ELECTRONIC SUPPLEMENTARY INFORMATION

Cyclic Metal(oid) Clusters Control Platinum-Catalysed Hydrosilylation Reactions: From Soluble to Zeolite and MOF Catalysts

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**Experimental Section.**

**General.**

Reagents were obtained from commercial sources and used without further purification unless otherwise indicated. Anhydrous solvents were obtained from a resin-exchanger apparatus. Reactions were performed in conventional round-bottomed flasks or sealed vials equipped with a magnetic stirrer. Most of the products have been previously described in the literature, and they are here characterized by GC-MS, $^1$H-, $^{13}$C or DEPT, and compared with the existing literature (all references provided with the compound). TLCs and flash chromatography were performed on silica and silica plates, respectively. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. $^1$H-, $^{13}$C and DEPT were recorded in a 300 MHz instrument using CDCl$_3$ as solvent unless otherwise indicated, containing TMS as internal standard. The metal content of the solids and filtrates was determined by the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) by disaggregation of the solid in aqueous acid mixture. X–ray photoelectron spectroscopy (XPS) measurements were recorded in a spectrometer using non–monochromatic Mg KR (1253.6 eV) X–ray source working at 50 W, after sticking, without sieving, the solid on a molybdenum plate with scotch tape film, followed by air drying. As an internal reference for the peak positions in the XPS spectra, the C1s peak has been set at 284.5 eV. The Fourier transform infrared (FTIR) using CO as a probe molecule was recorded on a spectrometer equipped with a homemade IR cell able to work at 77 K temperature range. Prior to CO adsorption experiments, the sample was evacuated at 298 K under vacuum ($10^{-6}$ mbar) for 1 h. Deconvolution of the IR spectra has been performed in the Origin software using Gaussian curves where the full width at half–maximum (fwhm) of the individual bands has been taken as constant. The peak areas are normalized to the sample weight. Electron microscopy studies were performed on a Jeol microscope operated at 100-200kV after impregnating a dispersion of the solid sample on a Cu grid and leaving to evaporate for, at least, 4 h.

**Procedures for the synthesis of Pt catalysts.**

$Pt/NaY$ 1 wt% was prepared by ionic exchange of a NaY zeolite. Typically, 10 g of the corresponding Y zeolite was suspended in 1 L of water and stirred for 12 h at 70 °C. A
0.01 M solution of Pt (NH₃)₄(NO₃)₂ was added at the rate of 1.5 x 10⁻⁴ mol Pt/h to give a suspension at 70 ºC with stirring. After addition of 50 mL (0.197 g of the platinum salt), the suspension was stirred for another 12 h at 70 ºC. Subsequently the support was filtered and re-suspended in 1 L of demineralized water at RT to remove nitrates, exchanged cations, and non-exchanged precursor. This procedure (filtered and washing) was repeated twice. After that, the zeolite was re-suspended in 250 mL of acetone at RT, and filtered again, and re-suspended in 250 mL of diethyl ether to improve the dry process. After filtering, the catalyst was calcined at 300 ºC for 2 h in an oven under air flow. The Pt loading of the catalysts was determined by the Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) technique after disaggregation of the solid in aqueous acid mixture, obtaining a 0.8% of platinum in the zeolite.

Pt₃/NaY 1 wt%: Pt/YNa 1 wt% was put into a 50 ml flask equipped with a septum and a balloon. CO (1 atmosphere) was introduced and the flask heated at 80 ºC during 20 hours. After that, the flask was evacuated at vacuum and a new portion of CO (1 atmosphere) was added and carbonylation was continued at 115 ºC during 50 hours. A pale purple solid was obtained.

PtCl₂/SiO₂ 1 wt% was obtained by incipient wetness impregnation of an aqueous solution of H₂PtCl₆.xH₂O over commercial SiO₂ nanopowder followed by 3 hours of drying at 100 ºC. The catalyst was calcined at 200 ºC in air for 16 hours and then at 300 ºC in air for 7 more hours.

Pt₁/MOF 52 was obtained after soaking crystals of the parent MOF Ni₂II{NiII₄[CuII₂(Me₃mpba)₂]₃} · 54H₂O (51.8 mg, 0.015 mmol) in a H₂O/CH₃OH (1:1) solution of [Pt(NH₃)₄](NO₃)₂ (5.8 mg, 0.015 mmol) for 12 hours. The process was repeated five more times to ensure the total replacement of Ni(II) cations by Pt(II) ones.

Supported Pt₁ catalyst was synthesized following the procedure in ref. 5b from the main text. In order to keep Pt₁ species in solution, Pt Karstedt’s catalyst was used in combination with TEMPO in order to avoid reduction-induced aggregation. Pt₃ species were synthesized following the procedures reported in ref. 9-11 from the main text.

Typical reaction procedures.

Typical reaction procedure for the hydrosilylation of alkynes.
Soluble Pt catalysts. A solution of the corresponding alkyne (0.5 mmol) and HSiEt₃ (0.6 mmol) in toluene (1.0 mL) was placed in a vial capped with a septum and magnetically stirred in an oil bath at 110 °C for 5 min. Then, the corresponding amount of Karstedt’s catalyst (dissolved in toluene or not) was added to the reaction mixture, together or not with 10 mol% of TEMPO, and aliquots (25 μL) were taken periodically for GC analysis after diluting with dichloromethane (1.0 mL), using n-dodecane (0.05 mmol) as an external standard. At the end of the reaction, the solvent was removed through rotary evaporation and the products were purified by flash column chromatography or preparative TLC on silica. Alternatively, 1,1,2,2-tetrachloroethane (0.5 mmol) was added to the crude as internal standard for ¹H-NMR yield quantification and the mixture was dissolved in 1 ml of CDCl₃.

Solid Pt catalysts. A solution of the corresponding alkyne (0.5 mmol) was placed in a vial containing the solid Pt-based catalyst, capped with a septum and magnetically stirred in an oil bath at 110 °C for 5 min. Then, silane (0.6 mmol) was added to the reaction mixture, and aliquots (25 μL) were taken periodically for GC analysis after diluting with dichloromethane (1.0 mL), using n-dodecane (0.05 mmol) as an external standard. At the end of the reaction, the solvent was removed through rotary evaporation and the products were purified by flash column chromatography or preparative TLC on silica. Alternatively, 1,1,2,2-tetrachloroethane (0.5 mmol) was added to the crude as internal standard for ¹H-NMR yield quantification and the mixture was dissolved in 1 ml of CDCl₃.

Typical reaction procedure for the hydrosilylation of alkenes.

Soluble Pt catalysts. A solution of the corresponding alkene (0.5 mmol), silane (0.6 mmol) and n-dodecane (0.05 mmol, internal standard) in toluene (1.0 mL) was placed in a vial capped with a septum and magnetically stirred in an oil bath at 110 °C for 5 min. Then, the corresponding amount of Pt catalyst dissolved in toluene was added to the reaction mixture, and aliquots (25 μL) were taken periodically for GC analysis after diluting with dichloromethane (1.0 mL). At the end of the reaction, the solvent was removed through rotary evaporation and the products were purified by flash column chromatography or preparative TLC on silica. Alternatively, 1,1,2,2-tetrachloroethane (0.5 mmol) was added to the crude as internal standard for ¹H-NMR yield quantification and the mixture was dissolved in 1 ml of CDCl₃.
Solid Pt catalysts. A solution of the corresponding alkene (0.5 mmol) in toluene (1.0 mL) was placed in a vial containing the solid Pt-based catalyst, capped with a septum and magnetically stirred in an oil bath at 110 °C for 5 min. Then, silane (0.6 mmol) was added to the reaction mixture, and aliquots (25 μL) were taken periodically for GC analysis after diluting with dichloromethane (1.0 mL), using n-dodecane (0.05 mmol) as an external standard. At the end of the reaction, the solvent was removed through rotary evaporation and the products were purified by flash column chromatography or preparative TLC on silica. Alternatively, 1,1,2,2-tetrachloroethane (0.5 mmol) was added to the crude as internal standard for 1H-NMR yield quantification and the mixture was dissolved in 1 ml of CDCl3.

Typical reaction procedure for the dehydrogenative hydrosilylation of alcohols.

Soluble Pt catalysts. A solution of the corresponding alcohol (0.25 mmol), silane (0.50 mmol) and n-dodecane (0.05 mmol, internal standard) in 1,4-dioxane (0.25 mL) was placed in a vial capped with a septum and magnetically stirred in an oil bath at 110 °C for 5 min. Then, the corresponding amount of Pt catalyst dissolved in 1,4-dioxane was added to the reaction mixture, and aliquots (10 μL) were taken periodically for GC analysis after diluting with dichloromethane (1.0 mL). At the end of the reaction, the solvent was removed through rotary evaporation and the products were purified by flash column chromatography or preparative TLC on silica. Alternatively, 1,1,2,2-tetrachloroethane (0.5 mmol) was added to the crude as internal standard for 1H-NMR yield quantification and the mixture was dissolved in 1 ml of CDCl3.

Solid Pt catalysts. A solution of the corresponding alcohol (0.25 mmol) in 1,4-dioxane (0.25 mL) was placed in a vial containing the solid Pt-based catalyst, capped with a septum and magnetically stirred in an oil bath at 110 °C for 5 min. Then, silane (0.50 mmol) was added to the reaction mixture, and aliquots (10 μL) were taken periodically for GC analysis after diluting with dichloromethane (1.0 mL), using n-dodecane (0.05 mmol) as an external standard. At the end of the reaction, the solvent was removed through rotary evaporation and the products were purified by flash column chromatography or preparative TLC on silica. Alternatively, 1,1,2,2-tetrachloroethane (0.5 mmol) was added to the crude as internal standard for 1H-NMR yield quantification and the mixture was dissolved in 1 ml of CDCl3.
Typical reaction procedure to obtain kinetic profiles.

The reactions were carried out following the aforementioned procedures but in larger scale (2 mmol of limiting reagent: alkyne, alkene or alcohol, respectively) inside 10 ml Biotage® microwave reaction vials sealed with a cap with septum (withstand pressures up to 30 bar) and using dodecane (0.5 mmol) as internal standard. After all the reagents were mixed with the solvent inside the vial containing the magnetic stirring bar, the vial was sealed with a cap with septum and heated at the desired temperature for 15 minutes before adding the catalyst. After the addition of the catalyst, aliquots were extracted through the septum with a Hamilton® syringe at the desired times, diluted with ethyl acetate and analysed by GC-FID.

Synthesis of para-substituted phenyldimethyl silanes.

(4-methyl)-phenyldimethyl silane (S1) and (4-bromo)-phenyldimethyl silane (S3) were prepared following reaction scheme a. 4-Bromotoluene (1.2 g, 7 mmol) was diluted with anhydrous THF (30 mL) into a 100 mL round bottom flask equipped with magnetic stirrer. n-BuLi diluted in hexanes (8.4 mmol, 1.2 eq.) was added slowly to the mixture at -78 ºC and stirred during 3 h. After this, ClMe2SiH (0.97 g, 10 mmol) was added to the mixture, taken to room temperature and stirred overnight. The same procedure was followed to obtain S3 using 1,4-dibromobenzene (3.0 g, 12.7 mmol) and the corresponding amounts of the other reagents. Products were purified by flash chromatography using silica as stationary phase and hexane as eluent.

(4-methoxy)-phenyldimethyl silane (S2) and (4-cyano)-phenyldimethyl silane (S4) were prepared following reaction scheme b. 4-Bromoanisole (1.2 mL, 10 mmol) was added to a 100 mL round bottom flask containing 30 ml of anhydrous THF, Mg turnings (290 mg, 12 mmol) and a magnetic stirrer. Two crystals of iodine were added to catalyse the reaction, which was taken to reflux for 1 hour under constant stirring and then placed into an ice bath at 0 ºC. ClMe2SiH (1.69 mL, 18.5 mmol) was added and reaction was stirred
overnight. The same procedure was followed to obtain S4 using 4-bromo benzonitrile (1.84 g, 10 mmol). Products were purified by flash chromatography using silica as stationary phase and hexane as eluent.

**Compound characterization.**

*Triethyl(1-phenylvinyl)silane 8a.* GC-MS (m/z, M+ 218.2), major peaks found: 218.2 (5%), 189.2 (79%), 161.2 (100%), 133.2 (48%), 107.2 (37%), 87.2 (20%), 59.2 (20%).

1H NMR (δ, ppm; J, Hz): 7.00-7.40 (5H, m), 5.78 (1H, d, J = 3.1), 5.48 (1H, d, J = 3.1), 0.87 (9H, m), 0.57 (6H, m). 13C NMR (δ, ppm; J, Hz): 150.5 (C), 145.5 (C), 128.8 (CH2), 128.1 (2 x CH), 126.7 (2 x CH), 126.1 (CH), 7.3 (3 x CH3), 3.3 (3 x CH2). HRMS (ESI) [M+, major peak; calculated for C14H22Si: 218.1491] found 218.1496 m/z.

*Dimethyl(phenyl)(1-phenylvinyl)silane 8b* (α + β). 1H NMR (δ, ppm; J, Hz): 7.58 – 6.97 (m, 27H), 6.86 (d, J = 19.1 Hz, 1H), 6.50 (d, J = 19.2 Hz, 1H), 5.90 (d, J = 2.9 Hz, 1H), 5.58 (d, J = 2.9 Hz, 1H), 0.54 – 0.30 (m, 10H). 13C NMR (δ, ppm; J, Hz): 153.36, 147.64, 146.49, 140.89, 140.59, 140.49, 140.16, 136.36, 136.31, 136.25, 131.44, 131.39, 131.36, 130.84, 130.55, 130.48, 130.42, 130.22, 130.18, 130.15, 130.12, 129.96, 129.43, 129.19, 128.83, 128.79, 128.71, 127.63, 0.00, -0.19.

*Phenyl(1-phenylvinyl)silane 8c* (α + β). 1H NMR (δ, ppm; J, Hz): 8.05 – 6.71 (m, 135H), 6.56 (dd, J = 19.1, 3.2 Hz, 1H), 6.42 (dt, J = 18.9, 3.2 Hz, 2H), 6.15 (d, J = 2.5 Hz, 1H), 5.74 (d, J = 2.4 Hz, 1H), 4.90 – 4.50 (m, 8H), 2.97 (s, 1H), 2.27 (s, 14H). 13C NMR (δ, ppm; J, Hz): 148.30, 136.82, 136.71, 134.54, 134.45, 132.21, 131.09, 128.84, 128.78, 128.00, 127.74, 127.61, 127.56, 127.53, 127.46, 127.26, 127.19, 127.07, 126.87, 125.94, 125.68, 125.65, 125.43, 124.27, 118.35, 76.41, 76.12, 75.98, 75.56, 20.42, 0.00.

*Triethyl(1-(o-tolyl)vinyl)silane 9.* IR (ν, cm⁻¹): 2953, 2876, 1737, 1366, 1217, 729. GC-MS (m/z, M+ 232.2), major peaks found: 232.2 (28%), 203.2 (100%), 175.2 (44%), 147.2 (45%), 115.2 (29%), 87.2 (59%), 59.2 (34%). 1H NMR (δ, ppm; J, Hz): 6.96 (4H, m), 5.60 (2H, q, J = 3.4), 2.11 (3H, s), 0.85 (9H, m), 0.54 (6H, m). 13C NMR (δ, ppm; J, Hz): 150.0 (C), 143.9 (C), 132.8 (C), 128.9 (CH), 127.9 (CH2), 126.6 (CH), 124.6 (CH), 124.1 (CH), 19.2 (CH3), 6.2 (3 x CH3), 1.5 (3 x CH2). HRMS (ESI) [M+, major peak; calculated for C15H24Si: 232.1647] found 232.1651 m/z.
(1-(2-Chlorophenyl)vinyl)triethylsilane 10.\textsuperscript{S3} GC-MS (m/z, M^• 252.1), major peaks found: 252.1 (<1%), 223.2 (100%), 195.1 (7%), 169.1 (12%), 141.1 (13%), 93.1 (7%), 59.2 (7%). \textsuperscript{1}H NMR (δ, ppm; J, Hz): 7.09 (4H, m), 5.68 (2H, dd, J = 8.6, 3.0), 0.85 (9H, m), 0.61 (6H, m). \textsuperscript{13}C NMR (δ, ppm; J, Hz): 149.4 (C), 144.4 (C), 133.0 (C), 131.6 (CH\textsubscript{2}), 129.7 (CH), 129.3 (CH), 127.0 (CH), 126.2 (CH), 7.2 (CH\textsubscript{3}), 3.5 (CH\textsubscript{2}).

(1-cyclohexylvinyl)triethylsilane \textit{11a} (α + β). \textsuperscript{1}H NMR (δ, ppm; J, Hz): 5.98 (dd, J = 18.9, 6.0 Hz, 1H), 5.48 (dd, J = 18.9, 1.5 Hz, 1H), 2.08 – 1.89 (m, 1H), 1.80 – 1.68 (m, 6H), 1.41 – 1.03 (m, 6H), 0.92 (t, J = 7.9 Hz, 9H), 0.54 (q, J = 7.9 Hz, 6H). \textsuperscript{13}C NMR (δ, ppm; J, Hz): 153.31 (CH), 120.95 (CH), 43.21 (CH), 31.52 (2 x CH\textsubscript{2}), 25.27 (2 x CH\textsubscript{2}), 25.03 (CH\textsubscript{2}), 6.35 (3 x CH\textsubscript{3}), 2.55 (3 x CH\textsubscript{2}).

(1-cyclohexylvinyl)dimethyl(phenyl)silane \textit{11b} (α + β). \textsuperscript{1}H NMR (δ, ppm; J, Hz): 7.74 – 6.90 (m, 28H), 6.00 (dd, J = 18.7, 5.9 Hz, 2H), 5.78 – 5.52 (m, 3H), 5.32 (d, J = 2.6 Hz, 1H), 1.93 (dt, J = 11.0, 3.1 Hz, 3H), 1.87 – 1.41 (m, 16H), 1.41 – 0.78 (m, 15H), 0.51 – 0.13 (m, 20H). \textsuperscript{13}C NMR (δ, ppm; J, Hz): 158.25, 157.23, 141.90, 141.28, 140.22, 136.38, 136.34, 136.22, 135.42, 132.01, 131.42, 131.18, 131.13, 130.62, 130.28, 130.24, 130.06, 130.02, 127.69, 126.68, 126.28, 79.83, 79.41, 78.98, 46.39, 45.73, 35.93, 34.74, 29.33, 28.68, 28.64, 28.44, 23.83, 2.37, 0.00, -0.02.

Benzyl(1-(3-methoxyphenyl)vinyl)dimethylsilane \textit{12}.\textsuperscript{S3} GC-MS (m/z, M^• 282.1), major peaks found: 282.1 (40%), 191.2 (100%), 165.2 (63%), 121.2 (10%), 91.2 (11%), 59.2 (7%). \textsuperscript{1}H NMR (δ, ppm; J, Hz): 6.81 (9H, m), 5.73 (1H, d, J = 2.8), 5.43 (1H, d, J = 2.8). 3.66 (3H, s), 2.08 (2H, s), 0.0 (6H, s). \textsuperscript{13}C NMR (δ, ppm; J, Hz): 159.4 (C), 151.7 (C), 146.1 (C), 139.6 (C), 129.1 (CH), 128.6 (CH\textsubscript{2}), 128.3 (2 x CH), 128.1 (2 x CH), 124.1 (CH), 119.4 (CH), 112.6 (CH), 111.8 (CH), 55.2 (CH\textsubscript{2}), 25.6 (CH\textsubscript{2}), -2.8 (2 x CH\textsubscript{3}).

\textit{Dimethyl(phenylethyl)(phenyl)silane 18}.\textsuperscript{S4} GC-MS (m/z, M^• 240.1), major peaks found: 240.1 (<1%), 225.3 (14%), 197.3 (6%), 163.3 (9%), 162.3 (56%), 136.3 (17%), 135.3 (100%), 121.3 (31%), 105.3 (12%). \textsuperscript{1}H NMR (δ, ppm; J, Hz): 7.11 (10H, m), 2.55 (2H, m), 1.04 (2H, m), 0.18 (6H, s).

\textit{Benzyl(dimethyl(phenethyl)silane 19}.\textsuperscript{S5} GC-MS (m/z, M^• 254.1), major peaks found: 254.1 (<1%), 239.2 (1%), 164.2 (15%), 163.2 (93%), 136.2 (13%), 135.2 (100%), 121.2 (14%), 91.2 (14%), 59.2 (36%). \textsuperscript{1}H NMR (δ, ppm; J, Hz): 7.13 (10H, m), 2.53 (2H, m), 2.03 (2H, s), 0.81 (2H, m) 0.01 (6H, s).
1,1,1,3,3-Pentamethyl-3-phenethylsiloxane 20. $^S^6$ $^1$H NMR ($\delta$, ppm; J, Hz): 7.11 (5H, m), 2.53 (2H, m), 0.80 (2H, m), 0.01 (9H, s), -0.05 (6H, s).

(4-Methoxyphenethyl)dimethylphenylsilane 21a. $^S^7$a GC-MS (m/z, M$^+$ 270.1), major peaks found: 270.1 (12%), 255.1 (4%), 227.2 (21%), 192.2 (69%), 167.2 (44%), 135.2 (100%), 122.2 (43%), 105.2 (10%). $^1$H NMR ($\delta$, ppm; J, Hz): 7.33 (9H, m), 3.91 (3H, s), 2.76 (2H, m), 1.30 (2H, m), 0.46 (6H, s).

(4-Bromophenethyl)dimethylphenylsilane 21b. $^S^7$b $^1$H NMR ($\delta$, ppm; J, Hz): 7.43-7.35 (d, J = 8.5, 2H), 7.25-7.17 (m, 3H), 7.07 (t, J = 7.1 Hz, 1H), 7.01-6.99 (m, 3H), 2.54 – 2.48 (m, 2H), 2.10i (s, 2H), 0.86 – 0.80 (m, 2H), -0.01 (s, 6H). $^{13}$C NMR ($\delta$, ppm; J, Hz): 143.9 (C), 140.0 (C), 131.5 (CH), 129.6 (CH), 128.4 (CH), 128.2 (CH), 124.0 (CH), 119.1 (C), 29.3(CH$_2$), 25.5(CH$_2$, 16.7(CH$_2$), -3.6 (2xCH$_3$).

$^{1}$H NMR ($\delta$, ppm; J, Hz): 7.16 (9H, m), 3.44 (2H, s), 2.50 (2H, m), 2.34 (2H, s), 0.84 (2H, m), 0.03 (6H, s).

Dimethyl(octyl)phenylsilane 24. $^S^8$ GC-MS (m/z, M$^+$ 248.2), major peaks found: 248.2 (<1%), 233.2 (6%), 170.2 (11%), 136.2 (14%), 135.2 (100%), 121.2 (26%), 105.2 (6%).

$^1$H NMR ($\delta$, ppm; J, Hz): 7.30 (5H, m), 1.17 (14H, m), 0.77 (3H, t, J = 6.7 Hz), 0.58 (6H, s).

2-(Phenylsilyl)bicycle[2.2.1]heptane 25. $^1$H NMR ($\delta$, ppm; J, Hz): 7.88 – 6.67 (m, 5H), 4.20 – 4.00 (m, 2H), 2.51 – 1.60 (m, 2H), 1.60 – 0.37 (m, 9H). $^{13}$C NMR ($\delta$, ppm; J, Hz): 135.46, 132.79, 129.48, 127.95, 38.84, 37.36, 37.31, 33.77, 33.58, 29.16, 24.22.

Dimethyl(octyloxy)phenylsilane 27. $^S^9$ GC-MS (m/z, M$^+$ 264.2), major peaks found: 264.2 (<1%), 251.2 (6%), 250.2 (23%), 249.2 (100%), 186.2 (23%), 137.2 (65%), 135.2 (36%), 121.2 (12%).

$^1$H NMR ($\delta$, ppm; J, Hz): 7.33 (5H, m), 3.47 (2H, m), 1.38 (4H, m), 1.10 (8H, m), 0.75 (3H, t, J = 5.5 Hz), 0.23 (6H, s).

Benzyldimethyl(octyloxy)silane 28. $^S^{10}$a GC-MS (m/z, M$^+$ 278.3), major peaks found: 278.3 (6%), 263.2 (2%), 189.2 (5%), 188.2 (18%), 187.3 (100%), 149.2 (19%), 121.2 (11%), 91.2 (10%), 89.2 (11%), 75.2 (51%), 69.2 (17%).

$^1$H NMR ($\delta$, ppm; J, Hz): 7.12
(2H, t, J = 7.5 Hz), 6.98 (3H, t, J = 6.7 Hz), 3.48 (2H, t, J = 6.7 Hz), 2.10 (2H, s), 1.42 (2H, m), 1.14 (10H, m), 0.81 (3H, t, J = 6.3 Hz), 0.00 (6H, m).

1,1,1,3,3-Pentamethyl-3-(octyloxy)disiloxane 29. GC-MS (m/z, M⁺ 276.1), major peaks found: 276.1 (<1%), 263.1 (5%), 262.1 (12%), 261.1 (45%), 177.1 (6%), 151.1 (8%), 150.1 (16%), 149.1 (100%), 147.1 (28%), 133.1 (31%), 71.2 (11%), 57.2 (12%), 43.2 (8%). ¹H NMR (δ, ppm; J, Hz): 3.55 (2H, t, J = 6.7 Hz), 1.44 (2H, m), 1.12 (10H, m) 0.78 (3H, t, J = 6.6 Hz), 0.00 (15H, s).

Triethyl octyl silicate 31. GC-MS (m/z, M⁺ 292.2), major peaks found: 292.2 (<1%), 247.1 (7%), 150.1 (11%), 149.1 (100%), 137.1 (77%), 135.1 (39%), 119.1 (30%), 105.1 (45%), 91.1 (24%), 69.2 (33%), 63.2 (31%). ¹H NMR (δ, ppm; J, Hz): 3.78 (6H, q, J = 7.0 Hz), 3.69 (2H, t, J = 6.6 Hz), 1.46 (2H, m), 1.15 (19H, m), 0.81 (3H, t, J = 6.7 Hz).

(Hexan-2-yloxy)diphenylsilane 32. GC-MS (m/z, M⁺ 284.2), major peaks found: 284.2 (<1%), 269.1 (3%), 227.2 (50%), 206.2 (23%), 199.2 (21%), 183.2 (100%), 181.2 (25%), 151.2 (10%), 128.1 (15%), 123.2 (47%), 105.2 (25%), 78.3 (9%).

1,1,1,3,3-Pentamethyl-3-(1-phenylethoxy)disiloxane 33. GC-MS (m/z, M⁺ 268.1), major peaks found: 269.1 (9%), 268.1 (35%), 172.2 (10%), 149.1 (44%), 133.1 (12%), 105.2 (100%), 77.2 (7%).

Benzyldimethyl(phenethoxy)silane 34. GC-MS (m/z, M⁺ 270.1), major peaks found: 270.1 (<1%), 255.2 (2%), 180.2 (17%), 179.2 (100%), 161.2 (20%), 149.2 (7%), 105.3 (27%), 99.2 (13%), 75.2 (21%).

Dimethyl(4-nitrophenoxy)phenylsilane 35. GC-MS (m/z, M⁺ 273.1), major peaks found: 274.1 (7%), 273.1 (33%), 260.1 (6%), 259.1 (22%), 258.1 (100%), 197.2 (11%), 135.2 (30%).

Dimethyl((4-methylpentan-2-yl)oxy)(phenyl)silane 36.¹H NMR (δ, ppm; J, Hz): 7.66-7.57 (2H, m), 7.44-7.36 (3H, m), 3.96-3.83 (1H, m), 1.76-1.63 (1H, m), 1.51-1.42 (1H, m), 1.25-1.15 (1H, m), 1.14 (d, 3H, J = 6.0 Hz), 0.87 (d, 3H, J = 6.6 Hz), 0.83 (d, 3H, J = 6.6 Hz), 0.36 (s, 6H). ¹³C NMR (δ, ppm; J, Hz): 138.5 (C), 133.5 (2XCH), 129.4 (CH), 127.8 (2CH), 67.2 (CH), 49.0 (CH₂), 24.6 (CH), 24.1 (CH₃), 23.1 (CH₃), 22.4 (CH₃), -1.0 (CH₃), -1.1 (CH₃).

S11
4-acetylphenyl triethyl silicate 37. $^1$H NMR ($\delta$, ppm; J, Hz): 7.89 (2H, d, J = 8.7 Hz), 6.92 (2H, d, J = 8.7 Hz), 3.96-3.72 (6H, m), 2.56 (3H, s), 1.25-1.18 (9H, m). $^{13}$C NMR ($\delta$, ppm; J, Hz): 198.0 (C), 161.4 (C), 131.1 (2xCH), 129.6 (C), 115.5 (2xCH), 59.2 (3xCH$_2$), 26.3 (CH$_3$), 17.9 (3xCH$_3$).

4-(Triethylsilyloxy)acetophenone 38. $^{1}$H NMR ($\delta$, ppm; J, Hz): 7.87 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 2.55 (s, 3H), 1.00 (t, J = 6.0 Hz, 9H), 0.77 (q, J = 6.0 Hz, 6H); $^{13}$C NMR ($\delta$, ppm; J, Hz): 198.5 (C), 161.4 (C), 131.2 (2xCH), 129.6 (C), 115.5 (2xCH), 26.3 (CH$_3$), 6.8 (3xCH$_3$), 6.4 (3xCH$_2$).

Computational details

All designed models were fully optimized at the oB97X-D theory level. We have previously shown that this approach provides reliable results for the thermochemistry and kinetics of Pt-based compounds. The def2-SVP basis set was used to describe all the atoms, except the Pt centres, where the core electrons were replaced by the effective core potentials to account for scalar relativistic effects without increasing the computational cost. For all calculations, we used an ultrafine grid for numerical density functional theory integration. The optimized structures were confirmed to be stable (real minima) or transitional state (saddle point) in the potential energy surface by analysing their vibrational modes. No imaginary frequency was obtained for the products and reactants, although a single imaginary frequency was obtained for the transitional state. In addition, relative energy curves along with the reaction were computed by monitoring the hydrosilylation phenomena. This is a relaxed potential energy scan over the oxidative addition. Because solvation might influence the reactivity of Pt compounds, environmental effects were included by using the polarizable continuum method of Tomasi and co-workers. All calculations were performed with Gaussian16.

Graphical method.

General discussion.

The graphical methodology described in the manuscript is applied, in general terms, as follows: 1) Different reactions changing one variable (T, $\sigma$, etc.) are set and followed kinetically over time. 2) Aliquots are analyzed using an appropriate experimental technique (GC, NMR, IR, etc.) to measure concentration. 3) The corresponding time-scale normalization is applied using a spreadsheet. 4) The desired value is found in an
iterative way giving different values until all kinetic profiles graphically overlay. 5) A more mathematically precise way to obtain the desired value along with the experimental error of the measurement is a) adjusting all the data, [P] vs. f to a polynomic function (depending on the case, normally 3rd grade is enough) and the values of the desired parameter are changed by iteration (for example using Solver function in Excel) until R² reach its maximum value, or b) minimizing the accumulated distance between nearest neighbors to ensure best overlay.

Calculation of the error for the graphical method for activation parameters is as follows:
1) Reaction profiles at two temperatures (X and Y) are obtained by GC or other quantitative technique (NMR, etc.). 2) Data points for each temperature are divided into two subsets (X1 and Y1). 3) Activation parameters are calculated for the entire profiles and for the four combinations of the subsets (i.e. X-Y, X1-Y1, X1-Y2, X2-Y1 and X2-Y2). 4) Weighted average of the 5 values is calculated (giving X-Y double the weight of the rest combinations) and error is calculated from the standard deviation. Error is calculated similarly for Hammett and KIE.

The concentration data for the simulated reactions shown in the figures of the manuscript have been calculated by using the theoretical rate equation for each individual kinetic profile (1st order, 2nd order, etc.) and the different kinetic rate constants have been calculated from the corresponding equation addressing the changes in temperature (Eyring-Polanyi), sigma values (Hammett) or kinetic isotopic effect (KIE), as described in the following sections. Numerical data for each simulation is provided at the end of this text.

**Simplicity and associated error.**

In traditional methodologies, every reaction at a determinate temperature gives one numeric value for rate or kinetic constant. In order to have statistically significant values for activation parameters, reactions have to be carried out at least at three different temperatures. In contrast to that, for this graphical analysis every point of the kinetic profile is a separate value that provides information for the calculation of the required value. For this reason, experiments at only two different temperatures are needed and a lower number of data points are necessary to obtain a more precise results of the desired values, i.e. activation parameters, than for initial rates methodology. In addition, for initial rates methodology, several data points are required to obtain a precise measure of the
initial rate (if possible) that minimize the transfer of uncertainty to the next step for the calculation of the values. However, in our methodology, values are obtained directly from raw concentration data, avoiding the propagation of error from the calculation of initial rates to the calculation of activation parameters.

The biggest limitation of graphical methodologies is that they do not provide a measure of the error associated to the calculated value (order of reagent or catalyst), which makes impossible a direct comparison with other methods in terms of accuracy. We can take advantage of the fact that every point of the kinetic profile is independent from the rest in order to calculate the errors. Data from the two temperatures X and Y are split into two different data sets for each temperature (X1 and X2; Y1 and Y2), as shown in Figure S9, and the activation parameters are calculated using the four possible combinations (X1-Y1, X1-Y2, X2-Y1 and X2-Y2). The correct values are obtained from the weighted average between the four subset combinations and the one calculated using the entire kinetic profiles and the standard deviation gives the measure of the uncertainty associated to the calculation.

In order to adjust the value to make the profiles overlay, three different approaches can be followed: 1) **Visual adjustment** is the simplest way to adjust the parameters for the overlay of the kinetic profiles and is good for a first approach or to give a rough estimate of the value without associated error, however, it is subjective and carries an unknown uncertainty that can jeopardize the calculation of the error. 2) **Adjustment to a polynomial equation** of the profile containing both X and Y is an alternative way to obtain the desired values. The procedure consists in changing the desired value (enthalpy, entropy, etc.) until the $R^2$ given in the adjustment of the equation is maximized. This can be done manually although is more tedious. An optimization algorithm (like Solver® in excel) can give the results much faster and with higher precision. This methodology can be very helpful, however, it is highly dependent on how well the data adjust to the polynomial equation and can produce misleading results. 3) Calculation of **Euclidean distance between consecutive points and minimization** of the summation of the distances for all the points. This methodology is based in the principle that the best overlay must minimize the distances between consecutive points. The procedure consists in the following steps:

1. Sort the data points by increasing [Product], calculating the function (f, g, etc.) for each point.
2. Normalize the X axis to reach a maximum of 1 (divide every f, g, etc. value for each point between the maximum value).

3. Calculate the Euclidean distance between each consecutive pair of data points (defined as \([(x_i - x_{i+1})^2 + (y_i - y_{i+1})^2]^{1/2}\)).

4. Calculate the summation of all the distances and change the value of the parameter (enthalpy, entropy, etc.) until finding the minimum value.

This latter method is the least biased of all three and therefore have been used throughout this work. Figure S19c shows the application of the methodology for the calculation of Hammett parameters.

**Enthalpy value.**

Eyring-Polanyi equation (Eq. 1) was used to extract the dependence of the kinetic constant with respect to temperature through activation parameters (transition state enthalpy and entropy).

\[
\text{[Eq. (1)] } \quad k(T) = \frac{k_B T}{h} e^{-\Delta S^\ddagger / R} e^{\Delta H^\ddagger / RT} 
\]

Reaction rate depends on concentration of the reagents and on the kinetic constant and therefore on reaction temperature. We can describe a function \( f \) to include the rate dependence with respect to all the parameters but kinetic constant and then integrate the inverse of this function to obtain the time dependence. Then, constant values are removed from the equation to get the normalized time-scale \( f \) that depends on time, temperature and transition state entropy. Time and temperature are known for each point of the kinetic profiles, remaining \( \Delta H^\ddagger \) as the only unknown variable that is calculated iteratively from the overlay of the kinetic profiles:

\[
-\frac{d[A]}{dt} = f([A],[B],...,k(T, \Delta H^\ddagger, \Delta S^\ddagger); k(T, \Delta H^\ddagger, \Delta S^\ddagger) = \frac{k_B T}{h} e^{-\Delta S^\ddagger / R} e^{\Delta H^\ddagger / RT}
\]

\[
\int_{[A]_0}^{[A]_t} f^{-1}([A],[B],...)d[A] = \int_0^t -kd\tau \]

\[
F^{-1}([A]_t,[A]_0,[B]_0,...) = -kt = -t \frac{k_B T}{h} e^{-\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}
\]
Entropy value.

Entropy appears in an exponential term that is not altered by temperature changes in Eq. (1), so cannot be calculated from the aforementioned time-scale normalization. For entropy calculation, we must perform a mathematical transformation to include dependence of $T$ in the entropy term by raising $k$ to the power of $T/T_m$ ($T_m =$ average $T$ used in measurements). Thus, if we simply raise Eq. (1) to the power of temperature, divided by average temperature of the experiments to have a manageable data, we obtain Eq. (3) where temperature dependence affects the entropy term.

\[
[f(t, T, \Delta H^\pm) = tTe^{-\Delta H^\pm/RT}]
\]

\[
[k^{T/T_m}(T) = \left(\frac{k_B T}{h}\right)^{T/T_m} e^{T\Delta S^\pm/RT_m} e^{-\Delta H^\pm/RT_m}]
\]

After performing an approximation ($T/T_m \approx 1$), $g$ can be defined as follows:

\[
\left(-\frac{d[A]}{dt}\right)^{T/T_m} = f^{T/T_m}([A], [B], ...) k^{T/T_m}(T, \Delta H^\pm, \Delta S^\pm); \quad k^{T/T_m}
\]

\[
\left(-\frac{d[A]}{dt}\right)^{T/T_m} = -\frac{d^{T/T_m}[A]}{dt^{T/T_m}} \approx -\frac{d[A]}{dt}
\]

\[
\int_{[A]_0}^{[A]_T} f^{-T/T_m}([A], [B], ...) d[A] = \int_0^t -k^{T/T_m} dt
\]

\[
G^{-1}([A]_T, [A]_0, [B]_0, ...) = -k^{T/T_m} t = -t \left(\frac{k_B T}{h}\right)^{T/T_m} e^{T\Delta S^\pm/RT_m} e^{-T_m\Delta H^\pm/R}
\]

\[
[g(t, T, \Delta H^\pm) = t \left(\frac{k_B T}{h}\right)^{T/T_m} e^{T\Delta S^\pm/RT_m}]
\]

A new normalized time-scale $g(t, T, \Delta S^\dagger)$ Eq. (4) is obtained and $\Delta S^\dagger$ is calculated directly by overlying product concentration profiles at different temperatures representing concentration versus $g$ at the correct $\Delta S^\dagger$ value, as shown in Figure 3 in the main text.
ΔH‡ and ΔS‡ can be calculated analogously for any reaction by applying the simple graphical method using the corresponding normalized time-scales in Eq. 2 and 4.

Now we can compare the graphical method with the initial rates in terms of error of the measurements to check if it is really superior. For that, 2% random error was included in the concentration data from the reaction in Figure 2 and both methods were applied (Figure S9). For the initial rates method, we used the data from the three different temperatures, obtaining values of 57 ± 3 KJ·mol⁻¹ and -152 ± 8 J·K⁻¹·mol⁻¹ for the enthalpy and entropy, respectively. Which involve a deviation from the real values of 14 and 11%, respectively. On the other hand, the graphical method only needs two temperatures (highest and lowest), obtaining a value of 51.8 ± 1.3 KJ·mol⁻¹ and -169 ± 4 J·K⁻¹·mol⁻¹ for the enthalpy and entropy, respectively. These values have much lower uncertainty and are much closer to the real values (50 and -170) than the calculated by initial rates method, confirming that our methodology is more precise using less data and experiments. The complete mathematical development is as follows:

A second order reaction is simulated in which two different compounds (A and B) react with each other in just one-step to give the product (P) at different temperatures according to Eq. (S1).

\[ \text{[Eq. (S1)]} \quad \text{A} + \text{B} \rightarrow \text{P} ; k_2(T) \]

Concentration of the reagents and product is calculated from the kinetic rate equation: Eq. (S2) and (S3) with initial concentrations of \([A]_0 = [B]_0 = 1.0\) M. Kinetic constants at different temperatures are calculated using Eyring-Polanyi equation: Eq. (S4) with transition state activation parameters \(\Delta H^\ddagger = 50\) KJ·mol⁻¹ and \(\Delta S^\ddagger = -170\) J·K⁻¹·mol⁻¹, as shown in Tables S1-S5.

\[ \text{[Eq. (S2)]} \quad \frac{d[p]}{dt} = k_2(T)[A][B] \]

\[ \text{[Eq. (S3)]} \quad \frac{1}{[A]} = \frac{1}{[A]_0} + k_2(T)t \]

\[ \text{[Eq. (S4)]} \quad k_2(T) = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT} \]
Hammett parameter.

Another powerful tool to extract information about organic reaction mechanisms are Linear Free Energy Relationships (LFER),\(^3\) based on electronic effects on a reactive functionality from different substituents. Hammett plot (Eq. 5) is a representative example of LFER and indicates how reaction rate and kinetic constant are affected by the electronic nature of a substituent (-X) linked to a reactive functionality, giving electronic information about the rate-determining step (rds) of the reaction. Application of the graphical methodology for Eq. 5 simply consists on representing product concentrations versus the normalized time-scale \(h(t, \rho, \sigma_X)\) Eq. (6), for reactions with different substituents (change in \(\sigma_X\)), and \(\rho\) is calculated iteratively until all profiles overlay. Please note that this analysis can be applicable to other LFERs, like Taft equation.

\[
\text{[Eq. (5)]} \quad \log \left( \frac{k_X}{k_H} \right) = \rho \sigma_X
\]

\[
\text{[Eq. (6)]} \quad h(t, \sigma_X, \rho) = t e^{\rho \sigma_X}
\]

Figure S19 and Table S10 shows the application of the described methodology compared to initial rates method in a simulated bimolecular reaction \(A + B \rightarrow P\) of aromatic compounds with different substituents with a \(\rho = 0.50\). The advantage of the graphical methodology is more evident for this fast reaction (\(t_{1/2} = 40 – 90\) s), where a reliable measure of initial rate (lower than 20% conversion) is technically difficult to obtain. Indeed, while the classical initial rates method gives a \(\rho\) value of 0.40 (Figure S19a), which supposes a 20% deviation from the correct value (0.50), the graphical method gives the exact value \(\rho = 0.50\) (Figure S19b). The mathematical development is as follows:

A bimolecular reaction of different \(para\)-substituted aromatic compounds \(A_X\) with \(B\) is shown to obtain product \(P_X\) (Eq. S5) and the methodology described in the paper is compared with the traditional initial rates methodology to obtain Hammett parameter rho (\(\rho\)).

\[
\text{[Eq. (S5)]} \quad A_X + B \rightarrow P_X ; k_2(T)
\]

Concentration of the reagents and product is calculated from the kinetic rate equation: Eq. (6) and (7) with initial concentrations of \([A_X]_0 = 0.6\) and \([B]_0 = 0.5\) M. Kinetic constants at different temperatures are calculated using Hammett equation: Eq. (8) with rho parameter equal to 0.5.
\[
\text{[Eq. (S6)]} \quad \frac{d[p]}{dt} = k_X[A_X][B] \\
\text{[Eq. (S7)]} \quad \ln \frac{[A]}{[B]} = \ln \frac{[A]_0}{[B]_0} + k_X([A]_0 - [B]_0)t \\
\text{[Eq. (S8)]} \quad \log \left( \frac{k_X}{k_H} \right) = \rho \sigma_X
\]

The initial rate method was carried out for comparison with the graphical analysis reported in the main text. For this, linear regression of the first three data points was performed in each case and the results for the slopes measured are presented in Table S7, the value of \( \rho \) is calculated using linear regression from the second (x) and fifth (y) columns of Table S10. Numeric data for the kinetic graphical analysis method is shown in Table S10.

**KIE values.**

Kinetic isotopic effects (KIE) are measured in organic chemistry to extract information about bond breaking/formation (or rehybridization) during the rds. These experiments normally involve comparison of the reaction rate for one of the reagents with the deuterated analogue \( k_H/k_D \) Eq. (7). Again, measurements must be performed at low conversions with intrinsic experimental errors, and analogously to the previous examples in the work, we can use the graphical method to calculate KIE by representing [P] vs. \( t \cdot KIE^{-1} \) Eq. (8) for both reactions (with –H and with –D) and iterating KIE different values until kinetic profiles overlay (see also Table S11).

\[
\text{[Eq. (7)]} \quad \left( \frac{k_H}{k_D} \right) = KIE \\
\text{[Eq. (8)]} \quad i(t, KIE) = t(KIE)^{-1}
\]
Hydrosilylation of alkynes. Kinetic experiments.

**Table S1.** Kinetic constants $k_2(T)$ calculated at different temperatures for Figure 3 in the main text.

| $T$ (°C) | 60  | 80  | 100 |
|----------|-----|-----|-----|
| $k_2(T)$ (M$^{-1}$.s$^{-1}$) | 0.000138 | 0.000406 | 0.00107 |

**Table S2.** Initial rates of reaction shown in Figure S9 calculated by linear regression.

| $T$ (°C) | $r_0$ (P) | $r^2$ |
|----------|-----------|-------|
| 60       | $0.776 \cdot 10^{-4}$ | 0.9997 |
| 70       | $1.301 \cdot 10^{-4}$ | 0.992 |
| 80       | $2.448 \cdot 10^{-4}$ | 0.995 |

**Table S3.** Numeric data for Figure 3a in the main text (transition state enthalpy).

| $T$ (°C) | time (s) | [P] (M) | $f(t, T, 0)$ | $f(t, T, 10)$ | $f(t, T, 100)$ | $f(t, T, 50)$ |
|----------|----------|---------|--------------|--------------|----------------|---------------|
| 60 °C    | 1000     | 0.1213  | 333000       | 9033         | 7.19E-11       | 0.00489       |
|          | 2000     | 0.2163  | 666000       | 18067        | 1.44E-10       | 0.00978       |
|          | 3000     | 0.2928  | 999000       | 27100        | 2.16E-10       | 0.01468       |
|          | 4000     | 0.3557  | 1332000      | 36134        | 2.87E-10       | 0.01957       |
|          | 5000     | 0.4083  | 1665000      | 45167        | 3.59E-10       | 0.02446       |
|          | 6000     | 0.4529  | 1998000      | 54201        | 4.31E-10       | 0.02935       |
|          | 8000     | 0.5247  | 2664000      | 72267        | 5.75E-10       | 0.03914       |
|          | 10000    | 0.5798  | 3330000      | 90334        | 7.19E-10       | 0.04892       |
|          | 12000    | 0.6235  | 3996000      | 108401       | 8.62E-10       | 0.05870       |
|          | 15000    | 0.6743  | 4995000      | 135501       | 1.08E-09       | 0.07338       |
|          | 18000    | 0.7130  | 5994000      | 162602       | 1.29E-09       | 0.08806       |

| $T$ (°C) | time (s) | [P] (M) | $f(t, T, 0)$ | $f(t, T, 10)$ | $f(t, T, 100)$ | $f(t, T, 50)$ |
|----------|----------|---------|--------------|--------------|----------------|---------------|
| 80 °C    | 200      | 0.0752  | 70600        | 2349         | 1.18E-10       | 0.00288       |
|          | 400      | 0.1398  | 141200       | 4699         | 2.35E-10       | 0.00576       |
|          | 600      | 0.1960  | 211800       | 7048         | 3.53E-10       | 0.00864       |
|          | 800      | 0.2454  | 282400       | 9398         | 4.70E-10       | 0.01153       |
|          | 1200     | 0.3278  | 423600       | 14097        | 7.06E-10       | 0.01729       |
|          | 1600     | 0.3940  | 564800       | 18796        | 9.41E-10       | 0.02305       |
|          | 2000     | 0.4484  | 706000       | 23495        | 1.18E-09       | 0.02882       |
|          | 3000     | 0.5494  | 1059000      | 35242        | 1.76E-09       | 0.04322       |
### Table S4. Numeric data for Figure 3b in the main text (transition state entropy).

| T (°C) | time (s) | [P] (M) | g(t, T, 0) | g(t, T, 100) | g(t, T, -100) | g(t, T, -170) |
|--------|----------|---------|------------|--------------|---------------|---------------|
| 60 °C  | 1000     | 0.1213  | 6.94E+15   | 1.14E+21     | 4.21E+10      | 9393019       |
|        | 2000     | 0.2163  | 1.39E+16   | 2.29E+21     | 8.42E+10      | 18786039      |
|        | 3000     | 0.2928  | 2.08E+16   | 3.43E+21     | 1.26E+11      | 28179058      |
|        | 4000     | 0.3557  | 2.78E+16   | 4.57E+21     | 1.68E+11      | 37572077      |
|        | 5000     | 0.4083  | 3.47E+16   | 5.71E+21     | 2.11E+11      | 46965097      |
|        | 6000     | 0.4529  | 4.16E+16   | 6.86E+21     | 2.53E+11      | 56358116      |
|        | 8000     | 0.5247  | 5.55E+16   | 9.14E+21     | 3.37E+11      | 75144155      |
|        | 10000    | 0.5798  | 6.94E+16   | 1.14E+22     | 4.21E+11      | 93930193      |
|        | 12000    | 0.6235  | 8.33E+16   | 1.37E+22     | 5.05E+11      | 112716232     |
|        | 15000    | 0.6743  | 1.04E+17   | 1.71E+22     | 6.32E+11      | 140895290     |
|        | 18000    | 0.7130  | 1.25E+17   | 2.06E+22     | 7.58E+11      | 169074348     |
| 80 °C  | 200      | 0.0752  | 1.20E+16   | 4.06E+21     | 3.54E+10      | 4758762       |
|        | 400      | 0.1398  | 2.50E+16   | 8.47E+21     | 7.37E+10      | 9922105       |
|        | 600      | 0.1960  | 3.84E+16   | 1.30E+22     | 1.13E+11      | 15250046      |
|        | 800      | 0.2454  | 5.21E+16   | 1.77E+22     | 1.54E+11      | 20687771      |
|        | 1200     | 0.3278  | 8.01E+16   | 2.71E+22     | 2.36E+11      | 31796624      |
|        | 1600     | 0.3940  | 1.09E+17   | 3.68E+22     | 3.21E+11      | 43134382      |
|        | 2000     | 0.4484  | 1.38E+17   | 4.66E+22     | 4.06E+11      | 54645451      |
|        | 3000     | 0.5494  | 2.12E+17   | 7.17E+22     | 6.24E+11      | 83988790      |
|        | 4000     | 0.6191  | 2.87E+17   | 9.72E+22     | 8.47E+11      | 113936766     |
|        | 5000     | 0.6702  | 3.64E+17   | 1.23E+23     | 1.07E+12      | 144342533     |
|        | 6000     | 0.7092  | 4.41E+17   | 1.49E+23     | 1.30E+12      | 175118166     |
| 100 °C | 80       | 0.0788  | 3.72E+16   | 2.59E+22     | 5.34E+10      | 4334018       |
|        | 160      | 0.1461  | 8.09E+16   | 5.64E+22     | 1.16E+11      | 9420641       |
| T (ºC) | time (s) | [P] (M) | g(t, T, 0) | g(t, T, 100) |
|-------|----------|---------|------------|--------------|
| 60    | 1000     | 0.1183  | 0.0023     | 11615534     |
|       | 2000     | 0.1998  | 0.0045     | 23231067     |
|       | 3000     | 0.2834  | 0.0068     | 34846601     |
|       | 4000     | 0.3366  | 0.0090     | 46462134     |
|       | 5000     | 0.4036  | 0.0113     | 58077668     |
|       | 6000     | 0.4645  | 0.0135     | 69693201     |
|       | 8000     | 0.5162  | 0.0180     | 92924268     |
|       | 10000    | 0.5867  | 0.0225     | 116155335    |
|       | 12000    | 0.6165  | 0.0270     | 139386402    |
|       | 15000    | 0.6689  | 0.0338     | 174233003    |
|       | 18000    | 0.6995  | 0.0405     | 209079604    |
| 80    | 200      | 0.0653  | 0.0014     | 5960291      |
|       | 400      | 0.1269  | 0.0028     | 12427316     |
|       | 600      | 0.2111  | 0.0042     | 19100497     |
|       | 800      | 0.2494  | 0.0055     | 25911182     |
|       | 1200     | 0.3261  | 0.0083     | 39824886     |
|       | 1600     | 0.4097  | 0.0111     | 54025289     |
|       | 2000     | 0.4291  | 0.0139     | 68442763     |
|       | 3000     | 0.5331  | 0.0208     | 105194939    |
|       | 4000     | 0.6269  | 0.0277     | 142704416    |
|       | 5000     | 0.6819  | 0.0346     | 180787270    |
|       | 6000     | 0.7137  | 0.0416     | 219333375    |
| 100   | 80       | 0.0760  | 0.0015     | 5497988      |
|       | 160      | 0.1625  | 0.0030     | 11950706     |
|       | 240      | 0.2224  | 0.0045     | 18820750     |
|       | 320      | 0.2481  | 0.0061     | 25976660     |
|       | 520      | 0.3695  | 0.0099     | 44747051     |
|       | 720      | 0.4423  | 0.0136     | 64427316     |
|       | 920      | 0.4891  | 0.0174     | 84783785     |

Table S5. Numeric data for Figure S9.
Table S6. Numeric data for Figure S10 (transition state enthalpy and entropy).

| T (°C) | time (s) | [C] (M) | [P] (M) | f(t, T, 54) | g(t, T, -150) |
|-------|----------|---------|---------|-------------|--------------|
| 60    | 333      | 100     | 0.0005  | 2408162     | 7442264      |
|       | 333      | 200     | 0.0018  | 4816324     | 14673624     |
|       | 333      | 300     | 0.0040  | 7224485     | 21827462     |
|       | 333      | 400     | 0.0069  | 9632647     | 28931417     |
|       | 333      | 500     | 0.0106  | 12040809    | 35998509     |
|       | 333      | 600     | 0.0149  | 14448971    | 43036362     |
|       | 333      | 700     | 0.0198  | 16857133    | 50049994     |
|       | 333      | 800     | 0.0252  | 19265294    | 57042956     |
|       | 333      | 900     | 0.0311  | 21673456    | 64017898     |
|       | 333      | 1000    | 0.0373  | 24081618    | 70976868     |
|       | 333      | 1500    | 0.0729  | 36122427    | 105580249    |
|       | 333      | 2000    | 0.1116  | 48163236    | 139942346    |
|       | 333      | 2500    | 0.1496  | 60204045    | 174126134    |
|       | 333      | 3500    | 0.2173  | 84285663    | 242093693    |
|       | 333      | 4500    | 0.2711  | 108367281   | 309656965    |
|       | 333      | 5500    | 0.3128  | 132448899   | 376909219    |
|       | 333      | 7500    | 0.3703  | 180612358   | 510695614    |
|       | 333      | 9500    | 0.4063  | 228775372   | 643740500    |
|       | 333      | 11500   | 0.4301  | 276938608   | 776205606    |
|       | 333      | 13500   | 0.4466  | 325101844   | 908194824    |
| 70    | 343      | 30      | 0.0001  | 13130832    | 3660441      |
|       | 343      | 60      | 0.0006  | 2626166     | 7365795      |
|       | 343      | 90      | 0.0013  | 3939250     | 11088291     |
|       | 343      | 120     | 0.0023  | 5252333     | 14821964     |
|       | 343      | 150     | 0.0035  | 6565416     | 18563970     |
|       | 343      | 180     | 0.0050  | 7878499     | 22312629     |
|       | 343      | 240     | 0.0087  | 10504666    | 29825786     |
|       | 343      | 300     | 0.0132  | 13130832    | 37355710     |
|       | 343      | 360     | 0.0184  | 15756998    | 44899024     |
|       | 343      | 560     | 0.0402  | 24510886    | 70115741     |
|       | 343      | 760     | 0.0663  | 33264774    | 95413828     |
|       | 343      | 960     | 0.0943  | 42018662    | 120771421    |
|       | 343      | 1160    | 0.1225  | 50772550    | 146176012    |
|       | 343      | 1660    | 0.1880  | 72657270    | 209845467    |
|       | 343      | 2160    | 0.2423  | 94541990    | 273687011    |
Table S7. Numeric data for Figure S11 (transition state enthalpy and entropy).

| T (ºC) | time (s) | [C] (M) | [P] (M) | f(t, T, 55.5) | g(t, T, -148) |
|--------|----------|---------|---------|--------------|--------------|
| 60     | 300      | 0.0024  | 4205505 | 27617870     |              |
|        | 600      | 0.0096  | 8411010 | 54453085     |              |
|        | 900      | 0.0222  | 12616515| 81000620     |              |
|        | 1500     | 0.0671  | 21027525| 133588668    |              |
|        | 2500     | 0.1462  | 35045875| 220318464    |              |
|        | 3500     | 0.2084  | 49064225| 306316515    |              |
|        | 5500     | 0.3066  | 77100925| 476896019    |              |
|        | 7500     | 0.3754  | 105137626| 646173383    |              |
|        | 9500     | 0.3970  | 133174326| 814512531    |              |
|        | 13500    | 0.4368  | 189247726| 1149121524   |              |
| 70     | 90       | 0.0088  | 2329570 | 14129286     |              |
|        | 180      | 0.0107  | 4659139 | 28431932     |              |
|        | 360      | 0.0248  | 9318279 | 57212709     |              |
Table S8. Kinetic constants $k_2(T)$ calculated at different temperatures for Figure S19.

| $T$ (°C) | time (s) | $k_2(T)$ (s$^{-1}$) |
|----------|----------|----------------------|
| 30       | 0.0077   | 1385989              |
| 70       | 0.0076   | 3233973              |
| 160      | 0.0219   | 7391939              |
| 260      | 0.0335   | 12011900             |
| 460      | 0.0715   | 21251824             |
| 560      | 0.1056   | 25871786             |
| 960      | 0.2021   | 44351633             |
| 1160     | 0.2211   | 53591556             |
| 1660     | 0.2924   | 76691365             |
| 2660     | 0.3870   | 122890982            |

Table S9. Initial rates of reaction shown in Figure S19 calculated by linear regression.

| $X$      | $\sigma_X$ | $r_0$ (PX) | $r^2$ | $\ln(r_0(P_X) / r_0(P_H))$ |
|----------|------------|------------|-------|-----------------------------|
| -NH$_2$  | -0.660     | 0.00458    | 0.998 | -0.273                      |
| -OMe     | -0.268     | 0.00540    | 0.998 | -0.109                      |
| -H       | 0.000      | 0.00602    | 0.997 | 0.000                       |
| -Br      | 0.232      | 0.00661    | 0.997 | 0.092                       |
| -CN      | 0.660      | 0.00779    | 0.996 | 0.257                       |
Table S10. Numeric data for Figure S19 (Hammet).

| -X  | time (s) | [P] (M) | h(t, σₓ, 0) | h(t, σₓ, -1) | h(t, σₓ, 0.5) |
|-----|----------|---------|-------------|--------------|---------------|
| -NH₂| 10       | 0.0491  | 10          | 19.35        | 7.19          |
|     | 20       | 0.0900  | 20          | 38.70        | 14.38         |
|     | 30       | 0.1247  | 30          | 58.04        | 21.57         |
|     | 40       | 0.1545  | 40          | 77.39        | 28.76         |
|     | 50       | 0.1803  | 50          | 96.74        | 35.95         |
|     | 70       | 0.2229  | 70          | 135.44       | 50.32         |
|     | 90       | 0.2565  | 90          | 174.13       | 64.70         |
|     | 110      | 0.2837  | 110         | 212.83       | 79.09         |
|     | 160      | 0.3333  | 160         | 309.57       | 115.03        |
|     | 210      | 0.3667  | 210         | 406.31       | 150.97        |
|     | 260      | 0.3907  | 260         | 503.05       | 186.92        |
|     | 360      | 0.4226  | 360         | 696.53       | 258.81        |
| -OMe| 10       | 0.0586  | 10          | 13.07        | 8.75          |
|     | 20       | 0.1057  | 20          | 26.15        | 17.49         |
|     | 30       | 0.1446  | 30          | 39.22        | 26.24         |
|     | 40       | 0.1771  | 40          | 52.29        | 34.98         |
|     | 50       | 0.2047  | 50          | 65.37        | 43.73         |
|     | 70       | 0.2490  | 70          | 91.51        | 61.22         |
|     | 90       | 0.2831  | 90          | 117.66       | 78.71         |
|     | 110      | 0.3100  | 110         | 143.81       | 96.20         |
|     | 160      | 0.3577  | 160         | 209.18       | 139.93        |
|     | 210      | 0.3888  | 210         | 274.54       | 183.66        |
|     | 260      | 0.4106  | 260         | 339.91       | 227.39        |
|     | 360      | 0.4389  | 360         | 470.64       | 314.85        |
| -H  | 10       | 0.0659  | 10          | 10           | 10            |
|     | 20       | 0.1176  | 20          | 20           | 20            |
|     | 30       | 0.1592  | 30          | 30           | 30            |
|     | 40       | 0.1934  | 40          | 40           | 40            |
|     | 50       | 0.2221  | 50          | 50           | 50            |
|     | 70       | 0.2672  | 70          | 70           | 70            |
|     | 90       | 0.3011  | 90          | 90           | 90            |
|     | 110      | 0.3275  | 110         | 110          | 110           |
|     | 160      | 0.3734  | 160         | 160          | 160           |
|     | 210      | 0.4028  | 210         | 210          | 210           |
|     | 260      | 0.4230  | 260         | 260          | 260           |
|     | 360      | 0.4488  | 360         | 360          | 360           |
| -Br | 10       | 0.0730  | 10          | 7.93         | 11.23         |
|     | 20       | 0.1287  | 20          | 15.86        | 22.46         |
|     | 30       | 0.1726  | 30          | 23.79        | 33.69         |
|     | 40       | 0.2081  | 40          | 31.72        | 44.92         |
| time (s) | [P] [M] | h(t, σ_x, 0) | h(t, σ_x, -1) | h(t, σ_x, 0.5) |
|----------|---------|---------------|---------------|----------------|
| 10       | 0.0876  | 10            | 5.17          | 13.91          |
| 20       | 0.1509  | 20            | 10.34         | 27.82          |
| 30       | 0.1987  | 30            | 15.51         | 41.73          |
| 50       | 0.2663  | 50            | 25.84         | 69.55          |
| 70       | 0.3116  | 70            | 36.18         | 97.37          |
| 90       | 0.3440  | 90            | 46.52         | 125.19         |
| 110      | 0.3683  | 110           | 56.85         | 153.01         |
| 160      | 0.4085  | 160           | 82.70         | 222.55         |
| 210      | 0.4329  | 210           | 108.54        | 292.10         |
| 260      | 0.4491  | 260           | 134.38        | 361.65         |
| 360      | 0.4687  | 360           | 186.07        | 500.75         |

**Table S11.** Numeric data for Figure 4 in the main text (KIE).

| time (s) | [P] [M] | i(t, 1.91) |
|----------|---------|------------|
| HSiEt₃   | 0.5     | 0.5        | 0.019       |
|          | 1       | 1          | 0.031       |
|          | 2       | 2          | 0.055       |
|          | 5       | 5          | 0.097       |
|          | 10      | 10         | 0.152       |
|          | 20      | 20         | 0.231       |
|          | 40      | 40         | 0.403       |
| DSiEt₃   | 0.5     | 0.26       | 0.012       |
|          | 1       | 0.52       | 0.021       |
|          | 2       | 1.05       | 0.033       |
|          | 5       | 2.62       | 0.060       |
|          | 10      | 5.24       | 0.099       |
|          | 20      | 10.47      | 0.153       |
|          | 40      | 20.94      | 0.243       |
**Figure S1.** Effect of catalyst concentration on hydrosilylation reaction rate. [Pt] is given in ppm with respect to the alkyne. Reaction conditions: alkyne 0.5 mmol, HSiEt₃ 0.6 mmol, toluene 1 mL, 110 ºC.

**Figure S2.** Reaction rate for different alkyne concentrations: A) phenylacetylene, B) 1-Octyne, HSiEt₃ 0.6 mmol, 1 mL of toluene and 2.5·10⁻⁵ mmol Pt.

**Figure S3.** Reaction rate for different silane concentrations. Phenylacetylene 0.5 mmol, 0.6 mmol of HSiEt₃, 1 mL of toluene and 2.5·10⁻⁵ mmol Pt Karstedt, 110 ºC.
**Figure S4.** Hammett plots for para-substituted dimethylphenylsilanes. A) \( \alpha \)-alkenylsilane B) \( \beta \)-alkenylsilane. Reaction conditions: phenylacetylene 0.5 mmol, \( p\)-R-PhMe\(_2\)SiH 0.6 mmol (R=OMe, H, CN), Pt Kardstedt 0.005 mol%, 1 mL of toluene, 110 °C.

**Figure S5.** Comparison of a-c) traditional methods to measure reaction kinetics based on concentration measurements and subsequent transformation to rate with d) the graphical analysis described in this work that uses concentration profiles to calculate different thermodynamic and kinetic parameters of chemical reactions.
**Figure S6.** a) Kinetic profiles, b) application of the graphical method with split of data in four subsets and c) comparison of initial rates method with the graphical method for a simulated bimolecular reaction. R² > 0.999 for the graphical method.
Figure S7. Simulation of a reaction with an induction time: a) chemical reaction involving two processes: (1) in-situ formation of active species by metal aggregation and (2) catalytic cycle in which reagents A and B form P catalysed by the active species; (3) correspond to the whole process (1) + (2). b) Reaction profile. c) Transition state enthalpy and entropy calculation by initial rates, in this case measuring the rate after the induction time. d) Transition state enthalpy and entropy calculation by the graphical method.

\[
\text{a) Reaction scheme}
\]

(1) \(2M \rightarrow C\)

(2) \(A + B \rightarrow P\)

\[\Delta H_1^\ddagger = 70; \Delta S_1^\ddagger = -70\]

\[\Delta H_2^\ddagger = 45; \Delta S_2^\ddagger = -125\]

\[\Delta H_3^\ddagger = ?; \Delta S_3^\ddagger = ?\]

\[
\text{b) Reaction profiles}
\]

\[
\text{c) Initial rates method}
\]

\[
\Delta H_3^\ddagger = 53\pm5 \text{ KJ} \cdot \text{mol}^{-1}
\]

\[
\Delta S_3^\ddagger = -165\pm15 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\]

\[
\text{d) This method}
\]

\[
\Delta H_3^\ddagger = 54.5 \text{ KJ} \cdot \text{mol}^{-1}
\]

\[
\Delta S_3^\ddagger = -150 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\]
Figure S8. Comparison of the graphical method (a) with the initial rates method (b) by introducing 2% random error in a simulated example of a reaction with induction time (from Figure S10) caused by in-situ catalyst formation. For the initial rates method, rate is measured after induction time at three different temperatures to obtain the activation parameters. For the graphical method, only two temperatures are necessary (the lowest and the highest) and data from concentration profile is divided into two subsets for each temperature. Activation parameters are calculated for the whole profiles and for each subset combination and the value is calculated from the weighted average with the error obtained from the standard deviation.
Figure S9. Graphical analysis method to calculate activation parameters in the Heck reaction catalysed by Pt(acac)2 that form the clusters in-situ under reaction conditions: a) Reaction scheme, b) Reaction profiles, and calculation of c) enthalpy and d) entropy. The Table at the bottom shows the results with different number of data points (N). * Measured initial rate instead of rate after induction time.
Figure S10. Application of the graphical method to the calculation of transition state enthalpy (a) and entropy (b) of phenylacetylene 1 and triethylsilane 2 catalysed by Pt\textsubscript{1} (Table 1, entry 1 in the main text).

Figure S11. Application of the graphical method to the calculation of transition state enthalpy (a) and entropy (b) of phenylacetylene 1 and triethylsilane 2 catalysed by Pt\textsubscript{3} (Table 1, entry 2 in the main text).

Figure S12. Application of the graphical method to the calculation of transition state enthalpy (a) and entropy (b) of 1-octyne 3 and triethylsilane 2 catalysed by Pt\textsubscript{1} (Table 1, entry 3 in the main text).
Figure S13. Application of the graphical method to the calculation of transition state enthalpy (a) and entropy (b) of 1-octyne 3 and triethyilsilane 2 catalysed by Pt$_3$ (Table 1, entry 4 in the main text).

Figure S14. Application of the graphical method to the calculation of transition state enthalpy (a) and entropy (b) of phenylacetylene 1 and 1,1,3,3-tetramethyldisiloxane 4 catalysed by Pt$_1$ (Table 1, entry 5 in the main text).

Figure S15. Application of the graphical method to the calculation of transition state enthalpy (a) and entropy (b) of phenylacetylene 1 and 1,1,3,3-tetramethyldisiloxane 4 catalysed by Pt$_3$ (Table 1, entry 6 in the main text).
Figure S16. Comparison of a) initial rates method with b) this graphical analysis to calculate Hammett parameter (ρ). A simulated bimolecular reaction was considered in which one of the reagents (A) is a para-substituted aromatic ring. c) Summation of the distances between consecutive points for different values of ρ. As can be seen the sum of the distances converge towards the real value of ρ (0.5), reaching the minimum at ρ = 0.4992, which constitutes a deviation of 0.1% with respect to the real value.
Hydrosilylation of alkynes. Reactivity, computational and mechanism.

**Table S12.** Partial charges of the alkyne carbon atoms for different alkynes calculated by Huckel model.

| Alkyne | $C_{\text{int}}$ | $C_{\text{ext}}$ | H  | $C_{\text{int}}-C_{\text{ext}}$ |
|--------|------------------|------------------|----|-------------------------------|
|        |                  |                  |    |                               |
|        | 0.107            | -0.255           | 0.053 | 0.362                        |
|        | -0.063           | -0.080           | -   | 0.017                         |
|        | 0.115            | -0.276           | 0.053 | 0.391                         |
|        | 0.136            | -0.306           | 0.052 | 0.442                         |
|        | -0.019           | -0.116           | -   | 0.097                         |
|        | 0.136            | -0.317           | 0.052 | 0.452                         |
|        | 0.139            | -0.3155          | 0.0515 | 0.455                       |
|        | 0.123            | -0.414           | 0.0515 | 0.537                       |
|        | 0.133            | -0.282           | 0.0515 | 0.415                       |
|        | **0.095**        | **-0.470**       | **1.163** | **0.565**                |
|        | -0.052           | -0.102           | -   | 0.050                         |
|        | 0.062            | -0.408           | 1.164 | 0.470                         |
Figure S17. Hydrosilylation of phenylacetylene (0.5 M) with triethylsilane using Pt\(_i\) (2.5 \cdot 10^{-5} \text{ M}) catalyst without (A) or with silanepyridine (B). Kardstedt's catalyst present an induction time.

Figure S18. Hammett plots for \textit{para-} and \textit{meta}-substituted ethynylbenzenes. A) \(\alpha\)-product, B) \(\beta\)-product. Reaction conditions: alkyne 0.5 mmol, HSiEt\(_3\) 0.6 mmol, Pt Kardstedt 0.005 mol\%, toluene (1 mL), 110 °C.
Figure S19. Reaction rate for the hydrosilylation of 1-octyne (left) and phenylacetylene (right) individually and together. Individual experiments conditions: alkyne 0.5 mmol, silane 0.6 mmol, Pt Kardstedt $2.5 \times 10^{-5}$ mmol, toluene 1 mL, 110 °C. Competitive experiments: 1-octyne 0.25 mmol, phenylacetylene 0.25 mmol, Pt Kardstedt $2.5 \times 10^{-5}$ mmol, toluene 1 mL, 110 °C.

Figure S20. Reaction rate for different substituted phenylacetylenes catalysed by Pt.
Figure S21. Scheme of different possibilities for migratory insertion through hydro- and silylplatination to yield α and β isomers catalysed by Pt₃ and steric factors affecting each one.

Figure S22. NOESY of the purified product between phenylacetylene 0.5 mmol and HSiEt₃ 0.6 mmol in 1 mL of toluene with Pt Kardstedt (0.005 mol%) at 110 °C.
Figure S23. NOESY of the purified product between phenylacetylene 0.5 mmol and DSiEt3 0.6 mmol in 1 mL of toluene with Pt Kardstedt (0.005 mol%) at 110 ºC.

Figure S24. NOESY of the purified product between deuterated phenylacetylene 0.5 mmol and HSiEt3 0.6 mmol in 1 mL of toluene with Pt Kardstedt (0.005 mol%) at 110 ºC.
Theoretical kinetic equation for Pt1 and discussion

Taking into consideration the mechanism for the reaction proposed in Figure 8 in the main text, we have calculated the theoretical kinetic equation for the hydrosilylation of alkynes catalysed by Pt1 using the corresponding approximations. Steady state approximation has been used for the concentration of reaction intermediates B-E. In the catalytic cycle, the concentration of these intermediates is supposed to stay equal once the equilibrium has been reached, since the amount of catalyst is more than 10,000 times lower than the amount of reagents (turnover number, TON is more than 10,000) and we can assume the reaction reach the equilibrium immediately after the start of the reaction.

\[
\frac{d[P]}{dt} = k_5[F][A]^2
\]

**Figure S25.** Decomposition of mechanism in single steps with their corresponding kinetic constants.

The intermediates B-F of the catalytic cycle are in equilibrium and steady state approximation was therefore applied to equations 1-5 of figure S5 in order to obtain the rate for every intermediate of the catalytic cycle.
\[
0 = \frac{d[F]}{dt} = k_4[E][A] - k_5[F][A]^2
\]
\[
0 = \frac{d[E]}{dt} = k_3[D] - k_4[E][A]
\]
\[
0 = \frac{d[D]}{dt} = k_2[C][S] - k_{-2}[D][A] - k_3[D]
\]
\[
0 = \frac{d[C]}{dt} = k_1[B][S] - k_{-1}[C][A] + k_2[C][S] - k_{-2}[D][A]
\]
\[
0 = \frac{d[B]}{dt} = k_5[F][A]^2 - k_1[B][S] + k_{-1}[C][A]
\]

\[
[Pt^0] = [B] + [C] + [D] + [E] + [F]
\]

These equations were worked out to obtain an equation for the rate of product formation, which is shown below:

\[
\frac{d[P]}{dt} = \frac{k_1k_2k_3k_4k_5}{\{(k_{-1}[A] + k_1[S])(k_{-2}[A] + k_3) + k_2(k_3k_5[A]^2 + k_4[S])[S]\}^2[A]^2[Pt^0]}
\]

Through kinetic measurements, we know that reaction rate always increases with higher silane concentration and decreases with alkyne concentration, at least in all experiments performed in the study. Therefore, we can omit the \([S]^2\) term in the denominator because it is irrelevant in a broad range of reaction conditions. The approximated equation will stay as follows:

\[
\frac{d[P]}{dt} = \frac{k_1k_2k_3}{(k_{-1}[A] + k_1[S])(k_{-2}[A] + k_3) + k_2(k_3k_5[A]^2 + k_4[S])[S]}[S]^2[Pt^0]
\]

Kinetic data measured fits well to the equation after performing the proper modifications and approximations convenient for each case and explains the quadratic dependence of reaction rate [silane] at low concentrations.
Theoretical kinetic equation for Pt₃ and discussion

Figure S26. Kinetic equation elucidation from elementary steps of the catalytic cycle for Pt₃ applying steady state approximation.

Steady state approximation was applied to equations 1-2 (intermediates B-E) in order to obtain the rate for every intermediate of the catalytic cycle. Equation 4 was used to obtain the rate of product formation.

\[
\text{rate} = \frac{d[P]}{dt} = k_4[E][A]^2
\]

\[
0 = \frac{d[E]}{dt} = k_3[D][A] - k_4[E][A]^2
\]

\[
0 = \frac{d[D]}{dt} = k_2[C] - k_{-2}[D][A] - k_3[D][A]
\]

\[
0 = \frac{d[C]}{dt} = k_2[B][S] + k_{-2[D][A]} - k_{-1}[C][A] - k_2[C]
\]

\[
0 = \frac{d[B]}{dt} = k_4[E][A]^2 + k_{-1}[C][A] - k_1[B][S]
\]

\[
[Pt^0] = [B] + [C] + [D] + [E]
\]

These equations were worked out to obtain an equation for the rate of product formation which is shown below.

\[
\text{rate} = \frac{d[P]}{dt} = \frac{k_1k_2k_3k_4}{k_2k_3 + (k_{-2} + k_3)(k_{-1}(A) + k_1[S])}k_4[A]^2 + k_1k_2k_4[A][S] + k_1k_2k_3[S][A]^2[Pt^0]
\]
Under the diverse conditions tested for the hydrosilylation of phenylacetylene with triethylsilane, experimental rate always increases with higher silane concentration and decreases or remains constant with higher alkyne concentration, showing the high affinity of the platinum for the alkyne. On this basis we can assume $[A]^2$ term is the most relevant in the denominator and excluding the other terms we obtain the following equation:

$$
\frac{d[P]}{dt} = \frac{k_1k_2k_3}{k_2k_3 + (k_{-2} + k_3)(k_{-1}[A] + k_1[S])[S][Pt^0]}
$$

Which very much resembles the experimental equation obtained with the preliminary kinetic study. Kinetic data measured fits well to the equation after performing the proper modifications and approximations convenient for each case. We have used the same equation for both Pt$_1$ and Pt$_3$ species, since the mechanism is similar, according to the experiments that have been carried out. Kinetic constants change for the different platinum species, but also change for different silanes, alkynes and even solvent, since every single step has a characteristic kinetic constant for the reagents.

**Movie 1.** Chalk-Harrod (CH, left) and TS-1 (right) intermediates for the formation of the alpha-product after hydride insertion.

**Movie 2.** Chalk-Harrod (CH, left) and TS-1 (right) intermediates for the formation of the alpha-product after silylation.
**Movie 3.** Chalk-Harrod (CH, left) and TS-1 (right) intermediates for the formation of the beta-product after hydride insertion.

![CH-beta-Si.mov](image)  ![TS-1-beta-Si.mov](image)

**Movie 4.** Chalk-Harrod (CH, left) and TS-1 (right) intermediates for the formation of the beta-product after silylation.
Hydrosilylation of alkenes.

**Figure S27.** Left: Kinetics for the hydrosilylation of styrene 16 (0.5 M) with dimethylphenylsilane 17 (1.2 equivalents) catalysed by Pt/MOF to give (2-phenylethyl)dimethylphenylsilane 18 in toluene at 110 ºC (blue diamonds) and after filtering the catalyst in hot at 15 min reaction time (pink triangles). Right: amplification of the points in the first 2 hours.

**Figure S28.** Kinetics for the hydrosilylation of styrene 16 (0.5 M) with dimethylphenylsilane 17 (1.2 equivalents) catalysed by Karstedt’s catalyst in toluene at 110 ºC.
Figure S29. Top: Deconvoluted platinum 4d X-ray photoelectron spectroscopy (XPS) peaks for Pt₁/NaY calcined at 100 °C (left) and 200 °C (right) for 24 h. The Pt(II)/Pt(0) ratio is ca. 20 and 10, respectively. The typical Pt 4f peaks were not employed because superimpose with the Al₂p peaks of the zeolite. Bottom left: CO-probe low temperature IR measurement of Pt₁/NaY calcined at 200 °C, at increasing CO doses. S17 Bottom right: Pt₄f XPS of Pt₁/MOF. S2

Dehydrogenative silylation of alcohols.

Table S13. Catalytic results for the hydrosilylation of 1-octanol 26 with dimethylphenylsilane 17 to give octyldimethylphenylsiloxane 27 in 1,4-dioxane solvent with different amounts of Karstedt’s catalyst. GC yields using n-dodecane as an internal standard. Tests with other solvents gave lower yields.
**Figure S30.** Kinetics for the dehydrogenative hydrosilylation of 1-octanol **26** with dimethylphenylsilane **17** to give octyldimethylphenylsiloxane **27**, with a Pt-supported solid catalyst in 1,4-dioxane at 110 °C, after filtering the solid catalyst in hot at 15 min reaction time (blue points) or not (red points). GC yields using n-dodecane as an internal standard.

| Entry | mmol 26 | mmol 17 | Karstedt (ppm) | Solvent volume (ml) | T (°C) | Time (h) | 27 (%) | TOF (h⁻¹) | TON |
|-------|---------|---------|----------------|---------------------|--------|----------|--------|------------|-----|
| 1     | 0.25    | 0.25    | 100            | 0.5                 | 100    | 24       | 8      | 33         | 790 |
| 2     | 0.25    | 0.25    | 100            | 1.0                 | 110    | 20       | 5      | 47         | 931 |
| 3     | 0.25    | 0.25    | 100            | 0.25                | 110    | 20       | 15     | 37         | 733 |
| 4     | 0.25    | 0.25    | 100            | 0.5                 | 110    | 20       | 9      | 45         | 894 |
| 5     | 0.25    | 0.25    | 200            | 0.5                 | 110    | 20       | 16     | 40         | 801 |
| 6     | 0.5     | 0.25    | 100            | 0.5                 | 110    | 20       | 19     | 95         | 1908|
| 7     | 0.25    | 0.5     | 100            | 0.5                 | 110    | 20       | 42     | 208        | 4154|
| 8     | 0.25    | 0.5     | 100            | 0.25                | 110    | 19       | 96     | 126        | 2389|
Figure S31. Tentative mechanism for the dehydrogenative silylation of alcohols based on metal(oid) cycles.

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