Supporting Information

# Semi-bridging σ-Silyls as *Z*-type Ligands

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## Synthetic Details and Spectroscopic Data

## General Considerations

All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free argon atmosphere using standard Schlenk, dry-box and vacuum line techniques, Glassware was flame-dried under vacuum prior to use. Solvents were dried by conventional methods. NMR spectra were recorded at 25°C on Bruker Avance 400 MHz and 600 MHz spectrometers. The chemical shifts (δ) for $^{1}$H and $^{13}$C spectra are given in ppm relative to residual signals of the solvent, $^{29}$Si relative to an internal $SiMe_4$ reference, and $^{31}$P relative to an external $H_3PO_4$ reference. Low resolution mass spectra were obtained on a ZAB-SEQ4F spectrometer by positive ion ESI techniques using an acetonitrile matrix by the mass spectrometry service of the Australian National University. Assignments were made relative to M, where M is the molecular cation. Elemental microanalysis was performed by the micro analytical service of the Australian National University. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer. The compounds **1**,[1] $[Pd_2(dba)_3]$,[2] $[Pt(nbe)_3]$[3] and $[Ni(cod)_2]$[4] were prepared according to published procedures. Other reagents were used as received from commercial suppliers.

## Synthesis of $[Pd_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (4)

To a purple solution of $[Pd_2(dba)_3.dba]$ (50 mg, 0.087 mmol) in thf (10 mL) was added the pro-ligand $HSiPh(CH_2PPh_2)_2C_6H_4$ (**3**: 53 mg, 0.087 mmol). The mixture was stirred at room temperature for 20 hours. The resulting orange solution was concentrated and pentane was added to induce precipitation. The orange precipitate was collected by filtration, washed with pentane and diethyl ether to remove excess dba and $H_2$dba and dried *in vacuo*. Although conversion was spectroscopically near quantitative, the isolated yield was diminished due to the requisite extensive washing with diethyl ether. Yield: 48 mg (77%). $^{1}$H NMR (600 MHz, $C_6D_6$): $\delta_H$ = 7.61 (d, 4 H, $^{3}J_{HH}$ = 7.2 Hz, $C_6H_4$), 7.30 (t, 4 H, $^{3}J_{HH}$ = 8.4 Hz, $C_6H_5$), 7.02 (t, 2 H, $^{3}J_{HH}$ = 7.2 Hz), 7.00 (t, 2 H, $^{3}J_{HH}$ = 7.2 Hz), 6.92-6.89 (m, 6H, $^{3}J_{HH}$ = 7.2 Hz), 6.87-6.79 (m, 16 H, $C_6H_5$), 6.74-6.70 (m, 8 H, $C_6H_5$), 6.65 (t, 6 H, $^{3}J_{HH}$ = 6.6 Hz), 6.61 (t, 4 H, $^{3}J_{HH}$ = 7.2 Hz), 6.51-66 (m, 6 H, $C_6H_5$), 4.37 (dd, 2 H, *J* = 13.2, 4.9 Hz, $PCH_2$), 4.02 (dt, 2 H, *J* = 13.3, 4.0 Hz, $PCH_2$), 3.87 (dd, 2 H, *J* = 13.1, 2.9 Hz, $PCH_2$), 3.45 (dt, 2 H, *J* = 13.1, 4.3 Hz, $PCH_2$). $^{13}$C{$^{1}$H} NMR (150 MHz, $C_6D_6$): $\delta_C$ = 144.0-143.8 (m), 142.6 (t, *J* = 10.5 Hz), 142.2 (t, *J* = 3 Hz), 139.8 (t, *J* = 10.5 Hz), 136.6 (d, *J* = 24 Hz), 136.4 (d, *J* = 28.5 Hz), 134.6 (t, *J* = 9 Hz), 134.1 (t, *J* = 7.5 Hz), 133.9, 133.0 (t, *J* = 6 Hz), 132.0 (t, *J* = 6 Hz), 129.7, 129.6, 129.1, 128.7, 128.5, 128.3, 127.9, 127.4, 118.4, 116.8, 108.6, 107.7, 48.2 (d, *J* = 30 Hz), 45.9 (t, *J* = 12 Hz). $^{31}$P{$^{1}$H} NMR (162 MHz, $C_6D_6$): $\delta_P$ = 44.91 (t, 2 P, *J* = 10.5 Hz), 25.13 (t, 2 P, *J* = 10.5 Hz). NB: The **AA'BB'** spin system manifests as two apparent triplet resonances (*cf.* $\mathbf{A_2B_2}$), the inference being that $J_{AB} \approx J_{AB'} << (\delta_A - \delta_B)$. $^{29}$Si NMR (79.5 MHz, 300 K, $C_6D_6$): $\delta_{Si}$ = 58.35 (m, 2Si). ESI-MS (low-res, +ve ion, MeCN): *m/z* = 1428 $[M]^+$. Anal. Found: C, 64.19; H, 4.76; N, 3.92%. Calcd. for $C_{76}H_{66}N_4P_4Si_2Pd_2$: C, 63.91; H, 4.66; N, 3.92%. Crystals of a benzene solvate **4**.$(C_6H_6)_2$ suitable for X-ray diffraction were grown by slow diffusion of hexane vapour into a benzene (CAUTION) solution of compound **4**. *Crystal data for* **4**.$(C_6H_6)_2$: $C_{88}H_{78}N_4P_4Pd_2Si_2$, $M_w$ = 1584.52 gmol$^{-1}$, orange block, 0.1903 × 0.1403 × 0.0611 mm$^3$, triclinic, space group *P*-1 (No. 2), *V* = 3724.1(2) Å$^3$, *Z* = 2, $D_{calcd}$ = 1.4129 Mgm$^{-3}$, *F*000 = 1636, Cu Kα radiation, λ = 1.54184 Å, μ = 5.398 mm$^{-1}$, *T* = 150.0(1)K, $2\theta_{max}$ = 144.9º, 21950 reflections collected, 14151 unique ($R_{int}$ = 0.0384), $R_1$ = 0.0558, $wR_2$ = 0.1515, *R* indices based on 12345 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 829 parameters, Lp and absorption corrections applied, CCDC 1517410.

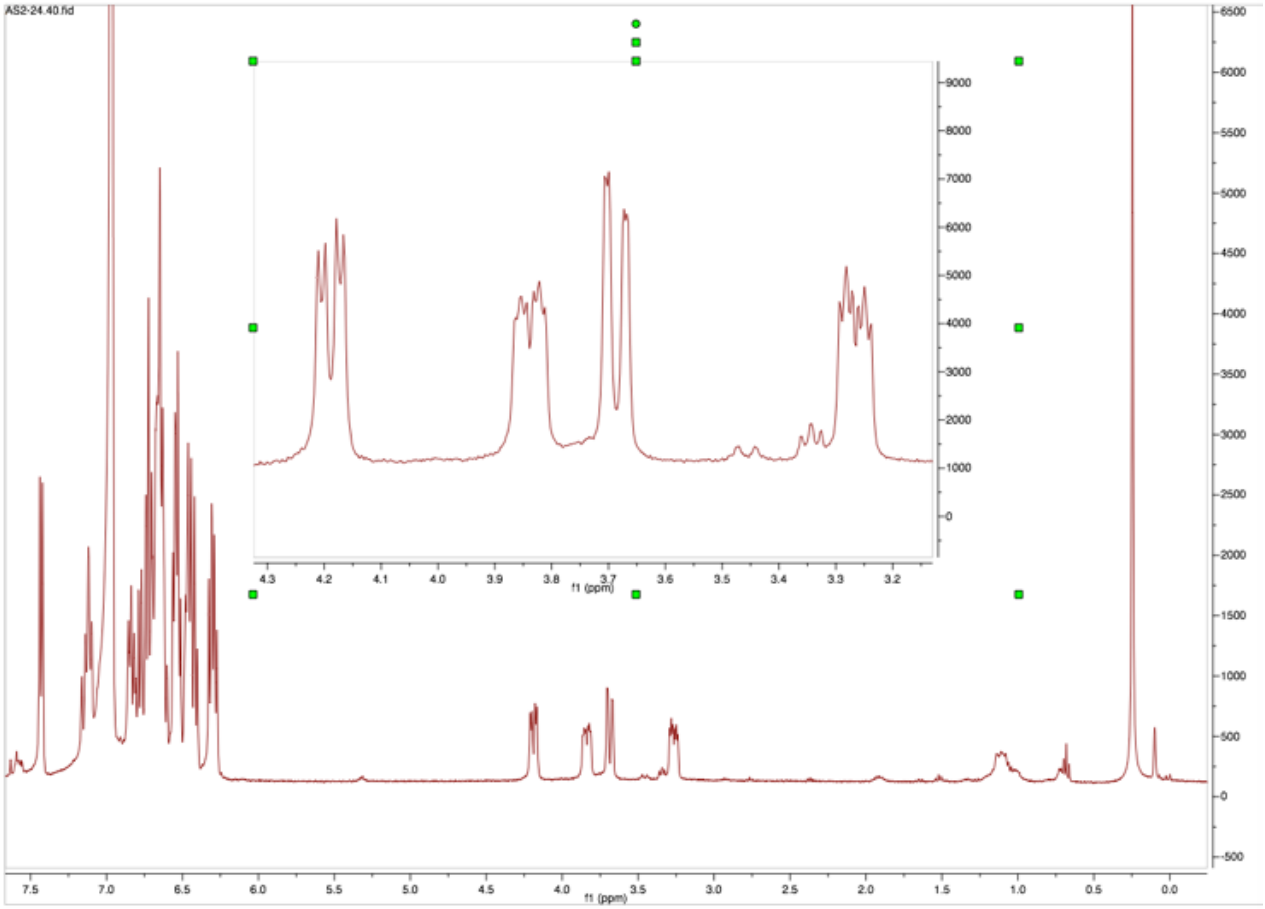


**Figure S1.** $^{1}H$ NMR Spectrum of **4** (400.1 MHz, 298 K, $C_6D_6$)


**Figure S2**. $^{1}H$-$^{1}H$ COSY NMR Spectrum of **4** ($PCH_2$ Region).

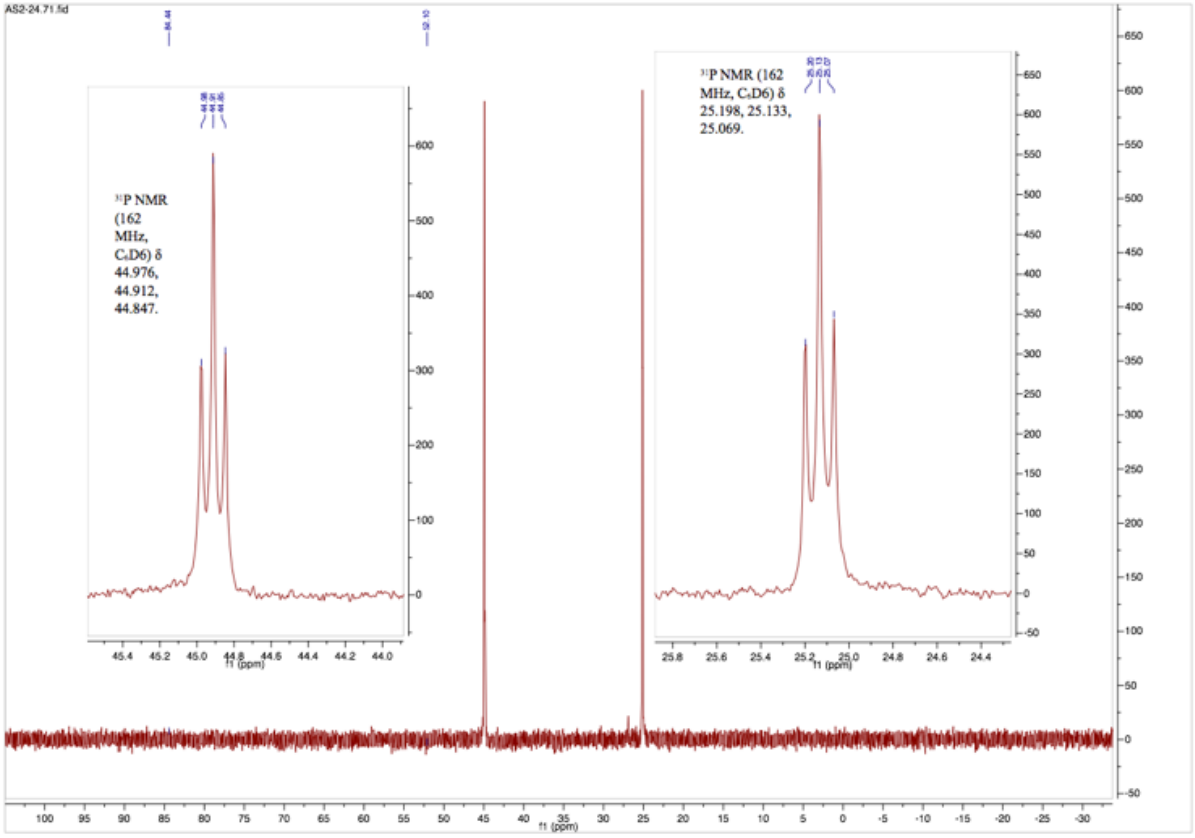


**Figure S3**. $^{31}P\{^{1}H\}$ NMR Spectrum of **4** (162 MHz, $C_6D_6$, 298 K)

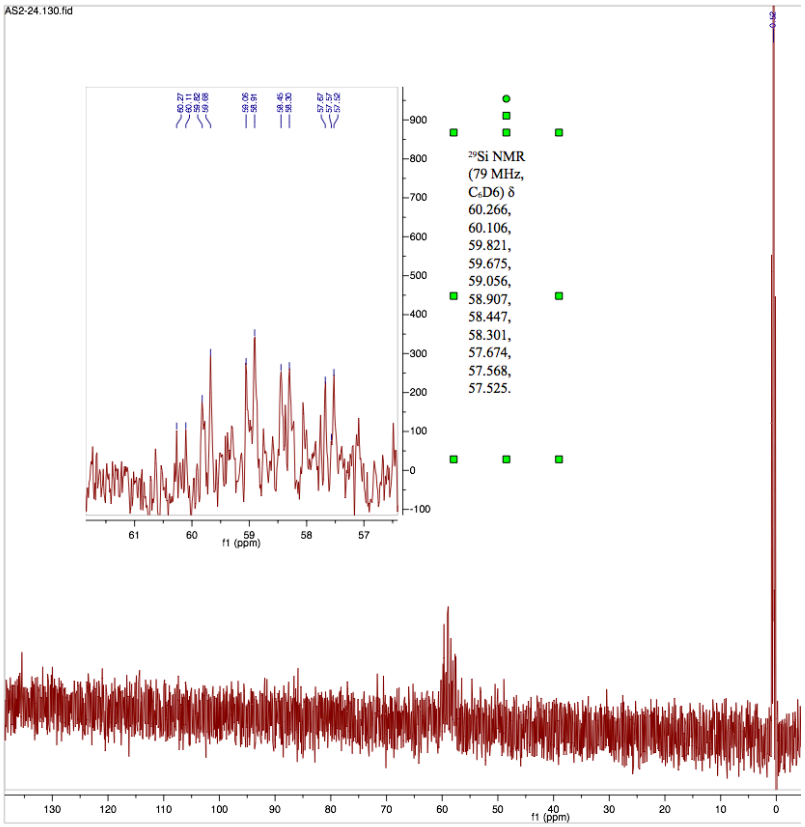


**Figure S4**. $^{29}Si\{^{1}H\}$ NMR Spectrum of **4** (162 MHz, $C_6D_6$, 298 K)

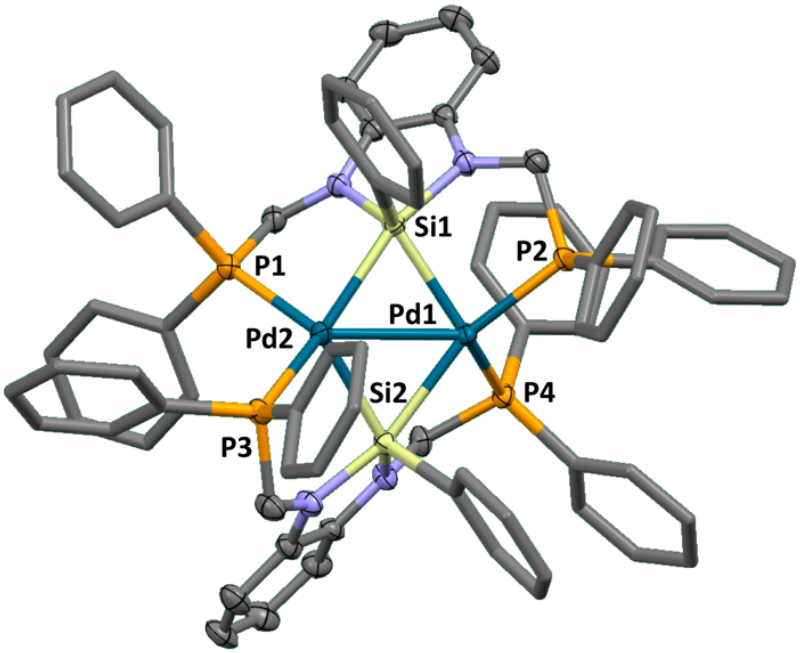


**Figure S5**. Molecular structure of **4** in a crystal of **4**.$(C_6H_6)_2$ (50% displacement ellipsoids, hydrogen atoms and solvent omitted, phenyl groups simplified). Selected bond lengths (Å) and angles (°): Pd1 Pd2 2.7856(4), Pd1–P1 2.3484(11), Pd1–P3 2.3507(11), Pd1–Si1 2.4730(11), Pd1–Si2 2.4068(11), Pd2–Pd2–P4 2.3458(10), Pd2–Si1 2.4128(11), Pd2–Si2 2.4732(11), P1–Pd1–Pd2 23.05(3), P1–Pd1–P3 105.41(4), P1–Pd1–Si1 81.73(4), P1–Pd1–Si2 130.60(4), P3–Pd1–Pd2 130.19(3), P3–Pd1–Si1 154.65(4), P3–Pd1–Si2 84.63(4), Si1–Pd1–Pd2 54.23(3), Si2–Pd1–Pd2 56.32(3), Si2–Pd1–Si1 109.51(4), P2–Pd2–Pd1 130.91(3), P2–Pd2–Si1 84.58(4), P2–Pd2–Si2 155.87(4), P4–Pd2–Pd1 122.45(3), P4–Pd2–P2 104.85(4), P4–Pd2–Si1 129.77(4), P4–Pd2–Si2 81.79(4), Si1–Pd2–Pd1 56.26(3), Si1–Pd2–Si2 109.31(4), Si2–Pd2–Pd1 54.08(3).

## Synthesis of $[Ni_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (5)

The pro-ligand $HSiPh(CH_2PPh_2)_2C_6H_4$ (**3**: 110 mg, 0.182 mmol) was added to a thf (10 mL solution of $[Ni(cod)_2]$ (50.0 mg, 0.182 mmol). Immediately the colour of the solution changed to dark reddish brown. After stirring at room temperature for 10 mins the solution was concentrated and pentane was added to induce precipitation. The resulting dark red-brown precipitate was washed with pentane and dried *in vacuo*. Yield: 105 mg (87%). $^1$H NMR (600 MHz, $C_6D_6$): $\delta_H$ = 7.798 (d, 4H, *J* = 7.2 Hz), 7.122 (dt, 4H, *J* = 7.8 Hz, *J* = 1.2 Hz), 7.074-7.026 (m, 10H), 6.934 (t, 4H, 7.2 Hz), 6.823-6.647 (m, 20H), 6.495-6.466 (m 8H), 6.419 (dt, 4H, *J* = 7.8 Hz, *J* = 1.2 Hz), 6.118 (t, 4H, *J* = 7.8 Hz), 4.111 (dd, 2H, *J* = 12 Hz, *J* = 6.2 Hz), 3.922 (dd, 2H, *J* = 13.1 Hz, *J* = 2.9 Hz), 3.716 (dd, 2H, *J* = 11.9 Hz, *J* = 2.5 Hz), 3.605 (dd, 2H, *J* = 13 Hz, *J* = 7.5 Hz). $^{13}$C NMR (150 MHz, $C_6D_6$): δ 143.5 (d, *J* = 16.5 Hz), 142.98 (d, *J* = 16.5 Hz), 140.21 (dd, *J* = 26 Hz, 13 Hz), 139.01, 138.85, 138.59, 138.34, 136.23, 135.23 (d, *J* = 30 Hz), 132.83, 132.75, 132.45, 132.41, 132.38, 132.18, 132.15, 132.12, 129.62, 129.29, 129.16, 129.03, 128.12, 128.00, 127.91, 127.86, 127.79, 127.77, 124.49 (d, *J* = 13 Hz), 118.59, 117.89, 109.20, 108.39, 48.07 (d, *J* = 27 Hz), 45.83 (d, *J* = 36 Hz). $^{31}$P NMR (162 MHz, $C_6D_6$): $\delta_P$ = 32.398 (dd, 2P, J = 11.7, 6.6 Hz), 23.768 (dd, 2P, J = 11.4, 6.3 Hz). $^{29}$Si NMR (79.5 MHz, $C_6D_6$): $\delta_{Si}$ = 55.99 (dddd, *J* = 60.1, 43.2, 16.2, 5.2 Hz, 2Si). Anal. Found: C, 65.91; H, 5.31; N, 4.07%. Calcd. for $C_{76}H_{66}N_4P_4Si_2Ni_2$: C, 68.49; H, 4.99; N, 4.20%. Satisfactory elemental data not acquired due to the compound undergoing rapid oxidation upon exposure to air. Calcd. for $C_{76}H_{66}N_4O_4P_4Si_2Ni_2$: C, 65.35; H, 4.76; N, 4.01%. ESI-MS (low-res., +ve ion, MeCN): *m/z* = 1273.32 $[(C_{38}H_{33}N_2P_2Si)_2Ni + H]^+$, 1332.24 $[M + H]^+$. Crystals of a benzene solvate **5**.$(C_6H_6)_{1.5}$ suitable for X-ray diffraction were grown by slow diffusion of hexane vapour into benzene (CAUTION) solution of compound **5**. *Crystal data for* **5**.$(C_6H_6)_{1.5}$: $C_{85}H_{75}N_4Ni_2P_4Si_2$, $M_w$ = 1450.06 gmol$^{-1}$, dark red-brown prism, 0.210 × 0.090 × 0.085 mm$^3$, triclinic, space group *P*-1 (No. 2), *a* = 12.6509(3), *b* = 16.9249(6), *c* = 17.6665(6) Å, $\alpha$ = 81.1890(12), $\beta$ = 77.4286(16), $\gamma$ = 73.2272(17)°, *V* = 3518.3(2) Å$^3$, *Z* = 2, $D_{calcd}$ = 1.369 Mgm$^{-3}$, *F*000 = 1514, Nonius KappaCCD, Mo Kα radiation, λ = 0.71073 Å, μ = 0.711 mm$^{-1}$, *T* = 200(1) K, $2\theta_{max}$ = 50.3º, 46219 reflections collected, 12476 unique ($R_{int}$ = 0.069). $R_1$ = 0.0438, $wR_2$ = 0.1071, *R* indices based on 9240 reflections with $I > 2.0\sigma(I)$ (refinement on $F^2$), 874 parameters, 0 restraints. Lp and absorption corrections applied, CCDC 1517411.

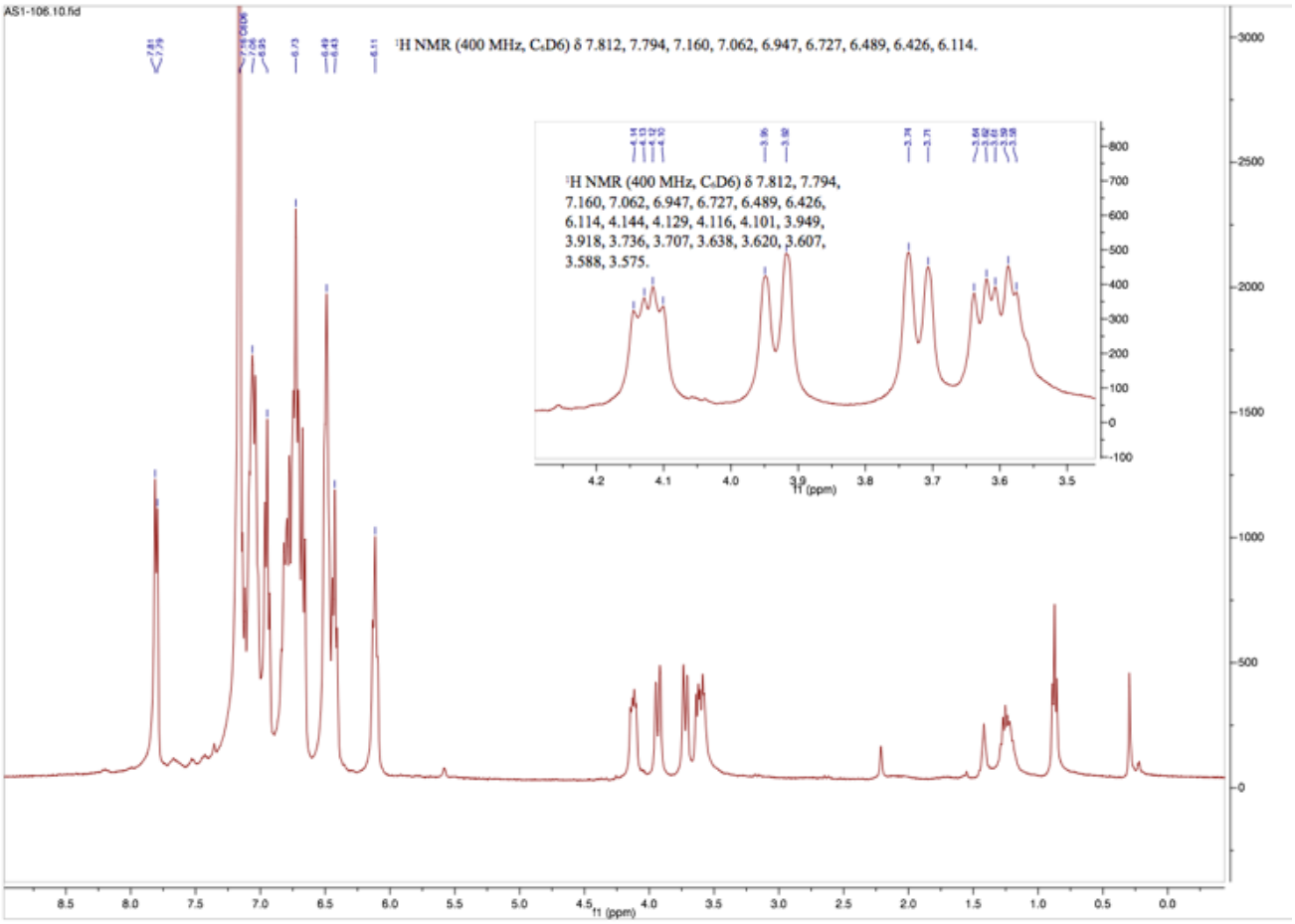


**Figure S6.** $^{1}H$ NMR spectrum of **5** (400 MHz, C6D6, 298 K)

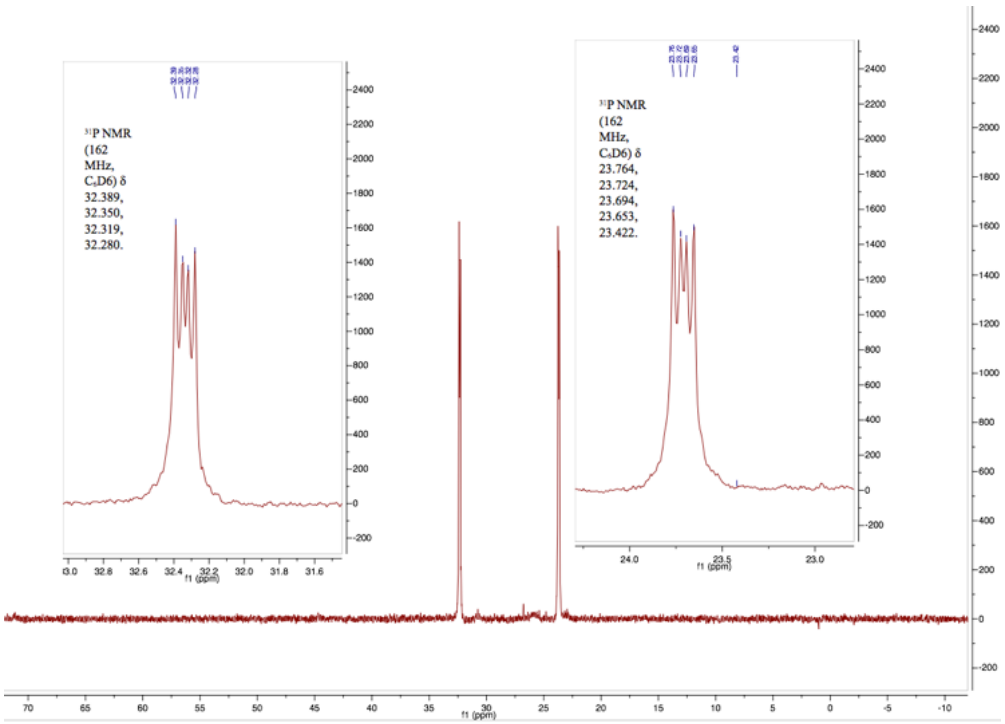


**Figure S7.** $^{31}P\{^{1}H\}$ NMR Spectrum of **5** (162 MHz, $C_6D_6$, 298 K)

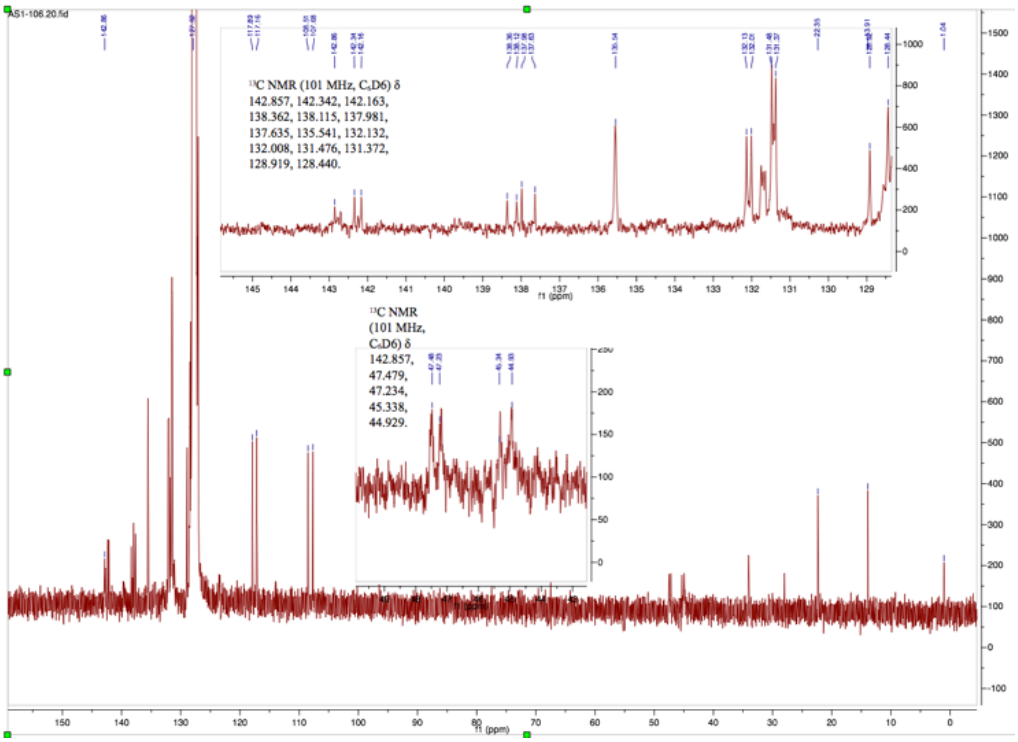


**Figure S8.** $^{13}C\{^1H\}$ NMR Spectrum of **5** (101 MHz, $C_6D_6$, 298 K)

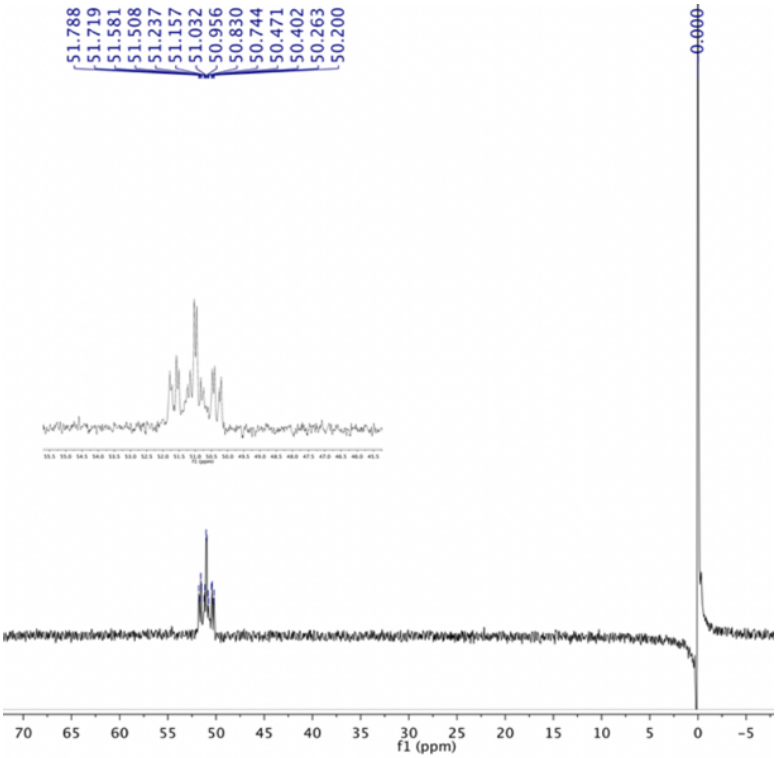


**Figure S9.** $^{29}Si\{^1H\}$ NMR Spectrum of **5** ($C_6D_6$, 298 K)

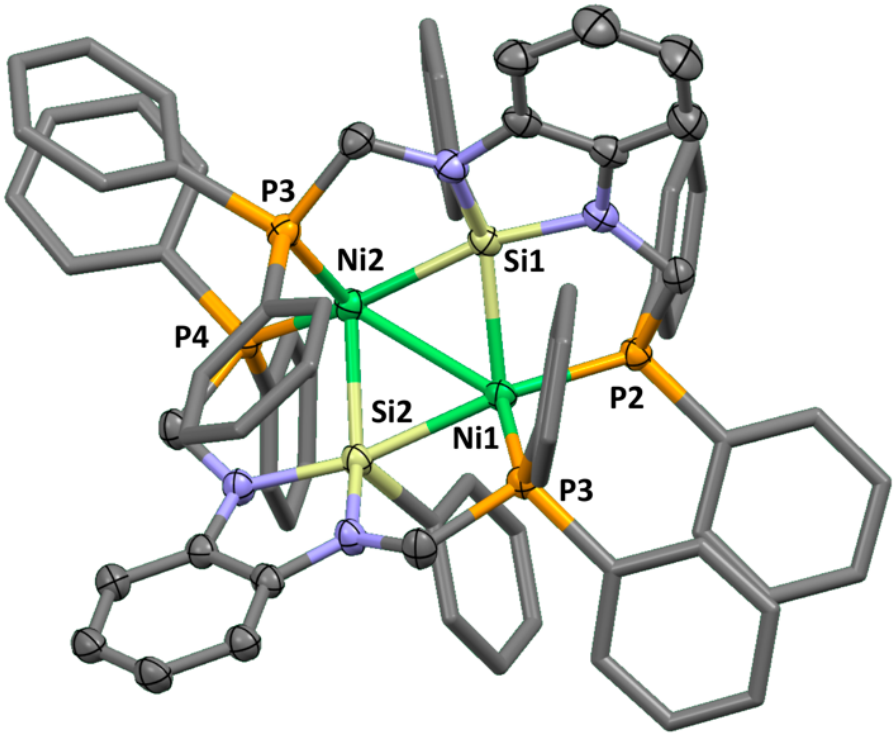


**Figure S10**. Molecular structure of **5** in a crystal of **5**.$(C_6H_6)_{1.5}$ (50% displacement ellipsoids, hydrogen atoms and solvent omitted, phenyl groups simplified). Selected bond lengths (Å) and angles (°): Ni1–Ni2 2.6020(5), Ni1–P1 2.2358(8), Ni1–P2 2.2189(9), Ni1–Si1 2.2906(9), Ni1–Si2 2.3131(9), Ni2–P3 2.2015(9), Ni2–P4 2.2013(9), Ni2–Si1 2.3213(9), Ni2–Si2 2.2937(9), P1–Ni1–Ni2 124.16(3), P1–Ni1–Si1 117.63(3), P1–Ni1–Si2 87.40(3), P2–Ni1–Ni2 123.61(3), P2–Ni1–P1 107.81(3), P2–Ni1–Si1 82.51(3), P2–Ni1–Si2 154.45(4), Si1–Ni1–Ni2 56.21(2), Si1–Ni1–Si2 109.02(3), Si2–Ni1–Ni2 55.26(2), P3–Ni2–Ni1 118.99(3), P3–Ni2–Si1 85.54(3), P3–Ni2–Si2 113.33(3), P4–Ni2–Ni1 126.52(3), P4–Ni2–P3 108.37(4), P4–Ni2–Si1 156.08(3), P4–Ni2–Si2 84.18(3), Si1–Ni2–Ni1 55.10(2), Si2–Ni2–Ni1 55.96(2), Si2–Ni2–Si1 108.62(3).

## Synthesis of $[Pt_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (6)

The pro-ligand $HSiPh(CH_2PPh_2)_2C_6H_4$ (**3**: 64 mg, 0.105 mmol) was added to a thf (10 mL) solution of $[Pt(nbe)_3]$ (50 mg, 0.105 mmol). The mixture was then stirred at room temperature for 6 hours. The resulting orange solution was concentrated and pentane was added to induce precipitation. The yellow-orange precipitate was collected by filtration, washed with pentane and dried under vacuo. Yield: 48 mg (92%). $^1$H NMR (600 MHz, $C_6D_6$, 298 K): $\delta_H$ = 7.88 (dd, 4 H, $^{3,4}J_{HH}$ = 7.8, 1.2 Hz, $C_6H_4$), 7.64 (t, 4 H, $^3J_{HH}$ = 9 Hz), 7.05-6.98 (m, 8 H, $C_6H_5$), 6.93-6.85 (m, 8 H, $C_6H_5$), 6.81 (t, 6 H, *J* = 7.8 Hz, $C_6H_5$), 6.77-6.71 (m, 14 H, $C_6H_5$), 6.64 (td, 2 H, $^{3,4}J_{HH}$ = 7.5, 1.8 Hz), 6.59-6.56 (m, 6 H, $C_6H_5$), 6.49-6.45 (m, 6 H, $C_6H_5$), 4.63-4.53 (m, 2 H, $PCH_2$), 4.53-4.49 (dd, 2 H, *J* = 12, 10.2 Hz, $PCH_2$), 4.42-4.39 (dd, 2 H, *J* = 12, 6 Hz, $PCH_2$), 3.28-3.24 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $C_6D_6$, 298 K): $\delta_C$ = 147.4, 142.9 (d, *J* = 15 Hz), 142. 7, 140.1 (d, *J* = 36 Hz), 138.4 (t, *J* = 18 Hz), 135.0 (d, *J* = 15 Hz), 134.4 (t, *J* = 9 Hz), 132.7, 132.6, 132.6, 132.5, 130.0 (d, *J* = 4.5 Hz), 129.3 (d, *J* = 4.5 Hz), 128.8 (t, *J* = 1.5 Hz), 128.7, 128.4, 128.3, 128.13, 128.10, 128.07, 127.9, 127.8 (d, *J* = 10.5 Hz), 127.6, 127.4, 118.0, 117.1, 109.0, 108.5, 51.55 (m), 46.40 (d, *J* = 36 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$, 298 K): $\delta(P_{A,A'})$ = 68.39 ($^1J(PtP_A)$ = 3500 Hz, $^2J(PtP_A)$ = 522 Hz, $^3J(P_AP_{A'})$ = 101 Hz), 43.83 ($^1J(PtP_B)$ = 2224 Hz, 2J(PBPB') and $^2J(P_AP_B)$ not resolved), See Figure S12 for *gNMR* simulation. $^{29}$Si NMR (79.5 MHz, $C_6D_6$, 298 K): $\delta_{Si}$ = 60.54 (t, $^2J_{SiP}$ = 4.9 Hz), 58.44 (t, $^2J_{SiP}$ = 5.6 Hz). Anal. Found: C, 56.86; H, 4.18; N, 3.55%. Calcd. for $C_{76}H_{66}N_4P_4Si_2Pt_2$: C, 56.85; H, 4.14; N, 3.49%. ESI-MS (low-res, +ve ion, MeCN): *m/z* = 1605.31 $[M]^+$, 803.66 $[(M/2)+H]^+$. Crystals of a benzene solvate **6**.$(C_6H_6)_2$ suitable for X-ray diffraction were grown by slow diffusion of hexane vapour into benzene (CAUTION) solution of compound **6**. *Crystal data for* **6**.$(C_6H_6)$: $C_{88}H_{78}N_4P_4Pt_2Si_2$, $M_w$ = 1761.78 gmol$^{-1}$, orange plate, 0.120 x 0.110 x 0.080 mm$^3$, triclinic, space group *P*-1 (No. 2), *a* = 12.9341(2), *b* = 15.4591(3), *c* = 20.0358(3) Å, $\alpha$ = 70.8529(9), $\beta$ = 79.0293(10), $\gamma$ = 88.9368(10)°, *V* = 3711.21(11) Å$^3$, *Z* = 2, $D_{calcd}$ = 1.577 Mgm$^{-3}$, *F*000 = 1756, Nonius KappaCCD, Mo K$\alpha$ radiation, $\lambda$ = 0.71073 Å, $\mu$ = 3.934 mm$^{-1}$, *T* = 200(1) K, 2$\theta_{max}$ = 55.0°, 84751 reflections collected, 16970 unique ($R_{int}$ = 0.085), $R_1$ = 0.0368, $wR_2$ = 0.0875, *R* indices based on 13109 reflections with $I > 2.0\sigma(I)$ (refinement on $F^2$), 847 parameters, 0 restraints. Lp and absorption corrections applied, CCDC 1517308.

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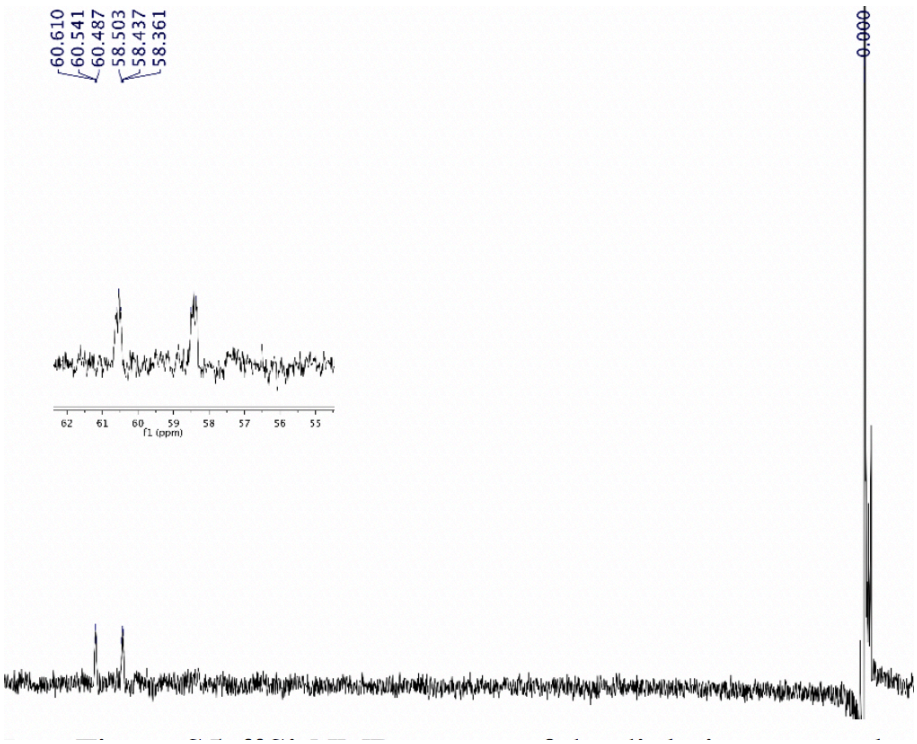



**Figure S11.** $^{29}Si\{^{1}H\}$ NMR Spectrum of **6** ($C_6D_6$, 298 K)

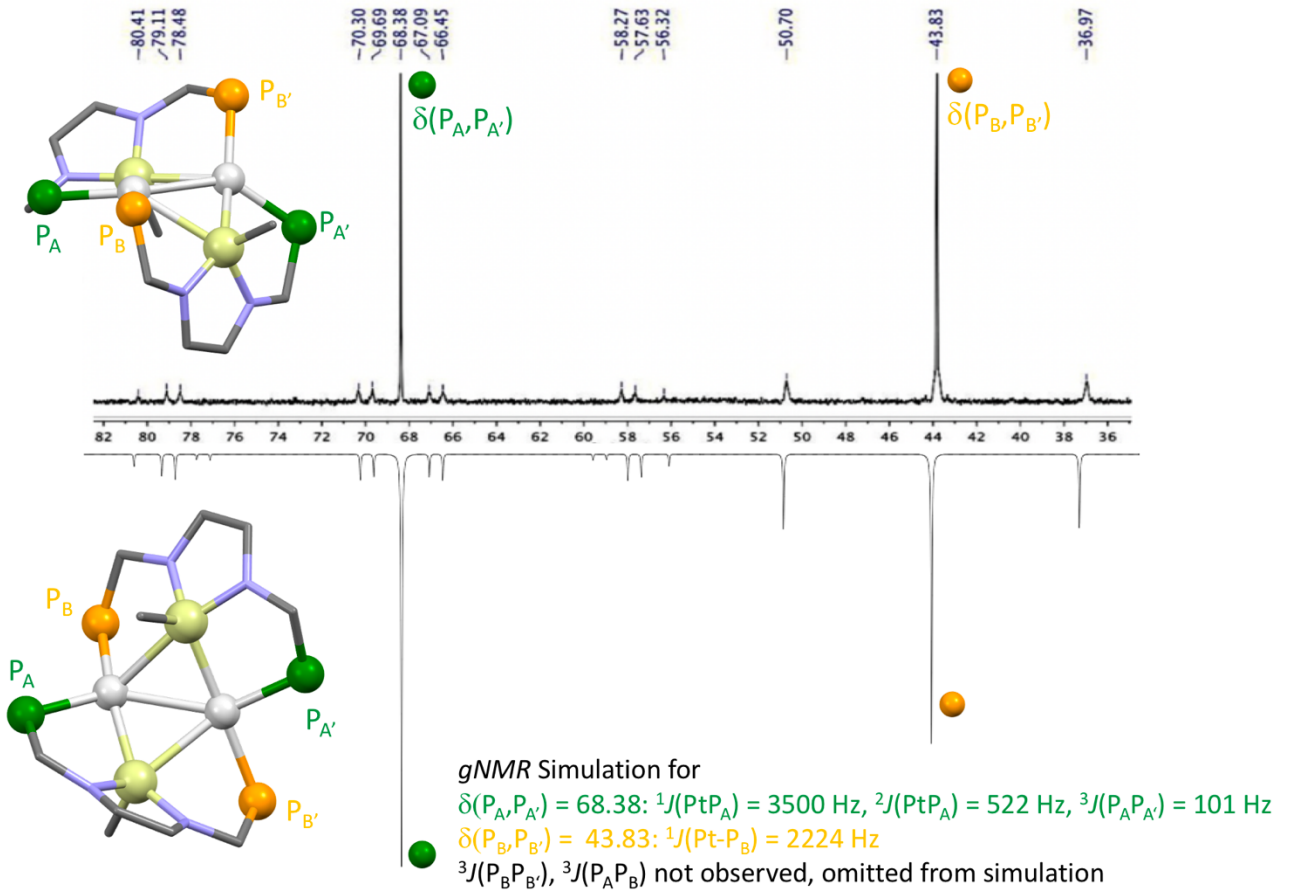



**Figure S12.** $^{31}P\{^{1}H\}$ NMR Spectrum of **6** ($C_6D_6$, 162 MHz, 298 K) (Simulated using gNMR: P. H. M. Budzelaar, *gNMR, version 5.1*, http://www.home.cc.umanitoba.ca/~budzelaa/gNMR/gNMR.html).

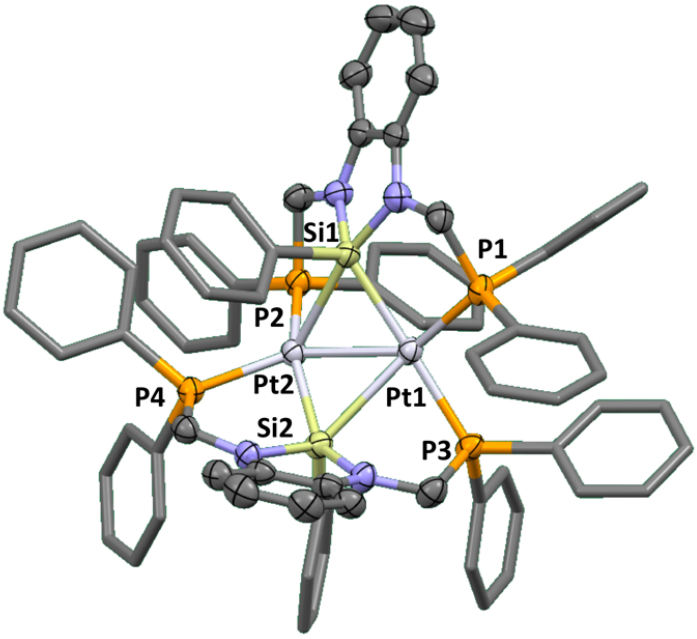



**Figure S13**. Molecular structure of **6** in a crystal of **6**.$(C_6H_6)_2$ (50% displacement ellipsoids, hydrogen atoms and solvent omitted, phenyl groups simplified). Selected bond lengths (Å) and angles (°): Pt1–P1 2.2841(12), Pt1–P3 2.3451(12), Pt1–Si1 2.3821(12), Pt1–Si2 2.7133(13), Pt2–P2 2.2805(11), Pt2–P4 2.2836(11), Pt2–Si1 2.6421(12), Pt2–Si2 2.3782(12), P1–Pt1–Pt2 145.24(3), P1–Pt1–P3 96.95(4), P1–Pt1–Si1 83.30(4), P1–Pt1–Si2 145.59(4), P3–Pt1–Pt2 117.74(3), P3–Pt1–Si1 178.21(4), P3–Pt1–Si2 76.12(4), Si1–Pt1–Pt2 61.96(3), Si1–Pt1–Si2 102.67(4), Si2–Pt1–Pt2 51.91(3), P2–Pt2–Pt1 107.93(3), P2–Pt2–P4 111.18(4), P2–Pt2–Si1 81.96(4), P2–Pt2–Si2 158.40(4), P4–Pt2–Pt1 140.19(3), P4–Pt2–Si1 126.31(4), P4–Pt2–Si2 81.62(4), Si1–Pt2–Pt1 52.73(3), Si2–Pt2–Pt1 63.90(3), Si2–Pt2–Si1 104.92(4).

(a) $Pd_2$ (Compound **4**) (b) $Ni_2$ (Compound **5**) (c) $Pt_2$ (Compound **6**)

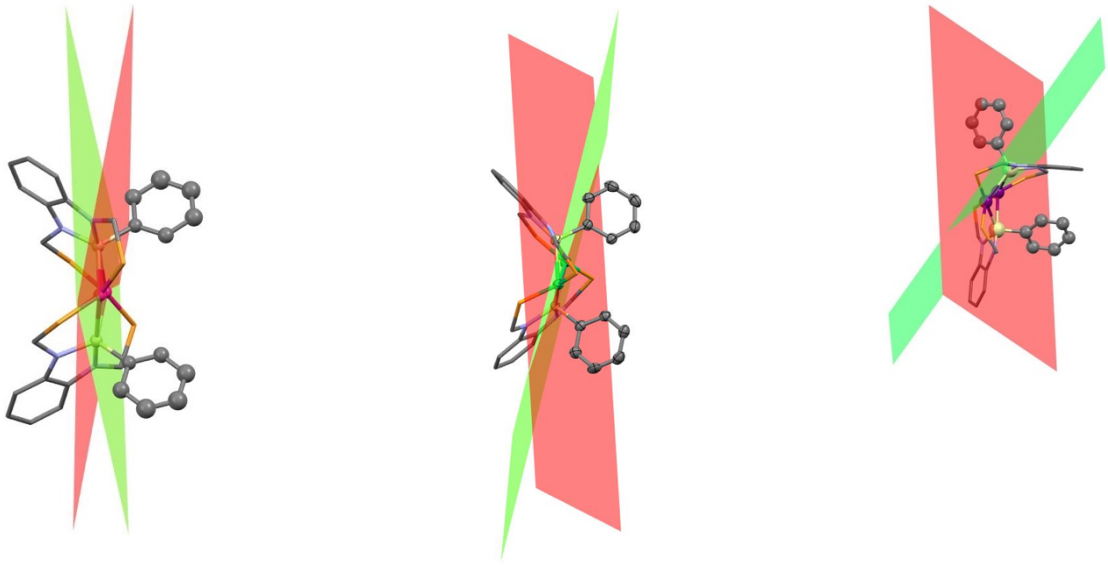
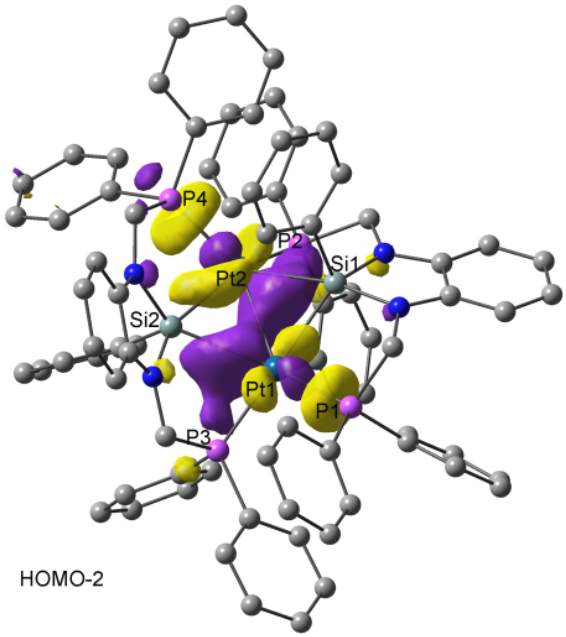


**Figure S14.** Folding of two $M_2Si$ planes across M-M vector. (a) M = Pd; (b) M = Ni; (c) M = Pt.

## Computational Details

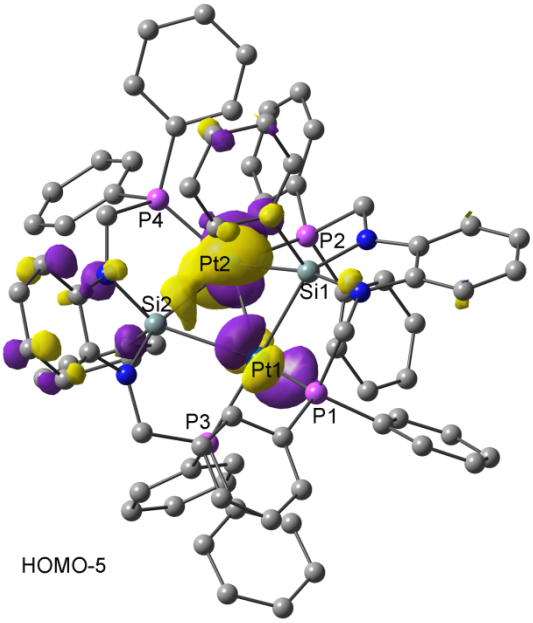
All computational work was performed by using the Gaussian 09 suite of programs.[5] The geometries of complexes **11**-**13** were optimized at the DFT level of theory using the exchange functional of Becke[6] in conjunction with the correlation functional of Perdew[7,8] (BP86). The Stuttgart basis set in combination with the 60-core-electron relativistic effective core potential (SDD)[9] was used for Ni, Pd and Pt; 6-31G(d)[10] basis sets were used for all other atoms. Frequency calculations were performed to confirm that optimized structures were minimal or saddle points at the BP86 level of theory. Single point energy calculations for all the optimized structures were carried out with a larger basis set viz the quadruple-ζ valence def2-QZVP[11] basis set on Ni, Pd and Pt along with the corresponding ECP and the 6-311+G(2d,p) basis set on other atoms. Single point calculations were also carried out at the M06, B97D and B3LYP level of theories, and found to follow similar trends. Natural bond orbital (NBO) analyses were carried out at the BP86 level of theory.

## $[Pt_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (6)

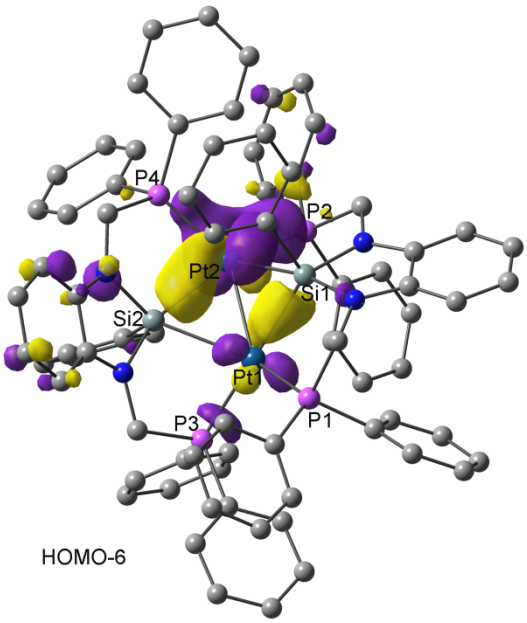


HOMO-2

For this complex, NBO analysis indicates that both the Pt-centers have five lone pairs with an electronic configuration of [Xe ]$5d^{9.5}6s^{0.5}6p^{0.5}$ and natural charges of -0.5. The Wiberg bond order and HOMO-2 closely represent a conventional Pt–Pt bond. NBO second order perturbation theory analysis (donor-acceptor) suggests that this bonding interaction comprises primarily the Pt2-P2 bond electron pair to the antibonding Pt1-P3 orbital, but hardly any contribution is found from either of the Si atoms. Therefore, this corresponds a 4-centered-2-electron type of bonding as described by Nova and Nazari which here involves P–Pt–Pt–P centers rather than Si–Pt–Pt–Si. NBO analysis shows that each of the Pt-centers have three different types of interactions with both the Si atoms. The almost degenerate HOMO-5 and HOMO-6 (332-331) orbitals reflect the polar-covalent bonding interaction which primarily comprises σ-back donation from a Pt-d lone pair to an orbital on the Si atom, while the other Si atom donates electron density to the of Pt-d orbital.

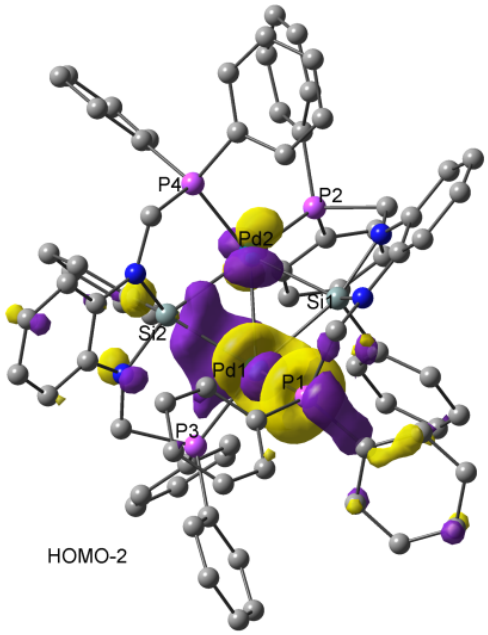


HOMO-5

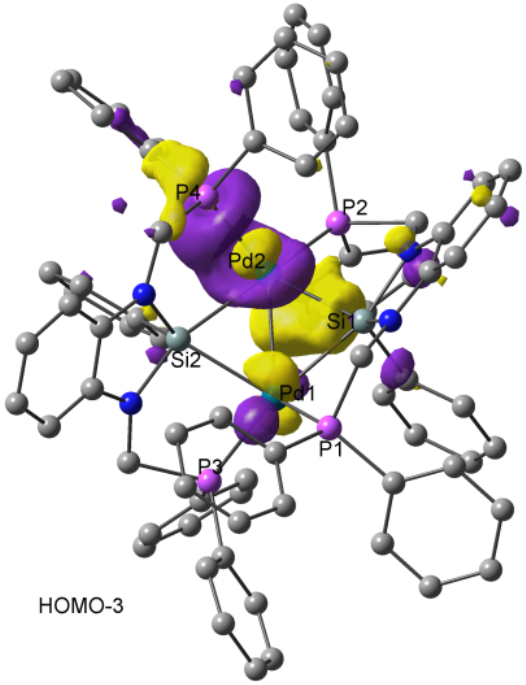


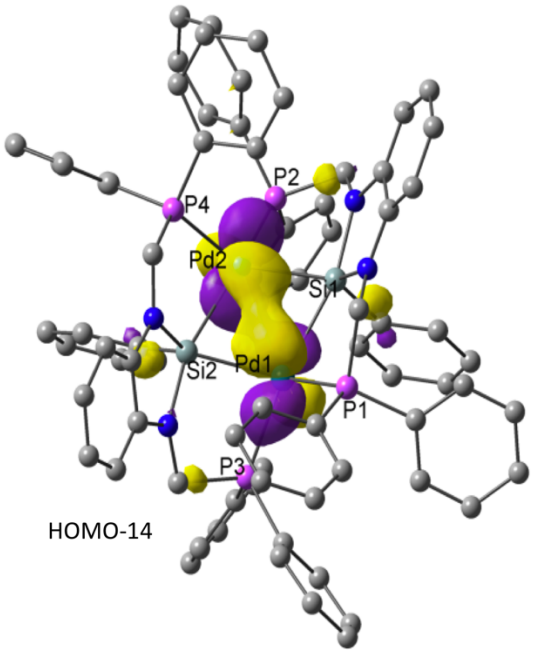
HOMO-6

## $[Pd_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (4)




In contrast to the observation of Nova and Nazari, NBO-NLMO analysis of the $Pd_2$-complex did not show any obvious 4c-2e bonding. Both the Pd-centers interact in two different ways to each of the Si-atoms. The almost degenerate HOMO-2 and HOMO-3 sets of orbitals reflect the bonding interaction due to the Pd-P bonding orbital interaction with the Si-*p* orbital, while HOMO-4 represent back donation from a Pd-d orbital to the Si-p orbital. The metal-metal bonding orbital is very low in energy and can be seen only in the HOMO-14. Each $Pd^{I}$ centre is thus a $d^9$ system due to this interaction).




## $[Ni_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (5)

Each nickel has five lone pairs, corresponding to HOMO, HOMO-4, HOMO-6, HOMO-7 and HOMO-8 the with electronic configuration of $3d^{9.4}4p^{0.7}5s^{0.3}$ and natural charges of -0.5. Each Ni-center is found to form covalent bonds only with the P-atoms of ligands while the Ni–Ni bond (HOMO-3; Ni-Ni bonding with from the Ni-P bonding to the Ni-d orbital) or Ni–Si bonds involve extended delocalization (HOMO-5 represent Ni to Si σ-back donation; (326) and HOMO-11 involves Si to Ni σ-donation). The primary component of the Ni–Ni σ-bond arises from HOMO-12.

## Cartesian Coordinates for $[Pd_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (4)

Optimised structure at the MO6L level of theory (SDD basis set for palladium with SDD core potential and 6-31g(d) for remaining elements)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | 1.373476 | -0.032203 | 0.131778 |
| 2 | 46 | 0 | -1.403038 | 0.013830 | 0.178978 |
| 3 | 15 | 0 | 2.664128 | -1.105069 | -1.560233 |
| 4 | 15 | 0 | -2.684533 | 1.349636 | -1.350026 |
| 5 | 15 | 0 | -2.859471 | -1.594695 | 1.169458 |
| 6 | 15 | 0 | 2.835966 | 1.371394 | 1.402657 |
| 7 | 14 | 0 | -0.128464 | -1.956267 | -0.434376 |
| 8 | 14 | 0 | 0.092867 | 2.012456 | -0.064434 |
| 9 | 7 | 0 | 0.395718 | -2.465655 | -2.076474 |
| 10 | 7 | 0 | -0.447666 | 2.783746 | -1.601597 |
| 11 | 7 | 0 | 1.544598 | 3.099615 | -0.179495 |
| 12 | 6 | 0 | 0.317261 | 4.442106 | -3.306047 |
| 13 | 6 | 0 | -0.354764 | -3.839005 | -4.015924 |
| 14 | 6 | 0 | -0.474979 | -3.331897 | -2.726466 |
| 15 | 6 | 0 | 0.428067 | 3.740574 | -2.110053 |
| 16 | 6 | 0 | 2.737180 | 1.253329 | -2.993542 |
| 17 | 6 | 0 | 2.504319 | 4.911924 | -1.605549 |
| 18 | 6 | 0 | -3.562990 | 0.307513 | -2.565120 |
| 19 | 7 | 0 | -1.593705 | -2.999947 | -0.722042 |
| 20 | 6 | 0 | -2.030290 | -1.104868 | 3.784395 |
| 21 | 6 | 0 | 2.155435 | 0.253416 | 3.851254 |
| 22 | 6 | 0 | -3.200257 | -3.192092 | 3.485482 |
| 23 | 6 | 0 | -2.698947 | -2.001192 | 2.945432 |
| 24 | 6 | 0 | -1.273404 | 2.586387 | 3.843911 |
| 25 | 6 | 0 | 1.285748 | 5.398884 | -3.642215 |
| 26 | 6 | 0 | 1.551840 | 3.954487 | -1.261707 |
| 27 | 6 | 0 | 0.788268 | -2.640858 | 2.215703 |
| 28 | 6 | 0 | 3.294925 | 2.255354 | -3.779562 |
| 29 | 6 | 0 | -0.793895 | 2.726164 | 1.453654 |
| 30 | 6 | 0 | 3.482598 | 0.116289 | -2.646266 |
| 31 | 6 | 0 | 3.034599 | 2.493421 | 4.007468 |
| 32 | 6 | 0 | 4.638436 | 1.173907 | 1.155817 |
| 33 | 6 | 0 | -1.597416 | -3.678199 | -1.924855 |
| 34 | 6 | 0 | -1.857384 | -1.391686 | 5.135753 |
| 35 | 6 | 0 | 5.360347 | 1.010561 | -3.881237 |
| 36 | 6 | 0 | -2.541034 | -4.579102 | -2.413908 |
| 37 | 6 | 0 | 4.801715 | 0.004498 | -3.094955 |
| 38 | 6 | 0 | 4.520204 | -3.226586 | -2.033721 |
| 39 | 6 | 0 | -2.589579 | -3.216191 | 0.286125 |
| 40 | 6 | 0 | -0.690211 | 2.068459 | 2.688576 |
| 41 | 6 | 0 | 2.680694 | 1.388712 | 3.224014 |
| 42 | 6 | 0 | -2.390786 | -5.110167 | -3.701102 |
| 43 | 6 | 0 | 2.361758 | 5.634648 | -2.795506 |
| 44 | 6 | 0 | 4.612398 | 2.134597 | -4.221878 |
| 45 | 6 | 0 | 2.835895 | 2.471265 | 5.385131 |
| 46 | 6 | 0 | -5.410522 | -0.782542 | 2.046068 |
| 47 | 6 | 0 | -1.480864 | 2.233136 | -2.438575 |
| 48 | 6 | 0 | 1.446673 | -3.409862 | 3.174393 |
| 49 | 6 | 0 | 1.549887 | -1.967927 | -2.772827 |
| 50 | 6 | 0 | 0.821569 | -2.978989 | 0.855083 |
| 51 | 6 | 0 | 1.971882 | 0.224761 | 5.230349 |
| 52 | 6 | 0 | -4.662679 | -1.330789 | 0.994959 |
| 53 | 6 | 0 | -1.315914 | -4.737904 | -4.499306 |
| 54 | 6 | 0 | -2.341252 | -2.588168 | 5.659188 |
| 55 | 6 | 0 | 5.456016 | 0.553354 | 2.108778 |
| 56 | 6 | 0 | 5.942611 | -4.107964 | -0.294192 |
| 57 | 6 | 0 | 3.957896 | -2.317835 | -1.128297 |

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|---|---|---|---|---|---|
| 58 | 6 | 0 | -2.849747 | -0.774880 | -3.103258 |
| 59 | 6 | 0 | 2.163800 | -4.538563 | 2.782782 |
| 60 | 6 | 0 | 5.194444 | 1.544869 | -0.076814 |
| 61 | 6 | 0 | -3.449039 | -1.641984 | -4.010140 |
| 62 | 6 | 0 | -3.013367 | -3.487058 | 4.832527 |
| 63 | 6 | 0 | 2.539343 | 3.132475 | 0.853341 |
| 64 | 6 | 0 | -2.001081 | 3.771724 | 3.777391 |
| 65 | 6 | 0 | -5.675093 | 4.551466 | 0.126328 |
| 66 | 6 | 0 | 6.800541 | 0.317313 | 1.836526 |
| 67 | 6 | 0 | -5.286012 | -1.535593 | -0.245026 |
| 68 | 6 | 0 | 7.346936 | 0.697334 | 0.613474 |
| 69 | 6 | 0 | 2.302327 | 1.339451 | 5.998341 |
| 70 | 6 | 0 | -1.507111 | 3.934907 | 1.418240 |
| 71 | 6 | 0 | -4.891373 | 0.506080 | -2.954100 |
| 72 | 6 | 0 | -5.862967 | 3.200227 | 0.412807 |
| 73 | 6 | 0 | -2.118157 | 4.444337 | 2.560122 |
| 74 | 6 | 0 | 2.203659 | -4.899315 | 1.435596 |
| 75 | 6 | 0 | -4.588515 | 4.946923 | -0.648479 |
| 76 | 6 | 0 | -4.778726 | -1.443035 | -4.381406 |
| 77 | 6 | 0 | -7.362972 | -0.665070 | 0.629559 |
| 78 | 6 | 0 | -3.693945 | 3.999846 | -1.141696 |
| 79 | 6 | 0 | 1.537179 | -4.130326 | 0.486251 |
| 80 | 6 | 0 | -3.874420 | 2.640501 | -0.861291 |
| 81 | 6 | 0 | -6.627116 | -1.207923 | -0.421806 |
| 82 | 6 | 0 | 5.500951 | -4.121354 | -1.616545 |
| 83 | 6 | 0 | -4.964282 | 2.254948 | -0.066704 |
| 84 | 6 | 0 | 6.540346 | 1.313543 | -0.341070 |
| 85 | 6 | 0 | 5.394219 | -3.205625 | 0.612915 |
| 86 | 6 | 0 | 4.398135 | -2.327127 | 0.200101 |
| 87 | 6 | 0 | -5.493074 | -0.368836 | -3.856909 |
| 88 | 6 | 0 | -6.750888 | -0.456319 | 1.864366 |
| 89 | 1 | 0 | 5.402145 | -0.859389 | -2.812145 |
| 90 | 1 | 0 | 6.390717 | 0.915601 | -4.222852 |
| 91 | 1 | 0 | 5.056486 | 2.923510 | -4.826947 |
| 92 | 1 | 0 | 2.705606 | 3.137879 | -4.025233 |
| 93 | 1 | 0 | 1.717359 | 1.363946 | -2.614423 |
| 94 | 1 | 0 | 3.926605 | -1.650482 | 0.916045 |
| 95 | 1 | 0 | 5.722829 | -3.199335 | 1.651118 |
| 96 | 1 | 0 | 6.711898 | -4.807806 | 0.028707 |
| 97 | 1 | 0 | 5.925781 | -4.828460 | -2.327073 |
| 98 | 1 | 0 | 4.196617 | -3.232396 | -3.075085 |
| 99 | 1 | 0 | 4.565154 | 2.004026 | -0.842487 |
| 100 | 1 | 0 | 6.954418 | 1.611486 | -1.303063 |
| 101 | 1 | 0 | 8.398843 | 0.511901 | 0.403292 |
| 102 | 1 | 0 | 7.425098 | -0.164205 | 2.587883 |
| 103 | 1 | 0 | 5.038600 | 0.252606 | 3.069891 |
| 104 | 1 | 0 | 3.469731 | 3.377491 | 3.541335 |
| 105 | 1 | 0 | 3.102385 | 3.340961 | 5.983118 |
| 106 | 1 | 0 | 2.147970 | 1.326326 | 7.076134 |
| 107 | 1 | 0 | 1.561998 | -0.667306 | 5.703032 |
| 108 | 1 | 0 | 1.879151 | -0.607552 | 3.240724 |
| 109 | 1 | 0 | 1.576801 | -4.420447 | -0.566430 |
| 110 | 1 | 0 | 2.764165 | -5.780977 | 1.124959 |
| 111 | 1 | 0 | 2.683756 | -5.141993 | 3.526069 |
| 112 | 1 | 0 | 1.396593 | -3.129251 | 4.227456 |
| 113 | 1 | 0 | 0.221703 | -1.756767 | 2.520129 |
| 114 | 1 | 0 | -1.581884 | 4.484824 | 0.478995 |
| 115 | 1 | 0 | -2.682169 | 5.375419 | 2.504769 |
| 116 | 1 | 0 | -2.468173 | 4.178839 | 4.673443 |
| 117 | 1 | 0 | -1.159242 | 2.064276 | 4.795460 |
| 118 | 1 | 0 | -0.121499 | 1.135873 | 2.731780 |
| 119 | 1 | 0 | -5.461671 | 1.338776 | -2.543609 |
| 120 | 1 | 0 | -6.529849 | -0.206263 | -4.150309 |
| 121 | 1 | 0 | -5.255558 | -2.127391 | -5.081302 |
| 122 | 1 | 0 | -2.878471 | -2.480644 | -4.407823 |
| 123 | 1 | 0 | -1.816001 | -0.951672 | -2.794710 |
| 124 | 1 | 0 | -5.107656 | 1.200579 | 0.172912 |
| 125 | 1 | 0 | -6.707576 | 2.878061 | 1.020271 |

| | | | | | |
|---|---|---|---|---|---|
| 126 | 1 | 0 | -6.371415 | 5.294567 | 0.511267 |
| 127 | 1 | 0 | -4.429115 | 6.001344 | -0.869673 |
| 128 | 1 | 0 | -2.836917 | 4.334689 | -1.725309 |
| 129 | 1 | 0 | -3.745814 | -3.891022 | 2.850721 |
| 130 | 1 | 0 | -3.397297 | -4.420801 | 5.239847 |
| 131 | 1 | 0 | -2.198387 | -2.821432 | 6.713184 |
| 132 | 1 | 0 | -1.339068 | -0.680067 | 5.777777 |
| 133 | 1 | 0 | -1.636843 | -0.180119 | 3.361047 |
| 134 | 1 | 0 | -4.718315 | -1.940388 | -1.085569 |
| 135 | 1 | 0 | -7.092080 | -1.370362 | -1.392893 |
| 136 | 1 | 0 | -8.410879 | -0.406300 | 0.486906 |
| 137 | 1 | 0 | -7.319254 | -0.035046 | 2.692515 |
| 138 | 1 | 0 | -4.936867 | -0.611038 | 3.012593 |
| 139 | 1 | 0 | -3.388497 | -4.877184 | -1.798386 |
| 140 | 1 | 0 | -3.127005 | -5.820716 | -4.072980 |
| 141 | 1 | 0 | -1.206830 | -5.150680 | -5.500520 |
| 142 | 1 | 0 | 0.490118 | -3.550732 | -4.639811 |
| 143 | 1 | 0 | 3.355065 | 5.100955 | -0.952521 |
| 144 | 1 | 0 | 3.106000 | 6.386233 | -3.053733 |
| 145 | 1 | 0 | 1.183618 | 5.959399 | -4.569653 |
| 146 | 1 | 0 | -0.522339 | 4.258529 | -3.974846 |
| 147 | 1 | 0 | -2.282142 | -3.978815 | 1.024433 |
| 148 | 1 | 0 | -3.539796 | -3.549845 | -0.153238 |
| 149 | 1 | 0 | -1.085859 | 1.503389 | -3.171365 |
| 150 | 1 | 0 | -1.995792 | 3.011609 | -3.021056 |
| 151 | 1 | 0 | 1.279082 | -1.241541 | -3.561963 |
| 152 | 1 | 0 | 2.089591 | -2.789957 | -3.271319 |
| 153 | 1 | 0 | 2.213985 | 3.730859 | 1.723116 |
| 154 | 1 | 0 | 3.484342 | 3.558487 | 0.490508 |

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## Cartesian Coordinates for $[Ni_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (5)

Optimised structure at the MO6L level of theory (SDD basis set for nickel with SDD core potential and 6-31g(d) for remaining elements)

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.041181 | 0.102229 | -0.028176 |
| 2 | 6 | 0 | 0.010670 | 0.106424 | 1.374271 |
| 3 | 6 | 0 | 1.185309 | 0.163050 | 2.114313 |
| 4 | 6 | 0 | 2.418759 | 0.216137 | 1.468657 |
| 5 | 6 | 0 | 2.463591 | 0.233853 | 0.078164 |
| 6 | 6 | 0 | 1.285888 | 0.185578 | -0.663702 |
| 7 | 6 | 0 | -2.461253 | -1.141102 | 0.055924 |
| 8 | 6 | 0 | -3.707689 | -0.844465 | 0.602129 |
| 9 | 6 | 0 | -4.401486 | -1.784641 | 1.364074 |
| 10 | 6 | 0 | -3.844194 | -3.041819 | 1.579547 |
| 11 | 6 | 0 | -2.593160 | -3.350901 | 1.041271 |
| 12 | 6 | 0 | -1.903577 | -2.406760 | 0.289686 |
| 13 | 6 | 0 | -1.108242 | -0.944486 | -2.447950 |
| 14 | 6 | 0 | -1.344466 | -0.871377 | -4.861433 |
| 15 | 6 | 0 | -0.736021 | -2.096792 | -5.119052 |
| 16 | 6 | 0 | -0.739317 | -2.605167 | -6.424063 |
| 17 | 6 | 0 | -1.358429 | -1.906037 | -7.453956 |
| 18 | 6 | 0 | -1.967525 | -0.667645 | -7.205349 |
| 19 | 6 | 0 | -1.936093 | -0.136601 | -5.921062 |
| 20 | 6 | 0 | -3.443578 | 1.735399 | -6.330372 |
| 21 | 6 | 0 | -5.607322 | 3.672062 | -6.228298 |
| 22 | 6 | 0 | -6.525238 | 4.478586 | -5.546940 |
| 23 | 6 | 0 | -7.639892 | 4.992202 | -6.200357 |
| 24 | 6 | 0 | -7.869735 | 4.674779 | -7.536572 |
| 25 | 6 | 0 | -6.977372 | 3.847860 | -8.215421 |
| 26 | 6 | 0 | -5.844229 | 3.358110 | -7.571248 |
| 27 | 6 | 0 | -2.950072 | 4.476631 | -5.687388 |
| 28 | 6 | 0 | -3.325422 | 5.803530 | -5.445830 |

| | | | | | |
|---|---|---|---|---|---|
| 29 | 6 | 0 | -2.414872 | 6.840822 | -5.622325 |
| 30 | 6 | 0 | -1.117703 | 6.567925 | -6.052037 |
| 31 | 6 | 0 | -0.738817 | 5.252303 | -6.304963 |
| 32 | 6 | 0 | -1.644085 | 4.212455 | -6.118584 |
| 33 | 6 | 0 | -0.897943 | 2.565995 | -3.340630 |
| 34 | 6 | 0 | -1.110178 | 3.922617 | -3.031741 |
| 35 | 6 | 0 | -0.049206 | 4.813545 | -2.869132 |
| 36 | 6 | 0 | 1.262239 | 4.363313 | -2.989230 |
| 37 | 6 | 0 | 1.505407 | 3.019120 | -3.279946 |
| 38 | 6 | 0 | 0.441353 | 2.139783 | -3.452519 |
| 39 | 6 | 0 | -0.822582 | 3.400628 | 1.132102 |
| 40 | 6 | 0 | 0.331686 | 3.289802 | 0.350068 |
| 41 | 6 | 0 | 1.588362 | 3.436588 | 0.927446 |
| 42 | 6 | 0 | 1.702509 | 3.667965 | 2.295627 |
| 43 | 6 | 0 | 0.557514 | 3.762454 | 3.085075 |
| 44 | 6 | 0 | -0.701868 | 3.642948 | 2.505159 |
| 45 | 6 | 0 | -2.852354 | 5.123969 | 0.277522 |
| 46 | 6 | 0 | -1.905750 | 6.046396 | -0.184624 |
| 47 | 6 | 0 | -2.217794 | 7.399306 | -0.272064 |
| 48 | 6 | 0 | -3.476464 | 7.853420 | 0.118329 |
| 49 | 6 | 0 | -4.418192 | 6.945723 | 0.595494 |
| 50 | 6 | 0 | -4.113622 | 5.589861 | 0.668640 |
| 51 | 6 | 0 | -3.637663 | 2.682880 | 1.517282 |
| 52 | 6 | 0 | -5.827798 | 1.629492 | 1.401438 |
| 53 | 6 | 0 | -5.981090 | 1.422804 | 2.767719 |
| 54 | 6 | 0 | -7.037673 | 0.628172 | 3.229961 |
| 55 | 6 | 0 | -7.919657 | 0.039225 | 2.331154 |
| 56 | 6 | 0 | -7.756322 | 0.214806 | 0.950984 |
| 57 | 6 | 0 | -6.703583 | 0.996226 | 0.481152 |
| 58 | 6 | 0 | -7.111848 | 0.719277 | -1.922334 |
| 59 | 6 | 0 | -7.351955 | 0.767918 | -4.733178 |
| 60 | 6 | 0 | -7.534868 | -0.231453 | -5.695366 |
| 61 | 6 | 0 | -8.537791 | -0.111279 | -6.655731 |
| 62 | 6 | 0 | -9.381852 | 0.994709 | -6.659966 |
| 63 | 6 | 0 | -9.217401 | 1.988834 | -5.697853 |
| 64 | 6 | 0 | -8.204804 | 1.881633 | -4.753743 |
| 65 | 6 | 0 | -5.283899 | -0.871965 | -3.472658 |
| 66 | 6 | 0 | -4.661110 | -1.341870 | -4.637659 |
| 67 | 6 | 0 | -3.981368 | -2.554072 | -4.644618 |
| 68 | 6 | 0 | -3.885465 | -3.304753 | -3.473797 |
| 69 | 6 | 0 | -4.476289 | -2.837184 | -2.302819 |
| 70 | 6 | 0 | -5.174602 | -1.631938 | -2.301441 |
| 71 | 6 | 0 | -5.653405 | 3.908238 | -1.755063 |
| 72 | 6 | 0 | -4.865784 | 4.955459 | -2.268699 |
| 73 | 6 | 0 | -5.417674 | 6.187054 | -2.624858 |
| 74 | 6 | 0 | -6.787753 | 6.394602 | -2.502894 |
| 75 | 6 | 0 | -7.601971 | 5.361611 | -2.029622 |
| 76 | 6 | 0 | -7.042251 | 4.142408 | -1.662487 |
| 77 | 7 | 0 | -6.327252 | 1.218801 | -0.831266 |
| 78 | 7 | 0 | -4.824908 | 2.354878 | 0.766713 |
| 79 | 7 | 0 | -2.508645 | 1.048195 | -5.479956 |
| 80 | 7 | 0 | -1.509257 | -0.254614 | -3.637470 |
| 81 | 15 | 0 | -1.550472 | 0.095430 | -0.957309 |
| 82 | 15 | 0 | -2.436169 | 3.331793 | 0.280748 |
| 83 | 15 | 0 | -6.047925 | 0.783718 | -3.443662 |
| 84 | 15 | 0 | -4.124945 | 3.112570 | -5.318349 |
| 85 | 14 | 0 | -4.889139 | 2.286293 | -1.058047 |
| 86 | 14 | 0 | -2.339493 | 1.341190 | -3.687423 |
| 87 | 28 | 0 | -2.641329 | 1.983137 | -1.466325 |
| 88 | 28 | 0 | -4.410174 | 2.255609 | -3.312469 |
| 89 | 1 | 0 | -0.947954 | 0.051788 | 1.892624 |
| 90 | 1 | 0 | 1.135908 | 0.165902 | 3.202265 |
| 91 | 1 | 0 | 3.339572 | 0.254441 | 2.048739 |
| 92 | 1 | 0 | 3.421250 | 0.286315 | -0.438865 |
| 93 | 1 | 0 | 1.344754 | 0.219716 | -1.750121 |
| 94 | 1 | 0 | -4.146080 | 0.129649 | 0.405211 |
| 95 | 1 | 0 | -5.375003 | -1.522812 | 1.779759 |
| 96 | 1 | 0 | -4.379930 | -3.783352 | 2.170369 |

| | | | | | |
|---|---|---|---|---|---|
| 97 | 1 | 0 | -2.152398 | -4.331871 | 1.213095 |
| 98 | 1 | 0 | -0.919093 | -2.650017 | -0.112758 |
| 99 | 1 | 0 | -0.025715 | -1.158386 | -2.446306 |
| 100 | 1 | 0 | -1.621853 | -1.918088 | -2.364856 |
| 101 | 1 | 0 | -0.289289 | -2.665592 | -4.304269 |
| 102 | 1 | 0 | -0.260000 | -3.561824 | -6.625665 |
| 103 | 1 | 0 | -1.366200 | -2.312665 | -8.463731 |
| 104 | 1 | 0 | -2.453697 | -0.119111 | -8.011545 |
| 105 | 1 | 0 | -2.971030 | 2.109691 | -7.255876 |
| 106 | 1 | 0 | -4.282702 | 1.080778 | -6.640322 |
| 107 | 1 | 0 | -6.367838 | 4.688358 | -4.488676 |
| 108 | 1 | 0 | -8.340283 | 5.622837 | -5.652575 |
| 109 | 1 | 0 | -8.749422 | 5.062256 | -8.048626 |
| 110 | 1 | 0 | -7.158350 | 3.589397 | -9.257607 |
| 111 | 1 | 0 | -5.142402 | 2.732791 | -8.122829 |
| 112 | 1 | 0 | -4.343600 | 6.025676 | -5.125350 |
| 113 | 1 | 0 | -2.723803 | 7.867763 | -5.430321 |
| 114 | 1 | 0 | -0.404150 | 7.378754 | -6.189666 |
| 115 | 1 | 0 | 0.275402 | 5.027000 | -6.631553 |
| 116 | 1 | 0 | -1.315269 | 3.184942 | -6.272285 |
| 117 | 1 | 0 | -2.135960 | 4.290341 | -2.980475 |
| 118 | 1 | 0 | -0.253506 | 5.865456 | -2.670038 |
| 119 | 1 | 0 | 2.093723 | 5.056668 | -2.867171 |
| 120 | 1 | 0 | 2.530160 | 2.660456 | -3.383495 |
| 121 | 1 | 0 | 0.640900 | 1.098688 | -3.714570 |
| 122 | 1 | 0 | 0.237160 | 3.072083 | -0.715338 |
| 123 | 1 | 0 | 2.478888 | 3.343332 | 0.307012 |
| 124 | 1 | 0 | 2.686459 | 3.767732 | 2.751812 |
| 125 | 1 | 0 | 0.645673 | 3.940627 | 4.155858 |
| 126 | 1 | 0 | -1.594555 | 3.748246 | 3.122742 |
| 127 | 1 | 0 | -0.911693 | 5.698223 | -0.466103 |
| 128 | 1 | 0 | -1.469780 | 8.103112 | -0.635298 |
| 129 | 1 | 0 | -3.720843 | 8.912517 | 0.053078 |
| 130 | 1 | 0 | -5.407286 | 7.288637 | 0.896009 |
| 131 | 1 | 0 | -4.880153 | 4.886967 | 0.994382 |
| 132 | 1 | 0 | -3.204579 | 1.786305 | 2.001986 |
| 133 | 1 | 0 | -3.841413 | 3.417733 | 2.315437 |
| 134 | 1 | 0 | -5.289680 | 1.885596 | 3.470732 |
| 135 | 1 | 0 | -7.168102 | 0.481352 | 4.300500 |
| 136 | 1 | 0 | -8.747617 | -0.566167 | 2.696140 |
| 137 | 1 | 0 | -8.443754 | -0.257588 | 0.250830 |
| 138 | 1 | 0 | -7.462647 | -0.311521 | -1.745951 |
| 139 | 1 | 0 | -8.012964 | 1.330409 | -2.110283 |
| 140 | 1 | 0 | -6.906180 | -1.119278 | -5.686957 |
| 141 | 1 | 0 | -8.665505 | -0.898289 | -7.397489 |
| 142 | 1 | 0 | -10.166123 | 1.083172 | -7.410019 |
| 143 | 1 | 0 | -9.867265 | 2.862649 | -5.694823 |
| 144 | 1 | 0 | -8.059904 | 2.681957 | -4.024068 |
| 145 | 1 | 0 | -4.690602 | -0.749765 | -5.552864 |
| 146 | 1 | 0 | -3.493923 | -2.889506 | -5.559221 |
| 147 | 1 | 0 | -3.331027 | -4.242658 | -3.472732 |
| 148 | 1 | 0 | -4.385776 | -3.398512 | -1.372619 |
| 149 | 1 | 0 | -5.612083 | -1.279154 | -1.368928 |
| 150 | 1 | 0 | -3.787094 | 4.813984 | -2.331849 |
| 151 | 1 | 0 | -4.766790 | 6.987701 | -2.976837 |
| 152 | 1 | 0 | -7.224044 | 7.356842 | -2.769116 |
| 153 | 1 | 0 | -8.675778 | 5.518925 | -1.928187 |
| 154 | 1 | 0 | -7.687496 | 3.362615 | -1.254297 |

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## Cartesian Coordinates for $[Pt_2\{SiPh(NCH_2PPh_2)_2C_6H_4\}_2]$ (6)

Optimised structure at the MO6L level of theory (SDD basis set for platinum with 60 electron SDD core potential and 6-31g(d) for remaining elements)

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|

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| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 8.475641 | 2.393452 | 1.875566 |
| 2 | 6 | 0 | 7.798470 | 1.779814 | 0.827162 |
| 3 | 6 | 0 | 8.303833 | 0.609029 | 0.263832 |
| 4 | 6 | 0 | 9.482814 | 0.058851 | 0.758713 |
| 5 | 6 | 0 | 10.160243 | 0.673216 | 1.808725 |
| 6 | 6 | 0 | 9.667293 | 1.852671 | 2.373935 |
| 7 | 6 | 0 | 9.457903 | 2.085676 | 5.143282 |
| 8 | 6 | 0 | 8.326002 | 2.838495 | 5.473570 |
| 9 | 6 | 0 | 7.462215 | 2.419704 | 6.478725 |
| 10 | 6 | 0 | 7.735990 | 1.249266 | 7.182816 |
| 11 | 6 | 0 | 8.868248 | 0.501053 | 6.869809 |
| 12 | 6 | 0 | 9.721403 | 0.910223 | 5.849428 |
| 13 | 6 | 0 | 12.158651 | 1.929971 | 3.821930 |
| 14 | 6 | 0 | 14.425640 | 2.649228 | 4.353783 |
| 15 | 6 | 0 | 15.089243 | 1.738376 | 3.538549 |
| 16 | 6 | 0 | 16.489975 | 1.763336 | 3.473018 |
| 17 | 6 | 0 | 17.212850 | 2.688948 | 4.213020 |
| 18 | 6 | 0 | 16.554064 | 3.607722 | 5.042467 |
| 19 | 6 | 0 | 15.165779 | 3.588232 | 5.121747 |
| 20 | 6 | 0 | 14.928936 | 5.567612 | 6.518641 |
| 21 | 6 | 0 | 13.445605 | 6.213771 | 8.919393 |
| 22 | 6 | 0 | 13.722198 | 4.909497 | 9.345094 |
| 23 | 6 | 0 | 13.510058 | 4.543874 | 10.670901 |
| 24 | 6 | 0 | 13.022225 | 5.473708 | 11.585092 |
| 25 | 6 | 0 | 12.749486 | 6.775935 | 11.169485 |
| 26 | 6 | 0 | 12.955719 | 7.144768 | 9.844455 |
| 27 | 6 | 0 | 14.397313 | 8.305337 | 7.244692 |
| 28 | 6 | 0 | 15.602423 | 8.468831 | 7.942120 |
| 29 | 6 | 0 | 16.215939 | 9.714602 | 8.000407 |
| 30 | 6 | 0 | 15.628242 | 10.814957 | 7.375370 |
| 31 | 6 | 0 | 14.428740 | 10.663061 | 6.688992 |
| 32 | 6 | 0 | 13.821378 | 9.411948 | 6.621505 |
| 33 | 6 | 0 | 11.784595 | 3.428731 | 7.049928 |
| 34 | 6 | 0 | 12.369671 | 2.288543 | 7.622687 |
| 35 | 6 | 0 | 11.878372 | 1.737804 | 8.804443 |
| 36 | 6 | 0 | 10.782883 | 2.320375 | 9.441005 |
| 37 | 6 | 0 | 10.176633 | 3.443966 | 8.883100 |
| 38 | 6 | 0 | 10.672278 | 3.982617 | 7.699356 |
| 39 | 6 | 0 | 12.670837 | 3.405054 | 0.565376 |
| 40 | 6 | 0 | 13.298733 | 2.352919 | -0.092321 |
| 41 | 6 | 0 | 12.611961 | 1.635408 | -1.070842 |
| 42 | 6 | 0 | 11.295828 | 1.970438 | -1.377884 |
| 43 | 6 | 0 | 10.663869 | 3.023516 | -0.721764 |
| 44 | 6 | 0 | 11.348613 | 3.761646 | 0.248687 |
| 45 | 6 | 0 | 8.980458 | 5.544828 | 0.648032 |
| 46 | 6 | 0 | 8.639774 | 5.656665 | -0.706228 |
| 47 | 6 | 0 | 7.378338 | 6.109496 | -1.079503 |
| 48 | 6 | 0 | 6.454299 | 6.488075 | -0.107226 |
| 49 | 6 | 0 | 6.792280 | 6.408983 | 1.240790 |
| 50 | 6 | 0 | 8.044782 | 5.932049 | 1.614825 |
| 51 | 6 | 0 | 11.551885 | 6.664510 | 0.598990 |
| 52 | 6 | 0 | 10.403943 | 8.768076 | 1.249080 |
| 53 | 6 | 0 | 9.933485 | 9.197730 | 0.011665 |
| 54 | 6 | 0 | 9.134744 | 10.342947 | -0.068930 |
| 55 | 6 | 0 | 8.816869 | 11.059564 | 1.076497 |
| 56 | 6 | 0 | 9.277332 | 10.632152 | 2.328212 |
| 57 | 6 | 0 | 10.050616 | 9.480078 | 2.426801 |
| 58 | 6 | 0 | 10.314722 | 9.519911 | 4.856156 |
| 59 | 6 | 0 | 8.428263 | 7.712823 | 5.989792 |
| 60 | 6 | 0 | 7.405602 | 8.552699 | 6.450320 |
| 61 | 6 | 0 | 6.071800 | 8.211629 | 6.254939 |
| 62 | 6 | 0 | 5.742362 | 7.027053 | 5.597108 |
| 63 | 6 | 0 | 6.752201 | 6.184456 | 5.142191 |
| 64 | 6 | 0 | 8.089989 | 6.522789 | 5.341062 |
| 65 | 6 | 0 | 10.215255 | 9.053284 | 7.750777 |
| 66 | 6 | 0 | 10.666395 | 10.366209 | 7.931376 |
| 67 | 6 | 0 | 10.739071 | 10.919643 | 9.208197 |

| | | | | | |
|---|---|---|---|---|---|
| 68 | 6 | 0 | 10.349900 | 10.176388 | 10.318781 |
| 69 | 6 | 0 | 9.893478 | 8.869464 | 10.149764 |
| 70 | 6 | 0 | 9.837939 | 8.309623 | 8.879969 |
| 71 | 6 | 0 | 13.377991 | 7.820377 | 3.380494 |
| 72 | 6 | 0 | 13.796108 | 9.158295 | 3.303097 |
| 73 | 6 | 0 | 15.147095 | 9.493535 | 3.285073 |
| 74 | 6 | 0 | 16.115719 | 8.491088 | 3.320695 |
| 75 | 6 | 0 | 15.725192 | 7.153956 | 3.367215 |
| 76 | 6 | 0 | 14.369968 | 6.827131 | 3.405364 |
| 77 | 7 | 0 | 11.220958 | 7.689382 | 1.532194 |
| 78 | 7 | 0 | 10.546049 | 8.881082 | 3.591092 |
| 79 | 7 | 0 | 13.058010 | 2.804198 | 4.518334 |
| 80 | 7 | 0 | 14.346529 | 4.433019 | 5.856088 |
| 81 | 15 | 0 | 10.665285 | 5.142403 | 1.221058 |
| 82 | 15 | 0 | 10.192455 | 8.195882 | 6.140765 |
| 83 | 15 | 0 | 10.489024 | 2.710805 | 3.769472 |
| 84 | 15 | 0 | 13.578111 | 6.674645 | 7.160387 |
| 85 | 14 | 0 | 11.533818 | 7.389765 | 3.303446 |
| 86 | 14 | 0 | 12.571805 | 4.236486 | 5.518319 |
| 87 | 78 | 0 | 10.977207 | 5.017493 | 3.531118 |
| 88 | 78 | 0 | 11.733561 | 6.512054 | 5.747581 |
| 89 | 1 | 0 | 8.080795 | 3.313008 | 2.310510 |
| 90 | 1 | 0 | 6.882861 | 2.229240 | 0.443378 |
| 91 | 1 | 0 | 7.780710 | 0.128251 | -0.561219 |
| 92 | 1 | 0 | 9.886020 | -0.853363 | 0.321058 |
| 93 | 1 | 0 | 11.081859 | 0.225428 | 2.178246 |
| 94 | 1 | 0 | 8.142817 | 3.775717 | 4.945813 |
| 95 | 1 | 0 | 6.589617 | 3.022335 | 6.727633 |
| 96 | 1 | 0 | 7.074920 | 0.926937 | 7.985669 |
| 97 | 1 | 0 | 9.097752 | -0.403023 | 7.431702 |
| 98 | 1 | 0 | 10.606048 | 0.316681 | 5.621035 |
| 99 | 1 | 0 | 12.451631 | 1.832165 | 2.760281 |
| 100 | 1 | 0 | 12.154664 | 0.907366 | 4.243866 |
| 101 | 1 | 0 | 14.523863 | 1.006790 | 2.961086 |
| 102 | 1 | 0 | 17.007865 | 1.044144 | 2.840388 |
| 103 | 1 | 0 | 18.300017 | 2.702396 | 4.158915 |
| 104 | 1 | 0 | 17.122450 | 4.329975 | 5.627647 |
| 105 | 1 | 0 | 15.579941 | 5.263940 | 7.356938 |
| 106 | 1 | 0 | 15.547772 | 6.169461 | 5.829347 |
| 107 | 1 | 0 | 14.083078 | 4.168464 | 8.632154 |
| 108 | 1 | 0 | 13.720129 | 3.522447 | 10.984526 |
| 109 | 1 | 0 | 12.856143 | 5.185279 | 12.621897 |
| 110 | 1 | 0 | 12.374156 | 7.511977 | 11.879725 |
| 111 | 1 | 0 | 12.738001 | 8.165270 | 9.525198 |
| 112 | 1 | 0 | 16.054393 | 7.617423 | 8.452404 |
| 113 | 1 | 0 | 17.154654 | 9.830679 | 8.539737 |
| 114 | 1 | 0 | 16.109071 | 11.790525 | 7.427371 |
| 115 | 1 | 0 | 13.967028 | 11.514787 | 6.188927 |
| 116 | 1 | 0 | 12.894491 | 9.274243 | 6.065085 |
| 117 | 1 | 0 | 13.234635 | 1.834646 | 7.131752 |
| 118 | 1 | 0 | 12.350572 | 0.853367 | 9.233324 |
| 119 | 1 | 0 | 10.398152 | 1.894275 | 10.367291 |
| 120 | 1 | 0 | 9.308610 | 3.893882 | 9.366049 |
| 121 | 1 | 0 | 10.183814 | 4.855634 | 7.255353 |
| 122 | 1 | 0 | 13.203220 | 3.945955 | 1.352850 |
| 123 | 1 | 0 | 14.323159 | 2.092481 | 0.169219 |
| 124 | 1 | 0 | 13.099950 | 0.809519 | -1.585600 |
| 125 | 1 | 0 | 10.745172 | 1.397300 | -2.122996 |
| 126 | 1 | 0 | 9.623528 | 3.250152 | -0.946773 |
| 127 | 1 | 0 | 9.371357 | 5.407064 | -1.475308 |
| 128 | 1 | 0 | 7.122572 | 6.187087 | -2.134929 |
| 129 | 1 | 0 | 5.475464 | 6.860789 | -0.404123 |
| 130 | 1 | 0 | 6.087405 | 6.730612 | 2.006202 |
| 131 | 1 | 0 | 8.328006 | 5.883078 | 2.669303 |
| 132 | 1 | 0 | 12.635037 | 6.459858 | 0.576146 |
| 133 | 1 | 0 | 11.232751 | 6.900544 | -0.423823 |
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| 135 | 1 | 0 | 8.777700 | 10.677536 | -1.041546 |

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| 136 | 1 | 0 | 8.213547 | 11.963125 | 1.010895 |
| 137 | 1 | 0 | 9.028735 | 11.209744 | 3.216722 |
| 138 | 1 | 0 | 11.121833 | 10.230647 | 5.119001 |
| 139 | 1 | 0 | 9.373582 | 10.089886 | 4.849503 |
| 140 | 1 | 0 | 7.658073 | 9.479421 | 6.967722 |
| 141 | 1 | 0 | 5.285757 | 8.872990 | 6.615745 |
| 142 | 1 | 0 | 4.697427 | 6.762313 | 5.442305 |
| 143 | 1 | 0 | 6.497128 | 5.258174 | 4.624057 |
| 144 | 1 | 0 | 8.900368 | 5.874940 | 4.985509 |
| 145 | 1 | 0 | 10.967465 | 10.967965 | 7.074993 |
| 146 | 1 | 0 | 11.098040 | 11.940153 | 9.331572 |
| 147 | 1 | 0 | 10.405406 | 10.612730 | 11.314656 |
| 148 | 1 | 0 | 9.597600 | 8.275821 | 11.013102 |
| 149 | 1 | 0 | 9.510796 | 7.274891 | 8.758943 |
| 150 | 1 | 0 | 13.042909 | 9.949437 | 3.255657 |
| 151 | 1 | 0 | 15.449011 | 10.540092 | 3.244516 |
| 152 | 1 | 0 | 17.173024 | 8.752128 | 3.303302 |
| 153 | 1 | 0 | 16.472217 | 6.359412 | 3.382502 |
| 154 | 1 | 0 | 14.070660 | 5.776266 | 3.461876 |

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