

## Using Ligand Bite Angles To Control the Hydricity of Palladium Diphosphine Complexes

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**Abstract:** A series of [Pd(diphosphine)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and Pd(diphosphine)<sub>2</sub> complexes have been prepared for which the natural bite angle of the diphosphine ligand varies from 78° to 111°. Structural studies have been completed for 7 of the 10 new complexes described. These structural studies indicate that the dihedral angle between the two planes formed by the two phosphorus atoms of the diphosphine ligands and palladium increases by over 50° as the natural bite angle increases for the [Pd(diphosphine)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> complexes. The dihedral angle for the Pd(diphosphine)<sub>2</sub> complexes varies less than 10° for the same range of natural bite angles. Equilibrium reactions of the Pd(diphosphine)<sub>2</sub> complexes with protonated bases to form the corresponding [HPd(diphosphine)<sub>2</sub>]<sup>+</sup> complexes were used to determine the pK<sub>a</sub> values of the corresponding hydrides. Cyclic voltammetry studies of the [Pd(diphosphine)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> complexes were used to determine the half-wave potentials of the Pd(II/I) and Pd(I/0) couples. Thermochemical cycles, half-wave potentials, and measured pK<sub>a</sub> values were used to determine both the homolytic ([HPd(diphosphine)<sub>2</sub>]<sup>+</sup> → [Pd(diphosphine)<sub>2</sub>]<sup>+</sup> + H•) and the heterolytic ([HPd(diphosphine)<sub>2</sub>]<sup>+</sup> → [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> + H<sup>-</sup>) bond-dissociation free energies, ΔG<sub>H•</sub><sup>o</sup> and ΔG<sub>H<sup>-</sup></sub><sup>o</sup>, respectively. Linear free-energy relationships are observed between pK<sub>a</sub> and the Pd(I/0) couple and between ΔG<sub>H•</sub><sup>o</sup> and the Pd(II/I) couple. The measured values for ΔG<sub>H•</sub><sup>o</sup> were all 57 kcal/mol, whereas the values of ΔG<sub>H<sup>-</sup></sub><sup>o</sup> ranged from 43 kcal/mol for [HPd(depe)<sub>2</sub>]<sup>+</sup> (where depe is bis-(diethylphosphino)ethane) to 70 kcal/mol for [HPd(EtXantphos)<sub>2</sub>]<sup>+</sup> (where EtXantphos is 9,9-dimethyl-4,5-bis-(diethylphosphino)xanthene). It is estimated that the natural bite angle of the ligand contributes approximately 20 kcal/mol to the observed difference of 27 kcal/mol for ΔG<sub>H<sup>-</sup></sub><sup>o</sup>.

### Introduction

Transition-metal phosphine complexes are used extensively as catalysts for many important industrial applications. Most of the early catalysts used simple monodentate phosphine ligands, and the reactivities of complexes are understood largely in terms of steric and electronic effects such as the  $\theta$  and  $\chi$  parameters developed by Tolman.<sup>1</sup> In many cases, researchers found that bidentate diphosphine ligands gave enhanced rates and selectivities for certain reactions when compared to the monophosphine ligands. Although Tolman cone angles can be applied to bidentate diphosphines, the constraints of the backbone of the ligand limit their applicability. To better explain the reactivity of chelating diphosphine ligands, Casey and Whiteker devised the concept of the natural bite angle.<sup>2</sup> They defined the natural bite angle as the chelation angle preferred by the ligand backbone. Casey and Whiteker used molecular mechanics calculations to determine the natural bite angle of various diphosphine ligands, and they found good agreement between calculated angles and observed angles in crystal

structures. Similarly, Dierkes and van Leeuwen performed a careful analysis of the Cambridge Structural Database and confirmed that the average bite angle in known crystal structures agrees with the values calculated using molecular mechanics.<sup>3</sup> The natural bite angles of a wide variety of diphosphine ligands used in catalysis have been calculated and range from 72° to 131°.

The concept of the natural bite angle of diphosphine ligands as applied to transition-metal phosphine catalysts has been reviewed recently by van Leeuwen and co-workers.<sup>4,5</sup> Ligand bite angles significantly affect the rates and selectivities of hydroformylation, hydrocyanation, allylic alkylation, and cross-coupling reactions. For example, van Leeuwen and co-workers have used a series of xanthene-based diphosphines to probe the effect of the natural bite angle without changing steric or electronic properties of the ligands.<sup>6</sup> In these studies, the natural bite angle was varied by changing the size of the middle ring

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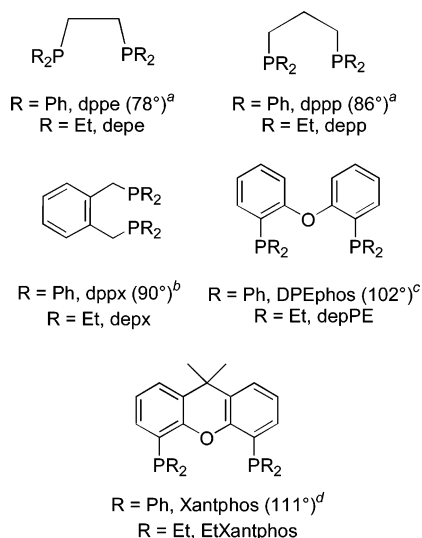
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**Chart 1.** Selected Diphosphine Ligands with Abbreviations and Calculated Natural Bite Angles

<sup>a</sup>Reference 7. <sup>b</sup>Reference 4. <sup>c</sup>Reference 3. <sup>d</sup>Reference 6.

of the xanthene backbone. For palladium-catalyzed allylic alkylation reactions, they found that Xantphos (see Chart 1) effected 100% selectivity for the desired linear products.<sup>7</sup> Although there are several influences on the selectivities of catalysts, the link with ligand bite angle is well established.<sup>8</sup>

Several groups have examined the kinetics of hydride transfer from transition-metal hydride complexes. Bullock and co-workers have examined the rates of hydride transfer for a variety of metal carbonyl hydrides, including some with phosphine ligands.<sup>9</sup> Very recently, Norton et al. investigated the rate of hydride transfer from ruthenium diphosphine complexes to iminium cations.<sup>10</sup> They found that smaller bite angles of the diphosphine ligand favored rapid hydride transfer.

Recently, we have investigated the thermodynamic properties of transition-metal hydride complexes containing diphosphine ligands.<sup>11–13</sup> Our work focused on nickel and platinum compounds containing ligands with backbones of two or three carbon atoms such as 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,3-bis(dimethylphosphino)propane (dmpp). General methods for the determination of solution bond-dissociation free energies (SDBFEs) of metal hydrides were exploited to obtain the values for the hydride donor abilities of a series of compounds.<sup>11,13</sup> Previously, we had also examined the relationship between the ligand bite angle and the electrochemical potentials of the II/I and I/O couples of nickel and palladium diphosphine complexes.<sup>14</sup> We found that larger bite angles caused distortions from square-planar geometry that resulted in the stabilization

of the Ni<sup>I</sup> or Pd<sup>I</sup> complexes. In this report, we investigate the link between the ligand bite angle of the diphosphine and the hydride donor ability in palladium complexes.

We selected a series of five known ligands with a range of natural bite angles of 33°. The ligands along with their bite angles are shown in Chart 1 (R = Ph). Although [Pd(dppe)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, [Pd(dppp)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, and [Pd(dppx)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> had been prepared previously,<sup>14</sup> investigations with the ligands DPEphos and Xantphos showed that the [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> complexes were not very stable. Therefore, we opted to use the analogous ligands in which ethyl groups have been substituted for the phenyl groups on the phosphines, as depicted in Chart 1. The resulting complexes are more stable, and the natural bite angles should be very similar because the backbones of the ligands are identical. Using the ligands with R = Et in Chart 1, we have synthesized and characterized the [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> and Pd(diphosphine)<sub>2</sub> complexes and determined the acidities and hydride donor abilities (hydricities) of the corresponding [HPd(diphosphine)<sub>2</sub>]<sup>+</sup> complexes in an effort to correlate the hydricity with the natural bite angle of the ligand.

## Experimental Section

**Syntheses.** All manipulations were performed under an inert atmosphere using standard Schlenk techniques or a glovebox. Solvents were distilled under nitrogen using standard procedures. Diphenyl ether (99%, Aldrich) was recrystallized from 90% EtOH, and acenaphthylene (75%, Aldrich) was sublimed (75 °C, 50 mTorr) prior to use. Lithium diethylphosphide was prepared by reacting diethylphosphine and butyllithium in hexane. Triethylammonium tetrafluoroborate and 1,1,3,3-tetramethylguanidinium tetrafluoroborate were prepared by reacting either triethylamine or 1,1,3,3-tetramethylguanidine with HBF<sub>4</sub>·OMe<sub>2</sub> in ether and washing the resulting solid with ether. All other materials were purchased and used as received.

**[Pd(depe)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>.** A solution of 0.45 g (1.0 mmol) of [Pd(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> in 20 mL of MeCN was added to a solution of 0.42 g (2.0 mmol) of 1,2-bis(diethylphosphino)ethane (depe) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting colorless solution was stirred overnight. The solution was reduced to dryness, and the solid was redissolved in 5 mL of MeCN. This solution was filtered, and 30 mL of EtOH was added to the filtrate. Upon cooling the filtrate for several hours at –20 °C, a precipitate formed. The resulting solid was collected by cannula filtration, washed with 2 × 20 mL of EtOH, and dried under vacuum. Yield = 0.54 g (77%) of a white powder. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.30–2.18 (m, PCH<sub>2</sub>CH<sub>3</sub>), 2.10–2.00 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 1.17 (m, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>3</sub>CN): δ 65.24 (s). Anal. Calcd for C<sub>20</sub>H<sub>48</sub>B<sub>2</sub>F<sub>8</sub>P<sub>4</sub>Pd: C, 34.69; H, 6.99; P, 17.89. Found: C, 34.52; H, 7.04; P, 17.69.

**Pd(depe)<sub>2</sub>.** Tris(dibenzylideneacetone)dipalladium(0) (0.44 g, 0.48 mmol, Aldrich) and depe (0.40 g, 1.9 mmol) were added to 35 mL of THF. The red-purple reaction solution was stirred for 4 h, during which the solution became orange-yellow. The solution was filtered to remove a small amount of black solid, and the filtrate was reduced to dryness. The solids were washed with 3 × 20 mL of MeCN to remove dibenzylideneacetone and dried under vacuum. Yield = 0.20 g (40%) of an off-white solid. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>): δ 1.55–1.38 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 1.34 (m, PCH<sub>2</sub>CH<sub>3</sub>), 1.08 (m, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P NMR (toluene-*d*<sub>8</sub>): δ 31.51 (s). Anal. Calcd for C<sub>20</sub>H<sub>48</sub>P<sub>4</sub>Pd: C, 46.29; H, 9.32; P, 23.88. Found: C, 46.37; H, 9.25; P, 23.65.

**[Pd(depp)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>.** A solution of 0.95 g (2.2 mmol) of [Pd(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> in 20 mL of MeCN was added to a solution of 0.95 g (4.4 mmol) of 1,3-bis(diethylphosphino)propane (depp) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting pale yellow solution was stirred overnight. The solution was reduced to dryness, and the solid was redissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was filtered, and 30 mL of EtOH was added to

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the filtrate. The volume was reduced by 5 mL, resulting in a white precipitate. The mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  overnight. The solid was then collected by cannula filtration, washed with  $2 \times 20\text{ mL}$  of EtOH, and dried under vacuum. Yield = 1.34 g (87%) of a white powder.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.21 (m,  $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 2.13–1.99 (m,  $\text{PCH}_2\text{CH}_3$  and  $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 1.18 (m,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.84 (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{52}\text{B}_2\text{F}_8\text{P}_4\text{Pd}$ : C, 36.67; H, 7.27; P, 17.19. Found: C, 36.66; H, 7.64; P, 16.99. Colorless rods suitable for X-ray diffraction were grown by layering ethanol on a solution of the complex in dichloromethane and storing at  $-20\text{ }^{\circ}\text{C}$ .

**Pd(depp)<sub>2</sub>**. A solution of sodium acenaphthylenide was prepared by reacting 42 mg (1.83 mmol) of sodium with 279 mg (1.83 mmol) of acenaphthylene in 50 mL of freshly distilled THF overnight. This brown solution was added dropwise to a pale yellow solution of 0.60 g (0.83 mmol) of  $[\text{Pd}(\text{depp})_2](\text{BF}_4)_2$  in 15 mL of MeCN that was cooled in an ice bath. Once the addition was complete, the ice bath was removed, and the green solution was stirred for 2 h while warming to room temperature. The solution was reduced to dryness, and the solids were extracted with  $3 \times 30\text{ mL}$  of ether. The extracts were passed through a Celite plug to remove  $\text{NaBF}_4$ . The ether solution was reduced to dryness, and the resulting brown oil was washed with  $3 \times 30\text{ mL}$  of cold ( $0\text{ }^{\circ}\text{C}$ ) MeCN to remove acenaphthylene. The remaining solid was dried for 2 h under vacuum. Yield = 250 mg (55%) of a pale yellow solid.  $^1\text{H}$  NMR (toluene- $d_8$ ):  $\delta$  1.79 (m,  $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 1.50 (m,  $\text{PCH}_2\text{CH}_3$ ), 1.34 (m,  $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 1.06 (m,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR (toluene- $d_8$ ):  $\delta$   $-2.60$  (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{52}\text{P}_4\text{Pd}$ : C, 48.31; H, 9.58; P, 22.65. Found: C, 48.10; H, 9.88; P, 22.47.

**$\alpha,\alpha'$ -Bis(diethylphosphino)xylene (depX)**. A solution of 2.34 g (13.4 mmol) of  $\alpha,\alpha'$ -dichloro-*o*-xylene in 30 mL of THF was added dropwise to a solution of 2.66 g (27.7 mmol) of  $\text{LiPEt}_2$  in 75 mL of THF at  $-78\text{ }^{\circ}\text{C}$ . The resulting solution was stirred for 3 h while warming to room temperature. An aqueous 0.1 M NaCl solution (100 mL) was added, and the organic layer was removed. The aqueous solution was washed with  $2 \times 50\text{ mL}$  of THF, and the combined THF solutions were dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the solvent was removed under vacuum to produce a white solid. The crude product was dissolved in a minimal amount of MeCN ( $\sim 50\text{ mL}$ ), and the resulting solution was filtered. The filtrate was stored at  $-20\text{ }^{\circ}\text{C}$  to produce a pure product as white needles. Yield = 2.78 g (74%). The product showed no detectable impurities by  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.08 (m, Ar-H), 2.93 (s, ArCH<sub>2</sub>P), 1.41 (m,  $\text{PCH}_2\text{CH}_3$ ), 1.03 (d of t,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ ,  $^3J_{\text{PH}} = 14.4\text{ Hz}$ ,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$   $-18.41$  (s).

**$[\text{Pd}(\text{depX})_2](\text{BF}_4)_2$** . A solution of 0.45 g (1.0 mmol) of  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$  in 30 mL of MeCN was added to a solution of 0.57 g (2.0 mmol) of depX in 30 mL of  $\text{CH}_2\text{Cl}_2$ . The homogeneous yellow solution was stirred, and, within 10 min, a precipitate began to form. The mixture was stirred 5 h. The product was isolated by cannula filtration and dried overnight under vacuum. Yield = 0.65 g (77%) of a pale yellow powder.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.20 (m, 4,5-H), 7.03 (br, 3,6-H), 3.37 (br, ArCH<sub>2</sub>P), 1.99 (br,  $\text{PCH}_2\text{CH}_3$ ), 1.24 (m,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  18.98 (broad). Anal. Calcd for  $\text{C}_{32}\text{H}_{56}\text{B}_2\text{F}_8\text{P}_4\text{Pd}$ : C, 45.50; H, 6.68; P, 14.67. Found: C, 45.56; H, 6.69; P, 14.52. Colorless prisms suitable for X-ray diffraction were grown by diffusion of ether into an acetonitrile solution of the complex.

**Pd(depX)<sub>2</sub>**. To a solution of 0.65 g (0.77 mmol) of  $[\text{Pd}(\text{depX})_2](\text{BF}_4)_2$  in 30 mL of MeCN was added 1.0 mL (31.9 mmol) of hydrazine via a syringe. The resulting solution turned from yellow to brown, and a white precipitate formed. The mixture was stirred overnight. The solid was isolated by cannula filtration, washed with  $3 \times 25\text{ mL}$  of MeCN, and dried under vacuum. Yield = 0.36 g (69%) of a white solid.  $^{31}\text{P}$  NMR (toluene- $d_8$ ):  $\delta$  1.3 (broad) and  $-0.4$  (broad).  $^1\text{H}$  NMR signals are extremely broad. Anal. Calcd for  $\text{C}_{32}\text{H}_{56}\text{P}_4\text{Pd}$ : C, 57.27; H, 8.41; P, 18.46. Found: C, 57.20; H, 8.29; P, 18.27. Colorless rods suitable for X-ray diffraction were grown by layering acetonitrile on a solution of the complex in dichloromethane.

**Bis(2-(diethylphosphino)phenyl)ether (depPE)**. The procedure for the analogous diphenylphosphino ligand, DPEphos, was followed.<sup>6</sup> A solution of 4.00 g (23.5 mmol) of diphenyl ether in 15 mL of THF was added dropwise to a mixture of 20.7 mL (51.7 mmol) of a 2.5 M solution of butyllithium in hexanes and 7.8 mL (51.7 mmol) of tetramethylethylenediamine (TMEDA). The reaction was stirred overnight. The reaction vessel was maintained at room temperature in a water bath, while a solution of 6.44 g (51.7 mmol) of  $\text{ClPEt}_2$  in 25 mL of hexane was added dropwise. A white precipitate had formed by the end of the addition, and the mixture was stirred overnight. Next, 30 mL of  $\text{CH}_2\text{Cl}_2$  was added, causing the precipitate to dissolve. Water (30 mL) was added, and the organic layer was removed. The organic solution was washed with an additional 30 mL of water and dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the solvent was removed from the filtrate, producing an orange liquid. The crude product was purified by vacuum distillation at  $110\text{ }^{\circ}\text{C}$  and 50 mTorr. Yield = 4.17 g (51%) of a yellow-orange, viscous liquid. The product was approximately 90% pure based on  $^1\text{H}$  and  $^{31}\text{P}$  NMR data.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.45–6.68 (m, Ar-H), 1.77 (m,  $\text{PCH}_2\text{CH}_3$ ), 0.99 (d of t,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ ,  $^3J_{\text{PH}} = 14.4\text{ Hz}$ ,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$   $-23.83$  (s).

**Pd(depPE)<sub>2</sub>**. A solution of 0.81 g (2.1 mmol) of depPE in 20 mL of MeCN was added to a solution of 0.45 g (1.0 mmol) of  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$  in 20 mL of MeCN, forming an orange solution. The reaction was stirred for 2 h, and then 1.0 mL (32 mmol) of hydrazine was added dropwise, resulting in a yellow precipitate. The mixture was stirred for 4 h. The solid was isolated by cannula filtration, washed with  $2 \times 20\text{ mL}$  of MeCN, and dried under vacuum overnight. Yield = 0.58 g (72%) of a yellow, microcrystalline solid.  $^1\text{H}$  NMR (toluene- $d_8$ ):  $\delta$  7.20 (d,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ , Ar-H), 6.99 (t,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ , Ar-H), 6.94 (t,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ , Ar-H), 6.86 (d,  $^3J_{\text{HH}} = 8.0\text{ Hz}$ , Ar-H), 1.50 (m,  $\text{PCH}_2\text{CH}_3$ ), 0.77 (m,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR (toluene- $d_8$ ):  $\delta$   $-1.33$  (s). Anal. Calcd for  $\text{C}_{40}\text{H}_{56}\text{O}_2\text{P}_4\text{Pd}$ : C, 60.11; H, 7.06; P, 15.50. Found: C, 60.12; H, 7.45; P, 13.21. Despite several attempts with independently prepared samples, the phosphorus analysis of this compound was consistently low. Yellow plates suitable for X-ray diffraction were grown by layering acetonitrile on a solution of the complex in dichloromethane.

**$[\text{Pd}(\text{depPE})_2](\text{BF}_4)_2 \cdot 2\text{THF}$** . To a yellow solution of 0.30 g (0.38 mmol) of  $\text{Pd}(\text{depPE})_2$  in 50 mL of THF was added 0.23 g (0.83 mmol) of ferrocenium tetrafluoroborate. The solution turned orange-brown, and an orange precipitate slowly formed. The reaction mixture was stirred overnight. The solid was isolated by cannula filtration, washed with  $2 \times 40\text{ mL}$  of THF to remove ferrocene, and dried briefly under vacuum. The solid was redissolved in a minimal amount of MeCN, and the solution was filtered. THF (100 mL) was added to the filtrate. Upon standing overnight, the product formed as orange crystals. It was isolated by filtration, washed with  $2 \times 20\text{ mL}$  of THF, and dried under vacuum overnight. Yield = 0.29 g (79%) of an orange, crystalline solid.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.67, 7.59, 7.46, and 7.26 (Ar-H), 2.14 ( $\text{PCH}_2\text{CH}_3$ ), 0.88 ( $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  22.1, 19.8, 6.6, 4.4, AB pattern with  $N = 350\text{ Hz}$  at  $-60\text{ }^{\circ}\text{C}$ . All NMR signals are broad at room temperature. Anal. Calcd for  $\text{C}_{48}\text{H}_{72}\text{B}_2\text{F}_8\text{O}_4\text{P}_4\text{Pd}$ : C, 51.61; H, 6.50; P, 11.09. Found: C, 51.43; H, 6.65; P, 10.86. The solvent content was confirmed by thermogravimetric analysis. Yellow plates suitable for X-ray diffraction were grown by the diffusion of ether into an acetonitrile solution of the compound.

**9,9-Dimethyl-4,5-bis(diethylphosphino)xanthene (EtXantphos)**. The procedure for the analogous diphenylphosphino ligand, Xantphos, was followed.<sup>6</sup> To a solution of 5.0 g (24 mmol) of 9,9-dimethylxanthene in 50 mL of ether was added 10.9 mL (72 mmol) of TMEDA. Next, 52 mL (72 mmol) of a 1.4 M solution of *sec*-butyllithium in cyclohexane was added dropwise. The reaction turned dark red with some precipitate. The mixture was stirred overnight. A solution of 8.96 g (72 mmol) of  $\text{ClPEt}_2$  in 15 mL of hexane was added dropwise, resulting in a white precipitate. The mixture was stirred overnight. The solvent was removed under vacuum, and the resulting yellow oil was redissolved in 100 mL of  $\text{CH}_2\text{Cl}_2$ . The solution was washed with  $2 \times$

100 mL of water, dried over  $\text{Na}_2\text{SO}_4$ , and reduced to dryness. The crude product was recrystallized from EtOH. Yield = 7.15 g (77%) of an off-white solid. The purity of the product was greater than 90% based on  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.46 (d of d,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.2$  Hz, 1,8-H), 7.21 (m, 3,6-H), 7.12 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2,7-H), 1.95–1.74 (m,  $\text{PCH}_2\text{CH}_3$ ), 1.57 (s,  $\text{CH}_3$ ), 1.01 (d of t,  $^3J_{\text{HH}} = 7.6$  Hz,  $^3J_{\text{PH}} = 14.0$  Hz,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  -26.18 (s).

**[Pd(EtXantphos) $_2$ ](BF $_4$ ) $_2$ .** A solution of 1.55 g (4.0 mmol) of EtXantphos in 50 mL of toluene was added to a solution of 0.88 g (2.0 mmol) of [Pd(MeCN) $_4$ ](BF $_4$ ) $_2$  in 20 mL of MeCN. The red homogeneous solution was stirred for 1 h and then reduced to dryness under vacuum. The resulting orange solid was recrystallized by dissolving in 15 mL of  $\text{CH}_2\text{Cl}_2$ , filtering the resulting solution, and adding 50 mL of EtOH to the filtrate. The resulting solution was stored at  $-20$  °C overnight. The product was isolated by cannula filtration and dried overnight under vacuum. Yield = 1.60 g (77%) of an orange powder.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.85 (d,  $^3J_{\text{HH}} = 7.6$  Hz, 1,8-H), 7.48 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2,7-H), 7.41 (br, 3,6-H), 2.11 and 1.85 (br,  $\text{PCH}_2\text{CH}_3$ ), 1.67 (s,  $\text{CH}_3$ ), 0.76 (br,  $\text{PCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  11.1 (broad). Anal. Calcd for  $\text{C}_{46}\text{H}_{64}\text{B}_2\text{F}_8\text{O}_2\text{P}_4\text{Pd}$ : C, 52.47; H, 6.13; P, 11.77. Found: C, 51.89; H, 6.18; P, 10.39. Orange-red prisms suitable for X-ray diffraction were grown by diffusion of ether into an acetonitrile solution of the complex.

**Pd(EtXantphos) $_2$ .** To a solution of 0.30 g (0.28 mmol) of [Pd-(EtXantphos) $_2$ ](BF $_4$ ) $_2$  in 30 mL of MeCN was added 0.2 mL (6.4 mmol) of hydrazine via a syringe. The resulting solution turned from orange to red, and a yellow precipitate formed. The mixture was stirred for 4 h. The solid was isolated by cannula filtration, washed with  $3 \times 20$  mL of MeCN, and dried under vacuum overnight. Yield = 0.16 g (64%) of a yellow solid.  $^{31}\text{P}$  NMR (toluene- $d_8$ ):  $\delta$  -0.92 (broad) and -9.87 (broad).  $^1\text{H}$  NMR signals are extremely broad. Anal. Calcd for  $\text{C}_{46}\text{H}_{64}\text{O}_2\text{P}_4\text{Pd}$ : C, 62.83; H, 7.34; P, 14.09. Found: C, 62.69; H, 7.45; P, 13.86. Yellow plates suitable for X-ray diffraction were grown by layering acetonitrile on a solution of the complex in benzonitrile.

**Physical Measurements.** NMR spectra were recorded on a Varian Inova 400 MHz spectrometer.  $^1\text{H}$  chemical shifts are reported relative to tetramethylsilane using residual solvent protons as a secondary reference.  $^{31}\text{P}$  chemical shifts are reported relative to external phosphoric acid. All electrochemical measurements were carried out under an  $\text{N}_2$  atmosphere in 0.3 M  $\text{Et}_4\text{NBF}_4$  in acetonitrile or in 0.3 M  $\text{Bu}_4\text{NBF}_4$  in benzonitrile or dichloromethane. Cyclic voltammetry experiments were carried out on a Cypress Systems computer-aided electrolysis system. The working electrode was a glassy carbon disk (2 mm diameter), and the counter electrode was a glassy carbon rod. A platinum wire immersed in a permethylferrocene/permethylferrocenium solution was used to fix the potential. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.

**$\text{p}K_{\text{a}}$  of [HPd(diphosphine) $_2$ ] $^+$ .** In a typical experiment, Pd(diphosphine) $_2$  and either triethylammonium tetrafluoroborate ( $\text{Et}_3\text{NH}^+\text{BF}_4^-$ ) or 1,1,3,3-tetramethylguanidium tetrafluoroborate ( $(\text{Me}_2\text{N})_2\text{CNH}_2^+\text{BF}_4^-$ ) were accurately weighed into an NMR tube and dissolved in benzonitrile. A known quantity of conjugate base (either triethylamine or tetramethylguanidine) was added via a gastight syringe. The solutions were mixed and monitored by  $^{31}\text{P}$  NMR (unlocked). The reactions came to equilibrium within 20 min and were checked every several hours for 24 h to ensure that the ratios had not changed. The signals of [HPd(diphosphine) $_2$ ] $^+$  and Pd(diphosphine) $_2$  were integrated, and the ratio was used to determine the equilibrium constant for the reaction. At least three separate experiments were run to confirm the result. The equilibrium constant was used to calculate the  $\text{p}K_{\text{a}}$  of the palladium hydride.

**X-ray Crystallography.** X-ray diffraction data from selected crystals were recorded on a Bruker Nonius SMART CCD diffractometer employing Mo  $K\alpha$  radiation (graphite monochromator). Selected details related to the crystallographic experiment for seven compounds are

**Table 1.** Crystallographic Data<sup>a</sup> for [Pd(depp) $_2$ ], [Pd(dep $x$ ) $_2$ ](BF $_4$ ) $_2$ , and Pd(dep $x$ ) $_2$

compound	[Pd(dep $x$ ) $_2$ ](BF $_4$ ) $_2$ <sup>c</sup>		
	EtOH	[Pd(dep $x$ ) $_2$ ](BF $_4$ ) $_2$	Pd(dep $x$ ) $_2$
formula	$\text{C}_{24}\text{H}_{58}\text{B}_2\text{F}_8\text{OP}_4\text{Pd}$	$\text{C}_{16}\text{H}_{28}\text{BF}_4\text{P}_2\text{Pd}_{0.5}$	$\text{C}_{32}\text{H}_{56}\text{P}_4\text{Pd}$
formula wt	766.60	422.33	671.05
<i>T</i> (K)	173	173	173
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P$
<i>a</i> (Å)	20.3790(8)	19.58(2)	10.035(5)
<i>b</i> (Å)	16.9052(7)	11.555(13)	10.316(5)
<i>c</i> (Å)	21.5603(8)	16.865(19)	18.247(9)
$\alpha$ (deg)	90	90	80.890(9)
$\beta$ (deg)	111.6720(10)	99.802(19)	79.214(9)
$\gamma$ (deg)	90	90	66.363(8)
<i>V</i> (Å $^3$ )	6902.7(5)	3759(7)	1692.6(15)
<i>Z</i>	8	8	2
<i>d</i> <sub>calc</sub> (g/cm $^3$ )	1.475	1.492	1.317
$\mu$ (mm $^{-1}$ )	0.785	0.727	0.757
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> < 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0522, 0.0908	0.0422, 0.1062	0.0377, 0.0913
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1166, 0.1098	0.0448, 0.1083	0.0450, 0.0950

<sup>a</sup> Obtained with graphite-monochromated Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation. <sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

listed in Tables 1 and 2. Unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections, and intensities were integrated from a series of frames ( $0.3^\circ$   $\omega$  rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS.<sup>15</sup> The structures were solved by using direct methods and refined (on  $F^2$ , using all data) by a full-matrix, weighted least-squares process. All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined by using a riding model. Standard Bruker Nonius control (SMART) and integration (SAINT) software was employed, and Bruker Nonius SHELXTL<sup>16</sup> software was used for structure solution and refinement. Thermal ellipsoid plots were generated with the program Ortep-3 for Windows.<sup>17</sup>

## Results

**Syntheses.** Both depe and depp are commercially available; however, the ligands dep $x$ , depPE, and EtXantphos had not been prepared previously. These ligands were prepared by variations of established literature procedures. The ligand dep $x$  was synthesized by reaction of lithium diethylphosphide with  $\alpha,\alpha'$ -dichloro-*o*-xylene. This procedure is similar to that used for other diethylphosphine ligands, such as in the synthesis of depp.<sup>13</sup> The ligands depPE and EtXantphos were prepared by methods nearly identical to those for the diphenylphosphino analogues.<sup>6</sup> Lithiation of either diphenyl ether or 9,9-dimethylxanthene followed by reaction with chlorodiethylphosphine produced the desired diphosphine molecules. The diphenyl ether ligand, depPE, was a viscous liquid, whereas the xanthene ligand, EtXantphos, was an off-white solid.

The most convenient route to the Pd<sup>II</sup> complexes was the reaction of [Pd(MeCN) $_4$ ](BF $_4$ ) $_2$  with 2 equiv of the ligands. The complexes [Pd(depe) $_2$ ](BF $_4$ ) $_2$ , [Pd(depp) $_2$ ](BF $_4$ ) $_2$ , [Pd(dep $x$ ) $_2$ ](BF $_4$ ) $_2$ , and [Pd(EtXantphos) $_2$ ](BF $_4$ ) $_2$  could be prepared by this method in yields of 77–87%. This procedure did not work well for depPE, which produced an oily product that despite several attempts could not be purified. It was found that the complex

(15) Sheldrick, G. M. *SADABS – a program for area detector absorption corrections*.

(16) Sheldrick, G. M. *SHELXTL*, v. 6.12; Bruker AXS: Madison, WI, 1999.

(17) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

**Table 2.** Crystallographic Data<sup>a</sup> for [Pd(depPE)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, Pd(depPE)<sub>2</sub>, [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, and Pd(EtXantphos)<sub>2</sub>

compound	[Pd(depPE) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> EtOH	Pd(depPE) <sub>2</sub>	[Pd(EtXantphos) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> 2MeCN·1/2Et <sub>2</sub> O	Pd(EtXantphos) <sub>2</sub>
formula	C <sub>42</sub> H <sub>62</sub> B <sub>2</sub> F <sub>8</sub> O <sub>3</sub> P <sub>4</sub> Pd	C <sub>40</sub> H <sub>56</sub> O <sub>2</sub> P <sub>4</sub> Pd	C <sub>104</sub> H <sub>150</sub> B <sub>4</sub> F <sub>16</sub> N <sub>4</sub> O <sub>5</sub> P <sub>3</sub> Pd <sub>2</sub>	C <sub>46</sub> H <sub>64</sub> O <sub>2</sub> P <sub>4</sub> Pd
formula wt	1018.82	799.13	2344.08	879.25
<i>T</i> (K)	173	173	164	173
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i>	<i>P</i>
<i>a</i> (Å)	12.423(10)	24.902(15)	14.0903(19)	11.087(2)
<i>b</i> (Å)	22.881(17)	10.638(6)	18.715(3)	14.170(3)
<i>c</i> (Å)	16.794(13)	17.118(10)	23.130(3)	15.859(3)
α (deg)	90	90	106.886(2)	90.503(3)
β (deg)	100.713(15)	118.091(9)	106.065(3)	109.192(3)
γ (deg)	90	90	90.951(3)	106.287(3)
<i>V</i> (Å <sup>3</sup> )	4690(6)	4000(4)	5577.1(13)	2244.7(7)
<i>Z</i>	4	4	2	2
<i>d</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.443	1.327	1.396	1.301
μ (mm <sup>-1</sup> )	0.601	0.656	0.516	0.591
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> < 2σ( <i>I</i> )] <sup>b</sup>	0.0674, 0.1700	0.0305, 0.0939	0.0775, 0.2142	0.0376, 0.0949
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1041, 0.1914	0.0328, 0.0973	0.1141, 0.2393	0.0421, 0.0978

<sup>a</sup> Obtained with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. <sup>b</sup> *R*<sub>1</sub> = Σ||*F*<sub>o</sub> − |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|, *wR*<sub>2</sub> = {Σ[*w*(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)]/Σ[*w*(*F*<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>.

[Pd(depPE)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> could be prepared in 79% yield by oxidation of the Pd<sup>0</sup> complex with ferrocenium tetrafluoroborate in THF.

The Pd<sup>II</sup> complexes were prepared primarily by reduction of the Pd<sup>II</sup> species. For the complexes [Pd(depX)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, [Pd(depPE)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, and [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, which have reduction potentials more positive than −1.0 V versus ferrocene (see below), hydrazine was a convenient reducing agent. Because the neutral Pd<sup>0</sup> complexes are insoluble in acetonitrile, reaction of the Pd<sup>II</sup> complexes with hydrazine in MeCN solution produced the desired products as pure, microcrystalline solids. Using this method, the compounds Pd(depX)<sub>2</sub> (69%) and Pd(EtXantphos)<sub>2</sub> (64%) were isolated in the indicated yields. Because of the problem of isolating the Pd<sup>II</sup> complex of depPE, the compound Pd(depPE)<sub>2</sub> was made directly by adding hydrazine to a solution of [Pd(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> and depPE in MeCN and isolating the yellow product in 72% yield. Because of its more negative reduction potential, the complex Pd(depp)<sub>2</sub> was prepared using the stronger reducing agent, sodium acenaphthylenide; workup afforded the product in 55% yield. Pd(depe)<sub>2</sub> was most readily prepared by reacting the Pd<sup>0</sup> starting material tris(dibenzylideneacetone)dipalladium(0) with 4 equiv of depe in THF solution.

The diethylphosphino ligands in Chart 1 were found to produce stable compounds with both Pd<sup>II</sup> and Pd<sup>0</sup>. Of all the compounds prepared, only Pd(depe)<sub>2</sub> and Pd(depp)<sub>2</sub> are very air-sensitive; they turn black within minutes of exposure to air. However, air was excluded from all samples due to the possibility of oxidizing the phosphine moieties on the ligands.

**NMR Spectroscopy.** All compounds were analyzed by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The <sup>31</sup>P shifts of the compounds are gathered in Table 3. The compounds [Pd(depe)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, Pd(depe)<sub>2</sub>, [Pd(depp)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, Pd(depp)<sub>2</sub>, and Pd(depPE)<sub>2</sub> exhibit simple <sup>31</sup>P NMR spectra at room temperature with single, sharp peaks indicative of all four phosphorus atoms being equivalent. The <sup>31</sup>P spectra are not as straightforward for the other compounds. [Pd(depX)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> have single broad peaks; the corresponding zero-valent compounds, Pd(depX)<sub>2</sub> and Pd(EtXantphos)<sub>2</sub>, have two broad peaks at room temperature (20 °C). All four species were examined at temperatures between −60 and +80 °C (neutral complexes − toluene-*d*<sub>8</sub>) or −40 and +60 °C (2+ complexes − CD<sub>3</sub>CN). At high temperatures, all spectra display a single,

**Table 3.** <sup>31</sup>P NMR Data for [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> and Pd(diphosphine)<sub>2</sub> at Various Temperatures

compound	solvent	<sup>31</sup> P δ (ppm) <sup>a</sup>		
		20 °C	low temp <sup>b</sup>	high temp <sup>c</sup>
[Pd(depe) <sub>2</sub> ] <sup>2+</sup>	CD <sub>3</sub> CN	65.24		
Pd(depe) <sub>2</sub>	toluene- <i>d</i> <sub>8</sub>	31.51		
[Pd(depp) <sub>2</sub> ] <sup>2+</sup>	CD <sub>3</sub> CN	2.84		
Pd(depp) <sub>2</sub>	toluene- <i>d</i> <sub>8</sub>	−2.60		
[Pd(depX) <sub>2</sub> ] <sup>2+</sup>	CD <sub>3</sub> CN	18.98(br)	23.59 <sup>d</sup>	18.13
			13.58 <sup>d</sup>	
Pd(depX) <sub>2</sub>	toluene- <i>d</i> <sub>8</sub>	1.3(br)	3.54 <sup>e</sup>	0.89
		−0.4(br)	−0.62 <sup>e</sup>	
[Pd(depPE) <sub>2</sub> ] <sup>2+</sup>	CD <sub>2</sub> Cl <sub>2</sub>	20.9 <sup>f</sup>	20.95 <sup>g</sup>	
		5.5 <sup>f</sup>	5.47 <sup>g</sup>	
Pd(depPE) <sub>2</sub>	toluene- <i>d</i> <sub>8</sub>	−1.33		
[Pd(EtXantphos) <sub>2</sub> ] <sup>2+</sup>	CD <sub>3</sub> CN	11.10(br)	15.71 <sup>h</sup>	11.89
			13.56 <sup>h</sup>	
Pd(EtXantphos) <sub>2</sub>	toluene- <i>d</i> <sub>8</sub>	−0.92(br)	0.60 <sup>i</sup>	−5.65
		−9.87(br)	−9.76 <sup>i</sup>	

<sup>a</sup> Peaks are sharp singlets except where indicated (br = broad). <sup>b</sup> Measured at −40 °C in CD<sub>3</sub>CN and CD<sub>2</sub>Cl<sub>2</sub> or −60 °C in toluene-*d*<sub>8</sub>. <sup>c</sup> Measured at +60 °C in CD<sub>3</sub>CN or +80 °C in toluene-*d*<sub>8</sub>. <sup>d</sup> Triplets with a splitting of 25.5 Hz. <sup>e</sup> Triplets with a splitting of 14.1 Hz. <sup>f</sup> Apparent AB quartet with broad peaks. <sup>g</sup> Apparent AB quartet with *N* = 350 Hz. <sup>h</sup> Apparent AB quartet with *N* = 348 Hz. <sup>i</sup> Triplets with a splitting of 19.6 Hz.

sharp peak due to equivalence of the phosphorus atoms. However, at low temperature, the phosphorus atoms become nonequivalent, and [Pd(depX)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, Pd(depX)<sub>2</sub>, and Pd(EtXantphos)<sub>2</sub> each have two well-separated triplets. This pattern is typical of a degenerate A<sub>2</sub>X<sub>2</sub> spin system. At −40 °C, [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> exhibits a pattern similar to an AB quartet, again consistent with a degenerate AA'XX' system, but one that has significantly larger coupling constants than the other three complexes. As discussed under structural studies, the two phosphorus atoms of each EtXantphos ligand occupy trans positions in a tetrahedrally distorted square-planar complex. The fact that the two nonequivalent phosphorus atoms of the same diphosphine ligand are trans to each other is consistent with a larger P–P coupling. At room temperature in CD<sub>3</sub>CN, [Pd(depPE)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> exhibits no signals in the <sup>31</sup>P spectrum, but in CD<sub>2</sub>Cl<sub>2</sub> has an apparent AB quartet similar to [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> at low temperature, suggesting similar structures in solution. The lack of peaks in acetonitrile is believed to be due to a fluxional process that exchanges the nonequivalent phos-

**Table 4.** Selected Structural Data for the Compounds in Tables 1 and 2

compound	average ligand bite angle (deg)	ligand-to-ligand dihedral angle (deg)	average Pd–P distance (Å)
[Pd(depp) <sub>2</sub> ] <sup>2+</sup>	87.0	22.3	2.3655(19)
[Pd(dep $x$ ) <sub>2</sub> ] <sup>2+</sup>	90.1	32.1	2.342(2)
[Pd(depPE) <sub>2</sub> ] <sup>2+</sup>	94.5	38.0	2.381(2)
[Pd(EtXantphos) <sub>2</sub> ] <sup>2+</sup>	139.7	89.0	2.338(3)
	95.8 <sup>a</sup>	55.4 <sup>b</sup>	
Pd(dep $x$ ) <sub>2</sub>	103.2	89.3	2.3404(13)
Pd(depPE) <sub>2</sub>	106.3	84.6	2.3371(10)
Pd(EtXantphos) <sub>2</sub>	108.3	80.6	2.3432(9)

<sup>a</sup> For the smallest P–Pd–P angle. <sup>b</sup> For the angle between the planes defined in footnote a.

phorus atoms of the diphosphine ligands. This process is promoted by acetonitrile and could occur by a chelation/dechelation mechanism or by acetonitrile promoting a conformational rearrangement.

In the crystal structures discussed below, conformations of the ligand backbones render the phosphorus atoms nonequivalent. In these distorted tetrahedral structures, the phosphorus atoms are not equivalent because one phosphorus atom of one ligand is closer to the ring backbone of the other ligand. Above room temperature, there is enough thermal energy to allow the ligand conformations to interconvert, thus causing the phosphorus atoms to become equivalent, as evidenced by the coalescence into one, sharp <sup>31</sup>P NMR peak in all four compounds. A similar type of nonequivalence is observed for [RuH(solvent)(diphosphine)<sub>2</sub>]<sup>+</sup> complexes using Xantphos-type ligands.<sup>18</sup> Another example is found in the compound ( $\mu$ -*o*-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>S)Fe<sub>2</sub>(CO)<sub>6</sub> where the *o*-xylyl group of the bridging dithiolate ligand is fixed in position, lowering the symmetry of the molecule.<sup>19</sup>

**Structural Studies.** Single-crystal X-ray structures have been obtained for seven compounds listed in Tables 1 and 2. Selected structural data are found in Table 4. Compounds [Pd(depp)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> have two cations and four anions in the asymmetric unit, and values are reported as the average for both cations.

The structures of four Pd<sup>II</sup> compounds have been obtained: [Pd(depp)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>·EtOH, [Pd(dep $x$ )<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, [Pd(depPE)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>·EtOH, and [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>·2MeCN·<sup>1</sup>/<sub>2</sub>Et<sub>2</sub>O. Figure 1 shows the structures of the cations [Pd(depp)<sub>2</sub>]<sup>2+</sup>, [Pd(dep $x$ )<sub>2</sub>]<sup>2+</sup>, [Pd(depPE)<sub>2</sub>]<sup>2+</sup>, and [Pd(EtXantphos)<sub>2</sub>]<sup>2+</sup>. The Pd<sup>II</sup> complexes all exhibit tetrahedrally distorted square-planar geometries typical of d<sup>8</sup> metals. The tetrahedral distortion increases with increasing ligand bite angle, as evidenced by the increase in the dihedral angle between the two planes defined by the palladium atom and the two phosphorus atoms of each diphosphine ligand (Table 4). The average Pd–P distance in these compounds ranges from 2.34 to 2.38 Å, which is typical of palladium phosphines.<sup>20,21</sup> The structure of [Pd(EtXantphos)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> is different in that the ligand has a very large bite angle of almost 140°, and the two phosphorus atoms of each

diphosphine ligand are trans to each other. However, the smallest average P–Pd–P angle is 95.8° with a dihedral angle between the planes defined by these angles of 55.4°, resulting in a geometry that is intermediate between square planar and tetrahedral.

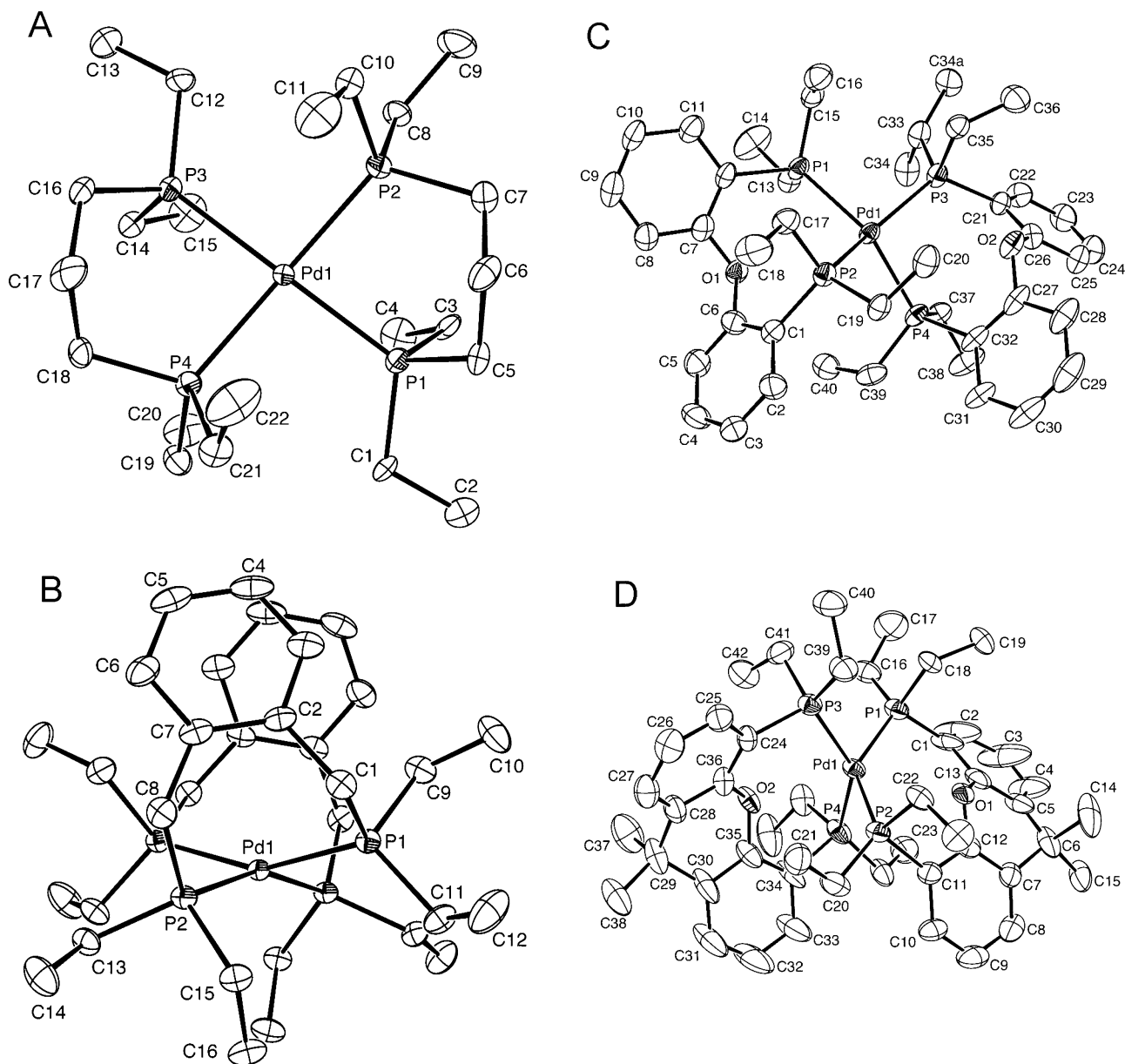
Crystal structures of three Pd<sup>0</sup> compounds were obtained: Pd(dep $x$ )<sub>2</sub>, Pd(depPE)<sub>2</sub>, and Pd(EtXantphos)<sub>2</sub>; Figure 2 shows the structures of these molecules. The three neutral species have distorted tetrahedral geometries typical of d<sup>10</sup> complexes. As seen from the data in Table 4, the ligands have bite angles that are larger than those in the Pd<sup>II</sup> species and closer to that expected for tetrahedral geometry (109.5°). For the same ligand, the bite angles increase by about 13° as the oxidation state of the metal changes from Pd<sup>II</sup> to Pd<sup>0</sup>. The dihedral angles between the ligand planes are between 80° and 90°. With an increase in the bite angle, there is a small decrease in the dihedral angle, presumably due to steric effects. All Pd–P distances are about 2.34 Å, which is similar to that observed for the Pd<sup>II</sup> compounds. Pd(depPE)<sub>2</sub> exhibits Pd–P bonds that are shorter by more than 0.04 Å when compared to [Pd(depPE)<sub>2</sub>]<sup>2+</sup>. The shortening of the M–P bond upon reduction has been observed previously.<sup>11</sup>

As mentioned above, the low-temperature NMR spectra of compounds containing dep $x$ , depPE, and EtXantphos display peaks characteristic of two sets of phosphorus atoms. It is evident from the structural analysis of the compounds that one phosphorus atom of one ligand is closer to the ring backbone of the other ligand. This is clearly apparent in the drawing of [Pd(dep $x$ )<sub>2</sub>]<sup>2+</sup> (Figure 1B), where P1 is closer than P2 to the xylene ring of the rear ligand. For all three ligands, the nonequivalence of the phosphorus atoms is a result of ring conformations of the ligand backbone that interconvert rapidly at high temperature in solution, but slowly at or below room temperature.

**Electrochemistry.** Cyclic voltammograms have been obtained for all compounds in at least two different solvents; the results are listed in Table 5. Except for [Pd(depp)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> in MeCN, all compounds exhibit reversible waves (*i*<sub>pa</sub> ≈ *i*<sub>pc</sub> and Δ*E*<sub>p</sub> = 60 mV) in all solvents. Because all compounds have at least some solubility in benzonitrile, it was possible to measure the cyclic voltammograms in this solvent, which enables facile comparison. The cyclic voltammograms of the five Pd<sup>II</sup> species in PhCN solution are shown in Figure 3. [Pd(depe)<sub>2</sub>]<sup>2+</sup> and [Pd(depp)<sub>2</sub>]<sup>2+</sup> exhibit a single two-electron wave at –1.47 and –1.23 V, respectively, for the reduction to the Pd<sup>0</sup> species. The other complexes exhibit two one-electron waves, with varying separations between the waves. The difference in the waves (Δ*E*<sub>1/2</sub> in Table 5) changes from 0 mV for [Pd(depp)<sub>2</sub>]<sup>2+</sup> to 410 mV for [Pd(EtXantphos)<sub>2</sub>]<sup>2+</sup> in benzonitrile. Across the series of compounds, there are small differences in the potentials of the 1+/0 couples and larger differences in the 2+/1+ couples. When comparisons are made in the same solvent, the cyclic voltammograms of the Pd<sup>II</sup> species were identical to those of the corresponding Pd<sup>0</sup> species.

As shown in Table 5, the wave separation changes slightly in different solvents, but these differences are minor. The more polar solvents display smaller wave separations, so the separation increases in the order MeCN < PhCN < CH<sub>2</sub>Cl<sub>2</sub>. On average, the Pd(II/I) couples become more negative by 68 mV on changing from dichloromethane to acetonitrile, and the Pd(I/0) couples become more positive by 72 mV. This leads to

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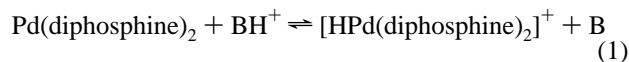


**Figure 1.** Structures of  $[\text{Pd}(\text{depp})_2]^{2+}$  (A),  $[\text{Pd}(\text{depX})_2]^{2+}$  (B),  $[\text{Pd}(\text{depPE})_2]^{2+}$  (C), and  $[\text{Pd}(\text{EtXantphos})_2]^{2+}$  (D) showing 50% probability ellipsoids and the atom numbering scheme. H atoms have been omitted for clarity. Half of the  $[\text{Pd}(\text{depX})_2]^{2+}$  cation is related by symmetry. In (D), labels on the carbons of the ethyl groups on P4 have been omitted for clarity.

expected potentials of  $-1.19$  and  $-1.23$  V, respectively, for the (I/0) and (II/I) couples of  $[\text{Pd}(\text{depp})_2]^{2+}$  as compared to a single wave at  $-1.22$  V in acetonitrile. We have used the value of  $-1.22$  V in our calculations of  $\Delta G_{\text{H}}^{\circ}$  and  $\Delta G_{\text{H}}^{\circ}$  discussed below as any errors introduced by this small difference in potential would be small (less than  $0.7$  kcal/mol).

**Acid–Base Equilibria and Solution Bond-Dissociation Free Energies.** The  $\text{p}K_{\text{a}}$  values of the palladium–hydride complexes were measured in benzonitrile solution by reacting  $\text{Pd}(\text{diphosphine})_2$  with an appropriate acid ( $\text{BH}^+$ ) of known  $\text{p}K_{\text{a}}$  according to reaction 1. It was found that triethylammonium ( $\text{p}K_{\text{a}} = 18.5$  in acetonitrile)<sup>22</sup> worked well for  $\text{Pd}(\text{depp})_2$ ,  $\text{Pd}(\text{depPE})_2$ , and  $\text{Pd}(\text{EtXantphos})_2$ , and 1,1,3,3-tetramethylguanidinium ( $\text{p}K_{\text{a}} = 23.3$  in acetonitrile)<sup>22</sup> worked well for  $\text{Pd}(\text{depe})_2$  and  $\text{Pd}(\text{depp})_2$ . All reactions came to equilibrium within 20 min

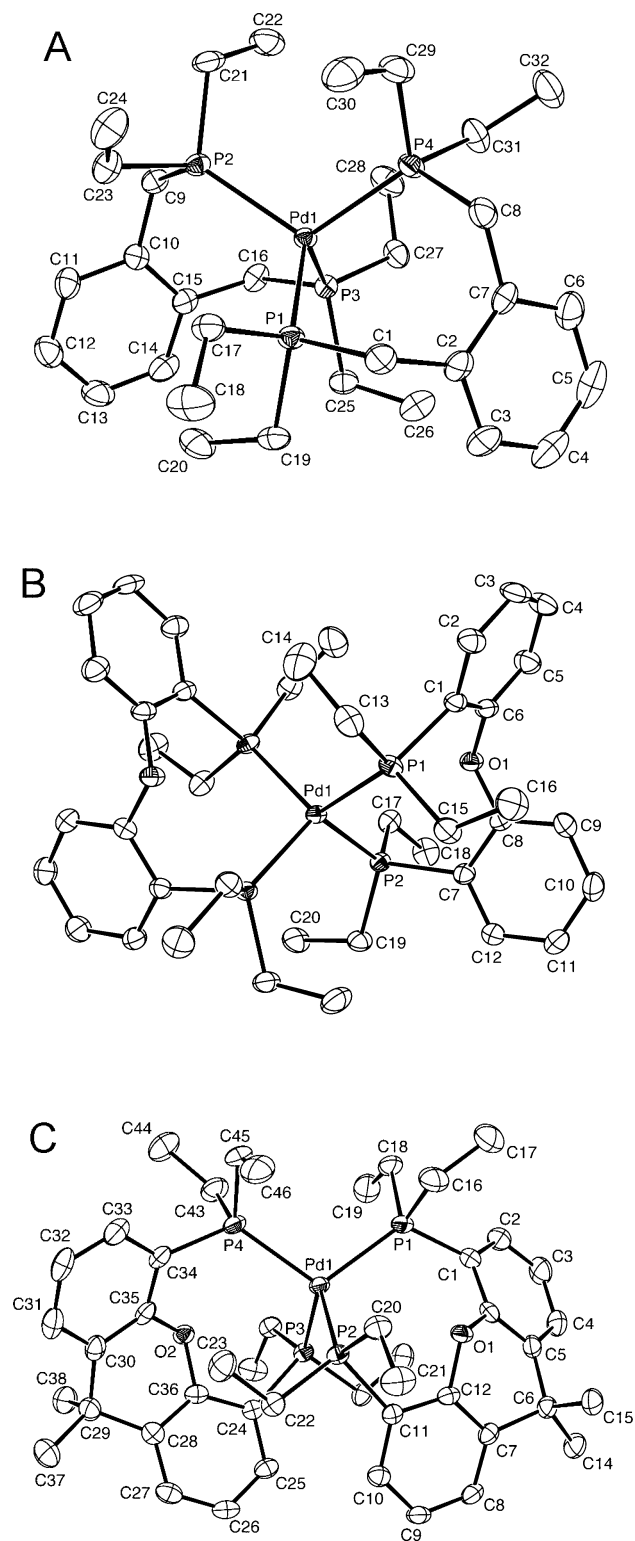
and maintained a constant ratio of  $[\text{HPd}(\text{diphosphine})_2]^+$  to  $\text{Pd}^0(\text{diphosphine})_2$  for at least 24 h. This ratio was determined by integration of the  $^{31}\text{P}$  NMR signals and used to calculate an equilibrium constant for the reaction. Using eq 2, the  $\text{p}K_{\text{a}}$  of the palladium hydrides in acetonitrile could be calculated using the  $\text{p}K_{\text{a}}$  values of the acids ( $\text{BH}^+$ ) above. These values are listed in Table 6. The larger errors assigned to the values for  $[\text{HPd}(\text{depPE})_2]^+$  and  $[\text{HPd}(\text{EtXantphos})_2]^+$  are due to the fact that the  $^{31}\text{P}$  peaks for the hydride and the  $\text{Pd}^0$  complexes overlap, resulting in the integration values being less accurate.



$$\text{p}K_{\text{a}} [\text{HPd}(\text{diphosphine})_2]^+ = \text{p}K_{\text{a}} (\text{BH}^+) + \log K_{\text{eq}} \quad (2)$$

The free energies associated with the heterolytic (reaction 3) and homolytic (reaction 5) cleavage of an  $\text{M}-\text{H}$  bond in solution

(22) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23–28.



**Figure 2.** Structures of Pd(depx)<sub>2</sub> (A), Pd(depPE)<sub>2</sub> (B), and Pd(EtXantphos)<sub>2</sub> (C) showing 50% probability ellipsoids and the atom numbering scheme. H atoms have been omitted for clarity. Half of the Pd(depPE)<sub>2</sub> molecule is related by symmetry. In (C), labels on the carbons of the ethyl groups on P3 have been omitted for clarity.

are given by eqs 4 and 6, respectively. Equations 4 and 6 are based on thermodynamic cycles,<sup>11,23</sup> and they require  $pK_a$  values and half-wave potentials for calculating the solution bond-

**Table 5.** Cyclic Voltammetry Data for [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> and Pd(diphosphine)<sub>2</sub><sup>a</sup>

compound	solvent	$E_{1/2}(I/II)$	$E_{1/2}(II/0)$	$E_{1/2}(I/0)$	$\Delta E_{1/2}$
[Pd(depe) <sub>2</sub> ] <sup>2+</sup>	MeCN		-1.48		
	PhCN		-1.47		
Pd(depe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>		-1.47		
	PhCN		-1.47		
[Pd(depp) <sub>2</sub> ] <sup>2+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	-1.16		-1.26	0.10
	MeCN		-1.22 <sup>b</sup>	-1.22 <sup>b</sup>	
	PhCN		-1.23	-1.23	
Pd(depp) <sub>2</sub>	PhCN		-1.23		
[Pd(depX) <sub>2</sub> ] <sup>2+</sup>	MeCN	-0.94		-1.02	0.08
	PhCN	-0.92		-1.01	0.09
Pd(depX) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-0.84		-1.06	0.22
	PhCN	-0.92		-1.02	0.10
[Pd(depPE) <sub>2</sub> ] <sup>2+</sup>	MeCN	-0.73		-0.92	0.19
	PhCN	-0.71		-0.93	0.22
Pd(depPE) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-0.66		-0.99	0.33
	PhCN	-0.71		-0.93	0.22
[Pd(EtXantphos) <sub>2</sub> ] <sup>2+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	-0.49		-1.02	0.53
	MeCN	-0.55		-0.94	0.39
	PhCN	-0.54		-0.95	0.41
Pd(EtXantphos) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-0.49		-1.01	0.52
	PhCN	-0.53		-0.95	0.42

<sup>a</sup> All potentials are reported as volts versus the ferrocene/ferrocenium couple and were measured at a scan rate of 50 mV/s. <sup>b</sup> Quasi-reversible ( $\Delta E_p = 110$  mV,  $i_{pa} \neq i_{pc}$ ).

dissociation free energies. For complexes with two one-electron processes,  $E_{1/2}(II/0)$  is the average of the two  $E_{1/2}$  values. The calculated values of  $\Delta G_{H^-}^\circ$  and  $\Delta G_{H^+}^\circ$  are found in Table 6.



$$\Delta G_{H^-}^\circ = 1.37 pK_a + 46.1 E_{1/2}(II/0) + 79.6 \quad (4)$$



$$\Delta G_{H^+}^\circ = 1.37 pK_a + 23.06 E_{1/2}(I/0) + 53.6 \quad (6)$$

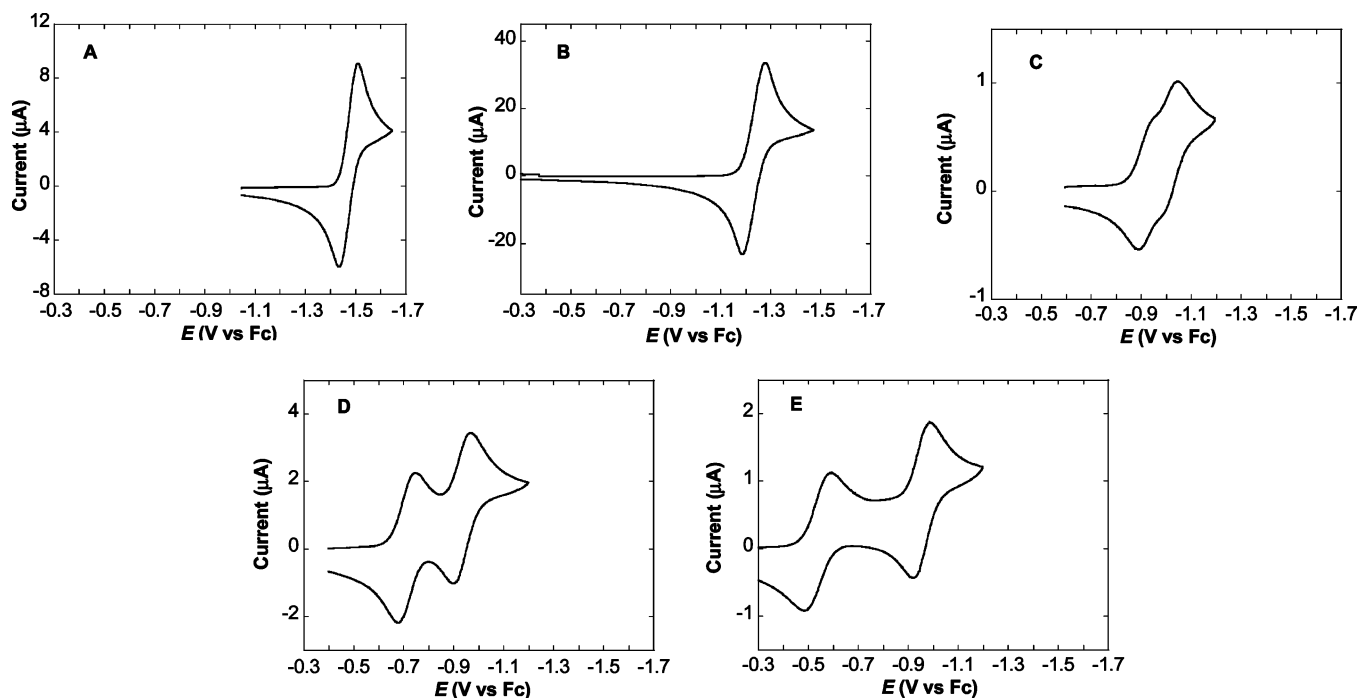
## Discussion

**Structural Studies.** The objective of this study is to determine the influence of the natural bite angle on the thermodynamic properties of [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> and [HPd(diphosphine)<sub>2</sub>]<sup>+</sup> complexes. To that end, structural determinations of these complexes are desirable for determining how natural bite angles actually contribute to important geometric features. Ten new palladium diphosphine compounds have been prepared, and seven have been characterized by X-ray crystallography. Of the three compounds without structural data, two are extremely air-sensitive, Pd(depe)<sub>2</sub> and Pd(depp)<sub>2</sub>, and purifications did not produce crystalline materials. The third, [Pd(depe)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, produced only microcrystalline material, despite numerous attempts to recrystallize it. Thus, structural data were obtained for complexes containing four of the five ligands studied.

[Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> complexes are normally regarded as square-planar complexes. However, as can be seen from the data for the four Pd(II) complexes in Table 4, many of these complexes are neither square nor planar. The observed bite angles actually vary from 87.0° to 139.7° (a range of 53°), whereas the natural bite angles vary from 86° to 111° (a range of 25°). As mentioned above, the compound [Pd(EtXantphos)<sub>2</sub>]<sup>2+</sup> is unique in that it contains a ligand bite angle of nearly 140°, which is much larger than the natural bite angle

(23) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6717. Correction: Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.





**Figure 3.** Cyclic voltammograms of 2 mM solutions of [Pd(depe)<sub>2</sub>]<sup>2+</sup> (A), [Pd(depp)<sub>2</sub>]<sup>2+</sup> (B), [Pd(depX)<sub>2</sub>]<sup>2+</sup> (C), [Pd(depPE)<sub>2</sub>]<sup>2+</sup> (D), and [Pd(EtXantphos)<sub>2</sub>]<sup>2+</sup> (E) in 0.3 M Bu<sub>4</sub>NBF<sub>4</sub> benzonitrile solution. Scan rate is 50 mV/s.

**Table 6.** Half-Wave Potentials of [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> Complexes and the Thermodynamic Properties of the Corresponding [HPd(diphosphine)<sub>2</sub>]<sup>+</sup> Complexes

diphosphine	$E_{1/2}(\text{II}/\text{I})^a$	$E_{1/2}(\text{I}/\text{I})^a$	$\text{p}K_a^b$	$\Delta G_{\text{H}}^{\circ,c}$	$G_{\text{H}}^{\circ,d}$	$\text{p}K_a(\text{H}_2)^e$	$\Delta \text{p}K_a^f$
depe	-1.48	-1.24 <sup>g</sup>	23.2 ± 0.2	43.2	56.8	23.9	-0.7
depp	-1.22	-1.22	22.9 ± 0.2	54.7	56.8	15.5	7.4
depX	-0.98	-1.02	19.8 ± 0.2	61.5	57.2	10.6	9.2
depPE	-0.83	-0.92	18.3 ± 0.5	66.4	57.5	7.0	11.3
EtXantphos	-0.75	-0.94	18.5 ± 0.5	70.4	57.3	4.1	14.4

<sup>a</sup> Potentials (V vs FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup>) for [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> in acetonitrile.  $E_{1/2}(\text{II}/\text{I})$  values are the average of  $E_{1/2}(\text{II}/\text{I})$  and  $E_{1/2}(\text{I}/\text{I})$  where two one-electron waves are present. <sup>b</sup> Values for [HPd(diphosphine)<sub>2</sub>]<sup>+</sup> determined experimentally from equilibrium reaction 1 and calculated from eq 2. <sup>c</sup> Calculated from eq 4; value is in kcal/mol. <sup>d</sup> Calculated from eq 6; value is in kcal/mol. <sup>e</sup> Calculated from eq 10. <sup>f</sup>  $\Delta \text{p}K_a = \text{p}K_a - \text{p}K_a(\text{H}_2)$ . <sup>g</sup> Calculated from eq 7.

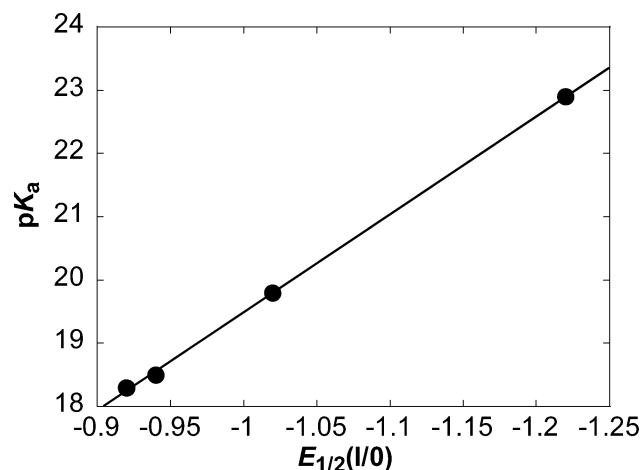
of 111° calculated for Xantphos. The flexibility range (the range of bite angles in which strain is less than 3 kcal/mol)<sup>2</sup> for this ligand is calculated to be 97–135°.<sup>6</sup> Apparently, the ligand cannot achieve an angle close to 90° in the distorted square-planar structure, and instead spans pseudo-trans positions with a P–Pd–P angle of 139.7°. The smallest P–Pd–P angle in the structure is 95.8° with an associated dihedral angle of 55.4°. These angles are consistent with a significantly distorted square-planar complex, but indicate a less dramatic distortion than suggested by the bite angles and dihedral angles based on the EtXantphos ligand.

Because crystals suitable for diffraction studies were not obtained for the [Pd(depe)<sub>2</sub>]<sup>2+</sup> cation, we were unable to obtain structural data for this complex. However, there are numerous examples of the analogous ligand dppe (see Chart 1), and a CSD search conducted in 1999 found that the average ligand bite angle for metal complexes containing this ligand was 82.6°.<sup>3</sup> For Pd(dppe)Cl<sub>2</sub> and Pd(dppe)(SCN)(NCS), the chelate angles are 85.8° and 85.1°, respectively.<sup>24,25</sup> To our knowledge, the organometallic compound (depe)Pd(2,2'-biphenyl) is the only

example of a palladium depe complex, and it has a P–Pd–P angle of 84.5°.<sup>21</sup> Therefore, the expected bite angle of depe in [Pd(depe)<sub>2</sub>]<sup>2+</sup> is approximately 85°. It is also anticipated that the dihedral angle between the two planes defined by the two depe ligands and Pd will be near 0°. In the analogous nickel complex, [Ni(depe)<sub>2</sub>]<sup>2+</sup>, the dihedral angle is 0.0°.<sup>11</sup> Thus, a chelate bite angle of 85° and a dihedral angle of near 0° is expected for [Pd(depe)<sub>2</sub>]<sup>2+</sup>. Using these estimated values for [Pd(depe)<sub>2</sub>]<sup>2+</sup>, the values for [Pd(EtXantphos)<sub>2</sub>]<sup>2+</sup> based on the smallest P–Pd–P angle, and the remaining values shown in Table 4, the average bite angle appears to increase monotonically from 85° to 96° and the dihedral angle from 0° to 55° as the natural bite angle increases from 86° to 111°. Clearly, the metal complex restricts the range of observed bite angles so that the natural bite angles are not completely expressed. A more pronounced manifestation of the natural bite angle for these [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> complexes is the dihedral angle, which increases from near 0° for [Pd(depe)<sub>2</sub>]<sup>2+</sup> to 55° for [Pd(EtXantphos)<sub>2</sub>]<sup>2+</sup>. This angle appears to amplify the natural bite angle. The large tetrahedral distortions observed for these [Pd(diphosphine)<sub>2</sub>]<sup>2+</sup> complexes have significant effects on the potentials of the Pd(II/I) redox couples of these complexes and on the hydride donor abilities of the corresponding [HPd(diphosphine)<sub>2</sub>]<sup>+</sup> complexes (as discussed below).

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**Figure 4.** Plot of  $pK_a$  values for  $[HPd(diphosphine)_2]^+$  in benzonitrile versus the potentials of the  $E_{1/2}(I/O)$  couple of the corresponding  $[Pd(diphosphine)_2]^{2+}$  complexes in benzonitrile. The line is the best linear fit of the data with eq 7.

For the Pd(0) complexes in Table 4, all of the geometries are best described as distorted tetrahedra. In an ideal tetrahedron, all of the P–Pd–P bond angles would be  $109.5^\circ$ , and the dihedral angles between the two planes defined by two sets of two phosphorus atoms and palladium should be  $90^\circ$ . For four-coordinate 18-electron ( $d^{10}$ ) complexes containing diphosphine ligands, the actual chelate bite angle adopted is a compromise between the ideal tetrahedral angle of  $109.5^\circ$  preferred by the metal and the natural bite angle of the ligand. The ligands with the smallest natural bite angles, depe and depp, are expected to deviate from the ideal tetrahedral angles the most. For  $Pd(depp)_2$ , estimates of the bite angle and dihedral angle are  $99 \pm 3^\circ$  and  $88 \pm 3^\circ$ , respectively. These estimates are based on observed bite angles for  $Pt(dmpp)_2$  ( $99.8^\circ$ ),<sup>11</sup>  $Pt(dppp)_2$  ( $97.8^\circ$ ),<sup>26</sup> and  $Pd(dppp)_2$  ( $97.6^\circ$ ).<sup>20</sup> The corresponding dihedral angles for  $Pt(dmpp)_2$  and  $Pt(dppp)_2$  are  $89.7^\circ$  and  $87.2^\circ$ , respectively. A slightly smaller bite angle is anticipated for  $Pd(depe)_2$ , but with a very similar dihedral angle. For the  $Pd(diphosphine)_2$  complexes described in this study, the observed bite angles vary by slightly more than  $10^\circ$  from ideal tetrahedral geometry depending on the natural bite angle of the diphosphine ligand, and the dihedral angles vary by approximately  $10^\circ$ . It therefore appears that the tetrahedral angles preferred for Pd(0) complexes also reduce the range of angles observed from those expected on the basis of natural bite angles alone. For Pd(0) complexes, the dihedral angle is much less sensitive to the natural bite angle than is observed for Pd(II) complexes.

**Thermodynamic Studies. Linear Free-Energy Correlation of  $pK_a$  with  $E_{1/2}(I/O)$ .** Angelici and co-workers have shown that heats of protonation for several series of complexes exhibit a linear correlation with the oxidation potentials of the complexes.<sup>27</sup> Similarly, for  $[HNi(diphosphine)_2]^+$  complexes, the  $pK_a$  values were shown to be linearly dependent on the potentials of the Ni(I/O) couple of the corresponding conjugate base of the hydride,  $Ni(diphosphine)_2$ .<sup>12</sup> A plot of the  $pK_a$  values of the  $[HPd(diphosphine)_2]^+$  complexes versus  $E_{1/2}(I/O)$  of the corresponding  $Pd(diphosphine)_2$  complexes shows an excellent linear correlation (see Figure 4 and eq 7). This correlation suggests

that both oxidation and protonation are similar processes involving the highest occupied molecular orbital (HOMO) of these tetrahedral  $M(diphosphine)_2$  complexes.

$$pK_a = -15.5 E_{1/2}(I/O) + 4.0 \quad (7)$$

Structural studies of the isoelectronic  $[Ir(dppf)_2]$  and  $[Ir(dppf)_2]^-$  complexes (where dppf is bis(diphenylphosphino)ferrocene) indicate that structural rearrangements associated with the ( $d^9/d^{10}$ ) couple are small with average chelate bite angles of  $99.9^\circ$  and  $102.3^\circ$ , respectively, and dihedral angles of  $74.7^\circ$  and  $85.0^\circ$ , respectively.<sup>28</sup> Because the geometries of the  $[Pd(diphosphine)_2]^+$  and  $Pd(diphosphine)_2$  complexes are expected to be very similar, it is anticipated that  $E_{1/2}(I/O)$  will not be strongly dependent on the chelate bite angle. As seen in Table 5, the potentials of the Pd(I/O) couples of  $[Pd(EtXantphos)_2]^{2+}$  ( $-0.94$  V) and  $[Pd(depPE)_2]^{2+}$  ( $-0.92$  V) are nearly the same. The same is true for the potentials of the (I/O) couples for  $[Pd(depp)_2]^{2+}$  ( $-1.22$  V) and  $[Pd(depe)_2]^+$  ( $-1.24$  V, see following paragraph). These data are consistent with our previous observations for  $[Ni(diphosphine)_2]^{2+}$  complexes, that the potential of the (I/O) couple is independent of the chelate bite angle for complexes with five- and six-membered chelate rings.

The same concepts appear to hold for protonation reactions, as well. Protonation of  $Pd(diphosphine)_2$  complexes to form  $[HPd(diphosphine)_2]^+$  derivatives results in electron transfer from palladium to the proton. On the basis of theoretical and X-ray diffraction studies of  $[HM(diphosphine)_2]^{n+}$  complexes [where  $M = Co$  ( $n = 0$ ),  $Pd$  ( $n = 1$ ), or  $Pt$  ( $n = 1$ )], these hydride complexes can be described as distorted trigonal bipyramidal or face-capped tetrahedral complexes.<sup>29–31</sup> The distorted tetrahedral arrangement of the phosphorus ligands in these structures demonstrates that protonation results in a relatively small structural rearrangement of the  $MP_4$  core. The variation in the  $pK_a$  values for the  $[HPd(diphosphine)_2]^+$  complexes shown in Table 6 and the  $E_{1/2}(I/O)$  values of the  $[Pd(diphosphine)_2]^{2+}$  complexes appear to arise from inductive effects of the substituents on the diphosphine ligands. As a result, the  $pK_a$  values of  $[HPd(EtXantphos)_2]^+$  (18.5) and  $[HPd(depPE)_2]^+$  (18.3) are nearly the same, as are those of  $[HPd(depp)_2]^+$  (22.9) and  $[HPd(depe)_2]^+$  (23.2). Substitution of the aryl bridge of  $[Pd(EtXantphos)_2]^{2+}$  and  $[Pd(depPE)_2]^{2+}$  with the trimethylene and ethylene bridges of  $[Pd(depp)_2]^{2+}$  and  $[Pd(depe)_2]^+$  results in more negative potentials for the (I/O) couples and larger  $pK_a$  values for the corresponding hydride complexes, as expected. Because oxidation and protonation of  $Pd(diphosphine)_2$  complexes involve removal of electron density from palladium and small structural rearrangements of the phosphorus atoms, both of these processes depend on ligand bite angles and ligand substituents in the same way, and a linear relationship between the potentials of the Pd(I/O) couples and  $pK_a$  values is reasonable.

Correlations such as those shown in Figure 4 and given by eq 7 are very useful for obtaining accurate estimates of

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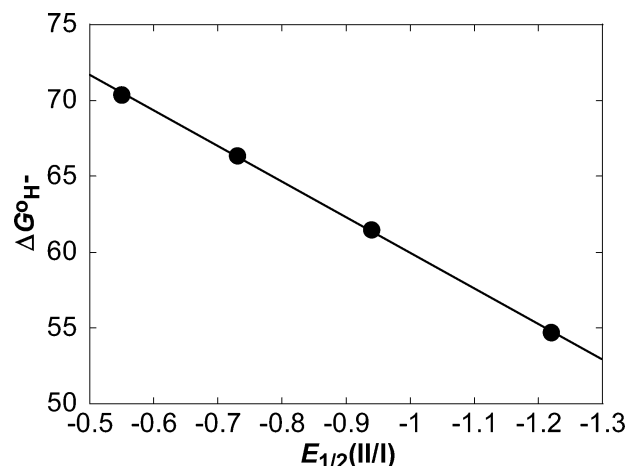
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thermodynamic properties that cannot be obtained directly by experiment or that have not been measured. For example, eq 7 can be used to calculate an  $E_{1/2}(I/O)$  potential of  $-1.24$  V for  $[\text{Pd}(\text{depe})_2]^{2+}$  from the measured  $\text{p}K_a$  value of 23.2 for  $[\text{HPd}(\text{depe})_2]^+$ . The potential of the (I/O) couple for  $[\text{Pd}(\text{depe})_2]^{2+}$  cannot be determined from cyclic voltammetry, because the observed wave is a two-electron wave. This estimated potential can be used in eq 6 to calculate a homolytic bond-dissociation free energy of 56.8 kcal/mol for  $[\text{HPd}(\text{depe})_2]^+$ , which agrees very well with those of the other complexes shown in Table 6. Similarly, the  $\text{p}K_a$  and homolytic bond-dissociation free energies of  $[\text{HPd}(\text{dppx})_2]^+$  (where dppx is  $\alpha, \alpha'$ -bis(diphenylphosphino)-xylene) can be predicted to be 12.8 (using eq 7) and 58 kcal/mol (using eq 6), respectively, on the basis of the observed potential of the (I/O) couple for this complex ( $-0.57$  V).<sup>14</sup> These estimates are expected to be accurate within 1.5  $\text{p}K_a$  units and within 2.5 kcal/mol for  $\Delta G_{\text{H}}^\circ$ .

**Homolytic Bond-Dissociation Free Energies.** The homolytic cleavage of the Pd–H bond of  $[\text{HPd}(\text{diphosphine})_2]^+$  complexes to form  $[\text{Pd}(\text{diphosphine})_2]^+$  species is not expected to produce a large structural rearrangement of the phosphorus atoms, as discussed in the two preceding paragraphs. Because there is no large change in geometry, the bite angle of the diphosphine ligand should have little effect on the homolytic bond-dissociation free energies. Similarly, because there is no change in charge, no large charge reorganization is expected, and ligand substituent effects should also be small. As seen in Table 6, neither the substituents nor the chelate bite sizes have a significant effect on the homolytic bond-dissociation free energies of  $[\text{HPd}(\text{diphosphine})_2]^+$  complexes, which are  $57 \pm 1$  kcal/mol for all of the complexes studied. For comparison, increasing the electron-donating ability of the diphosphine ligands from all aryl substituents for  $[\text{HNi}(\text{dppv})_2]^+$  (where dppv is bis(diphenylphosphino)ethene) to all alkyl substituents for  $[\text{HNi}(\text{dmpe})_2]^+$  (where dmpe is bis(dimethylphosphino)ethane) increased the homolytic bond-dissociation free energies by 3 kcal/mol.<sup>12</sup> For these same two complexes, the  $\text{p}K_a$  values increased by 12 units, and the  $\Delta G_{\text{H}}^\circ$  values decreased by 16 kcal/mol. Clearly, substituent effects have a much larger effect on  $\text{p}K_a$  and  $\Delta G_{\text{H}}^\circ$  values than on homolytic bond-dissociation free energies. The somewhat greater sensitivity to substituents of the homolytic bond-dissociation free energies of  $[\text{HNi}(\text{diphosphine})_2]^+$  complexes as compared to  $[\text{HPd}(\text{diphosphine})_2]^+$  complexes may be a reflection of the slightly higher electronegativity of  $\text{Pd}^{\text{II}}$  ( $\chi_{\text{P}} = 2.20$ ) as compared to  $\text{Ni}^{\text{II}}$  ( $\chi_{\text{P}} = 1.91$ ).<sup>32</sup>

**Linear Free-Energy Correlation of  $\Delta G_{\text{H}}^\circ$  and  $E_{1/2}(\text{II/I})$ .** The hydride donor abilities of the palladium hydride complexes exhibit a linear dependence on the potentials of the (II/I) couples of the corresponding  $[\text{Pd}(\text{diphosphine})_2]^{2+}$  complexes (Figure 5 and eq 8). Similar correlations have been observed previously for  $[\text{HNi}(\text{diphosphine})_2]^+$  complexes.<sup>12</sup> The potentials of the (II/I) couples of the  $[\text{Pd}(\text{diphosphine})_2]^{2+}$  complexes are a measure of the energy of the lowest unoccupied molecular orbital (LUMO) of these complexes. This orbital is the  $d_{x^2-y^2}$  orbital in ligand field theory, and it is antibonding with respect to ligand  $\sigma$  orbitals. The energy of this orbital will be affected by the basicity of the phosphine ligands, which is controlled by the



**Figure 5.** Plot of  $\Delta G_{\text{H}}^\circ$  for  $[\text{HPd}(\text{diphosphine})_2]^+$  versus the potential of the  $E_{1/2}(\text{II/I})$  couples for the corresponding  $[\text{Pd}(\text{diphosphine})_2]^{2+}$  complexes in benzonitrile. The line is the best linear fit of the data with eq 8.

electron-donating ability of the substituents on phosphorus. The energy of this orbital will also be affected by the ligand bite angle. For the  $[\text{Pd}(\text{diphosphine})_2]^{2+}$  complexes, as the natural bite angle increases, there is an increase in the dihedral angle between the planes defined by the phosphorus atoms of the ligand and the metal. As the natural bite angle is increased, the geometry becomes increasingly tetrahedral. This tetrahedral distortion decreases the overlap between the  $d_{x^2-y^2}$  orbital and the ligand  $\sigma$  orbitals, lowering the energy of the LUMO. Based on these simple arguments, the potential of the (II/I) couple is expected to depend on both the substituents on phosphorus and the chelate bite angle of the diphosphine ligand. Because the binding of a hydride by  $[\text{Pd}(\text{diphosphine})_2]^{2+}$  complexes involves a change in charge and geometry very similar to that of a one-electron reduction, the excellent linear correlation observed for these two thermodynamic properties is expected.

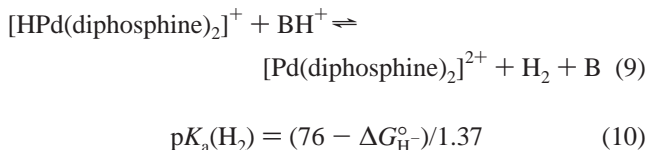
$$\Delta G_{\text{H}}^\circ = 23.5 E_{1/2}(\text{II/I}) + 83.4 \quad (8)$$

Equation 8 can be used to calculate an  $E_{1/2}(\text{II/I})$  potential of  $-1.71$  V for  $[\text{Pd}(\text{depe})_2]^{2+}$  from the measured  $\Delta G_{\text{H}}^\circ$  value of 43.2 kcal/mol for  $[\text{HPd}(\text{depe})_2]^+$ . As discussed above, the potential of the (I/O) couple ( $-1.24$  V) for  $[\text{Pd}(\text{depe})_2]^{2+}$  was calculated using eq 7 and the  $\text{p}K_a$  value of  $[\text{HPd}(\text{depe})_2]^+$ . These results indicate that the potential of the (II/I) couple is 0.47 V negative of the (I/O) couple, which is consistent with the two-electron reduction wave observed experimentally. It is important to note that the average of the two calculated values ( $-1.48$  V) agrees well with the experimentally measured potential ( $-1.47$  V). The hydride donor ability of  $[\text{HPd}(\text{dppx})_2]^+$  (70 kcal/mol) can also be estimated from eq 8 and the previously reported (II/I) potential ( $-0.57$  V).<sup>14</sup>

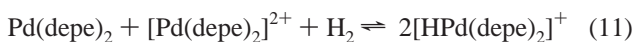
**Acidity, Hydricity, and  $\text{p}K_a$  Stability Ranges.** With an acid of sufficient strength, hydride complexes become unstable with respect to loss of hydrogen, according to reaction 9. A thermodynamic cycle generates eq 10, which uses  $\Delta G_{\text{H}}^\circ$  to calculate  $\text{p}K_a(\text{H}_2)$ , the  $\text{p}K_a$  required to protonate the hydride to form  $\text{H}_2$  and  $[\text{Pd}(\text{diphosphine})_2]^{2+}$ .<sup>12,13</sup> Thus, the hydricity value of  $[\text{HPd}(\text{dppx})_2]^+$  can be used in eq 10 to determine a  $\text{p}K_a(\text{H}_2)$  value of 4.4.  $[\text{HPd}(\text{dppx})_2]^+$  should be stable to acids with  $\text{p}K_a$  values higher than 4.4, and it should be unstable with respect to hydrogen evolution in the presence of acids with  $\text{p}K_a$  values

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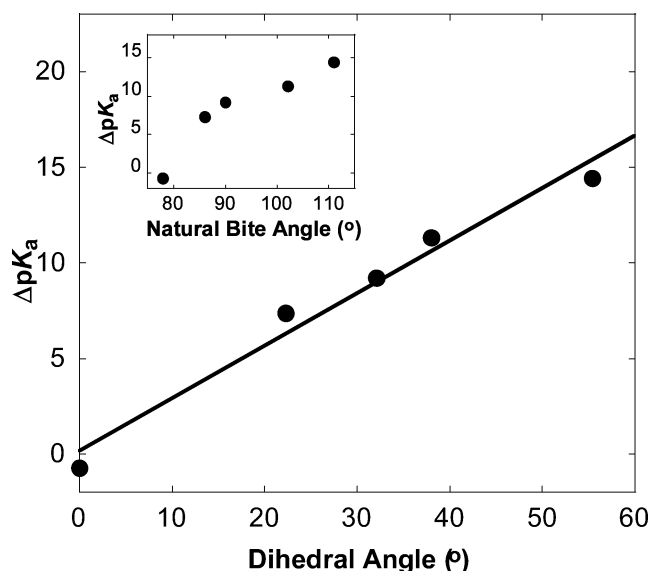
in acetonitrile of less than 4.4. Because  $[\text{HPd}(\text{dppx})_2]^+$  is expected to have a  $\text{p}K_a$  value of 12.8, as discussed above, it will be deprotonated in solutions containing bases with  $\text{p}K_a(\text{BH}^+)$  values higher than 12.8. Thus,  $[\text{HPd}(\text{dppx})_2]^+$  is expected to be stable over a  $\text{p}K_a$  range from 12.8 to 4.4 in acetonitrile. This can be very useful when designing synthetic reactions to prepare such a hydride.



Similarly, the hydricity of  $[\text{HPd}(\text{depe})_2]^+$  can be used to calculate a  $\text{p}K_a(\text{H}_2)$  of 23.9 for  $\text{H}_2$  formation from this hydride. Because the  $\text{p}K_a$  of this complex is 23.2, it is unstable with respect to itself (by  $-0.7$   $\text{p}K_a$  units); that is, it is acidic enough to cause elimination of  $\text{H}_2$ . Indeed, an equimolar mixture of  $[\text{Pd}(\text{depe})_2]^{2+}$  and  $\text{Pd}(\text{depe})_2$  in benzonitrile under an atmosphere of hydrogen results in an equilibrium mixture of  $[\text{Pd}(\text{depe})_2]^{2+}$ ,  $\text{Pd}(\text{depe})_2$ , and  $[\text{HPd}(\text{depe})_2]^+$  (as observed by  $^{31}\text{P}$  NMR) according to eq 11, with  $K_{\text{eq}} = 0.01$ . Reaction 11 could occur either by formation of  $\text{Pd}(\text{I})$  intermediates followed by homolytic  $\text{H}_2$  cleavage or by heterolytic cleavage in which the  $\text{Pd}(\text{O})$  complex acts as a base. Heterolytic activation of  $\text{H}_2$  using nitrogen bases and  $[\text{M}(\text{diphosphine})_2]^{2+}$  (where  $\text{M} = \text{Ni}$  and  $\text{Pt}$ ) has been observed previously.<sup>13</sup>



The hydricities of the remaining complexes in Table 6 can be used to calculate the  $\text{p}K_a(\text{H}_2)$  at which hydrogen formation will occur from these hydrides. The values of  $\text{p}K_a(\text{H}_2)$  and the  $\text{p}K_a$  values of the hydrides give a  $\text{p}K_a$  range,  $\Delta\text{p}K_a$ , for each of these complexes over which the hydrides are stable. These  $\Delta\text{p}K_a$  values are shown in the last column of Table 6. As discussed above, the  $\text{p}K_a$  values of the  $[\text{HPd}(\text{diphosphine})_2]^+$  complexes are dependent on the electron-donating ability of the substituents on phosphorus, and they are independent of the chelate bite size. The hydride donor abilities depend on both the substituents on phosphorus and the chelate bite size. The  $\text{p}K_a$  range over which these hydrides are stable is therefore dependent only on the chelate bite effects. The  $\Delta\text{p}K_a$  values shown in Table 6 represent the difference in the hydricities and acidities if the substituents remain the same and only the bite angle of the ligand is changed. Figure 6 shows a plot of  $\Delta\text{p}K_a$  as a function of the observed dihedral angle, which appears to be the geometric parameter that is a manifestation of the natural bite angle. The inset plot also shows  $\Delta\text{p}K_a$  as a function of the calculated natural bite angle. It is apparent that the plot of  $\Delta\text{p}K_a$  versus the dihedral angle is more linear than the plot of  $\Delta\text{p}K_a$  versus the natural bite angle, but both plots are relatively smooth and well behaved. From the plot in Figure 6 and the data in Table 6, it can be seen that  $\Delta\text{p}K_a$  varies from  $-0.7$  to 14.4 on changing the natural bite angle from  $78^\circ$  to  $111^\circ$ . This means that this range of natural bite angles can be used to decouple the acidity and hydricity of these complexes by 20 kcal/mol. The combination of natural bite angles and substituent effects



**Figure 6.** Plot of  $\Delta\text{p}K_a$  versus ligand-to-ligand dihedral angle for the compounds in this study; the line is the best linear fit to the data ( $\Delta\text{p}K_a = 0.27$  angle + 0.18). Inset: Plot of  $\Delta\text{p}K_a$  versus natural ligand bite angle.

results in a total variation of the hydricities for these  $[\text{HPd}(\text{diphosphine})_2]^+$  complexes of 27 kcal/mol. Clearly, chelate bite effects can rival or exceed substituent effects in controlling the hydride donor abilities of these complexes. The ability to use the natural bite angle to control hydricity while having a minimal effect on acidity provides an attractive approach to designing complexes that have tailored combinations of acidities and hydricities suitable for a specific application.

## Summary

A series of five diphosphine ligands with natural ligand bite angles ranging between  $78^\circ$  and  $111^\circ$  have been used to prepare compounds  $[\text{Pd}(\text{diphosphine})_2]^n$  ( $n = 2+, 0$ ). Values of  $\text{p}K_a$  and  $\Delta G_{\text{H}^-}^\circ$  have been determined for the corresponding  $[\text{HPd}(\text{diphosphine})_2]^+$  complexes. It was found that the acidity of the compounds varies with the electron-donating or -withdrawing ability of the substituents on phosphorus, but that it is independent of the natural bite angle of the ligand. The homolytic bond-dissociation free energies of these  $[\text{HPd}(\text{diphosphine})_2]^+$  complexes are independent of both the phosphine substituents and the natural bite angle. The hydricities of these compounds vary over a range of 27 kcal/mol, and they are dependent on both the natural bite angle and the phosphine substituents. The origin of the dependence of the hydricities and potentials of the  $\text{Pd}(\text{II/I})$  redox couples on the natural bite angles can be traced to structural distortions. With increasing natural bite angles, the geometry around the metal becomes more distorted toward a tetrahedron. In palladium(II) complexes, the geometry of complexes with small bite angles is very close to square planar, but is more intermediate between square planar and tetrahedral for complexes containing diphosphine ligands with large bite angles. This tetrahedral distortion stabilizes the LUMO and results in compounds that are easier to reduce and that are energetically more favorable for binding a hydride ligand. Thus, palladium diphosphine hydride complexes with large bite angles are good hydride acceptors and poor hydride donors. By varying the natural bite angle over a range of  $33^\circ$ , the hydride donor abilities can be tuned over a range of 27 kcal/

mol. The variation of the hydricity of metal hydrides with the natural bite angle is undoubtedly important in many catalytic processes.

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**Supporting Information Available:** X-ray structural data for the compounds listed in Tables 1 and 2, including tables of crystal and refinement data, atomic positional and thermal parameters, and interatomic distances and angles (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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