The Mechanism of the Hydroalkoxycarbonylation of Ethene and Alkene-Co
Copolymerization Catalyzed by Pd(II)-Diphosphine Cations

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Experimental details

All manipulations were carried out under dry oxygen-free nitrogen atmosphere using Schlenk techniques. All solvents were carefully purified by appropriate procedures. CD$_2$Cl$_2$ was subjected to three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. Air sensitive compounds were stored under nitrogen at 243 K. $^3$P{$_1^1$H}, $^{13}$C{$_1^1$H} and $^1$H NMR spectra were recorded on a Bruker AMX2-200 WB spectrometer at 193 K unless otherwise specified. $^{13}$CO (99%) was used in experiments in which $^{13}$C NMR data was recorded; for simplicity, CO is used to designate both natural abundance and enriched carbon monoxide. $^{13}$CO was purchased from ISOTEK, ethene from BOC. All other chemicals were purchased from Aldrich. 1,3-bis(di-isobutylphosphino)propane (dibpp) was prepared by reaction of di-isobutylphosphate 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)(CH$_3$)$_2$] was synthesized as described in the literature.$^{2,3}$ [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ was prepared following the method of Drent.$^4$

X-Ray Crystallography. Crystallographic data for [{Pd(dibpp)(µ-OH)}$_2$](OTf)$_2$ were recorded on a Bruker Smart Apex diffractometer using MoK$_\alpha$-radiation ($\lambda = 0.71073$ Å) at $T = 100$ K. The structure was solved by Direct Methods and refined by full-matrix least squares against $R^2$ using all data (SHELX). The crystal was of rather poor quality and weakly diffracting. Thus, the data were truncated at $2\theta = 45^\circ$ and only Pd, P and S atoms were refined anisotropically. H-atoms were fixed in calculated positions at parent atoms, including those of the hydroxide units. Disordered atom positions, incl. one triflate ion, three methyl groups and the central C-atom of one propylene unit, were split on two positions and refined using similar distance and similar $U$ restraints. Crystal data: C$_{40}$H$_{86}$F$_6$O$_8$P$_4$Pd$_2$S$_2$, $M = 1209.89$, $T = 100$ K, $P$-1, $a = 9.872(3)$, $b = 12.504(3)$, $c= 21.947(6)$ Å, $\alpha = 88.350(4)$, $\beta = 89.165(4)$, $\gamma = 83.170(5)^\circ$, $V = 2688.5(12)$ Å$^3$, $Z = 2$, $\mu$(MoK$_\alpha$) = 0.930, 6898 independent reflections ($R_{int} = 0.068$), $R1 (I > 2\sigma(I)) = 0.094$, $wR2$ (all data) = 0.246.
1. Synthesis of palladium monomethyl complexes

**[Pd(dibpp)(CH₃)(OTf)] (1-OTf).** 64 mg (0.14 mmol) [Pd(dibpp)(CH₃)₂] was dissolved in 2 mL CH₂Cl₂ in a 10 mm NMR tube and then cooled to 195 K. 7 µL (0.14 mmol) CF₃SO₃H (1 equivalent) 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. ³¹P{¹H} NMR: δ 11.0 (d, ²J(PP) = 41 Hz); -15.6 (d, ²J(PP) = 41 Hz). ¹H NMR(CD₂Cl₂): δ 0.36 (d, ³J(HP) = 7 Hz, Pd-CH₃).

**[Pd(dibpp)(CH₃)(OTs)] (1-OTs).** 1-OTs was synthesized in an analogous manner to 1-OTf using 20 mg (0.043 mmol) [Pd(dibpp)(CH₃)₂] and 8 mg CH₃C₆H₄SO₃H. ³¹P{¹H} NMR: δ 17.2 (d, ²J(PP) = 42 Hz); -12.2 (d, ²J(PP) = 42 Hz).

**[Pd(dibpp)(CH₃)(TFA)] (1-TFA).** 1-TFA was synthesized in an analogous manner to 1-OTf using 38 mg (0.08 mmol) [Pd(dibpp)(CH₃)₂] and 6.5 µl of CF₃CO₂H. ³¹P{¹H} NMR: δ 12.7 (d, ²J(PP) = 41 Hz); -11.4 (d, ²J(PP) = 41 Hz). ¹H NMR(CD₂Cl₂): δ 0.27 (d, ³J(HP) = 7 Hz, Pd-CH₃).

**[Pd(dibpp)(CH₃)(Cl)] (1-Cl).** 1-Cl was synthesized by adding [Bu₄N]Cl (9 mg, 0.04 mmol, 1 equivalent) to 1-TFA generated in situ as described above from 19 mg (0.04 mmol) [Pd(dibpp)(CH₃)₂] and 3.2 µl of CF₃CO₂H. ³¹P{¹H} NMR: δ 11.4 (d, ²J(PP) = 41 Hz); -12.9 (d, ²J(PP) = 41 Hz).

**[Pd(dibpp)(CH₃)(PPh₃)](TFA) (1-PPh₃).** 1-PPh₃ was synthesized by adding Ph₃P (20.9 mg, 0.08 mmol, 1 equivalent) to 1-TFA generated in situ as described above from 38 mg (0.08 mmol) [Pd(dibpp)(CH₃)₂] and 6.4 µl of CF₃CO₂H. ³¹P{¹H} NMR: δ 32.0 (PPh₃, dd, ²Jₓᵧ (PP) = 356 Hz, ²Jₓᵧ (PP) = 34 Hz); -3.7 (dd, ²Jₓᵧ (PP) = 356 Hz, ²Jₓᵧ (PP) = 49 Hz); -14.8 (dd, ²Jₓᵧ (PP) = 49 Hz, ²Jₓᵧ (PP) = 34 Hz).

**[Pd(dibpp)(CH₃)(CH₃CN)](OTf) ([1-CH₃CN](OTf)).** 23 mg (0.049 mmol) [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 195 K; 3.5 µL CF₃SO₃H 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. ³¹P{¹H} NMR: δ
11.0 (d, $^2J(PP) = 41$ Hz); -15.6 (d, $^2J(PP) = 41$ Hz). $^1$H NMR (CD$_2$Cl$_2$/CD$_3$CN): $\delta$ 0.34 (d, $^3J(HP) = 7$ Hz, Pd-CH$_3$).

$[$Pd(dibpp)(CH$_3$)(CH$_3$CN)](OTs)([1-CH$_3$CN](OTs)).$ Compound [1-CH$_3$CN](OTs) was synthesized in the same manner as [1-CH$_3$CN](OTf) using 23 mg (0.049 mmol) [Pd(dibpp)(CH$_3$)$_2$] and 9 mg CH$_3$C$_6$H$_4$SO$_3$H. $^{31}$P{$_1$H} NMR: $\delta$ 11.1 (d, $^2J(PP) = 42$ Hz); -15.7 (d, $^2J(PP) = 42$ Hz).

$[$Pd(dibpp)(CH$_3$)(CH$_3$CN)](TFA)([1-CH$_3$CN](TFA)).$ Compound [1-CH$_3$CN](TFA) was synthesized in the same manner as [1-CH$_3$CN](OTf) using 22 mg (0.047 mmol) [Pd(dibpp)(CH$_3$)$_2$] and 3.5 µL of CF$_3$CO$_2$H. $^{31}$P{$_1$H} NMR: $\delta$ 10.8 (d, $^2J(PP) = 41$ Hz); -15.6 (d, $^2J(PP) = 41$ Hz).

$[$Pd(dibpp)(CH$_3$)(CH$_3$OH)](OTf) ([1-CH$_3$OH](OTf)).$ 27 mg (0.058 mmol) [Pd(dibpp)(CH$_3$)$_2$] was dissolved in a mixture of 1.8 mL CH$_2$Cl$_2$ and 0.2 mL CH$_3$OH in a 10 mm NMR tube and then cooled to 195 K; 3.5 µL (1 equivalent) CF$_3$SO$_3$H was then added and the solution warmed to room temperature briefly until the $^{31}$P{$_1$H} NMR spectrum indicated that the reaction had gone to completion. $^{31}$P{$_1$H} NMR: $\delta$ 18.8 (d, $^2J(PP) = 41$ Hz); -14.2 (d, $^2J(PP) = 41$ Hz).

$[$Pd(dibpp)(CH$_3$)(CH$_3$OH)](OTs)([1-CH$_3$OH](OTs)).$ Compound [1-CH$_3$OH](OTs) was synthesized in the same manner as [1-CH$_3$OH](OTf) using 18 mg (0.038 mmol) [Pd(dibpp)(CH$_3$)$_2$] and 7.7 mg CH$_3$C$_6$H$_4$SO$_3$H. $^{31}$P{$_1$H} NMR: $\delta$ 18.9 (d, $^2J(PP) = 42$ Hz); -14.3 (d, $^2J(PP) = 42$ Hz).

### 2. Propagation reactions in the “hydride” cycle

**Comments on the reactions with CO and ethene** The palladium monomethyl complexes prepared above were used as precursors to demonstrate the alternating CO/ethylene insertion (propagation) reactions in single or mixed solvents under the desired conditions. All experiments were carried out in 10 mm NMR tubes and using ca 2 mL of the specified solvent; gaseous reactants were bubbled through the solutions and the progress of the reaction was monitored by $^{31}$P{$_1$H} and $^{13}$C{$_1$H} NMR spectroscopy at 193 K unless otherwise stated.

**Synthesis of [Pd(dibpp)(CH$_3$)(CO)]X (1-CO, X = OTf, OTs TFA).** Carbon monoxide was bubbled briefly (a few seconds) through solutions of 1-OTf (84.5 mg, 0.14 mmol), 1-OTs (26.9 mg,
0.04 mmol), and 1-TFA (45.4 mg, 0.08 mmol) in dichloromethane at 195 K; the $^{31}$P{$^1$H} NMR spectra revealed the formation, in situ, of [1-CO](OTf), [1-CO](OTs), [1-CO](TFA) respectively.

$^{[\text{Pd(dibpp)(CH3)(CO)}](\text{OTf})} ([1-\text{CO}](\text{OTf}))$. $^{31}$P{$^1$H} NMR: $\delta$ -0.5 (d, $^2$J(PP) = 47 Hz); -12.3 (d, $^2$J(PP) = 47 Hz); $^{13}$C{$^1$H} NMR: $\delta$ 181.6 (dd, $^2$J(P$_{\text{trans CO}}$) = 114 Hz, $^2$J(P$_{\text{cis CO}}$) = 16 Hz).

$^{[\text{Pd(dibpp)(CH3)(CO)}](\text{OTs})} ([1-\text{CO}](\text{OTs}))$. $^{31}$P{$^1$H} NMR: $\delta$ -0.6 (d, $^2$J(PP) = 47 Hz); -13.4 (d, $^2$J(PP) = 47 Hz); $^{13}$C{$^1$H} NMR: $\delta$ 181.7 (dd, $^2$J(P$_{\text{trans CO}}$) = 114 Hz, $^2$J(P$_{\text{cis CO}}$) = 16 Hz).

$^{[\text{Pd(dibpp)(CH3)(CO)}](\text{TFA})} ([1-\text{CO}](\text{TFA}))$. $^{31}$P{$^1$H} NMR: $\delta$ -0.8 (d, $^2$J(PP) = 48 Hz); -13.5 (d, $^2$J(PP) = 48 Hz); $^{13}$C{$^1$H} NMR: $\delta$ 181.6 (dd, $^2$J(P$_{\text{trans CO}}$) = 114 Hz, $^2$J(P$_{\text{cis CO}}$) = 16 Hz).

Synthesis of $^{[\text{Pd(dibpp)(C(O)CH}_3)(\text{CH}_3\text{OH})](\text{OTf})} ([2-\text{CH}_3\text{OH}](\text{OTf}))$. CO was bubbled thoroughly (a few minutes) through a solution of $^{[1-\text{CH}_3\text{OH}]}$(OTf) (86.8 mg, 0.14 mmol) in a mixture of dichloromethane and methanol (9:1) at 195 K, the solution was then warmed to 243 K when the $^{31}$P{$^1$H} NMR revealed the formation, in situ, of $^{[2-CO]}$(OTf) and $^{[2-\text{CH}_3\text{OH}]}$(OTf).

$^{[\text{Pd(dibpp)(C(O)CH}_3)(CO)](\text{OTf})} ([2-CO](\text{OTf}))$. $^{31}$P{$^1$H} NMR: $\delta$ -6.7 (d, $^2$J(PP) = 73 Hz); -19.2 (d, $^2$J(PP) = 73 Hz); $^{13}$C{$^1$H} NMR: $\delta$ 235.2 (dd, $^2$J(P$_{\text{trans C(O)CH}_3}$) = 88 Hz, $^2$J(P$_{\text{cis C(O)CH}_3}$) = 5 Hz); 176.9 (dd, $^2$J(P$_{\text{trans CO}}$) = 80 Hz, $^2$J(P$_{\text{cis CO}}$) = 20 Hz).

$^{[\text{Pd(dibpp)(C(O)CH}_3)(\text{CH}_3\text{OH})](\text{OTf})} ([2-\text{CH}_3\text{OH}](\text{OTf}))$. $^{31}$P{$^1$H} NMR: $\delta$ 13.4 (d, $^2$J(PP) = 66 Hz); -19.1 (d, $^2$J(PP) = 66 Hz); $^{13}$C{$^1$H} NMR: $\delta$ 243.0 (dd, $^2$J(P$_{\text{trans C(O)CH}_3}$) = 116 Hz, $^2$J(P$_{\text{cis C(O)CH}_3}$) = 12 Hz).

Synthesis of $^{[\text{Pd(dibpp)(C(O)CH}_3)(\text{TFA})]}(2\text{-TFA})$. CO was bubbled thoroughly (a few minutes) through a solution of 1-TFA (45.4 mg, 0.08 mmol) in dichloromethane at 195 K. The solution was warmed to 243 K for 1 hour when the $^{31}$P{$^1$H} NMR revealed the quantitative formation of 2-TFA. $^{31}$P{$^1$H} NMR: $\delta$ 10.0 (d, $^2$J(PP) = 67 Hz); -15.8 (d, $^2$J(PP) = 67 Hz); $^{13}$C{$^1$H} NMR: $\delta$ 247.8 (dd, $^2$J(P$_{\text{trans C(O)CH}_3}$) = 125 Hz, $^2$J(P$_{\text{cis C(O)CH}_3}$) = 10 Hz). $^1$H NMR(CD$_2$Cl$_2$): $\delta$ 2.25 (d, $^2$J(CH) = 4 Hz, Pd-$^{13}$C(O)CH$_3$).
Synthesis of \([\text{Pd(dibpp)}(\text{C}(O)\text{CH}_3)(\text{OTs})]\) (2-\text{OTs}). CO was bubbled thoroughly (a few minutes) through a solution of 1-\text{OTs} (26.9 mg, 0.04 mmol) in dichloromethane at 195 K. The solution was warmed to 243 K for 1 hour, then purged with nitrogen at 195 K for 10 minutes when the $^{31}\text{P} \{^1\text{H}\}$ NMR revealed the quantitative formation of 2-\text{OTs}. $^{31}\text{P} \{^1\text{H}\}$ NMR: $\delta$ 12.5 (d, $^2J(\text{PP}) = 70$ Hz); $-16.6$ (d, $^2J(\text{PP}) = 70$ Hz); $^{13}\text{C} \{^1\text{H}\}$ NMR: $\delta$ 244.6 (dd, $^2J(\text{P}_{\text{transC}}(\text{O})\text{CH}_3) = 122$ Hz, $^2J(\text{P}_{\text{cisC}}(\text{O})\text{CH}_3) = 12$ Hz).

Synthesis of \([\text{Pd(dibpp)}(\text{C}(O)\text{CH}_3)(\text{CH}_3\text{CN})]\text{X}\) (2-\text{CH}_3\text{CN}, \text{X} = \text{OTf}, \text{OTs}, \text{TFA}). Carbon monoxide was bubbled thoroughly (a few minutes) through a solution of [1-\text{CH}_3\text{CN}](\text{X}) (31.6 mg, 0.049 mmol); [1-\text{CH}_3\text{CN}](\text{OTs}) (32.6 mg, 0.049 mmol); or [1-\text{CH}_3\text{CN}](\text{TFA}) (28.6 mg, 0.047 mmol) in a mixture of dichloromethane and acetonitrile (9:1) at 195 K, the solution was warmed to 243 K for 1 hour when the $^{31}\text{P} \{^1\text{H}\}$ NMR revealed the quantitative formation of [2-\text{CH}_3\text{CN}](\text{X}).

\([\text{Pd(dibpp)}(\text{C}(O)\text{CH}_3)(\text{CH}_3\text{CN})](\text{OTf})\) ([2-\text{CH}_3\text{CN}](\text{OTf})). $^{31}\text{P} \{^1\text{H}\}$ NMR: $\delta$ 5.4 (d, $^2J(\text{PP}) = 70$ Hz); $-19.6$ (d, $^2J(\text{PP}) = 70$ Hz); $^{13}\text{C} \{^1\text{H}\}$ NMR: $\delta$ 242.6 (dd, $^2J(\text{P}_{\text{transC}}(\text{O})\text{CH}_3) = 112$ Hz, $^2J(\text{P}_{\text{cisC}}(\text{O})\text{CH}_3) = 10$ Hz). $^1\text{H}$ NMR(CD$_2$Cl$_2$/CD$_3$CN): $\delta$ 2.42 (d, $^2J(\text{CH}) = 4$ Hz, Pd-$^{13}\text{C}(\text{O})\text{CH}_3$).

\([\text{Pd(dibpp)}(\text{C}(O)\text{CH}_3)(\text{CH}_3\text{CN})](\text{TFA})\) ([2-\text{CH}_3\text{CN}](\text{TFA})). $^{31}\text{P} \{^1\text{H}\}$ NMR: $\delta$ 4.9 (d, $^2J(\text{PP}) = 70$ Hz); $-19.7$ (d, $^2J(\text{PP}) = 70$ Hz); $^{13}\text{C} \{^1\text{H}\}$ NMR: $\delta$ 242.8(dd, $^2J(\text{P}_{\text{transC}}(\text{O})\text{CH}_3) = 112$ Hz, $^2J(\text{P}_{\text{cisC}}(\text{O})\text{CH}_3) = 16$ Hz).

\([\text{Pd(dibpp)}(\text{C}(O)\text{CH}_3)(\text{CH}_3\text{CN})](\text{OTs})\) ([2-\text{CH}_3\text{CN}](\text{OTs})). $^{31}\text{P} \{^1\text{H}\}$ NMR: $\delta$ 4.9 (d, $^2J(\text{PP}) = 70$ Hz); $-19.7$ (d, $^2J(\text{PP}) = 70$ Hz); $^{13}\text{C} \{^1\text{H}\}$ NMR: $\delta$ 242.6 (dd, $^2J(\text{P}_{\text{transC}}(\text{O})\text{CH}_3) = 113$ Hz, $^2J(\text{P}_{\text{cisC}}(\text{O})\text{CH}_3) = 10$ Hz).

Synthesis of \([\text{Pd(dibpp)}(\text{C}(O)\text{CH}_3)(\text{CO})]\text{X}\) (2-\text{CO}, \text{X} = \text{OTf}; \text{OTs}). Excess carbon monoxide was bubbled thoroughly (a few minutes) through a solution of 1-\text{OTf} (84.5 mg, 0.14 mmol) or 1-\text{OTs} (26.9 mg, 0.04 mmol) in dichloromethane at 195 K. The solution was then warmed to 243 K for 1 hour when the $^{31}\text{P} \{^1\text{H}\}$ NMR spectra revealed the quantitative formation, \textit{in situ}, of [2-\text{CO}](\text{OTf}) and [2-\text{CO}](\text{OTs}) respectively.
[Pd(dibpp)(C(O)CH₃)(CO)][OTf] ([2-CO][OTf]). \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta -6.7\) (d, \(^2J\text{(PP)} = 73\) Hz); -19.2 (d, \(^2J\text{(PP)} = 73\) Hz); \(^{13}\text{C}\{^1\text{H}\}\) NMR: \(\delta 235.2\) (dd, \(^2J\text{(PtransC(O)CH₃)} = 88\) Hz, \(^2J\text{(PcisC(O)CH₃)} = 5\) Hz); 176.9 (dd, \(^2J\text{(PtransCO)} = 80\) Hz, \(^2J\text{(PcisCO)} = 20\) Hz).

[Pd(dibpp)(C(O)CH₃)(CO)][OTs] ([2-CO][OTs]). \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta -6.8\) (d, \(^2J\text{(PP)} = 73\) Hz); -18.6 (d, \(^2J\text{(PP)} = 73\) Hz); \(^{13}\text{C}\{^1\text{H}\}\) NMR: \(\delta 235.5\) (dd, \(^2J\text{(PtransC(O)CH₃)} = 88\) Hz, \(^2J\text{(PcisC(O)CH₃)} = 5\) Hz); 176.9 (dd, \(^2J\text{(PtransCO)} = 80\) Hz, \(^2J\text{(PcisCO)} = 20\) Hz).

Synthesis of [Pd(dibpp)(C(O)CH₃)(CO)][TFA] ([2-CO][TFA]). Excess carbon monoxide was bubbled thoroughly (a few minutes) through a solution of 1-TFA (45.4 mg, 0.08 mmol) in a mixture of dichloromethane and methanol (9:1) at 195 K. The solution was then warmed to 243 K for 1 hour when the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra revealed the formation, \textit{in situ}, of \([2-CO]\)[TFA]. \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta -6.1\) (d, \(^2J\text{(PP)} = 73\) Hz); -18.5 (d, \(^2J\text{(PP)} = 73\) Hz); \(^{13}\text{C}\{^1\text{H}\}\) NMR: \(\delta 234.7\) (dd, \(^2J\text{(PtransC(O)CH₃)} = 88\) Hz, \(^2J\text{(PcisC(O)CH₃)} = 6\) Hz); 176.9 (dd, \(^2J\text{(PtransCO)} = 79\) Hz, \(^2J\text{(PcisCO)} = 20\) Hz).

[Pd(dibpp)(CH₂CH₂C(O)CH₃)][OTf] (3). Ethene was bubbled at 195 K through a solution of \([2-\text{CH₃CN}]\)(OTf) prepared as described above, and the progress of the reaction was monitored by \(^{31}\text{P}\{^1\text{H}\}\) NMR. 3 started to form after 15 minutes at 195 K, the reaction went to completion after 10 hrs at 243 K. \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta 12.7\) (d, \(^2J\text{(PP)} = 46\) Hz); -13.5 (d, \(^2J\text{(PP)} = 46\) Hz); \(^{13}\text{C}\{^1\text{H}\}\) NMR: \(\delta 236.0\) (d, \(^2J\text{(PCH₂CH₂C(O)CH₃)} = 10\) Hz).

[Pd(dibpp)(C(O)CH₂CH₂C(O)CH₃)(CH₃CN)][OTf] (4-CH₃CN). Exposure of a solution containing 3, prepared as above, to CO at 243 K resulted in an equilibrium mixture of 3 and 4-CH₃CN. \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta 3.9\) (d, \(^2J\text{(PP)} = 69\) Hz); -19.1 (d, \(^2J\text{(PP)} = 69\) Hz); \(^{13}\text{C}\{^1\text{H}\}\) NMR: \(\delta 240.3\) (dd, \(^2J\text{(PtransC(O)CH₂CH₂C(O)CH₃)} = 115\) Hz, \(^2J\text{(PcisC(O)CH₂CH₂C(O)CH₃)} = 10\) Hz), 208.0 (s, C(O)CH₂CH₂C(O)CH₃).

[Pd(dibpp)(C(O)CH₂CH₂C(O)CH₃)(CO)][OTf] (4-CO). On exposure of a solution containing 3 prepared as above to excess CO at 243 K, 3 is partially converted to a mixture of 4-CH₃CN and 4-CO. \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta -7.3\) (d, \(^2J\text{(PP)} = 72\) Hz); -18.9 (d, \(^2J\text{(PP)} = 72\) Hz); \(^{13}\text{C}\{^1\text{H}\}\) NMR: \(\delta 235.6\) (dd,
\[ \text{\( J(P_{\text{trans}}C(O)CH_2CH_2C(O)CH_3) = 90\) Hz, \( J(P_{\text{cis}}C(O)CH_2CH_2C(O)CH_3) = 4\) Hz); 177.8 (dd,}
\[ \text{\( J(P_{\text{trans}}CO) = 80\) Hz, \( J(P_{\text{cis}}CO) = 20\) Hz); 207.7 (s, C(O)CH_2CH_2C(O)CH_3).} \]

\[ \{\text{Pd(dibpp)CH}_2\text{CH}_2\text{(C(O)CH}_2\text{CH}_2\text{C(O)CH}_3\})\text{(OTf) (5). 4 prepared above was converted to 5 on}
\[ \text{bubbling ethene for 5 minutes through the solution at 243 K. Some 3, formed by deinsertion of CO from}
\[ \text{4, was also observed. } 31\text{P}\{\text{1H}\} \text{NMR: } \delta 14.7 \text{ (d, } J(PP) = 47\) Hz); -13.6 \text{ (d, } J(PP) = 47\) Hz);
\[ \text{13C}\{\text{1H}\} \text{NMR: } \delta 237.4 \text{ (d, } J(P,CH_2CH_2C(O)CH_2CH_2C(O)CH_3) = 10\) Hz), 206.4 (s).} \]

\text{3. Preparation of palladium carbomethoxy complexes}

\[ \{\text{Pd(dibpp)(OCH}_3\text{)(CH}_3\text{CN)\text{(OTf) (6). [Pd(dibpp)(CH}_3\text{CN)}\text{2)(OTf)}\text{_2 (42 mg, 0.05 mmol) was}
\[ \text{dissolved in a CH}_2\text{Cl}_2/\text{CH}_3\text{OH/CH}_3\text{CN (9:1:(5 equivalent)) mixture and cooled to 193 K, 1 equivalent}
\[ \text{Et}_3\text{N (6.5 } \mu\text{L) was added to give a pale yellow solution, 6 and 7 were detected as major products by}
\[ 31\text{P}\{\text{1H}\} \text{NMR at 193 K. } 31\text{P}\{\text{1H}\} \text{NMR: } \delta 3.7 \text{ (d, } J(PP) = 28\) Hz); 15.0 \text{ (d, } J(PP) = 28\) Hz).
\]

\[ \{\text{Pd(dibpp)(Et}_3\text{N)(CH}_3\text{CN)\text{(OTf) (7). [Pd(dibpp)(CH}_3\text{CN)}\text{2)(OTf)}\text{_2 (42 mg, 0.05 mmol) was}
\[ \text{dissolved in a CH}_2\text{Cl}_2/\text{CH}_3\text{OH/CH}_3\text{CN (9:1:5) mixture cooled to 193 K, 1 equivalent Et}_3\text{N (6.5 } \mu\text{L) was}
\[ \text{then added to give a pale yellow solution, 6 and 7 were detected as major products by } 31\text{P}\{\text{1H}\} \text{NMR at}
\[ 193 K. } 31\text{P}\{\text{1H}\} \text{NMR: } \delta 8.0 \text{ (d, } J(PP) = 35\) Hz); 11.7 \text{ (d, } J(PP) = 35\) Hz).
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\[ \{\text{Pd(dibpp)(C(O)OCH}_3\text{)(CH}_3\text{CN)\text{(OTf) (8-CH}_3\text{CN). [Pd(dibpp)(CH}_3\text{CN)}\text{2)(OTf)}\text{_2 (42 mg, 0.05}
\[ \text{mmol) was dissolved in a CH}_2\text{Cl}_2/\text{CH}_3\text{OH/CH}_3\text{CN (9:1:trace) mixture saturated with CO at 193 K, 1}
\[ \text{equivalent Et}_3\text{N (6.5 } \mu\text{L) was then added to give a clear yellow solution. Further CO was then bubbled}
\[ \text{through the solution to drive the reaction to completion in } ca. \text{ 10 minutes. The solvents were evaporated}
\[ \text{quickly and the red oily residue was extracted into 2 mL CH}_2\text{Cl}_2 \text{to give a yellow solution. } 31\text{P}\{\text{1H}\} \text{NMR: } \delta 8.3 \text{ (d, } J(PP) = 47\) Hz); -15.5 \text{ (d, } J(PP) = 47\) Hz); 13C\{\text{1H}\} \text{NMR: } \delta 191.7 \text{ (dd,}
\[ \text{J(P_{\text{trans}}C(O)OCH}_3) = 167\) Hz, \text{J(P_{\text{cis}}C(O)OCH}_3) = 9\) Hz).
\]

\[ \{\text{Pd(dibpp)(C(O)OCH}_3\text{)(CO)\text{(OTf) (8-CO). 8-CO was synthesized by an analogous procedure to}
\[ \text{8-CH}_3\text{CN using a 1:1 mixture of CH}_2\text{Cl}_2 \text{and CH}_3\text{OH as solvent. When excess CO was passed through}
the solution, 8-CO was the only product obtained. $^{31}$P$^1$H NMR: $\delta$ -1.4 (d, $^2J$(PP) = 49 Hz); -14.1 (d, $^2J$(PP) = 49 Hz); $^{13}$C$^1$H NMR: $\delta$ 185.5 (dd, $^2J$(Ptrans-C(O)OCH$_3$) = 141 Hz, $^2J$(Pcis-C(O)OCH$_3$) = 9 Hz); $\delta$ 177.3 (dd, $^2J$(PtransCO) = 98 Hz, $^2J$(PcisCO) = 12 Hz).

[Pd(dppp)(C(O)OCH$_3$)(CH$_3$CN)](OTf) (9). 9 was synthesized in an analogous manner to 8-CH$_3$CN using 63 mg (0.07mmol) [Pd(dppp)(CH$_3$CN)$_2$](OTf)$_2$ and 10 µL Et$_3$N using methanol as solvent. $^{31}$P$^1$H NMR: $\delta$ 11.8 (d, $^2J$(PP) = 57 Hz); -3.8 (d, $^2J$(PP) = 57 Hz); $^{13}$C$^1$H NMR: $\delta$ 190.3 (dd, $^2J$(PtransC(O)OCH$_3$) = 174 Hz, $^2J$(PcisC(O)OCH$_3$) = 18 Hz).

[Pd(dibpp)(13C(O)OCH$_3$)$_2$] (10). 10 was synthesized in a similar manner to 8 but using 2 equivalents Et$_3$N. $^{31}$P$^1$H and $^{13}$C NMR spectroscopy shows a AA’XX’ pattern. The chemical shifts and coupling constants were obtained from simulation of the experimental spectrum using gNMR 4.1. $^{31}$P$^1$H NMR: $\delta$ -8.2; $^{13}$C$^1$H NMR: $\delta$ 203.0; $^2J$(PP) = 45.2 Hz, $^2J$(PtransC) = 151.7 Hz, $^2J$(PcisC) = 12.3 Hz, $^2J$(CC) = 6.2 Hz).

4. Investigation of the mechanism of the formation of 8

[Pd(dibpp)(C(O)O13CH$_3$)(CH$_3$CN)](OTf)(8-CH$_3$CN). [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ (62 mg, 0.076 mmol) was dissolved in a mixture of 1.8 mL CH$_2$Cl$_2$ and 20 µL CH$_3$CN (5 equivalents), the mixture was saturated with $^{13}$CO at 193 K, 0.1 mL $^{13}$CH$_3$OH and 10.5 µL Et$_3$N (1 equivalent) were then added. The solution was kept at 243 K for 3 hours to give a clear yellow solution. $^{31}$P$^1$H NMR: $\delta$ 8.3 (d, $^2J$(PP) = 47 Hz); -15.5 (d, $^2J$(PP) = 47 Hz); $^{13}$C$^1$H NMR: $\delta$ 191.7 (dd, $^2J$(PtransC(O)OCH$_3$) = 167 Hz, $^2J$(PcisC(O)OCH$_3$) = 9 Hz, $^2J$(PcisC(O)OCH$_3$) = 4 Hz) (Figure S9).

[Pd(dibpp)(C(O)O13CH$_3$)(PPh$_3$)](OTf)(8-PPh$_3$). [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ (48 mg, 0.059 mmol) was dissolved in a mixture of 1.5 mL CH$_2$Cl$_2$, 0.1 mL $^{13}$CH$_3$OH and 15 µL CH$_3$CN (5 equivalents), the mixture was saturated with $^{13}$CO at 193 K, 8 µL Et$_3$N (1 equivalent) was then added and the solution was kept at 243 K for 4 hours. Then the solution was purged with nitrogen for 5 minutes and 15 mg Ph$_3$P (1 equivalent to Pd) was added as a solid, A clear yellow solution 8-PPh$_3$ was
formed immediately as indicated by $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectroscopies. $^{31}$P{$^1$H} NMR: δ 13.3 (PPh$_3$, dd, $^2J_{trans}$ (PPh$_3$P) = 298 Hz, $^2J_{cis}$ (PPh$_3$P) = 36 Hz); -4.3 (dibpp, dd, $^2J_{trans}$ (PPh$_3$P) = 298 Hz, $^2J_{cis}$ (PP) = 50 Hz); -17.8 (dibpp, dd, $^2J_{cis}$ (PP) = 50 Hz, $^2J_{cis}$ (PPh$_3$P) = 36 Hz); $^{13}$C{$^1$H} NMR: δ 192.8 (ddd, $^2J_{trans}$ C(O)OCH$_3$) = 153 Hz, $^2J_{cis}$ C(O)OCH$_3$) = 5 Hz, $^2J_{cis}$ (PPh$_3cis$ C(O)OCH$_3$) = 3 Hz).

Scrambling of $^{12}$CO with $^{13}$C-enriched 8-CH$_3$CN [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ (25 mg, 0.03 mmol) was dissolved in a mixture of 1.5 mL CH$_2$Cl$_2$, 0.2 mL CH$_3$OH and 70 µL CH$_3$CN (50 equivalents), and the mixture saturated with $^{13}$CO at 193 K, 4.1 µL Et$_3$N (1 equivalent) was then added and the solution kept at 243 K for 4 hours until NMR spectroscopy confirmed the formation of 8-CH$_3$CN. The solution was then purged thoroughly with nitrogen to remove residual $^{13}$CO, $^{12}$CO was bubbled through the solution for 5 minutes at 193 K, the tube capped, and the reaction monitored by $^{31}$P{$^1$H} NMR at time intervals of 1, 2.5 and 60 hours at 243 K.

Scrambling of $^{12}$CO with 8-PPh$_3$ [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ (20 mg, 0.024 mmol) was dissolved in a mixture of 1.5 mL CH$_2$Cl$_2$, 0.2 mL CH$_3$OH and 7 µL CH$_3$CN (5 equivalents), and the mixture saturated with $^{13}$CO at 193 K, 3.8 µL Et$_3$N (1 equivalent) was then added and the solution was kept at 243 K for 4 hours until NMR spectroscopy revealed that the formation of 8-CH$_3$CN had occurred. 7 mg PPh$_3$ was then added to convert 8-CH$_3$CN to 8-PPh$_3$. The solution was then purged with nitrogen thoroughly to remove residual $^{13}$CO, $^{12}$CO was bubbled through the solution for 5 minutes at 193 K, the tube was capped and the reaction monitored by $^{31}$P{$^1$H} NMR at time intervals of 1, 2.5 and 60 hours at 243 K.

5. Propagation reactions in the “carbomethoxy” cycle

$\text{[Pd(dibpp)(CH$_2$CH$_2$C(O)OCH$_3$)](OTf)}$ (11). Ethene was passed through a solution of 3 prepared as above, at 195 K for 2 minutes, and the solution then slowly warmed to 243 K. The $^{31}$P{$^1$H} NMR spectroscopy revealed that 11 was formed quantitatively after 1.5 hrs at 243 K. $^{31}$P{$^1$H} NMR: δ
13.3 (d, $^2J_{(PP)} = 46$ Hz); -12.0 (d, $^2J_{(PP)} = 46$ Hz); $^{13}C\{^1H\}$ NMR: $\delta$ 193.3 (d, $^2J(P,CH_2CH_2C(O)OCH_3) = 10$ Hz).

$[\text{Pd(dppp)}(\text{CH}_2\text{CH}_2\text{C}(O)\text{OCH}_3)](\text{OTf})$ (12). 12 was synthesized from 9 in an analogous manner to 11 but using pure methanol as solvent. $^{31}P\{^1H\}$ NMR: $\delta$ 29.4 (d, $^2J_{(PP)} = 57$ Hz); -3.9 (d, $^2J_{(PP)} = 57$ Hz); $^{13}C\{^1H\}$NMR: $\delta$ 192.4 (d, $^2J(P,CH_2CH_2C(O)OCH_3) = 12$ Hz).

$[\text{Pd(dibpp)}(\text{CH}_2\text{CH}_2\text{C}(O)\text{OCH}_3)(\text{CH}_3\text{CN})](\text{OTf})$ (13). 0.05 mL CH$_3$CN was added to the solution of 11 prepared above to give 13. $^{31}P\{^1H\}$ NMR: $\delta$ 12.7 (d, $^2J_{(PP)} = 46$ Hz); -12.6 (d, $^2J_{(PP)} = 46$ Hz); $^{13}C\{^1H\}$NMR: $\delta$ 179.0 (dd, $^4J_{transCH_2CH_2C(O)OCH_3} = 4$ Hz, $^4J_{cisCH_2CH_2C(O)OCH_3} = 2$ Hz).

$[\text{Pd(dibpp)}(\text{C}(O)\text{CH}_2\text{CH}_2\text{C}(O)\text{OCH}_3)(\text{CH}_3\text{CN})](\text{OTf})$ (14-CH$_3$CN) and $[\text{Pd(dibpp)}(\text{C}(O)\text{CH}_2\text{CH}_2\text{C}(O)\text{OCH}_3)(\text{CH}_3\text{CN})](\text{OTf})$ (14-CO). On bubbling CO through a CH$_2$Cl$_2$ solution of 11 prepared as described above, a mixture of 14-CH$_3$CN and 14-CO was formed as revealed by NMR spectroscopy. 14-CH$_3$CN: $^{31}P\{^1H\}$ NMR: $\delta$ 4.1 (d, $^2J_{(PP)} = 68$ Hz); -18.6 (d, $^2J_{(PP)} = 68$ Hz); $^{13}C\{^1H\}$NMR: $\delta$ 241.5 (dd, $^2J_{transC(O)(C_2H_4)C(O)OCH_3} = 116$ Hz, $^2J_{cisC(O)(C_2H_4)C(O)OCH_3} = 9$ Hz); 173.0 (s, C(O)(C$_2$H$_4$)C(O)OCH$_3$); 14-CO: $^{31}P\{^1H\}$ NMR: $\delta$ -7.1 (d, $^2J_{(PP)} = 71$ Hz), -18.6 (d, $^2J_{(PP)} = 71$ Hz); $^{13}C\{^1H\}$NMR: $\delta$ 234.9 (dd, $^2J_{transCO} = 91$ Hz, $^2J_{cisCO} = 5$ Hz); $\delta$ 176.7 (dd, $^2J_{transCO} = 81$ Hz, $^2J_{cisCO} = 20$ Hz), 172.7 (s, C(O)(C$_2$H$_4$)C(O)OCH$_3$).

$[\text{Pd(dibpp)}\text{CH}_2\text{CH}_2(\text{C}(O)\text{CH}_2\text{CH}_2\text{C}(O)\text{OCH}_3)](\text{OTf})$ (15). Ethene was bubbled through a solution of 14-CH$_3$CN, prepared as above, for a few minutes. After 1 hr at 243 K, 15 was detected as the major species. $^{31}P\{^1H\}$ NMR: $\delta$ 13.2 (d, $^2J_{(PP)} = 46$ Hz), -13.7 (d, $^2J_{(PP)} = 46$ Hz); $^{13}C\{^1H\}$ NMR: $\delta$ 237.5 (d, $^2J(P, CH_2CH_2C(O)CH_2CH_2C(O)OCH_3) = 10$ Hz); 174.0 (s, CH$_2$CH$_2$C(O)(C$_2$H$_4$)C(O)OCH$_3$).

6. Termination of the “hydride” cycle by methanolysis of palladium-acyls

Methanolysis of $[\text{Pd(dibpp)}(\text{C}(O)\text{CH}_3)(\text{CH}_3\text{CN})]X$ (2-CH$_3$CN, X = OTf, TFA, OTs). 0.2 mL CH$_3$OH was added to a solution of 2-CH$_3$CN in a mixture of CH$_2$Cl$_2$ and CH$_3$CN (9:1) at 195 K, the
solution was then warmed to 243 K and the reactions followed by $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR. No methyl acetate or any other organic product was observed by $^{13}\text{C}\{^1\text{H}\}$ NMR after 20 hours at 243 K. On warming the solutions to room temperature, 1-CH$_3$CN was detected as the only new species by $^{31}\text{P}\{^1\text{H}\}$ NMR indicating that decarbonylation reactions dominate.

**Methanolysis of [Pd(dibpp)(C(O)CH$_3$)(TFA]) (2-TFA).** 0.2 mL CH$_3$OH was added to a CH$_2$Cl$_2$ solution of 2-TFA, prepared as above, at 195 K, and the mixture allowed to warm up to 243 K. Progress of the reaction was followed by $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR and progressive formation of methyl acetate was observed by $^{13}\text{C}\{^1\text{H}\}$ NMR over a period of tens of minutes.

**Methanolysis of [Pd(dibpp)(C(O)CH$_3$)(OTs)] (2-OTs).** 0.2 mL CH$_3$OH was added to a CH$_2$Cl$_2$ solution of 2-OTs, prepared as above, at 195 K, and the reaction mixture warmed to 243 K. The reactions were followed by $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR, [2-CH$_3$OH][OTs] was detected as an intermediate and progressive formation of methyl acetate was observed by $^{13}\text{C}\{^1\text{H}\}$ NMR over a period of tens of minutes.

**Methanolysis of [Pd(dibpp)(C(O)CH$_3$)(CO)]X (2-CO, X = TFA, OTs).** 0.2 mL CH$_3$OH was added to a CH$_2$Cl$_2$ solution of 2-CO, prepared as above, at 195 K, and the solutions were warmed to 243 K. The reactions were followed by $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR and progressive formation of methyl acetate was observed by $^{13}\text{C}\{^1\text{H}\}$ NMR over a period of tens of minutes.

**Methanolysis of [Pd(dibpp)(C(O)CH$_3$)(CO)][OTf] ([2-CO][OTf]).** 0.2 mL CH$_3$OH was added to a CH$_2$Cl$_2$ solution of [2-CO][OTf] prepared as above, at 195 K, and the solution warmed to 243 K. [Pd(dibpp)C(O)CH$_3$(CH$_3$OH)][OTf] ([2-CH$_3$OH][OTf]) was detected as an intermediate and its decay was followed by $^{31}\text{P}\{^1\text{H}\}$ NMR. (Figure S13) Progressive formation of methyl acetate was observed by $^{13}\text{C}\{^1\text{H}\}$ NMR over a period of tens of minutes. The organometallic product of the methanolysis is presumably the Pd-hydride [Pd$_2$(µ-H)(µ-CO)(dibpp)$_2$]$^{2+}$ by analogy with Bianchini’s reports. However, the major organometallic species isolated after the methanolysis reaction is [{Pd(dibpp)(µ-OH)$_2$}]OTf$_2$. An X-ray crystal structure determination showed that the crystals contain the dicationic complex [{Pd(dibpp)(µ-OH)$_2$}]$^{2+}$ in which the two Pd(II) centres are bridged by two hydroxide ions.
Coordination to the bidentate diphosphine ligands completes the square planar environment of the Pd centres. The Pd-O distances within the planar four-membered Pd₂O₂ ring are on average 2.10 Å and thus similar to those of related complexes \([Pd(L\cdot L)(\mu-OH)]_{2}{\text{^2}^+}\) containing diphosphine ligands.⁶⁻⁸ There are two triflate ions for every dicaticonic complex in the crystal structure. Both interact via hydrogen bonds with the hydroxide ions of the Pd complex (Figure S15). \([Pd(dibpp)(\mu-OH)]_{2}\text{OTf}_2\) is presumably formed via a decomposition pathway involving adventitious water. Other bond lengths and interbond angles mirror those reported by Bianchini for similar μ-OH species.

7. Termination of the “hydride” cycle by methanolysis of chelating palladium-alkyls

Chain crossover to the “carboalkoxy” cycle

Methanolysis of 3 and 5. 0.2 mL CH₃OH was added to the mixture of palladium complexes, 3 and 5 prepared above at 243 K. Methanolysis occurred on the timescale of hours at room temperature, and was monitored by \(^{31}\text{P}\{^1\text{H}\}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR. After several hours, an additional resonance at 209.0 ppm was observed in the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum (Figure S17c), together with an increase in intensity of the resonance at 211.8 ppm. These resonances can be attributed to heptan-2,5-dione, the diketone product of methanolysis of the 3rd generation β-chelate 5. The remaining resonances in the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum may be due to CO/ethene multiple insertion products which are unavoidable even though the solution was purged thoroughly with nitrogen at low temperatures in an effort to remove residual CO and/or ethene. No deposition of metallic palladium was observed after 3 days at room temperature. Butan-2-one and heptan-2, 5-dione were detected as the principal organic products of the methanolysis. (Figure S16, S17)

After bubbling CO through this solution, 8 and some unidentified species were detected by \(^{31}\text{P}\{^1\text{H}\}\) NMR (Figure S18). NMR data: for palladium enolate: \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta\) 12.5 (d, \(^2J(PP) = 52\) Hz); -16.5 (d, \(^2J(PP) = 52\) Hz); \(^{13}\text{C}\{^1\text{H}\}\)NMR: \(\delta\) 206.3 (s); for 8: \(^{31}\text{P}\{^1\text{H}\}\) NMR: \(\delta\) 8.3 (d, \(^2J(PP) = 47\) Hz); -15.5 (d, \(^2J(PP) = 47\) Hz); \(^{13}\text{C}\{^1\text{H}\}\)NMR: \(\delta\) 191.7 (dd, \(^2J(\text{trans},\text{C}(O)\text{OCH}_3) = 167\) Hz, \(^2J(\text{cis},\text{C}(O)\text{OCH}_3) = 9\) Hz).
Hz); for the organic products: $^{13}\text{C}^{1}\text{H}$ NMR: $\delta$ 209.0, (s, CH$_3$C(O)CH$_2$CH$_2$-); 211.8 (s, CH$_3$CH$_2$C(O)CH$_2$CH$_2$-).

8. Termination of the “carboalkoxy” cycle

Methanolysis of 11. 0.2 mL CH$_3$OH was added to a solution of 11, prepared as above, and the progress of the reaction monitored by $^{31}\text{P}^{1}\text{H}$ and $^{13}\text{C}^{1}\text{H}$ NMR spectroscopy. No deposition of metallic palladium was observed after 3 days at room temperature; 8 was regenerated on bubbling CO through this solution. (Figure S19) Methyl propanoate was detected as the only organic product by $^{13}\text{C}^{1}\text{H}$ NMR, singlet at 173.0 (s) ppm.
List of Supplementary Figures

Figure S1. $^{13}$C{$_1^H$} NMR spectra recorded at 193 K of key stages in the “hydride” cycle: (a) [Pd(dibpp)(CH$_3$(CH$_2$CN))(OTf)] (1-CH$_3$CN) after $^{13}$CO bubble at 213 K, 1 minute; (b) bubble $^{13}$CO at 213 K, 5 minutes then purge with N$_2$ at 213 K; (c) bubble C$_2$H$_4$ at 213 K, 5 minutes then purge with N$_2$ at 213 K.

Figure S2. Plot of ln(K) versus 1/T for the equilibrium of Equation 1, K=([$1^\text{TFA}$][CH$_3$CN])/([1-CH$_3$CN][TFA]) over the temperature ranging from 193 K to 243 K.

Figure S3. $^{31}$P{$_1^H$} NMR spectra of the reaction of [Pd(dibpp)(CH$_3$)(OTs)] (1-OTs) with $^{13}$CO (a) bubble excess $^{13}$CO through the solution of 1-OTs; (b) purge the solution with N$_2$ for 1 minute; (c) purge the solution with N$_2$ for 5 minutes.

Figure S4. $^{13}$C{$_1^H$} NMR spectra of the reaction of [Pd(dibpp)(CH$_3$)(OTs)] (1-OTs) with CO (a) bubble excess $^{13}$CO through the solution of 1-OTs; (b) purge the solution with N$_2$ for 1 minute; (c) purge the solution with N$_2$ for 5 minutes.

Figure S5. $^{31}$P{$_1^H$} NMR spectra of key stages in the second pass “hydride” cycle: (a) [Pd(dibpp)(CH$_2$CH$_2$C(O)CH$_3$)](OTf) (3); (b) bubble $^{13}$CO at 213 K, then purge with N$_2$ at 213 K; (c) bubble C$_2$H$_4$ at 213 K.

Figure S6. $^{13}$C{$_1^H$} NMR spectra of key stages in the second pass “hydride” cycle: (a) [Pd(dibpp)(CH$_2$CH$_2$C(O)CH$_3$)][CF$_3$SO$_3$]; (b) bubble $^{15}$CO at 213 K, then purge with N$_2$ at 213 K; (c) bubble C$_2$H$_4$ at 213 K.

Figure S7. Experimental(up) and simulated(down) $^{31}$P{$_1^H$} and $^{13}$C{$_1^H$} NMR spectra for 10.

Figure S8. $^{31}$P{$_1^H$} NMR spectra of the reaction of [Pd(dibpp)(MeCN)$_4$][OTf]$_2$ with : (a) 1 equivalent NaOCH$_3$; (b) $^{13}$CO 5 min at 213 K; (c) $^{13}$CO overnight at 243K.

Figure S9. $^{13}$C{$_1^H$} NMR spectrum of [Pd(dibpp)[($^{13}$C(O)O$^{13}$CH$_3$)(MeCN)] [OTf]] prepared in a similar manner to 8 but using $^{13}$CH$_3$OH as reactant.

Figure S10. Experimental(up) and simulated(down) $^{31}$P{$_1^H$} NMR spectra for 8-PPh$_1$.

Figure S11. $^{31}$P{$_1^H$} NMR spectra recorded in dichloromethane: CH$_3$CN (9:1) at 193 K of key stages in the “carboalkoxy” cycle: (a) [Pd(dibpp)[($^{13}$C(O)OCH$_3$)(MeCN)](OTf) (8-CH$_3$CN) and [Pd(dibpp)[($^{13}$C(O)OCH$_3$)]($^{13}$CO)](OTf) (8-CO); (b) purge with N$_2$ at 213 K; (c) bubble C$_2$H$_4$ at 213 K, 5 minutes then purge with N$_2$ at 213 K.

Figure S12. $^{31}$P{$_1^H$} NMR spectra recorded in dichloromethane at 193 K of chain propagation stages in the “carbomethoxy” cycle: (a) 11 was synthesized by successive addition of $^{13}$CO and ethene into 8 formed in situ; (b) $^{13}$CO bubbled through the solution then at 243 K for 2 hours; (c) purged with nitrogen and then bubbled with ethene at 213 K, warmed up to 243 K for 2 hours.
**Figure S13.** $^{31}$P{$^1$H} NMR spectra of the methanolysis of 2-CO showing 2-CH$_3$OH as an intermediate: (a) [2-CO](OTf) in 1.8 ml CH$_2$Cl$_2$ at 193 K plus 0.2 ml CH$_3$OH; (b) after 45 minutes at 243 K.

**Figure S14.** $^{13}$C{$^1$H} NMR spectra of the methanolysis of 2-CO showing 2-CH$_3$OH as an intermediate: (a) [2-CO]OTf in 1.8 mL CH$_2$Cl$_2$ at 193 K with 0.2 mL CH$_3$OH added; (b) warmed to 243 K and then after 45 minutes at that temperature.

**Figure S15.** Crystal structure of [(L-L)Pd (µ-OH)]$_2$(CF$_3$SO$_3$)$_2$.

**Figure S16.** $^{31}$P{$^1$H} NMR spectra of the methanolysis of 3 and 5, showing the difference in reactivity of the β-chelates: CD$_3$OD was added to the mixture of 3 and 5 at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d). (spectra (a) and (b) are recorded at 253 K, spectra (c) and (d) recorded at room temperature).

**Figure S17.** $^{13}$C{$^1$H} NMR spectra of the methanolysis of 3 and 5, showing the difference in reactivity of the β-chelates: CD$_3$OD was added to the mixture of 3 and 5 at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d). (spectra (a) and (b) are recorded at 253 K, spectra (c) and (d) recorded at room temperature).

**Figure S18.** $^{31}$P{$^1$H} and $^{13}$C{$^1$H} NMR spectra of the methanolysis of 3 in the presence of CO (crossover reaction to carboalkoxy cycle).

**Figure S19.** $^{31}$P{$^1$H} NMR spectra of methanolysis of chelate in carboalkoxy cycle showing methanolysis of the β-chelate giving reinitiation: (a) a mixture of 11 and 12 generated in the presence of 4 equivalents CH$_3$CN following the procedure described above otherwise; (b) after 1 day at room temperature, $^{13}$CO was bubbled through the solution at 213 K and then kept at 243 K for 1.5 hrs (both spectra taken at 193K).
**Figure S1.** $^{13}$C$\{^1$H$\}$ NMR spectra recorded at 193 K of key stages in the “hydride” cycle: (a) [Pd(dibpp)(CH$_3$)(CH$_3$CN)](OTf) (I-CH$_3$CN) after $^{13}$CO bubble at 213 K, 1 minute; (b) bubble $^{13}$CO at 213 K, 5 minutes then purge with N$_2$ at 213 K; (c) bubble C$_2$H$_4$ at 213 K, 5 minutes then purge with N$_2$ at 213 K.
Figure S2. Plot of $\ln(K)$ versus $1/T$ for the equilibrium of Equation 1, $K=([\text{1-TFA}][\text{CH}_3\text{CN}])/([\text{1-CH}_3\text{CN}][\text{TFA}])$ at the temperature ranging from 193 K to 243 K.

\begin{equation}
1-\text{CH}_3\text{CN} + \text{TFA} \quad 1-\text{TFA} + \text{CH}_3\text{CN}
\end{equation}

\begin{align*}
y &= -1898.5x + 13.021 \\
R^2 &= 1
\end{align*}
Figure S3. $^{31}$P {$^1$H} NMR spectra of the reaction of $[\text{Pd(dibpp)}(\text{CH}_3)(\text{OTs})] \ (\text{1-OTs})$ with CO (a) bubble excess $^{13}$CO through the solution of 1-OTs; (b) purge the solution with N$_2$ for 1 minute; (c) purge the solution with N$_2$ for 5 minutes.
**Figure S4.** $^{13}C\{^1H\}$ NMR spectra of the reaction of [Pd(dibpp)(CH$_3$)(OTs)] (1-OTs) with CO (a) bubble excess $^{13}$CO through the solution of 1-OTs; (b) purge the solution with N$_2$ for 1 minute; (c) purge the solution with N$_2$ for 5 minutes.
Figure S5. $^{31}\text{P} \{^1\text{H}\}$ NMR spectra of key stages in the second pass “hydride” cycle: (a) $[\text{Pd}(\text{dibpp})(\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3)](\text{OTf})$ (3); (b) bubble $^{13}\text{CO}$ at 213 K, then purge with $\text{N}_2$ at 213 K; (c) bubble $\text{C}_2\text{H}_4$ at 213 K.
Figure S6. $^{13}$C{H} NMR spectra of key stages in the second pass “hydride” cycle: (a) [Pd(dibpp)(CH$_2$CH$_2$C(O)CH$_3$)][CF$_3$SO$_3$]; (b) bubble $^{15}$CO at 213 K, then purge with N$_2$ at 213 K; (c) bubble C$_2$H$_4$ at 213 K.
**Figure S7.** Experimental (up) and simulated (down) $^{31}$P{H} and $^{13}$C{H} NMR spectra of the 10.
Figure S8. $^{31}$P-$^{1}$H NMR spectra of the reaction of $[\text{Pd(dibpp)(MeCN)}]_2[\text{OTf}]_2$ with: (a) 1 equivalent NaOCH$_3$; (b) $^{13}$CO 5 min at 213 K; (c) $^{13}$CO overnight at 243 K.
Figure S9. $^{13}\text{C}^{1}\text{H}$ NMR spectrum of $[\text{Pd(dibpp)}(^{13}\text{C(O)O}^{13}\text{CH}_3)(\text{MeCN})] \ [\text{OTf}]$ prepared in a similar manner to 8 but using $^{13}\text{CH}_3\text{OH}$ as reactant.
Figure S10. Experimental (up) and simulated (down) $^{31\text{P}}\{^{1\text{H}}\}$ NMR spectra for 8-PPh$_3$
Figure S11. $^{31}$P{${}^{1}$H} NMR spectra recorded in dichloromethane: CH$_3$CN (9:1) at 193 K of key stages in the “carboalkoxy” cycle: (a) [Pd(dibpp)(${}^{13}$C(O)OCH$_3$)(MeCN)](OTf) (8-CH$_3$CN) and [Pd(dibpp)(${}^{13}$C(O)OCH$_3$)(${}^{13}$CO)](OTf) (8-CO); (b) purge with N$_2$ at 213 K; (c) bubble C$_2$H$_4$ at 213 K, 5 minutes then purge with N$_2$ at 213 K. 

![NMR spectra](image_url)
Figure S12. $^{31}$P{¹H} NMR spectra recorded in dichloromethane at 193 K of chain propagation stages in the “carbomethoxy” cycle: (a) 11 was synthesized by successive addition of $^{13}$CO and ethene into 8 formed in situ; (b) $^{13}$CO bubbled through the solution then at 243 K for 2 hours; (c) purged with nitrogen and then bubbled with ethene at 213 K, warmed to 243 K for 2 hours.
Figure S13. $^{31}$P{H} NMR spectra of the methanolysis of 2-CO showing 2-CH$_3$OH as an intermediate: (a) [2-CO](OTf) in 1.8 ml CH$_2$Cl$_2$ at 193 K plus 0.2 ml CH$_3$OH; (b) after 45 minutes at 243 K.
Figure S14. $^{13}$C{¹H} NMR spectra of the methanolysis of 2-CO showing 2-CH$_3$OH as an intermediate: (a) [2-CO]OTf in 1.8 mL CH$_2$Cl$_2$ at 193 K with 0.2 mL CH$_3$OH added; (b) warmed to 243 K and then after 45 minutes at that temperature.
Figure S15. Crystal structure of $[(\text{L-L})\text{Pd (µ-OH)}^2](\text{CF}_3\text{SO}_3)^2$. 
**Figure S16.** $^{31}$P{$^1$H} NMR spectra of the methanolation of 3 and 5, showing the difference in reactivity of the $\beta$-chelates: CD$_3$OD was added to the mixture of 3 and 5 at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d). (spectra (a) and (b) recorded at 253 K, spectra (c) and (d) recorded at room temperature).
Figure S17. $^{13}$C{$_1^1$H} NMR spectra of the methanolysis of 3 and 5, showing the difference in reactivity of the $\beta$-chelates: CD$_3$OD was added to the mixture of 3 and 5 at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d). (spectra (a) and (b) recorded at 253 K, spectra (c) and (d) recorded at room temperature).
Figure S18. $^{31}$P{$^1$H} and $^{13}$C{$^1$H} NMR spectra of the methanolysis of 3 in the presence of CO (crossover reaction to carboalkoxy cycle).
Figure S19. $^{31}\text{P}^1\text{H}$ NMR spectra of methanolysis of chelate in carbomethoxy cycle showing methanolysis of the β-chelate giving reinitiation: (a) a mixture of 11 and 12 generated in the presence of 4 equivalents CH$_3$CN following the procedure described above otherwise; (b) after 1 day at room temperature, $^{13}$CO was bubbled through the solution at 213 K and then kept at 243 K for 1.5 hrs (both spectra taken at 193K).
References

Collection of $^{31}$P{$_1$H} and $^{13}$C{$_1$H} NMR spectra

Representative $^{31}$P{$_1$H} and/or $^{13}$C{$_1$H} NMR spectra of following compounds are listed here:

$[{\text{1-CH}_3\text{CN}}](\text{OTf})$, 1-OTf, 1-TFA, 1-PPh$_3$, 1-Cl, 1-H$_2$O,
2-TFA,2-OTs,2-CH$_3$CN](OTf), [2-CO](OTf)$_3$, [4-CH$_3$CN](OTf)$_5$
[8-CH$_3$CN](OTf), [8-CO](OTf), [8-PPh$_3](OTf)$,9,11,12,13, [14-CO](OTf),
[14-CH$_3$CN](OTf), 15

The spectra of all other compounds, transient intermediates and sequential reactions are given **Figure 1,2,3** in main text and **Figure S1-S19** above, which are not reproduced here.
$^{31}$P$^{[1}H\} NMR spectrum of [1-CH$_3$CN](OTf) recorded at 193 K in dichloromethane
$^{31}\text{P}^{1\text{H}}$ NMR spectrum of 1-OTf recorded at 193 K in dichloromethane

* 1-H$_2$O
$^{31}\text{P}$ NMR spectrum of a mixture of $1\text{-H}_2\text{O}$ and $1\text{-OTf}$ recorded at 193 K in dichloromethane (1-H$_2$O formed due to trace of water in triflic acid is identified by the significant growth of those resonances (top spectrum) by addition of 1 eq H$_2$O to a “dry” solution of 1-OTf (bottom spectrum))
$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of **1-TFA** recorded at 193 K in dichloromethane
$^{31}$P{$^1$H} NMR spectrum of 1-PPh$_3$ recorded at 193 K in dichloromethane
(1-PPh$_3$ prepared by addition of 1 eq. PPh$_3$ to 1-TFA, [1-PPh$_3$]/[1-TFA]=12.3 by integration of corresponding resonances)
$^{31}$P$^1$H NMR spectrum of 1-Cl recorded at 193 K in dichloromethane
(1-Cl prepared by addition of 1 eq. Bu$_4$NCl to 1-TFA, [1-Cl]/[1-TFA]=1.7 by integration of corresponding resonances)

* (dibpp)Pd(TFA)$_2$

♦ 1-TFA
$^{31}\text{P}{^{1}\text{H}}} \text{ NMR spectrum of } 1\text{-CH}_3\text{OH recorded at 193 K in dichloromethane}
$^{31}\text{P}^{[\text{H}]}$ NMR spectrum of 1-OTS recorded at 193 K in dichloromethane
$^{31}$P{$^1$H} NMR spectrum of 2-TFA recorded at 193 K in dichloromethane

* (dibpp)Pd(TFA)$_2$
$^{13}\text{C}^{1\text{H}}$ NMR spectrum of 2-TFA recorded at 193 K in dichloromethane
$^{31}\text{P}^{1\text{H}}$ NMR spectrum of 2-OTs recorded at 193 K in dichloromethane

* (dibpp)Pd(OTs)$_2$
$^{13}\text{C}[^1\text{H}]$ NMR spectrum of 2-OTs recorded at 193 K in dichloromethane
$^{31}$P$^1$H NMR spectrum of [2-CH$_3$CN](OTf) recorded at 193 K in dichloromethane
$^{13}$C-$^1$H NMR spectrum of [2-CH$_3$CN][OTf] recorded at 193 K in dichloromethane

* residual 2-CO
$^{31}$P$[^1]$H NMR spectrum of [2-CO](OTf) recorded at 193 K in dichloromethane
$^{13}$C$^1$H NMR spectrum of \textbf{[2-CO](OTf)} recorded at 193 K in dichloromethane
$^{31}\text{P}$$^{1\text{H}}$ NMR spectrum of 3 recorded at 193 K in dichloromethane
$^{13}$C-$^1$H NMR spectrum of 3 recorded at 193 K in dichloromethane

* ethylene
$^{31}$P{$^1$H} NMR spectrum of 3 and [4-CH$_3$CN](OTf) recorded at 193 K in dichloromethane (insertion of CO into 3 can not go to completion under conditions employed)
$^{13}$C$^1$H NMR spectrum of $[4$-$\text{CH}_3\text{CN}]$(OTf) recorded at 193 K in dichloromethane

* 3
♦ pendent carbonyl on the chain
$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of 3 and 5 recorded at 193 K in dichloromethane
(a mixture of 3 and 5 (ca. 1:1) were obtained in equilibrium under current conditions employed, see main text)
$^{13}$C-$^1$H NMR spectrum of 5 recorded at 193 K in dichloromethane
$^{31}$P-$^1$H NMR spectrum of [8-CH$_3$CN](OTf) recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{13}$C-\textsuperscript{1}H NMR spectrum of [8-CH\textsubscript{3}CN](OTf) recorded at 193 K in CH\textsubscript{2}Cl\textsubscript{2}/\textsuperscript{12}CH\textsubscript{3}OH/CH\textsubscript{3}CN
$^{13}$C$_{1H}$ NMR spectrum of [8-CH$_3$CN](OTf) recorded at 193 K in CH$_2$Cl$_2$/$^{13}$CH$_3$OH/CH$_3$CN
($^{13}$CH$_3$O resonance is obscured by strong solvent peak, but additional coupling from which to carbonyl is clearly observed in extended carbonyl region)
$^{31}$P-$^1$H NMR spectrum of a mixture of [8-CO](OTf) and [8-CH₃CN](OTf) recorded at 193 K in CH₂Cl₂/CH₃OH/CH₃CN.
$^{13}$C{$_{^1}$H} NMR spectrum of a mixture of [8-CO](OTf) and [8-CH$_3$CN](OTf) recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN.
$^{31}\text{P}^1\text{H}$ NMR spectrum of [8-PPh$_3$](OTf) recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{13}\text{C}^{1\text{H}}$ NMR spectrum of $[8\text{-PPPh}_3](\text{OTf})$ recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{31}$P{$^1$H} NMR spectrum of 9 recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN

*(dppp)Pd(CH$_3$CN)(OTf)$_2$
$^{13}$C{$_{\text{1H}}$} NMR spectrum of 9 recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{31}\text{P}^{1\text{H}}$ NMR spectrum of 11 recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 11 recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{31}$P-{$^1$H} NMR spectrum of 12 recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{13}$C{$^1$H} NMR spectrum of **12** recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{31}$P/$^1$H NMR spectrum of 13 recorded at 293 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{13}$C-$^1$H NMR spectrum of 13 recorded at 293 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{31}$P{$^1$H} NMR spectrum of a mixture of 11 and 14-CO recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH

*(dibppp)Pd(CH$_3$CN)$_2$(OTf)$_2$
$^{13}$C-$^1$H NMR spectrum of 14-CO recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH
$^{31}$P{${^1}$H} NMR spectrum of 14-CH$_3$CN recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{13}$C{$^1$H} NMR spectrum of 14-CH$_3$CN recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{31}\text{P}^{{}^1\text{H}}$ NMR spectrum of 15 recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{13}\text{C}^{1\text{H}}$ NMR spectrum of 15 recorded at 193 K in CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN
$^{31}$P{$_1$H} NMR spectrum of the reaction of [Pd(dibpp)(OTf)2] with Et3N:
(a) in CD2Cl2/CH2Cl2; (b) after addition of Et3N