SUPPLEMENTARY INFORMATION

Unexpected bond activations promoted by palladium nanoparticles

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1. Experimental part

General

Samples for TEM were prepared depositing a drop of solution on a holey carbon grid and removing the excess of THF. The nanoparticles size distribution and average diameter were directly determined from TEM images by Image-J software associated to a Microsoft Excel macro developed by Christian Pradel. GC-MS analyses were performed on a Perkin–Elmer Clarus 500 chromatograph fitted with a FID and MS-detector and a SGE BPX5 capillary column (30 m x 0.32 mm x 0.25 mm): injector temperature 250 °C; flow 20 mL*min^{-1}; temperature programme of 40 °C for 2 min followed by 10 °C min^{-1} to 300 °C and hold for 5 min. GC-MS was also performed on Thermo-Electron Trace GC Ultra fitted with a FID and MS-detector and a DB-5MS capillary column (30 m x 0.32 mm x 0.25 mm): injector temperature 260 °C; flow 1 mL*min^{-1}; temperature programme of 50 °C for 4 min followed by 20 °C min^{-1} to 300 °C and hold for 15 min. XPS spectra of Pd 3d and S 2p core level shown coupling spin-orbit, the doublet separation was set to 1.21 eV and 5.29 eV The XPS error is based considering a detection limit estimated to be 0.1% in mass and uncertain propagation. For the deconvolution analysis the uncertainty was estimated at 5% of the binding energy. FAB$^+$ mass spectrum was acquired in a JEOL SX102A inverse geometry spectrometer using 3-nitrobenzylalcohol matrix. High-resolution mass spectrum was obtained on an Agilent G1969A electrospray-ionization time-off light mass spectrometer.

Synthesis of XPS reference materials:

[PdCl$_2$2]. Similar procedure as for [PdCl$_2$**1**][1] was followed using ligand **2** instead: A schlenk was charged with [PdCl$_2$(NCCH$_3$)$_2$] (39 mg, 0.150 mmol), **2** (69 mg, 0.158 mmol) and dry CH_2Cl_2 (15 mL). The mixture was stirred for 24 h at room temperature and then, the solvent was evaporated under reduced pressure. The residue was washed with Et_2O and dried under vacuum to give a yellow solid. Yield: 79%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ= 7.85 (m, 1H, *3-H$_{ar}$*), 7.74 (m, 4H, *3-H$_{ph}$*), 7.59 (m, 1H, *4-H$_{ar}$*), 7.53 (m, 2H, *4-H$_{ph}$*), 7.47 (m, 1H, *6-H$_{ar}$*), 7.46 (m, 1H, *5-H$_{ar}$*), 7.45 (m, 4H, *2-H$_{ph}$*), 3.37 (m, 2H, SC*H$_2$*-), 1.90 (2H, broad, SCH$_2$C*H$_2$*-), 1.05-1.26 (m, 10H, SCH$_2$CH$_2$(C*H$_2$*)$_5$CH$_2$CH$_2$CH$_3$), 1.24 (m, 2H, S(CH$_2$)$_8$C*H$_2$*CH$_3$), 1.18 (m, 10H, S(CH$_2$)$_7$C*H$_2$*CH$_2$CH$_3$), 0.86 (3H, t, S(CH$_2$)$_9$C*H$_3$,* J=6.75Hz). ^{13}C NMR ($CDCl_3$, 77.5 MHz): δ= 138.36 (d, *1-C$_{ar}$*, J$_{C-P}$= 22.8 Hz), 137.57 (d, *2-C$_{ar}$*, J$_{C-}$

$_P$= 56.1 Hz), 134.66 (d, *6*-C_{ar}, J_{C-P}=19.5 Hz), 133.92 (d, *3*-C_{ph}, J_{C-P}= 10.9 Hz), 132.57 (4-C_{ph}), 132.52 (5-C_{ar}), 131.71 (d, *3*-C_{ar}, J_{C-P}=16.3 Hz), 131.33 (d, *4*-C_{ar}, J_{C-P}=6.8 Hz), 129.16 (d, *2*-C_{ph}, J_{C-P}=13.0 Hz), 127.89 (d, *1*-C_{ph}, J_{C-P}=58.0 Hz), 43.89 (SCH_2), 31.89 ($S(CH_2)_7CH_2CH_2CH_3$), 30.62 (SCH_2CH_2-), 28.67-29.44 ($SCH_2CH_2(CH_2)_5CH_2CH_2CH_3$), 22.76 ($S(CH_2)_8CH_2CH_3$), 14.20 ($S(CH_2)_9CH_3$). ^{31}P NMR ($CDCl_3$, 121 MHz,): δ= 57.68 ppm. IR (ATR): 3053, 2922, 2851, 1456, 1434, 1098, 721, 688, 542, 512 cm^{-1}. MS (FAB): m/z = 575 for $[C_{28}H_{35}ClPPdS]^+$. HRMS (ESI-TOF$^+$): m/z Calcd. For $[C_{28}H_{35}ClPPdS]^+$: 575.0920; found: 575.0915.

$[Pd(SC_{10}H_{21})_2]_n$ was prepared according to the following procedure. 1-Decylthiol (0.371 mmol, 0.082 mL) in dichloromethane (1 mL) was added dropwise over 10 minutes to a solution of dichloro(norbornadiene)palladium(II) (0.185 mmol, 50 mg,) and triethylamine (0.371 mmol, 0.052 mL) in dichloromethane (10 mL). The solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure to dryness. Hexanes were added to the residue and the suspension was filtered over celite. The solvent was evaporated and the orange solid was dried under vacuum. Yield: 86%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ= 2.40 (m, 2H, SCH_2), 1.00 -1.80 (m, 12H, $SCH_2(CH_2)_6CH_2CH_2CH_3$), 1.23 (m, 2H, $S(CH_2)_8CH_2CH_3$), 1.18 (m, 2H, $S(CH_2)_7CH_2CH_2CH_3$), 0.81 (3H, broad, $S(CH_2)_9CH_3$). ^{13}C NMR ($CDCl_3$, 77.5 MHz): δ= 32.14 ($S(CH_2)_7CH_2CH_2CH_3$), 29.55 (SCH_2-), 28.9-30.5 ($SCH_2(CH_2)_6CH_2CH_2CH_3$), 22.92 $S(CH_2)_8CH_2CH_3$), 14.3 $S(CH_2)_9CH_3$). IR (ATR): 2957, 2917, 2848, 2873, 1466, 1377, 1260, 799, 720 cm^{-1}. E.A. Calcd. For $C_{20}H_{42}PdS_2$: C, 53.02; H, 9.34; S, 14.15%; found: C, 53.11, H, 9.02, S, 13.65%.

2. Figures

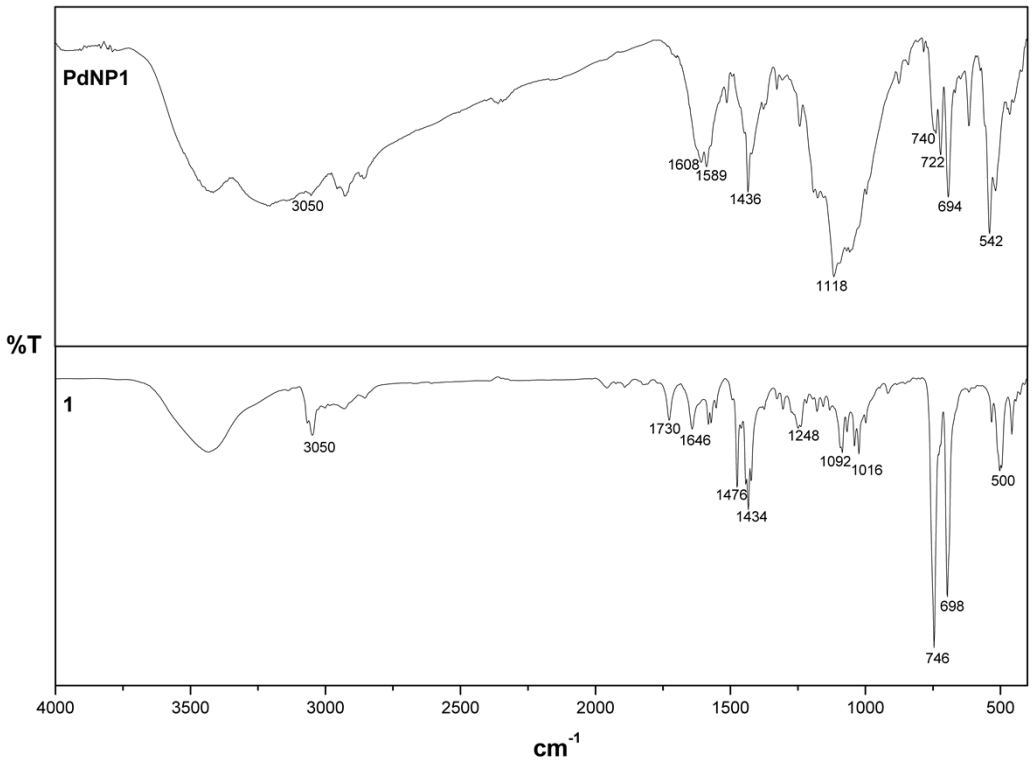

Fig. S1 IR spectra (recorded on KBr pellets) of **PdNP1** (top) and ligand **1** (bottom).

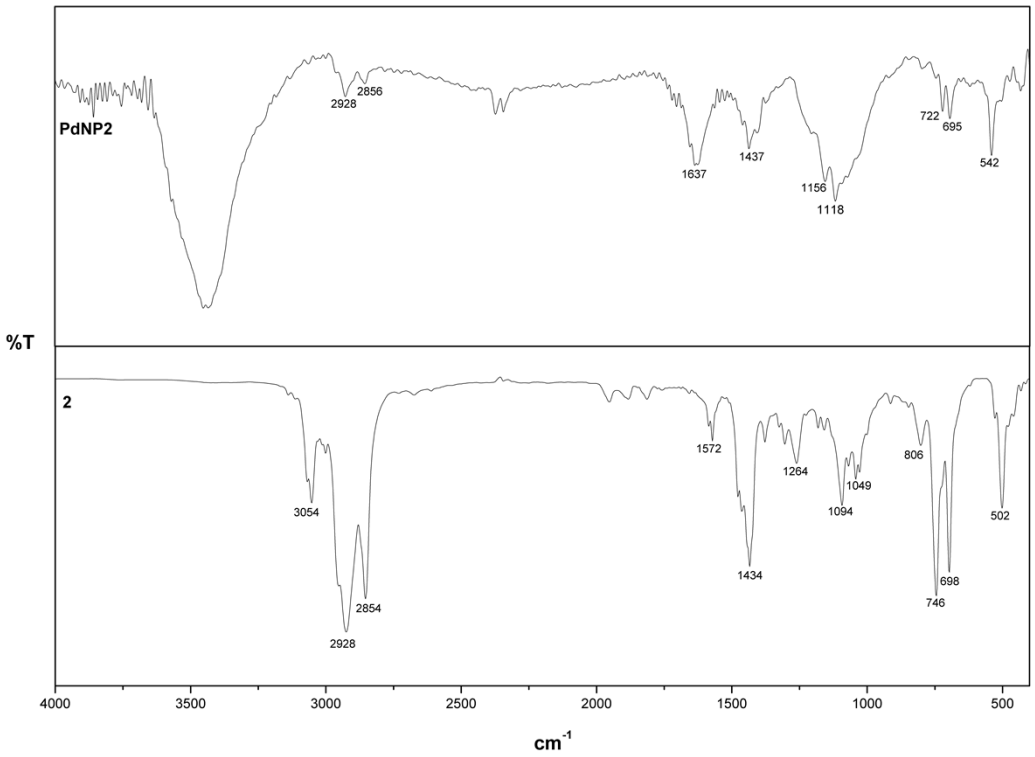

Fig. S2 IR spectra (recorded on KBr pellets) of **PdNP2** (top) and ligand **2** (bottom).

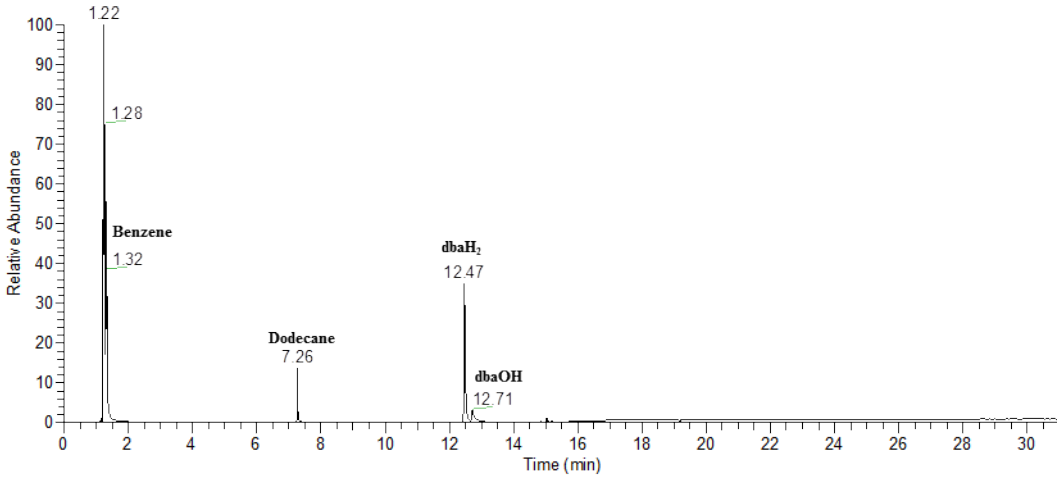

Fig. S3 GC-MS analysis of organic phase for the formation of **PdNP1** (dodecane used as internal standard).

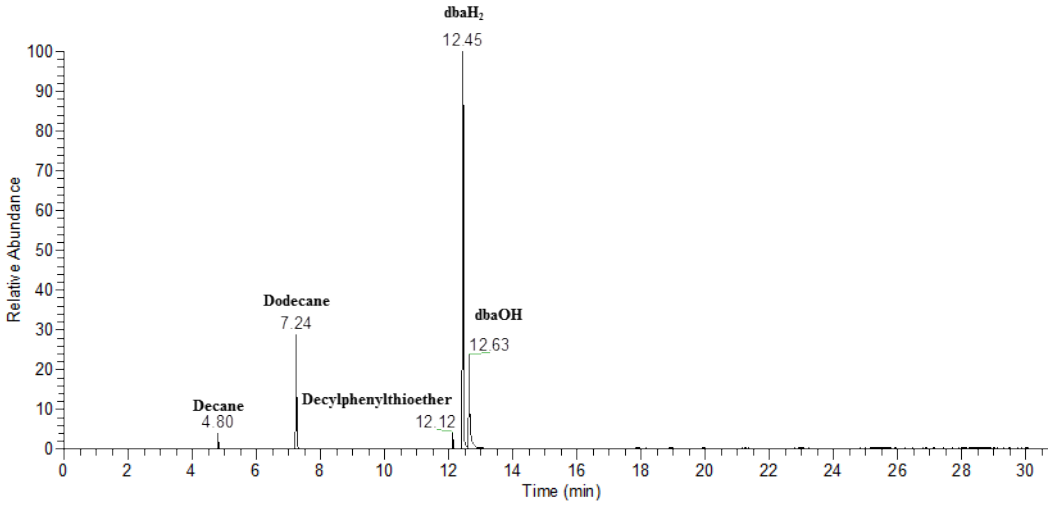

Fig. S4 GC-MS analysis of organic phase for the formation of **PdNP2** (dodecane used as internal standard).

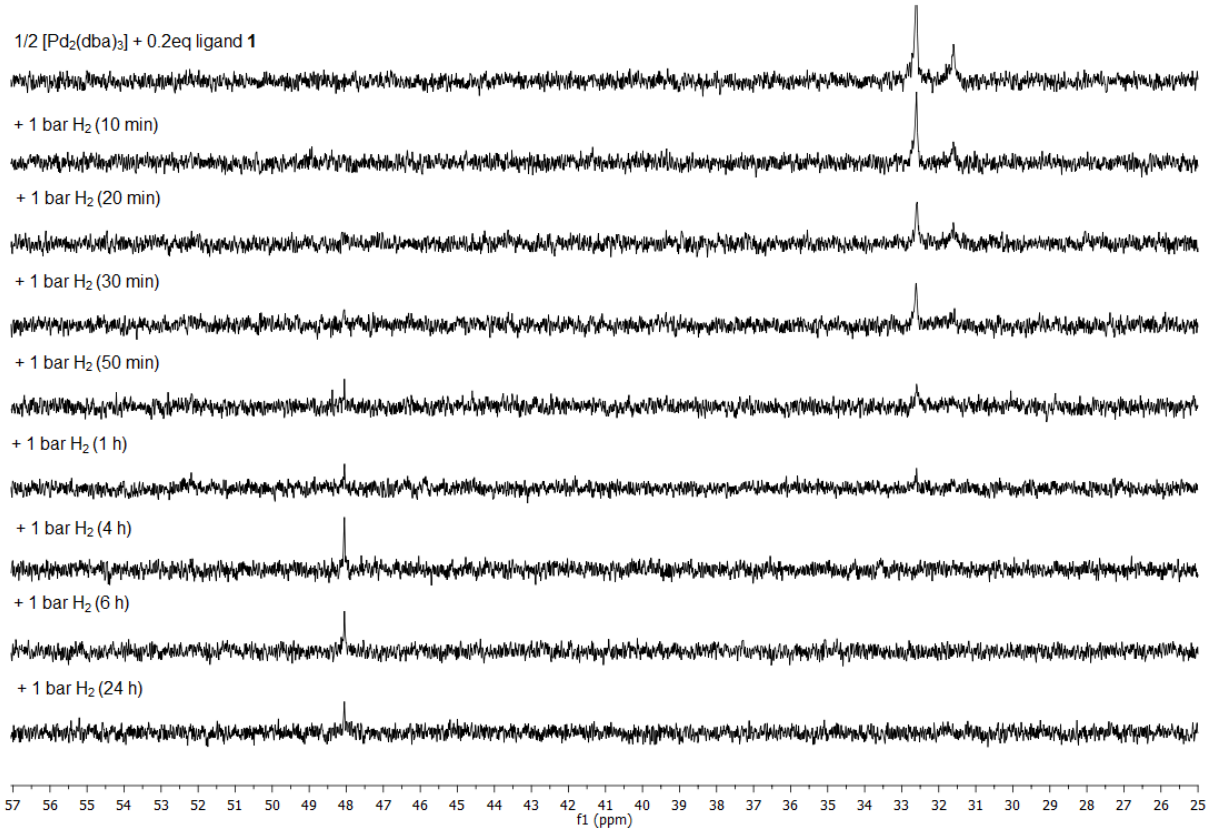

Fig. S5 Formation of **PdNP1** monitored by ^{31}P NMR.

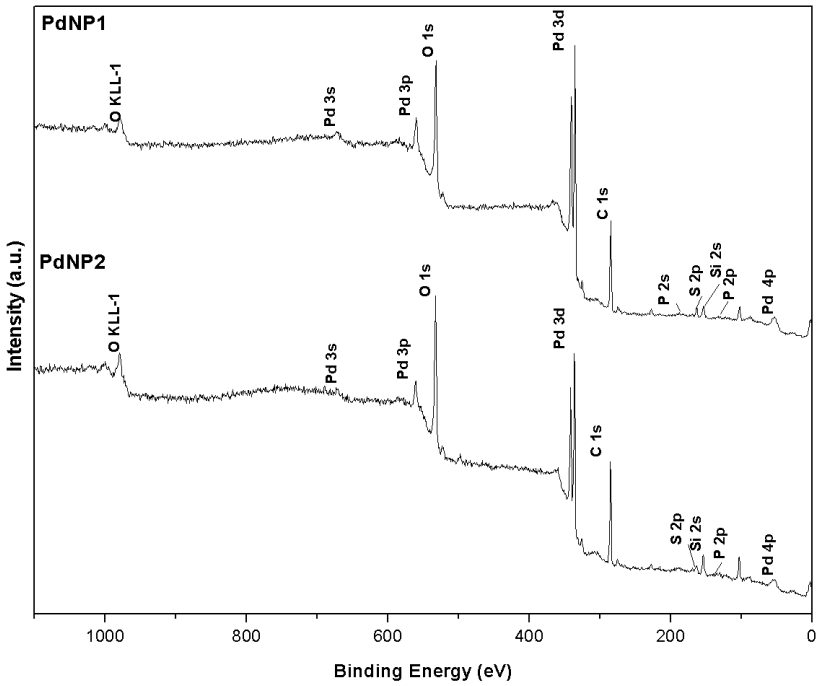

Fig. S6 XPS survey spectra for **PdNP1** and **PdNP2.**

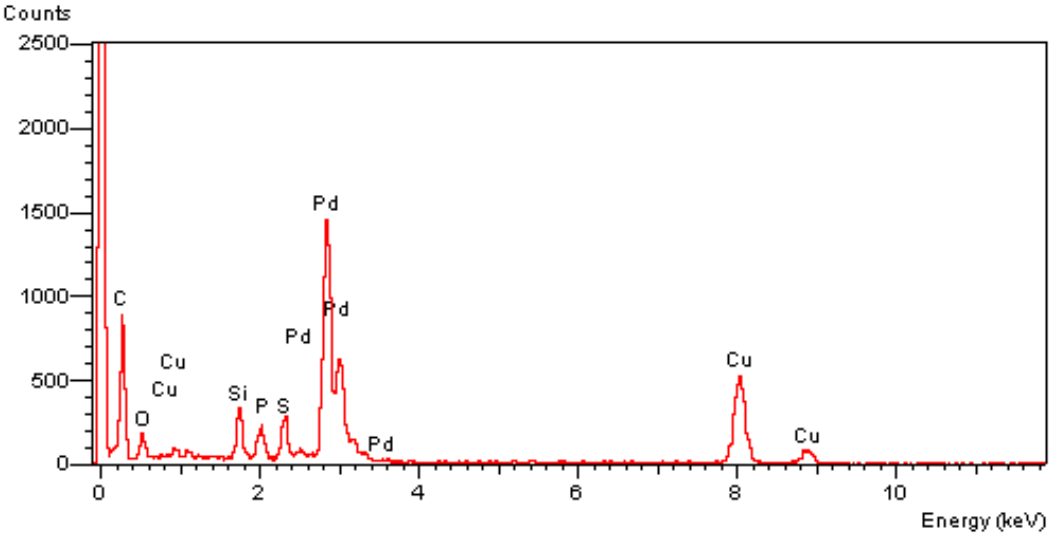

Fig. S7 EDX spectrum for **PdNP1.**

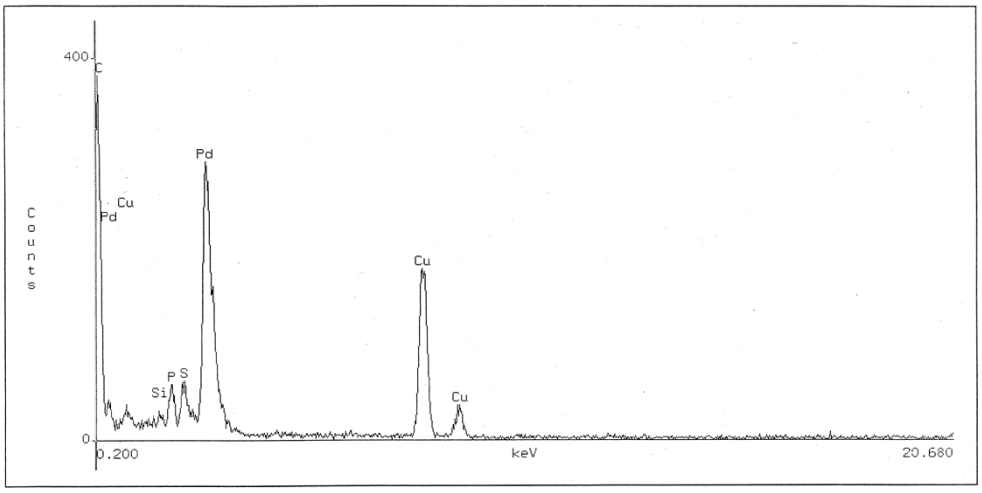

Fig. S8 EDX spectrum for **PdNP2.**

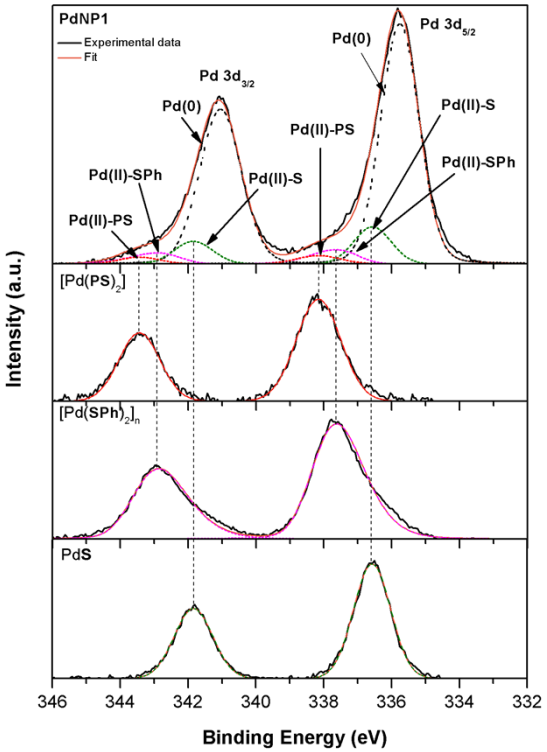

Fig. S9 High-resolution XPS spectra of Pd 3d for **PdNP1**, $[Pd(PS)_2]$, $[Pd(SPh)_2]_n$ and PdS.

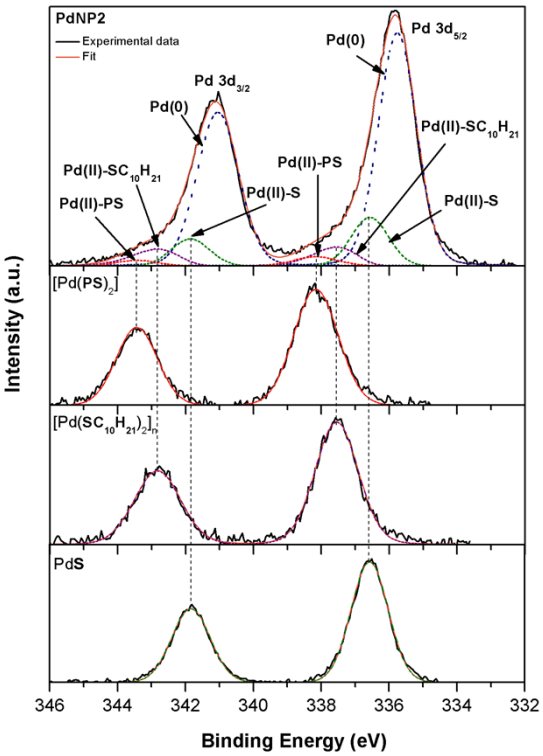

Fig. S10 High-resolution XPS spectra of Pd 3d for **PdNP2**, $[Pd(PS)_2]$, $[Pd(SC_{10}H_{21})_2]_n$ and PdS.

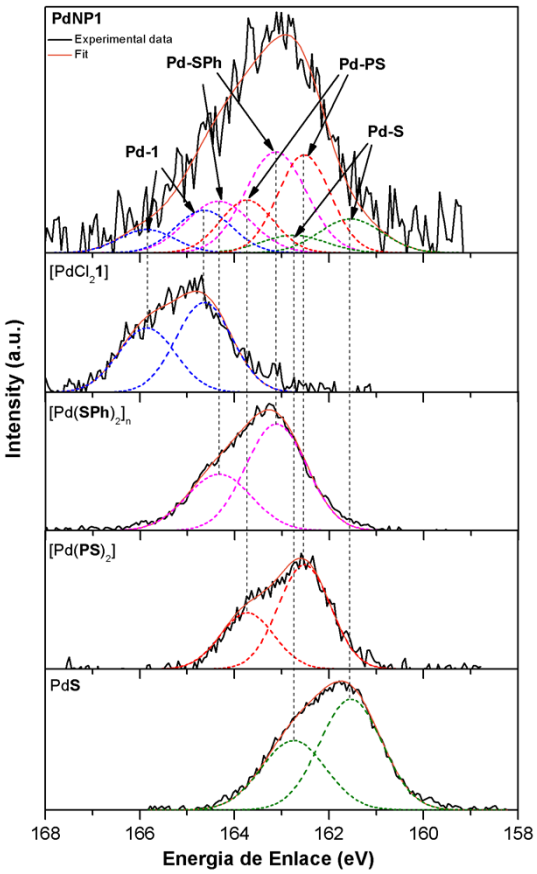

Fig. S11 High-resolution XPS spectra of S $2p_{3/2}$ for **PdNP1**, $[PdCl_2\mathbf{1}]$, $[Pd(PS)_2]$, $[Pd(SPh)_2]_n$ and PdS.

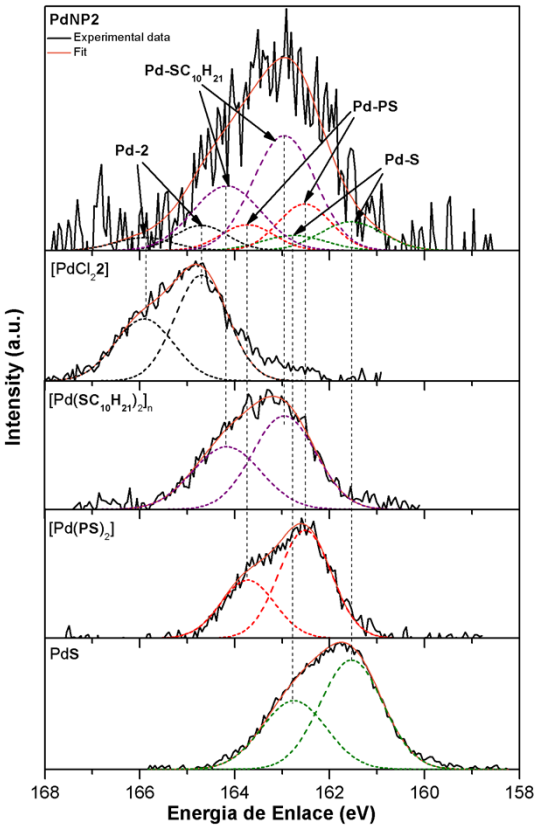

Fig. S12 High-resolution XPS spectra of S $2p_{3/2}$ for **PdNP2**, [$PdCl_2$**2**], [$Pd(PS)_2$], [$Pd(SC_{10}H_{21})_2]_n$ and PdS.

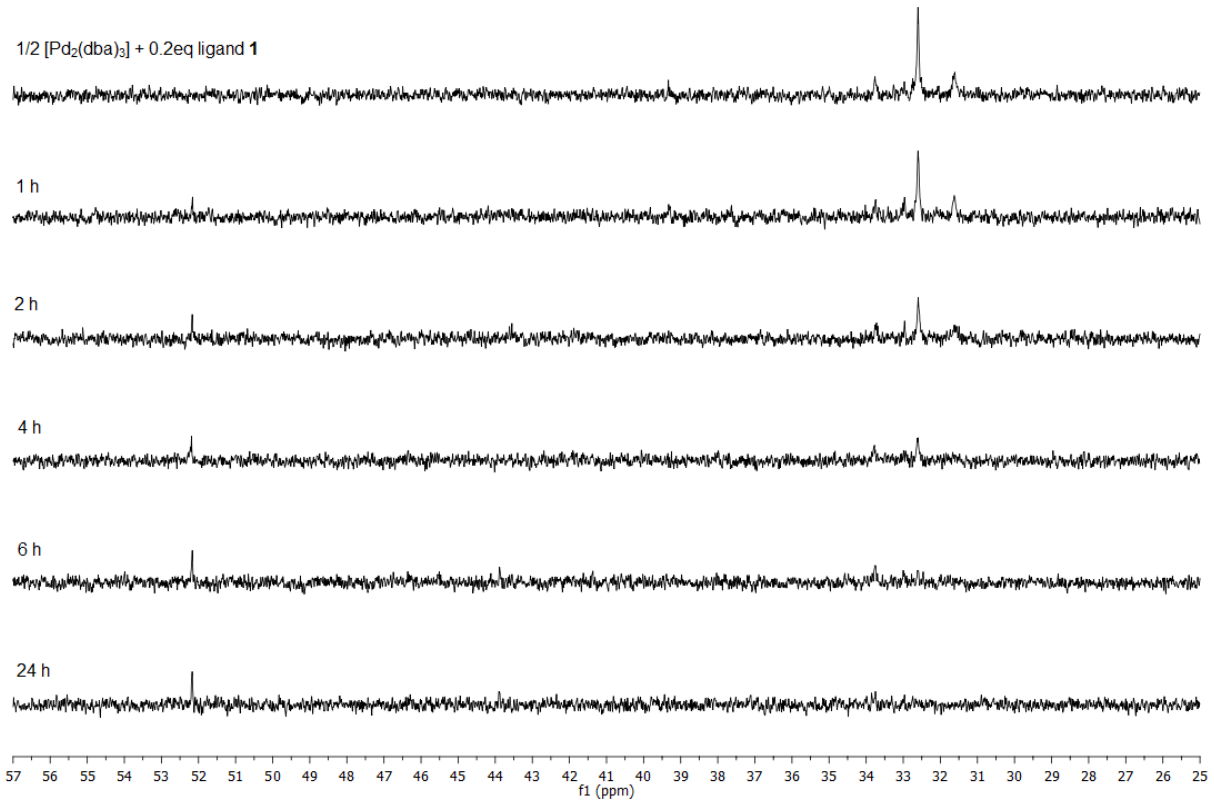

Fig. S13 Reaction between [$Pd_2(dba)_3$] and **1** (ratio Pd:L of 1:0.2) in the absence of H_2 monitored by ^{31}P NMR.

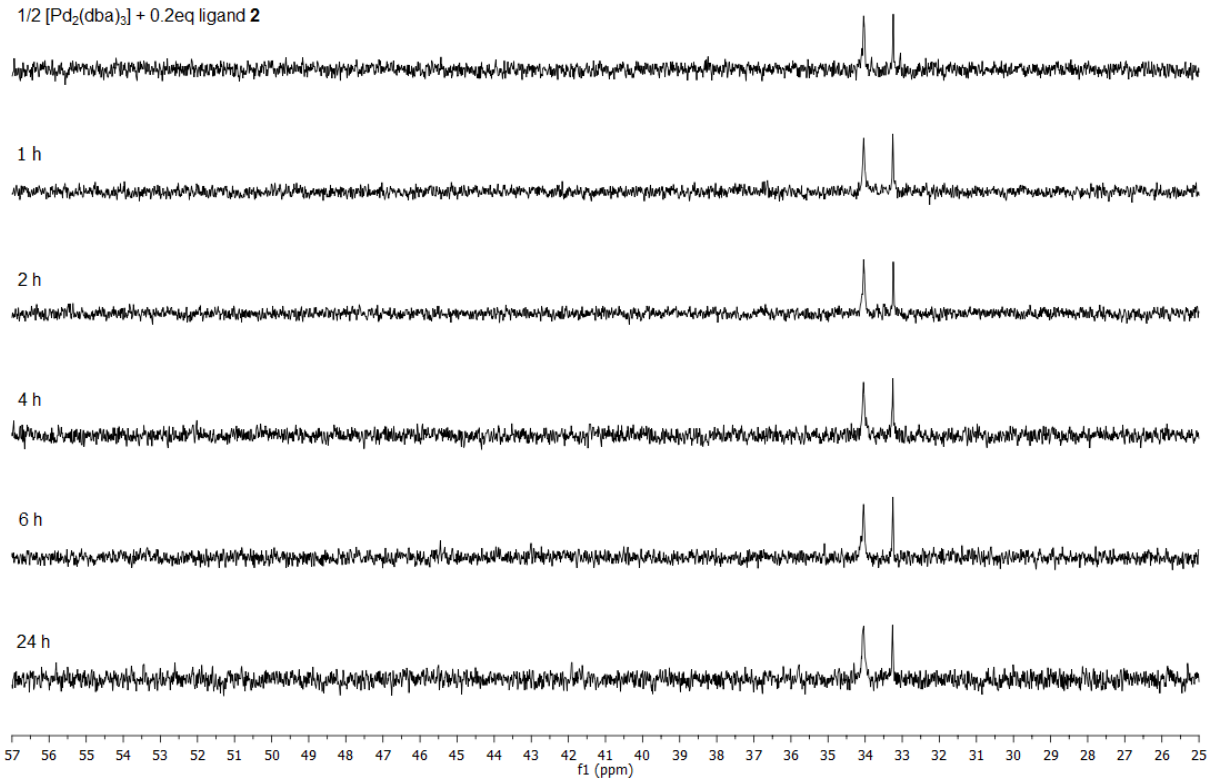

Fig. S14 Reaction between $[Pd_2(dba)_3]$ and **2** (ratio Pd:L of 1:0.2) in the absence of H_2monitored by ^{31}P NMR.

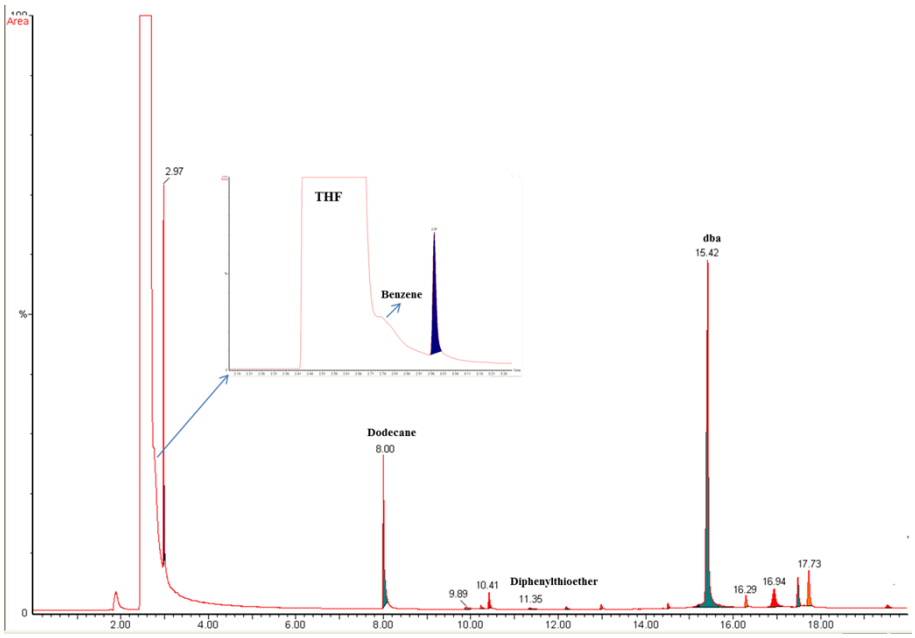

Fig. S15 GC-MS analysis of reaction between $[Pd_2(dba)_3]$ and **1** (ratio Pd:L of 1:0.2) in the absence of H_2.

3. Tables

Table S1. Binding energy values for Pd 3d.

Asignation	**PdNP1** Pd 3d (BE, eV)		**PdNP2** Pd 3d (BE, eV)		**PdNP@BMI·PF_6**[2] Pd 3d (BE, eV)
	5/2	3/2	5/2	3/2	5/2
Pd(0); Pd(0)-**L**	335.76	341.05	335.76	341.05	335
Pd(0)-**PPh_3**[3]	335.3	340.6	335.3	340.6	
Pd(II)-**PS**	338.16	343.44	338.16	343.44	
Pd(II)-**SR**	337.65	342.93	337.55	342.83	
Pd(II)-**S**	336.57	341.85	336.57	341.85	
Pd-F	-	-	-	-	336.7

Table S2. Binding energy values for S 2p.

Assignation	**PdNPs1** S 2p (BE, eV)		**PdNPs2** S 2p (BE, eV)		**PdNP@SC_{12}**[4] S 2p (BE, eV)
	3/2	1/2	3/2	1/2	3/2
Pd-**L**	164.64	165.85	164.70	165.91	
Pd-**PS**	162.52	163.73	162.52	163.73	
Pd-**SR**	163.12	164.33	162.95	164.16	162.9
Pd-**S**	161.54	162.75	161.54	162.75	162.8

References

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3. X. Feng, Z. Zhao, F. Yang, T. Jin, Y. Ma, MBao *J. Organomet. Chem.,* 2011, **696**, 1479.
4. G. Corthey, A. A. Rubert, A. L. Picone, G. Casillas, L. J. Giovanetti, J. M. Ramallo-López, E. Zelaya, G. A. Benitez, R. G. Requejo, M. José-Yacamán, R. C. Salvarezza and M. H. Fonticelli, *J. Phys. Chem. C,* 2012, **116,** 9830