

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. CH₂Cl₂ and CH₃CN was distilled over CaH₂ under nitrogen and CH₃OH over Mg(OCH₃)₂ under nitrogen before use. Air sensitive compounds were stored under nitrogen at -30 °C. ¹³C¹⁸O was purchased from Isotec Inc (USA), ethene from Linde gas UK. CF₃SO₃H (HOTf), CF₃CO₂H (TFA) and p-CH₃(C₆H₄)SO₃H (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.^[1] The palladium dimethyl complex, [Pd(dibpp)(CH₃)₂], was synthesized as described in the literature.^[2, 3] A solution of dibpp in acetone was added to a solution of [Pd(TMEDA)(CH₃)₂] 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. ³¹P{¹H} and ¹³C{¹H}NMR spectra were recorded on a Bruker AMX 200 NMR machine with a CD₂Cl₂ capillary lock at 193 K unless specified otherwise. ¹³C{¹H}NMR spectra were obtained by using ¹³C- enriched carbon monoxide.

Table 1. Palladium diphosphine compounds prepared in this work

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

*OTs=CH₃C₆H₄SO₃

Synthesis of [Pd(dibpp)(CH₃)X](1a, X = CF₃SO₃⁻; 1e, X = CF₃CO₂⁻; 1h, X = CH₃C₆H₄SO₃⁻) [Pd(dibpp)(CH₃)₂] was dissolved in 2 ml CH₂Cl₂ in a 10 mm NMR tube and then cooled to -78 °C; one equivalent of the corresponding acid, CF₃SO₃H,

CF₃CO₂H or CH₃C₆H₄SO₃H was then added and the solution warmed to room temperature briefly until the ³¹P{¹H} NMR spectrum indicated that the reaction had gone to completion.

[Pd(dibpp)(CH₃)(CF₃SO₃)](1a) ³¹P{¹H} NMR: **d** 18.8 (d, *J*(P,P) = 41 Hz); -16.6 (d, *J*(P,P) = 41 Hz).

[Pd(dibpp)(CH₃)(CF₃CO₂)](1e) ³¹P{¹H} NMR: **d** 12.7 (d, *J*(P,P) = 41 Hz); -11.4 (d, *J*(P,P) = 41 Hz).

[Pd(dibpp)(CH₃)(CH₃C₆H₄SO₃)](1h) ³¹P{¹H} NMR: **d** 17.2 (d, *J*(P,P) = 42 Hz); -12.2 (d, *J*(P,P) = 42 Hz).

Synthesis of [Pd(dibpp)(CH₃)(CH₃CN)]Y (1b, Y = CF₃SO₃⁻; 1f, Y = CF₃CO₂⁻; 1i, Y = CH₃C₆H₄SO₃⁻) [Pd(dibpp)(CH₃)₂] was dissolved in a mixture of 1.8 ml CH₂Cl₂ and 0.2 ml CH₃CN in a 10 mm NMR tube and then cooled to -78 °C; one equivalent of the corresponding acid CF₃SO₃H, CF₃CO₂H or CH₃C₆H₄SO₃H was then added and the solution warmed to room temperature briefly until the ³¹P{¹H} NMR spectrum indicated that the reaction had gone to completion.

[Pd(dibpp)(CH₃)(CH₃CN)][CF₃SO₃] (1b) ³¹P{¹H} NMR: **d** 11.0 (d, *J*(P,P) = 41 Hz); -15.6 (d, *J*(P,P) = 41 Hz).

[Pd(dibpp)(CH₃)(CH₃CN)][CF₃CO₂] (1f) ³¹P{¹H} NMR: **d** 10.8 (d, *J*(P,P) = 41 Hz); -15.6 (d, *J*(P,P) = 41 Hz).

[Pd(dibpp)(CH₃)(CH₃CN)][CH₃C₆H₄SO₃] (1i) ³¹P{¹H} NMR: **d** 11.1 (d, *J*(P,P) = 42 Hz); -15.7 (d, *J*(P,P) = 42 Hz).

Synthesis of [Pd(dibpp)(CH₃)(CH₃OH)]Y (1d, Y = CF₃SO₃⁻; 1j, Y = CH₃C₆H₄SO₃⁻) [Pd(dibpp)(CH₃)₂] was dissolved in a mixture of 1.8 ml CH₂Cl₂ and 0.2 ml CH₃OH in a 10 mm NMR tube and then cooled to -78 °C; one equivalent of the corresponding acid CF₃SO₃H, CH₃C₆H₄SO₃H was then added and the solution warmed to room temperature briefly until the ³¹P{¹H} NMR spectrum indicated that the reaction had gone to completion.

[Pd(dibpp)(CH₃)(CH₃OH)][CF₃SO₃] (1d) ³¹P{¹H} NMR: **d** 18.8 (d, *J*(P,P) = 41 Hz); -14.2 (d, *J*(P,P) = 41 Hz).

[Pd(dibpp)(CH₃)(CH₃OH)][CH₃C₆H₄SO₃] (1j) ³¹P{¹H} NMR: **d** 18.9 (d, *J*(P,P) = 42 Hz); -14.3 (d, *J*(P,P) = 42 Hz).

Synthesis of [Pd(dibpp)(CH₃)(CO)]Y (1c, Y = CF₃SO₃⁻; 1g, Y = CF₃CO₂⁻; 1k, Y = CH₃C₆H₄SO₃⁻) CO was bubbled briefly through a solution of **1a**, **1e** or **1h** in dichloromethane at -78 °C; ³¹P{¹H} NMR spectroscopies revealed the formation, in situ, of **1c**, **1g** or **1k** correspondingly.

[Pd(dibpp)(CH₃)(CO)][CF₃SO₃] (1c) ³¹P{¹H} NMR: **d** -0.5 (d, *J*(P,P) = 47 Hz); -12.3 (d, *J*(P,P) = 47 Hz); ¹³C{¹H} NMR: **d** 181.6 (dd, *J*(P_{trans},C) = 114 Hz *J*(P_{cis},C) = 16 Hz).

[Pd(dibpp)(CH₃)(CO)][CF₃CO₂] (1g) ³¹P{¹H} NMR: **d** -0.8 (d, *J*(P,P) = 48 Hz); -13.5 (d, *J*(P,P) = 48 Hz); ¹³C{¹H} NMR: **d** 181.6 (dd, *J*(P_{trans},C) = 114 Hz *J*(P_{cis},C) = 16 Hz).

[Pd(dibpp)(CH₃)(CO)][CH₃C₆H₄SO₃] (1k) ³¹P{¹H} NMR: **d** -0.6 (d, *J*(P,P) = 47 Hz); -13.4 (d, *J*(P,P) = 47 Hz); ¹³C{¹H} NMR: **d** 181.7 (dd, *J*(P_{trans},C) = 114 Hz *J*(P_{cis},C) = 16 Hz).

Synthesis of [Pd(dibpp)(C(O)CH₃)(CH₃OH)][CF₃SO₃] (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 ³¹P{¹H} NMR spectroscopies revealed the formation, in situ, of **2c** and **2d**.

[Pd(dibpp)(C(O)CH₃)(CO)][CF₃SO₃] (2c) ³¹P{¹H} NMR: **d** -6.7 (d, *J*(P,P) = 73 Hz); -19.2 (d, *J*(P,P) = 73 Hz); ¹³C{¹H} NMR: **d** 235.2 (dd, *J*(P_{trans},C) = 88 Hz *J*(P_{cis},C) = 5 Hz); 176.9 (dd, *J*(P_{trans},C) = 80 Hz *J*(P_{cis},C) = 20 Hz).

[Pd(dibpp)(C(O)CH₃)(CH₃OH)][CF₃SO₃] (2d) ³¹P{¹H} NMR: **d** 13.4 (d, *J*(P,P) = 66 Hz); -19.1 (d, *J*(P,P) = 66 Hz); ¹³C{¹H} NMR of **2d**: **d** 243.0 (dd, *J*(P_{trans},C) = 116 Hz *J*(P_{cis},C) = 12 Hz).

Synthesis of [Pd(dibpp)(C(O)CH₃)(CF₃CO₂)] (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 ³¹P{¹H} NMR spectrum revealed the quantitative formation of **2e**. ³¹P{¹H} NMR: **d** 10.0 (d, *J*(P,P) = 67 Hz); -15.8 (d, *J*(P,P) = 67 Hz); ¹³C{¹H} NMR: **d** 247.8 (dd, *J*(P_{trans},C) = 125 Hz *J*(P_{cis},C) = 10 Hz).

Synthesis of [Pd(dibpp)(C(O)CH₃)(CH₃C₆H₄SO₃)] (2h) CO was bubbled thoroughly through a solution of **1h** in dichloromethane at -78°C . The solution was then warmed to -30°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°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)CH₃)(CH₃CN)]Y (2b, Y = CF₃SO₃⁻; 2f, Y = CF₃CO₂⁻; 2i, Y = CH₃C₆H₄SO₃⁻) CO was bubbled thoroughly through a solution of **1b**, **1f**, or **1i** in a mixture of dichloromethane and acetonitrile (9:1) at -78°C , the solution was warmed to -30°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)CH₃)(CH₃CN)][CF₃SO₃] (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)CH₃)(CH₃CN)][CF₃CO₂] (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)CH₃)(CH₃CN)][CH₃C₆H₄SO₃] (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)CH₃)(CO)]Y (2c, Y = CF₃SO₃⁻; 2k, Y = CH₃C₆H₄SO₃⁻) Excess CO was bubbled thoroughly through a solution of **1a** or **1h** in dichloromethane at -78°C . The solution was then warmed to -30°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)CH₃)(CO)][CF₃SO₃] (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)CH₃)(CO)][CH₃C₆H₄SO₃] (2k) ³¹P{¹H} NMR: **d** -6.8 (d, $J(\text{P,P}) = 73 \text{ Hz}$); -18.6 (d, $J(\text{P,P}) = 73 \text{ Hz}$); ¹³C{¹H} NMR: **d** 235.5 (dd, $J(\text{P}_{\text{trans}},\text{C}) = 88 \text{ Hz}$ $J(\text{P}_{\text{cis}},\text{C}) = 5 \text{ Hz}$); 176.9 (dd, $J(\text{P}_{\text{trans}},\text{C}) = 80 \text{ Hz}$ $J(\text{P}_{\text{cis}},\text{C}) = 20 \text{ Hz}$).

Synthesis of [Pd(dibpp)(C(O)CH₃)(CO)][CF₃CO₂] (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 ³¹P{¹H} NMR spectra revealed the formation, in situ, of **2g**. ³¹P{¹H} NMR: **d** -6.1 (d, $J(\text{P,P}) = 73 \text{ Hz}$); -18.5 (d, $J(\text{P,P}) = 73 \text{ Hz}$); ¹³C{¹H} NMR: **d** 234.7 (dd, $J(\text{P}_{\text{trans}},\text{C}) = 88 \text{ Hz}$ $J(\text{P}_{\text{cis}},\text{C}) = 6 \text{ Hz}$); 176.9 (dd, $J(\text{P}_{\text{trans}},\text{C}) = 79 \text{ Hz}$ $J(\text{P}_{\text{cis}},\text{C}) = 20 \text{ Hz}$).

Synthesis of [Pd(dibpp)(C(O)CH₃)(CH₃OH)][CH₃C₆H₄SO₃] (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 ³¹P{¹H} NMR spectrum revealed the formation, in situ, of **2j**. ³¹P{¹H} NMR: **d** 13.4 (d, $J(\text{P,P}) = 66 \text{ Hz}$); -19.2 (d, $J(\text{P,P}) = 66 \text{ Hz}$); ¹³C{¹H} NMR: **d** 245.5 (dd, $J(\text{P}_{\text{trans}},\text{C}) = 117 \text{ Hz}$ $J(\text{P}_{\text{cis}},\text{C}) = 12 \text{ Hz}$).

Methanolysis of [Pd(dibpp)(C(O)CH₃)(CH₃CN)]Y (2b, Y = CF₃SO₃⁻; 2f, Y = CF₃CO₂⁻; 2i, Y = CH₃C₆H₄SO₃⁻) 0.2 ml CH₃OH was added to a solution of **2b**, **2f** or **2i** in a mixture of CH₂Cl₂ and CH₃CN (9:1) at -78 °C, the solution then warmed to -30 °C and the reactions followed by ¹³C{¹H} and ³¹P{¹H} NMR spectroscopies. No methyl acetate or any other organic product was observed by ¹³C{¹H} 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 ³¹P{¹H} NMR indicating decarbonylation reactions dominate.

Methanolysis of [Pd(dibpp)(C(O)CH₃)(X)] (2e, X = CF₃CO₂⁻; 2h, X = CH₃C₆H₄SO₃⁻) 0.2 ml CH₃OH was added to a CH₂Cl₂ solution of **2e** or **2h** at -78 °C, and the solutions warmed up to -30 °C. The reactions were followed by ¹³C{¹H} and ³¹P{¹H} NMR spectroscopies, progressive formation of methyl acetate was observed by ¹³C{¹H} NMR for both **2e** and **2h**.

Methanolysis of [Pd(dibpp)(C(O)CH₃)(CO)]Y (2g, Y = CF₃CO₂⁻; 2k, Y = CH₃C₆H₄SO₃⁻) 0.2 ml CH₃OH was added to a CH₂Cl₂ solution of **2g** or **2k** at -78 °C, and the solutions were warmed to -30 °C. The reactions were followed by ¹³C{¹H} and ³¹P{¹H} NMR spectroscopies. Progressive formation of methyl acetate was observed by ¹³C{¹H} NMR for both **2g** and **2k**.

Methanolysis of [Pd(dibpp)(C(O)CH₃)(CO)][CF₃SO₃] (2c) 0.2 ml CH₃OH was added to a CH₂Cl₂ solution of **2c** or **2h** at -78 °C, then the solutions were warmed to -30 °C. [Pd(dibpp)C(O)CH₃(CH₃OH)](CF₃SO₃) (**2d**) was detected as an intermediate and its decay was followed by ³¹P{¹H} NMR spectroscopies. Progressive formation of methyl acetate was observed by ¹³C{¹H} NMR.

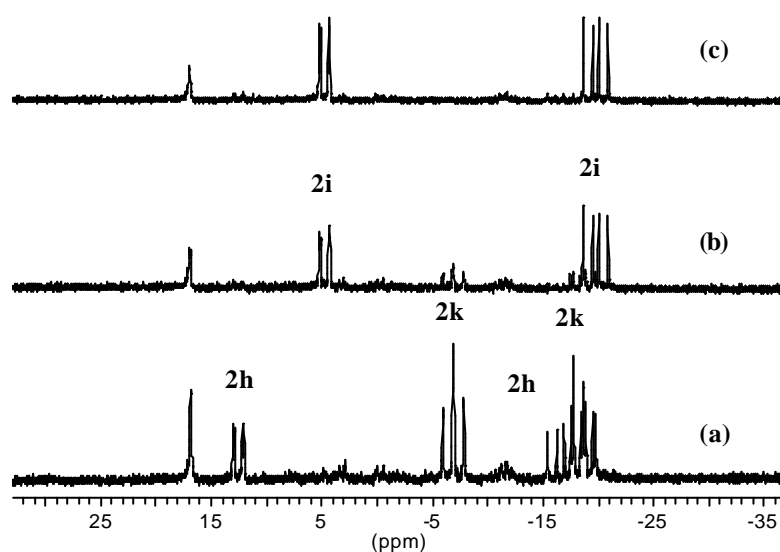


Figure 1. The relative affinity of OTs, CH₃CN and CO for the palladium center in Pd(dibpp)-acyl complexes. (a) ¹³CO was bubbled through a solution of [Pd(dibpp)CH₃(OTs)] (**1h**) at 193K for 5 minutes, [Pd(dibpp)(C(O)CH₃)(OTs)] (**2h**) and [Pd(dibpp)(C(O)CH₃)(CO)][OTs] (**2k**) are formed; (b) 1 equivalent CH₃CN was added at 193K to the solution prepared in (a), [Pd(dibpp)(C(O)CH₃)(CH₃CN)][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.

References:

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