Supporting Information: A Mechanistic Study of Allene Carboxylation with CO_2 Resulting in the Development of a Pd(II) Pincer Complex for the Catalytic Hydroboration of CO_2

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Experimental details

General experimental methods and procedures

All experiments were carried out under a dinitrogen atmosphere using standard Schlenk techniques or in an MBraun glovebox (under standard glovebox conditions purging was not performed between uses of pentane, diethyl ether, benzene, toluene and THF; thus when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles). Solvents for air- and moisture-sensitive reactions were deoxygenated and dried by sparging with dinitrogen followed by passage through a column of activated alumina from Innovative Technology Inc. All commercial chemicals were used as received unless noted otherwise. Anhydrous carbon dioxide and ethylene were obtained from Airgas, Inc. 1,1-dimethylallene was purchased from VWR International. $AlEt_3$ was obtained from Strem Chemicals, Inc. C_6D_6 and d_8-toluene were purchased from Cambridge Isotopes Laboratories, Inc., dried over sodium/benzophenone ketyl and vacuum transferred prior to use. $LiEt_3BH$ and AgOTf were purchased from Acros Organics. NMR spectra were recorded on Bruker AMX-400 and -500 spectrometers or Agilent DD2 -400, -500, -600 spectrometers at ambient probe temperatures. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ NMR spectra, or to an external standard for $^{31}P\{^1H\}$ (85% H_3PO_4 in D_2O at δ 0.0 ppm),$^{29}Si\{^1H\}$ spectra ($SiMe_4$ in C_6D_6 at δ 0.0 ppm) and $^{19}F\{^1H\}$ (CF_3CO_2H in $CDCl_3$ at δ -76.55 ppm). Elemental analyses were performed by Robertson Microlit Laboratories, Inc. under inert atmosphere. The compounds (^{Cy}PSiP)PdCl, (^{Cy}PSiP)PdH (**1**) and (^{Cy}PSiP)Pd{OC(O)H} (**2**) were synthesized following literature procedures.[1]

Synthesis and Characterization of Compounds

*(^{Cy}PSiP)Pd(η^1-prenyl) (**3**)*

To a solution of **1** (85.5 mg, 0.123 mmol) in 4 mL of benzene, 1.15 equivalents of 1,1-dimethylallene (14 μL, 9.72 mg, 0.142 mmol) was added. The solution instantly changed from colorless to bright orange. The volatiles were removed under reduced pressure, and the remaining solids were dissolved in cold pentane and recrystallized at -35 °C to give **3** as an orange solid. Yield 68 mg (73 %). In C_6D_6, **3** rearranged to **4**. Complete conversion was observed after 3 days at room temperature.

^{1}H NMR (C_6D_6, 400.0 MHz): 8.19 (2H, d, Ar*H*, *J* = 7.2 Hz), 7.54 (2H, d, Ar*H*, *J* = 7.7 Hz), 7.33 (2H, t, Ar*H*, *J* = 7.4 Hz), 7.23 (2H, t, Ar*H*, *J* = 7.4 Hz), 6.44 (1H, t, $CH_2CH(CH_3)_2$, *J* = 9.0 Hz), 2.57-2.48 (6H, Cy*H* and $CH_2CH(CH_3)_2$), 2.14 (3H, s, CH_3), 2.11 (2H, Cy*H*), 2.05 (3H, s, CH_3), 1.97-1.85 (4H, Cy*H*), 1.75 (2H, d, Cy*H*, *J* = 11.7 Hz) 1.68-1.59 (6H, Cy*H*), 1.52-0.80 (26H, Cy*H*), 0.76 (3H, s, Si*Me*). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): 158.4 (t, J = 26.4 Hz), 143.7 (t, *J* = 19.8 Hz), 136.1, 133.3 (t, *J* = 11.3 Hz), 131.3, 129.9, 128.13 (t, *J* = 2.4 Hz), 112.5, 37.6 (t, *J* = 11.1 Hz), 36.6 (t, *J* = 11.1 Hz), 31.6 (t, *J* = 4.0 Hz), 29.7, 28.8, 28.7, 27.9 (t, *J* = 7.3 Hz), 27.7-27.4 (overlapping resonances), 27.2, 26.4, 18.5, 16.15 (t, *J* = 8.6 Hz), 8.57. ^{31}P{^{1}H} NMR (C_6D_6, 202.0 MHz): 61.0. ^{29}Si{^{1}H} NMR (C_6D_6, 99.3 MHz): 63.9 (t, *J* = 6.6 Hz). Anal. Found (calcd for $C_{42}H_{64}P_2PdSi$): C, 66.13 (65.91); H, 8.49 (8.43).

(κ^2-$Cy_2PC_6H_4SiMe(prenyl)$)Pd(κ^2-$Cy_2PC_6H_4$) (***4***)

To a solution of **1** (38.5 mg, 0.055 mmol) in 5 mL of pentane, approximately 10 equivalents of 1,1-dimethylallene (50 μL, 0.51mmol) was added. The solution was heated at 50 °C for one hour until the solution became colorless. The volatiles were removed and the product was precipitated from pentane at -35 °C to yield **4** as an off-white powder. Yield 30.5 mg (72 %). Further recrystallization from pentane at room temperature yielded a colorless crystalline solid suitable for X-ray crystallography.

^{1}H NMR (C_6D_6, 400.0 MHz): 8.30 (1H, m, Ar*H*), 7.84 (1H, d, Ar*H*, *J* = 7.1 Hz), 7.46-7.39 (2H, m, Ar*H*), 7.31 (1H, td, Ar*H*, *J* = 7.4, 3.0 Hz), 7.22-7.19 (3H, m, Ar*H*), 5.49 (1H, t, $CH_2CH(CH_3)_2$, *J* = 8.4 Hz), 2.53 (1H, dd, $CH_2CH(CH_3)_2$, *J* = 13.2, 8.7 Hz), 2.35 (1H, m, $CH_2CH(CH_3)_2$), 2.28-1.98 (8H, Cy*H*), 1.91 (1H, br d, Cy*H*, *J* = 13.2 Hz), 1.83 (2H, br d, Cy*H*, *J* = 11.3 Hz), 1.72-1.51 (15H, Cy*H*), 1.61 (3H, s, $CH_2CH(CH_3)_2$), 1.49 (3H, s, $CH_2CH(CH_3)_2$), 1.45-1.07 (18H, Cy*H*), 1.01 (3H, d, Si*Me*, *J* = 3.2 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): 168.9 (dd, *J* = 110.3, 5.1 Hz), 161.7 (dd, *J* = 60.1, 7.3 Hz), 149.9 (dd, *J* = 33.7, 4.6 Hz), 139.5 (dd, *J* = 42.2, 7.6 Hz), 135.5 (dd, *J* = 22.3, 4.3 Hz), 134.0 (dd, *J* = 24.2, 3.1 Hz), 130.1, 130.0, 129.7 (d, *J* = 7.9 Hz), 129.4 (dd, *J* = 6.4, 4.2 Hz), 125.7, 124.7, 124.4 (d, *J* = 5.3 Hz), 36.9 (d, *J* = 16.7, 2.3 Hz), 34.6 (d, *J* = 17.3, 1.7 Hz), 33.4, 32.0, 30.8 (d, *J* = 9.2 Hz), 30.7 (d, *J* = 8.4 Hz), 30.2 (m), 30.0 (d, *J* = 6.2 Hz), 29.4 (d, *J* = 3.8 Hz), 29.2, 28.6, 28.0-26.4 (overlapping resonances), 26.2, 23.8 (d, *J* = 6.8 Hz), 18.2, 3.8 (d, *J* = 8.4 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 202.0 MHz): 68.7 (d, *J* =

19.2 Hz), -39.4 (d, J = 18.7 Hz). $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99.3 MHz): 35.5 (dd, J = 164.7, 10.6 Hz). Anal. Found (calcd for $C_{42}H_{64}P_2PdSi$): C, 65.65 (65.91); H, 8.37 (8.43).

(^{Cy}PSiP)Pd(carboxylate) (***5***)

3 (50.0 mg, 0.065 mmol) was dissolved in 0.5 mL of d_8-toluene in a J. Young NMR Tube at room temperature under N_2 atmosphere. The solution was degassed and an excess of 1 atm carbon dioxide was added via a dual manifold Schlenk line. The solution changed from bright orange to colorless over 15 minutes. The volatiles were removed under reduced pressure, and the remaining solids were washed with pentane (2 x 1 mL) to give **5** as a white powder. Yield 40.1 mg (77 %). Recrystallization from benzene-pentane at room temperature gave a colorless crystalline solid suitable for X-ray crystallography.

^{1}H NMR (C_6D_6, 400 MHz): 7.99 (2H, d, Ar*H*, J = 7.4 Hz), 7.39 (2H, d, Ar*H*, J = 7.4 Hz) 7.29 (2H, t, Ar*H*, J = 7.3 Hz), 7.18 (2H, t, Ar*H*, J = 7.7 Hz), 6.89 (1H, dd, $C(CH_3)_2CHCH_2$, J = 17.6, 10.7 Hz), 5.29 (1H, dd, *trans-H*, J = 17.6, 1.8 Hz), 5.15 (1H, dd, *cis-H*, J = 10.8, 1.8 Hz), 2.67 (2H, t, Cy*H, J* = 11.5 Hz), 2.42-2.34 (4H, Cy*H*), 2.16 (2H, d, Cy*H*, J = 12.9 Hz), 1.75 (6H, s, $C(CH_3)_2CHCH_2$), 1.74-1.18 (32H, Cy*H*), 1.02 (2H, qt, Cy*H*, J = 12.5, 3.2 Hz), 0.96 (2H, qt, Cy*H*, J = 12.9, 3.6 Hz), 0.79 (3H, s, Si*Me*). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.6 MHz): 179.4, 156.9 (t, J = 26.8 Hz), 149.2, 140.4 (t, J = 19.9 Hz), 133.0 (t, J = 11.8 Hz), 131.4, 130.4, 128.9 (t, J = 3.0 Hz), 108.4, 47.1, 36.3 (t, J = 10.6 Hz), 35.9 (t, J = 10.5 Hz), 29.9 (t, J = 3.2 Hz), 29.3, 29.2, 27.8 (t, J = 5.4 Hz), 27.4 (m), 26.8, 26.6, 26.1, 8.90. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz): 57.2. $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99.3 MHz): 50.7. Anal. Found (calcd for $C_{43}H_{64}O_2P_2PdSi$): C, 63.59 (63.81); H, 7.98 (7.97).

(^{Cy}PSiP)Pd(Et) (***6***)

To a solution of **2** (74.6 mg, 0.101 mmol) in 4 mL toluene at -35°C, 1 equivalent of $AlEt_3$ (0.6M in heptanes, 0.17 mL, 0.102 mmol) was added dropwise. The color of the solution changed from colorless to yellow immediately. The solution was warmed to room temperature over 5 minutes. Subsequently, the volatiles were removed under reduced pressure. Recrystallization at -35°C from diethyl ether yielded **6** as a yellow solid. Yield 31.2 mg (42 %). The isolated product contains (^{Cy}PSiP)Pd{OCH(O)$AlEt_3$)} (**9**) as an impurity (see NMR spectra in Figures S1-S4), and was not characterized by elemental analysis. Furthermore, **6** is unstable in solution at room temperature and complete ligand rearrangement to **7** was observed at room temperature over two

and a half days. Recrystallization from diethyl ether at -35°C gave a yellow crystalline solid suitable for X-ray crystallography.

^{1}H NMR (C_6D_6, 500 MHz): 8.24 (2H, d, Ar*H*, *J* = 7.3 Hz), 7.57 (2H, d, Ar*H*, *J* = 7.7 Hz), 7.35 (2H, t, Ar*H*, *J* = 7.3 Hz), 7.24 (2H, t, Ar*H*, *J* = 7.5 Hz), 2.60 (2H, m, Cy*H*), 2.46 (2H, t, Cy*H*, *J* = 12.4 Hz), 2.27 (2H, d, Cy*H*, *J* = 12.6 Hz), 2.07 (3H, t, PdCH$_2$C*H*$_3$, *J* = 7.7 Hz), 2.04 (2H, m, Cy*H*), 1.84 (2H, d, Cy*H*, *J* = 12.9 Hz), 1.75-0.90 (39H, overlapping resonances, Cy*H* and Pd C*H*$_2$CH$_3$), 0.74 (3H, s, Si*Me*). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz): 153.7 (t, *J* = 25.5 Hz), 137.7 (t, *J* = 21.7 Hz), 132.8 (t, *J* = 11.6 Hz), 131.9, 131.1, 129.8, 36.1 (t, *J* = 10.9 Hz), 35.7 (t, *J* = 10.5 Hz), 30.9, 30.0, 29.8, 29.0, 27.3 (t, *J* = 5.5 Hz), 27.2-27.0 (overlapping resonances), 26.5, 26.1, 10.8, 9.02, 1.54. ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): 61.8. ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): 64.9 (t, *J* = 7.5 Hz).

(κ^2-Cy$_2$PC$_6$H$_4$SiMeEt)Pd(κ^2-Cy$_2$PC$_6$H$_4$) (7)

(**1** + ethylene): To a degassed solution of **1** (30 mg, 0.043 mmol) in 0.5 mL of C_6D_6 in a J. Young tube, an excess of 1 atm ethylene was added. After five minutes, the volatiles were removed under vacuum to yield colorless oil, which was subsequently dissolved in pentane and recrystallized at -35 °C. Compound **7** was isolated as a white powder. Yield 28.4 mg (89 %). X-ray quality crystals were obtained from slow evaporation of pentane at room temperature. For unknown reasons satisfactory elemental analysis was not obtained for **7**, and therefore NMR spectra are provided below.

(**1** + AlEt$_3$): A suspension of **1** (10.0 mg, 0.013 mmol) in 3 mL acetonitrile was heated until all solids dissolved. Subsequently, the solution was slowly cooled to room temperature to yield colorless crystalline solids. The formation of **7** was confirmed by ^{1}H and ^{31}P NMR spectroscopy.

^{1}H NMR (C_6D_6, 400 MHz): 8.26 (1H, m, Ar*H*), 7.79 (1H, d, Ar*H*, *J* = 7.3 Hz), 7.43 (2H, app t, Ar*H*, *J* = 6.0 Hz), 7.32 (1H, td, Ar*H*, *J* = 7.1, 2.8 Hz), 7.23 (1H, br t, Ar*H*, *J* = 7.2 Hz), 7.19 (2H, t, Ar*H*, *J* = 7.4 Hz), 2.30-2.07 (7H, Cy*H*), 2.00 (1H, d, Cy*H*, *J* = 14.1 Hz), 1.92 (1H, d, Cy*H*, *J* = 13.2 Hz), 1.81 (2H, d, Cy*H*, *J* = 12.8 Hz), 1.74-0.92 (35H, Cy*H* and SiC*H*$_2$CH$_3$), 1.23 (3H, t, SiCH$_2$C*H*$_3$, *J* = 7.6 Hz), 0.99 (3H, d, Si*Me*, *J* = 3.1 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): 169.0 (dd, *J* = 109.9, 5.0 Hz), 161.9 (dd, *J* = 60.6, 7.1 Hz), 150.1 (dd, *J* = 33.7, 4.6 Hz), 139.8 (dd, *J* = 41.7, 7.8 Hz), 135.5 (dd, *J* = 22.2, 4.0 Hz), 133.6 (dd, *J* = 24.1, 2.9 Hz), 130.2, 130.2 (d, *J* = 2.6 Hz), 129.7 (d, *J* = 7.4 Hz), 129.4 (dd, *J* = 6.2, 4.3 Hz), 127.9 (d, *J* = 2.4 Hz), 124.4 (d, *J* =

5.1 Hz), 37.0 (dd, *J* = 109.9, 5.0 Hz), 34.6 (dd, *J* = 17.3, 2.3 Hz), 33.5, 32.1, 30.9 (d, *J* = 7.2 Hz), 30.7 (d, *J* = 9.1 Hz), 30.2 (t, *J* = 5.5 Hz), 30.1 (d, *J* = 3.1 Hz), 30.1, 29.6 (d, *J* = 4.0 Hz), 29.2, 28.6, 27.8, 27.7 (d, *J* = 13.4 Hz), 27.7, 27.6 (d, *J* = 3.0 Hz), 27.4 (d, *J* = 4.2 Hz), 27.3, 27.3, 27.2, 27.0, 26.7, 26.7, 26.5, 13.9 (d, *J* = 7.2 Hz), 11.4, 3.85 (d, *J* = 8.1 Hz). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz): 69.0 (d, *J* = 19.2 Hz), -38.7 (d, *J* = 19.2 Hz). $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99.3 MHz): 41.1 (dd, *J* = 160.4, 9.8 Hz).

(^{Cy}PSiP)Pd($HAlEt_3$) (***8***)

A solution of **1** (30.0 mg, 0.039 mmol) in 2 mL of pentane was treated with 1 equivalent of $AlEt_3$ (0.6 M in heptanes, 65 μL, 0.039 mmol). The volatiles were removed under vacuum to yield white solid, which was subsequently dissolved in pentane, concentrated, and recrystallized at -35 °C to give **8** as colorless crystalline solid. Yield 30.5 mg (87 %). For unknown reasons satisfactory elemental analysis was not obtained for **8**, and therefore NMR spectra are provided below.

^{1}H NMR (C_6D_6, 400 MHz): 7.97 (2H, d, Ar*H*, *J* = 7.3 Hz), 7.37 (2H, d, Ar*H*, *J* = 6.5 Hz), 7.29 (2H, t, Ar*H*, *J* = 7.3 Hz), 7.17 (2H, t, Ar*H*, *J* = 7.5 Hz), 2.72 (2H, t, Cy*H, J* = 10.3 Hz), 2.30 (2H, br s, Cy*H*), 2.19-2.14 (6H, Cy*H*), 1.97-1.92 (4H, m, Cy*H*), 1.79 (9H, t, $AlCH_2CH_3$, *J* = 8.0 Hz), 1.62-1.55 (8H, Cy*H*), 1.48 (2H, d, Cy*H*, *J* = 13.1 Hz), 1.37-1.17 (12H, Cy*H*), 1.04-0.82 (8H, Cy*H*), 0.79 (3H, s, Si*Me*), 0.63 (6H, q, $AlCH_2CH_3$, *J* = 8.1 Hz), 0.30 (1H, t, Al-*H*, *J* = 14.1 Hz). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.6 MHz): 155.8 (t, *J* = 26.2 Hz), 140.9 (t, *J* = 20.3 Hz), 133.2 (t, *J* = 12.0 Hz), 133.2, 131.5, 129.0 (t, *J* = 2.7 Hz), 37.0 (t, *J* = 10.5 Hz), 35.9 (t, *J* = 12.3 Hz), 31.3, 29.7, 29.2, 28.2, 27.4, 27.3 (t, *J* =7.4 Hz), 27.2 (t, *J* = 6.5 Hz), 26.9 (t, *J* = 6.3 Hz), 26.7, 26.4, 11.9, 9.0, 3.1. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.0 MHz): 67.2. $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99 MHz): 63.9.

(^{Cy}PSiP)Pd{OCH(O)$AlEt_3$)} (***9***)

Stoichiometric reaction: To a solution of **2** (8 mg, 0.0108 mmol) in 0.5 mL of d_8-toluene at -95°C, 1.0 equivalent $AlEt_3$ (0.6M solution in heptane, 18 μL, 0.0108 mmol) was added. Immediate formation of products was observed by ^{1}H NMR spectroscopy at room temperature. The resulting spectra showed that **9** along with (^{Cy}PSiP)Pd(Et) (**6**) had formed in an approximate ratio of 1:1. Over 12 hours, NMR spectroscopy showed full conversion of **9** to the **6**. A small amount of **7** was also observed as a side product.

Recrystallization: A solution of **2** (20 mg, 0.027 mmol) in 1 mL toluene was charged with $AlEt_3$ (0.6M solution in heptane, 45 μL, 0.027 mmol), and subsequently layered with 1.5 mL of pentane at -35°C to yield colorless crystals of **9** of X-ray quality.

Characteristic resonances for **9**: ^{1}H NMR (d_8-toluene, 500 MHz): 8.88 (2H, s), 7.83 (2H, d, J = 7.4 Hz), 7.28 (2H, br d, J = 7.7 Hz), 0.69 (3H, s, Si*Me*) 0.42 (4H, q, AlCH_2CH$_3$, J = 8.1 Hz). ^{31}P{^{1}H} NMR (d_8-toluene, 202 MHz): 57.4. ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): 50.6.

(^{Cy}PSiP)Pd(OTf) (***10***)

To a solution of (^{Cy}PSiP)PdCl (50.0 mg, 0.0683 mmol) in 4 mL of benzene at room temperature, AgOTf (17.6 mg, 0.0684 mmol) was added. A precipitate was immediately observed. The solution was sonicated for 1 hour, and subsequently filtered through Celite to yield a colorless solution. The volatiles were removed under reduced pressure and the residue was triturated with cold pentane to yield **10** as an off-white solid. Yield 52.6 mg (91 %). X-ray quality crystals were obtained from slow evaporation of pentane at room temperature.

^{1}H NMR (C_6D_6, 400 MHz): 7.85 (2H, d, Ar*H*, J = 7.3), 7.32 (2H, app d, Ar*H*, J = 7.7 Hz), 7.25 (2H, t, Ar*H*, J = 7.4 Hz), 7.15 (2H, t, Ar*H*, J = 7.6 Hz), 2.73 (2H, t, 2H, J = 12.2 Hz), 2.61 (2H, t, 2H, J = 12.2 Hz), 2.44 (2H, app s), 2.26 (2H, app d, J = 13.0 Hz), 1.71-1.07 (36H, overlapping resonances), 0.72 (3H, s, Si*Me*). ^{13}C{^{1}H} NMR (C_6D_6, 76 MHz): 154.8 (t, J = 25.6 Hz), 138.5 (t, J = 20.8 Hz), 132.9 (t, J = 11.5 Hz), 132.0, 130.8, 129.5 (t, J = 3.1 Hz), 36.0 (t, J = 10.7 Hz), 35.4 (t, J = 10.5 Hz), 30.7 (t, J = 3.3 Hz), 29.8 (t, J = 1.6 Hz), 29.7, 29.2, 27.4 (t, J = 5.7 Hz), 27.2-27.0 (overlapping resonances), 26.7, 26.0, 9.25. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): 57.1. ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): 99.3. ^{19}F{^{1}H} NMR (C_6D_6, 376 MHz): -77.2. Anal. Found (calcd for $C_{38}H_{55}F_3O_3P_2PdSSi$): C, 53.79 (53.99); H, 6.45 (6.56).

(^{Cy}PSiP)Pd{OTf(AlEt$_3$)} (***11***)

To a solution of **10** (32 mg, 0.039 mmol) in 4 mL benzene, $AlEt_3$ (0.6 M in heptane, 65 μL, 0.039 mmol) was added dropwise at room temperature. The solution was immediately filtered through Celite and the volatiles were removed under reduced pressure. The remaining residue was washed with cold pentane and dried *in vacuo* to give **11** as a white powder. Yield 27.5 mg (74 %). For unknown reasons satisfactory elemental analysis was not obtained for **10**, and therefore NMR spectra are provided below.

^{1}H NMR (d_8-toluene, 400 MHz): 7.80 (2H, d, Ar*H*, *J* = 7.1), 7.29 (2H, br d, Ar*H*, *J* = 7.1 Hz), 7.25 (2H, t, Ar*H*, *J* = 7.5 Hz), 7.16 (2H, t, Ar*H*, *J* = 7.5 Hz), 2.54 (4H, m, Cy*H*), 2.30 (2H, br s, Cy*H*), 2.22 (2H, br d, Cy*H*, *J* = 13.1 Hz), 1.78 (m, Cy*H*), 1.66-0.95 (48H, overlapping resonances), 0.69 (3H, s, Si*Me*), 0.49 (4H, q, AlCH_2CH$_3$, *J* = 8.4 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz): 153.7 (t, *J* = 25.5 Hz), 137.7 (t, *J* = 21.6 Hz), 132.8 (t, *J* = 11.6 Hz), 131.9, 131.1, 129.8, 36.1 (t, *J* = 10.8 Hz), 35.7 (t, *J* = 10.5 Hz), 30.7, 30.0, 29.8, 29.0, 27.3 (t, *J* = 5.6 Hz), 27.2-27.0 (overlapping resonances), 26.5, 26.1, 10.8, 9.02, 1.54. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): 56.7. ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): 51.7. ^{19}F{^{1}H} NMR (C_6D_6, 376 MHz): -77.0.

Catalytic Procedures

General procedure for the carboxylation of 1,1,-dimethylallene (Table 1)

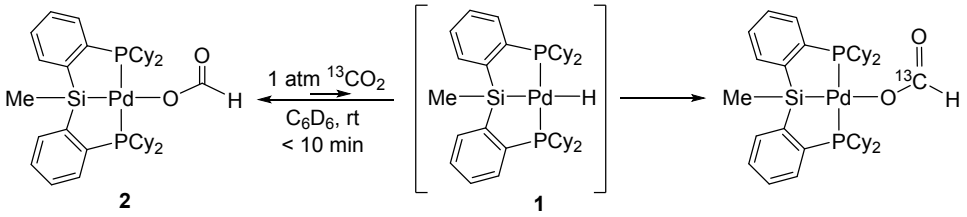
A 25 mL Schlenk flask was charged with a solution of [Pd] catalyst (1.4 mg, 0.002 mmol) and 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol, internal standard) in 0.40 mL of C_6D_6 under an N_2 atmosphere. The solution was frozen and 1,1-dimethylallene (1M solution in C_6D_6, 0.10 mL, 0.10 mmol) was added to the side of the Schlenk flask. The N_2 atmosphere was replaced with 1 atm of CO_2 using a dual manifold Schlenk line. The reaction mixture was warmed to room temperature and $AlEt_3$ (0.6M solution in heptanes, 0.25 mL, 0.15 mmol) was added via a syringe. The reaction was stirred at 50°C for 24 hours. An aliquot was taken directly out of Schlenk flask to a screw cap NMR tube for quantification using ^{1}H NMR spectroscopy. In some cases, following the work up procedures described by Iwasawa and co-workers,[2] (addition of HCl (0.4 M in diethyl ether), extraction with diethyl ether and NaOH (aq), washing with saturated NaCl(aq) and drying over magnesium sulfate), the crude carboxylic acid was isolated and quantified. This confirmed the yields determined using ^{1}H NMR spectroscopy.

General procedure for the hydroboration of CO_2 (Table 2)

A solution of **1** (1-0.001 mol%), HB(pin) (7.2 μL, 0.050 mmol) and 1,3,5-trimethoxybenzene (0.050 mmol, internal standard) in 0.5 mL of C_6D_6 was added to a J. Young NMR tube. The sample was degassed using three freeze-pump-thaw cycles and 1 atm of CO_2 was introduced via a Schlenk line. The formation of (pin)BOC(O)H was monitored over time using ^{1}H NMR spectroscopy.

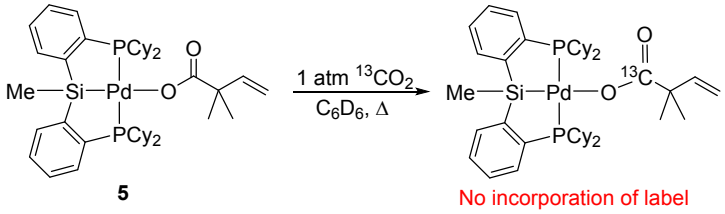
Supplementary experimental details

*Reversibility of CO_2 insertion into (^{Cy}PSiP)Pd{OC(O)H} (**2**)*



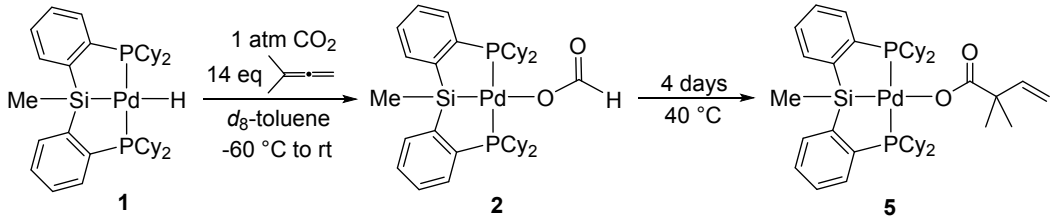
A solution of (^{Cy}PSiP)Pd{OC(O)H} (**2**) (3 mg, 0.0040 mmol) in 0.5 mL C_6D_6 was transferred to a J. Young NMR tube, and degassed through three freeze-pump-thaw cycles. Subsequently, 1 atm of $^{13}CO_2$ was introduced via a dual manifold Schlenk line at room temperature. Within minutes, $^{13}CO_2$ incorporation was observed by ^{1}H NMR spectroscopy. The characteristic formate proton resonance was observed as a doublet at 9.50 ppm (J = 186.5 Hz). The rapid exchange suggests that although **2** does not decompose under vacuum, CO_2 insertion/deinsertion into (^{Cy}PSiP)PdH (**1**) is facile a process in solution under ambient conditions.

*Reaction of (^{Cy}PSiP)Pd(carboxylate) (**5**) with $^{13}CO_2$*



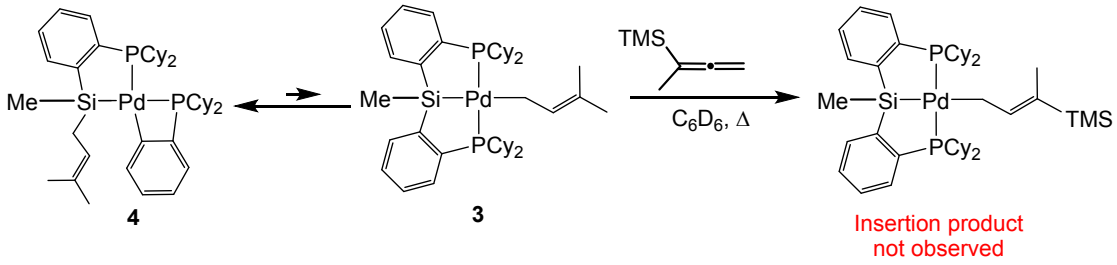
(^{Cy}PSiP)Pd(carboxylate) (**5**) (5.0 mg, 0.0062 mmol) was dissolved in 0.5 mL of C_6D_6 at room temperature and transferred to a J. Young NMR tube. The sample was degassed by three freeze-pump-thaw cycles, and 1 atmosphere of $^{13}CO_2$ was added via a dual manifold Schlenk line. No reaction was observed at room temperature after 24 hours. The temperature was increased once a day from 30°C, 50°C, to 70°C, but no incorporation of $^{13}CO_2$ was observed using $^{13}C\{^1H\}$ NMR spectroscopy. At 90 °C, product decomposition was observed with accumulation of Pd black.

*Competitive reaction of (^{Cy}PSiP)PdH (**1**) with CO_2 and 1,1-dimethylallene*



(^{Cy}PSiP)PdH (**1**) (5.0 mg, 0.0072 mmol) was dissolved in 0.5 mL d_8-toluene and transferred to a J. Young NMR tube. The sample was degassed using three freeze-pump-thaw cycles on a Schlenk line. A second J. Young NMR tube was charged with approximately 14 equivalents of 1,1-dimethylallene (10.0 µL, 0.102 mmol) and degassed as well. 1 atm of CO_2 was introduced to the tube containing 1,1-dimethylallene and subsequently the contents of this tube were vacuum transferred to the NMR tube containing the frozen solution of **1**. The frozen sample was taken to the NMR spectrometer in a liquid N_2 bath and warmed up in the spectrometer to -60 °C. At this point ^{31}P NMR spectroscopy indicated that **1** had been fully converted to a mixture containing predominantly **2**, with a small amount of **5**. Over 4 days the reaction mixture was heated at 50 °C, and full conversion to **5** was observed by both ^{1}H and ^{31}P NMR spectroscopy.

*Reaction of (^{Cy}PSiP)Pd(η^1-prenyl) (**3**) with 1-methyl-1-(trimethylsilyl)allene*



In order to determine if the insertion of 1,1-dimethylallene into (^{Cy}PSiP)PdH (**1**) was reversible, we dissolved an isolated sample of (^{Cy}PSiP)Pd(η^1-prenyl) (**3**) (3.0 mg, 0.0039 mmol) in 0.5 mL of C_6D_6 in a screw cap NMR tube. A slight excess of 1-methyl-1-(trimethylsilyl)allene (0.7 µL, 0.0042 mmol) was added to the solution using a micro syringe. If the insertion of 1,1-dimethylallene is reversible, it was expected that a product consistent with the insertion of 1-methyl-1-(trimethylsilyl)allene into (^{Cy}PSiP)PdH (**1**) would have been observed, assuming that the products formed from the insertion of 1,1-dimethylallene and 1-methyl-1-(trimethylsilyl)allene are approximately equally thermodynamically favorable. However there was no evidence for a product consistent with the insertion of 1-methyl-1-(trimethylsilyl)allene and incremental increases in temperature only showed formation of the ligand rearranged product **4** by ^{1}H NMR spectroscopy. At 90 °C, decomposition of the product was observed.

*Reaction between (^{Cy}PSiP)Pd(η^1-prenyl) (**3**) and $AlEt_3$*

(^{Cy}PSiP)Pd(η^1-prenyl) (**3**) (2.0 mg, 0.0026 mmol) was dissolved in 0.5 mL of C_6D_6 and transferred to a screw cap NMR tube. One equivalent of $AlEt_3$ (0.6 M in heptanes, 4.4 µL, 0.026

mmol) was added using a micro syringe and the reaction mixture was left to sit at room temperature for 10 minutes. No apparent reaction was observed by ^{1}H and ^{31}P NMR spectroscopy. When the reaction mixture was heated to 50 °C, only the formation of **4** was observed. No further reaction was observed when the reaction mixture containing $AlEt_3$ and **4** was left to sit in the 50 °C oil bath for an hour.

*Reaction of (^{Cy}PSiP)Pd(carboxylate) (**5**) and $AlEt_3$ (Scheme 5)*

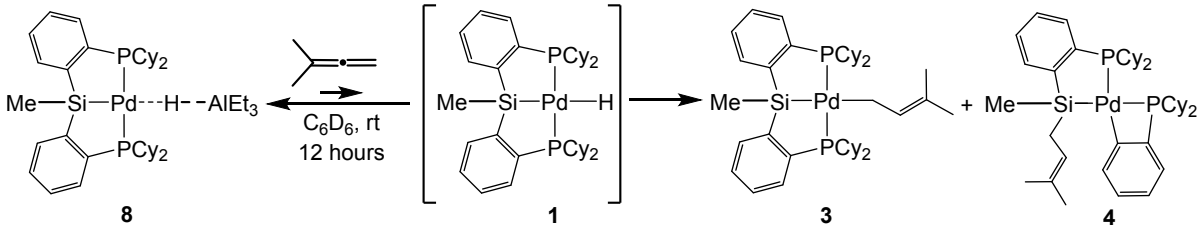
(**5** + 1 eq. $AlEt_3$): A solution of (^{Cy}PSiP)Pd(carboxylate) (**5**) (3.4 mg, 0.00421 mmol) in 0.5 mL of C_6D_6 was transferred to a screw cap NMR tube, and 1 equivalent of $AlEt_3$ (0.6 M in toluene, 7.0 µL, 0.00421 mmol) was added using a micro syringe. An instantaneous reaction was observed accompanied by the solution turning bright yellow. After 10 minutes, less than 3% of the starting material was observed in the ^{1}H NMR spectrum. In addition, a new set of carboxylate peaks were present (characteristic resonances at 5.84 (dd, J = 17.3, 10.6 Hz), 4.95 (d, J = 17.4 Hz), and 4.91 (d, J = 10.5 Hz)), which were assigned to an Al carboxylate. The addition of acid resulted in the appearance of peaks consistent with 2,2-dimethylbut-3-enoic acid. The resulting Pd complex was identified as **6** by ^{1}H and ^{31}P NMR spectroscopy. Upon addition of an additional equivalent of $AlEt_3$, the solution became colorless. Within 2 hours, the ^{1}H NMR spectrum showed formation of **8** along with the release of ethylene.

(**5** + 2 eq. $AlEt_3$): A solution of (^{Cy}PSiP)Pd(carboxylate) (**5**) (3.4 mg, 0.00421 mmol) in 0.5 mL of C_6D_6 was transferred to a screw cap NMR tube, and 2 equivalents of $AlEt_3$ (0.6 M in toluene, 14.0 µL, 0.00842 mmol) were added using a micro syringe. After 2 hours, complete conversion to **8** was observed by ^{1}H and ^{31}P NMR spectroscopy.

*Reaction of (^{Cy}PSiP)Pd{OC(O)H} (**2**) with excess $AlEt_3$*

(^{Cy}PSiP)Pd{OC(O)H} (**2**) (2 mg, 0.00270 mmol) was dissolved in 0.5 mL of C_6D_6 and 10 equivalents of $AlEt_3$ (0.6 M in toluene, 45.0 µL, 0.0270 mmol) were added at room temperature. The solution was heated at 50 °C for 5 hours upon which 83% conversion to (^{Cy}PSiP)Pd($HAlEt_3$) (**8**) was observed by ^{1}H and ^{31}P NMR spectroscopy along with unidentifiable side product. Further conversion to **8** was not observed.

*Reaction of (^{Cy}PSiP)Pd(HAlEt$_3$) (**8**) with 1,1-dimethylallene*



(^{Cy}PSiP)Pd(HAlEt$_3$) (**8**) (3 mg, 0.0037mmol) was dissolved in C_6D_6 at room temperature, and one equivalent of 1,1-dimethylallene (0.5M solution in C_6D_6, 7.4 μL, 0.0037 mmol) was added using a micro syringe. The solution was left to stand at room temperature for 12 hours. The products of allene insertion into (^{Cy}PSiP)PdH (**1**), **3** and **4**, were observed by ^{1}H and ^{31}P NMR spectroscopy.

*Reaction of (^{Cy}PSiP)Pd(Et) (**6**) and (^{Cy}PSiP)Pd{OCH(O)AlEt$_3$)} (**9**) with 1,1-dimethylallene (Scheme 7)*

A solution containing (^{Cy}PSiP)Pd(Et) (**6**) and (^{Cy}PSiP)Pd{OCH(O)AlEt$_3$)} (**9**) was prepared *in situ* through the reaction of **2** (10 mg, 0.014 mmol) in 0.5 mL of C_6D_6 with 1 equivalent of AlEt$_3$ (0.6 M in heptanes, 23 μL, 0.014 mmol) at room temperature. Subsequently approximately 3.8 equivalents of 1,1-dimethylallene (5.0 μL, 0.051 mmol) was added to the reaction mixture. Near complete conversion of the unknown product to **3** was confirmed by ^{1}H and ^{31}P NMR spectroscopy within 1 hour, along with **4** and a trace amount of **6** (1:0.26:0.06). This is considerably faster than the reaction of **2** with 1,1-dimethylallene, which suggests that AlEt$_3$ plays an active role in facilitating the transformation. After 18 hours at room temperature, further conversion of **3** to **4** was observed.

Selected NMR Spectra

NMR Spectra of ***6***

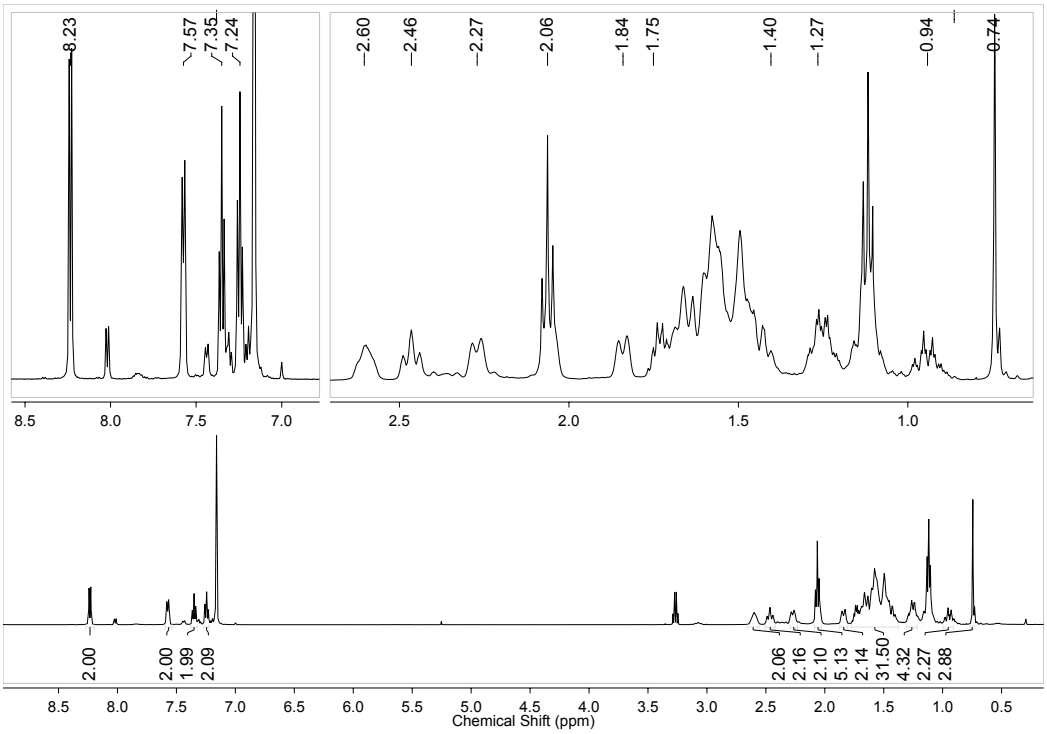


Figure S1: ^{1}H NMR spectrum of **6** (with 18% **9** and solvent, diethyl ether).

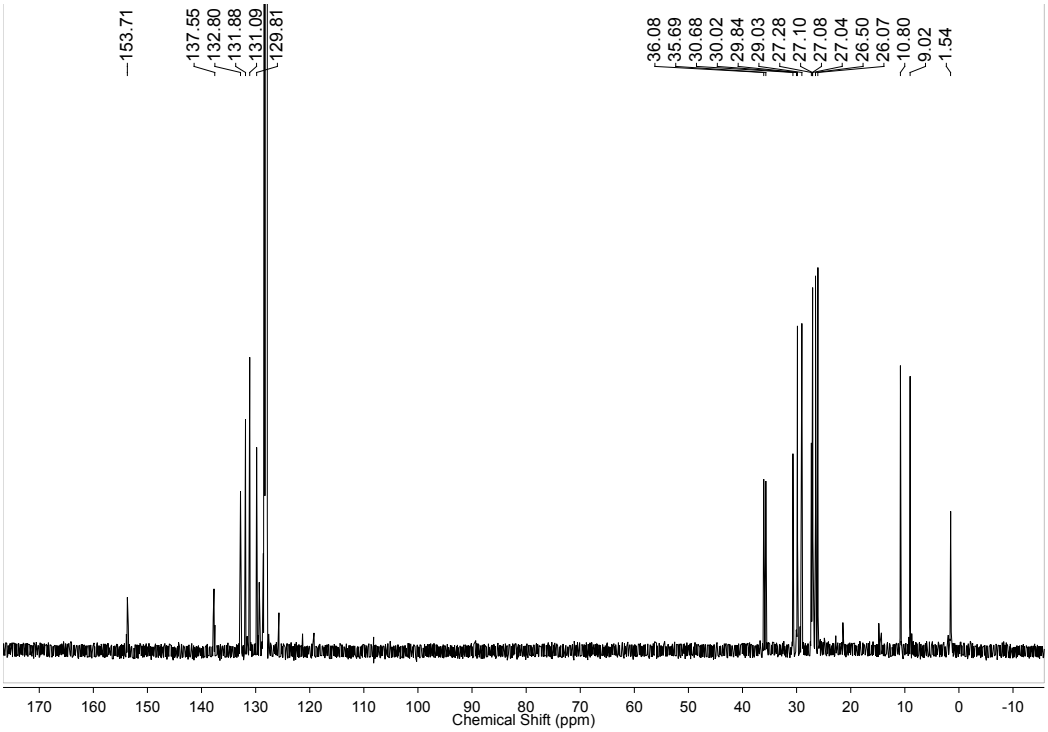


Figure S2: ^{13}C{^{1}H} NMR spectrum of **6**.

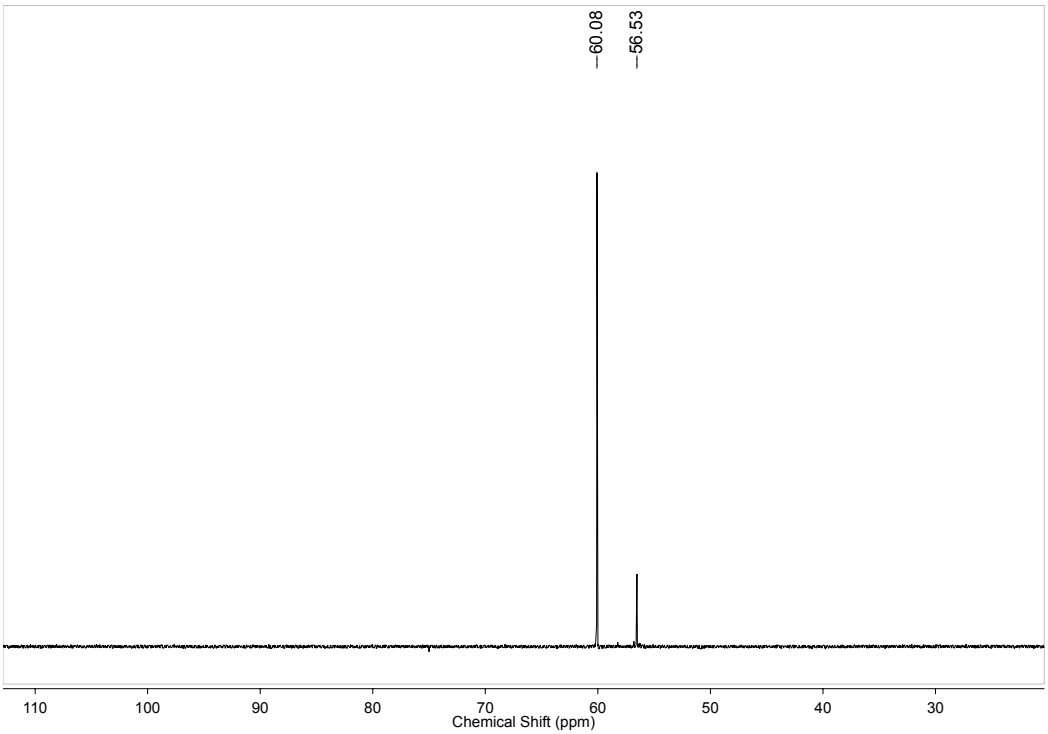


Figure S3: $^{31}P\{^{1}H\}$ NMR spectrum of **6**.

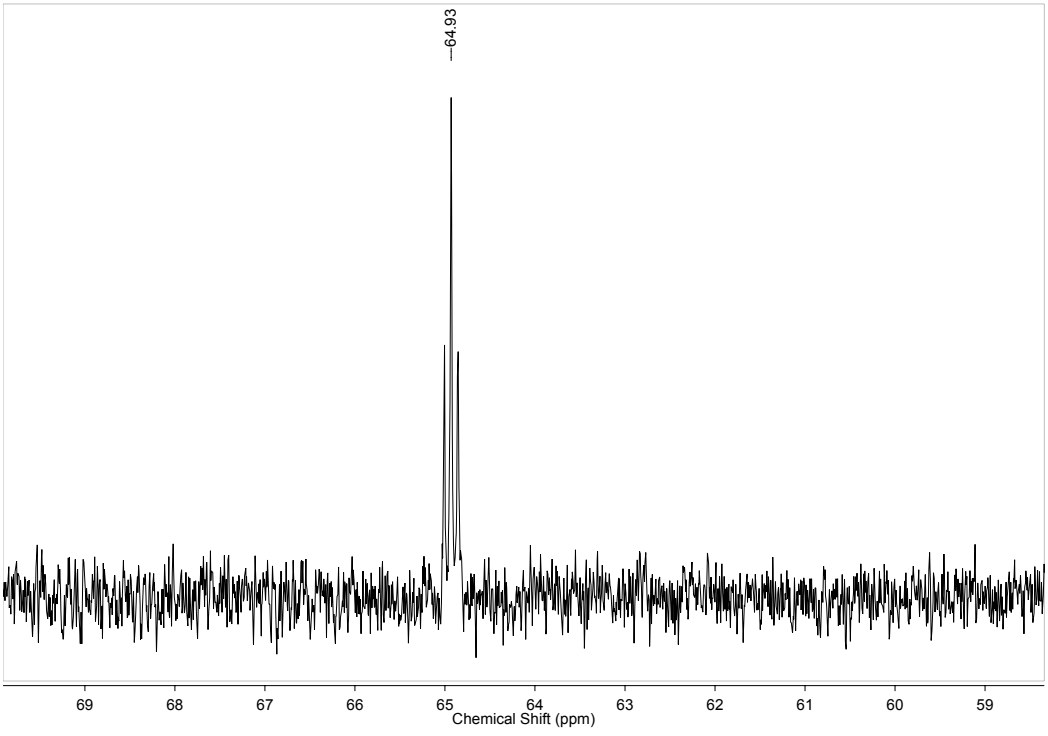


Figure S4: $^{29}Si\{^{1}H\}$ NMR spectrum of **6**.

NMR Spectra of 7

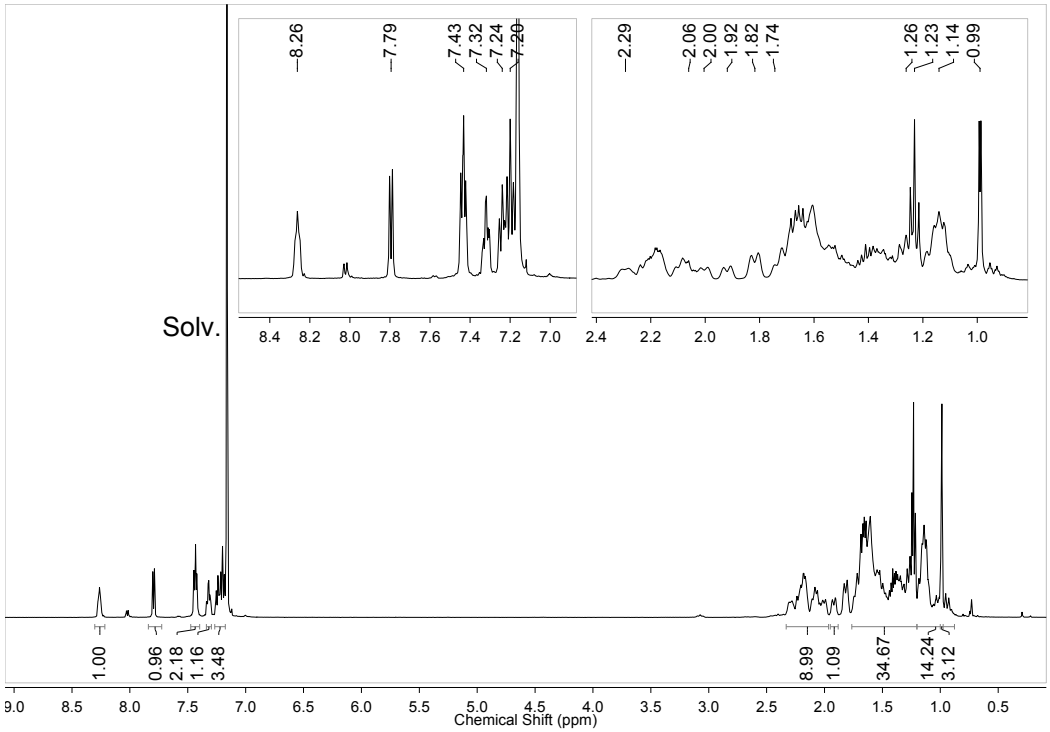


Figure S5: ^{1}H NMR spectrum of **7**.

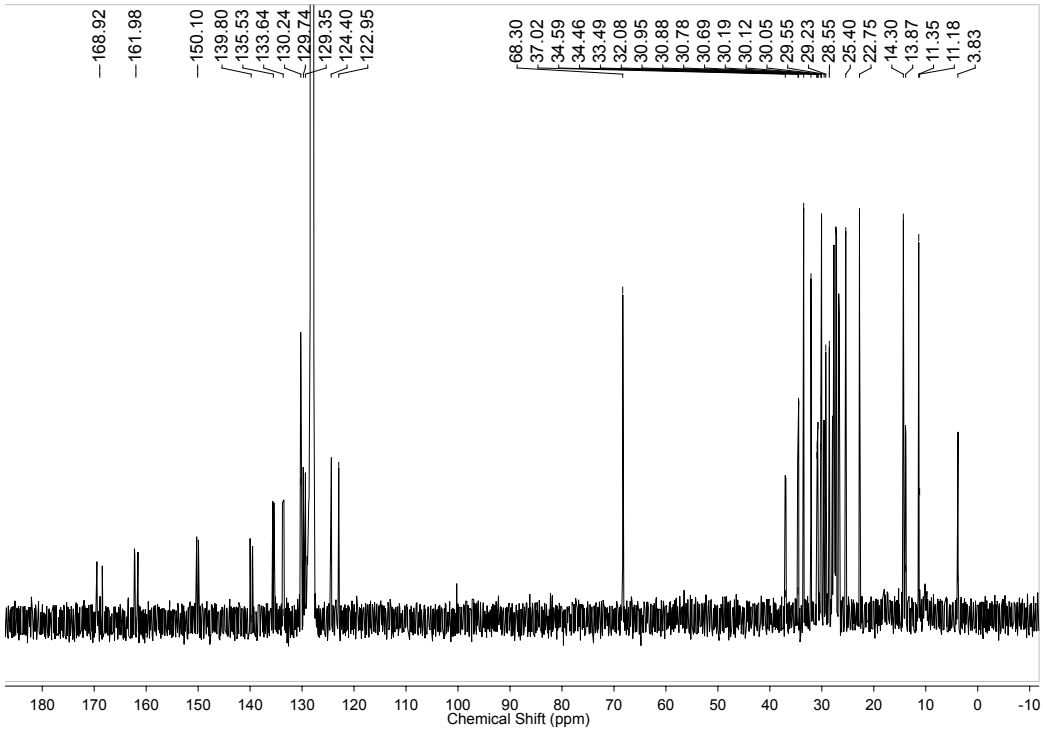


Figure S6: ^{13}C{^{1}H} NMR spectrum of **7**.

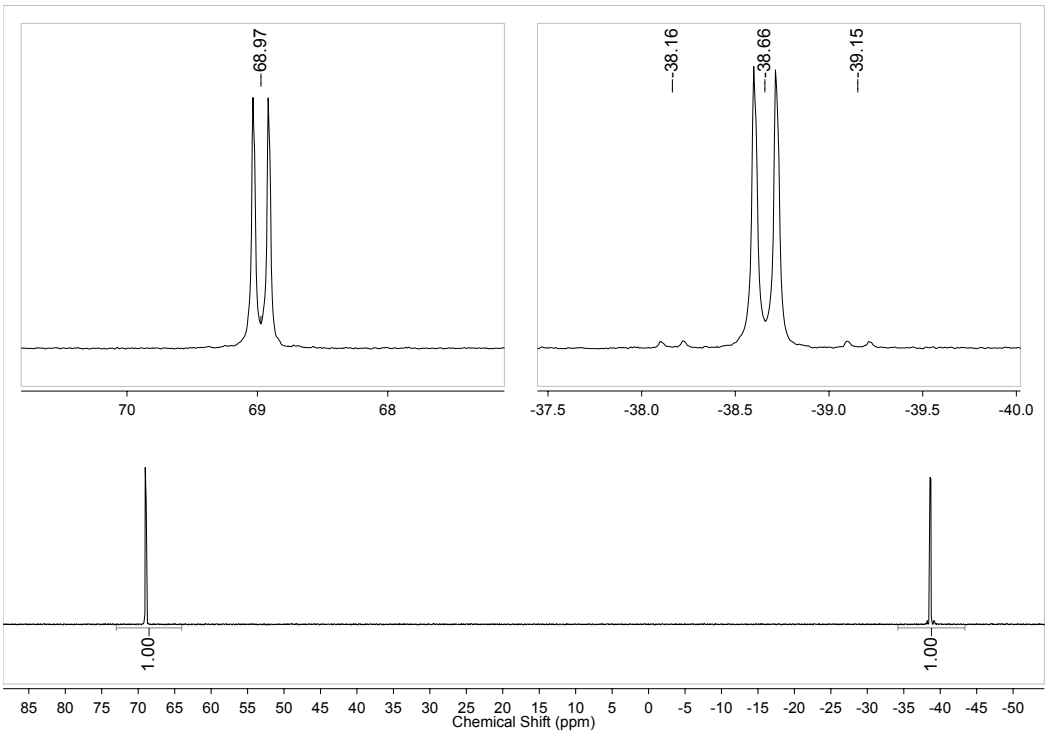


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of **7**.

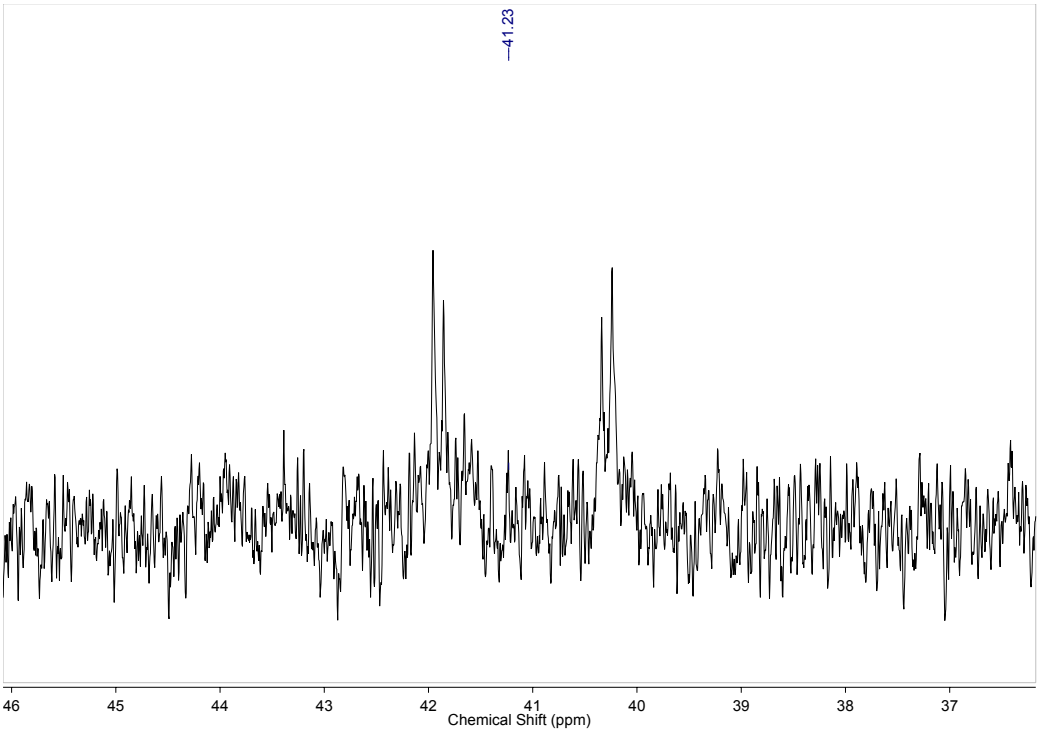


Figure S8: $^{29}Si\{^{1}H\}$ NMR spectrum of **7**.

*NMR Spectra of **8***

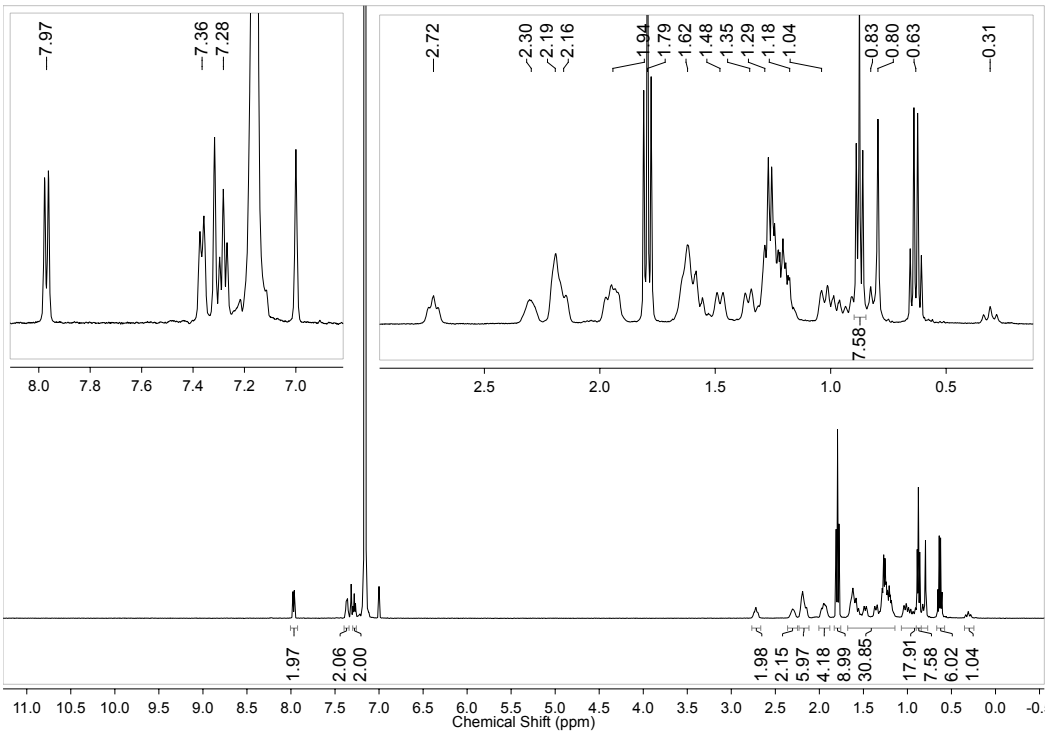


Figure S9: ^{1}H NMR spectrum of **8**. Pentane is present in the NMR spectrum.

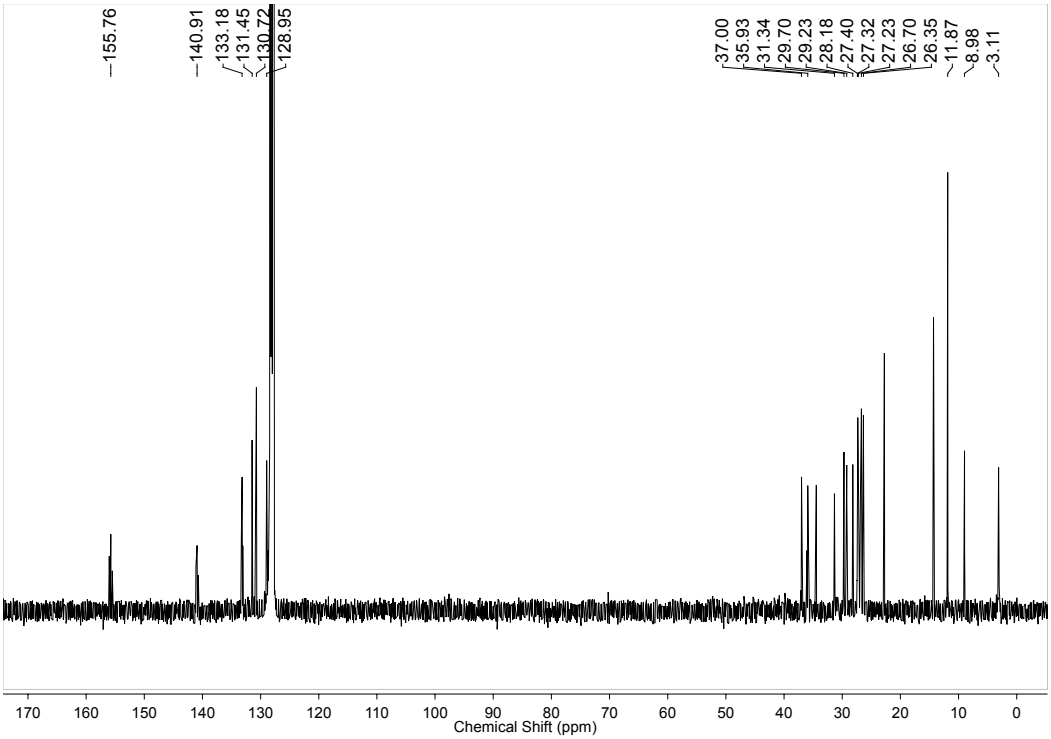


Figure S10: ^{13}C{^{1}H} NMR spectrum of **8**.

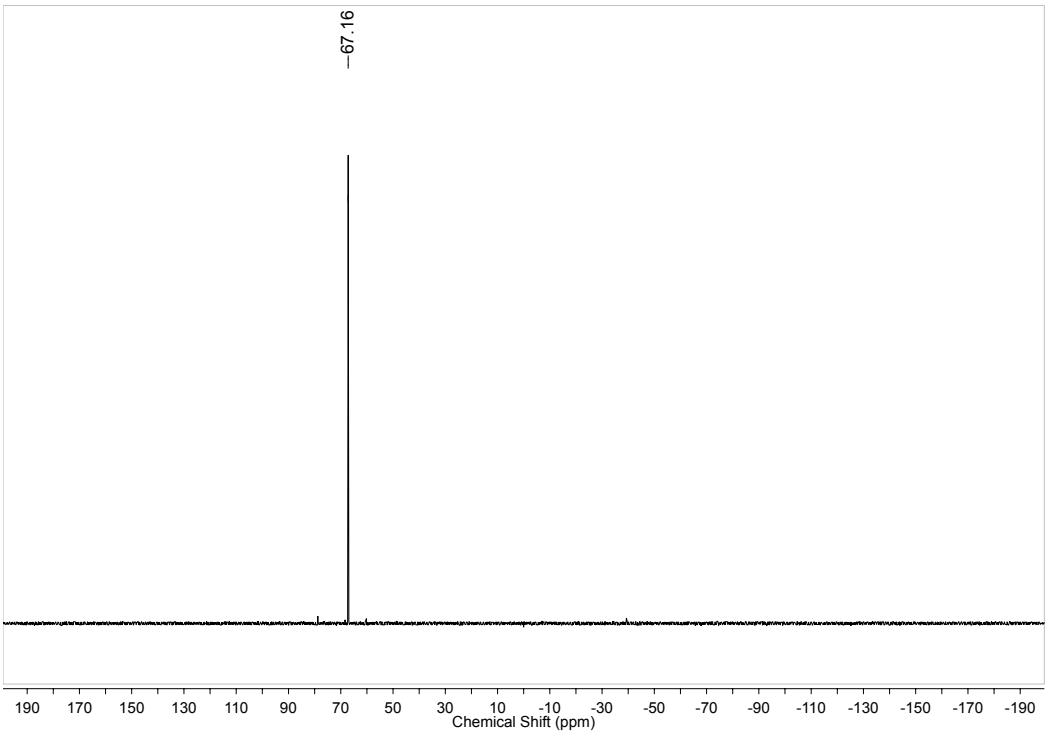


Figure S11: $^{31}P\{^{1}H\}$ NMR spectrum of **8**.

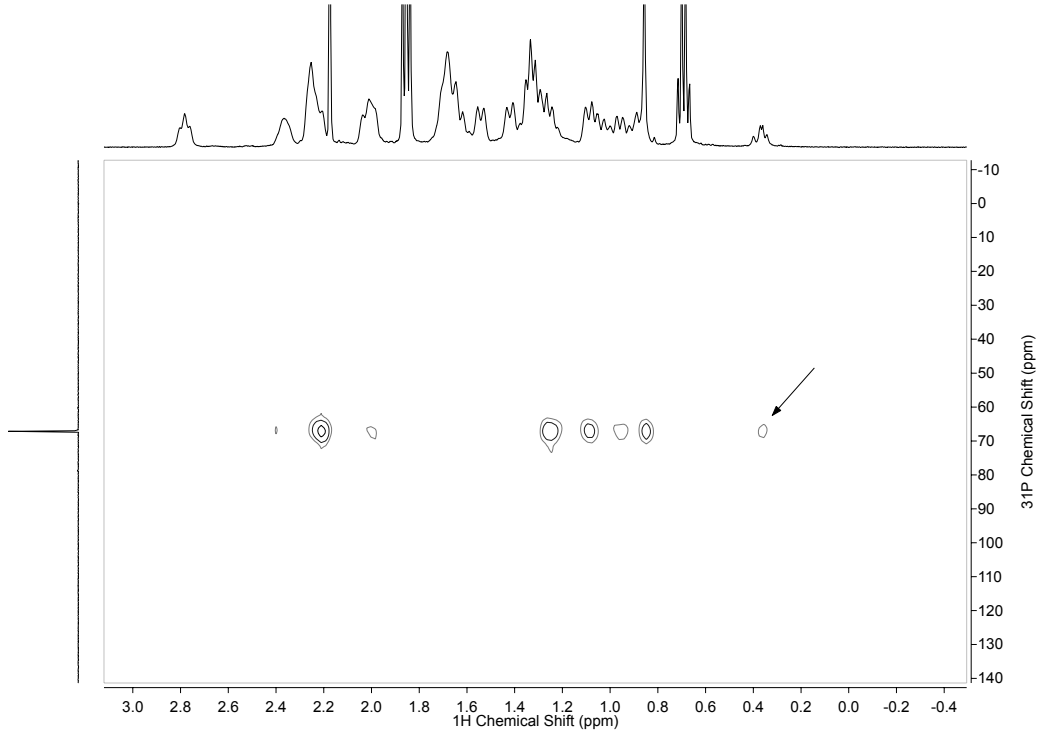


Figure S12: ^{1}H-^{31}P COSY NMR spectrum of **8** showing the Pd-H coupled to the pincer ligand.

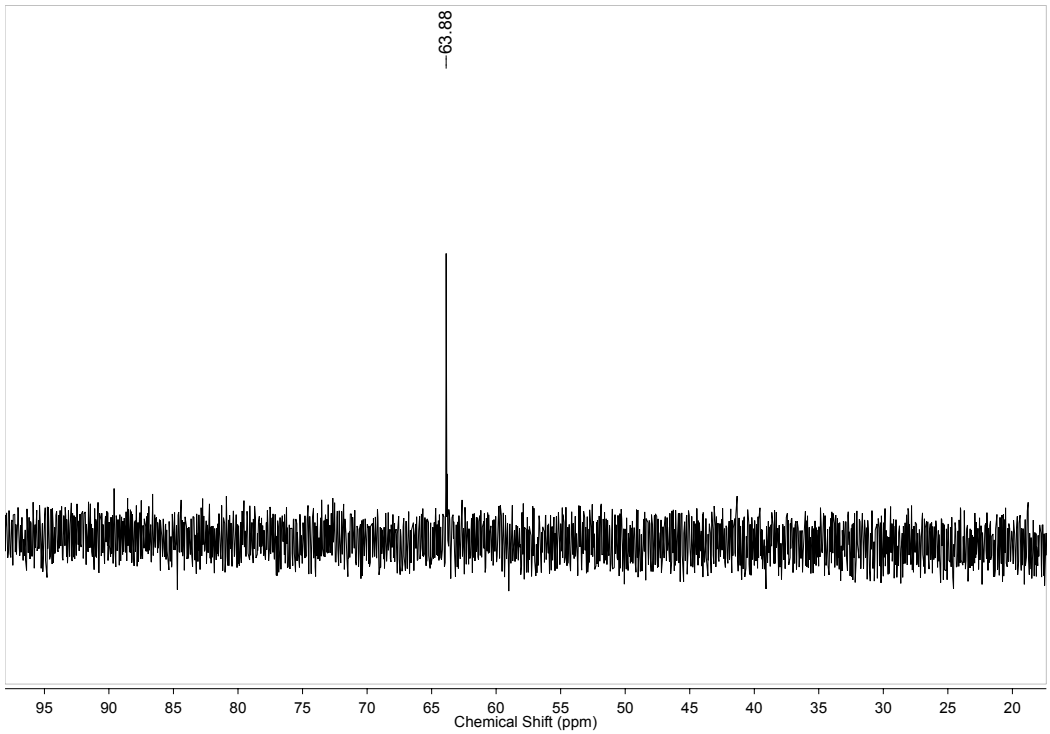


Figure S13: $^{29}Si\{^{1}H\}$ NMR spectrum of **8**.

*NMR Spectra of **10***

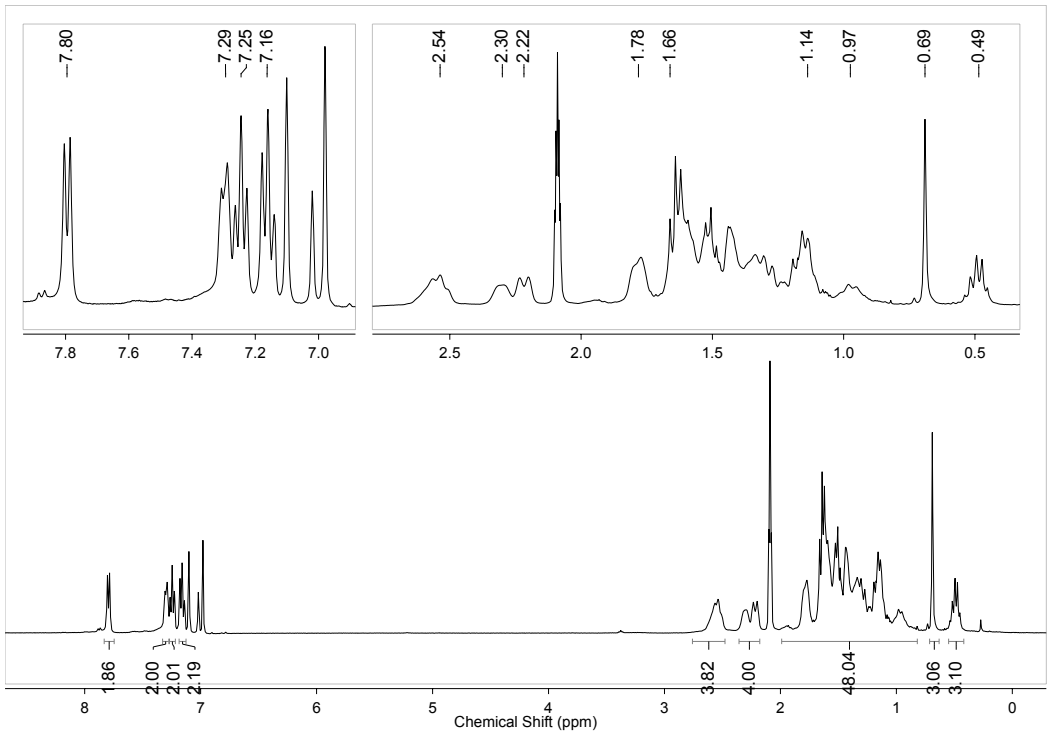


Figure S14: ^{1}H NMR spectrum of **10** in d_8-toluene.

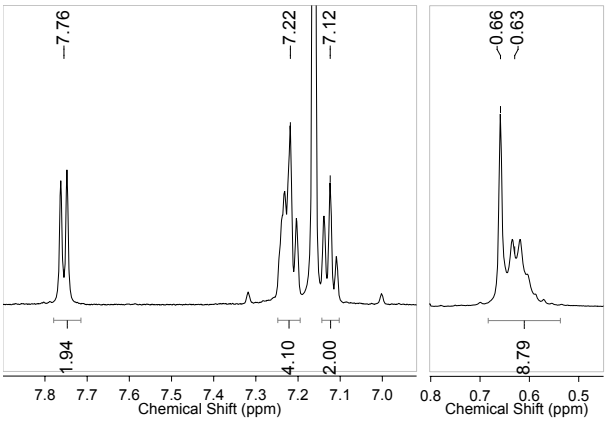


Figure S15: ^{1}H NMR spectrum in C_6D_6.

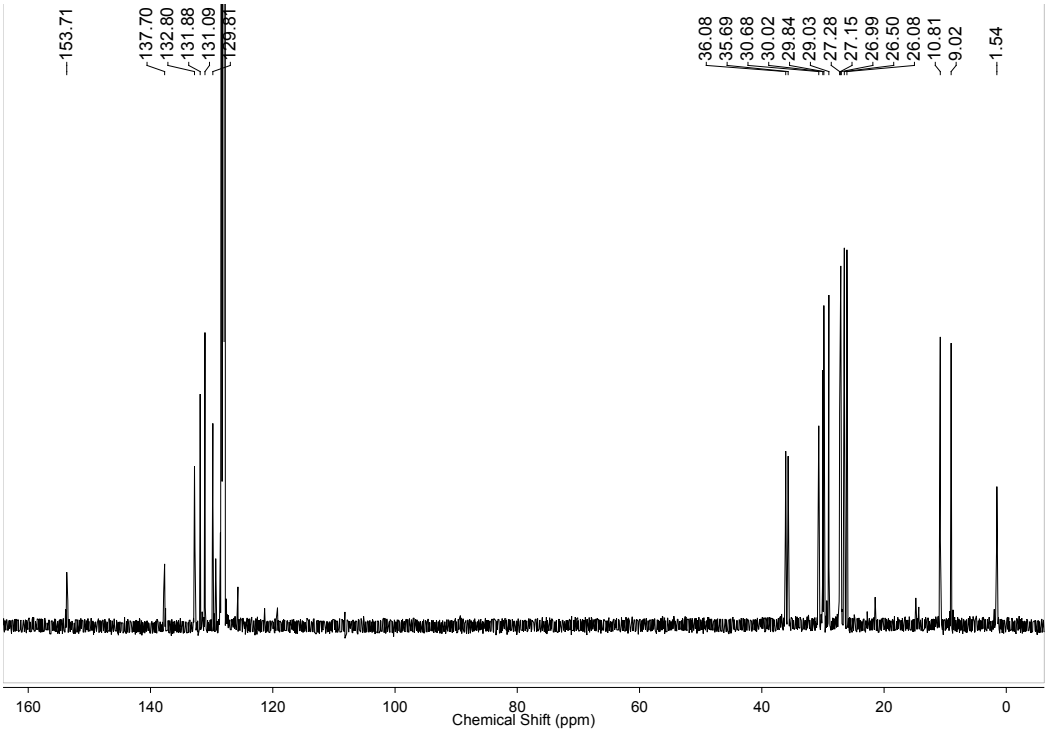


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of **10**. Residual pentane peaks are present in the aliphatic region.

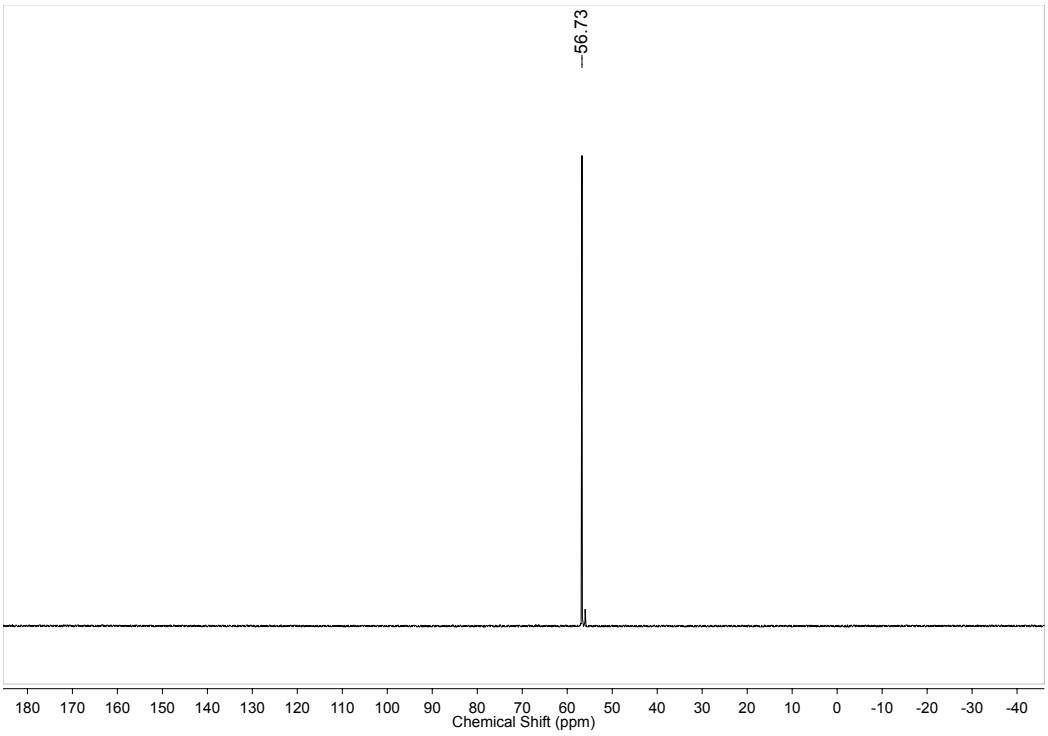


Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of **10**.

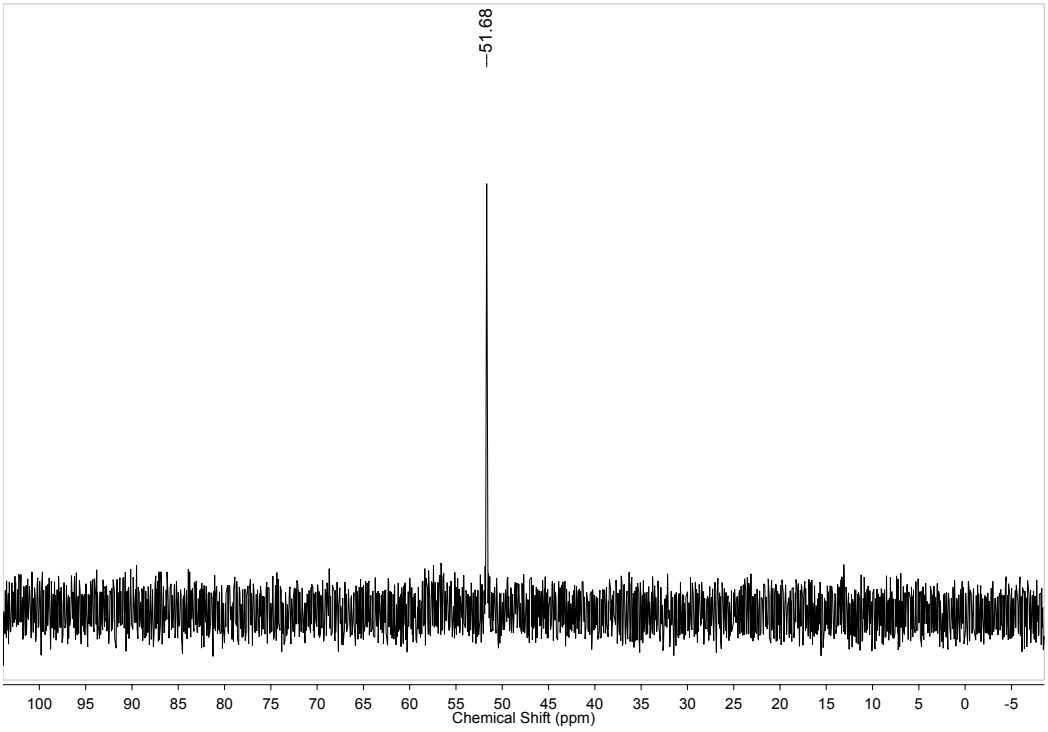


Figure S18: $^{29}Si\{^{1}H\}$ NMR spectrum of **10**.

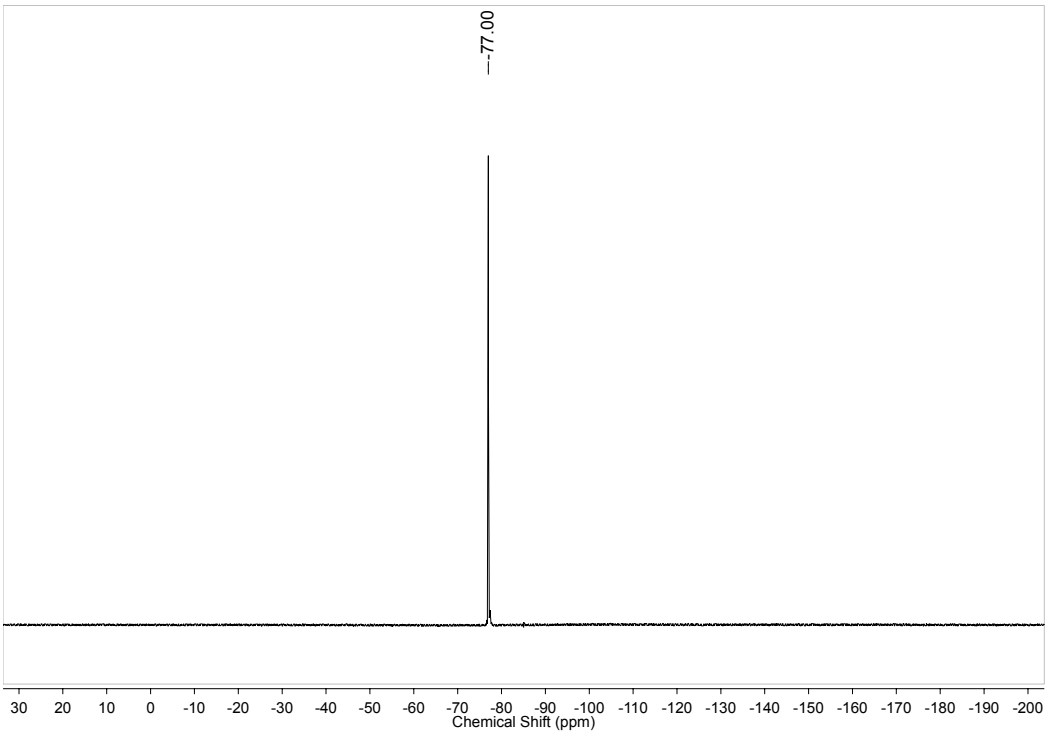


Figure S19: $^{19}F\{^{1}H\}$ NMR spectrum of **10**.

X-Ray Crystallography

Low temperature diffraction data was collected on either a Rigaku R-AXIS RAPID diffractometer coupled to a R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) or a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα radiation (λ = 1.54178 Å). The crystals were mounted on MiTeGen polyimide loops with immersion oil. The data frames were processed using Rigaku CrystalClear and corrected for Lorentz and polarization effects. Using Olex2[3] the structure was solved with the XS[4] structure solution program by direct methods and refined with the XL[4] refinement package using least-squares minimization. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Details of the crystal structure and refinement data for **3**, **4**, **5**, **6**, **7**, **8**, **9** and **10** are given below.

ORTEP of (^{Cy}PSiP)Pd(HAlEt$_3$) (***8***)

A low quality crystal of **8** was obtained from a concentrated solution of **8** in pentane at -35 °C. Three molecules of **8** co-crystallized in a single unit cell. Four pentane solvent molecules were also present in the asymmetric unit. Despite the low quality data, connectivity between (^{Cy}PSiP)PdH and AlEt$_3$ could be confirmed. The hydride on Pd was only located in the diffraction map in one of the three independent molecules in the unit cell.

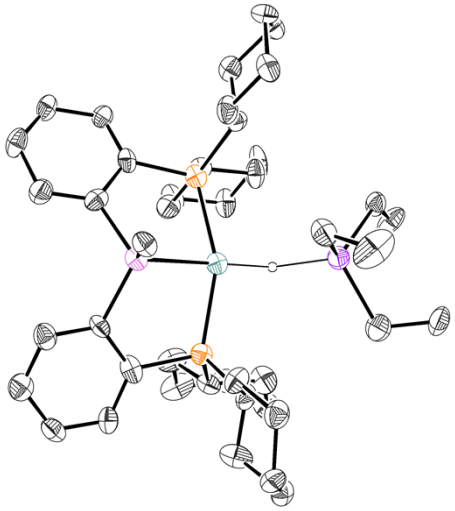


Figure S20: ORTEP of **8**. Selected hydrogen atoms are omitted for clarity.

X-Ray Data for (^{Cy}PSiP)Pd(η^1-prenyl) (***3***)

Compound **3** crystallized with one molecule of pentane in the asymmetric unit, which was disordered over two positions. The short H···H contact Level B alert in the checkcif is a result of this disorder.

Table S1: Crystal data and structure refinement for **3**.

Empirical formula	$C_{23.5}H_{38}PPd_{0.5}Si_{0.5}$
Formula weight	418.75
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.8954(3)
b/Å	18.9114(3)
c/Å	16.6032(12)
α/°	90.00
β/°	106.453(7)
γ/°	90.00
Volume/Å^3	4485.5(3)
Z	8
ρ_{calc}mg/mm^3	1.240
m/mm^{-1}	4.477
F(000)	1792.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
2Θ range for data collection	7.04 to 127.38°
Index ranges	$-16 \le h \le 17$, $-20 \le k \le 21$, $-19 \le l \le 18$
Reflections collected	52296
Independent reflections	7332[R(int) = 0.0419]
Data/restraints/parameters	7332/37/465
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.1061
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.1077
Largest diff. peak/hole / e Å^{-3}	0.97/-0.99

Table S2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	8434.17(14)	3035.80(11)	8018.86(12)	21.70(9)
P1	6878.3(5)	2763.1(4)	7509.0(4)	21.50(16)
P2	9326.6(5)	2599.0(4)	7097.8(4)	22.95(17)
Si1	8035.5(6)	3470.6(4)	9165.4(5)	26.74(19)
C38	8920(2)	1337.5(16)	6176.2(18)	28.3(6)
C12	6200(2)	3059.6(15)	8209.1(19)	25.1(6)
C25	10277(2)	2956.6(15)	7936.6(19)	26.0(7)
C11	5221(2)	3036.1(16)	7998(2)	30.1(7)
C26	11249(2)	2950.7(17)	8062(2)	32.1(7)
C42	9689(2)	1236.9(16)	7730.0(18)	28.2(6)
C2	8670(3)	2999.8(19)	10173(2)	39.5(8)

C39	9167(2)	566.6(17)	6063.7(19)	32.2(7)
C30	9854(2)	3271.9(16)	8496.7(18)	26.4(6)
C40	9250(2)	139.4(17)	6854.2(19)	32.6(7)
C10	4760(2)	3278.9(18)	8562(2)	33.8(7)
C8	6238(2)	3569.7(17)	9544.7(19)	31.6(7)
C7	6725(2)	3340.6(16)	8981.0(18)	26.4(6)
C27	11815(2)	3286.3(18)	8765(2)	35.2(7)
C29	10451(2)	3621.5(17)	9192.1(19)	30.2(7)
C37	9625(2)	1672.1(16)	6939.9(17)	24.9(6)
C32	10204(2)	2926.2(17)	5818(2)	32.5(7)
C31	9335(2)	3046.0(15)	6113.7(19)	26.8(7)
C19	6266(2)	3172.0(15)	6491.3(17)	24.0(6)
C20	6636(2)	2897.6(17)	5780.7(18)	29.1(7)
C14	7068(2)	1388.9(16)	8167.7(19)	29.1(7)
C41	9947(2)	470.5(17)	7617.8(19)	31.2(7)
C15	7001(2)	595.4(17)	7998(2)	35.1(7)
C24	6359(2)	3975.5(16)	6570.7(18)	28.8(7)
C36	9163(2)	3841.1(16)	6178(2)	30.9(7)
C1	8240(2)	4444.2(18)	9402(2)	37.9(8)
C13	6666(2)	1806.4(16)	7354.6(18)	24.4(6)
C23	5886(2)	4346.1(17)	5741.2(19)	33.8(7)
C3	8569(2)	2219.4(19)	10157(2)	34.4(7)
C9	5274(2)	3538.1(17)	9340(2)	34.8(7)
C18	5645(2)	1577.6(17)	6955(2)	36.4(8)
C28	11413(2)	3626.4(17)	9317(2)	33.8(7)
C21	6179(2)	3275.6(18)	4950.7(18)	32.2(7)
C22	6275(2)	4076.7(17)	5042.5(19)	34.4(7)
C16	6006(2)	355.2(18)	7547(2)	37.9(8)
C33	10111(3)	3291.3(19)	4979(2)	38.4(8)
C17	5593(2)	790.6(18)	6760(2)	40.1(8)
C35	9066(3)	4209.5(18)	5342(2)	39.3(8)
C4	8198(2)	1807(2)	10626(2)	47.9(10)
C34	9921(3)	4080.4(18)	5032(2)	41.1(8)
C5	7816(3)	2104(3)	11308(3)	77.2(17)
C6	8106(4)	1022(3)	10495(3)	77.6(16)
C1A	13048(4)	4932(3)	8570(3)	71.9(13)
C1B	12559(4)	4767(3)	7665(3)	74.3(13)
C1C	12263(4)	6301(3)	7047(4)	92.8(19)
C1D	11626(4)	5918(3)	7459(5)	107(2)
C1W	11630(3)	5107(3)	7390(4)	79.7(15)

Table S3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Pd1	21.03(14)	24.69(15)	17.88(13)	-0.67(7)	3.07(9)	0.13(7)
P1	21.3(4)	24.4(4)	17.7(3)	-0.1(3)	3.6(3)	2.1(3)
P2	23.2(4)	24.4(4)	21.6(4)	-0.4(3)	6.9(3)	-0.2(3)
Si1	28.0(4)	32.2(4)	18.1(4)	-2.7(3)	3.4(3)	0.4(3)
C38	30.8(16)	30.0(17)	24.0(15)	-0.1(12)	7.8(12)	-1.9(13)
C12	26.7(16)	24.1(16)	25.4(15)	2.6(11)	9.0(13)	3.1(11)

C25	25.1(16)	23.0(15)	27.6(16)	3.8(12)	3.5(13)	-2.8(11)
C11	29.6(17)	30.8(18)	30.0(17)	-1.7(12)	8.8(14)	0.9(12)
C26	27.2(17)	34.8(18)	35.0(18)	3.6(13)	9.9(14)	-1.8(13)
C42	30.7(16)	27.5(16)	24.2(15)	0.3(12)	4.0(12)	-4.3(12)
C2	38(2)	56(2)	20.8(16)	-0.9(14)	2.1(14)	0.2(15)
C39	43.9(19)	27.8(17)	27.2(16)	-3.1(13)	14.0(14)	-3.2(14)
C30	30.1(16)	22.7(15)	25.3(15)	3.4(12)	6.0(12)	0.3(12)
C40	43.0(19)	26.4(17)	30.9(16)	0.2(13)	14.6(14)	-3.7(13)
C10	29.6(17)	35.0(18)	41.0(18)	3.3(15)	17.2(14)	2.9(14)
C8	42.8(19)	30.9(17)	23.1(15)	1.1(12)	12.9(13)	1.1(14)
C7	33.2(16)	25.6(16)	22.1(14)	2.6(12)	10.7(12)	3.4(12)
C27	22.8(16)	39.0(19)	40.9(18)	4.6(15)	4.2(13)	-5.2(14)
C29	28.9(16)	30.2(17)	27.3(15)	-2.2(12)	0.8(12)	-3.2(13)
C37	23.4(14)	25.4(16)	25.9(15)	2.2(12)	6.9(11)	-2.4(12)
C32	38.9(19)	29.4(17)	34.2(17)	1.8(13)	18.3(15)	2.6(13)
C31	28.7(16)	26.6(17)	26.1(16)	-1.2(11)	9.4(13)	-0.4(11)
C19	26.0(15)	24.7(15)	19.3(14)	-0.1(11)	3.3(11)	3.4(12)
C20	35.3(17)	29.0(16)	21.6(15)	-2.1(12)	5.9(13)	5.6(13)
C14	27.4(15)	32.6(17)	25.8(15)	5.4(13)	4.8(12)	2.0(13)
C41	34.4(17)	28.2(17)	29.7(16)	4.6(13)	6.9(13)	-1.3(13)
C15	35.2(18)	30.5(18)	37.6(18)	8.9(14)	7.2(14)	0.9(14)
C24	36.7(17)	26.3(16)	23.7(15)	0.5(12)	9.0(13)	4.8(13)
C36	35.2(17)	24.0(16)	34.7(17)	-0.2(13)	11.9(13)	0.7(13)
C1	36.6(18)	40(2)	36.0(18)	-9.0(14)	7.9(14)	-2.0(14)
C13	21.7(15)	27.5(15)	21.9(15)	0.1(12)	2.5(11)	1.2(12)
C23	42.2(18)	28.1(17)	28.3(16)	3.4(13)	5.2(14)	7.9(13)
C3	24.6(16)	51(2)	25.4(16)	8.3(14)	2.7(13)	8.3(14)
C9	46(2)	32.6(18)	34.2(17)	3.3(13)	24.8(15)	3.7(14)
C18	26.7(17)	31.4(18)	41.6(18)	2.2(14)	-5.8(14)	-1.3(13)
C28	31.7(17)	32.0(18)	31.8(16)	0.8(13)	-0.5(13)	-9.1(13)
C21	38.9(18)	35.4(18)	20.2(15)	1.3(13)	5.0(13)	4.4(14)
C22	42.1(19)	35.2(18)	23.5(15)	4.2(13)	5.2(13)	4.2(14)
C16	39.2(19)	31.7(18)	42.8(19)	2.9(15)	11.7(15)	-5.5(14)
C33	53(2)	35.1(19)	34.6(17)	3.5(15)	24.3(16)	1.0(16)
C17	35.7(18)	31.6(18)	44.5(19)	-1.4(15)	-2.6(15)	-7.8(14)
C35	51(2)	30.8(18)	40.5(19)	8.3(14)	20.9(16)	5.2(15)
C4	26.5(18)	72(3)	40(2)	23.9(19)	1.6(15)	4.4(17)
C34	56(2)	31.5(19)	41.9(19)	8.2(15)	24.3(17)	-0.6(16)
C5	43(3)	146(5)	50(3)	34(3)	26(2)	10(3)
C6	72(3)	69(3)	78(3)	38(3)	-2(3)	-7(2)
C1A	86(3)	68(3)	62(3)	-5(2)	22(2)	-16(3)
C1B	84(3)	67(3)	74(3)	0(3)	26(3)	-8(3)
C1C	90(4)	88(4)	87(4)	6(3)	4(3)	-35(3)
C1D	78(4)	77(4)	173(7)	-11(4)	48(4)	-4(3)
C1W	51(3)	63(3)	122(4)	-14(3)	20(3)	-7(2)

Table S4: Bond Lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.2896(7)	C8	C9	1.381(5)

Pd1	P2	2.4370(7)	C27	C28	1.386(5)
Pd1	Si1	2.3007(8)	C29	C28	1.388(5)
Pd1	C30	2.085(3)	C32	C31	1.526(4)
P1	C12	1.831(3)	C32	C33	1.525(4)
P1	C19	1.847(3)	C31	C36	1.534(4)
P1	C13	1.842(3)	C19	C20	1.528(4)
P2	C25	1.813(3)	C19	C24	1.528(4)
P2	C37	1.845(3)	C20	C21	1.530(4)
P2	C31	1.843(3)	C14	C15	1.525(5)
Si1	C2	1.895(3)	C14	C13	1.532(4)
Si1	C7	1.905(3)	C15	C16	1.529(5)
Si1	C1	1.889(3)	C24	C23	1.528(4)
C38	C39	1.528(4)	C36	C35	1.523(4)
C38	C37	1.535(4)	C13	C18	1.538(4)
C12	C11	1.400(5)	C23	C22	1.524(5)
C12	C7	1.403(4)	C3	C4	1.329(5)
C25	C26	1.402(5)	C18	C17	1.521(5)
C25	C30	1.397(5)	C21	C22	1.525(5)
C11	C10	1.387(5)	C16	C17	1.519(5)
C26	C27	1.385(5)	C33	C34	1.526(5)
C42	C37	1.528(4)	C35	C34	1.522(5)
C42	C41	1.524(4)	C4	C5	1.512(7)
C2	C3	1.483(5)	C4	C6	1.501(7)
C39	C40	1.516(4)	C1A	C1B	1.505(6)
C30	C29	1.407(4)	C1B	C1W	1.476(6)
C40	C41	1.527(4)	C1C	C1D	1.504(8)
C10	C9	1.392(5)	C1D	C1W	1.539(7)
C8	C7	1.404(4)			

Table S5: Bond Angles for **3**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
P1	Pd1	P2	111.50(3)	C12	C7	Si1	118.4(2)
P1	Pd1	Si1	85.12(3)	C12	C7	C8	117.8(3)
Si1	Pd1	P2	162.71(3)	C8	C7	Si1	123.5(2)
C30	Pd1	P1	179.13(8)	C26	C27	C28	119.7(3)
C30	Pd1	P2	68.71(9)	C28	C29	C30	120.8(3)
C30	Pd1	Si1	94.60(9)	C38	C37	P2	111.9(2)
C12	P1	Pd1	112.28(10)	C42	C37	P2	110.4(2)
C12	P1	C19	103.54(14)	C42	C37	C38	110.4(2)
C12	P1	C13	106.56(14)	C33	C32	C31	111.1(3)
C19	P1	Pd1	115.46(11)	C32	C31	P2	115.9(2)
C13	P1	Pd1	112.87(9)	C32	C31	C36	110.0(3)
C13	P1	C19	105.25(13)	C36	C31	P2	110.1(2)
C25	P2	Pd1	80.67(11)	C20	C19	P1	111.8(2)
C25	P2	C37	107.25(13)	C20	C19	C24	111.1(3)
C25	P2	C31	108.06(14)	C24	C19	P1	109.2(2)
C37	P2	Pd1	127.38(10)	C19	C20	C21	111.8(3)
C31	P2	Pd1	122.87(10)	C15	C14	C13	110.8(3)
C31	P2	C37	104.33(13)	C42	C41	C40	110.8(3)

C2	Si1	Pd1	112.42(12)	C14	C15	C16	112.7(3)
C2	Si1	C7	108.29(15)	C23	C24	C19	111.8(2)
C7	Si1	Pd1	108.29(9)	C35	C36	C31	111.0(3)
C1	Si1	Pd1	117.14(11)	C14	C13	P1	112.0(2)
C1	Si1	C2	105.28(15)	C14	C13	C18	109.1(3)
C1	Si1	C7	104.90(14)	C18	C13	P1	116.5(2)
C39	C38	C37	111.2(3)	C22	C23	C24	110.8(3)
C11	C12	P1	123.6(2)	C4	C3	C2	129.1(4)
C11	C12	C7	120.8(3)	C8	C9	C10	120.2(3)
C7	C12	P1	115.5(2)	C17	C18	C13	110.6(3)
C26	C25	P2	131.3(3)	C27	C28	C29	121.2(3)
C30	C25	P2	105.6(2)	C22	C21	C20	111.6(3)
C30	C25	C26	123.1(3)	C23	C22	C21	111.3(3)
C10	C11	C12	120.0(3)	C17	C16	C15	111.1(3)
C27	C26	C25	118.5(3)	C32	C33	C34	111.1(3)
C41	C42	C37	111.3(3)	C16	C17	C18	111.3(3)
C3	C2	Si1	115.4(2)	C34	C35	C36	111.2(3)
C40	C39	C38	111.5(3)	C3	C4	C5	121.9(4)
C25	C30	Pd1	104.8(2)	C3	C4	C6	122.1(4)
C25	C30	C29	116.5(3)	C6	C4	C5	116.0(4)
C29	C30	Pd1	138.6(2)	C35	C34	C33	111.3(3)
C39	C40	C41	111.7(3)	C1W	C1B	C1A	111.4(5)
C11	C10	C9	119.8(3)	C1C	C1D	C1W	115.5(6)
C9	C8	C7	121.3(3)	C1B	C1W	C1D	115.7(5)

X-Ray Data for (κ^2-$Cy_2PC_6H_4SiMe(prenyl))Pd(\kappa^2$-$Cy_2PC_6H_4$) (***4***)

Compound **4** crystallized with one molecule of pentane in the asymmetric unit.

Table S6: Crystal data and structure refinement for **4**.

Empirical formula	$C_{23.5}H_{38}PPd_{0.5}Si_{0.5}$
Formula weight	418.75
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.8954(3)
b/Å	18.9114(3)
c/Å	16.6032(12)
α/°	90.00
β/°	106.453(7)
γ/°	90.00
Volume/Å^3	4485.5(3)
Z	8
ρ_{calc}mg/mm^3	1.240
m/mm^{-1}	4.477
F(000)	1792.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
2Θ range for data collection	7.04 to 127.38°
Index ranges	-16 ≤ h ≤ 17, -20 ≤ k ≤ 21, -19 ≤ l ≤ 18

Reflections collected	52296
Independent reflections	7332[R(int) = 0.0419]
Data/restraints/parameters	7332/37/465
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.1061
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.1077
Largest diff. peak/hole / e $Å^{-3}$	0.97/-0.99

Table S7: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	8434.17(14)	3035.80(11)	8018.86(12)	21.70(9)
P1	6878.3(5)	2763.1(4)	7509.0(4)	21.50(16)
P2	9326.6(5)	2599.0(4)	7097.8(4)	22.95(17)
Si1	8035.5(6)	3470.6(4)	9165.4(5)	26.74(19)
C38	8920(2)	1337.5(16)	6176.2(18)	28.3(6)
C12	6200(2)	3059.6(15)	8209.1(19)	25.1(6)
C25	10277(2)	2956.6(15)	7936.6(19)	26.0(7)
C11	5221(2)	3036.1(16)	7998(2)	30.1(7)
C26	11249(2)	2950.7(17)	8062(2)	32.1(7)
C42	9689(2)	1236.9(16)	7730.0(18)	28.2(6)
C2	8670(3)	2999.8(19)	10173(2)	39.5(8)
C39	9167(2)	566.6(17)	6063.7(19)	32.2(7)
C30	9854(2)	3271.9(16)	8496.7(18)	26.4(6)
C40	9250(2)	139.4(17)	6854.2(19)	32.6(7)
C10	4760(2)	3278.9(18)	8562(2)	33.8(7)
C8	6238(2)	3569.7(17)	9544.7(19)	31.6(7)
C7	6725(2)	3340.6(16)	8981.0(18)	26.4(6)
C27	11815(2)	3286.3(18)	8765(2)	35.2(7)
C29	10451(2)	3621.5(17)	9192.1(19)	30.2(7)
C37	9625(2)	1672.1(16)	6939.9(17)	24.9(6)
C32	10204(2)	2926.2(17)	5818(2)	32.5(7)
C31	9335(2)	3046.0(15)	6113.7(19)	26.8(7)
C19	6266(2)	3172.0(15)	6491.3(17)	24.0(6)
C20	6636(2)	2897.6(17)	5780.7(18)	29.1(7)
C14	7068(2)	1388.9(16)	8167.7(19)	29.1(7)
C41	9947(2)	470.5(17)	7617.8(19)	31.2(7)
C15	7001(2)	595.4(17)	7998(2)	35.1(7)
C24	6359(2)	3975.5(16)	6570.7(18)	28.8(7)
C36	9163(2)	3841.1(16)	6178(2)	30.9(7)
C1	8240(2)	4444.2(18)	9402(2)	37.9(8)
C13	6666(2)	1806.4(16)	7354.6(18)	24.4(6)
C23	5886(2)	4346.1(17)	5741.2(19)	33.8(7)
C3	8569(2)	2219.4(19)	10157(2)	34.4(7)
C9	5274(2)	3538.1(17)	9340(2)	34.8(7)
C18	5645(2)	1577.6(17)	6955(2)	36.4(8)
C28	11413(2)	3626.4(17)	9317(2)	33.8(7)
C21	6179(2)	3275.6(18)	4950.7(18)	32.2(7)
C22	6275(2)	4076.7(17)	5042.5(19)	34.4(7)
C16	6006(2)	355.2(18)	7547(2)	37.9(8)

C33	10111(3)	3291.3(19)	4979(2)	38.4(8)
C17	5593(2)	790.6(18)	6760(2)	40.1(8)
C35	9066(3)	4209.5(18)	5342(2)	39.3(8)
C4	8198(2)	1807(2)	10626(2)	47.9(10)
C34	9921(3)	4080.4(18)	5032(2)	41.1(8)
C5	7816(3)	2104(3)	11308(3)	77.2(17)
C6	8106(4)	1022(3)	10495(3)	77.6(16)
C1A	13048(4)	4932(3)	8570(3)	71.9(13)
C1B	12559(4)	4767(3)	7665(3)	74.3(13)
C1C	12263(4)	6301(3)	7047(4)	92.8(19)
C1D	11626(4)	5918(3)	7459(5)	107(2)
C1W	11630(3)	5107(3)	7390(4)	79.7(15)

Table S8: Anisotropic Displacement Parameters ($Å^2×10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Pd1	21.03(14)	24.69(15)	17.88(13)	-0.67(7)	3.07(9)	0.13(7)
P1	21.3(4)	24.4(4)	17.7(3)	-0.1(3)	3.6(3)	2.1(3)
P2	23.2(4)	24.4(4)	21.6(4)	-0.4(3)	6.9(3)	-0.2(3)
Si1	28.0(4)	32.2(4)	18.1(4)	-2.7(3)	3.4(3)	0.4(3)
C38	30.8(16)	30.0(17)	24.0(15)	-0.1(12)	7.8(12)	-1.9(13)
C12	26.7(16)	24.1(16)	25.4(15)	2.6(11)	9.0(13)	3.1(11)
C25	25.1(16)	23.0(15)	27.6(16)	3.8(12)	3.5(13)	-2.8(11)
C11	29.6(17)	30.8(18)	30.0(17)	-1.7(12)	8.8(14)	0.9(12)
C26	27.2(17)	34.8(18)	35.0(18)	3.6(13)	9.9(14)	-1.8(13)
C42	30.7(16)	27.5(16)	24.2(15)	0.3(12)	4.0(12)	-4.3(12)
C2	38(2)	56(2)	20.8(16)	-0.9(14)	2.1(14)	0.2(15)
C39	43.9(19)	27.8(17)	27.2(16)	-3.1(13)	14.0(14)	-3.2(14)
C30	30.1(16)	22.7(15)	25.3(15)	3.4(12)	6.0(12)	0.3(12)
C40	43.0(19)	26.4(17)	30.9(16)	0.2(13)	14.6(14)	-3.7(13)
C10	29.6(17)	35.0(18)	41.0(18)	3.3(15)	17.2(14)	2.9(14)
C8	42.8(19)	30.9(17)	23.1(15)	1.1(12)	12.9(13)	1.1(14)
C7	33.2(16)	25.6(16)	22.1(14)	2.6(12)	10.7(12)	3.4(12)
C27	22.8(16)	39.0(19)	40.9(18)	4.6(15)	4.2(13)	-5.2(14)
C29	28.9(16)	30.2(17)	27.3(15)	-2.2(12)	0.8(12)	-3.2(13)
C37	23.4(14)	25.4(16)	25.9(15)	2.2(12)	6.9(11)	-2.4(12)
C32	38.9(19)	29.4(17)	34.2(17)	1.8(13)	18.3(15)	2.6(13)
C31	28.7(16)	26.6(17)	26.1(16)	-1.2(11)	9.4(13)	-0.4(11)
C19	26.0(15)	24.7(15)	19.3(14)	-0.1(11)	3.3(11)	3.4(12)
C20	35.3(17)	29.0(16)	21.6(15)	-2.1(12)	5.9(13)	5.6(13)
C14	27.4(15)	32.6(17)	25.8(15)	5.4(13)	4.8(12)	2.0(13)
C41	34.4(17)	28.2(17)	29.7(16)	4.6(13)	6.9(13)	-1.3(13)
C15	35.2(18)	30.5(18)	37.6(18)	8.9(14)	7.2(14)	0.9(14)
C24	36.7(17)	26.3(16)	23.7(15)	0.5(12)	9.0(13)	4.8(13)
C36	35.2(17)	24.0(16)	34.7(17)	-0.2(13)	11.9(13)	0.7(13)
C1	36.6(18)	40(2)	36.0(18)	-9.0(14)	7.9(14)	-2.0(14)
C13	21.7(15)	27.5(15)	21.9(15)	0.1(12)	2.5(11)	1.2(12)
C23	42.2(18)	28.1(17)	28.3(16)	3.4(13)	5.2(14)	7.9(13)
C3	24.6(16)	51(2)	25.4(16)	8.3(14)	2.7(13)	8.3(14)
C9	46(2)	32.6(18)	34.2(17)	3.3(13)	24.8(15)	3.7(14)

C18	26.7(17)	31.4(18)	41.6(18)	2.2(14)	-5.8(14)	-1.3(13)
C28	31.7(17)	32.0(18)	31.8(16)	0.8(13)	-0.5(13)	-9.1(13)
C21	38.9(18)	35.4(18)	20.2(15)	1.3(13)	5.0(13)	4.4(14)
C22	42.1(19)	35.2(18)	23.5(15)	4.2(13)	5.2(13)	4.2(14)
C16	39.2(19)	31.7(18)	42.8(19)	2.9(15)	11.7(15)	-5.5(14)
C33	53(2)	35.1(19)	34.6(17)	3.5(15)	24.3(16)	1.0(16)
C17	35.7(18)	31.6(18)	44.5(19)	-1.4(15)	-2.6(15)	-7.8(14)
C35	51(2)	30.8(18)	40.5(19)	8.3(14)	20.9(16)	5.2(15)
C4	26.5(18)	72(3)	40(2)	23.9(19)	1.6(15)	4.4(17)
C34	56(2)	31.5(19)	41.9(19)	8.2(15)	24.3(17)	-0.6(16)
C5	43(3)	146(5)	50(3)	34(3)	26(2)	10(3)
C6	72(3)	69(3)	78(3)	38(3)	-2(3)	-7(2)
C1A	86(3)	68(3)	62(3)	-5(2)	22(2)	-16(3)
C1B	84(3)	67(3)	74(3)	0(3)	26(3)	-8(3)
C1C	90(4)	88(4)	87(4)	6(3)	4(3)	-35(3)
C1D	78(4)	77(4)	173(7)	-11(4)	48(4)	-4(3)
C1W	51(3)	63(3)	122(4)	-14(3)	20(3)	-7(2)

Table S9: Bond Lengths for **4**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pd1	P1	2.2896(7)	C8	C9	1.381(5)
Pd1	P2	2.4370(7)	C27	C28	1.386(5)
Pd1	Si1	2.3007(8)	C29	C28	1.388(5)
Pd1	C30	2.085(3)	C32	C31	1.526(4)
P1	C12	1.831(3)	C32	C33	1.525(4)
P1	C19	1.847(3)	C31	C36	1.534(4)
P1	C13	1.842(3)	C19	C20	1.528(4)
P2	C25	1.813(3)	C19	C24	1.528(4)
P2	C37	1.845(3)	C20	C21	1.530(4)
P2	C31	1.843(3)	C14	C15	1.525(5)
Si1	C2	1.895(3)	C14	C13	1.532(4)
Si1	C7	1.905(3)	C15	C16	1.529(5)
Si1	C1	1.889(3)	C24	C23	1.528(4)
C38	C39	1.528(4)	C36	C35	1.523(4)
C38	C37	1.535(4)	C13	C18	1.538(4)
C12	C11	1.400(5)	C23	C22	1.524(5)
C12	C7	1.403(4)	C3	C4	1.329(5)
C25	C26	1.402(5)	C18	C17	1.521(5)
C25	C30	1.397(5)	C21	C22	1.525(5)
C11	C10	1.387(5)	C16	C17	1.519(5)
C26	C27	1.385(5)	C33	C34	1.526(5)
C42	C37	1.528(4)	C35	C34	1.522(5)
C42	C41	1.524(4)	C4	C5	1.512(7)
C2	C3	1.483(5)	C4	C6	1.501(7)
C39	C40	1.516(4)	C1A	C1B	1.505(6)
C30	C29	1.407(4)	C1B	C1W	1.476(6)
C40	C41	1.527(4)	C1C	C1D	1.504(8)
C10	C9	1.392(5)	C1D	C1W	1.539(7)
C8	C7	1.404(4)			

Table S10: Bond Angles for **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pd1	P2	111.50(3)	C12	C7	Si1	118.4(2)
P1	Pd1	Si1	85.12(3)	C12	C7	C8	117.8(3)
Si1	Pd1	P2	162.71(3)	C8	C7	Si1	123.5(2)
C30	Pd1	P1	179.13(8)	C26	C27	C28	119.7(3)
C30	Pd1	P2	68.71(9)	C28	C29	C30	120.8(3)
C30	Pd1	Si1	94.60(9)	C38	C37	P2	111.9(2)
C12	P1	Pd1	112.28(10)	C42	C37	P2	110.4(2)
C12	P1	C19	103.54(14)	C42	C37	C38	110.4(2)
C12	P1	C13	106.56(14)	C33	C32	C31	111.1(3)
C19	P1	Pd1	115.46(11)	C32	C31	P2	115.9(2)
C13	P1	Pd1	112.87(9)	C32	C31	C36	110.0(3)
C13	P1	C19	105.25(13)	C36	C31	P2	110.1(2)
C25	P2	Pd1	80.67(11)	C20	C19	P1	111.8(2)
C25	P2	C37	107.25(13)	C20	C19	C24	111.1(3)
C25	P2	C31	108.06(14)	C24	C19	P1	109.2(2)
C37	P2	Pd1	127.38(10)	C19	C20	C21	111.8(3)
C31	P2	Pd1	122.87(10)	C15	C14	C13	110.8(3)
C31	P2	C37	104.33(13)	C42	C41	C40	110.8(3)
C2	Si1	Pd1	112.42(12)	C14	C15	C16	112.7(3)
C2	Si1	C7	108.29(15)	C23	C24	C19	111.8(2)
C7	Si1	Pd1	108.29(9)	C35	C36	C31	111.0(3)
C1	Si1	Pd1	117.14(11)	C14	C13	P1	112.0(2)
C1	Si1	C2	105.28(15)	C14	C13	C18	109.1(3)
C1	Si1	C7	104.90(14)	C18	C13	P1	116.5(2)
C39	C38	C37	111.2(3)	C22	C23	C24	110.8(3)
C11	C12	P1	123.6(2)	C4	C3	C2	129.1(4)
C11	C12	C7	120.8(3)	C8	C9	C10	120.2(3)
C7	C12	P1	115.5(2)	C17	C18	C13	110.6(3)
C26	C25	P2	131.3(3)	C27	C28	C29	121.2(3)
C30	C25	P2	105.6(2)	C22	C21	C20	111.6(3)
C30	C25	C26	123.1(3)	C23	C22	C21	111.3(3)
C10	C11	C12	120.0(3)	C17	C16	C15	111.1(3)
C27	C26	C25	118.5(3)	C32	C33	C34	111.1(3)
C41	C42	C37	111.3(3)	C16	C17	C18	111.3(3)
C3	C2	Si1	115.4(2)	C34	C35	C36	111.2(3)
C40	C39	C38	111.5(3)	C3	C4	C5	121.9(4)
C25	C30	Pd1	104.8(2)	C3	C4	C6	122.1(4)
C25	C30	C29	116.5(3)	C6	C4	C5	116.0(4)
C29	C30	Pd1	138.6(2)	C35	C34	C33	111.3(3)
C39	C40	C41	111.7(3)	C1W	C1B	C1A	111.4(5)
C11	C10	C9	119.8(3)	C1C	C1D	C1W	115.5(6)
C9	C8	C7	121.3(3)	C1B	C1W	C1D	115.7(5)

X-Ray Data for (^{Cy}PSiP)Pd(carboxylate) (***5***)

5 crystallized with disorder in the carboxylate over two positions. The occupancies were refined freely and converged at 0.695.

Table S11: Crystal data and structure refinement for **5**.

Empirical formula	$C_{43}H_{64}O_2P_2PdSi$
Formula weight	809.37
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.6994(16)
b/Å	25.260(3)
c/Å	13.3608(17)
α/°	90.00
β/°	105.432(7)
γ/°	90.00
Volume/Å^3	4131.5(9)
Z	4
ρ_{calc}mg/mm^3	1.301
m/mm^{-1}	0.590
F(000)	1712.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
2Θ range for data collection	6.1 to 48.22°
Index ranges	$-14 \le h \le 14$, $-29 \le k \le 29$, $-15 \le l \le 15$
Reflections collected	59463
Independent reflections	6568[R(int) = 0.1550]
Data/restraints/parameters	6568/115/472
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0597, wR_2 = 0.1117
Final R indexes [all data]	R_1 = 0.0760, wR_2 = 0.1191
Largest diff. peak/hole / e Å^{-3}	0.56/-0.69

Table S12: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	8363.5(3)	3569.61(13)	8028.3(3)	26.44(13)
P1	9744.4(10)	2964.6(5)	8600.6(10)	28.9(3)
P2	7279.6(10)	4303.1(5)	8041.2(9)	27.1(3)
Si1	7954.9(11)	3359.1(5)	9524.3(10)	27.7(3)
C31	6969(3)	4367.5(17)	9296(3)	26.4(11)
O2	7365(3)	3437.3(16)	5713(3)	65.2(12)
O1	8933(3)	3740.5(13)	6663(2)	38.2(8)
C38	5981(4)	4280.3(18)	7013(3)	30.8(11)
C30	6443(4)	4803.3(19)	9582(4)	33.1(12)
C26	7329(3)	3951.7(17)	10003(4)	27.7(11)
C10	11944(4)	4144.8(19)	8403(4)	44.9(14)
C27	7106(4)	3985.4(19)	10964(4)	36.6(12)
C16	9001(5)	1371.9(19)	7968(4)	48.1(15)
C14	9762(4)	2295.5(17)	8085(4)	31.5(11)
C18	9660(5)	1740(2)	6499(5)	52.9(16)
C32	7891(4)	4948.4(18)	7881(4)	30.0(11)
C36	8748(4)	5490.3(19)	6712(4)	39.9(13)

C11	13038(4)	3852(2)	8680(4)	42.7(13)
C28	6589(4)	4418(2)	11244(4)	38.5(13)
C42	4397(4)	3699(2)	6170(4)	49.0(15)
C39	5218(4)	4759(2)	6878(4)	41.1(13)
C34	9458(4)	5575.8(19)	8627(4)	39.4(13)
C2	8677(4)	3734(2)	4826(4)	42.5(12)
C13	12029(4)	2990.0(19)	8621(5)	42.8(14)
C25	9238(4)	3102.2(17)	10457(4)	30.2(11)
C8	10952(4)	3288.4(17)	8343(4)	31.6(11)
C29	6261(4)	4829.3(19)	10550(4)	37.5(12)
C23	10340(4)	2803(2)	12116(4)	44.1(14)
C20	10009(4)	2880.4(17)	9993(3)	30.2(11)
C24	9428(4)	3059.2(19)	11523(4)	37.0(12)
C15	8926(4)	1929.0(18)	8369(4)	39.6(13)
C43	5367(4)	3771.9(19)	7110(4)	39.2(13)
C41	3635(4)	4173(2)	5990(4)	52.7(16)
C9	11091(4)	3847.3(19)	8785(4)	40.0(13)
C33	8898(4)	5057.3(17)	8793(4)	33.5(12)
C1	8264(4)	3623.4(18)	5807(4)	34.9(12)
C37	8173(4)	4978.6(19)	6849(4)	36.3(12)
C7	6920(4)	2824.7(18)	9485(4)	36.8(12)
C35	9759(4)	5575(2)	7613(4)	43.0(13)
C21	10904(4)	2597.7(18)	10602(4)	34.8(12)
C19	9583(4)	2301.5(18)	6911(4)	39.8(13)
C22	11074(4)	2565.5(18)	11659(4)	36.5(13)
C40	4248(4)	4677(2)	5921(4)	48.7(15)
C17	8848(5)	1374(2)	6808(5)	58.6(17)
C12	12900(4)	3297(2)	8264(5)	48.0(14)
C6A	10678(18)	3428(9)	5057(17)	72(6)
C5	8973(7)	4322(3)	4835(6)	39(2)
C3	7760(8)	3611(4)	3858(6)	71(3)
C6	8575(7)	4674(3)	4147(7)	57(2)
C4	9671(9)	3407(4)	4866(8)	77(3)
C3A	8378(16)	3262(6)	4112(12)	42.5(12)
C5A	9956(12)	3747(8)	5208(13)	42.5(12)
C4A	8270(20)	4249(7)	4358(16)	58(5)

Table S13: Anisotropic Displacement Parameters ($Å^2×10^3$) for **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	29.8(2)	28.5(2)	21.3(2)	1.10(15)	7.23(16)	2.11(16)
P1	31.0(7)	27.8(7)	28.3(7)	-0.4(5)	8.8(6)	1.2(5)
P2	27.7(7)	31.4(7)	22.0(6)	1.9(5)	6.3(5)	0.6(5)
Si1	31.1(7)	28.5(7)	23.3(7)	1.4(6)	6.6(6)	0.6(6)
C31	23(2)	28(3)	29(3)	0(2)	8(2)	-4(2)
O2	67(3)	83(3)	50(3)	-17(2)	24(2)	-39(2)
O1	40(2)	48(2)	29(2)	5.6(16)	13.4(17)	5.5(17)
C38	35(3)	36(3)	20(2)	0(2)	5(2)	-3(2)
C30	31(3)	34(3)	35(3)	-3(2)	9(2)	0(2)
C26	24(3)	29(3)	29(3)	-1(2)	7(2)	-4(2)

C10	42(3)	31(3)	61(4)	-4(3)	12(3)	-7(2)
C27	40(3)	39(3)	34(3)	3(2)	17(2)	6(2)
C16	56(4)	34(3)	54(4)	-3(3)	14(3)	-9(3)
C14	32(3)	26(3)	35(3)	-3(2)	5(2)	2(2)
C18	68(4)	43(3)	58(4)	-20(3)	35(3)	-11(3)
C32	26(3)	31(3)	32(3)	5(2)	7(2)	0(2)
C36	50(3)	40(3)	32(3)	7(2)	16(3)	2(3)
C11	37(3)	47(3)	45(3)	3(3)	14(3)	-5(3)
C28	38(3)	52(3)	28(3)	-4(2)	14(2)	-1(3)
C42	47(3)	53(4)	43(3)	-1(3)	5(3)	-15(3)
C39	38(3)	42(3)	39(3)	7(2)	3(3)	4(2)
C34	43(3)	40(3)	34(3)	0(2)	8(2)	-6(2)
C2	59(3)	46(3)	28(2)	1(2)	21(2)	-7(2)
C13	38(3)	32(3)	63(4)	4(3)	20(3)	5(2)
C25	36(3)	26(3)	27(3)	0(2)	5(2)	3(2)
C8	36(3)	27(3)	33(3)	-2(2)	13(2)	-2(2)
C29	38(3)	35(3)	40(3)	-10(2)	10(2)	-2(2)
C23	52(4)	45(3)	26(3)	4(2)	-5(3)	-2(3)
C20	33(3)	29(3)	26(3)	-2(2)	4(2)	-3(2)
C24	47(3)	40(3)	23(3)	1(2)	7(2)	4(2)
C15	38(3)	37(3)	42(3)	-1(2)	9(3)	-5(2)
C43	36(3)	40(3)	39(3)	2(2)	6(2)	-2(2)
C41	32(3)	80(4)	40(3)	10(3)	-2(3)	-5(3)
C9	37(3)	39(3)	47(3)	-7(2)	16(3)	1(2)
C33	36(3)	30(3)	34(3)	-1(2)	9(2)	-2(2)
C1	46(3)	30(3)	30(3)	0(2)	13(2)	1(2)
C37	42(3)	38(3)	29(3)	5(2)	9(2)	-1(2)
C7	40(3)	39(3)	31(3)	2(2)	9(2)	-5(2)
C35	46(3)	39(3)	46(3)	2(2)	16(3)	-5(3)
C21	35(3)	31(3)	36(3)	7(2)	5(2)	2(2)
C19	48(3)	34(3)	40(3)	-7(2)	17(3)	-4(2)
C22	31(3)	33(3)	39(3)	8(2)	-3(2)	1(2)
C40	32(3)	58(4)	49(4)	18(3)	-1(3)	1(3)
C17	74(4)	43(3)	63(4)	-24(3)	25(3)	-13(3)
C12	43(3)	47(3)	61(4)	8(3)	26(3)	5(3)
C6A	65(11)	93(16)	64(14)	20(12)	30(12)	17(11)
C5	48(5)	47(4)	28(5)	1(3)	19(4)	-9(4)
C3	110(7)	70(7)	27(4)	-3(4)	10(5)	-41(6)
C6	73(6)	51(5)	53(5)	0(4)	28(5)	-13(5)
C4	115(8)	76(7)	65(7)	19(6)	66(6)	41(6)
C3A	59(3)	46(3)	28(2)	1(2)	21(2)	-7(2)
C5A	59(3)	46(3)	28(2)	1(2)	21(2)	-7(2)
C4A	89(14)	59(8)	41(13)	11(8)	42(11)	18(11)

Table S14: Bond Lengths for **5**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.2983(13)	C32	C33	1.538(6)
Pd1	P2	2.3110(13)	C32	C37	1.515(6)
Pd1	Si1	2.2581(14)	C36	C37	1.520(6)

Pd1	O1	2.177(3)	C36	C35	1.524(7)
P1	C14	1.828(4)	C11	C12	1.503(7)
P1	C8	1.849(5)	C28	C29	1.381(7)
P1	C20	1.814(5)	C42	C43	1.518(7)
P2	C31	1.829(5)	C42	C41	1.516(7)
P2	C38	1.845(4)	C39	C40	1.535(7)
P2	C32	1.842(4)	C34	C33	1.534(6)
Si1	C26	1.885(5)	C34	C35	1.502(7)
Si1	C25	1.884(5)	C2	C1	1.561(7)
Si1	C7	1.875(5)	C2	C5	1.531(9)
C31	C30	1.393(6)	C2	C3	1.525(8)
C31	C26	1.405(6)	C2	C4	1.497(9)
O2	C1	1.210(6)	C2	C3A	1.510(12)
O1	C1	1.266(6)	C2	C5A	1.567(15)
C38	C39	1.530(6)	C2	C4A	1.475(13)
C38	C43	1.526(6)	C13	C8	1.519(6)
C30	C29	1.374(7)	C13	C12	1.527(7)
C26	C27	1.389(6)	C25	C20	1.406(6)
C10	C11	1.530(7)	C25	C24	1.384(6)
C10	C9	1.515(7)	C8	C9	1.523(6)
C27	C28	1.377(6)	C23	C24	1.377(7)
C16	C15	1.518(6)	C23	C22	1.381(7)
C16	C17	1.510(8)	C20	C21	1.404(6)
C14	C15	1.532(6)	C41	C40	1.508(7)
C14	C19	1.523(6)	C21	C22	1.373(7)
C18	C19	1.535(6)	C6A	C5A	1.278(18)
C18	C17	1.520(7)	C5	C6	1.283(11)

Table S15: Bond Angles for **5**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pd1	P2	159.06(5)	C5	C2	C1	107.7(5)
Si1	Pd1	P1	83.32(5)	C5	C2	C5A	75.3(8)
Si1	Pd1	P2	84.52(5)	C3	C2	C1	108.9(5)
O1	Pd1	P1	90.93(9)	C3	C2	C5	109.6(6)
O1	Pd1	P2	100.29(9)	C3	C2	C5A	140.5(8)
O1	Pd1	Si1	173.83(9)	C4	C2	C1	109.9(5)
C14	P1	Pd1	125.06(16)	C4	C2	C5	109.4(6)
C14	P1	C8	104.2(2)	C4	C2	C3	111.3(7)
C8	P1	Pd1	103.95(15)	C4	C2	C3A	69.8(9)
C20	P1	Pd1	109.62(16)	C4	C2	C5A	37.8(7)
C20	P1	C14	105.1(2)	C3A	C2	C1	107.8(7)
C20	P1	C8	107.9(2)	C3A	C2	C5	142.2(8)
C31	P2	Pd1	110.62(15)	C3A	C2	C3	45.2(7)
C31	P2	C38	108.5(2)	C3A	C2	C5A	106.7(11)
C31	P2	C32	103.2(2)	C4A	C2	C1	110.9(8)
C38	P2	Pd1	112.66(15)	C4A	C2	C5	37.3(10)
C32	P2	Pd1	115.98(16)	C4A	C2	C3	73.7(11)
C32	P2	C38	105.2(2)	C4A	C2	C4	134.2(10)
C26	Si1	Pd1	109.29(15)	C4A	C2	C3A	115.3(12)

C25	Si1	Pd1	107.71(16)	C4A	C2	C5A	109.4(13)
C25	Si1	C26	114.7(2)	C8	C13	C12	110.6(4)
C7	Si1	Pd1	117.99(16)	C20	C25	Si1	115.3(3)
C7	Si1	C26	103.0(2)	C24	C25	Si1	126.2(4)
C7	Si1	C25	104.3(2)	C24	C25	C20	118.1(4)
C30	C31	P2	123.9(4)	C13	C8	P1	118.2(3)
C30	C31	C26	120.0(4)	C13	C8	C9	111.1(4)
C26	C31	P2	116.0(3)	C9	C8	P1	110.8(3)
C1	O1	Pd1	114.7(3)	C30	C29	C28	120.0(5)
C39	C38	P2	118.4(3)	C24	C23	C22	120.8(5)
C43	C38	P2	109.8(3)	C25	C20	P1	116.4(3)
C43	C38	C39	110.7(4)	C21	C20	P1	123.7(4)
C29	C30	C31	120.6(5)	C21	C20	C25	119.9(4)
C31	C26	Si1	117.2(3)	C23	C24	C25	121.3(5)
C27	C26	Si1	124.8(4)	C16	C15	C14	111.1(4)
C27	C26	C31	117.8(4)	C42	C43	C38	110.6(4)
C9	C10	C11	111.3(4)	C40	C41	C42	111.0(4)
C28	C27	C26	121.9(5)	C10	C9	C8	110.4(4)
C17	C16	C15	110.8(4)	C34	C33	C32	111.0(4)
C15	C14	P1	112.7(3)	O2	C1	O1	124.9(5)
C19	C14	P1	111.4(3)	O2	C1	C2	120.2(5)
C19	C14	C15	109.7(4)	O1	C1	C2	114.9(4)
C17	C18	C19	110.6(4)	C32	C37	C36	113.0(4)
C33	C32	P2	110.7(3)	C34	C35	C36	110.5(4)
C37	C32	P2	111.1(3)	C22	C21	C20	120.5(5)
C37	C32	C33	111.3(4)	C14	C19	C18	110.7(4)
C37	C36	C35	110.8(4)	C21	C22	C23	119.3(5)
C12	C11	C10	110.6(4)	C41	C40	C39	112.1(4)
C27	C28	C29	119.6(5)	C16	C17	C18	111.7(5)
C41	C42	C43	112.3(4)	C11	C12	C13	112.4(4)
C38	C39	C40	109.5(4)	C6	C5	C2	128.2(8)
C35	C34	C33	111.6(4)	C6A	C5A	C2	131.3(19)
C1	C2	C5A	106.4(7)				

*X-Ray Data for (^{Cy}PSiP)Pd(Et) (**6**)*

Compound **6** crystallized with 14% (^{Cy}PSiP)PdCl impurity.

Table S16: Crystal data and structure refinement for **6**.

Empirical formula	$C_{39}H_{60}P_2PdSi$
Formula weight	725.30
Temperature/K	223
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.9946(4)
b/Å	14.2318(4)
c/Å	20.8681(15)
α/°	90
β/°	100.188(7)
γ/°	90

Volume/Å^3	3798.4(3)
Z	4
ρ_{calc}mg/mm^3	1.270
m/mm^{-1}	0.639
F(000)	1536.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection	6.06 to 54.962°
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -26 ≤ l ≤ 27
Reflections collected	64882
Independent reflections	8675 [R_{int} = 0.0464, R_{sigma} = 0.0265]
Data/restraints/parameters	8675/0/390
Goodness-of-fit on F^2	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0793
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.0827
Largest diff. peak/hole / e Å^{-3}	1.21/-0.41

Table S17: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	3164.2(2)	7997.7(2)	8172.6(2)	29.58(6)
P1	1897.8(5)	8968.8(4)	8440.7(3)	30.73(14)
P2	4005.3(5)	6630.4(4)	7982.4(3)	30.86(14)
Si1	2935.0(5)	7204.7(5)	9108.9(3)	31.26(15)
C27	1218.7(19)	8422.6(18)	9053.8(12)	34.4(5)
C22	1627.5(19)	7569.0(18)	9318.5(12)	36.7(6)
C3	3452(2)	6249.0(18)	7144.9(12)	34.8(5)
C23	1089(2)	7102(2)	9751.5(15)	53.4(8)
C29	1681(2)	10807.4(17)	8992.5(13)	38.5(6)
C20	3149(2)	5901.1(17)	9005.1(13)	35.9(6)
C15	3733.4(19)	5669.0(17)	8521.3(12)	33.8(5)
C16	4119(2)	4757.2(19)	8486.0(14)	43.9(6)
C4	2258(2)	6210(2)	7048.9(15)	52.6(8)
C33	3407(2)	9968.4(18)	9275.6(14)	41.8(6)
C9	5442.9(19)	6574.1(18)	8037.0(12)	35.7(5)
C34	772(2)	9262(2)	7788.3(13)	41.2(6)
C26	311(2)	8792(2)	9229.5(14)	42.5(6)
C14	5992(2)	6768(3)	8738.5(15)	55.0(8)
C28	2431.9(18)	10116.4(16)	8756.5(12)	31.0(5)
C10	5826(2)	7245(2)	7562.8(16)	49.9(7)
C19	2958(3)	5190(2)	9433.5(15)	50.6(7)
C30	2233(2)	11739.4(18)	9202.4(13)	39.8(6)
C25	-204(2)	8308(2)	9650.8(15)	50.5(7)
C21	3897(2)	7460(2)	9878.8(14)	46.8(7)
C31	3196(2)	11588.0(19)	9715.4(14)	45.5(7)
C32	3940(2)	10899.2(19)	9489.8(16)	49.4(7)
C8	3872(2)	5349(2)	6885.8(14)	45.8(7)
C17	3908(3)	4071(2)	8910.5(15)	53.2(8)
C24	175(3)	7462(2)	9906.3(16)	58.3(8)
C11	7011(2)	7212(3)	7624.7(17)	58.4(8)

C5	1787(3)	6077(3)	6331.9(17)	64.2(9)
C35	1016(2)	9995(3)	7300.3(15)	57.2(8)
C18	3324(3)	4285(2)	9383.4(16)	57.9(8)
C7	3400(3)	5219(3)	6164.0(15)	60.6(9)
C6	2213(3)	5214(2)	6053.7(16)	60.7(9)
C39	339(3)	8358(3)	7449.5(19)	71.5(10)
C12	7562(3)	7391(3)	8316.3(19)	68.6(10)
C13	7186(2)	6719(3)	8792.0(17)	68.5(10)
C36	68(3)	10172(3)	6763.6(19)	79.4(12)
C38	-589(4)	8554(4)	6912(3)	107.8(17)
C37	-310(4)	9268(4)	6427(2)	108.2(18)
C2	3218(4)	8718(3)	6664(3)	65.3(13)
C1	3566(7)	8939(6)	7387(4)	38.6(13)
Cl1	3490(16)	8799(15)	7240(11)	104(12)

Table S18: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **6**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Pd1	30.75(10)	26.31(9)	33.41(10)	-3.54(8)	10.42(7)	-1.66(7)
P1	30.1(3)	27.6(3)	35.4(3)	-3.6(3)	8.0(3)	-0.9(2)
P2	31.7(3)	29.5(3)	32.7(3)	-5.1(3)	9.3(3)	-0.5(2)
Si1	34.3(3)	28.6(3)	32.5(4)	-1.4(3)	10.3(3)	0.9(3)
C27	34.0(13)	34.1(13)	36.9(14)	-3.6(11)	11.6(11)	-3.3(10)
C22	36.5(14)	38.4(14)	37.5(14)	-2.4(11)	12.8(11)	1.9(11)
C3	38.3(13)	32.7(13)	33.2(13)	-3.5(10)	5.8(11)	-2.6(10)
C23	57.6(18)	52.0(18)	57.2(18)	16.1(15)	28.2(15)	10.8(14)
C29	36.8(14)	33.2(13)	44.8(15)	-4.0(11)	5.3(11)	5.7(11)
C20	37.1(13)	29.8(13)	41.8(14)	-1.3(11)	9.9(11)	-0.7(10)
C15	35.5(13)	30.7(12)	35.3(13)	-3(1)	6.7(10)	-0.5(10)
C16	52.8(17)	38.3(15)	42.2(15)	-1.9(12)	12.6(13)	8.3(12)
C4	36.4(15)	59.6(19)	60.2(19)	-18.4(16)	3.9(14)	1.3(14)
C33	40.1(15)	29.3(13)	51.1(16)	-2.8(12)	-5.4(12)	5.4(11)
C9	33.0(13)	37.7(14)	37.0(14)	-9.0(11)	8.0(11)	1.1(11)
C34	29.9(13)	51.5(16)	40.7(15)	-2.7(12)	2.0(11)	-1.7(11)
C26	36.0(14)	41.7(15)	52.4(17)	1.6(13)	15.0(12)	5.9(11)
C14	40.5(16)	81(2)	43.1(17)	-13.0(15)	6.7(13)	-6.4(15)
C28	31.2(12)	27.3(12)	34.4(13)	-1(1)	5.5(10)	0.7(9)
C10	40.5(15)	53.4(18)	58.7(19)	1.8(14)	16.7(14)	-1.0(13)
C19	65(2)	37.7(15)	55.9(18)	4.9(13)	28.9(16)	2.2(14)
C30	45.4(15)	29.7(13)	44.3(15)	-2.0(11)	8.0(12)	6.6(11)
C25	41.2(15)	59.5(18)	56.6(18)	4.6(15)	24.5(14)	6.8(13)
C21	51.5(17)	44.2(16)	42.4(16)	-2.6(13)	2.4(13)	1.2(13)
C31	58.8(18)	27.9(13)	45.9(16)	-3.4(12)	-1.6(13)	-2.7(12)
C32	42.0(16)	35.7(15)	62.7(19)	-5.5(13)	-11.8(14)	2.3(12)
C8	45.0(16)	47.2(16)	44.5(16)	-17.2(13)	6.3(13)	3.8(13)
C17	73(2)	31.6(14)	56.5(18)	1.4(13)	16.4(16)	11.1(14)
C24	54.3(18)	65(2)	64(2)	16.3(17)	35.6(16)	5.6(16)
C11	40.8(16)	71(2)	68(2)	1.1(17)	21.4(15)	-4.1(15)
C5	46.5(18)	69(2)	69(2)	-12.6(18)	-13.5(16)	1.1(16)
C35	48.5(18)	74(2)	45.4(17)	8.7(16)	-1.0(14)	1.0(16)

C18	81(2)	33.0(15)	64(2)	12.3(14)	26.7(18)	3.5(15)
C7	65(2)	71(2)	45.3(18)	-25.0(16)	9.0(15)	-5.7(17)
C6	61(2)	64(2)	51.0(19)	-17.6(16)	-6.7(15)	-9.6(16)
C39	57(2)	69(2)	80(3)	-19(2)	-13.5(19)	-14.2(18)
C12	39.7(17)	79(2)	88(3)	-23(2)	13.5(17)	-14.2(17)
C13	41.5(17)	106(3)	54(2)	-15(2)	-2.7(15)	-7.1(18)
C36	60(2)	112(3)	59(2)	14(2)	-9.6(18)	13(2)
C38	75(3)	122(4)	107(4)	-24(3)	-36(3)	-27(3)
C37	83(3)	154(5)	69(3)	-16(3)	-36(2)	7(3)
C2	104(4)	51(2)	48(3)	5(2)	33(2)	2(2)
C1	42(3)	32(2)	46(3)	11(2)	17.1(18)	-1.3(19)
Cl1	71(10)	83(10)	170(30)	-14(9)	47(12)	9(6)

Table S19: Bond Lengths for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.2929(6)	C4	C5	1.525(4)
Pd1	P2	2.3004(6)	C33	C28	1.529(3)
Pd1	Si1	2.3207(7)	C33	C32	1.525(4)
Pd1	C1	2.249(6)	C9	C14	1.536(4)
Pd1	Cl1	2.36(2)	C9	C10	1.521(4)
P1	C27	1.849(3)	C34	C35	1.530(4)
P1	C34	1.861(3)	C34	C39	1.527(4)
P1	C28	1.850(2)	C26	C25	1.380(4)
P2	C3	1.850(3)	C14	C13	1.537(4)
P2	C15	1.845(3)	C10	C11	1.523(4)
P2	C9	1.853(3)	C19	C18	1.383(4)
Si1	C22	1.900(3)	C30	C31	1.511(4)
Si1	C20	1.894(3)	C25	C24	1.372(4)
Si1	C21	1.888(3)	C31	C32	1.510(4)
C27	C22	1.400(4)	C8	C7	1.534(4)
C27	C26	1.399(3)	C17	C18	1.381(4)
C22	C23	1.404(4)	C11	C12	1.515(5)
C3	C4	1.530(4)	C5	C6	1.505(5)
C3	C8	1.528(4)	C35	C36	1.532(4)
C23	C24	1.383(4)	C7	C6	1.519(5)
C29	C28	1.527(3)	C39	C38	1.520(5)
C29	C30	1.535(4)	C12	C13	1.520(5)
C20	C15	1.405(3)	C36	C37	1.505(6)
C20	C19	1.402(4)	C38	C37	1.523(7)
C15	C16	1.398(3)	C2	C1	1.529(9)
C16	C17	1.378(4)			

Table S20: Bond Angles for **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pd1	P2	159.30(2)	C19	C20	C15	117.9(2)
P1	Pd1	Si1	83.29(2)	C20	C15	P2	116.72(18)
P1	Pd1	Cl1	98.7(5)	C16	C15	P2	123.2(2)
P2	Pd1	Si1	82.51(2)	C16	C15	C20	120.0(2)
P2	Pd1	Cl1	96.1(5)	C17	C16	C15	120.7(3)
Si1	Pd1	Cl1	177.1(5)	C5	C4	C3	110.8(3)

C1	Pd1	P1	95.1(2)	C32	C33	C28	111.4(2)
C1	Pd1	P2	101.5(2)	C14	C9	P2	110.15(18)
C1	Pd1	Si1	169.8(3)	C10	C9	P2	112.04(19)
C27	P1	Pd1	111.49(8)	C10	C9	C14	110.9(2)
C27	P1	C34	101.01(12)	C35	C34	P1	114.28(19)
C27	P1	C28	108.64(11)	C39	C34	P1	109.1(2)
C34	P1	Pd1	117.52(9)	C39	C34	C35	111.7(3)
C28	P1	Pd1	112.26(8)	C25	C26	C27	120.4(3)
C28	P1	C34	105.03(12)	C9	C14	C13	110.7(2)
C3	P2	Pd1	107.10(8)	C29	C28	P1	117.54(17)
C3	P2	C9	105.34(11)	C29	C28	C33	110.9(2)
C15	P2	Pd1	111.97(8)	C33	C28	P1	110.03(16)
C15	P2	C3	105.90(12)	C9	C10	C11	111.6(3)
C15	P2	C9	103.31(12)	C18	C19	C20	121.5(3)
C9	P2	Pd1	122.04(9)	C31	C30	C29	111.5(2)
C22	Si1	Pd1	108.32(8)	C24	C25	C26	120.3(3)
C20	Si1	Pd1	109.67(8)	C32	C31	C30	111.6(2)
C20	Si1	C22	116.69(12)	C31	C32	C33	111.8(2)
C21	Si1	Pd1	117.29(10)	C3	C8	C7	110.0(2)
C21	Si1	C22	103.64(12)	C16	C17	C18	120.0(3)
C21	Si1	C20	101.39(12)	C25	C24	C23	119.9(3)
C22	C27	P1	116.34(18)	C12	C11	C10	112.1(3)
C26	C27	P1	123.5(2)	C6	C5	C4	111.6(3)
C26	C27	C22	120.1(2)	C34	C35	C36	111.3(3)
C27	C22	Si1	116.00(18)	C17	C18	C19	119.9(3)
C27	C22	C23	117.9(2)	C6	C7	C8	111.7(3)
C23	C22	Si1	125.9(2)	C5	C6	C7	111.7(3)
C4	C3	P2	110.49(18)	C38	C39	C34	111.5(3)
C8	C3	P2	118.47(19)	C11	C12	C13	111.3(3)
C8	C3	C4	109.9(2)	C12	C13	C14	111.1(3)
C24	C23	C22	121.4(3)	C37	C36	C35	110.8(3)
C28	C29	C30	110.8(2)	C39	C38	C37	111.2(4)
C15	C20	Si1	114.92(18)	C36	C37	C38	110.9(4)
C19	C20	Si1	126.0(2)	C2	C1	Pd1	122.0(5)

X-Ray Data for (κ^2-$Cy_2PC_6H_4SiMeEt$)Pd(κ^2-$Cy_2PC_6H_4$) (7)

Table S21: Crystal data and structure refinement for **7**.

Empirical formula	$C_{39}H_{60}P_2PdSi$
Formula weight	725.30
Temperature/K	153
Crystal system	orthorhombic
Space group	Pbca
a/Å	19.3281(9)
b/Å	19.6232(9)
c/Å	19.8527(14)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	7529.7(7)

Z	8
ρ_{calc}mg/mm^3	1.280
m/mm^{-1}	0.635
F(000)	3072.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
2Θ range for data collection	6.2 to 51.36°
Index ranges	$-23 \le h \le 23$, $-23 \le k \le 23$, $-22 \le l \le 24$
Reflections collected	140954
Independent reflections	7137[R(int) = 0.1840]
Data/restraints/parameters	7137/0/391
Goodness-of-fit on F^2	1.183
Final R indexes [I>=2σ (I)]	R_1 = 0.0856, wR_2 = 0.1255
Final R indexes [all data]	R_1 = 0.1066, wR_2 = 0.1325
Largest diff. peak/hole / e Å^{-3}	0.94/-0.59

Table S22: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **7**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	9460.0(2)	2076.1(2)	6734.7(2)	30.47(14)
P2	8528.7(7)	2776.0(7)	6896.7(7)	28.4(3)
Si1	10016.7(9)	3039.9(8)	6366.5(9)	39.5(4)
P1	9275.5(8)	897.6(7)	7085.0(8)	31.3(4)
C4	10365(3)	1511(3)	6674(3)	33.3(13)
C27	7389(3)	1893(3)	6846(3)	34.9(14)
C23	7736(3)	2476(3)	5766(3)	35.6(13)
C9	10209(3)	887(3)	6975(3)	31.3(13)
C2	10417(4)	3003(3)	5519(3)	53.6(18)
C10	8937(3)	262(3)	6482(3)	33.4(13)
C39	9353(3)	3752(3)	6318(3)	35.0(14)
C28	8350(3)	2909(3)	7803(3)	32.5(13)
C16	9106(3)	573(3)	7941(3)	34.1(14)
C21	9373(3)	1103(3)	8448(3)	41.9(15)
C22	7686(3)	2549(3)	6536(3)	27.8(12)
C7	11379(3)	508(3)	6938(3)	41.7(15)
C35	8189(3)	4143(3)	6523(3)	34.4(14)
C37	9004(3)	4903(3)	6032(3)	43.7(16)
C38	9496(3)	4396(3)	6061(3)	43.2(15)
C34	8686(3)	3629(3)	6556(3)	29.4(13)
C6	11549(3)	1107(3)	6606(3)	43.3(15)
C24	7040(3)	2292(3)	5460(3)	39.8(15)
C36	8344(3)	4774(3)	6260(3)	40.3(15)
C33	7716(3)	3341(3)	7978(3)	41.3(15)
C8	10703(3)	390(3)	7121(3)	40.3(15)
C15	9192(4)	-462(3)	6594(3)	42.6(16)
C29	8989(3)	3189(3)	8165(3)	44.9(16)
C17	8337(3)	421(3)	8057(3)	39.6(15)
C18	8198(3)	232(3)	8792(3)	47.1(17)
C25	6747(3)	1643(3)	5771(3)	44.5(16)
C32	7596(4)	3342(4)	8739(3)	51.7(18)
C20	9205(4)	917(3)	9175(3)	48.3(17)

C1	10722(3)	3342(3)	6981(4)	60(2)
C26	6690(3)	1712(3)	6533(3)	43.1(16)
C31	8225(4)	3632(4)	9096(3)	58(2)
C19	8441(4)	782(3)	9269(3)	51.4(18)
C5	11057(3)	1603(3)	6486(3)	41.2(15)
C11	9091(4)	493(3)	5763(3)	45.2(17)
C13	9078(4)	-726(3)	5367(3)	52.5(18)
C12	8814(4)	-11(4)	5242(3)	62(2)
C30	8867(4)	3228(4)	8925(3)	54.4(19)
C14	8913(4)	-960(3)	6073(3)	49.1(17)
C3	10062(4)	2542(4)	5053(4)	61(2)

Table S23: Anisotropic Displacement Parameters ($Å^2×10^3$) for **7**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Pd1	28.3(2)	24.1(2)	39.0(3)	1.58(19)	0.7(2)	0.53(19)
P2	29.6(8)	23.4(7)	32.1(8)	2.1(6)	0.2(6)	-0.6(6)
Si1	32.8(9)	31.3(9)	54.5(11)	4.9(8)	5.7(8)	1.5(7)
P1	30.9(8)	25.1(8)	37.9(8)	2.2(6)	0.9(6)	1.7(6)
C4	34(3)	30(3)	36(3)	-1(3)	-1(3)	3(2)
C27	36(3)	33(3)	36(3)	5(2)	-3(3)	-8(3)
C23	41(3)	34(3)	32(3)	-3(2)	0(3)	2(3)
C9	31(3)	27(3)	36(3)	-1(2)	-1(2)	6(2)
C2	62(5)	44(4)	55(4)	0(3)	16(4)	8(4)
C10	32(3)	28(3)	41(3)	-3(3)	-4(3)	0(3)
C39	35(4)	30(3)	40(3)	3(3)	2(3)	-3(3)
C28	38(3)	32(3)	27(3)	-3(2)	-1(2)	-1(3)
C16	38(4)	29(3)	36(3)	3(3)	-1(3)	5(3)
C21	42(4)	37(3)	46(4)	-8(3)	-5(3)	0(3)
C22	25(3)	25(3)	34(3)	1(2)	0(2)	1(2)
C7	36(4)	43(4)	47(4)	-1(3)	-7(3)	13(3)
C35	31(3)	36(3)	36(3)	0(3)	0(2)	3(3)
C37	52(4)	27(3)	52(4)	7(3)	1(3)	-4(3)
C38	41(4)	36(3)	52(4)	0(3)	3(3)	-2(3)
C34	37(3)	21(3)	30(3)	0(2)	1(2)	-2(2)
C6	33(3)	48(4)	49(4)	-1(3)	-2(3)	6(3)
C24	46(4)	38(3)	35(3)	-1(3)	-9(3)	-2(3)
C36	42(4)	26(3)	53(4)	1(3)	-4(3)	3(3)
C33	40(4)	42(4)	42(4)	-1(3)	1(3)	4(3)
C8	47(4)	31(3)	43(4)	-1(3)	-1(3)	6(3)
C15	65(4)	27(3)	36(4)	3(3)	-1(3)	-1(3)
C29	46(4)	46(4)	42(4)	-1(3)	-10(3)	-5(3)
C17	34(3)	41(4)	44(4)	3(3)	2(3)	1(3)
C18	39(4)	49(4)	54(4)	11(3)	4(3)	6(3)
C25	49(4)	33(3)	52(4)	-1(3)	-19(3)	-6(3)
C32	59(5)	57(4)	39(4)	-7(3)	4(3)	9(4)
C20	61(5)	47(4)	37(4)	-5(3)	-6(3)	9(3)
C1	37(4)	42(4)	102(6)	-13(4)	-1(4)	-15(3)
C26	43(4)	35(3)	51(4)	6(3)	-6(3)	-11(3)
C31	83(6)	51(4)	40(4)	-2(3)	0(4)	-2(4)

C19	61(5)	53(4)	40(4)	3(3)	4(3)	20(4)
C5	38(4)	35(3)	50(4)	0(3)	-1(3)	-2(3)
C11	67(5)	32(3)	36(4)	1(3)	-7(3)	4(3)
C13	69(5)	45(4)	44(4)	-8(3)	-2(3)	0(4)
C12	85(6)	59(5)	42(4)	1(4)	-11(4)	6(4)
C30	67(5)	51(4)	45(4)	-1(3)	-19(4)	-9(4)
C14	61(5)	32(4)	54(4)	-4(3)	6(3)	-7(3)
C3	76(5)	61(5)	48(4)	6(4)	4(4)	0(4)

Table S24: Bond Lengths for **7**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P2	2.2869(15)	C28	C33	1.529(8)
Pd1	Si1	2.2956(17)	C28	C29	1.532(8)
Pd1	P1	2.4409(15)	C16	C21	1.535(8)
Pd1	C4	2.074(5)	C16	C17	1.534(8)
P2	C28	1.851(5)	C21	C20	1.525(8)
P2	C22	1.835(5)	C7	C6	1.387(8)
P2	C34	1.830(5)	C7	C8	1.376(8)
Si1	C2	1.854(6)	C35	C34	1.396(7)
Si1	C39	1.900(6)	C35	C36	1.376(8)
Si1	C1	1.923(7)	C37	C38	1.377(8)
P1	C9	1.818(6)	C37	C36	1.378(8)
P1	C10	1.848(6)	C6	C5	1.382(8)
P1	C16	1.843(6)	C24	C25	1.523(8)
C4	C9	1.395(7)	C33	C32	1.530(8)
C4	C5	1.400(8)	C15	C14	1.520(8)
C27	C22	1.539(7)	C29	C30	1.529(8)
C27	C26	1.530(8)	C17	C18	1.528(8)
C23	C22	1.538(7)	C18	C19	1.511(9)
C23	C24	1.521(8)	C25	C26	1.522(8)
C9	C8	1.394(8)	C32	C31	1.517(9)
C2	C3	1.465(9)	C20	C19	1.511(9)
C10	C15	1.521(7)	C31	C30	1.512(10)
C10	C11	1.526(8)	C11	C12	1.527(9)
C39	C38	1.391(8)	C13	C12	1.513(9)
C39	C34	1.393(8)	C13	C14	1.509(9)

Table S25: Bond Angles for **7**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P2	Pd1	Si1	85.35(6)	C33	C28	P2	116.6(4)
P2	Pd1	P1	114.45(5)	C33	C28	C29	110.0(5)
Si1	Pd1	P1	160.01(6)	C29	C28	P2	110.8(4)
C4	Pd1	P2	173.12(16)	C21	C16	P1	108.1(4)
C4	Pd1	Si1	91.53(16)	C17	C16	P1	112.3(4)
C4	Pd1	P1	68.48(16)	C17	C16	C21	111.0(5)
C28	P2	Pd1	111.63(19)	C20	C21	C16	112.8(5)
C22	P2	Pd1	119.89(18)	C27	C22	P2	112.2(4)
C22	P2	C28	104.3(2)	C23	C22	P2	110.7(4)
C34	P2	Pd1	111.48(19)	C23	C22	C27	110.1(4)
C34	P2	C28	105.2(3)	C8	C7	C6	119.6(6)

C34	P2	C22	103.0(2)	C36	C35	C34	121.2(6)
C2	Si1	Pd1	116.9(2)	C38	C37	C36	119.6(6)
C2	Si1	C39	105.4(3)	C37	C38	C39	122.3(6)
C2	Si1	C1	106.9(3)	C39	C34	P2	116.0(4)
C39	Si1	Pd1	107.79(19)	C39	C34	C35	119.7(5)
C39	Si1	C1	106.5(3)	C35	C34	P2	124.3(4)
C1	Si1	Pd1	112.6(2)	C5	C6	C7	121.0(6)
C9	P1	Pd1	80.31(18)	C23	C24	C25	111.5(5)
C9	P1	C10	105.4(3)	C35	C36	C37	119.4(6)
C9	P1	C16	106.4(3)	C28	C33	C32	110.2(5)
C10	P1	Pd1	120.40(18)	C7	C8	C9	118.5(6)
C16	P1	Pd1	127.99(19)	C14	C15	C10	112.7(5)
C16	P1	C10	107.5(3)	C30	C29	C28	110.8(5)
C9	C4	Pd1	105.3(4)	C18	C17	C16	111.2(5)
C9	C4	C5	115.7(5)	C19	C18	C17	111.8(5)
C5	C4	Pd1	138.7(4)	C26	C25	C24	110.8(5)
C26	C27	C22	111.0(5)	C31	C32	C33	109.9(6)
C24	C23	C22	111.2(5)	C19	C20	C21	111.6(5)
C4	C9	P1	104.8(4)	C25	C26	C27	111.2(5)
C8	C9	P1	131.5(5)	C30	C31	C32	110.9(6)
C8	C9	C4	123.7(5)	C20	C19	C18	110.5(5)
C3	C2	Si1	113.7(5)	C6	C5	C4	121.4(6)
C15	C10	P1	114.9(4)	C10	C11	C12	111.9(5)
C15	C10	C11	110.5(5)	C14	C13	C12	111.2(6)
C11	C10	P1	109.7(4)	C13	C12	C11	111.9(6)
C38	C39	Si1	123.5(5)	C31	C30	C29	112.0(6)
C38	C39	C34	117.8(5)	C13	C14	C15	111.2(5)
C34	C39	Si1	118.7(4)				

*X-Ray Data for (^{Cy}PSiP)Pd{OCH(O)AlEt$_3$)} (**9**)*

Table S26: Crystal data and structure refinement for **9**.

Empirical formula	$C_{44}H_{71}AlO_2P_2PdSi$
Formula weight	855.41
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.632(3)
b/Å	23.5987(7)
c/Å	19.2983(14)
α/°	90
β/°	105.726(11)
γ/°	90
Volume/Å^3	4660.9(16)
Z	4
ρ_{calc}mg/mm^3	1.219
m/mm^{-1}	0.544
F(000)	1816.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71075)

2Θ range for data collection	6.108 to 49.378°
Index ranges	$-12 \le h \le 12$, $-27 \le k \le 27$, $-22 \le l \le 22$
Reflections collected	127755
Independent reflections	7904 [R_{int} = 0.1205, R_{sigma} = 0.0473]
Data/restraints/parameters	7904/25/459
Goodness-of-fit on F^2	1.110
Final R indexes [I>=2σ (I)]	R_1 = 0.0903, wR_2 = 0.2513
Final R indexes [all data]	R_1 = 0.1108, wR_2 = 0.2748
Largest diff. peak/hole / e Å^{-3}	3.38/-1.26

Table S27: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **9**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	3402.7(5)	3299.8(2)	8716.1(3)	35.7(3)
Si1	5225(2)	3348.5(8)	8321.6(11)	37.8(5)
P1	4868.0(18)	3062.9(8)	9798.6(10)	38.9(5)
P2	2471.1(18)	3841.5(8)	7709.5(10)	37.9(5)
Al1	-156(3)	1937.2(11)	7907.6(14)	54.8(7)
O1	1636(5)	3202(2)	9125(3)	42.9(12)
O2	1006(5)	2483(2)	8369(3)	49.9(13)
C14	7569(7)	3303(3)	10427(4)	42.4(18)
C13	6495(7)	3296(3)	9798(4)	38.1(16)
C21	6017(8)	4148(3)	7366(4)	49.0(19)
C25	3759(7)	4166(3)	7374(4)	36.8(16)
C15	8771(7)	3478(3)	10386(4)	43.9(18)
C20	5021(7)	3937(3)	7642(4)	38.9(16)
C11	6032(9)	1369(4)	10026(6)	61(2)
C27	2065(7)	2947(3)	6722(4)	43.5(17)
C18	6679(7)	3453(3)	9136(4)	37.7(16)
C17	7929(7)	3626(3)	9118(4)	44.7(18)
C7	5083(7)	2323(3)	10132(4)	40.0(17)
C19	5506(7)	2674(4)	7873(4)	49.4(19)
C12	5866(9)	1978(4)	9723(5)	59(2)
C22	5783(8)	4589(4)	6870(4)	52(2)
C37	181(7)	4285(3)	7993(5)	45.6(18)
C36	-520(8)	4800(3)	8170(5)	56(2)
C24	3525(8)	4615(3)	6874(4)	46.4(18)
C26	1383(7)	3458(3)	6953(4)	40.5(16)
C28	1147(8)	2595(3)	6151(4)	48.7(19)
C32	1540(7)	4448(3)	7908(4)	43.0(17)
C8	3782(8)	2047(3)	10085(5)	48.9(19)
C23	4559(8)	4831(4)	6631(4)	52(2)
C10	4750(8)	1082(3)	9964(5)	54(2)
C2	4576(9)	4122(3)	10368(5)	57(2)
C33	2333(8)	4745(3)	8588(5)	52(2)
C9	3961(9)	1439(4)	10363(5)	58(2)
C6	4802(11)	3316(4)	11258(5)	63(2)
C30	-245(8)	3456(4)	5727(4)	50.3(19)
C3	3949(11)	4482(4)	10827(6)	75(3)
C1	4345(8)	3486(4)	10479(5)	52(2)

C35	262(9)	5103(4)	8835(5)	61(2)
C31	712(8)	3816(3)	6295(4)	50.2(19)
C39	-1246(7)	2302(4)	7152(5)	76(3)
C16	8962(7)	3640(3)	9742(4)	45.6(18)
C29	431(8)	2944(4)	5501(4)	52(2)
C34	1609(8)	5262(4)	8770(6)	62(2)
C43	889(10)	1404(4)	7545(6)	81(3)
C41	-1227(10)	1695(4)	8535(5)	67(3)
C5	4133(11)	3686(4)	11715(5)	71(3)
C4	4342(12)	4313(5)	11593(6)	83(3)
C44	2208(11)	1234(6)	8113(6)	94(4)
C42	-2344(12)	1268(5)	8140(6)	94(4)
C38	873(7)	2825(3)	8854(4)	43.5(18)
C40	-1651(7)	2974(4)	7387(5)	76(3)

Table S28: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **9**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Pd1	33.3(4)	37.5(4)	34.7(4)	0.3(2)	6.6(3)	0.0(2)
Si1	33.6(11)	42.4(11)	35.5(11)	-0.8(8)	6.3(9)	0.0(8)
P1	37.2(10)	42.0(11)	34.7(10)	2.7(8)	5.0(8)	1.0(8)
P2	35.4(10)	38.6(10)	37.3(10)	1.3(8)	5.9(8)	0.1(8)
Al1	56.7(15)	54.3(15)	47.3(14)	-5.4(12)	3.9(12)	-7.7(12)
O1	33(3)	48(3)	45(3)	-4(2)	6(2)	-4(2)
O2	48(3)	55(3)	46(3)	-6(3)	11(2)	-10(3)
C14	44(4)	47(4)	33(4)	4(3)	4(3)	2(3)
C13	32(4)	38(4)	40(4)	-1(3)	3(3)	4(3)
C21	38(4)	59(5)	47(5)	2(4)	8(4)	-3(4)
C25	39(4)	41(4)	28(3)	4(3)	4(3)	-5(3)
C15	39(4)	47(4)	40(4)	-11(3)	1(3)	1(3)
C20	40(4)	42(4)	36(4)	0(3)	12(3)	-2(3)
C11	54(5)	44(5)	88(7)	3(4)	25(5)	2(4)
C27	40(4)	46(4)	41(4)	0(3)	7(3)	8(3)
C18	33(4)	38(4)	42(4)	2(3)	10(3)	2(3)
C17	43(4)	47(4)	43(4)	1(3)	11(3)	2(3)
C7	48(4)	36(4)	32(4)	4(3)	2(3)	5(3)
C19	35(4)	63(5)	49(5)	-9(4)	8(3)	1(4)
C12	56(5)	44(5)	82(7)	10(4)	26(5)	7(4)
C22	48(5)	61(5)	49(5)	3(4)	15(4)	-18(4)
C37	34(4)	40(4)	60(5)	-3(4)	8(3)	3(3)
C36	48(5)	45(5)	76(6)	-6(4)	18(4)	-2(4)
C24	48(4)	48(4)	42(4)	3(3)	11(4)	-2(3)
C26	36(4)	45(4)	36(4)	-1(3)	2(3)	-4(3)
C28	51(5)	47(5)	46(5)	-6(3)	11(4)	-4(4)
C32	39(4)	43(4)	45(4)	-2(3)	7(3)	-1(3)
C8	46(4)	48(5)	54(5)	-4(4)	16(4)	4(4)
C23	61(5)	50(5)	46(5)	7(4)	17(4)	-7(4)
C10	59(5)	43(4)	53(5)	9(4)	6(4)	7(4)
C2	64(5)	38(4)	70(6)	-4(4)	20(5)	-4(4)
C33	44(4)	48(5)	62(5)	-17(4)	13(4)	5(4)

C9	57(5)	46(5)	78(6)	5(4)	29(5)	-2(4)
C6	80(7)	69(6)	41(5)	-2(4)	18(5)	2(5)
C30	45(4)	55(5)	43(5)	-1(4)	-2(4)	2(4)
C3	100(8)	64(6)	71(7)	-6(5)	38(6)	17(6)
C1	52(5)	53(5)	55(5)	6(4)	19(4)	4(4)
C35	60(5)	52(5)	78(6)	-9(4)	28(5)	10(4)
C31	49(5)	48(5)	50(5)	2(4)	9(4)	4(4)
C39	13(2)	114(6)	105(5)	86(5)	20(3)	15(3)
C16	32(4)	47(5)	56(5)	-5(4)	8(4)	-3(3)
C29	49(5)	53(5)	48(5)	-4(4)	4(4)	-3(4)
C34	54(5)	45(5)	80(7)	-18(4)	7(5)	-3(4)
C43	89(7)	58(6)	83(7)	-16(5)	-1(5)	2(5)
C41	72(6)	70(6)	56(6)	-1(4)	11(5)	-15(5)
C5	110(8)	61(6)	45(5)	0(4)	27(5)	2(5)
C4	99(8)	88(8)	62(6)	-25(6)	21(6)	8(6)
C44	88(7)	100(9)	86(7)	-12(6)	10(6)	21(6)
C42	99(8)	104(8)	74(7)	-2(6)	16(6)	-45(7)
C38	40(4)	55(5)	36(4)	8(4)	10(3)	6(4)
C40	13(2)	114(6)	105(5)	86(5)	20(3)	15(3)

Table S29: Bond Lengths for **9**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pd1	Si1	2.269(2)	C27	C26	1.534(10)
Pd1	P1	2.3108(19)	C27	C28	1.509(11)
Pd1	P2	2.3121(19)	C18	C17	1.399(10)
Pd1	O1	2.238(5)	C17	C16	1.393(11)
Si1	C20	1.881(7)	C7	C12	1.529(11)
Si1	C18	1.899(7)	C7	C8	1.509(11)
Si1	C19	1.874(8)	C22	C23	1.381(12)
P1	C13	1.816(8)	C37	C36	1.513(11)
P1	C7	1.853(7)	C37	C32	1.546(10)
P1	C1	1.850(9)	C36	C35	1.506(12)
P2	C25	1.833(7)	C24	C23	1.404(11)
P2	C26	1.837(7)	C26	C31	1.531(11)
P2	C32	1.838(7)	C28	C29	1.522(11)
Al1	O2	1.838(6)	C32	C33	1.525(11)
Al1	C39	1.815(8)	C8	C9	1.527(12)
Al1	C43	1.929(11)	C10	C9	1.534(12)
Al1	C41	1.959(11)	C2	C3	1.507(12)
O1	C38	1.222(9)	C2	C1	1.545(11)
O2	C38	1.273(9)	C33	C34	1.533(11)
C14	C13	1.424(10)	C6	C1	1.503(12)
C14	C15	1.367(11)	C6	C5	1.545(13)
C13	C18	1.392(10)	C30	C31	1.534(11)
C21	C20	1.400(10)	C30	C29	1.530(11)
C21	C22	1.389(11)	C3	C4	1.478(14)
C25	C20	1.408(10)	C35	C34	1.519(12)
C25	C24	1.409(10)	C39	C40	1.737(8)
C15	C16	1.367(11)	C43	C44	1.580(12)

C11	C12	1.543(12)	C41	C42	1.587(11)
C11	C10	1.497(12)	C5	C4	1.525(15)

Table S30: Bond Angles for **9**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Si1	Pd1	P1	83.55(7)	C10	C11	C12	112.5(7)
Si1	Pd1	P2	84.28(7)	C28	C27	C26	112.5(6)
P1	Pd1	P2	157.47(7)	C13	C18	Si1	116.1(5)
O1	Pd1	Si1	176.80(14)	C13	C18	C17	118.1(7)
O1	Pd1	P1	94.64(14)	C17	C18	Si1	125.6(6)
O1	Pd1	P2	98.28(14)	C16	C17	C18	121.2(7)
C20	Si1	Pd1	108.9(2)	C12	C7	P1	110.9(5)
C20	Si1	C18	113.4(3)	C8	C7	P1	111.1(5)
C18	Si1	Pd1	107.8(2)	C8	C7	C12	110.9(7)
C19	Si1	Pd1	111.7(3)	C7	C12	C11	108.8(7)
C19	Si1	C20	107.9(4)	C23	C22	C21	121.1(7)
C19	Si1	C18	107.3(3)	C36	C37	C32	110.9(6)
C13	P1	Pd1	109.6(3)	C35	C36	C37	112.4(7)
C13	P1	C7	104.9(3)	C23	C24	C25	119.6(8)
C13	P1	C1	107.9(4)	C27	C26	P2	111.9(5)
C7	P1	Pd1	122.1(2)	C31	C26	P2	116.1(5)
C1	P1	Pd1	104.6(3)	C31	C26	C27	110.1(6)
C1	P1	C7	107.1(4)	C27	C28	C29	112.5(7)
C25	P2	Pd1	109.7(2)	C37	C32	P2	113.5(5)
C25	P2	C26	107.1(3)	C33	C32	P2	109.5(5)
C25	P2	C32	104.1(3)	C33	C32	C37	109.7(6)
C26	P2	Pd1	115.5(3)	C7	C8	C9	111.1(6)
C26	P2	C32	106.9(3)	C22	C23	C24	119.4(8)
C32	P2	Pd1	112.8(3)	C11	C10	C9	108.8(7)
O2	Al1	C43	104.8(4)	C3	C2	C1	110.8(8)
O2	Al1	C41	109.4(3)	C32	C33	C34	111.6(7)
C39	Al1	O2	104.9(4)	C8	C9	C10	111.9(7)
C39	Al1	C43	108.8(5)	C1	C6	C5	110.2(8)
C39	Al1	C41	106.4(4)	C29	C30	C31	111.7(7)
C43	Al1	C41	121.5(5)	C4	C3	C2	112.7(9)
C38	O1	Pd1	116.5(5)	C2	C1	P1	109.7(6)
C38	O2	Al1	127.4(5)	C6	C1	P1	119.2(6)
C15	C14	C13	120.0(7)	C6	C1	C2	112.1(8)
C14	C13	P1	123.1(6)	C36	C35	C34	111.3(7)
C18	C13	P1	116.9(5)	C26	C31	C30	110.9(7)
C18	C13	C14	120.0(7)	C40	C39	Al1	111.9(6)
C22	C21	C20	121.1(7)	C15	C16	C17	120.1(7)
C20	C25	P2	116.0(5)	C28	C29	C30	111.2(7)
C20	C25	C24	120.9(7)	C35	C34	C33	111.4(7)
C24	C25	P2	123.1(6)	C44	C43	Al1	113.8(7)
C14	C15	C16	120.7(7)	C42	C41	Al1	111.9(7)
C21	C20	Si1	124.9(6)	C4	C5	C6	110.6(8)
C21	C20	C25	117.9(7)	C3	C4	C5	113.7(9)
C25	C20	Si1	117.2(5)	O1	C38	O2	125.8(7)

*X-Ray Data for (^{Cy}PSiP)Pd(OTf) (**10**)*

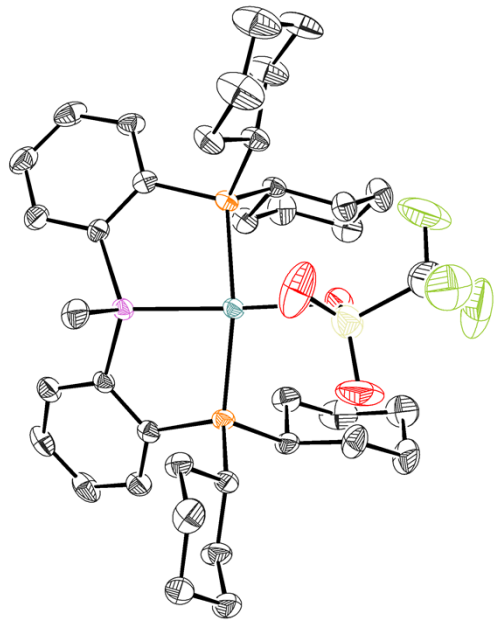


Figure S17: ORTEP of **10**. Selected hydrogen atoms are omitted for clarity.

Table S31: Crystal data and structure refinement for **10**.

Empirical formula	$C_{38}H_{55}F_3O_3P_2PdSSi$
Formula weight	845.31
Temperature/K	223
Crystal system	orthorhombic
Space group	Pbca
a/Å	23.517(18)
b/Å	21.766(18)
c/Å	14.710(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7530(10)
Z	8
ρ_{calc}mg/mm^3	1.491
m/mm^{-1}	0.717
F(000)	3520.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection	6.098 to 51.362°

Index ranges	$-25 \le h \le 28$, $-26 \le k \le 25$, $-17 \le l \le 17$
Reflections collected	24546
Independent reflections	7105[R(int) = 0.0635]
Data/restraints/parameters	7105/0/443
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	$R_1 = 0.0634$, $wR_2 = 0.1291$
Final R indexes [all data]	$R_1 = 0.0970$, $wR_2 = 0.1433$
Largest diff. peak/hole / e $Å^{-3}$	1.32/-0.81

Table S32: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **10**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	3669.0(2)	628.3(2)	2582.1(3)	30.57(14)
P1	4132.1(6)	-264.8(6)	2480.4(9)	32.4(3)
Si1	3189.6(6)	177.6(7)	3696.4(10)	33.0(4)
P2	3403.9(6)	1496.8(6)	3300.9(10)	33.8(3)
C18	3520(2)	-564(2)	3966(4)	34.2(13)
C13	3933(2)	-767(2)	3386(4)	35.9(13)
C20	3172(2)	712(2)	4672(4)	33.5(12)
C21	3073(2)	556(3)	5573(4)	45.8(15)
C7	4882(2)	-170(3)	2669(4)	34.9(13)
C16	3612(3)	-1478(3)	4800(5)	61(2)
C26	2831(2)	1950(3)	2857(4)	37.8(13)
C24	3258(2)	1737(3)	5152(4)	46.7(15)
C25	3258(2)	1314(3)	4477(4)	34.9(13)
C31	2323(2)	1576(3)	2650(4)	44.5(15)
C14	4193(3)	-1311(3)	3525(4)	45.8(15)
C27	2676(2)	2501(3)	3403(5)	52.3(17)
C28	2235(3)	2870(3)	2920(5)	57.5(18)
C8	5004(2)	-5(3)	3643(4)	47.4(15)
C12	5132(2)	293(3)	2031(4)	50.3(16)
C22	3089(3)	981(3)	6239(4)	54.3(17)
C29	1733(3)	2497(3)	2704(5)	57.2(18)
C15	4033(3)	-1667(3)	4236(4)	56.9(18)
C30	1884(3)	1948(3)	2172(5)	60.3(19)
C17	3357(3)	-939(3)	4665(4)	48.2(16)
C9	5627(3)	69(3)	3806(5)	60.2(19)
C10	5871(3)	521(3)	3178(5)	63(2)
C23	3184(3)	1566(4)	6038(4)	59.5(19)
C11	5758(3)	367(4)	2204(5)	66(2)
S1	3466.6(9)	1133.7(10)	578.8(13)	68.5(6)
O1	3928.0(19)	996(2)	1216(3)	57.2(12)
C33	4150(3)	2249(3)	2439(5)	62.5(19)
C1	4060(2)	-645(3)	1399(4)	43.3(14)
C32	3999(2)	2011(3)	3364(4)	42.2(14)
C2	3445(3)	-816(3)	1235(4)	52.1(17)
C37	4499(2)	1694(3)	3763(5)	52.4(17)
O2	3053(2)	670(3)	486(5)	111(2)
C6	4433(3)	-1139(4)	1173(5)	74(2)
F1	3488(3)	1208(3)	-1144(3)	113.2(19)

F3	4082(3)	603(3)	-563(4)	155(3)
C19	2470(2)	5(3)	3331(5)	53.3(17)
O3	3250(3)	1719(3)	633(4)	104(2)
C34	4661(3)	2646(4)	2462(6)	79(2)
F2	4216(3)	1552(3)	-444(5)	154(3)
C5	4348(3)	-1344(4)	186(5)	74(2)
C36	5016(3)	2095(4)	3772(6)	77(2)
C3	3374(3)	-1056(4)	269(6)	89(3)
C4	3749(3)	-1517(4)	21(6)	93(3)
C35	5148(3)	2312(4)	2837(7)	86(3)
C38	3829(5)	1111(5)	-448(6)	96(3)

Table S33: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **10**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Pd1	28.2(2)	31.5(2)	32.0(2)	-0.85(19)	2.23(19)	3.27(18)
P1	29.4(7)	35.4(7)	32.4(7)	-3.7(7)	-0.4(6)	4.8(6)
Si1	28.6(8)	33.7(8)	36.6(8)	-4.2(7)	3.3(7)	-1.9(7)
P2	26.9(7)	29.3(7)	45.2(8)	-4.6(7)	2.1(7)	0.4(6)
C18	34(3)	33(3)	36(3)	-1(3)	-3(2)	-6(3)
C13	36(3)	35(3)	37(3)	-2(3)	-8(3)	-1(3)
C20	24(3)	37(3)	39(3)	-4(3)	2(2)	0(2)
C21	39(3)	52(4)	47(3)	0(3)	6(3)	4(3)
C7	27(3)	37(3)	41(3)	-6(3)	1(2)	6(2)
C16	100(6)	39(4)	45(4)	7(3)	1(4)	-8(4)
C26	28(3)	37(3)	48(3)	2(3)	3(3)	6(3)
C24	43(4)	42(3)	55(4)	-18(3)	5(3)	-10(3)
C25	24(3)	39(3)	41(3)	-7(3)	-1(2)	-2(2)
C31	35(3)	37(3)	62(4)	-3(3)	-3(3)	-2(3)
C14	53(4)	36(3)	48(4)	3(3)	-5(3)	14(3)
C27	35(3)	39(3)	82(5)	-7(3)	-2(3)	5(3)
C28	42(4)	40(3)	91(5)	5(4)	11(4)	5(3)
C8	41(4)	53(4)	49(4)	-7(3)	-4(3)	-4(3)
C12	39(4)	62(4)	50(4)	-1(3)	-2(3)	-8(3)
C22	43(4)	83(5)	37(3)	-10(4)	9(3)	-2(4)
C29	36(3)	53(4)	82(5)	18(4)	8(3)	17(3)
C15	84(5)	36(4)	50(4)	4(3)	-21(4)	7(4)
C30	36(4)	66(5)	79(5)	11(4)	-15(3)	-4(3)
C17	63(4)	39(3)	43(3)	-1(3)	5(3)	-7(3)
C9	43(4)	79(5)	58(4)	1(4)	-18(3)	-9(4)
C10	36(4)	75(5)	78(5)	-10(4)	-12(4)	-7(4)
C23	51(4)	81(5)	47(4)	-33(4)	9(3)	-13(4)
C11	43(4)	89(5)	65(4)	-6(4)	2(3)	-19(4)
S1	71.8(13)	76.0(13)	57.6(11)	10.9(10)	8.4(10)	16.3(11)
O1	62(3)	67(3)	42(2)	15(2)	3(2)	18(2)
C33	41(4)	62(4)	85(5)	19(4)	-2(4)	-14(3)
C1	33(3)	50(4)	47(3)	-15(3)	-2(3)	3(3)
C32	32(3)	31(3)	64(4)	-4(3)	5(3)	-3(3)
C2	35(3)	69(4)	52(4)	-24(3)	1(3)	-6(3)
C37	32(3)	50(4)	76(4)	-5(4)	-6(3)	1(3)

O2	76(4)	123(5)	134(5)	47(4)	-34(4)	-59(4)
C6	57(5)	91(6)	73(5)	-34(5)	-16(4)	18(4)
F1	158(5)	118(4)	64(3)	13(3)	-29(3)	18(4)
F3	238(8)	132(5)	97(4)	-7(4)	42(5)	113(5)
C19	37(3)	51(4)	73(4)	-3(4)	-3(3)	-12(3)
O3	138(5)	80(4)	94(4)	-7(3)	2(4)	71(4)
C34	46(4)	73(5)	119(7)	14(5)	18(5)	-24(4)
F2	116(5)	168(6)	177(7)	87(5)	26(4)	-38(5)
C5	66(5)	91(6)	65(5)	-45(4)	-10(4)	27(4)
C36	38(4)	72(5)	122(7)	-27(5)	-27(5)	-5(4)
C3	50(5)	126(8)	91(6)	-57(6)	-25(4)	-2(5)
C4	72(6)	109(7)	99(7)	-63(6)	-19(5)	9(5)
C35	34(4)	76(6)	147(9)	-10(6)	14(5)	-15(4)
C38	135(9)	89(7)	65(5)	15(5)	2(6)	30(7)

Table S34: Bond Lengths for **10**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.233(2)	C14	C15	1.355(8)
Pd1	Si1	2.2183(18)	C27	C28	1.491(8)
Pd1	P2	2.254(2)	C28	C29	1.468(9)
Pd1	O1	2.247(4)	C8	C9	1.493(8)
P1	C13	1.786(6)	C12	C11	1.501(8)
P1	C7	1.798(5)	C22	C23	1.327(9)
P1	C1	1.801(6)	C29	C30	1.473(9)
Si1	C18	1.834(6)	C9	C10	1.468(9)
Si1	C20	1.848(5)	C10	C11	1.495(9)
Si1	C19	1.815(6)	S1	O1	1.465(5)
P2	C26	1.794(6)	S1	O2	1.408(5)
P2	C25	1.808(6)	S1	O3	1.374(5)
P2	C32	1.794(6)	S1	C38	1.735(10)
C18	C13	1.365(8)	C33	C32	1.500(9)
C18	C17	1.369(8)	C33	C34	1.479(9)
C13	C14	1.348(7)	C1	C2	1.512(8)
C20	C21	1.389(8)	C1	C6	1.426(8)
C20	C25	1.354(7)	C32	C37	1.484(8)
C21	C22	1.348(8)	C2	C3	1.523(9)
C7	C8	1.504(8)	C37	C36	1.496(9)
C7	C12	1.499(8)	C6	C5	1.532(9)
C16	C15	1.354(10)	F1	C38	1.317(10)
C16	C17	1.332(9)	F3	C38	1.266(10)
C26	C31	1.477(8)	C34	C35	1.464(10)
C26	C27	1.488(8)	F2	C38	1.323(12)
C24	C25	1.355(7)	C5	C4	1.478(10)
C24	C23	1.366(9)	C36	C35	1.487(11)
C31	C30	1.490(8)	C3	C4	1.386(10)

Table S35: Bond Angles for **10**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pd1	P2	153.69(6)	C26	C31	C30	110.9(5)
P1	Pd1	O1	96.78(12)	C13	C14	C15	119.5(6)

Si1	Pd1	P1	84.97(7)	C26	C27	C28	110.3(6)
Si1	Pd1	P2	83.32(7)	C29	C28	C27	111.4(5)
Si1	Pd1	O1	162.96(13)	C9	C8	C7	111.5(5)
O1	Pd1	P2	101.29(13)	C7	C12	C11	110.5(5)
C13	P1	Pd1	110.8(2)	C23	C22	C21	120.2(6)
C13	P1	C7	102.3(3)	C28	C29	C30	111.7(5)
C13	P1	C1	110.6(3)	C16	C15	C14	120.1(6)
C7	P1	Pd1	111.62(19)	C29	C30	C31	111.0(6)
C7	P1	C1	106.4(3)	C16	C17	C18	120.7(6)
C1	P1	Pd1	114.4(2)	C10	C9	C8	110.7(6)
C18	Si1	Pd1	109.45(18)	C9	C10	C11	112.5(6)
C18	Si1	C20	113.3(2)	C22	C23	C24	119.6(6)
C20	Si1	Pd1	107.83(19)	C10	C11	C12	111.2(6)
C19	Si1	Pd1	110.3(2)	O1	S1	C38	100.8(4)
C19	Si1	C18	106.1(3)	O2	S1	O1	115.3(3)
C19	Si1	C20	109.9(3)	O2	S1	C38	103.5(5)
C26	P2	Pd1	119.9(2)	O3	S1	O1	115.3(4)
C26	P2	C25	109.1(3)	O3	S1	O2	114.5(4)
C25	P2	Pd1	108.45(19)	O3	S1	C38	105.0(4)
C32	P2	Pd1	109.4(2)	S1	O1	Pd1	116.4(3)
C32	P2	C26	105.2(3)	C34	C33	C32	112.0(6)
C32	P2	C25	103.6(3)	C2	C1	P1	110.2(4)
C13	C18	Si1	116.9(4)	C6	C1	P1	119.6(5)
C13	C18	C17	118.4(5)	C6	C1	C2	111.4(5)
C17	C18	Si1	124.6(5)	C33	C32	P2	110.7(4)
C18	C13	P1	117.0(4)	C37	C32	P2	110.4(4)
C14	C13	P1	122.1(5)	C37	C32	C33	109.4(5)
C14	C13	C18	120.9(5)	C1	C2	C3	109.9(5)
C21	C20	Si1	126.2(5)	C32	C37	C36	112.1(6)
C25	C20	Si1	116.2(4)	C1	C6	C5	111.2(6)
C25	C20	C21	117.7(5)	C35	C34	C33	110.7(6)
C22	C21	C20	121.4(6)	C4	C5	C6	110.7(7)
C8	C7	P1	111.2(4)	C35	C36	C37	110.3(6)
C12	C7	P1	111.4(4)	C4	C3	C2	115.2(7)
C12	C7	C8	111.2(5)	C3	C4	C5	112.3(7)
C17	C16	C15	120.4(6)	C34	C35	C36	110.0(7)
C31	C26	P2	112.2(4)	F1	C38	S1	111.9(8)
C31	C26	C27	111.1(5)	F1	C38	F2	107.9(8)
C27	C26	P2	115.5(4)	F3	C38	S1	111.8(7)
C25	C24	C23	121.0(6)	F3	C38	F1	108.9(9)
C20	C25	P2	116.4(4)	F3	C38	F2	108.1(10)
C20	C25	C24	120.1(5)	F2	C38	S1	108.3(7)
C24	C25	P2	123.5(5)				

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