

Palladium catalysed hydrogenation: detection of palladium hydrides, a joint study using parahydrogen enhanced NMR spectroscopy and density functional theory.

Joaquín López-Serrano, Simon B. Duckett* and Agustí Lledós ^a

Department of Chemistry, University of York, Heslington, YO10 5DD, York, United Kingdom.

^a Departament de Química, Universitat Autònoma de Barcelona, 08193 Barcelona, Spain.

Supporting Information

Experimental Section

General Conditions. All manipulations were carried out under inert atmosphere conditions, using standard Schlenk techniques (with vacuum of up to 10^{-2} mbar, with N₂ or Ar as an inert atmosphere) or high vacuum techniques (10^{-4} mbar). Dry N₂ and Ar for Schlenk lines was purchased from BOC Gases. Storage and manipulation of samples was carried out using standard glove box techniques, under an atmosphere of N₂, using an Alvic Scientific Gas Shield glove box, equipped with a freezer (-32 °C), vacuum pump and N₂ purge facilities. Solvents were obtained as Analytical Grade from Fisher. Diethyl ether was dried by refluxing under nitrogen over sodium wire, dichloromethane and methanol by refluxing over calcium hydride. Deuterated solvents (d_4 -MeOD and CD₂Cl₂) were purchased from Aldrich, degassed and used without further purification. Pd(PhCN)₂Cl₂ was prepared as described in the literature¹ (PdCl₂ was purchased from Johnson Matthey, and PhCN from Lancaster). PEt₃ and AgOTf were obtained from Strem and Aldrich respectively and used as received.

Syntheses of the complexes described in this paper were carried out using modified literature procedures.²

NMR spectra were obtained on Bruker DRX 400 and Bruker DSX 700 spectrometers. Samples were prepared using NMR tubes fitted with Young's taps and solvents were transferred using high vacuum techniques or in globe box and then degassed prior to addition of *p*-H₂.

Synthesis of *cis*-[Pd(PEt₃)₂(Cl)₂]. A solution of [Pd(NCPh)₂(Cl)₂] (400 mg, 1.04 mmol) in CH₂Cl₂ (10 mL) was added another dichloromethane (5 mL) solution of PEt₃ (310 µL, 2.6 mmol). The pale yellow solution was stirred for 2h and then concentrated to ca. 1 mL. Diethyl ether addition (10 mL) caused the formation of a precipitate, the mixture was cooled in an ice bath to complete the precipitation. The solid was collected by filtration, washed with cold diethyl ether (3x2 mL) and

dried in vacuo to give the title complex as a pale yellow powder. Yield: 275 mg, 64 %. ^1H NMR (400 MHz, CDCl_3): δ 2.03-1.94 (m, 12 H, CH_2), 1.21-1.06 (m, 18 H, CH_3). $^{31}\text{P}\{\text{H}\}$ (161 MHz, CDCl_3): δ 14.86 (s, PEt₃). The spectroscopic data obtained for this complex matches that reported in the literature.²

Synthesis of *cis*-[Pd(PEt₃)₂(OTf)₂] (1). To a solution of *trans*-[Pd(PEt₃)₂(Cl)₂] (200 mg, 0.48 mmol) in CH_2Cl_2 (10 mL) was added AgOTf (274 mg, 1.06 mmol). The reaction mixture was stirred for 18 h with the exclusion of light. The resulting suspension was filtered; the solution concentrated to ca. 2 mL and n-pentane (10 mL) added to precipitate the product which was collected, washed with n-pentane and dried in vacuo. Yield: 270 mg, 88 %. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.06-1.98 (m, 12 H, CH_2), 1.38-1.29 (m, 18 H, CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 17.50-17.00 (m, CH_2), 8.52 (s, CH). $^{31}\text{P}\{\text{H}\}$ NMR (161 MHz, CD_2Cl_2): δ 48.08 (s). The spectroscopic data obtained for this complex matches that reported in the literature.²

GC/MS data studies were performed on a Varian SATURN GC/MS 2000 gas chromatograph coupled to a mass spectrometer detector. A Factor-FormTM VF-6mg capillary column (30 m x 0.25 mm ID and 0.25 μm film thickness) was used for GC separation. The initial oven temperature was 100 °C, the temperature was then raised from 100 to 145 °C at 2.5 K/min, and from there to 250 °C at 30 K/min, with the maximum temperature being held for 50 min. Helium was used as the carrier gas (flow rate 1.0 mL/min). Mass spectra were recorded in the EI mode (70 eV) on the 30-650 *m/z* range.

For the GC/MS measurements, a dichloromethane or methanol solution (1 mL) of the palladium complex (ca. 3 mg) and diphenylacetylene (ca. 40 fold excess, 22 mg) was degassed and placed under a H₂ atmosphere (4 atm). The mixture was heated at 37 °C, and the reaction monitored after 1h (the sample was shaken every 15 min to mimic the NMR conditions).

In order to obtain a relative response factor for the different species formed in this reaction, a control sample containing known amounts of diphenylacetylene, *cis*-stilbene, *trans*-stilbene and 1,2-diphenylethane in CH_2Cl_2 was analysed.

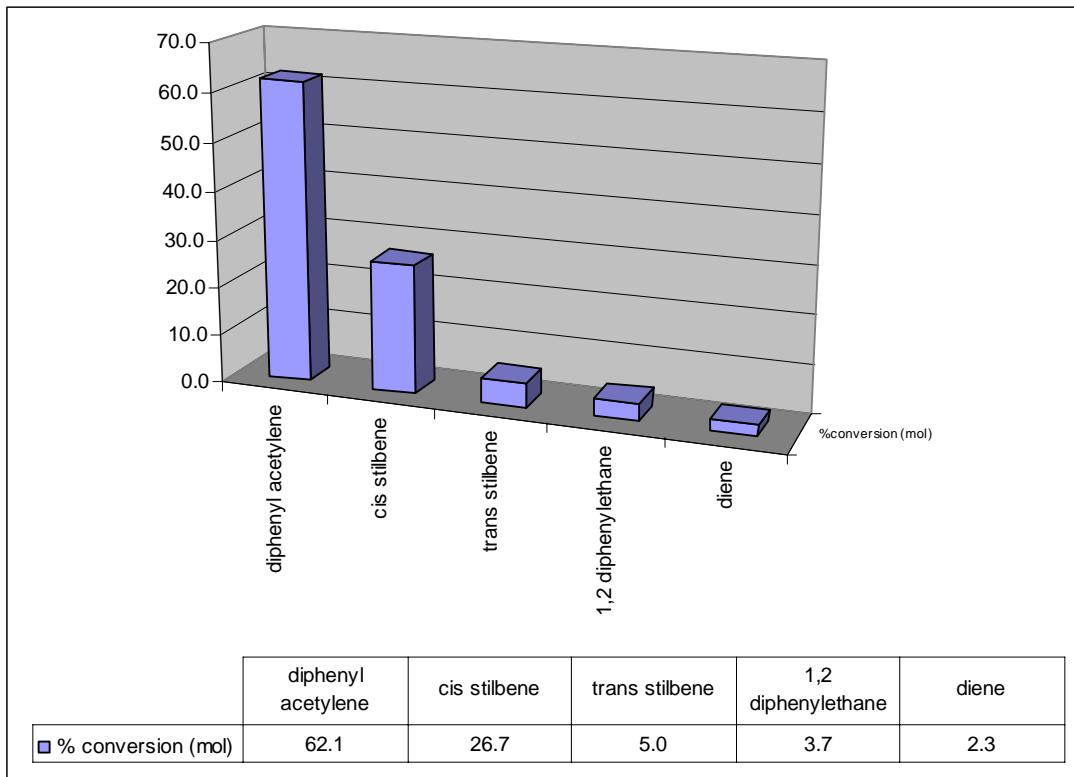
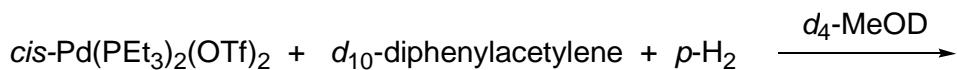


Figure S1. Conversion (% in moles) from diphenylacetylene to the different reaction products after 1h at 37 °C in methanol.



Species	^1H δ , assign (multiplicity), J	^{31}P	^{13}C
2	4.47, CHPh , $J_{\text{HH}} = 10$ Hz, $J_{\text{HP}} = 6.5$ Hz, $J_{\text{HC}} = 78.6$ Hz, $J_{\text{HH}} = 10$ Hz, $J_{\text{HC}} = 157$ Hz 3.22, CH_2Ph , $J_{\text{HC}} = 130$ Hz 2.99, CH_2Ph , $J_{\text{HC}} = 130$ Hz	25.90 (d), $J_{\text{PP}} = 54$ Hz 8.40 (d), $J_{\text{PP}} = 54$ Hz	67.14 (d), CH , $J_{\text{PC}} = 44$ Hz 35.30 (t), CH_2 , $J_{\text{PC}} = 15$ Hz
3	3.52, CH_2 , 3.38, CH_2 , 3.34, CH , alkyl ligand -9.18 hydride (dddad), $J_{\text{HH}} = -3.50$ Hz, $J_{\text{HP}} = 19, 71, 89$ Hz	7.64 4.63, $J_{\text{PP}} = 75$ Hz 3.41, $J_{\text{PP}} = 75$ Hz	49.70, CH_2 49.58, CH , (dd), $J_{\text{PC}} = 24, 55$ Hz
4a	6.35 -7.77 (ddad), $J_{\text{HH}} = 4$ Hz, $J_{\text{HP}} = 18, 82$ Hz	10.72 11.92	-
4b	5.35 -10.65 (tad), $J_{\text{HH}} = 4$ Hz, $J_{\text{HP}} = 15.8$ Hz	19.29	-
Cluster	-18.69 (s)	-	-

Table S1. NMR data for the species observed in the reactions of **1** with diphenylacetylene and H_2 in $d_4\text{-MeOD}$ (a = antiphase, d = doublet, t = triplet).

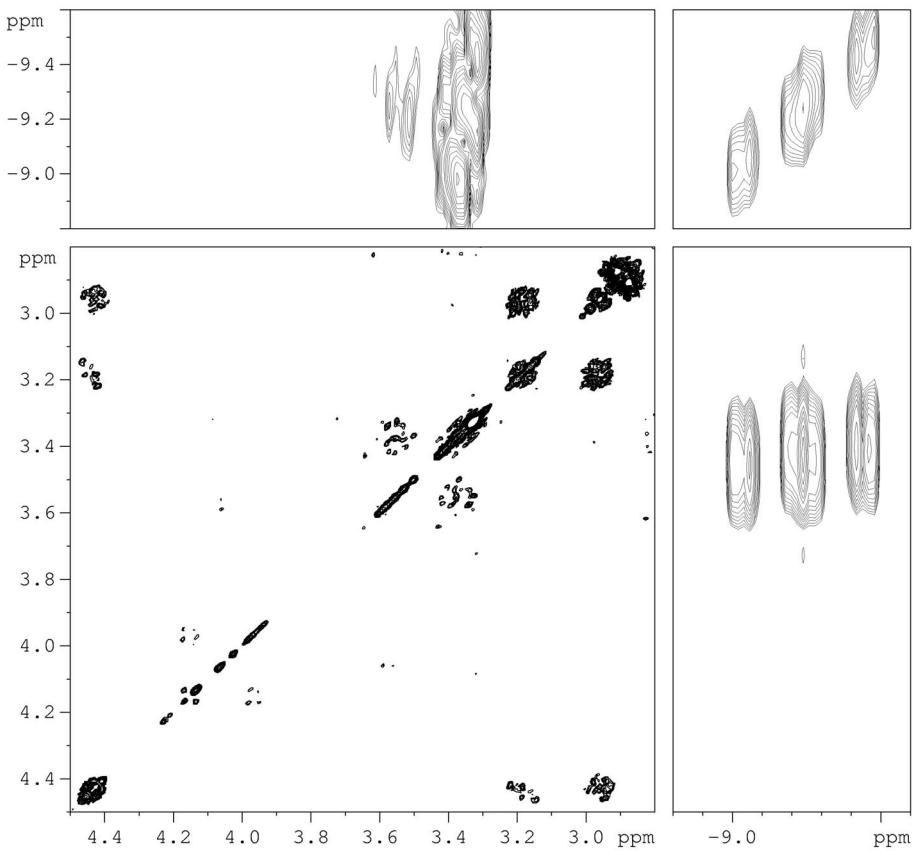
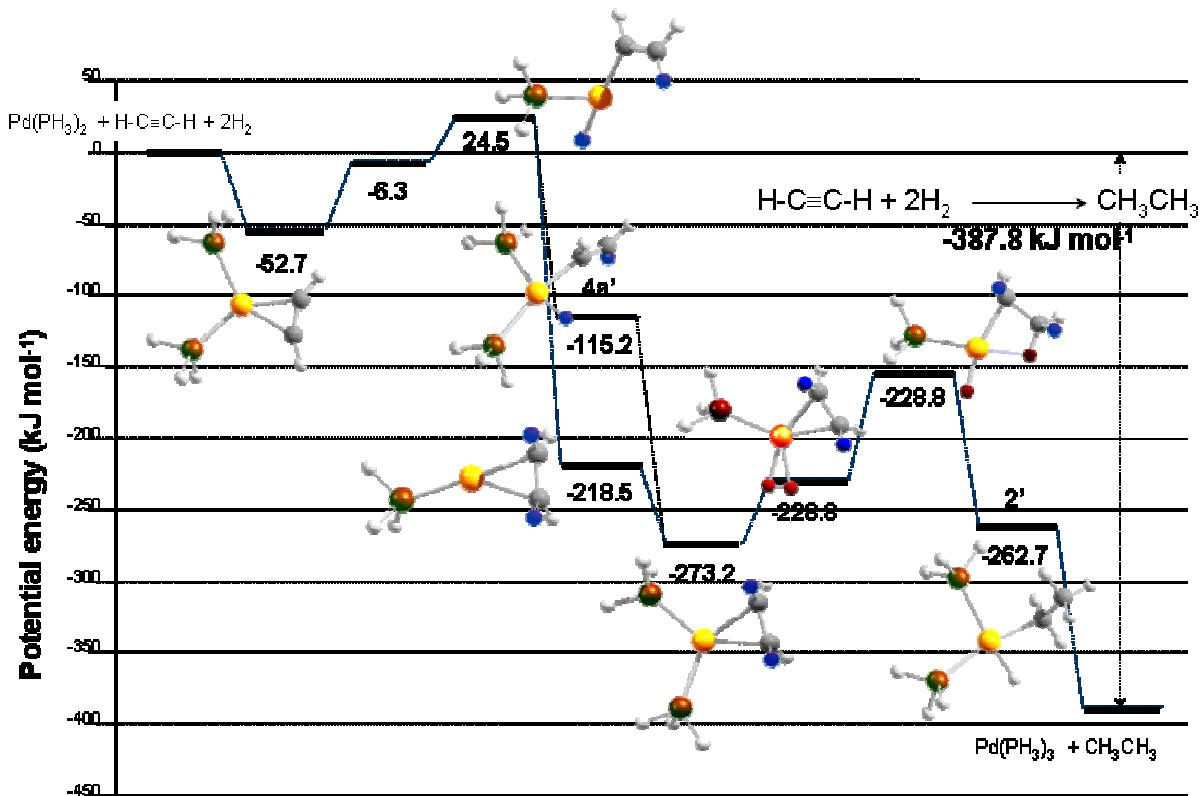


Figure S2. Combination of traces from several COSY spectra obtained during the reaction of **1** with diphenylacetylene and *p*-H₂ in *d*₄ MeOD showing cross peaks between the hydride signal of **3**, at δ -9.18, and the signals for the corresponding alkyl ligand (δ 3.34, 3.52 and 3.38). The resolution required to resolve the alkyl signals in the F2 dimension, and the relative short lifetime of the contributing signals, made it necessary to acquire separate high resolution spectra for the alkyl region. Cross peaks for the alkyl ligand of **2** (δ 4.47, 3.22 and 2.99) are shown from this spectrum.

Computational Details.

All calculations were performed using the GAUSSIAN 03 series of programs³ together with the B3LYP functional.^{4,5} An effective core potential⁶ and its associated double- ζ LANL2DZ³ basis set were used for the palladium and phosphorus atoms, and in the case of phosphorus the core potential was supplemented by a d shell.⁷ Hydride atoms and H atoms involved in hydrogenation processes were represented by means of the 6-31G(d,p) basis set, whereas for the rest of H atoms the 6-31G basis set was used. C atoms were represented by the 6-31G(d) basis set.⁸⁻¹⁰ All geometry optimisations were carried out without restrictions and in gas-phase. Stationary points located in the potential energy hypersurface were characterised as true minima through vibrational analysis.



Scheme S1. DFT based potential energy diagram (thermodynamics) for acetylene hydrogenation by a palladium bisphosphine complex. Energies for the model species are in kJ mol^{-1} and relative to $\text{Pd}(\text{PH}_3)_2 + \text{H-C}\equiv\text{C-H} + 2\text{H}_2$. Energy values therefore account for the energy contributions of the absent compounds in each case. The large energy difference between the first and last step of the cycle is a consequence of the very exothermic C-H bond formation in the hydrogenation process, the overall reaction energy for the double hydrogenation in gas phase being $-387.8 \text{ kJ mol}^{-1}$. It should also be noted that acetylene exchange in $\text{Pd}(\text{PH}_3)_2(\text{CH}_2=\text{CH}_2)$ to give $\text{Pd}(\text{PH}_3)_2(\text{H-C}\equiv\text{C-H})$ and ethene is favourable by 4.1 kJ mol^{-1} . This would therefore explain why the main compound of the experimental reaction is the semihydrogenation product *cis* stilbene.

Literature

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Tables of the optimized geometries (Cartesian coordinates, in Angstroms) for the calculated species.

Energies (in Hartrees) in parenthesis.

Table S2. $\text{Pd}(\text{PH}_3)_2^{2+}$

(-142.668970219)

46	0.000000000	0.720074000	0.000000000
15	1.667930000	-0.867553000	0.000000000
1	1.707062000	-1.700053000	1.143739000
1	1.707062000	-1.700053000	-1.143739000
15	-1.668094000	-0.874388000	0.000000000
1	-2.460632000	-0.634349000	1.151335000
1	-2.460632000	-0.634349000	-1.151335000
1	2.847799000	-0.076056000	0.000000000
1	-1.338193000	-2.249434000	0.000000000

Table S3. $\text{Pd}_2(\text{PH}_3)_3(\text{H})(\text{CH}_2\text{CH}_3)^{2+}$ model compound for **3**

(-357.704516688)

46	-1.506676000	0.033554000	-0.162607000
46	1.696726000	-0.157149000	0.008095000
1	-0.107097000	-0.039187000	0.651649000
15	-2.098024000	-0.380630000	1.986016000
1	-1.583193000	-1.581487000	2.522792000
1	-1.695736000	0.612273000	2.906769000
15	-3.709908000	0.137807000	-1.281647000
1	-4.508960000	-1.031361000	-1.273070000
1	-4.635924000	1.111026000	-0.833574000
1	-3.493440000	-0.488587000	2.189732000
1	-3.659482000	0.425898000	-2.669262000
15	2.409366000	2.058382000	0.100446000
1	3.705731000	2.346022000	-0.390973000
1	1.638253000	3.022450000	-0.593539000
1	2.470297000	2.635788000	1.392061000
6	3.535301000	-0.956741000	-0.531937000
1	4.246853000	-0.736027000	0.262875000
1	3.810709000	-0.547553000	-1.503007000
6	2.846611000	-2.277121000	-0.502024000
1	2.797294000	-2.763400000	-1.478865000
1	3.223938000	-2.946261000	0.274542000
1	1.735464000	-2.164425000	-0.219003000

Table S4. Pd(PH₃)₂ (-143.409892733)

46	0.000000000	0.001853000	0.000000000
15	2.312551000	0.062381000	0.000000000
1	3.066879000	-0.529179000	1.056335000
1	3.066879000	-0.529179000	-1.056335000
15	-2.312602000	-0.066515000	0.000000000
1	-3.069848000	0.521505000	1.056234000
1	-3.069848000	0.521505000	-1.056234000
1	3.022396000	1.299699000	0.000000000
1	-3.015701000	-1.307584000	0.000000000

Table S5. Pd(PH₃)₂(H)₂ (-144.572440541)

46	0.000000000	0.623541000	0.000000000
1	0.851030000	1.943349000	0.000000000
1	-0.932480000	1.891350000	0.000000000
15	-1.924022000	-0.846617000	0.000000000
15	1.935108000	-0.828392000	0.000000000
1	2.176125000	-1.753476000	1.058526000
1	3.236001000	-0.255233000	0.000000000
1	2.176125000	-1.753476000	-1.058526000
1	-2.857411000	-0.677595000	1.060412000
1	-1.958271000	-2.275072000	0.000000000
1	-2.857411000	-0.677595000	-1.060412000

Table S6. Pd(PH₃)₂(η²-HC≡CH) (-220.757805970)

46	0.000053000	0.251979000	-0.000163000
15	1.912136000	-1.166951000	0.000034000
15	-1.913465000	-1.164913000	0.000067000
6	0.631003000	2.280450000	0.000229000
6	-0.627836000	2.281534000	0.000179000
1	-1.585928000	2.766310000	0.000162000
1	1.589755000	2.763942000	0.000314000
1	-2.876135000	-1.076928000	-1.050426000
1	-2.870753000	-1.082944000	1.055951000
1	-1.858638000	-2.593642000	-0.004176000
1	1.855749000	-2.595625000	-0.003444000
1	2.869644000	-1.085475000	1.055755000
1	2.874812000	-1.080619000	-1.050597000

Table S7. Pd(PH₃)₂(η²-HC≡CH)

(-213.615375651)

46	0.239735000	-0.322842000	-0.000046000
15	-2.036267000	0.356525000	0.000013000
6	2.273745000	0.315250000	0.000154000
6	1.544589000	1.337128000	-0.000046000
1	1.349064000	2.392237000	-0.000179000
1	3.209628000	-0.209034000	0.000342000
1	-2.369692000	1.742787000	-0.001859000
1	-2.931953000	0.009173000	1.055812000
1	-2.933929000	0.005897000	-1.053028000
1	0.537746000	-2.187589000	0.000150000
1	-0.254689000	-2.164867000	0.000039000

Table S8. Pd(PH₃)(H)(CH=CH₂)

(-213.603649422)

46	0.015430000	-0.560851000	-0.018696000
15	-1.699796000	0.811709000	0.057399000
6	2.570300000	0.810037000	0.389681000
6	1.585162000	0.668873000	-0.510012000
1	1.755769000	1.031362000	-1.528156000
1	3.560713000	1.195113000	0.131288000
1	-1.574036000	2.190902000	-0.269733000
1	-2.353668000	0.939677000	1.308569000
1	-2.815258000	0.491756000	-0.756382000
1	2.446699000	0.536379000	1.439231000
1	-1.165855000	-1.635155000	0.396195000

Table S9. cis-Pd(PH₃)₂(H)(CH=CH₂) model compound for 4a

(-221.960167598)

46	0.103786000	-0.350795000	-0.097924000
1	0.328227000	-1.905520000	-0.168364000
15	2.477828000	-0.109170000	0.164108000
1	3.305781000	-0.653077000	-0.857081000
1	3.210118000	1.106550000	0.327048000
1	3.083199000	-0.800693000	1.249911000
15	-0.824536000	1.906602000	-0.013456000
1	-1.634902000	2.291566000	-1.116498000
1	-1.806255000	2.107644000	0.994804000
1	-0.159899000	3.162973000	0.142421000
6	-1.806226000	-1.026578000	-0.366562000
1	-2.042800000	-1.355157000	-1.380331000
6	-2.771675000	-1.069867000	0.557084000

1	-3.781267000	-1.405076000	0.312049000
1	-2.608316000	-0.795428000	1.597638000

Table S10. *trans-Pd(PH₃)₂(H)(CH=CH₂)* model compound for **4b** (-221.952364364)

46	0.090866000	-0.385571000	0.014754000
15	-2.198263000	-0.646174000	-0.016449000
1	-2.901974000	-0.358960000	1.183060000
1	-2.914460000	0.219907000	-0.883929000
1	-2.855580000	-1.863957000	-0.344721000
6	-0.265910000	1.642977000	0.488056000
1	-0.021172000	1.953885000	1.510255000
6	-0.734043000	2.592680000	-0.331979000
1	-0.8611151000	3.631656000	-0.017529000
1	-1.006667000	2.389737000	-1.368485000
1	0.354048000	-1.956030000	-0.347145000
15	2.384772000	-0.123207000	-0.050237000
1	3.243798000	-1.105588000	0.510793000
1	2.964007000	-0.077203000	-1.346535000
1	3.021390000	1.029599000	0.489386000

Table S11. *Pd(PH₃)(η²-H₂C=CH₂)* (-213.696293782)

46	0.119933000	-0.121050000	0.002862000
1	2.509850000	-1.013513000	-0.933022000
15	-2.180673000	0.115314000	-0.002660000
1	-3.017889000	-1.040277000	-0.038378000
1	-2.877602000	0.754608000	1.065077000
1	-2.860856000	0.807544000	-1.047784000
6	2.314038000	-0.478299000	-0.007286000
1	2.517567000	-1.019656000	0.913190000
6	2.121598000	0.883986000	-0.001435000
1	2.158297000	1.454126000	0.922688000
1	2.149981000	1.461623000	-0.921212000

Table S12. *Pd(PH₃)₂(η²-H₂C=CH₂)* (-222.020415899)

46	0.006637000	0.175936000	-0.006749000
15	1.827571000	-1.349463000	0.000676000
15	-2.046791000	-1.015420000	0.000863000
6	0.922029000	2.201411000	0.007736000
6	-0.461271000	2.345746000	0.006518000
1	-0.995811000	2.569800000	-0.912654000

1	1.489507000	2.304842000	0.928682000
1	-0.997373000	2.563551000	0.926306000
1	1.492617000	2.311055000	-0.910526000
1	-3.320102000	-0.420015000	-0.260987000
1	-2.472047000	-1.676792000	1.193990000
1	-2.273775000	-2.144375000	-0.846587000
1	1.737214000	-2.752772000	-0.263947000
1	2.961036000	-1.149818000	-0.846122000
1	2.597170000	-1.508258000	1.193676000

Table S13. Pd(PH₃)(H)₂(η²-H₂C=CH₂)

(-214.878756177)

46	-0.172943000	-0.360422000	0.000011000
15	2.070838000	0.392335000	-0.000009000
6	-2.308196000	0.228064000	-0.000055000
6	-1.525201000	1.376533000	0.000026000
1	-1.350360000	1.929280000	-0.919115000
1	-2.754499000	-0.139663000	0.920001000
1	2.389977000	1.783331000	-0.001256000
1	2.976643000	0.057200000	-1.052114000
1	2.976027000	0.059229000	1.053264000
1	-0.518332000	-2.212436000	0.000131000
1	0.278598000	-2.199782000	-0.000146000
1	-2.754433000	-0.139574000	-0.920177000
1	-1.350448000	1.929201000	0.919230000

Table S14. Pd(PH₃)(H)(CH₂CH₃)

(-214.849969001)

46	-0.102347000	-0.382137000	-0.000001000
15	1.997814000	0.408311000	0.000004000
6	-2.411435000	0.153562000	-0.000004000
6	-1.443987000	1.278869000	0.000002000
1	-1.390924000	1.874440000	-0.908833000
1	-3.023947000	0.064104000	0.899660000
1	2.356519000	1.789909000	0.000010000
1	2.830773000	-0.003497000	-1.073172000
1	2.830772000	-0.003506000	1.073178000
1	-1.876067000	-0.920030000	-0.000005000
1	0.561037000	-1.880894000	-0.000007000
1	-3.023943000	0.064109000	-0.899671000
1	-1.390927000	1.874433000	0.908840000

Table S15. *cis*-Pd(PH₃)₂(H)(CH₂CH₃) model compound for **2** (-223.194977984)

46	-0.086383000	-0.337405000	-0.149491000
1	-0.236955000	-1.895485000	-0.314285000
15	-2.468400000	-0.304880000	0.232416000
1	-3.331825000	0.806605000	0.491393000
1	-3.279130000	-0.884326000	-0.783798000
15	0.501723000	2.026498000	0.010245000
1	1.858820000	2.408749000	-0.194588000
1	-0.065392000	2.991047000	-0.874051000
1	0.302029000	2.791873000	1.197491000
1	-2.951939000	-1.114348000	1.298631000
6	1.911696000	-0.893727000	-0.522334000
1	1.958858000	-1.868533000	-1.007099000
1	2.281717000	-0.153800000	-1.243304000
6	2.753373000	-0.890596000	0.754389000
1	2.746482000	0.081685000	1.262594000
1	2.394853000	-1.632188000	1.474973000
1	3.805865000	-1.128965000	0.536389000