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## Coordinated Water/Anion Hydrogen Bonds and Pd-H Bond Acidity in Cationic Palladium(II) Aquo Hydrides and the X-ray Crystal and Molecular Structures of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(H<sub>2</sub>O)]BF<sub>4</sub>

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Palladium(II) bis(tricyclohexylphosphine) cationic hydrides have been obtained by oxidative addition of the strong acids [H<sub>3</sub>O<sup>+</sup>][BF<sub>3</sub>OH<sup>-</sup>] or [H<sub>3</sub>O<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] to (PCy<sub>3</sub>)<sub>2</sub>Pd, 1; by this route, the compounds *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(H<sub>2</sub>O)]X (X = BF<sub>3</sub>OH, 2; X = BF<sub>4</sub>, 4) have been isolated and characterized. A strong dependence of the stability of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(L)]X complexes upon the L-X combinations was observed. When L = H<sub>2</sub>O, stable cationic hydrides are obtainable only with fluorine-containing anions (BF<sub>3</sub>OH<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, or PF<sub>6</sub><sup>-</sup>), while immediate decomposition to 1 was observed when the metathesis of X<sup>-</sup> with BPh<sub>4</sub><sup>-</sup> or B(*n*-Bu)<sub>4</sub><sup>-</sup> was attempted. Stable complexes with X = BPh<sub>4</sub> could be isolated when L = MeCN. No reaction was observed when 1 was reacted with [Et<sub>2</sub>OH<sup>+</sup>][BF<sub>4</sub><sup>-</sup>]. These findings can be explained in principle by two hypotheses: (i) when the strength of the M-L bond is not sufficient to stabilize the [(R<sub>3</sub>P)<sub>2</sub>Pd(H)(L)]X complexes, further thermodynamic assistance is furnished by hydrogen-bond formation between the metal-bonded ligand L and the X counteranion, and/or (ii) depending upon the nature of L, the cationic hydrides are sufficiently acidic to decompose reactive anions such as BPh<sub>4</sub><sup>-</sup> or B(*n*-Bu)<sub>4</sub><sup>-</sup>. IR and crystallographic data on *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(H<sub>2</sub>O)]BF<sub>4</sub> show the existence, in the solid state, of strong hydrogen bonds between the Pd-bound water molecule and the BF<sub>4</sub><sup>-</sup> anion. A conductivity study on 4 and on the related hydride *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(MeCN)]BF<sub>4</sub>, 5, shows the existence of large concentrations of ions both in 4 and 5 solutions, though the values of Λ<sub>M</sub> (10–20% lower for 4 as compared to 5) could account for the presence in 4 of appreciable amounts of the hydrogen-bonded species. The aquohydride 4 has evidenced its acidic behavior by protonating strong and weak bases (Ph<sub>3</sub>C<sup>-</sup>, OH<sup>-</sup>, Et<sub>3</sub>N, and PCy<sub>3</sub>), and further information on its acid-base behavior has been obtained through the study of exchange reactions with D<sub>2</sub>O. The aquodeuteride *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(D)(H<sub>2</sub>O)]BF<sub>4</sub>, 9, can in fact be obtained by reacting for a few minutes a solution of complex 4 with D<sub>2</sub>O while the *d*<sub>3</sub> derivative *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(D)(D<sub>2</sub>O)]BF<sub>4</sub>, 10, can only be obtained after prolonged reaction times. Complex 2 behaves similarly, and *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(D)(H<sub>2</sub>O)]BF<sub>3</sub>OD, 11, or *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(D)(D<sub>2</sub>O)]BF<sub>3</sub>OD, 12, can be prepared by controlling the reaction times with D<sub>2</sub>O. These data suggest that the acidity of the hydridic hydrogen is higher than the acidity of the hydrogens of the PdOH<sub>2</sub> moiety. The last hypothesis is further confirmed by the reaction of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(D)(H<sub>2</sub>O)]BF<sub>4</sub> with Ph<sub>3</sub>CLi, which yields a 70/30 Ph<sub>3</sub>C-*d*/Ph<sub>3</sub>C-*h* mixture. Crystals of 4 are monoclinic, C2/c, *a* = 30.587 (6) Å, *b* = 13.408 (4) Å, *c* = 19.121 (5) Å, β = 99.23 (3)°, *V* = 7740.2 Å<sup>3</sup>, *Z* = 8, *R* = 0.040 for 3077 reflections with *F*<sub>o</sub> > 4σ(*F*<sub>o</sub>).

### Introduction

A rapidly growing interest in the reactivity of the O-H bond toward late transition metals (LTMs) can be perceived in the recent literature. This is not surprising if one thinks that relevant reactions catalyzed by LTM complexes need a LTM/OH bond interaction; representative examples are the Wacker oxidation reaction,<sup>2</sup> the water gas shift (WGS) reaction,<sup>3</sup> olefin hydrocarboxylations,<sup>4</sup> olefin, alkyl halide and alcohol carboxylations,<sup>2,5</sup> carbonyl compound hydrogenations<sup>2</sup> and alcohol dehydrogenations,<sup>2</sup> and nitrile<sup>2,6</sup> and olefin<sup>2,7</sup> hy-

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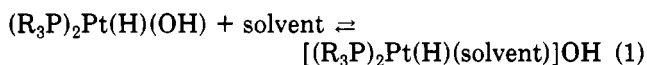
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drations. Comprehensive studies in this area have been delayed by the common belief that the LTM–oxygen bond should be weak; this opinion was contradicted by both synthetic<sup>2</sup> and thermodynamic<sup>2,8</sup> studies, and Bryndza and Tam have exhaustively reviewed syntheses, structures, and reactivity of LTM alkoxides and hydroxides.<sup>2</sup>

A remarkable subset of the above topic is represented by LTM reactions with the water O–H bond; the photolytic splitting of water<sup>9</sup> and the activated C–H bond deuteration by D<sub>2</sub>O,<sup>6a,10</sup> as well as many of the catalytic reactions listed previously, proceed through H<sub>2</sub>O–LTM interactions. Only a few water oxidative addition reactions to LTM have been observed, and the first completely characterized mononuclear hydrido–hydroxy derivative of a group 8 system, *cis*-[Ir(H)(OH)(PMe<sub>3</sub>)<sub>4</sub>]PF<sub>6</sub>, has been recently reported by Milstein.<sup>11</sup> The neutral Pt derivatives *trans*-[(Pt(H)(OH)(PR<sub>3</sub>)<sub>2</sub>] have been spectroscopically detected in solution<sup>3b,6,12</sup> in the presence of a strong excess of water, but they could not be isolated pure, while a cationic rhodium amino complex, *trans*-[Rh(en)<sub>2</sub>(H)(OH)]<sup>+</sup>, was reported to form upon electrochemical reduction of *trans*-[Rh(en)<sub>2</sub>Cl]<sup>+</sup> in aqueous solution.<sup>13</sup> The Ru derivative (Ph<sub>3</sub>P)<sub>2</sub>Ru(H)(OH)(solvent) was prepared by reacting the corresponding chloride with NaOH.<sup>14</sup>

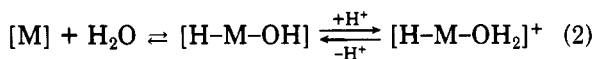
Some formal water oxidative addition reactions result in the formation of cationic hydrides, with the hydroxide ion acting as a nonbonded anion: [RhH<sub>2</sub>(Py)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]OH,<sup>15</sup> [RhH<sub>2</sub>(PR<sub>3</sub>)<sub>3</sub>]OH,<sup>15</sup> [PtH(PR<sub>3</sub>)<sub>3</sub>]OH<sup>3b,6a,16</sup> and [PdH(PR<sub>3</sub>)<sub>3</sub>]OH<sup>17</sup> fall in this class. All of these compounds can be handled in solution, but they can be isolated as pure compounds only after metathesis of the hydroxide ion, usually with NaBPh<sub>4</sub>.

Inner- and outer-sphere hydroxides of [L<sub>n</sub>MH]<sup>+</sup> fragments can be interconverted: this has been verified<sup>3b,6</sup> for the Pt phosphino derivatives (see eq 1), and the catalytic

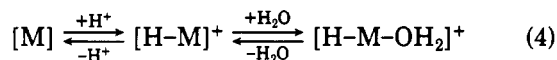
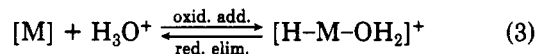


efficiency of these systems has been successfully tested in the WGS reaction<sup>3b</sup> in activated C–H bond deuteration by D<sub>2</sub>O,<sup>6a</sup> and in olefin and nitrile hydration.<sup>6</sup>

Neutral hydrido–hydroxo complexes are related, through an acid–base equilibrium (eq 2), to cationic aquo hydride complexes that are generally prepared by protonation of a basic LTM complex with strong acids in the presence of water.



The possible decomposition pathways of cationic aquo hydride complexes, which are formally derived from the oxidative addition of the oxonium ion H<sub>3</sub>O<sup>+</sup> (eq 3), are represented by equilibria 2–4, which take into account the influence of the relative acidities of the M–H and M(HO–H) hydrogens.



To the best of our knowledge, the known cationic LTM aquo hydride complexes are [Ir(benzoquinolato)-(PR<sub>3</sub>)<sub>2</sub>(H)(H<sub>2</sub>O)]<sup>+</sup>,<sup>18a</sup> [Ir(H)<sub>2</sub>(H<sub>2</sub>O)(L)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (L = THF, olefin, H<sub>2</sub>O),<sup>18b,c</sup> [Ir(H)(H<sub>2</sub>O)(CO)(Cl)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>,<sup>19a,b</sup> [Ru(H)(H<sub>2</sub>O)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>,<sup>19c</sup> [Rh(en)<sub>2</sub>(H)(H<sub>2</sub>O)]<sup>2+</sup>,<sup>13</sup> and [(R<sub>3</sub>P)<sub>2</sub>Pt(H)(H<sub>2</sub>O)]<sup>+</sup>.<sup>6b,20,21</sup>

## Experimental Section

**General Procedures.** Unless otherwise stated, all procedures were carried out by using standard Schlenk techniques, under an atmosphere of prepurified nitrogen or argon. Nujol mulls of oxygen- or moisture-sensitive compounds were prepared in a glovebox.

**Materials.** HBF<sub>4</sub> (37% aqueous) (Merck), HBF<sub>4</sub>·54% ether (Fluka), BF<sub>3</sub>·Et<sub>2</sub>O (Aldrich), AgBF<sub>4</sub> (Aldrich), NaPF<sub>6</sub> (Aldrich), NaBPh<sub>4</sub> (C. Erba), and Et<sub>3</sub>N (Aldrich) were used as purchased. H<sub>2</sub>O and D<sub>2</sub>O were distilled from KMnO<sub>4</sub>. All other reagents were refluxed on a proper drying agent (in parentheses), distilled under nitrogen, and used immediately or stored on molecular sieves: Py, CH<sub>3</sub>CN, and CD<sub>3</sub>CN (CaH<sub>2</sub>), CH<sub>3</sub>OH and CD<sub>3</sub>OD (Mg or Na corresponding alkoxide), THF and THF-*d*<sub>3</sub> (LiAlH<sub>4</sub>), toluene (Na), C<sub>6</sub>D<sub>6</sub>, *n*-hexane and Et<sub>2</sub>O (Na/K benzophenone), CH<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> (P<sub>2</sub>O<sub>5</sub>), and acetone and acetone-*d*<sub>6</sub> (Na<sub>2</sub>CO<sub>3</sub>). When strictly anhydrous conditions were required, the distilled solvent or reagent was again refluxed on the drying agent and distilled.

PCy<sub>3</sub>,<sup>22a</sup> (Cy<sub>3</sub>P)<sub>2</sub>Pd,<sup>22b</sup> LiB(*n*-Bu)<sub>4</sub>,<sup>23</sup> and Ph<sub>3</sub>ClI<sup>24</sup> were prepared as previously described, Ph<sub>3</sub>C-*d* was prepared for comparison purposes by reacting Ph<sub>3</sub>ClI with D<sub>2</sub>O in anhydrous thf.

**Physical Measurements.** IR spectra were recorded with a Perkin-Elmer 283-B spectrometer. Liquid samples were placed in 0.1-mm cells that were flushed with nitrogen before use. Solid samples were prepared as Nujol mulls. Fourier transform <sup>1</sup>H NMR spectra were recorded on a Varian XL-100 spectrometer at 100 MHz or a Varian XR-300 instrument at 299.945 MHz; <sup>19</sup>F, <sup>31</sup>P, and <sup>2</sup>H NMR spectra were recorded on a Varian XR-300 spectrometer at 282.203, 121.421, and 46.044 MHz, respectively. Chemical shifts are reported relative to internal Me<sub>4</sub>Si (<sup>1</sup>H), CFCl<sub>3</sub> (<sup>19</sup>F), and CDCl<sub>3</sub> (<sup>2</sup>H) or external H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), positive chemical shifts being downfield of the reference.

Gas chromatographic analyses were performed with a Dani 8400 instrument equipped with a 10% OV-101 on Chromosorb W-AW (80/100-mesh, 2-m) column.

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**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(H<sub>2</sub>O)]BF<sub>3</sub>OH (2).** A solution of BF<sub>3</sub>·Et<sub>2</sub>O (0.231 mL, 1.88 mmol) in toluene (5 mL) and water (0.17 mL, 9.44 mmol) was dropped into a solution of (Cy<sub>3</sub>P)<sub>2</sub>Pd (1.252 g, 1.88 mmol) in toluene (15 mL). A colorless crystalline solid began to precipitate during the addition; the suspension was vigorously stirred 2 h at room temperature, and the solid was then filtered and vacuum dried (1.125 g, 1.46 mmol, 77.7% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 3.26 [1:3:3:1 q, <sup>3</sup>J<sub>HF</sub> = 8 Hz, 1 H, BF<sub>3</sub>OH], 2.20–1.00 [m, 66 H, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>], –20.65 [br s, 1 H, PdH]. IR (Nujol, cm<sup>-1</sup>): 3520 s [ν<sub>OH(ass,H<sub>2</sub>O)</sub>], 3430 s [ν<sub>OH(ass,H<sub>2</sub>O)</sub>], 3220 s [ν<sub>OH(BF<sub>3</sub>OH)</sub>], 2110 w [ν<sub>PdH</sub>], 1630 m [δ<sub>HOH</sub>], 1120 vs, 1050 vs, 1000 s, 980 vs [ν<sub>BF</sub>], 720 m [δ<sub>PdH</sub>]. Anal. Calcd for C<sub>36</sub>H<sub>70</sub>BF<sub>3</sub>O<sub>2</sub>P<sub>2</sub>Pd: C, 56.07; H, 9.15, F, 7.39. Found: C, 55.75; H, 8.88, F, 7.27.

**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(CH<sub>3</sub>CN)]BF<sub>3</sub>OH (3).** Compound 2 (154 mg; 0.20 mmol) was dissolved in CH<sub>3</sub>CN (10 mL); the solution was stirred 1.5 h at room temperature, and the solvent was removed under vacuum. After recrystallization from thf/Et<sub>2</sub>O, 3 (87.3 mg, 0.11 mmol, 55% yield) was isolated as a colorless crystalline solid. IR (Nujol, cm<sup>-1</sup>): 3220 s [ν<sub>OH</sub>], 2320 vw, 2280 w [ν<sub>CN</sub>], 2080 w [ν<sub>PdH</sub>], 1050 vs [ν<sub>BF</sub>]. Anal. Calcd for C<sub>38</sub>H<sub>71</sub>BF<sub>3</sub>NOP<sub>2</sub>Pd: C, 57.47; H, 9.01; N, 1.76. Found: C, 57.02; H, 8.93; N, 1.69.

**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(H<sub>2</sub>O)]BF<sub>4</sub> (4). Method a.** A solution of AgBF<sub>4</sub> (26 mg, 0.133 mmol) in MeOH (5 mL) was dropped into a solution of 2 (103 mg, 0.133 mmol) in MeOH (8 mL). A small amount of a black powder precipitated and was filtered away; the filtrate was concentrated to ca. 2 mL, and 10 mL of Et<sub>2</sub>O was added. A white powder formed and was filtered off and vacuum dried (33 mg, 0.043 mmol, 32% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 43.2 s (room temperature), the spectrum is unchanged if recorded at –90 °C. <sup>19</sup>F{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>; room temperature): δ –151.08 (s, 1 F, *h*<sub>1/2</sub> = 2.3 Hz), –151.03 (s, 4 F, *h*<sub>1/2</sub> = 2.6 Hz); the spectrum was practically unchanged at –90 °C, the integral ratio of the two signals is 1:4, equal to the <sup>10</sup>B/<sup>11</sup>B isotopic ratio (natural isotopic abundance: <sup>10</sup>B = 19.4%, <sup>11</sup>B = 80.6%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ –18.34 [t, <sup>2</sup>J<sub>PH</sub> = 4.3 Hz, 1 H, PdH], 2.10–1.20 [m, 66 H, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>], 3.07 [s, 3 H, H<sub>2</sub>O]. IR (Nujol, cm<sup>-1</sup>): 3530 s [ν<sub>OH,ass</sub>], 3440 s [ν<sub>OH,ass</sub>], 2115 w [ν<sub>PdH</sub>], 1630 m [δ<sub>HOH</sub>], 1120 vs, 1050 vs, 1000 vs, 990 sh [ν<sub>BF</sub>], 720 m [δ<sub>PdH</sub>]. Anal. Calcd for C<sub>36</sub>H<sub>69</sub>BF<sub>4</sub>OP<sub>2</sub>Pd: C, 55.92; H, 9.00. Found: C, 56.06; H, 8.97.

**Method b.** Aqueous (35%) HBF<sub>4</sub> (0.160 mL; 0.784 mmol) was added to a solution of (Cy<sub>3</sub>P)<sub>2</sub>Pd (517 mg, 0.775 mmol) in toluene (15 mL). The solution was vigorously stirred overnight at room temperature, and the white powder that formed was filtered and vacuum dried (450 mg, 0.582 mmol, 75.1% yield). IR and NMR spectra were indistinguishable from those of the product obtained by method a. Single crystals for the X-ray crystal and molecular structure determination were grown by recrystallization from an acetone/Et<sub>2</sub>O mixture.

**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(CH<sub>3</sub>CN)]BF<sub>4</sub> (5).** Compound 4 (180 mg; 0.233 mmol) was dissolved in CH<sub>3</sub>CN (15 mL); the solution was stirred for 1 h at room temperature and then concentrated to a small volume. Ten milliliters of Et<sub>2</sub>O was added, and a white crystalline solid precipitated; the solid was filtered and vacuum dried (145 mg, 0.182 mmol, 78.2% yield). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ –15.27 [s, 1 H, PdH], 2.10–1.20 [m, 60 H, P[CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>], 2.15 [tt, *J*<sub>1</sub> = 11 Hz, *J*<sub>2</sub> = 3 Hz, 6 H, P[CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>], 2.87 [s, 3 H, CH<sub>3</sub>CN]. <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 43.82 s. IR (Nujol, cm<sup>-1</sup>): 2310 vw [ν<sub>CN</sub>], 2280 w [ν<sub>CN</sub>], 2080 w [ν<sub>PdH</sub>], 1050 vs [ν<sub>BF</sub>]. Anal. Calcd for C<sub>38</sub>H<sub>70</sub>BF<sub>4</sub>NP<sub>2</sub>Pd: C, 57.32; H, 8.86; N, 1.76. Found: C, 57.45; H, 9.00; N, 1.84.

**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(Py)]BF<sub>4</sub> (6).** Compound 4 (92 mg; 0.119 mmol) was dissolved in acetone (10 mL), and 0.01 mL of pyridine (0.124 mmol) was added. The solution was concentrated to a small volume, and 6 mL of Et<sub>2</sub>O was added; a pink solid precipitated and was filtered and vacuum dried (64.5 mg, 0.0773 mmol, 65% yield). IR (Nujol, cm<sup>-1</sup>): 2050 br w [ν<sub>PdH</sub>], 1600 m [ν<sub>CC</sub>], 1050 vs [ν<sub>BF</sub>]. Anal. Calcd for C<sub>41</sub>H<sub>72</sub>BF<sub>4</sub>NP<sub>2</sub>Pd: C, 59.03; H, 8.70; N, 1.68. Found: C, 59.41; H, 8.66; N, 1.72.

**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(H<sub>2</sub>O)]PF<sub>6</sub> (7).** Compound 4 (240 mg; 0.31 mmol) and NaPF<sub>6</sub> (208 mg; 1.24 mmol) were dissolved in MeOH (15 mL). From the yellow solution, a colorless powder precipitated and was filtered away. The filtrate

was concentrated and 15 mL of Et<sub>2</sub>O was added; the colorless crystalline solid that formed was filtered and vacuum dried (152 mg, 0.183 mmol, 59% yield). IR (Nujol, cm<sup>-1</sup>): 3595 s [ν<sub>OH,ass</sub>], 3520 s [ν<sub>OH,ass</sub>], 2120 w [ν<sub>PdH</sub>], 1630 m [δ<sub>HOH</sub>], 840 vs [ν<sub>PF</sub>], 550 m. Anal. Calcd for C<sub>36</sub>H<sub>69</sub>F<sub>6</sub>OP<sub>3</sub>Pd: C, 52.01; H, 8.37. Found: C, 52.44; H, 8.16.

**Preparation of *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(H)(CH<sub>3</sub>CN)]BPh<sub>4</sub> (8).** Compound 4 (105 mg; 0.136 mmol) was dissolved in CH<sub>3</sub>CN (20 mL); 47 mg (0.137 mmol) of NaBPh<sub>4</sub> was added, and the colorless powder, which precipitated in a few minutes, was filtered away. The filtrate was concentrated, and 5 mL of Et<sub>2</sub>O was added; a colorless crystalline solid precipitated and was filtered and vacuum dried (110 mg, 0.106 mmol, 78% yield). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ –15.44 [br s, 1 H, PdH], 2.10–1.20 [m, 60 H, P[CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>], 2.13 [tt, *J*<sub>1</sub> = 11 Hz, *J*<sub>2</sub> = 3 Hz, 6 H, P[CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>], 2.88 [s, 3 H, CH<sub>3</sub>CN], 6.79 [t, *J* = 7 Hz, 4 H, BPh<sub>4</sub> (*p*-H)], 6.92 [t, *J* = 7 Hz, 8 H, BPh<sub>4</sub> (*o*-H)], 7.40–7.30 [m, 8 H, BPh<sub>4</sub> (*m*-H)]. <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>): δ 44.71 s. IR (Nujol, cm<sup>-1</sup>): 3050 m [ν<sub>CH</sub>], 2300 w, 2280 w [ν<sub>CN</sub>], 2090 vw [ν<sub>PdH</sub>], 1580 m [ν<sub>CC</sub>]. Anal. Calcd for C<sub>62</sub>H<sub>90</sub>BNP<sub>2</sub>Pd: C, 72.40; H, 8.82; N, 1.36. Found: C, 72.11; H, 8.72; N, 1.40.

**Attempted Reaction of (Cy<sub>3</sub>P)<sub>2</sub>Pd with HBF<sub>4</sub>·Et<sub>2</sub>O.** Compound 1 (214 mg; 0.321 mmol) and an Et<sub>2</sub>O solution (54%) of HBF<sub>4</sub> (0.050 mL; 0.347 mmol) were dissolved in toluene (10 mL). In some cases, the presence of adventitious water caused the precipitation of a few milligrams of 4, which were filtered away. The solution was stirred at room temperature, and after 2 days, the IR (Nujol) and NMR (C<sub>6</sub>D<sub>6</sub> solution) spectra of the solid obtained by taking to dryness a portion of the solution were still essentially the spectrum of unreacted 1. At this point, a few drops of water were added to the bulk solution and 4 precipitated in high yield. If CH<sub>3</sub>CN or pyridine was added instead of water to solutions obtained following the same procedure, complexes 5 and 6 were respectively isolated in good yields.

**Reactions of 4 with NaBPh<sub>4</sub> or LiB(*n*-Bu)<sub>4</sub>.** A solution of NaBPh<sub>4</sub> (95 mg, 0.278 mmol) in MeOH (5 mL) was dropped into a solution of 4 (215 mg, 0.278 mmol) in MeOH (15 mL). A brown solid started to precipitate after 0.5 h; the suspension was allowed to stand 2 h at room temperature and 2 h at –78 °C; the solid was then filtered, vacuum dried, and identified from its IR and NMR spectra as (Cy<sub>3</sub>P)<sub>2</sub>Pd (135 mg, 0.203 mmol, 73% yield). The volatile fractions in the filtrate were collected by trap-to-trap distillation and analyzed by GLC, and the presence of relevant amounts of benzene was detected. The solid residue was analyzed by TLC and was shown to contain BPh<sub>3</sub> by comparison with an authentic sample.

The same procedure was used starting from 260 mg (0.336 mmol) of 4 and 83 mg (0.337 mmol) in LiB(*n*-Bu)<sub>4</sub> (27 mL total MeOH volume). A similar trend was observed and 157 mg of (Cy<sub>3</sub>P)<sub>2</sub>Pd obtained.

**Exchange Reactions of 4 with D<sub>2</sub>O.** Compound 4 (350 mg) was dissolved in an acetone (25 mL)/D<sub>2</sub>O (10 mL) mixture. The solution was stirred at room temperature, and the progress of the reaction was followed by IR (Nujol) spectroscopy of 0.7-mL portions of the solution taken to dryness. After 15 min, the complete disappearance of the ν<sub>PdH</sub> band at 2115 cm<sup>-1</sup> was observed, 15 mL of the bulk solution was evaporated and vacuum dried, and *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd(D)(H<sub>2</sub>O)]BF<sub>4</sub>, 9, was isolated. IR (Nujol, cm<sup>-1</sup>): 3520 s [ν<sub>OH,ass</sub>], 3440 s [ν<sub>OH,s</sub>], 1630 m [δ<sub>HOH</sub>], 1520 w [ν<sub>PdD</sub>], 1120 vs, 1050 vs, 1000 s, 990 sh [ν<sub>BF</sub>], 535 m [δ<sub>PdD</sub>]. No hydride signals were observed in the <sup>1</sup>H NMR spectrum.

Complete deuteration of the Pd(H<sub>2</sub>O) moiety proved to be much slower, and after 2 weeks, a compound containing ca. 1/1 D<sub>2</sub>O/H<sub>2</sub>O was isolated. The *d*<sub>3</sub> derivative, *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd-(D)(D<sub>2</sub>O)]BF<sub>4</sub>, 10, was obtained by reacting 1 with HBF<sub>4</sub>·Et<sub>2</sub>O in toluene with D<sub>2</sub>O excess. IR (Nujol, cm<sup>-1</sup>): 2620 s [ν<sub>OD,ass</sub>], 2520 s [ν<sub>OD,s</sub>], 1520 w [ν<sub>PdD</sub>], 1120 vs, 1050 vs, 1000 s, 990 sh [ν<sub>BF</sub>], 535 m [δ<sub>PdD</sub>]. No hydride signals were observed in the <sup>1</sup>H NMR spectrum. <sup>2</sup>H NMR (thf): δ 3.0 (s, PdOD<sub>2</sub>), –20.3 (s, PdD).

**Exchange Reaction of 10 with H<sub>2</sub>O.** *trans*-[(Cy<sub>3</sub>P)<sub>2</sub>Pd-(D)(D<sub>2</sub>O)]BF<sub>4</sub> (50 mg) was dissolved in 5 mL of wet THF. The solution was stirred 45 min at room temperature, the solvent was evaporated, and the residue was identified as pure 4 by its IR and NMR spectra. The same reaction was performed in a NMR tube in anhydrous THF and submitted to <sup>2</sup>H NMR analysis. The complete disappearance of the PdD absorption at –20.3 ppm a

few minutes after the addition for 24  $\mu\text{L}$  of  $\text{H}_2\text{O}$  was observed, while the absorption at 3.0 ppm is shifted to 2.1 ppm.

**Exchange Reactions of 2 with  $\text{D}_2\text{O}$ .** Compound 2 (115 mg; 0.149 mmol) was dissolved in 10 mL of THF, and 0.1 mL of  $\text{D}_2\text{O}$  was added. The solution was vigorously stirred and the reaction periodically monitored by IR spectroscopy. After 4 h, the solvent was evaporated and *trans*-[( $\text{C}_3\text{P}$ ) $_2\text{Pd}(\text{D})(\text{H}_2\text{O})\text{BF}_3\text{OD}$ ], 11, was isolated. Longer reaction times (weeks) are necessary to observe significant deuteration of the Pd( $\text{H}_2\text{O}$ ) moiety. The  $d_4$  derivative, *trans*-[( $\text{C}_3\text{P}$ ) $_2\text{Pd}(\text{D})(\text{D}_2\text{O})\text{BF}_3\text{OD}$ ], 12, is best obtained by reacting 1 with  $\text{BF}_3\cdot\text{Et}_2\text{O}$  and  $\text{D}_2\text{O}$  in toluene solution. 11: IR (Nujol,  $\text{cm}^{-1}$ ): 3520 s [ $\nu_{\text{OH}(\text{H}_2\text{O})_{\text{as}}}$ ], 3440 s [ $\nu_{\text{OH}(\text{H}_2\text{O})_{\text{s}}}$ ], 2400 s [ $\nu_{\text{OD}(\text{BF}_3\text{OD})}$ ], 1630 m [ $\delta_{\text{HOH}}$ ], 1520 w [ $\nu_{\text{PdD}}$ ], 1120 vs, 1050 vs, 1000 s, 980 sh [ $\nu_{\text{BF}}$ ], 530 m [ $\delta_{\text{PdD}}$ ]. 12: IR (Nujol,  $\text{cm}^{-1}$ ): 2620 s [ $\nu_{\text{OD}(\text{D}_2\text{O})_{\text{as}}}$ ], 2520 s [ $\nu_{\text{OD}(\text{D}_2\text{O})_{\text{s}}}$ ], 2400 s [ $\nu_{\text{OD}(\text{BF}_3\text{OD})}$ ], 1520 w [ $\nu_{\text{PdD}}$ ], 1120 vs, 1050 vs, 1000 s, 980 sh [ $\nu_{\text{BF}}$ ], 530 m [ $\delta_{\text{PdD}}$ ]. No hydride signals were observed in the  $^1\text{H}$  NMR spectra of 11 and 12.

**Conductance Measurements on 4 and 5.** A Metrohm conductometer E 382 (range 0.01–100 k $\Omega$ ) and a conductivity cell with sealed-in platinum electrodes were used for conductance measurements. The cell constant, determined with a 0.01 M aqueous KCl solution,<sup>25</sup> was 0.835  $\text{cm}^{-1}$ . The dry solvents used (acetone, thf and methylene chloride) exhibited specific conductance less than  $4 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ . Conductivity measurements were carried out at 20  $^\circ\text{C}$ .

**Reactions of 4 with Bases.** Compound 4 (200–250 mg) was reacted with an equimolar amount of the base in 10 mL of  $\text{CH}_3\text{OH}$  ( $\text{Et}_3\text{N}$ , NaOH), acetone ( $\text{PCy}_3$ ), or THF ( $\text{Ph}_3\text{CLi}$ ). After a few minutes, 1 precipitated in high yields from the  $\text{CH}_3\text{OH}$  solutions. The acetone or THF solutions of the reactions with  $\text{PCy}_3$  or  $\text{Ph}_3\text{CLi}$  were evaporated to small volume 15 min after the end of the addition of the base solution; 5 mL of *n*-hexane was added and the filtered solutions were kept 2 h at  $-78^\circ\text{C}$ . The solid that precipitated in high yield was filtered, vacuum dried, and identified as pure 1.

**Reaction of *trans*-[( $\text{C}_3\text{P}$ ) $_2\text{Pd}(\text{D})(\text{H}_2\text{O})\text{BF}_4$  with  $\text{Ph}_3\text{CLi}$ .** Compound 9 (201 mg; 0.260 mmol) was dissolved in 10 mL of anhydrous THF. An equimolar amount of  $\text{Ph}_3\text{CLi}$  dissolved in 5 mL of THF was then slowly added at  $-50^\circ\text{C}$ . The red color of the carbanion solution instantaneously disappeared when the two solutions came in contact. At the end of the addition, the solution was slowly warmed to room temperature and stirred for 30 min. The solution was then evaporated to a small volume, and the residue was chromatographed on silica gel (eluent: *n*-hexane). The fractions containing the  $\text{Ph}_3\text{CH}/\text{Ph}_3\text{CD}$  mixture were identified by comparison of their TLC response with those of authentic samples ( $R_f = 0.32$ ); after evaporation of the solvent, 51 mg (80.3% yield) of a  $\text{Ph}_3\text{CH}/\text{Ph}_3\text{CD}$  mixture was collected. The  $\text{Ph}_3\text{CH}/\text{Ph}_3\text{CD}$  ratio was estimated to be ca. 30/70 by comparison of IR and NMR spectra with those of pure  $\text{Ph}_3\text{CH}$  and  $\text{Ph}_3\text{CD}$  and of mixtures of them.

**Crystallographic Analysis.** The data collection crystal was mounted on a thin glass fiber. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using Mo  $K\alpha$  radiation. The unit cell was refined from 25 reflections in the range  $20 < 2\theta < 25^\circ$ . Crystal data, data collection parameters, and results of the analysis are listed in Table I. Absorption corrections were applied by the Walker and Stuart method.<sup>26</sup> Neutral atom scattering factors were obtained by standard sources.<sup>27</sup> The Pd, P, and O atoms were located by direct methods (SHELX86)<sup>28</sup> and the remaining non-H atoms from subsequent difference Fourier synthesis (SHELX76).<sup>29</sup> Hydride and O-bound hydrogen atoms also were located in difference Fourier maps and not refined, except for their thermal parameters [0.06, 0.08, and 0.03  $\text{\AA}^2$  for H(1), H(2), and H(3), respectively]. All the remaining hydrogen atoms were placed in idealized positions on the cyclohexyl carbon atoms (C–H 1.08  $\text{\AA}$ , H–C–H 109.5 $^\circ$ ) and allowed to ride on these atoms with a common isotropic thermal parameter that was refined (0.078  $\text{\AA}^2$ ). Thermal vibration was treated an-

Table I. Crystallographic Data for *trans*-[( $\text{C}_3\text{P}$ ) $_2\text{Pd}(\text{H})(\text{H}_2\text{O})\text{BF}_4$

(a) Crystal Parameters	
formula	$\text{C}_{36}\text{H}_{69}\text{OPd}\cdot\text{BF}_4$
mol wt	711.12
cryst system	monoclinic
space group	$C2/c$
$a$ , $\text{\AA}$	30.587 (6)
$b$ , $\text{\AA}$	13.408 (4)
$c$ , $\text{\AA}$	19.121 (5)
$\beta$ , deg	99.23 (3)
$V$ , $\text{\AA}^3$	7740.2
$Z$	8
$\mu$ , $\text{cm}^{-1}$	5.19
$\rho$ , $\text{g cm}^{-3}$ (calcd)	1.22
size, mm	$0.12 \times 0.21 \times 0.3$
(b) Data Collection	
radiation	Mo $K\alpha$
$\lambda$ , $\text{\AA}$	0.71069
monochromator	graphite
$2\theta$ scan range, deg	5–50
scan type	$\omega/2\theta$
$\omega$ scan width, deg	0.8
std reflns	3
(c) Data Reduction and Refinement	
reflns collected	7325
unique reflns	5549
unique reflns with $F_o > 4\sigma(F_o)$	3077
abs correction	Walker and Stuart <sup>26</sup>
transmission coeff max, min	1.0, 0.65
$R$ value	0.040
$R_w$ value ( $g$ value)	0.041 (0.00069)
highest peak, final diff Fourier, $e \text{\AA}^{-3}$	0.5
largest shift/error, value of final cycle	0.02

isotropically for all non-H atoms. The structure was refined to converge by using full-matrix least squares. The weighting scheme employed ( $w = K/[\sigma^2(F_o) + |g|F_o^2]$ ) gave satisfactory agreement analyses. Fractional atomic coordinates are reported in Table II.

## Results and Discussion

Despite the relative abundance of data on the  $(\text{R}_3\text{P})_n\text{Pt}/\text{H}_2\text{O}$  systems, the parent Pd systems are quite unexplored; it has been known for several years that tetrakis- or tris(phosphine)-Pd(0) complexes react with aqueous acids to give  $[(\text{R}_3\text{P})_3\text{PdH}]\text{X}$  complexes,<sup>4,16,17,30</sup> but scarce, if any, are the reports on the reactivity of bis(phosphine)-Pd(0) derivatives with water.

We have investigated the reactivity of  $(\text{C}_3\text{P})_2\text{Pd}$ , 1, with the strong acid  $[\text{H}_3\text{O}^+][\text{BF}_3\text{OH}^-]$ , obtained by mixing  $\text{BF}_3\cdot\text{Et}_2\text{O}$  with an excess of water in organic solvents. The quantitative formation of the cationic Pd aquo hydride complex *trans*-[( $\text{C}_3\text{P}$ ) $_2\text{Pd}(\text{H})(\text{H}_2\text{O})\text{BF}_3\text{OH}$ ], 2, was observed.<sup>31</sup> The coordination to Pd of the  $\text{BF}_3\text{OH}^-$  anion, which was suggested in the preliminary communication,<sup>31</sup> has been excluded by further experiments discussed hereafter.

The metal-bound water molecule can be substituted by reacting complex 2 with  $\text{CH}_3\text{CN}$ ; the resulting cationic hydride *trans*-[( $\text{C}_3\text{P}$ ) $_2\text{Pd}(\text{H})(\text{CH}_3\text{CN})\text{BF}_3\text{OH}$ ], 3, was isolated in high yield. The complex *trans*-[( $\text{C}_3\text{P}$ ) $_2\text{Pd}(\text{H})(\text{H}_2\text{O})\text{BF}_4$ ], 4, was prepared by two independent routes, i.e., by anion metathesis, reacting 2 with  $\text{AgBF}_4$ , and by addition of aqueous  $\text{HBF}_4$  to a toluene solution of complex 1. The formation of a palladium hydride by reaction of complex 1 with  $\text{HBF}_4$  occurs only in the presence of water or other strong ligands for Pd; if the etherate acid

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Table II. Fractional Atomic Coordinates and Thermal Parameters ( $\text{\AA}^2$ )

atom	x	y	z	$U_{eq}$
Pd	0.12467 (2)	0.24265 (4)	0.34535 (3)	0.0370 (3)
P(1)	0.13280 (5)	0.08829 (12)	0.29202 (9)	0.0328 (9)
P(2)	0.10490 (6)	0.39592 (13)	0.38660 (10)	0.0388 (10)
O	0.1833 (2)	0.2135 (4)	0.4261 (3)	0.056 (3)
C(1)	0.1797 (2)	0.0865 (5)	0.2424 (3)	0.041 (4)
C(2)	0.1734 (2)	0.1673 (6)	0.1848 (4)	0.056 (5)
C(3)	0.2114 (3)	0.1623 (7)	0.1411 (4)	0.077 (6)
C(4)	0.2560 (3)	0.1729 (7)	0.1881 (5)	0.078 (6)
C(5)	0.2616 (2)	0.0943 (8)	0.2459 (5)	0.076 (6)
C(6)	0.2244 (2)	0.0988 (6)	0.2898 (4)	0.059 (5)
C(7)	0.0853 (2)	0.0320 (5)	0.2313 (3)	0.036 (4)
C(8)	0.0990 (2)	-0.0382 (5)	0.1741 (4)	0.044 (4)
C(9)	0.0585 (2)	-0.0897 (6)	0.1323 (4)	0.059 (5)
C(10)	0.0245 (2)	-0.0176 (6)	0.0986 (4)	0.059 (5)
C(11)	0.0110 (2)	0.0542 (5)	0.1541 (4)	0.052 (5)
C(12)	0.0512 (2)	0.1078 (5)	0.1961 (4)	0.048 (4)
C(13)	0.1449 (2)	-0.0030 (5)	0.3647 (3)	0.036 (4)
C(14)	0.1520 (2)	-0.1117 (5)	0.3428 (4)	0.043 (4)
C(15)	0.1632 (2)	-0.1788 (5)	0.4085 (4)	0.051 (4)
C(16)	0.1276 (2)	-0.1734 (5)	0.4548 (4)	0.054 (5)
C(17)	0.1207 (3)	-0.0674 (5)	0.4781 (4)	0.052 (5)
C(18)	0.1097 (2)	0.0009 (5)	0.4132 (4)	0.042 (4)
C(19)	0.0536 (2)	0.3896 (5)	0.4259 (3)	0.040 (4)
C(20)	0.0593 (2)	0.3209 (5)	0.4912 (4)	0.052 (4)
C(21)	0.0172 (3)	0.3214 (6)	0.5256 (4)	0.061 (5)
C(22)	-0.0233 (3)	0.2912 (6)	0.4728 (5)	0.068 (5)
C(23)	-0.0290 (2)	0.3574 (6)	0.4073 (4)	0.061 (5)
C(24)	0.0130 (2)	0.3588 (6)	0.3726 (4)	0.058 (5)
C(25)	0.0932 (3)	0.4902 (5)	0.3161 (4)	0.054 (5)
C(26)	0.1192 (4)	0.4868 (7)	0.2597 (5)	0.095 (7)
C(27)	0.1061 (3)	0.5574 (6)	0.1990 (4)	0.060 (5)
C(28)	0.0945 (4)	0.6596 (7)	0.2208 (5)	0.119 (9)
C(29)	0.0658 (3)	0.6625 (6)	0.2737 (5)	0.076 (6)
C(30)	0.0769 (3)	0.5911 (5)	0.3351 (4)	0.058 (5)
C(31)	0.1474 (2)	0.4443 (5)	0.4593 (4)	0.041 (4)
C(32)	0.1339 (2)	0.5305 (5)	0.5046 (4)	0.049 (5)
C(33)	0.1710 (3)	0.5533 (6)	0.5657 (4)	0.060 (5)
C(34)	0.2139 (3)	0.5767 (6)	0.5399 (4)	0.059 (5)
C(35)	0.2274 (2)	0.4925 (6)	0.4950 (4)	0.061 (5)
C(36)	0.1907 (2)	0.4725 (5)	0.4325 (4)	0.052 (5)
B	0.1936 (4)	0.1941 (8)	0.6070 (5)	0.061 (6)
F(1)	0.2295 (2)	0.2317 (5)	0.5817 (3)	0.124 (5)
F(2)	0.1679 (2)	0.1446 (6)	0.5551 (3)	0.157 (6)
F(3)	0.2044 (3)	0.1457 (7)	0.6646 (4)	0.198 (9)
F(4)	0.1701 (3)	0.2709 (7)	0.6224 (6)	0.212 (10)

$[\text{Et}_2\text{OH}^+][\text{BF}_4^-]$  is reacted with 1 under strictly anhydrous conditions, only unreacted 1 is recovered after long reaction times. The subsequent addition of water,  $\text{CH}_3\text{CN}$ , or pyridine to the solution containing unreacted 1 and  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  gives quantitatively complex 4 or, respectively, *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{CH}_3\text{CN})]\text{BF}_4$ , 5, and *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{Py})]\text{BF}_4$ , 6.

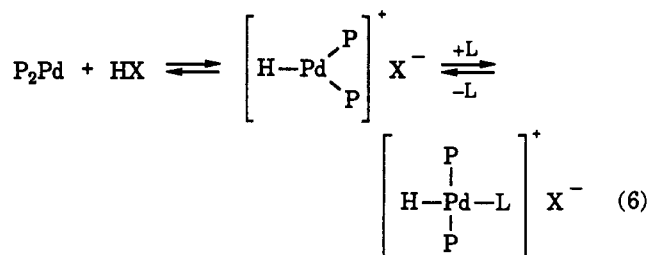
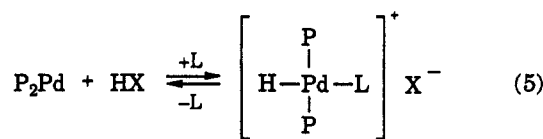
While the  $\text{BF}_4^-$  anion in complex 4 can be successfully metathesized with  $\text{NaPF}_6$ , giving in good yields *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{H}_2\text{O})]\text{PF}_6$ , 7, attempted metathesis with  $\text{NaBPh}_4$  or  $\text{LiB}(n\text{-Bu})_4$  resulted in a quick decomposition both of complex 4 to  $\text{Pd}(\text{PCy}_3)_2$  and of the borate anions to benzene and  $\text{BPh}_3$  and, respectively, to *n*-butane.

The decomposition of the  $\text{BR}_4^-$  anions was unexpected since stable tetraphenyl borate salts of *trans*- $[(\text{Cy}_3\text{P})_2\text{M}(\text{H})(\text{L})]^+$  cations ( $\text{M} = \text{Ni}, \text{Pd}$ ;  $\text{L} = \text{pyridines, pyrazole, imidazole}$ )<sup>32</sup> can be obtained, and we ourselves observed that *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{CH}_3\text{CN})]\text{BPh}_4$  can be isolated in good yields as a thermally and air-stable crystalline solid by reacting 4 with  $\text{NaBPh}_4$  in the presence of  $\text{CH}_3\text{CN}$ .

Two hypotheses could be considered to justify the above reported behavior. The first one takes into consideration the possibility of hydrogen bond formation between the

coordinated water molecule and the anion. When the M-L bond strength is not sufficient to stabilize the reaction products, a substantial contribution to the thermodynamic balance of the reaction could arise from the hydrogen bond formation. In this light, the stability of the aquo hydrides reported here should be ascribed to the formation of hydrogen bonds between the Pd-coordinated water molecule and the fluorine-containing anions ( $\text{BF}_4^-$ ,  $\text{BF}_3\text{OH}^-$ ,  $\text{PF}_6^-$ ); lacking this interaction ( $\text{BR}_4^-$  anions), the stability of the complexes falls off.

The second hypothesis, which does not exclude the former but could be cooperative with it, is that the acidity of the Pd-H bond depends on the nature of the ligand L. When the acid HX ( $\text{X}$  is a noncoordinating anion) is reacted with  $(\text{Cy}_3\text{P})_2\text{Pd}$ , a two-electron ligand ( $\text{MeCN}$ ,  $\text{Py}$ ,  $\text{H}_2\text{O}$ ,  $\text{R}_2\text{O}$ ) can saturate the fourth coordination position around the metal. The reaction can be depicted as an acid-base equilibrium involving oxidative addition/reductive elimination of the acid  $[\text{H}(\text{L})]^+\text{X}^-$  (eq 5) or protonation of  $(\text{Cy}_3\text{P})_2\text{Pd}$  followed by coordination of the ligand L to the intermediate tricoordinate hydride (eq 6).



In both cases, the position of the overall equilibrium is related to the strength of the M-L bond. Ligands forming strong bonds to the metal ( $\text{L} = \text{MeCN}, \text{Py}, \text{Im}$ ) should push to the right equilibrium 5 or 6, giving the less acidic hydrides and stable  $\text{BR}_4^-$  salts. Weak Pd-L bonds should correspond to more acidic hydrides, the acidity being related to the reductive elimination of  $[\text{H}(\text{L})]^+$  (eq 5) or to the generation of the tricoordinate hydride shown in eq 6. To this purpose, it has to be mentioned that in the case of analogous Pt systems, the tricoordinate platinum hydrides  $[(\text{R}_3\text{P})_2\text{PtH}]\text{X}$  could be isolated and were shown to be strong acids.<sup>21</sup>

According to eqs 5 and 6, the anhydrous acid  $[\text{Et}_2\text{OH}^+][\text{BF}_4^-]$  fails to react because  $\text{Et}_2\text{O}$  is a "stronger base" than  $(\text{Cy}_3\text{P})_2\text{Pd}$ , a quite puzzling basicity order being observed between the employed bases (for instance,  $\text{Et}_2\text{O}$  is a stronger base than  $\text{Py}$ ). In fact the reactions of  $[\text{H}(\text{L})]^+\text{X}^-$  with  $\text{P}_2\text{Pd}$  fragments are not simple proton-transfer reactions, the position of the "acid-base" equilibrium depending on the Pd-L bond strength in addition to the L-H and Pd-H bond strengths.

The "basicity" scale of the ligands L employed in these reactions is not necessarily correlated to the basicity scale observed in traditional proton-transfer reactions. If the matter is seen under this perspective, the reversal of the basicities of  $\text{Et}_2\text{O}$  and  $\text{Py}$  is not surprising.

The lack of stability of the  $\text{BR}_4^-$  anions when  $\text{L} = \text{H}_2\text{O}$  must be ascribed, according to this picture, to the acidic properties of the aquo hydride cation; actually the instability of  $\text{BR}_4^-$  anions in acidic media is well documented.<sup>33</sup>

**Hydrogen Bonding.** The possible thermodynamic relevance of hydrogen bonding in the oxidative addition of phenol<sup>34</sup> to  $(\text{Cy}_3\text{P})_2\text{Pd}$  has been outlined by some of us; a quantitative estimation of the thermodynamics of the hydrogen bond formation reaction between rhodium aryl oxides and phenols has been made by Bergman and co-workers,<sup>35</sup> who measured association heats up to 15 kcal/mol. The kinetic relevance of intramolecular hydrogen bonds has been evaluated by Bercaw<sup>36</sup> in some reactions of early transition-metal complexes with water.

The hydrogen bond formation energy probably has a significant influence on the stabilization of complex 4, at least in the solid state. A single-crystal X-ray study has, in fact, revealed that the water molecule in complex 4 is strongly hydrogen-bonded to two  $\text{BF}_4^-$  anions (see Crystallographic Analysis). This is consistent with the change of symmetry from  $T_d$  to  $C_{2v}$  of the  $\text{BF}_4^-$  ion in 4, which is evidenced by its IR spectrum [ $\nu_{\text{BF}}$  (Nujol) 1120 vs, 1050 vs, 1000 vs, 990 sh  $\text{cm}^{-1}$ ].<sup>37</sup>

<sup>19</sup>F NMR<sup>38a</sup> and conductance studies were performed in order to estimate the extent of hydrogen bonding in solutions of 4.

The <sup>19</sup>F NMR spectrum of 4 consists of two singlets at  $-151.08$  ( $h_{1/2} = 2.3$  Hz) and  $-151.03$  ( $h_{1/2} = 2.6$  Hz) ppm of approximate 4:1 intensity ratio. This pattern is not significantly influenced by the temperature, and the spectrum is practically the same at room temperature and at  $-90$  °C. The proximity of the two signals ( $\Delta\delta = 16$  Hz), their insensitivity to the temperature, and the strong similarities with the <sup>19</sup>F spectrum of  $[\text{n-Bu}_4\text{N}][\text{BF}_4]$  ( $\delta = -150.65$  s,  $h_{1/2} = 5.0$  Hz;  $-150.59$  s,  $h_{1/2} = 5.4$  Hz; intensity ratio = 4/1) recorded at the same conditions, are in agreement with a <sup>10</sup>B-<sup>11</sup>B isotopic shift effect.<sup>39</sup> Such an effect has rarely been reported for compounds containing B-F bonds but could be often masked by line broadening. We have, in fact, observed two singlets only in acetone-*d*<sub>6</sub> solution. The <sup>19</sup>F NMR spectrum of 4 in  $\text{CDCl}_3$  exhibits a singlet with  $h_{1/2} = 45$  Hz, a line width larger than the  $\Delta\delta$  between the two signals observed in acetone-*d*<sub>6</sub>.

Due to the lack of information on the <sup>19</sup>F NMR spectra with regard to hydrogen bond formation in solution,<sup>38a</sup> the molar conductance of *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{L})]\text{BF}_4$  (L = H<sub>2</sub>O, 4; L = CH<sub>3</sub>CN, 5; ca. 10<sup>-3</sup> M solutions) was measured in different solvents, and the  $\Lambda_M$  values observed were 128 (acetone), 6.50 (THF), and 30.7 (CH<sub>2</sub>Cl<sub>2</sub>)  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for complex 4 and 146 (acetone), 6.75 (THF), and 37.2 (CH<sub>2</sub>Cl<sub>2</sub>)  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for complex 5. While the  $\Lambda_M$  values measured for 5 are in complete agreement with those re-

Table III. Relevant Bond Distances (Å) and Angles (deg) for 4

Pd-O	2.206 (5)	P(2)-C(31)	1.861 (7)
Pd-P(1)	2.338 (2)	O-H(2)	1.09
Pd-P(2)	2.316 (2)	O-H(3)	0.96
Pd-H(1)	1.51	B-F(1)	1.36 (1)
P(1)-C(1)	1.843 (6)	B-F(2)	1.34 (1)
P(1)-C(7)	1.867 (6)	B-F(3)	1.27 (1)
P(1)-C(13)	1.844 (6)	B-F(4)	1.32 (1)
P(2)-C(19)	1.848 (6)	F(2)···H(2)	1.77
P(2)-C(25)	1.841 (7)	F(1)···H(3)	1.90
P(1)-Pd-P(2)	170.3 (1)	F(1)-B-F(2)	109 (1)
O-Pd-P(1)	91.0 (1)	F(1)-B-F(3)	112 (1)
O-Pd-P(2)	98.4 (1)	F(1)-B-F(4)	107 (1)
O-Pd-H(1)	166	F(2)-B-F(3)	115 (1)
H(2)-O-H(3)	101	F(2)-B-F(4)	106 (1)
		F(3)-B-F(4)	106 (1)

ported for strong electrolytes,<sup>40</sup> the aquo complex 4 exhibits  $\Lambda_M$  values 10–20% lower. These results indicate that complex 4 is largely dissociated in solution though they do not exclude the presence of ion pairs in low concentration.

**Acidity of Pd-H Bonds.** Either or both the Pd-H and the Pd(OH<sub>2</sub>) units can be expected to give H/D exchange when 4 is reacted with D<sub>2</sub>O. The platinum derivatives *trans*- $[(\text{R}_3\text{P})_2\text{Pt}(\text{H})(\text{H}_2\text{O})]\text{X}$  have been reported to react with D<sub>2</sub>O to give *trans*- $[(\text{R}_3\text{P})_2\text{Pt}(\text{H})(\text{D}_2\text{O})]\text{X}$ ,<sup>6b</sup> i.e., the product arising from the deuteration of the Pt(OH<sub>2</sub>) moiety. We have observed for 4 a quite different behavior: short reaction times (ca. 5 min) of complex 4 with excess D<sub>2</sub>O in acetone or THF solution yield *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{D})(\text{H}_2\text{O})]\text{BF}_4$ , while a 2-week reaction time is necessary to observe over 50% deuterium incorporation into the Pd(OH<sub>2</sub>) moiety.

The reverse exchange was studied by reacting *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{D})(\text{D}_2\text{O})]\text{BF}_4$  with H<sub>2</sub>O; in this case, we observed the quantitative formation of 4 in a few minutes. This would suggest an unlikely huge isotopic effect, but sound conclusions on this point will be possible only after careful quantitative measurements of the rates of H/D-exchange reactions.

A similar trend was observed in the H/D-exchange reactions involving complex 2: *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{D})(\text{H}_2\text{O})]\text{BF}_3\text{OD}$  or *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{D})(\text{D}_2\text{O})]\text{BF}_3\text{OD}$  was isolated dependently on the reaction time of 2 with D<sub>2</sub>O.

These results suggest that the H/D exchange of the Pd-H and of the Pd(OH<sub>2</sub>) moieties are independent processes and rule out the oxidative addition/reductive elimination mechanisms of eqs 3 and 5 for acid-base processes involving complex 4.

The acid behavior of complex 4 was tested by reacting it with bases of different strength (Ph<sub>3</sub>C<sup>-</sup>, OH<sup>-</sup>, Et<sub>3</sub>N, Py, PCy<sub>3</sub>); apart from the reaction with pyridine, which gives *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{Py})]\text{BF}_4$ , we have always observed deprotonation of 4 and the formation of  $(\text{Cy}_3\text{P})_2\text{Pd}$  in high yield.

When the reaction with Ph<sub>3</sub>CLi was performed on *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{D})(\text{H}_2\text{O})]\text{BF}_4$ , the formation of a 70/30 mixture of Ph<sub>3</sub>CD and Ph<sub>3</sub>CH was observed, thus confirming the hypothesis of a higher acidity of the hydridic hydrogen compared to that of the hydrogens of the Pd-coordinated water molecule.

The line width of the hydride absorption in the <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>) of *trans*- $[(\text{Cy}_3\text{P})_2\text{Pd}(\text{H})(\text{H}_2\text{O})]\text{BF}_4$ , 4, was shown to be influenced by the water content of the solvent; a well-resolved triplet ( $\delta = 18.39$ , <sup>2</sup>J<sub>PH</sub> = 4.3 Hz)

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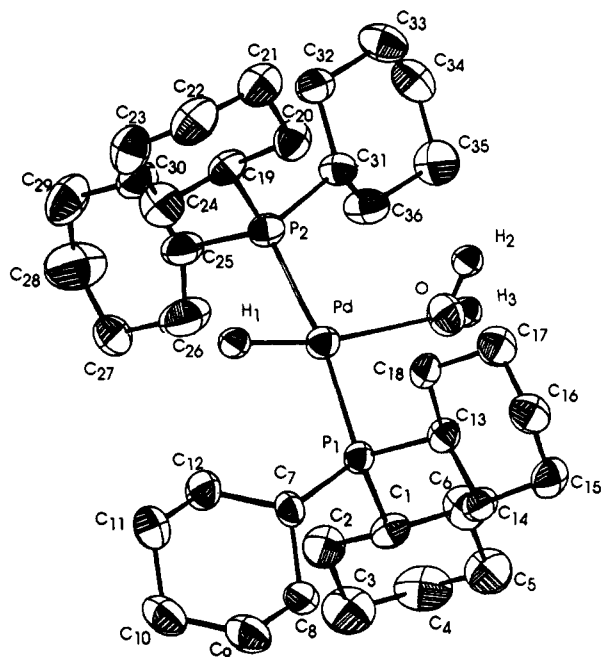
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(38) (a) Slow exchange between terminal and hydrogen-bonded F atoms in  $[\text{L}_n\text{M}-\text{OH}_2\cdots\text{BF}_4]$  systems should influence the <sup>19</sup>F NMR spectra and different chemical shifts, and eventually, *J*<sub>FF</sub> couplings should be observed. However, it must be taken into account that when the  $\text{BF}_4^-$  ions interact directly with the metal of unsaturated cationic fragments, a signal splitting is observed only in a few cases and at low temperatures,<sup>38b-d</sup> due to the spinning of the anions; in hydrogen-bonded systems, the anion spinning is probably more difficult to freeze and the <sup>19</sup>F NMR spectra may be uninformative. (b) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* 1989, 28, 2869. (c) Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* 1989, 111, 6056. (d) Sunkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* 1983, 252, 187.

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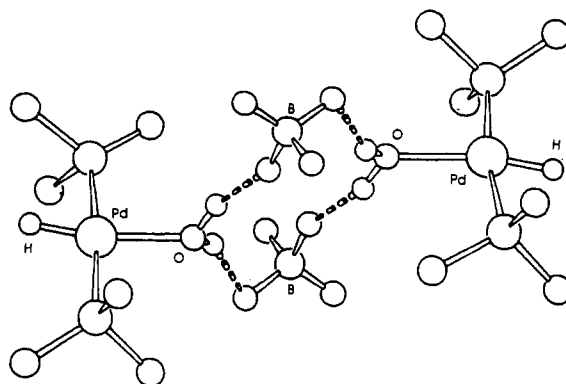
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**Figure 1.** ORTEP view of the geometry around Pd in 4, showing the atom numbering scheme.

can be observed only in strictly anhydrous acetone- $d_6$ , while the presence of adventitious water considerably broadens the signal probably due to a Pd-H/external  $H_2O$  exchange process. Such an effect is not determined by the addition of anhydrous  $CF_3SO_3H$  to an anhydrous acetone- $d_6$  solution of 4. A small amount of the protonated phosphine  $Cy_3PH^+$  was observed in the NMR spectra of 2 and 4 in  $CDCl_3$  and THF- $d_6$  [ $^1H$  NMR  $\delta$  ( $CDCl_3$ ) 5.85 (dd,  $^1J_{PH} = 475$  Hz;  $^3J_{HH} = 4$  Hz);  $^{31}P$  NMR ( $CDCl_3$ )  $\delta$  28.32 (d,  $^1J_{PH} = 475$  Hz)], further supporting the acidic behavior of these systems.

**Structural Characterization of 4.** An ORTEP diagram showing the coordination geometry around Pd in 4 is shown in Figure 1 together with the atomic labeling. Relevant structural parameters are reported in Table III. The Pd atom possesses a distorted square-planar coordination: two trans sites are occupied by the  $PCy_3$  ligands [Pd-P mean distance 2.33 Å, P-Pd-P angle  $170.3(1)^\circ$ ], while the other two sites are occupied by a water molecule and by the H (hydride) atom. These two latter ligands deserve a more careful scrutiny. Although the H atom positioning is based on an X-ray diffraction experiment and as such is largely uncertain, the Pd-H distance [1.51 (1) Å] compares well with the values previously observed in the other two palladium hydrides characterized to date by *trans*- $[(Cy_3P)_2Pd(H)(OC_6H_5)] \cdot C_6H_5OH$  [Pd-H 1.57 (2) Å] and *trans*- $[(Cy_3P)_2Pd(H)(OC_6F_5)] \cdot C_6F_5OH$  [Pd-H 1.46 (2) Å]. The  $H_2O$  molecule is bound to the Pd center through the O atom [Pd-O 2.206 (5) Å, O-Pd-H  $166(1)^\circ$ ]. The H( $H_2O$ ) hydrogen atoms could also be located in the Fourier maps; the H-O distances were found to be 1.09 and 0.96 Å. The  $H_2O$  geometry is not substantially affected by the two interactions as shown by the H-O-H angle of  $101(1)^\circ$ , as well as the tetrahedral coordination



**Figure 2.** ORTEP diagram of 4.

expected for an O atom interacting with the Pd atom via one of its lone pairs H2-O-H3  $101(1)^\circ$ , H2-O 1.09 (1) Å, H3-O 0.96 (1) Å, H2-O-Pd  $116(1)^\circ$ , H3-O-Pd  $123(1)^\circ$  [these structural parameters have to be taken with a grain of salt, being based on the H atom positions].

The Pd-O distance appears to be slightly longer than in the phenoxy and perfluorophenoxy hydrides mentioned above [2.135 (2) and 2.181 (2) Å respectively],<sup>34</sup> while the Pd-P distances are strictly comparable [mean 2.33 versus 2.32, 2.33 Å]. Finally it is worth noting that two  $BF_4^-$  counterions are found to "bridge" two *trans*- $[(Cy_3P)_2Pd(H)(H_2O)]^+$  cations. These contact ion pair interactions are established via H bridging between two F atoms of each  $BF_4^-$  and the O atoms of the coordinated  $H_2O$  molecule, thus constituting a sort of "dimeric"  $\{trans-[(Cy_3P)_2Pd(H)(H_2O)][BF_4^-]\}_2$  system in the solid state (see Figure 2). The two moieties are related by a crystallographic inversion center. The F...H interactions are not symmetric: each  $BF_4^-$  showing one "short" (1.77-Å) and one "long" (1.90-Å) F-H distance. These interactions cause loss of  $T_d$  idealized symmetry for the  $BF_4^-$  anion as also evidenced by the spectroscopic results discussed above. The two B-F bonds involving the H-bridged F atoms are on the average longer than the other two [1.35 versus 1.30 Å]. This water counterion H bridge has precedent in some rhenium carbonyl aqua species with  $AsF_6^-$  and  $BF_4^-$  anions,<sup>41</sup> as well as in the complexes  $[Mo(acac)(H_2O)(\eta^7-C_7H_7)]BF_4$ <sup>42</sup> and  $[(Ph_3P)_2(CO)Cl(H)Ir(H_2O)]BF_4$ .<sup>19b</sup>

**Acknowledgment.** We thank the Ministero della Pubblica Istruzione and the CNR (Rome) for financial support.

**Supplementary Material Available:** Tables of fractional coordinates for the hydrogen atoms (Table 1S), anisotropic thermal parameters (Table 2S), and complete bond distances and angles (Table 3S), IR spectra (Nujol) of complexes 2, 4, 9, 10, and 11 (Figures 1S-5S), and  $^1H$  NMR spectra of complex 4 in wet (Figure 6S) and anhydrous (Figure 7S) acetone- $d_6$  and in the presence of excess  $CF_3SO_3H$  (Figure 8S) (60 pages); a table of observed and calculated structure factors (Table 4S) (18 pages). Ordering information is given on any current masthead page.

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