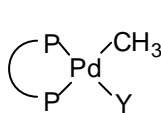
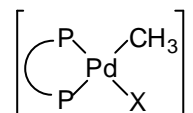
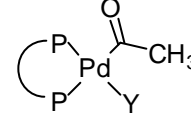
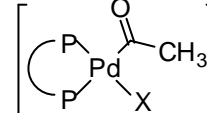


**General procedures** All reactions and manipulations were carried out under dry oxygen-free nitrogen atmosphere using Schlenk techniques. All solvents were carefully purified by appropriate procedures. CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN was distilled over CaH<sub>2</sub> under nitrogen and CH<sub>3</sub>OH over Mg(OCH<sub>3</sub>)<sub>2</sub> under nitrogen before use. Air sensitive compounds were stored under nitrogen at -30 °C. <sup>13</sup>C<sup>18</sup>O was purchased from Isotec Inc (USA), ethene from Linde gas UK. CF<sub>3</sub>SO<sub>3</sub>H (HOTf), CF<sub>3</sub>CO<sub>2</sub>H (TFA) and p-CH<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>)SO<sub>3</sub>H (HOTs).were purchased from Aldrich and used as received. 1, 3-bis(di-isobutylphosphino)propane (dibpp) was prepared by reaction of di-isobutylphosphine with 1, 3-dibromopropane to give the double HBr salt which was subsequently neutralized with sodium hydroxide and distilled to give the diphosphine product.<sup>[1]</sup> The palladium dimethyl complex, [Pd(dibpp)(CH<sub>3</sub>)<sub>2</sub>], was synthesized as described in the literature.<sup>[2, 3]</sup> A solution of dibpp in acetone was added to a solution of [Pd(TMEDA)(CH<sub>3</sub>)<sub>2</sub>] in 30 ml acetone, and the mixture stirred for 18 hr. The solution was then taken to dryness in vacuo at 0 °C, washed with cold hexane and dried in vacuo. <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H}NMR spectra were recorded on a Bruker AMX 200 NMR machine with a CD<sub>2</sub>Cl<sub>2</sub> capillary lock at 193 K unless specified otherwise. <sup>13</sup>C{<sup>1</sup>H}NMR spectra were obtained by using <sup>13</sup>C- enriched carbon monoxide.

**Table 1. Palladium diphosphine compounds prepared in this work**

							
Y	X	Y	Y	X	Y		
<b>1a</b> CF <sub>3</sub> SO <sub>3</sub>	<b>1b</b> MeCN	CF <sub>3</sub> SO <sub>3</sub>		<b>2b</b> MeCN	CF <sub>3</sub> SO <sub>3</sub>		
	<b>1c</b> CO	CF <sub>3</sub> SO <sub>3</sub>		<b>2c</b> CO	CF <sub>3</sub> SO <sub>3</sub>		
	<b>1d</b> CH <sub>3</sub> OH	CF <sub>3</sub> SO <sub>3</sub>		<b>2d</b> CH <sub>3</sub> OH	CF <sub>3</sub> SO <sub>3</sub>		
<b>1e</b> CF <sub>3</sub> CO <sub>2</sub>	<b>1f</b> MeCN	CF <sub>3</sub> CO <sub>2</sub>	<b>2e</b> CF <sub>3</sub> CO <sub>2</sub>	<b>2f</b> MeCN	CF <sub>3</sub> CO <sub>2</sub>		
	<b>1g</b> CO	CF <sub>3</sub> CO <sub>2</sub>		<b>2g</b> CO	CF <sub>3</sub> CO <sub>2</sub>		
<b>1h</b> OTs*	<b>1i</b> MeCN	OTs	<b>2h</b> OTs	<b>2i</b> MeCN	OTs		
	<b>1k</b> CO	OTs		<b>2k</b> CO	OTs		
	<b>1j</b> CH <sub>3</sub> OH	OTs		<b>2j</b> CH <sub>3</sub> OH	OTs		

\*OTs=CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>

**Synthesis of [Pd(dibpp)(CH<sub>3</sub>)X](1a, X = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; 1e, X = CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>; 1h, X = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** [Pd(dibpp)(CH<sub>3</sub>)<sub>2</sub>] was dissolved in 2 ml CH<sub>2</sub>Cl<sub>2</sub> in a 10 mm NMR tube and then cooled to -78 °C; one equivalent of the corresponding acid, CF<sub>3</sub>SO<sub>3</sub>H,

CF<sub>3</sub>CO<sub>2</sub>H or CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H was then added and the solution warmed to room temperature briefly until the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum indicated that the reaction had gone to completion.

**[Pd(dibpp)(CH<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>)](1a)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 18.8 (d, *J*(P,P) = 41 Hz); -16.6 (d, *J*(P,P) = 41 Hz).

**[Pd(dibpp)(CH<sub>3</sub>)(CF<sub>3</sub>CO<sub>2</sub>)](1e)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 12.7 (d, *J*(P,P) = 41 Hz); -11.4 (d, *J*(P,P) = 41 Hz).

**[Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)](1h)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 17.2 (d, *J*(P,P) = 42 Hz); -12.2 (d, *J*(P,P) = 42 Hz).

**Synthesis of [Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>CN)]Y (1b, Y = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; 1f, Y = CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>; 1i, Y = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** [Pd(dibpp)(CH<sub>3</sub>)<sub>2</sub>] was dissolved in a mixture of 1.8 ml CH<sub>2</sub>Cl<sub>2</sub> and 0.2 ml CH<sub>3</sub>CN in a 10 mm NMR tube and then cooled to -78 °C; one equivalent of the corresponding acid CF<sub>3</sub>SO<sub>3</sub>H, CF<sub>3</sub>CO<sub>2</sub>H or CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H was then added and the solution warmed to room temperature briefly until the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum indicated that the reaction had gone to completion.

**[Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>CN)][CF<sub>3</sub>SO<sub>3</sub>] (1b)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 11.0 (d, *J*(P,P) = 41 Hz); -15.6 (d, *J*(P,P) = 41 Hz).

**[Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>CN)][CF<sub>3</sub>CO<sub>2</sub>] (1f)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 10.8 (d, *J*(P,P) = 41 Hz); -15.6 (d, *J*(P,P) = 41 Hz).

**[Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>CN)][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (1i)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 11.1 (d, *J*(P,P) = 42 Hz); -15.7 (d, *J*(P,P) = 42 Hz).

**Synthesis of [Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>OH)]Y (1d, Y = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; 1j, Y = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** [Pd(dibpp)(CH<sub>3</sub>)<sub>2</sub>] was dissolved in a mixture of 1.8 ml CH<sub>2</sub>Cl<sub>2</sub> and 0.2 ml CH<sub>3</sub>OH in a 10 mm NMR tube and then cooled to -78 °C; one equivalent of the corresponding acid CF<sub>3</sub>SO<sub>3</sub>H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H was then added and the solution warmed to room temperature briefly until the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum indicated that the reaction had gone to completion.

**[Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>OH)][CF<sub>3</sub>SO<sub>3</sub>] (1d)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 18.8 (d, *J*(P,P) = 41 Hz); -14.2 (d, *J*(P,P) = 41 Hz).

**[Pd(dibpp)(CH<sub>3</sub>)(CH<sub>3</sub>OH)][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (1j)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 18.9 (d, *J*(P,P) = 42 Hz); -14.3 (d, *J*(P,P) = 42 Hz).

**Synthesis of [Pd(dibpp)(CH<sub>3</sub>)(CO)]Y (1c, Y = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; 1g, Y = CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>; 1k, Y = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** CO was bubbled briefly through a solution of **1a**, **1e** or **1h** in dichloromethane at -78 °C; <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies revealed the formation, in situ, of **1c**, **1g** or **1k** correspondingly.

**[Pd(dibpp)(CH<sub>3</sub>)(CO)][CF<sub>3</sub>SO<sub>3</sub>] (1c)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** -0.5 (d, *J*(P,P) = 47 Hz); -12.3 (d, *J*(P,P) = 47 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 181.6 (dd, *J*(P<sub>trans</sub>,C) = 114 Hz *J*(P<sub>cis</sub>,C) = 16 Hz).

**[Pd(dibpp)(CH<sub>3</sub>)(CO)][CF<sub>3</sub>CO<sub>2</sub>] (1g)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** -0.8 (d, *J*(P,P) = 48 Hz); -13.5 (d, *J*(P,P) = 48 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 181.6 (dd, *J*(P<sub>trans</sub>,C) = 114 Hz *J*(P<sub>cis</sub>,C) = 16 Hz).

**[Pd(dibpp)(CH<sub>3</sub>)(CO)][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (1k)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** -0.6 (d, *J*(P,P) = 47 Hz); -13.4 (d, *J*(P,P) = 47 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 181.7 (dd, *J*(P<sub>trans</sub>,C) = 114 Hz *J*(P<sub>cis</sub>,C) = 16 Hz).

**Synthesis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>OH)][CF<sub>3</sub>SO<sub>3</sub>] (2d)** CO was bubbled thoroughly through a solution of **1d** in a mixture of dichloromethane and methanol (9:1) at -78 °C. The solution was then warmed to -30 °C when the <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies revealed the formation, in situ, of **2c** and **2d**.

**[Pd(dibpp)(C(O)CH<sub>3</sub>)(CO)][CF<sub>3</sub>SO<sub>3</sub>] (2c)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** -6.7 (d, *J*(P,P) = 73 Hz); -19.2 (d, *J*(P,P) = 73 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 235.2 (dd, *J*(P<sub>trans</sub>,C) = 88 Hz *J*(P<sub>cis</sub>,C) = 5 Hz); 176.9 (dd, *J*(P<sub>trans</sub>,C) = 80 Hz *J*(P<sub>cis</sub>,C) = 20 Hz).

**[Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>OH)][CF<sub>3</sub>SO<sub>3</sub>] (2d)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 13.4 (d, *J*(P,P) = 66 Hz); -19.1 (d, *J*(P,P) = 66 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR of **2d**: **d** 243.0 (dd, *J*(P<sub>trans</sub>,C) = 116 Hz *J*(P<sub>cis</sub>,C) = 12 Hz).

**Synthesis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CF<sub>3</sub>CO<sub>2</sub>)] (2e)** CO was bubbled thoroughly through a solution of **1e** in dichloromethane at -78 °C. The solution was warmed to -30 °C for 1 hour when the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed the quantitative formation of **2e**. <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 10.0 (d, *J*(P,P) = 67 Hz); -15.8 (d, *J*(P,P) = 67 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 247.8 (dd, *J*(P<sub>trans</sub>,C) = 125 Hz *J*(P<sub>cis</sub>,C) = 10 Hz).

**Synthesis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)] (2h)** CO was bubbled thoroughly through a solution of **1h** in dichloromethane at  $-78^{\circ}\text{C}$ . The solution was then warmed to  $-30^{\circ}\text{C}$  for 1 hour when the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum revealed the formation of a mixture of **2h** and **2k**, on purging the solution with nitrogen at  $-78^{\circ}\text{C}$  for 10 minutes, **2h** was formed quantitatively ( $^{31}\text{P}\{^1\text{H}\}$  NMR).  $^{31}\text{P}\{^1\text{H}\}$  NMR: **d** 12.5 (d,  $J(\text{P},\text{P}) = 70$  Hz); -16.6 (d,  $J(\text{P},\text{P}) = 70$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR: **d** 244.6 (dd,  $J(\text{P}_{\text{trans}},\text{C}) = 122$  Hz  $J(\text{P}_{\text{cis}},\text{C}) = 12$  Hz).

**Synthesis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>CN)]Y (2b, Y = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; 2f, Y = CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>; 2i, Y = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** CO was bubbled thoroughly through a solution of **1b**, **1f**, or **1i** in a mixture of dichloromethane and acetonitrile (9:1) at  $-78^{\circ}\text{C}$ , the solution was warmed to  $-30^{\circ}\text{C}$  for 1 hour when the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum revealed the quantitative formation of **2b**, **2f** or **2i** respectively.

**[Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>CN)][CF<sub>3</sub>SO<sub>3</sub>] (2b)**  $^{31}\text{P}\{^1\text{H}\}$  NMR: **d** 5.4 (d,  $J(\text{P},\text{P}) = 70$  Hz); -19.6 (d,  $J(\text{P},\text{P}) = 70$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR: **d** 242.6 (dd,  $J(\text{P}_{\text{trans}},\text{C}) = 112$  Hz  $J(\text{P}_{\text{cis}},\text{C}) = 10$  Hz).

**[Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>CN)][CF<sub>3</sub>CO<sub>2</sub>] (2f)**  $^{31}\text{P}\{^1\text{H}\}$  NMR: **d** 4.9 (d,  $J(\text{P},\text{P}) = 70$  Hz); -19.7 (d,  $J(\text{P},\text{P}) = 70$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR: **d** 242.8 (dd,  $J(\text{P}_{\text{trans}},\text{C}) = 112$  Hz  $J(\text{P}_{\text{cis}},\text{C}) = 16$  Hz).

**[Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>CN)][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (2i)**  $^{31}\text{P}\{^1\text{H}\}$  NMR: **d** 4.9 (d,  $J(\text{P},\text{P}) = 70$  Hz); -19.7 (d,  $J(\text{P},\text{P}) = 70$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR: **d** 242.6 (dd,  $J(\text{P}_{\text{trans}},\text{C}) = 113$  Hz  $J(\text{P}_{\text{cis}},\text{C}) = 10$  Hz).

**Synthesis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CO)]Y (2c, Y = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; 2k, Y = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** Excess CO was bubbled thoroughly through a solution of **1a** or **1h** in dichloromethane at  $-78^{\circ}\text{C}$ . The solution was then warmed to  $-30^{\circ}\text{C}$  for 1 hour when the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra revealed the quantitative formation, in situ, of **2c** or **2k**.

**[Pd(dibpp)(C(O)CH<sub>3</sub>)(CO)][CF<sub>3</sub>SO<sub>3</sub>] (2c)**  $^{31}\text{P}\{^1\text{H}\}$  NMR: **d** -6.7 (d,  $J(\text{P},\text{P}) = 73$  Hz); -19.2 (d,  $J(\text{P},\text{P}) = 73$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR: **d** 235.2 (dd,  $J(\text{P}_{\text{trans}},\text{C}) = 88$  Hz  $J(\text{P}_{\text{cis}},\text{C}) = 5$  Hz); 176.9 (dd,  $J(\text{P}_{\text{trans}},\text{C}) = 80$  Hz  $J(\text{P}_{\text{cis}},\text{C}) = 20$  Hz).

**[Pd(dibpp)(C(O)CH<sub>3</sub>)(CO)][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (2k)** <sup>31</sup>P{<sup>1</sup>H} NMR: **d** -6.8 (d, *J*(P,P) = 73 Hz); -18.6 (d, *J*(P,P) = 73 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 235.5 (dd, *J*(P<sub>trans</sub>,C) = 88 Hz *J*(P<sub>cis</sub>,C) = 5 Hz); 176.9 (dd, *J*(P<sub>trans</sub>,C) = 80 Hz *J*(P<sub>cis</sub>,C) = 20 Hz).

**Synthesis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CO)][CF<sub>3</sub>CO<sub>2</sub>] (2g)** Excess CO was bubbled thoroughly through a solution of **1e** in a mixture of dichloromethane and methanol (9:1) at -78 °C. The solution was then warmed to -30 °C for 1 hour when the <sup>31</sup>P{<sup>1</sup>H} NMR spectra revealed the formation, in situ, of **2g**. <sup>31</sup>P{<sup>1</sup>H} NMR: **d** -6.1 (d, *J*(P,P) = 73 Hz); -18.5 (d, *J*(P,P) = 73 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 234.7 (dd, *J*(P<sub>trans</sub>,C) = 88 Hz *J*(P<sub>cis</sub>,C) = 6 Hz); 176.9 (dd, *J*(P<sub>trans</sub>,C) = 79 Hz *J*(P<sub>cis</sub>,C) = 20 Hz).

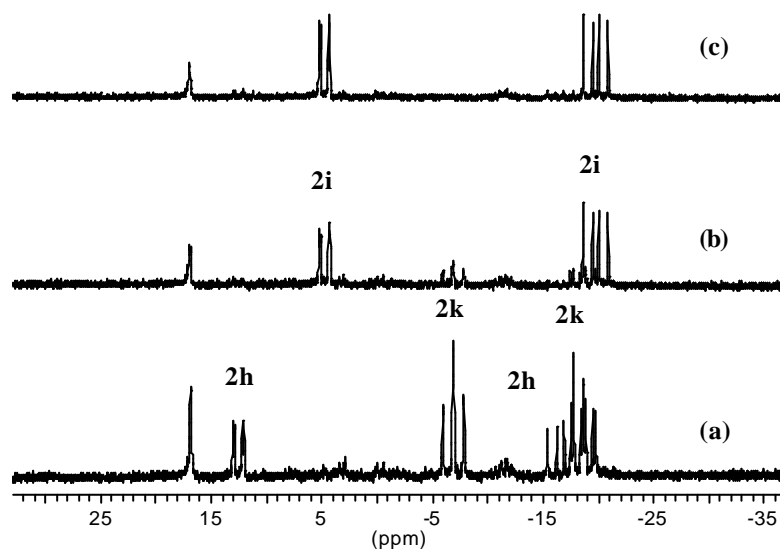
**Synthesis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>OH)][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (2j)** CO was bubbled thoroughly through a solution of **1j** in a mixture of dichloromethane and methanol (9:1) at -78 °C, the solution was then warmed to -30 °C when the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed the formation, in situ, of **2j**. <sup>31</sup>P{<sup>1</sup>H} NMR: **d** 13.4 (d, *J*(P,P) = 66 Hz); -19.2 (d, *J*(P,P) = 66 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR: **d** 245.5 (dd, *J*(P<sub>trans</sub>,C) = 117 Hz *J*(P<sub>cis</sub>,C) = 12 Hz).

**Methanolysis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>CN)]Y (2b, Y = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>; 2f, Y = CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>; 2i, Y = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** 0.2 ml CH<sub>3</sub>OH was added to a solution of **2b**, **2f** or **2i** in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN (9:1) at -78 °C, the solution then warmed to -30 °C and the reactions followed by <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies. No methyl acetate or any other organic product was observed by <sup>13</sup>C{<sup>1</sup>H} NMR after 20 hours at -30 °C. On warming the solutions to room temperature, **1b**, **1f** or **1i** were detected as the only new species by <sup>31</sup>P{<sup>1</sup>H} NMR indicating decarbonylation reactions dominate.

**Methanolysis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(X)] (2e, X = CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>; 2h, X = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** 0.2 ml CH<sub>3</sub>OH was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of **2e** or **2h** at -78 °C, and the solutions warmed up to -30 °C. The reactions were followed by <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies, progressive formation of methyl acetate was observed by <sup>13</sup>C{<sup>1</sup>H} NMR for both **2e** and **2h**.

**Methanolysis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CO)]Y (2g, Y = CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>; 2k, Y = CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>)** 0.2 ml CH<sub>3</sub>OH was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of **2g** or **2k** at -78 °C, and the solutions were warmed to -30 °C. The reactions were followed by <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies. Progressive formation of methyl acetate was observed by <sup>13</sup>C{<sup>1</sup>H} NMR for both **2g** and **2k**.

**Methanolysis of [Pd(dibpp)(C(O)CH<sub>3</sub>)(CO)][CF<sub>3</sub>SO<sub>3</sub>] (2c)** 0.2 ml CH<sub>3</sub>OH was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of **2c** or **2h** at -78 °C, then the solutions were warmed to -30 °C. [Pd(dibpp)C(O)CH<sub>3</sub>(CH<sub>3</sub>OH)](CF<sub>3</sub>SO<sub>3</sub>) (**2d**) was detected as an intermediate and its decay was followed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies. Progressive formation of methyl acetate was observed by <sup>13</sup>C{<sup>1</sup>H} NMR.



**Figure 1.** The relative affinity of OTs, CH<sub>3</sub>CN and CO for the palladium center in Pd(dibpp)-acyl complexes. (a) <sup>13</sup>CO was bubbled through a solution of [Pd(dibpp)CH<sub>3</sub>(OTs)] (**1h**) at 193K for 5 minutes, [Pd(dibpp)(C(O)CH<sub>3</sub>)(OTs)] (**2h**) and [Pd(dibpp)(C(O)CH<sub>3</sub>(CO)][OTs] (**2k**) are formed; (b) 1 equivalent CH<sub>3</sub>CN was added at 193K to the solution prepared in (a), [Pd(dibpp)(C(O)CH<sub>3</sub>)(CH<sub>3</sub>CN)][OTs] (**2i**) is formed, a small amount of **2k** and **2h** remain; (c) the solution in (b) was purged with nitrogen at -78 °C for 10 minutes, essentially quantitative conversion to **2i** is observed.

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