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Supporting Information

for

Platinum(0) olefin complexes of a bulky terphenylphosphine ligand. Synthetic, structural and reactivity studies

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I. <u>General considerations</u>

All preparations and manipulations were carried out under oxygen free argon or nitrogen using conventional Schlenk techniques and, when specified, at low temperature. Solvents were rigorously dried and degassed before use. Toluene, pentane and benzene were distilled under nitrogen over sodium. Tetrahydrofuran was distilled under nitrogen over sodium/benzophenone and dichloromethane was distilled under nitrogen over CaH₂ and stored over activated 4Å molecular sieves. Solution NMR spectra were recorded on Bruker Avance DPX-300, Avance DRX-400, Avance DRX-500, and 400'54 Ascend/R spectrometers. The ¹H and ¹³C resonances of the solvent were used as the internal standard and the chemical shifts are reported relative to TMS. NMR simulations were performed employing the TopSpin V 3.1 package, Bruker. Yields of the metal complexes are based on platinum. Commercially available chemicals were used as received. CCDC nos. 1416067-1416069 contain the crystallographic data for compounds 2a, and 3, and 4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. Experimental details for X-ray analyses, and synthesis and analytical data for complexes 2a, 2b, 3 and 4, and ligand 1 are included in the Supporting Information.

II. Synthesis and characterization data

Synthesis of PMe₂Ar^{Dipp₂} (1). This ligand was prepared in *ca*. 55 % yield using the procedure already described in detail¹ for the analogous phosphine PMe₂Ar^{Xyl₂}, but utilizing the Grignard reagent Mg(Ar^{Dipp₂})Br.² Yield: 8.72 g (54%). Anal. Calcd. for C₃₂H₄₃P: C, 83.80; H, 9.45. Found: C, 83.8; H, 9.9. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 0.70 (d, ²*J*_{HP} = 5.0 Hz, 6H, (CH₃)₂–P), 1.05 (d, ³*J*_{HH} = 6.8 Hz, 12H, CH₃–Dipp), 1.25 (d, ³*J*_{HH} = 6.8 Hz, 12H, CH₃–Dipp), 2.66 (h, ³*J*_{HH} = 6.8 Hz, 4H, CH–Dipp), 7.05 (dd, ³*J*_{HH} = 7.6 Hz, ⁴*J*_{HP} = 2.0 Hz, 2H, *m*–C₆H₃), 7.19 (d, ³*J*_{HH} = 7.7 Hz, 4H, *m*–Dipp), 7.30 (t, ³*J*_{HH} = 7.6 Hz, 1H, *p*–C₆H₃), 7.36 (t, ³*J*_{HH} = 7.7 Hz, 2H, *p*–Dipp) ppm. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 25 °C): δ 13.7 (d, ¹*J*_{CP} = 14 Hz, (CH₃)₂–P), 22.6 (s, CH₃–Dipp), 25.7 (s, CH₃–Dipp), 31.2 (s, CH–Dipp), 122.8 (s, *m*–Dipp), 127.0 (s, *p*–C₆H₃), 140.4 (d, ³*J*_{CP} = 4 Hz, *ipso*–Dipp), 145.2 (d, ²*J*_{CP} = 15 Hz, *o*–C₆H₃), 147.1 (s, *o*–Dipp) ppm. ³¹P{¹H</sup> NMR (160 MHz, CD₂Cl₂, 25 °C): δ -41.3 (s) ppm.

Synthesis of [PtCl₂(PMe₂Ar^{Dipp₂})]. A solution of ligand 1 (570 mg, 1.24 mmol) in toluene (10 mL) was added to a suspension of PtCl₂ (300 mg, 1.13 mmol) in toluene (10 mL). The reaction mixture was heated at 80 °C and stirred for three days. The resulting orange solution was taken to dryness under reduced pressure and the solid residue was washed with pentane (3 \times 20 mL), dried under vacuum for 1 h, and identified as [PtCl₂(PMe₂Ar^{Diip2})]. Yield: 730 mg (89 %). Anal. Calcd. for C₃₂H₄₃Cl₂PPt: C, 53.04; H, 5.98. Found: C, 52.9; H, 6.0. ¹H NMR (300 MHz, 25 °C, CD₂Cl₂): δ 0.96 (d, 6 H, ${}^{3}J_{\rm HH} = 6.6$ Hz, Me-Dipp), 1.01 (d, 6 H, ${}^{3}J_{\rm HH} = 7.1$ Hz, Me-Dipp), 1.31 (d, 6 H, ${}^{3}J_{\rm HH} =$ 7.1 Hz, Me-Dipp), 1.51 (d, 6 H, ${}^{2}J_{HP} = 12.0$ Hz, ${}^{4}J_{HPt} = 26.4$ Hz, PMe₂), 1.63 (d, 6 H, ${}^{3}J_{\text{HH}} = 7.1$ Hz, Me-Dipp), 2.34 (sept, 4 H, ${}^{3}J_{\text{HH}} = 6.6$ Hz, CH-Dipp), 6.75 (d, 1 H, ${}^{3}J_{\text{HH}} =$ 7.7 Hz, *m*-Dipp'), 7.23 (m, 3 H, *m*-C₆H₃ and *m*-Dipp'), 7.31 (d, 2 H, ${}^{3}J_{HH} = 8.2$ Hz, *m*-Dipp), 7.50 (m, 2H, p-Dipp), 7.88 (t, 1 H, ${}^{3}J_{HH} = 8$ Hz, $p-C_{6}H_{3}$) ppm. ${}^{13}C{}^{1}H$ NMR (75.4 MHz, 25°C, CD₂Cl₂): δ 13.4 (d, ${}^{1}J_{CP}$ = 45 Hz, ${}^{2}J_{CPt}$ = 26 Hz, PMe₂), 21.7 (s, Me-Dipp), 24.2 (s, ${}^{4}J_{CPt} = 22$ Hz, Me-Dipp), 25.4 (s, ${}^{4}J_{CPt} = 18.3$ Hz, Me-Dipp), 26.6 (s, Me-Dipp), 31.7 (s, CH-Dipp), 34.6 (s, CH-Dipp), 123.6 (s, *m*-Dipp), 126.6 (s, ⁴J_{CPt} = 25 Hz, m-C₆H₃), 130.5 (s, *p*-Dipp'), 131.2 (d, J_{CP} = 15 Hz, *m*-Dipp'), 132.3 (s, *p*-Dipp'), 133.3 (d, ${}^{3}J_{CP} = 7$ Hz, *m*-Dipp'), 138.1 (s, ${}^{5}J_{CPt} = 34$ Hz, *p*-C₆H₃), 147.5 (s), 148.5 (s) ppm.³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂, 25 °C): δ 10.9 (s, ¹*J*_{PPt} = 3189 Hz) ppm. Solid-state structural data for this complex will be reported in a forthcoming publication.



Synthesis of $[Pt(C_2H_4)_2(PMe_2Ar^{Dipp_2})]$, (2a). The chloride precursor $[PtCl_2(PMe_2Ar^{Dip_2})]$ (40 mg, 0.06 mmol) was dissolved in THF (5 mL) and Zn powder (50 mg, 0.76 mmol) was added to the solution at room temperature. The reaction mixture was kept under a C_2H_4 atmosphere (1.5 atm) overnight at room temperature. Excess metallic zinc was removed by filtration and the dark brown solution was taken to dryness under reduced pressure. The resulting solid was extracted with pentane (2 × 2 mL), which was then

removed by evaporation under reduced pressure, giving rise to a dark brown solid. Crystallization of the crude, which contains a mixture of **2a** and **2b**, from a saturated pentane solution under an ethylene atmosphere at -23° C afforded pure complex **2a**. Yield: 25 mg (64%). Anal. Calcd. for C₃₆H₅₁PPt: C, 60.91; H, 7.24. Found: C, 61.2; H, 7.6 %. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 0.95 (d, ³*J*_{HH} = 6.6 Hz, 12 H, CH₃–Dipp), 1.27 (d, ³*J*_{HH} = 6.6 Hz, 12 H, CH₃–Dipp), 1.32 (d, ²*J*_{HP} = 7.7 Hz, ³*J*_{HP} = 32.2 Hz, 6 H, (CH₃)₂–P), 2.34 (br s, ²*J*_{HPt} = 53.1 Hz, 8 H, C₂H₄), 2.84 (sept, ³*J*_{HH} = 7.0 Hz, 4 H, CH–Dipp), 6.96 (t, ³*J*_{HH} = 7.7 Hz, 1 H, *p*–C₆H₃), 7.00 – 7.05 (m, 2 H, *m*–C₆H₃), 7.07 (d, ³*J*_{HH} = 7.3 Hz, 4 H, *p*–Dipp), 7.24 (t, ³*J*_{HH} = 7.5 Hz, 2 H, *p*–Dipp) ppm. ¹³C {¹H} NMR (100.6 MHz, C₆D₆, 25 °C: δ 20.6 (d, ¹*J*_{CP} = 30 Hz, ²*J*_{CPt} = 40 Hz, (CH₃)₂–P), 22.8 (s, CH₃–Dipp), 25.9 (s, CH₃–Dipp), 31.3 (s, CH–Dipp), 38.5 (br s, ¹*J*_{CPt} = 153 Hz, C₂H₄), 123.0 (s, *p*–Dipp), 126.6 (d, ⁴*J*_{CP} = 1 Hz, *p*–C₆H₃), 128.9 (s, *p*–Dipp), 133.6 (s, ³*J*_{CP} = 6 Hz, *m*–C₆H₃), 135.1 (d, ¹*J*_{CP} = 24 Hz, ²*J*_{CPt} = 13 Hz, *o*–C₆H₃), 140.9 (d, ³*J*_{CP} = 3 Hz, *ipso*–Dipp), 143.5 (d, ²*J*_{CP} = 9 Hz, ³*J*_{CPt} = 13 Hz, *o*–C₆H₃), 147.1 (s, *o*–Dipp) ppm.

As explained in the main text, complex **2a** looses C_2H_4 in solution and converts into **2b**. Although complex **2b** was not isolated in a pure form, characteristic NMR data were identified by analyzing mixtures of **2a** and **2b** and are reported here. ¹H NMR (300 MHz, C_6D_6 , 25 °C): δ 2.18 (br s, ²J_{HPt} = 69.6 Hz, 4 H, C_2H_4). ¹³C{¹H}NMR (100.6 MHz, C₆D₂, 25°C): δ 42.5 (d, ²*J*_{CP} = 16 Hz, ²*J*_{CPt} = 270 Hz, C₂H₄) ppm. ³¹P{¹H}NMR (121.44 MHz, C₆D₂, 25°C): δ 24.1 (s, ¹*J*_{PPt} = 4333 Hz) ppm.



Synthesis of $[Pt(CH_2=CH'Bu)(PMe_2Ar^{Dipp_2})]$, (3). Complex $[PtCl_2(PMe_2Ar^{Diip_2})]$ (100 mg, 0.14 mmol) was dissolved in dry THF (5 mL) in an ampoule under inert atmosphere. Zn powder (0.090 g, 1.4 mmol) and 3,3dimethyl-1-butene (0.27 mL, 2.07 mmol) were added to the solution at room temperature. The reaction mixture was stirred at room temperature for 48 h and was then filtered

volatiles were removed under vacuum to give a dark brown solid that was washed with pentane at -80°C. For further purification the product can be crystalized from a saturated pentane solution at -23°C. Yield: 64 mg (62%). Anal. Calcd. for C₃₈H₅₅PPt: C, 61.85; H, 7.51. Found: C, 61.5; H, 7.8.¹H NMR (400 MHz, C₆D₆, 25 °C): δ 0.63 (t, ${}^{3}J_{\text{HH}} = 9.7 \text{ Hz}, {}^{3}J_{\text{HH}} = 9.0 \text{ Hz}, {}^{2}J_{\text{HPt}} = 18.4 \text{ Hz}, 1\text{H}, \text{H}_{\text{B}}), 0.91 \text{ (d}, {}^{3}J_{\text{HH}} = 6.7 \text{ Hz}, 6\text{H}, \text{CH}_{3}$ -Dipp), 0.96 (d, ${}^{3}J_{HH} = 6.7$ Hz, 6H, CH₃-Dipp), 1.12 (s, (CH₃)₃C), 1.22 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6H, CH₃-Dipp), 1.30 (br, 7H, CH₃-Dipp and H_A), 1.38 (d, ${}^{2}J_{HP} = 7.6$ Hz, ${}^{3}J_{HPt} = 57.6$ Hz, 3H, CH₃-P), 1.45 (d, ${}^{2}J_{HP} = 7.1$ Hz, ${}^{3}J_{HPt} = 49.8$ Hz, 3H, CH₃-P), 2.39 (br, 4H, CH-Dipp), 3.92 (ddd, ${}^{3}J_{HH} = 10$ Hz, ${}^{3}J_{HH} = 12$ Hz, ${}^{3}J_{HP} = 3.3$ Hz, ${}^{2}J_{HPt} = 110.8$ Hz, 1H, H_C), 6.95 (br, 3H_{arom}), 7.11 (br, 4H_{arom}), 7.23 (br, 2H_{arom}) ppm. ¹H NMR (400 MHz, CD₂Cl₂, -40 °C): $\delta -0.28$ (t, ${}^{3}J_{\text{HP}} = 9.3$ Hz, ${}^{3}J_{\text{HH}} = 9.3$ Hz, ${}^{2}J_{\text{HPt}} = 28$ Hz, 1H, H_B), 0.70 (s, 9H, $(CH_3)_3C$, 0.77 (m, 7H, CH₃-Dipp and H_A), 0.89 (d, ${}^{3}J_{HH} = 7.4$ Hz, 3H, CH₃-Dipp), 0.91 (d, ${}^{3}J_{HH} = 7.7$ Hz, 3H, CH₃-Dipp), 0.94 (d, ${}^{3}J_{HH} = 6.5$ Hz, 3H, CH₃-Dipp), 0.98(d, ${}^{3}J_{HH}$ = 6.8 Hz, 3H, CH₃-Dipp), 1.17 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 3H, CH₃-Dipp), 1.20 (d, ${}^{3}J_{HH}$ = 6.4 Hz, 6H, CH₃-Dipp), 1.25 (d, ${}^{2}J_{HP}$ =8.2 Hz, ${}^{3}J_{HPt}$ = 56.2 Hz, 3H, CH₃-P), 1.33 (d, ${}^{2}J_{HP}$ =7.2 Hz, ${}^{3}J_{HPt}$ = 48.4 Hz, 3H, CH₃-P), 1.84 (sept, ${}^{3}J_{HH}$ = 6.7 Hz, 1H, CH-Dipp), 1.91 (sept, ${}^{3}J_{HH} = 6.7$ Hz, 1H, CH-Dipp), 2.40 (sept, ${}^{3}J_{HH} = 6.5$ Hz, 1H, CH-Dipp), 2.41 (sept, ${}^{3}J_{HH} = 6.5$ Hz, 1H, CH-Dipp), 3.31 (td, ${}^{3}J_{HH} = 10.6$ Hz, ${}^{3}J_{HP} = 3.0$ Hz, ${}^{2}J_{HP} =$ 109.1 Hz, 1H, H_C), 6.71 (t, ${}^{3}J_{HH} = 7.6$ Hz, 1H, *p*-Dipp'), 6.94 (d, ${}^{3}J_{HH} = 7.5$ Hz, 1H, *m*-Dipp'), 6.99 (d, ${}^{3}J_{HH} = 7.7$ Hz, 1H, *m*-Dipp), 7.07 (d, ${}^{3}J_{HH} = 7.4$ Hz, 1H, *m*-C₆H₃), 7.22 (d, ${}^{3}J_{HH} = 7.3$ Hz, 2H, *m*-Dipp), 7.27 (d, ${}^{3}J_{HH} = 7.9$ Hz, 1H, *m*-Dipp'), 7.32 (t, ${}^{3}J_{HH} = 7.4$ Hz, 1H, *p*-C₆H₃), 7.38 (t, ${}^{3}J_{HH} = 7.8$ Hz, 1 H, *p*-Dipp) ppm. ${}^{13}C{}^{1}H$ NMR (96.6 MHz,

CD₂Cl₂, -40°C): δ 17.6 (d, ¹*J*_{CP} =26 Hz, CH₃-P), 18.3 (d, ¹*J*_{CP} = 26 Hz, CH₃-P), 21.4 (s, CH₃-Dipp), 24.7 (s, CH₃-Dipp), 26.1 (s, CH₃-Dipp), 26.2 (s, CH₃-Dipp), 31.0 (s, CH-Dipp), 31.1 (s, CH-Dipp), 32.1 (s, CH-Dipp), 33.0 (s, CH-Dipp), 31.6 (s, ²*J*_{CPt} = 63 Hz, (CH₃)₃C), 34.7 (s, CH₃)₃C), 45.6 (d, ²*J*_{CP} = 38 Hz, CH₂), 78.0 (d, ¹*J*_{CPt} = 460 Hz, ²*J*_{CP} = 4 Hz, CH₂=CH⁴Bu), 117.0 (s, C_{ipso}-Dipp') 121.0 (s, *p*-Dipp'), 121.5 (s, *m*-Dipp'), 122.5 (s, *m*-Dipp), 122.6 (s, *m*-Dipp), 124.2 (s, *m*-Dipp'), 125.9 (s, *o*-Dipp'), 128.7 (s, *p*-C₆H₃), 128.9 (s, *p*-Dipp), 131.4 (s, *m*-C₆H₃), 131.8 (s, *m*-C₆H₃), 137.7 (s, C_{ipso}-Dipp), 139.1 (s, *o*-Dipp'), 143.9 (d, ¹*J*_{CP} = 33 Hz, C_{ipso}-C₆H₃) 144.8 (s, *o*-C₆H₃), 146.9 (s, *o*-Dipp), 147.1 (s, *o*-Dipp) 147.4 (d, ²*J*_{CP} = 41 Hz, *o*-C₆H₃) ppm. ³¹P{¹H} NMR (161.9 MHz, C₆D₆, 25 °C): δ 23.9 (s, ¹*J*_{PPt} = 4457 Hz) ppm. ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂, -40°C °C): δ 23.7 (s, ¹*J*_{PPt} = 4414 Hz) ppm.



Synthesis of $[Pt_3(\mu-CO)_3(PMe_2Ar^{Dipp_2})_3]$, (4). Complex 3 (0.1 g, 0.14 mmol) was dissolved in C₆H₆ (5 mL) and through this solution CO was bubbled for 5 minutes at room temperature. The product was precipitated as an orange solid, which was filtered and washed with hexane and dried under vacuum. Yield: 68 mg (71%). Single crystals

were obtained by crystallization from CH₂Cl₂:C₆H₁₄ solvent mixtures. Anal. Calcd. for C₉₉H₁₂₉O₃P₃Pt₃: C, 58.14; H, 6.36. Found: C, 58.4; H, 6.8 %. IR (CH₂Cl₂): v_{CO} 1780 cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂, -10° C): δ 0.31 (d, ³J_{HH} = 6.5 Hz, 18 H, CH₃–Dipp), 0.77 (d, ³J_{HH} = 6.5 Hz, 18 H, CH₃–Dipp), 0.81 (d, ³J_{HH} = 6.5 Hz, 18 H, CH₃–Dipp), 0.94 (br, 18 H, CH₃–P), 1.21 (d, ³J_{HH} = 6.5 Hz, 18 H, CH₃–Dipp), 2.46 (sept, ³J_{HH} = 6.7 Hz, 6 H, CH–Dipp), 2.93 (sept, ³J_{HH} = 6.6 Hz, 6 H, CH–Dipp), 7.01 (d, ³J_{HH} = 7.8 Hz, 6 H, *m*–Dipp), 7.07 (d, ³J_{HH} = 6.8 Hz, 6 H, *m*–Dipp), 7.08 (d, ³J_{HH} = 6.8 Hz, 6 H, *m*–C₆H₃), 7.26 (t, ³J_{HH} = 7.8 Hz, 6 H, *p*–Dipp), 7.28 (t, ³J_{HH} = 7.4 Hz, 3 H, *p*–C₆H₃) ppm. ¹³C{¹H} NMR (125.72 MHz, CD₂Cl₂, -10° C): δ 18.2 (m, CH₃–P), 22.0 (s, CH₃–Dipp), 30.8 (s, CH–Dipp), 122.2 (s, *m*–Dipp), 123.2 (s, *m*–Dipp), 126.9 (*p*–C₆H₃), 128.3 (*p*–Dipp), 131.8 (s, *m*–C₆H₃), 135.5 (m, C_{ipso}–C₆H₃), 140.3 (s, *o*–Dipp), 142.8 (m, *o*–C₆H₃), 146.7 (s, C_{ipso}–Dipp), 147.6 (s, C_{ipso}–Dipp), 182.6 (s, CO) ppm. ³¹P{¹H} NMR (121.44 MHz, CD₂Cl₂, 25°C): δ 41.2 (s, ¹J_{PPt} = 4440 Hz, ²J_{PPt} = 504 Hz, ³J_{PP} = 72 Hz) ppm.

III. Platinum catalized hydrosilylation of alkynes

In a NMR tube under N₂ the alkyne (1.35 mmol), the silane (1.35 mmol), hexamethylbenzene (0.07 mmol, internal standard) and **3** (1.35 µmol) were dissolved in C₆D₆ (0.5 mL). The reaction was heated at 80 °C. Selectivities and conversions were determined by ¹H NMR spectroscopy and GC-MS analysis. Alkenylsilane selectivity was unambiguously determined from the coupling constants between the olefinic protons appearing at 5-7.5 ppm, since larger values were found for *E*-vinylsilanes (³*J*_{HH} = 18-20 Hz) than for the *Z*- (³*J*_{HH} = 12-16 Hz) and α -isomers (²*J*_{HH} = 2-3 Hz).³ The identity of the major *E*-isomer was further confirmed by comparison with previously reported data (entries 1,⁴ 2,⁵ 3,⁴ 4,⁶ 5,⁷ 6,⁵ 7,⁵ 8,⁸ 9,⁹ 10,¹⁰ and 12⁹, Table 1).

Hydrisilylation product from entry 11



¹H NMR (400 MHz, C₆D₆, 25°C): δ 0.63 (q, ³*J*_{HH} = 8.0 Hz, 6H, Si-CH₂), 1.01 (t, ³*J*_{HH} = 8.4 Hz, 9H, CH₃), 1.47 (m, 2H, H_A), 1.54 (m, 2H, H_B), 2.01 (m, 2H, H_C), 2.09 (m, 1H, H_H), 5.68 (d, ³*J*_{HH}= 19.2 Hz, 1H, H_F), 5.71 (s, 2H, H_E and H_D), 6.65 (d, ³*J*_{HH}= 19.2 Hz, 1H, H_G) ppm. ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25°C): δ 4.2 (s, Si-CH₂), 7.8 (s,

CH₃), 23.0 (s, C_A), 23.1 (s, C_B), 24.5 (s, C_H), 26.4 (s, C_C), 120.2 (s, C_F), 130.8 (s,C_E), 137.9 (s, C_D), 149.6 (s, C_G) ppm. ²⁹Si{¹H} NMR (49.46 MHz, C₆D₆, 25°C): δ –0.65 (s) ppm. HRMS (CI) *m/z* calcd. (expt.) C₁₄H₂₆Si: 222.4470 (222.1795).

IV. X-Ray structural characterization of new compounds

Crystals of compounds 2a, 3, and 4 were mounted in oil on glass fibres and fixed in a cold nitrogen stream. Data were measured on a Bruker APEX II CCD diffractometer equipped with Ag-K α radiation and graphite monochromator and processed with APEX-W2D-NT (Bruker, 2004), cell refinement and data reduction with SAINT-Plus (Bruker, 2004) and the absorption was corrected by multiscan method applied by SADABS. The structures of the three samples were determined by the direct methods routines in the SHELXS program and refined by full-matrix least-squares methods on F², in SHELXL-97.¹¹ The non-hydrogen atoms were refined anisotropically. Except for the ethylenic hydrogen atoms of compound 2a, which were refined freely, all hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms.

In compound **3**, the tbe ligand is disordered over two positions. All atoms of both molecules were included with partial occupancy and were refined with anisotropic thermal parameters.

In compound **4**, the diffused electron densities resulting from residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.

A summary of the fundamental crystal and refinement data are given in the Table S1. Figures S1 and S2 show the Ortep views of complexes **3** (molecule **B**) and **4**, respectively. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files.

Compound	2a	3	4
Empirical formula	C36 H51 P Pt	C38 H55 P Pt	C49.50 H64.50 O1.50
_			P1.50 Pt1.50
Formula weight	709.83	737.88	1022.60
Temperature	100(2) K	173(2) K	95(2) K
Wavelength	0.71073 Å	0.71073 Å	0.56086 Å
Crystal system	Monoclinic	Triclinic	Hexagonal
Space group	P 2 ₁ /c	P -1	P 63/m
Unit cell dimensions	a = 13.7573(4) Å	a = 9.9449(6) Å	a = 18.9177(4) Å
	$\alpha = 90^{\circ}$	$\alpha = 82.197(2)^{\circ}$	$\alpha = 90^{\circ}$
	b = 11.3705(3) Å	b = 12.8244(7) Å	b = 18.9177(4) Å
	$\beta = 98.1820(10)^{\circ}$	$\beta = 86.808(2)^{\circ}$	β=90°
	c = 20.9159(5) Å	c = 14.3077(8) Å	c = 17.4660(4) Å
	$\gamma = 90^{\circ}$	$\gamma = 72.959(2)^{\circ}$	$\gamma = 120^{\circ}$
Volume	3238.52(15) Å ³	1728.25(17) Å ³	5413.3(2) Å ³
Ζ	4	2	4
Density (calculated)	1.456 Mg/m ³	1.418 Mg/m ³	1.255 Mg/m ³
Absorption coefficient	4.404 mm ⁻¹	4.129 mm ⁻¹	2.150 mm ⁻¹
F(000)	1440	752	2052
Crystal size	$0.21\times0.19\times0.15\ mm^3$	$0.19\times0.12\times0.08\ mm^3$	$0.21\times0.16\times0.12\ mm^3$
Theta range for data	1.97 to 30.65°	2.07 to 28.38°	1.34 to 22.25°
collection			
Index ranges	-19<=h<=19	-13<=h<=13	-25<=h<=19
	-16<=k<=16	-17<=k<=16	-15<=k<=25
	-27<=]<=29	-18<=1<=19	-22<=]<=23
Reflections collected	28865	13503	43366
Independent reflections	9981 [R(int) = 0.0445]	8429 [R(int) = 0.0161]	4797 [R(int) = 0.0619]
Completeness to theta $= 30.65^{\circ}$	99.6 %	97.4 %	99.6 %
Absorption correction	Semi-empirical from	Semi-empirical from	Semi-empirical from
	equivalents	equivalents	equivalents
Max. and min.	0.7461 and 0.5028	0.7457 and 0.4910	0.7447 and 0.6331
	0001 / 0 / 205	8420 / 21 / 441	4707 / 0 / 177
parameters	9981/0/385	8429/21/441	4/9//0/1//
Goodness-of-fit on F ²	0.904	1.284	0.644
Final R indices	R1 = 0.0268	R1 = 0.0489	R1 = 0.0237
[I>2sigma(I)]	wR2 = 0.0556	wR2 = 0.0914	wR2 = 0.0760
R indices (all data)	R1 = 0.0406	R1 = 0.0653	R1 = 0.0302
	wR2 = 0.0608	wR2 = 0.0993	wR2 = 0.0830
Largest diff. peak and hole	1.317 and -1.726 e.Å ⁻³	1.352 and -1.318 e.Å ⁻³	0.931 and -1.222 e.Å ⁻³

Table S1: Crystal data and structure refinement for compounds 2a, 3, and 4.



Figure S1. ORTEP view of the solid structure of 2a with ellipsoids drawn at the 50% probability level. Selected bond distances [Å] and angles [°]: Pt1–P1 2.2866(6), Pt1–C1 2.117(3), Pt1–C2 2.115(3), Pt1–C3 2.121(3), Pt1–C4 2.115(3), C1–C2 1.425(4), C3–C4 1.414(4), P1-Pt1-centroid(C1-C2) 113.82, P1-Pt1-centroid(C3-C4) 113.22, centroid(C3-C4)-Pt1-centroid(C1-C2) 132.67.



Figure S2. ORTEP view of the solid structure of **3** (molecule **A**) with ellipsoids drawn at the 30% probability level. Selected bond distances [Å] and angles [°]: Pt0–P1 2.193(2), Pt0–C1 2.10(1), Pt0–C2 2.063(8), Pt0–C27 2.314(4), C1–C2 1.40(1); P1-Pt0-centroid(C1-C2) 141.6, C27-Pt0-centroid(C1-C2) 135.1, C27-Pt0-P1 83.1(1).



Figure S3. ORTEP view of the solid structure of 3 (molecule B) with ellipsoids drawn at the 30% probability level. Selected bond distances [Å] and angles [°]: Pt1–P1 2.276(2), Pt1–C1 2.11(1), Pt1–C2 2.14(1), Pt1–C27 2.257(4), C1–C2 1.40(1); P1-Pt1-centroid(C1-C2) 134.9, centroid(C27-C32)-Pt1-centroid(C1–C2) 129.9, centroid(C27-C32)-Pt1-P1 92.7.



Figure S4. ORTEP view of the solid structure of **4** with ellipsoids drawn at the 30% probability level. Selected bond distances [Å] and angles [°]: Pt1–P1 2.258(1), Pt1–C21 2.076(4), Pt1–C21' 2.036(4), Pt1–Pt1' 2.6462(2), C21-Pt1-Pt1' 109.3(1), C21-Pt1-Pt1'' 49.3(1), C21-Pt1-P1 94.4(1), C21'-Pt1-P1 105.7(1), Pt1'-Pt1-Pt1'' 60.0.

V. <u>References</u>

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