

Supporting Information

Interaction of Alkynes with Palladium POCOP-Pincer Hydride Complexes and Its Unexpected Relation to Palladium-Catalyzed Hydrogenation of Alkynes

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Procedures for the DLS Experiments. Under an argon atmosphere, in two separate J. Young NMR tubes, complex **5b** (0.0125 mmol) was dissolved in 0.5 mL of toluene- d_8 . One of the samples (**B**) was degassed by a freeze-pump-thaw cycle and then mixed with 1 atm of H_2 , while the other sample (**A**) was kept under argon. After 12 h at room temperature, sample **B** changed from colorless to faint yellow while sample **A** remained colorless even after 48 h. Neither 1H NMR nor $^{31}P\{^1H\}$ NMR spectra of the two samples showed any sign of decomposition. Both samples were diluted with toluene and examined by a particle size analyzer using dynamic light scattering techniques (toluene was used as reference). Sample **B** revealed particles distributed in the range of 0.18-0.30 μm . When centrifuged, sample **B** also showed some black particles. Appearance of the two samples before centrifugation is shown in Fig. S1.

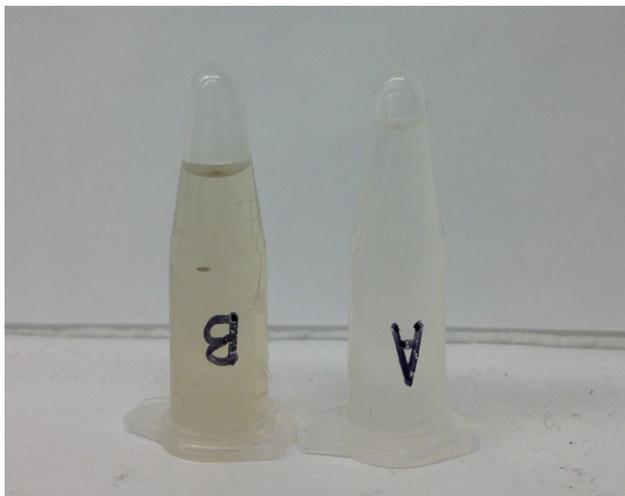


Fig. S1 Toluene solutions of **5b** with (sample **B**) and without (sample **A**) exposure to H_2 .

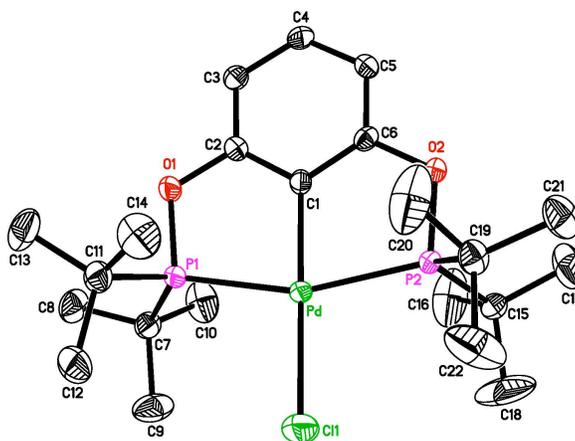


Fig. S2 ORTEP drawing of $[2,6-(tBu_2PO)_2C_6H_3]PdCl$ (**1a**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

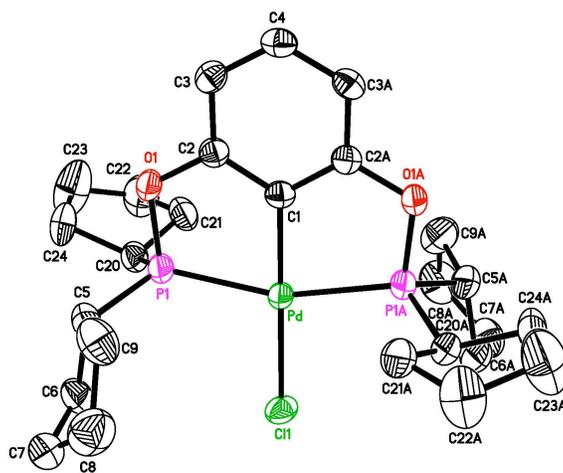


Fig. S2 ORTEP drawing of [2,6-(ⁱPe₂PO)₂C₆H₃]PdCl (**1c**) at the 50% probability level.
Hydrogen atoms are omitted for clarity.

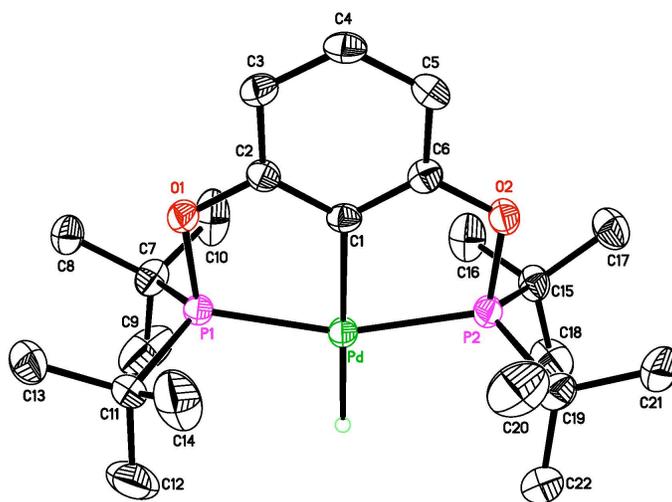


Fig. S3 ORTEP drawing of [2,6-(^tBu₂PO)₂C₆H₃]PdH (**2a**) at the 50% probability level.
Hydrogen atoms are omitted for clarity.

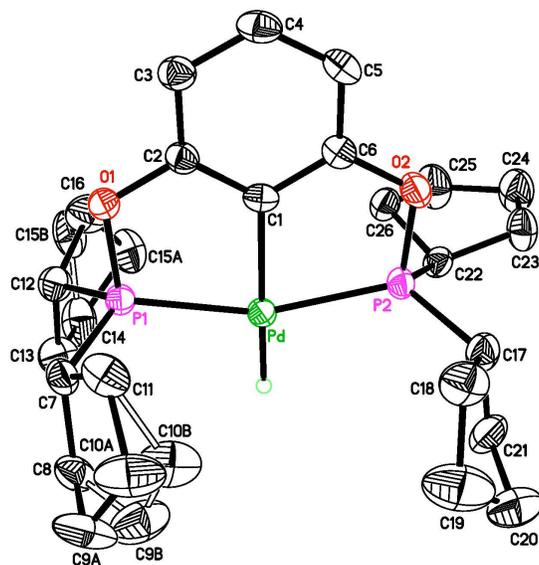


Fig. S4 ORTEP drawing of $[2,6-(^{\text{Pe}}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdH}$ (**2c**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

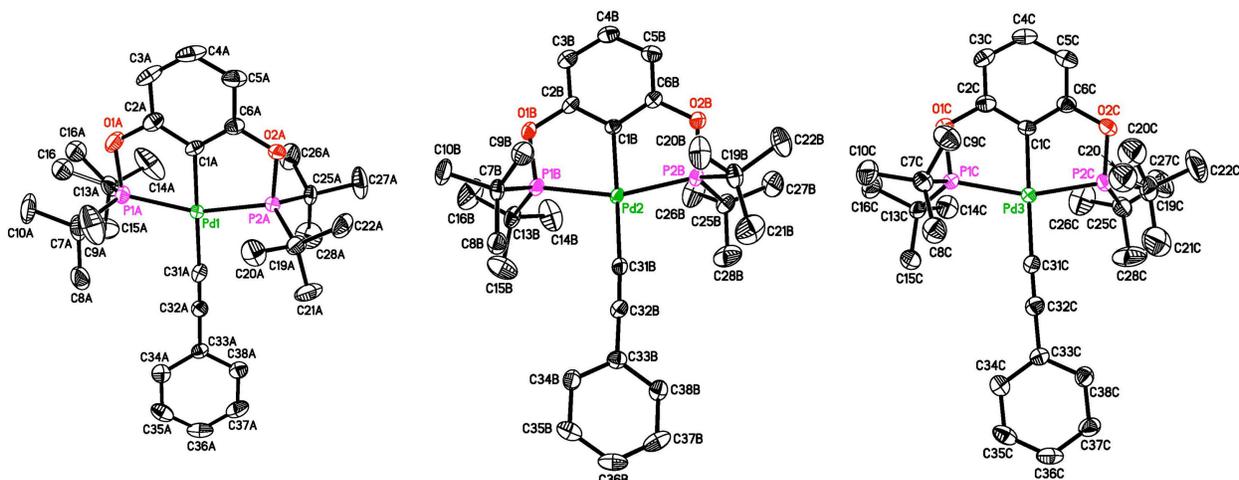


Fig. S5 ORTEP drawing of $[2,6-(^{\text{tBu}}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdC}\equiv\text{CPh}$ (**3a**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

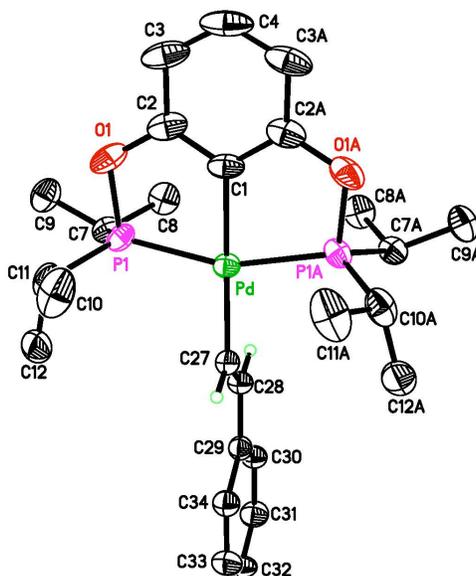


Fig. S6 ORTEP drawing of (*E*)-[2,6-(*i*Pr₂PO)₂C₆H₃]PdCH=CHPh (**4b**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

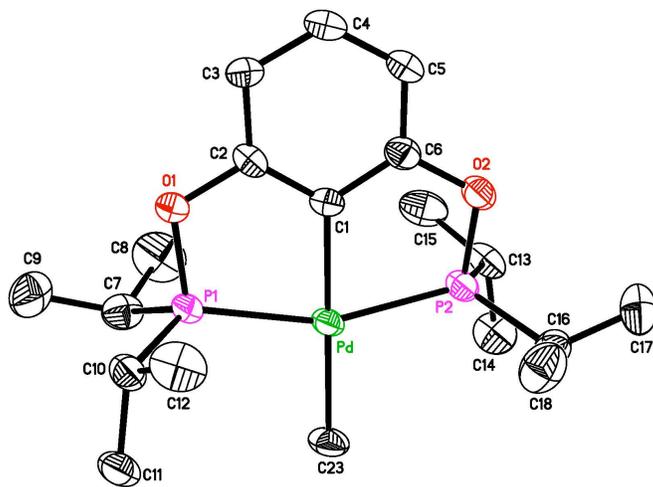


Fig. S7 ORTEP drawing of [2,6-(*i*Pr₂PO)₂C₆H₃]PdCH₃ (**5b**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S1 Summary of crystallographic data

	1a	1c	2a	2c	3a	4b	5b
empirical formula	C ₂₂ H ₃₉ O ₂ P ₂ ClP	C ₂₆ H ₃₉ O ₂ P ₂ ClPd	C ₂₂ H ₄₀ O ₂ P ₂ Pd	C ₂₆ H ₄₀ O ₂ P ₂ Pd	3(C ₃₀ H ₄₄ O ₂ P ₂ Pd)	C ₂₆ H ₃₈ O ₂ P ₂ Pd	C ₁₆ H ₃₄ O ₂ P ₂ Pd
formula weight	539.32	587.36	504.88	552.92	1814.98	550.90	462.80
temp, K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
crystal system	triclinic	tetragonal	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	P-1	I-42d	P2 ₁ /c	P2 ₁ /n	Pc	P2 ₁ /n	P-1
a, Å	8.3191(2)	21.578(2)	16.4881(2)	12.2605(2)	26.224(3)	7.8023(2)	8.0315(2)
b, Å	12.0094(2)	21.578(2)	10.6035(1)	17.3087(4)	15.8839(18)	14.4839(4)	10.3766(2)
c, Å	13.3760(2)	11.5095(13)	15.7094(2)	12.3482(2)	11.0864(12)	12.0669(3)	14.2789(3)
α, deg	100.296(1)	90	90	90	90	90	100.667(1)
β, deg	96.127(1)	90	114.927(1)	99.811(1)	96.9650(16)	101.659(2)	103.372(1)
γ, deg	103.903(1)	90	90	90	90	90	101.595(1)
Volume, Å ³	1260.55(4)	5358.8(9)	2490.65(5)	2582.13(8)	4583.9(9)	1335.52(6)	1100.12(4)
Z	2	8	4	4	2	2	2
d _{calc} , g/cm ³	1.421	1.456	1.346	1.422	1.315	1.370	1.397
λ, Å	1.54178	0.88560	1.54178	1.54178	0.77490	1.54178	1.54178
μ, mm ⁻¹	8.220	1.650	7.319	7.115	0.915	6.878	8.235
no. of data collected	10578	24904	20794	21918	57801	10793	9168
no. of unique data	4321	2737	4482	4651	22449	2453	3781
R _{int}	0.0187	0.0987	0.0337	0.0470	0.0558	0.0300	0.0278
Goodness-of-fit on F ²	1.050	1.049	1.043	1.047	1.023	1.055	1.057
R1, wR2 (I > 2σ(I))	0.0284, 0.0755	0.0298, 0.0756	0.0270, 0.0688	0.0339, 0.0815	0.0389, 0.0861	0.0273, 0.0693	0.0315, 0.0803
R1, wR2 (all data)	0.0301, 0.0766	0.0313, 0.0763	0.0308, 0.0710	0.0458, 0.0876	0.0540, 0.0926	0.0318, 0.0720	0.0347, 0.0827