

# Reductive Routes to Dinuclear $d^{10}$ – $d^{10}$ Palladium(0) Complexes and Their Redistribution Equilibria in Solution

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**Summary:** The reaction of hydrazine with  $(dcpe)PdCl_2$  or  $(dippe)Pd(OAc)_2$  leads to high yields of the isolated dinuclear complexes  $[(\mu-dcpe)Pd]_2$  and  $[(\mu-dippe)Pd]_2$ , respectively. In solution, these dinuclear complexes undergo a monomer–dimer equilibrium with their corresponding 14-electron  $(P-P)Pd$  fragments. Solutions containing both  $[(\mu-dcpe)Pd]_2$  and  $[(\mu-dippe)Pd]_2$  give near statistical amounts of the novel “mixed” dimer  $(\mu-dcpe)(\mu-dippe)Pd_2$ .

The activation of aromatic carbon–halogen bonds by coordinatively unsaturated complexes of palladium(0) is a critical step in a number of important catalytic reactions, including the Heck reaction<sup>1</sup> and cross-coupling reactions of aryl halides.<sup>2</sup> Reactions involving difficult bond activations such as the C–Cl bond of chloroarenes often involve palladium(0) catalyst precursors in the presence of chelating, and usually sterically congested, bis-phosphine ligands. The C–Cl activation step is believed to involve the extremely reactive 14-electron dicoordinate intermediate  $(P-P)Pd$ . Milstein and Portnoy, for example, demonstrated directly an equilibrium giving rise to  $(dipp)Pd$ ,<sup>3a</sup> the key intermediate in the catalytic carbonylation,<sup>3b</sup> formylation,<sup>3c</sup> and reduction<sup>3d</sup> of aryl chlorides. Fryzuk and co-workers have similarly identified  $(dippe)Pd$  as the putative and highly reactive 14-electron fragment in the catalytic reductive dechlorination of chlorobenzene by  $[(dippe)Pd]_2(\mu-dippe)$  ( $dipp = 1,3$ -bis(diisopropylphosphino)propane;  $dippe = 1,2$ -bis(diisopropylphosphino)ethane).<sup>4</sup>

Sources of catalytically active palladium(0) typically arise from ligand dissociation from coordinatively more saturated  $Pd(0)$  complexes<sup>2b,5–8</sup> or from reduction of a

$Pd(II)$  species.<sup>9</sup> A potentially cleaner and more direct route to catalytically active  $(P-P)Pd$  fragments is offered through the dissociation of the dinuclear complexes  $[(\mu-P-P)Pd]_2$ . We have previously reported the synthesis of the dinuclear complex  $[(\mu-dcpe)Pd]_2$  (**1**) from the photolysis of  $(dcpe)Pd(C_2O_4)$  ( $dcpe = 1,2$ -bis(dicyclohexylphosphino)ethane).<sup>10</sup> In solution, the dinuclear complex **1** exists in a facile equilibrium with  $(dcpe)Pd$ , thereby acting as a “bottled” source of this highly reactive 14-electron intermediate. As a consequence, the reaction of **1** with chlorobenzene was found to give  $(dcpe)PdPhCl$  rapidly at room temperature.

Instances of these dinuclear complexes, however, are relatively rare. A closely related derivative  $[(\mu-dippe)Pd]_2$  (**2**) was tentatively identified by the groups of Fryzuk<sup>4</sup> and Pörschke<sup>11</sup> in reaction mixtures but never isolated in pure form. Jolly et al. have structurally characterized the complex  $[(\mu-dippm)Pd]_2$ , which was isolated as a reaction side product.<sup>12</sup> Very recently, we have obtained the complexes  $[(\mu-dcpm)Pd]_2$  and  $[(\mu-dtbpm)Pd]_2$  from the reductive elimination of ethane from dimethylpalladium(II) complexes ( $dippm =$  bis(diisopropylphosphino)methane;  $dcpm =$  bis(dicyclohexylphosphino)methane;  $dcpm =$  bis(di-*tert*-butylphosphino)methane).<sup>13</sup>

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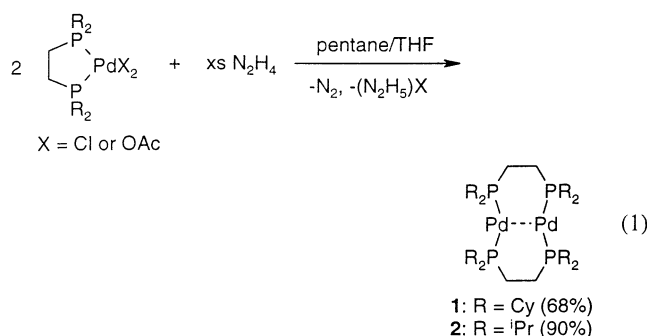
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Detailed investigations of these dinuclear complexes have hereto been limited by the availability of general and scalable synthetic routes. For example, the photolysis of the oxalate, (dcpe)Pd(C<sub>2</sub>O<sub>4</sub>), could not be successfully scaled to generate more than ~50 mg of pure **1**. On the other hand, the synthesis of complexes from reductive elimination of ethane is highly dependent on the bis-phosphine ligand.<sup>14</sup> We now report a much more efficient and improved synthesis that allows **1** and **2** to be isolated in multigram quantities. The preliminary reaction chemistry of **2** indicates that it also dissociates in solution to give highly reactive (dippe)Pd fragments, a finding that is corroborated by the direct spectroscopic observation of a novel "mixed" dimer that exists in equilibrium with mixtures of both **1** and **2**.

Rapid addition of excess N<sub>2</sub>H<sub>4</sub><sup>15</sup> to suspensions of either (dcpe)PdCl<sub>2</sub><sup>16</sup> in THF or (dippe)Pd(OAc)<sub>2</sub> in pentane quickly gave rise to bright red solutions containing essentially pure **1** or **2**, respectively (eq 1).<sup>17,18</sup>



After filtration of the hydrazinium chloride and removal of solvent, high yields of both **1** and **2** were obtained as highly air-sensitive orange-red microcrystalline solids. The new compound **2** was fully characterized by NMR,

(14) The reductive elimination of ethane from [R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>]<sub>2</sub>PdMe<sub>2</sub> to give dipalladium complexes is limited to cases where n = 1.<sup>13</sup>

(15) To our knowledge, only two other reports describe the synthesis of Pd(0) complexes via hydrazine reduction of Pd(II) starting materials: that for (Ph<sub>3</sub>P)<sub>4</sub>Pd (Malatesta, L.; Angoletta, M. *J. Chem. Soc.* **1957**, 1186) and that for (1,2-(diphenylphosphinoethynyl)benzene)<sub>2</sub>Pd (Coalter, N. L.; Concolino, T. E.; Streib, W. E.; Hughes, C. G.; Rheingold, A. L.; Zaleski, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3112).

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(17) Synthesis of **1**: A vigorously stirred suspension of (dcpe)PdCl<sub>2</sub> (3.225 g, 5.376 mmol) in 28 mL of THF was treated at once with N<sub>2</sub>H<sub>4</sub> (3.446 g, 107.520 mmol). Within 30 s, the color began to change to orange-red. After 20 min, 30 mL of pentane was added and the dark orange-red mixture was filtered through a bed of Celite. Volatiles were removed completely from the filtrate by prolonged exposure to vacuum (16 h) to leave a dark orange-red microcrystalline solid that was pure, as judged by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR: yield 1.921 g (68%). <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR match the reported data.<sup>10</sup> Synthesis of **2**: A vigorously stirred suspension of (dippe)Pd(OAc)<sub>2</sub> (5.649 g, 11.603 mmol) in 40 mL of pentane was treated at once with N<sub>2</sub>H<sub>4</sub> (5.578 g, 174.045 mmol), whereupon immediate rapid gas evolution and a color change to deep orange-red was observed. After 30 min, the mixture was filtered through a bed of Celite. Volatiles were removed completely from the filtrate by prolonged exposure to vacuum (16 h) to leave a dark orange-red solid; yield 3.868 g (90%). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) of this crude product showed that it contained 2–3% [(dippe)Pd]<sub>2</sub>(μ-dippe). Crystallization from Et<sub>2</sub>O at –78 °C afforded the pure product as red-orange crystals that were dried in vacuo: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.33 (m, 24, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (m, 4, PCH<sub>2</sub>CH<sub>2</sub>P), 1.81 (m, 4, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 20.93 (br, CH(CH<sub>3</sub>)<sub>2</sub>), 22.60 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 26.64 (m, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 33.80 (s); UV–vis (hexane) λ<sub>max</sub> 455 nm; HRMS (EI, 70 eV) *m/z* calcd for C<sub>28</sub>H<sub>64</sub>P<sub>4</sub><sup>106</sup>Pd<sup>108</sup>Pd 738.2032, found 738.2011 (M<sup>+</sup>); Anal. Calcd for C<sub>28</sub>H<sub>64</sub>P<sub>4</sub>Pd<sub>2</sub>: C, 45.60; H, 8.75. Found: C, 45.57; H, 8.80.

(18) Attempted reductions with Mg sand led to no reactions, and those with K<sub>8</sub> gave irreproducible and low yields of the products.

combustion analysis, and mass spectrometry.<sup>19</sup> The <sup>31</sup>P chemical shift of 33.8 ppm is identical with that ascribed to it by Fryzuk and Pörschke on the basis of reaction mixtures.<sup>4,11</sup> The high-resolution mass spectrum and elemental analysis of **2** are in full accord with a dinuclear structure. The mass spectrum (EI, 70 eV) shows a molecular ion at 738 amu and a high-mass fragment (695 amu, 2.4%) arising from the loss of one isopropyl group. A small fragment ion at 368 amu (3.4%) corresponding to the monomer (dippe)Pd is also observed. The intense red color of complex **2** arises from a long-wavelength absorption band at λ<sub>max</sub> = 455 nm, which is attributed to a dσ\* → pσ transition<sup>20</sup> typical of bimetallic bonding interactions in d<sup>10</sup>–d<sup>10</sup> model systems (M = Pd, Pt).<sup>21</sup> The long-wavelength absorption for **2** is virtually identical with that observed for **1**, which suggests a high degree of structural and bonding similarity between the two complexes.

The preliminary reaction chemistry of **2** suggests the intermediacy of a highly reactive mononuclear complex, (dippe)Pd, in equilibrium with **2** in solution (Scheme 1). For example, the activation of the carbon–chlorine bond in PhCl by **2** in toluene proceeded smoothly at room temperature to furnish the mononuclear insertion product (dippe)Pd(Ph)Cl (**3**) in excellent isolated yield. Not surprisingly, these mild conditions contrast sharply with those reported previously (100 °C, overnight) by Portnoy and Milstein for the synthesis of **3** from the coordinatively saturated (dippe)<sub>2</sub>Pd.<sup>22</sup> Addition of PhSiH<sub>3</sub> to **2** in benzene led to the high-yield formation of the white crystalline solid (dippe)Pd(SiH<sub>2</sub>Ph)<sub>2</sub> (**4**), a very rare example<sup>23</sup> of an isolated Pd(II) *cis*-bis(silyl) complex.<sup>24</sup> In contrast to the related air-stable (dcpe)Pd(SiH<sub>2</sub>Ph)<sub>2</sub>,<sup>23f</sup> **4** is reactive toward oxygen and is stable in air for only brief periods of time.

Further support for the existence of facile monomer–dimer equilibria for complexes **1** and **2** is given from redistribution processes involving mixtures of both species in solution (Scheme 2). Separate solutions of **1** and **2** each exhibit a sharp singlet in <sup>31</sup>P{<sup>1</sup>H} NMR spectra at δ 23.40 and 33.80, respectively. Dissolution of approximately equimolar amounts of **1** and **2** in toluene-*d*<sub>8</sub> gave, after 3 days at 20 °C, an equilibrium mixture of **1**, **2**, and the "mixed dimer" (μ-dcpe)(μ-dippe)-

(19) A preliminary X-ray crystallographic analysis of **2** has been performed and supports the dinuclear structure shown in eq 1. A successful refinement could not be obtained due to chemical disorder within the crystal.

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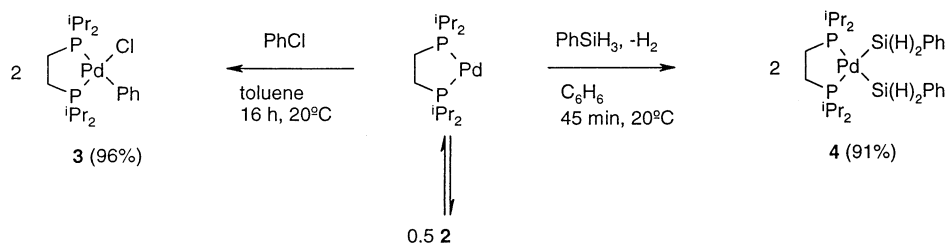
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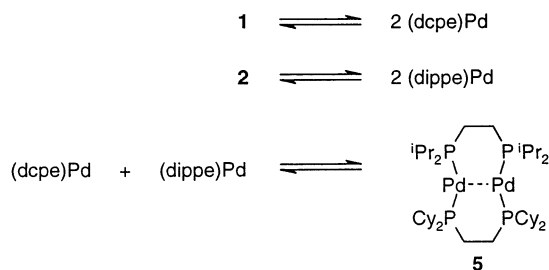
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(24) Synthesis of **4**: A stirred orange-red solution of **2** (300 mg, 0.407 mmol) in 10 mL of benzene was treated with PhSiH<sub>3</sub> (528 mg, 4.881 mmol), whereupon a rapid color change to pale amber occurred. After 45 min, the product had crystallized from the reaction mixture as fine white needles. Pentane (20 mL) was added to induce further crystallization. The mother liquor was siphoned from the crystals, which were then suspended in pentane, collected by filtration, washed with 3 × 5 mL of pentane, and dried in vacuo; yield 432 mg (91%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) 1.03 (m, 24, CH(CH<sub>3</sub>)<sub>2</sub>), 1.80 (m, 4, PCH<sub>2</sub>CH<sub>2</sub>P), 2.28 (m, 4, CH(CH<sub>3</sub>)<sub>2</sub>), 4.46 (m, 4, Si–H, *J*<sub>SiH</sub> = 82), 7.17 (m, 6, Ph), 7.59 (m, 4, Ph); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 65.25 (s). Anal. Calcd for C<sub>26</sub>H<sub>46</sub>P<sub>2</sub>PdSi<sub>2</sub>: C, 53.55; H, 7.95. Found: C, 53.48; H, 8.20.

Scheme 1. Reactivity of [(dippe)Pd]<sub>2</sub> (2)

## Scheme 2. Formation of “Mixed Dimer” 5



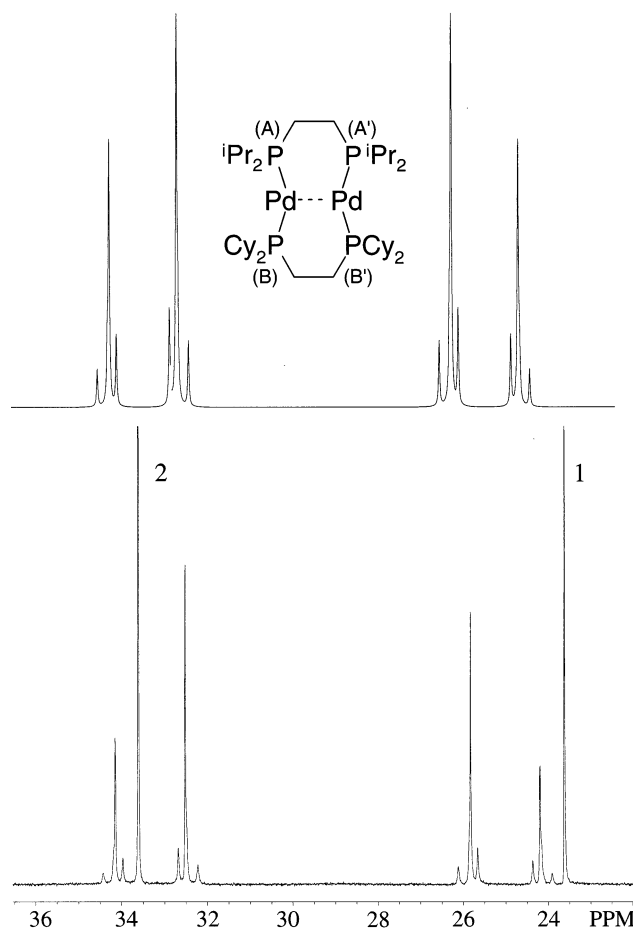
Pd<sub>2</sub> (5), in an approximate 1.0:3.0:3.7 composition. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this mixture is presented in Figure 1 along with a computer simulation of resonances for 5 that were analyzed as an AA'BB' spin system.<sup>25</sup> The derived chemical shift values of 25.1 and 33.3 ppm are nearly the same as the values of the pure complexes 1 and 2, respectively. A large coupling constant of 267.45 Hz for |J<sub>AB</sub>| is also consistent with structure 5, in which the *trans* phosphorus nuclei are inequivalent. Additional coupling constants listed below Figure 1 are in general agreement with those found for AA'BB' spin systems of other dipalladium complexes that contain bridging bisphosphine ligands.<sup>26</sup>

We have disclosed a highly efficient synthesis of the dinuclear palladium complexes 1 and 2 in which *multi-gram* quantities of these complexes can now be prepared and investigated. The formation of the “mixed dimer” 5 unequivocally establishes a monomer–dimer equilibrium of 1 and 2 in solution, a finding that illustrates the propensity of these dimers to serve as “bottled” sources of the highly reactive 14-electron fragments (P–P)Pd. We are currently exploring the generality of hydrazine reduction routes to other related dinuclear palladium complexes which contain chelating bisphosphine ligands as well as the relevance of these complexes to catalytic processes.

**Acknowledgment.** We thank Dow Corning Corp. and the Tulane Center for Bioenvironmental Research

(25) After subspectral analysis, starting data and the experimental spectrum for 5 were used for iterative, least-squares optimization of chemical shifts and coupling constants using the gNMR 4.1 software package (Budzelaar, P. H. M. Cherwell Scientific Limited, 1999).

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**Figure 1.** (Bottom) 161.96 MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of an equilibrium mixture containing 1, 2, and 5 in toluene-*d*<sub>8</sub>. The resonances for 1 and 2 appear as singlets and are labeled as such. The remaining AA'BB' multiplet is attributed to complex 5. (Top) Simulated and fitted AA'BB' pattern for 5 with δ<sub>A</sub> 33.25, δ<sub>B</sub> 25.10, J<sub>AB</sub> = ±267.45 Hz, J<sub>AB'</sub> = ±3.37 Hz, J<sub>AA'</sub> = ±35.11 Hz, and J<sub>BB'</sub> = ±40.95 Hz.

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**Supporting Information Available:** Detailed experimental procedures for (dippe)Pd(OAc)<sub>2</sub> and 4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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