 (Cy, CH_2), 25.8 (Cy, CH_2), 23.9−22.8 (CH_2). IR: 2919, 2837, 1560, 1443, 720, 691.

$[Pd_2(\mu\text{-}PPh_2)(\mu\text{-}dcpm)(PPh_2H)_2][I]$ (5). To a slurry of Pd(dcpm)(Ph)(I) (148 mg, 0.21 mmol) in 2 mL of THF was added PPh_2H (57 mg, 0.31 mmol). The remaining solid dissolved, forming a yellow solution. After 12 h the solution, now dark orange, was filtered. The solvent was removed under vacuum, and the residue was redissolved in toluene (5 mL). The dark orange solution was filtered and allowed to stand at room temperature. After 2 days the crude product precipitated as 85 mg of orange solid, which was a mixture of **5** (major) and $Pd(dcpm)I_2$ (minor, identified by the independent synthesis below). Orange crystals of **5** separated manually from this material were used for X-ray crystallography, but the bulk material could not be obtained analytically pure and free of $Pd(dcpm)I_2$.

$^{31}P\{^1H\}$ NMR (CD_3CN): δ 222.5 (tt, $^2J_{PP} = 192$, 26), 9.5 (dm, $^2J_{PP} = 192$), −14.5 (m). ^1H NMR (CD_2Cl_2): δ 7.40−7.17 (m, 30H, Ph), 6.46 (m, 2H, PH), 3.23 (m, 2H, CH_2), 2.40−1.01 (m, 44H, Cy). IR: 3048, 2924, 2849, 2292, 1479, 1435, 1179, 1094, 850, 735.

$Pd(dcpm)I_2$. To $Pd(cod)Cl_2$ (73 mg, 0.26 mmol) in 2 mL of toluene was added dcpm (105 mg, 0.26 mmol), and the resulting slurry was stirred for 5 min. The solution was decanted and the solid was washed with 3 × 10 mL of petroleum ether and dried under vacuum to give $Pd(dcpm)Cl_2$ as 147 mg (98% yield) of off-white solid, which was used without additional purification. To a white slurry of $Pd(dcpm)(Cl)_2$ (53 mg, 0.09 mmol) in 3 mL of toluene was added NaI (at least a 2-fold excess). After 30 min of stirring, the yellow solution was decanted and the solid residue was washed with ether and dried under vacuum. The yellow solid was recrystallized from CH_2Cl_2/ether at −25 °C to give 59 mg (85% yield) of yellow crystalline solid. Anal. Calcd for $C_{25}H_{46}P_2I_2Pd$: C, 39.06; H, 6.03. Found: C, 39.49; H, 6.14.

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^{1}H NMR (CD_2Cl_2): δ 3.14 (t, 2H, $^2J_{PH}$ = 10, CH_2), 2.44–2.28 (m, 8H, Cy), 2.23–2.11 (m, 4H, Cy), 2.04–1.90 (m, 8H, Cy), 1.84–1.75 (m, 4H, Cy), 1.67–1.24 (m, 20H, Cy). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −42.1. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 36.9 (m, CH), 29.4, 28.4, 27.2 (m), 26.8 (m), 26.0, 21.5 (t, $^1J_{PC}$ = 20, CH_2). IR: 2928, 2850, 2666, 1623, 1445, 1346, 1326, 1293, 1268, 1199, 1179, 1114, 1001, 916, 888, 851, 821, 770.

Pd(dmpe)(Me)(Cl). This complex was reported previously by Yamamoto and co-workers.[15] We describe an alternative synthesis and additional (^{31}P and ^{13}C NMR) spectroscopic characterization. To a white slurry of Pd(cod)(Me)(Cl) (525 mg, 1.98 mmol) in 5 mL of toluene was added dmpe (330 μL, 1.98 mmol) via microliter syringe. The color of the slurry immediately changed to beige. After 1 h of stirring the slurry was filtered on a frit. The solid residue was washed with 4 × 5 mL of petroleum ether and dried in vacuo to give the product as 403 mg (1.31 mmol, 66% yield) of gray solid. Anal. Calcd for $C_7H_{19}ClP_2Pd$: C, 27.38; H, 6.24. Found: C, 27.32; H, 6.27.

^{1}H NMR (CD_2Cl_2): δ 2.00–1.55 (m, 4H, CH_2), 1.53 (d, $^2J_{PH}$ = 11, 6H, Me), 1.43 (d, $^2J_{PH}$ = 9, 6H, Me), 0.30 (dd, $^3J_{PH}$ = 4, 8, 3H, Me). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 39.8 (d, $^2J_{PP}$ = 23), 26.8 (d, $^2J_{PP}$ = 23). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 31.2 (dd, J_{PC} = 21, 15, CH_2), 25.4 (dd, J_{PC} = 16, 6, CH_2), 13.7 (d, $^1J_{PC}$ = 20, Me), 12.0 (d, $^1J_{PC}$ = 11, Me), 3.4 (dd, $^2J_{PC}$ = 69, 3, Me).

[Pd(μ-PPh$_2$)(dmpe)]$_2$[OTf]$_2$ (6). 1. Pd(dmpe)(Me)(Cl) (43 mg, 0.14 mmol) was suspended in 2 mL of 1:1 THF/MeCN. AgOTf (36 mg, 0.14 mmol) and PPh_2H (26 mg, 0.14 mmol) were added. The solution was stirred for 5 min and filtered. The resulting yellow solution was kept at room temperature for 1 day, petroleum ether was added, and cooling to −30 °C gave the crude product as 48 mg (93% yield) of orange solid contaminated with a small amount of [Pd$_2$(dmpe)$_2$(μ-H)(μ-PPh$_2$)][OTf]$_2$ (**7**). ^{31}P{^{1}H} NMR (acetone-d_6): δ 168.3 (t, $^2J_{PP}$ = 285), 43.3–40.7 (m). Selected ^{1}H NMR (acetone-d_6): δ −6.04 (dt, $^2J_{PH}$ = 80, 17).

2. To a slurry of [Pd(Cl)(μ-PPh$_2$)(PPh$_2$H)]$_2$ (74 mg, 0.07 mmol) in 2 mL of THF were added AgOTf (37 mg, 0.14 mmol) and dmpe (22 mg, 0.14 mmol). The resulting yellow solution was allowed to stand for 12 h and then filtered. Petroleum ether was added, and cooling to −30 °C gave the product as 65 mg (76% yield) of orange solid. Anal. Calcd for $C_{38}H_{52}P_6F_6S_2O_6Pd_2$: C, 38.63; H, 4.44. Found: C, 38.39; H, 4.37.

^{1}H NMR (CD_2Cl_2): δ 7.60–7.51 (m, 8H, Ph), 7.32–7.21 (m, 12H, Ph), 2.04–1.81 (m, 8H, CH_2), 1.16–1.13 (m, 24H, Me). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 38.8–33.6 (m), −109.4 to −117.2 (m). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 135.8 (m), 133.4–133.1 (m), 130.4, 129.2 (m), 28.5–27.9 (m), 13.0–12.6 (m). IR: 3052, 2987, 2908, 1631, 1582, 1475, 1435, 1260, 1223, 1153, 1094, 1030, 941, 901, 844, 798, 747.

Synthesis and Decomposition of [Pd(dmpe)(Me)(PCy$_2$H)][OTf]. To a white slurry of Pd(dmpe)(Me)(Cl) (60 mg, 0.20 mmol) in 5:1 THF/MeCN was added AgOTf (50 mg, 0.20 mmol) in 1 mL of THF, then PCy_2H (39 mg, 0.20 mmol) via microliter syringe. The resulting gray slurry was stirred for 5 min and filtered to give a yellow solution, containing [Pd(dmpe)(Me)(PCy$_2$H)][OTf]. ^{31}P{^{1}H} NMR (THF): δ 31.8 (dd, $^2J_{PP}$ = 374, 25), 20.0 (dd, $^2J_{PP}$ = 36, 25), 8.5 (dd, $^2J_{PP}$ = 374, 36).

The solvent was removed under vacuum, and the resulting oily residue was washed with petroleum ether, dried, and dissolved in 2 mL of THF, then filtered to give a tan solution. No visible change in the solution occurred after 1 day of standing, but the ^{31}P{^{1}H} NMR spectrum showed decomposition of [Pd(dmpe)(Me)(PCy$_2$H)][OTf] and formation of at least three new products.

[Pd$_2$(dmpe)$_2$(μ-H)(μ-PCy$_2$)][OTf]$_2$ (8). 1. To a slurry of Pd(dmpe)(Me)(Cl) (75 mg, 0.24 mmol) in 2 mL of 5:1 THF/MeCN were added AgOTf (63 mg, 0.24 mmol) and PCy_2H (49 mg, 0.24 mmol). The solvent was removed under vacuum, the solid residue was dissolved in THF (2 mL), petroleum ether was added, and the solution was stored at −25 °C for 3 weeks to give a single clear crystal used for the crystal structure determination.

2. To a slurry of Pd(dba)$_2$ (89 mg, 0.15 mmol) in 3 mL of THF was added dmpe (25 μL, 0.15 mmol) via microliter syringe. After 20 min of stirring the dark solution was filtered and PCy_2H (31 mg, 0.15 mmol) was added via microliter syringe. In a separate flask, to a slurry of Pd(cod)Cl$_2$ (44 mg, 0.15 mmol) in 3 mL of THF was added dmpe (25 μL, 0.15 mmol), and the slurry was stirred for 30 min. AgOTf (80 mg, 0.31 mmol) was added to the slurry in 1 mL of THF. A gray precipitate formed, and the yellow solution was filtered and added to the Pd(dba)$_2$/dmpe/PCy$_2$H solution immediately after the addition of PCy_2H. No visible reaction occurred. The dark orange solution was allowed to stand at room temperature for 5 days, during which time black solid precipitated. The solution was decanted, and the solid residue was washed with 3 × 5 mL of ether and dried under vacuum. The solid was suspended in 5 mL of CH_2Cl_2 and stirred for 1 h, then filtered. Ether was added to the clear solution, and cooling to −25 °C gave the product as 7 mg (9% yield) of beige solid, which still contained impurities.

^{1}H NMR (CD_2Cl_2): δ 2.48–2.10 (m, 8H, CH_2), 1.96–1.66 (m), 1.40–1.22 (m), 1.10–0.96 (m), −6.39 (td, $^2J_{PH}$ = 17, 77, 1H, PH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 244.2 (t, $^2J_{PP}$ = 266, PCy$_2$), 38.3 (m, *trans*-dmpe), 38.1 (m, *cis*-dmpe).

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 1. The systematic absences in the diffraction data for **8** and **4** are uniquely consistent for the reported space group. No evidence of symmetry higher than triclinic was observed in the diffraction data for **3**. The centrosymmetric space group $P\bar{1}$ was chosen for **3**, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. SADABS empirical absorption corrections were applied to all four structures.

The asymmetric unit of **3** contains a palladium dimer complex and a THF molecule. All non-hydrogen atoms of **3**, except C(9), C(35), C(36), C(44), and C(45), which persistently remained nonpositive definite, and the non-hydrogen atoms of the THF molecule were refined with anisotropic displacement parameters. All phenyl rings of **3** were fixed as rigid planar groups. The bridging hydrogen atom was located from a difference map in which the coordinate was free to refine and the thermal parameter was set as an idealized contribution. All other hydrogen atoms of **3** were treated as idealized contributions. The asymmetric unit of **4** contains half of a palladium dimer, which lies on an inversion center. All non-hydrogen atoms of **8** and **4** were refined with anisotropic displacement coefficients. The bridging hydrogen atom of **8** and the phosphine hydrogen atom of **4** were located from the difference map.

For **5**, diffraction symmetry was restricted to the monoclinic crystal system, and systematic absences in the data indicated the space groups *I*2, *Im*, or *I*2/*m*. E-statistics strongly suggested a noncentrosymmetric setting; *I*2 was initially chosen based on its higher frequency of occurrence and later confirmed by the results of the refinement process. The structure was solved by direct methods. The asymmetric unit consists of two independent cations and two iodide counterions, one located in a general position and the other divided between two 2-fold sites. The hand reported was confirmed by refinement of the Flack parameter, 0.10(5). All phenyl rings were treated as rigid, planar hexagons. The low quality of the data due to a very high mosaic spread in all specimens examined allowed anisotropic refinement of only the Pd and P atoms. All H atoms were treated as idealized contributions (d(CH) = 0.95, d(P–

H) = 1.40 Å). All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library.[27]

Acknowledgment. We thank the NSF Career Program, DuPont, and Union Carbide (Innovation Recognition Award) for support, the Department of Education for a GAANN fellowship for M.A.Z, and Jeff Nagle (Bowdoin College) for a helpful discussion. The University of Delaware acknowledges the NSF (Grant CHE-9628768) for their support of the purchase of the CCD-based diffractometer.

Supporting Information Available: Details of the crystal structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] Sheldrick, G. *SHELXTL*; Siemens XRD: Madison, WI.