

Electronic Supplementary Information for the paper

Entitled

Synthesis of a homoleptic tris(silylene)-palladium(0) complex and a silylyne-bridged tetranuclear palladium cluster

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Table of Contents

| | |
|--|------------|
| 1- General procedure | S2 |
| 2- Experimental procedures and characterization data | S2 |
| 2.1 Synthesis of tris(silylene) palladium(0) complex 2 | S2 |
| 2.2 Reaction of [PdMe₂(tmeda)] with 1 | S5 |
| 3- Crystallographic data collection and structure determination | S8 |
| 4- Computational details | S10 |
| 5- Plausible formation mechanism for 3 | S14 |
| 6- XPS study for 3 | S15 |
| 7- References | S16 |

1- General procedure

Unless otherwise noted, all experiments were carried out under an argon atmosphere by using standard Schlenk techniques or in a UNICO glovebox. All solvents were dried by 4A molecular sieves or potassium mirror before use. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Bruker AVANCE-400 (400, 101, and 162 MHz, respectively) spectrometer, and ^{29}Si NMR spectra were recorded on a Bruker AVANCE-500 (99 MHz) spectrometer. All melting points were determined on a Mel-Temp capillary tube apparatus and were uncorrected. Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University. X-ray photoelectron spectra (XPS) were acquired on a Kratos AXIS-NOVA spectrometer with a monochromatic Al $K\alpha$ X-ray source (1486.6 eV) using a pass energy of 20 eV. To provide a precise energy calibration, the XPS binding energies were referenced to the C 1s peak at 284.6 eV. All materials were obtained from commercial supplier and used without further purification except chlorosilylene **1**^{S1}, $[\text{Pd}(\text{PPh}_3)_4]$ ^{S2}, and $[\text{PdMe}_2(\text{tmeda})]$ ^{S3}, which were prepared by the respective literature procedures.

2- Experimental procedures and characterization data

2-1 Synthesis of tris(silylene) palladium(0) complex **2**

In a Schlenk tube, $[\text{Pd}(\text{PPh}_3)_4]$ (507.0 mg, 0.44 mmol) and silylene **1** (688.6 mg, 1.77 mmol) were dissolved into toluene (7 mL) at ambient temperature. The resulting brown solution was stirred for 1 h at the temperature. All volatiles were removed under reduced pressure, and the residue was washed with Et_2O (ca. 10.0 mL) and dried under reduced pressure to give tris(silylene) palladium(0) complex **2** (513.1 mg, 92%) as reddish brown crystals. Mp. 236–237 °C (decomp.). ^1H NMR (C_6D_6 , 400 MHz): δ 1.50 (s, 54H, CH_3), 7.10–7.20 (m, 3H, Ar), 7.21–7.26 (m, 6H, Ar), 7.36–7.41 (m, 3H, Ar), 7.58 (br s, 6H, Ar), 8.47–7.53 (m, 6H, Ar), 8.82 (br s, 6H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 101 MHz): δ 32.6 (d, $J_{\text{CP}} = 6$ Hz, CH_3), 53.5 (C), 128.7

(d, $J_{CP} = 122$ Hz, CH_{Ar}), 128.8 (d, $J_{CP} = 13$ Hz, CH_{Ar}), 131.5 (d, $J_{CP} = 94$ Hz, C_{Ar}), 131.6 (d, $J_{CP} = 84$ Hz, C_{Ar}), 132.5 (br, CH_{Ar}), 132.5 (br, CH_{Ar}), 134.7 (d, $J_{CP} = 12$ Hz, CH_{Ar}), 136.0 (d, $J_{CP} = 13$ Hz, CH_{Ar}). $^{29}Si\{^1H\}$ NMR (C_6D_6 , 99 MHz): δ 75.8 (d, $J_{SiP} = 9$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6 , 202 MHz): δ 40.3 (s). Anal. Calcd for $C_{60}H_{84}N_6Si_3P_3Cl_3Pd$: C, 56.33; H, 6.62; N, 6.57. Found: C, 56.51; H, 6.59; N, 6.33.

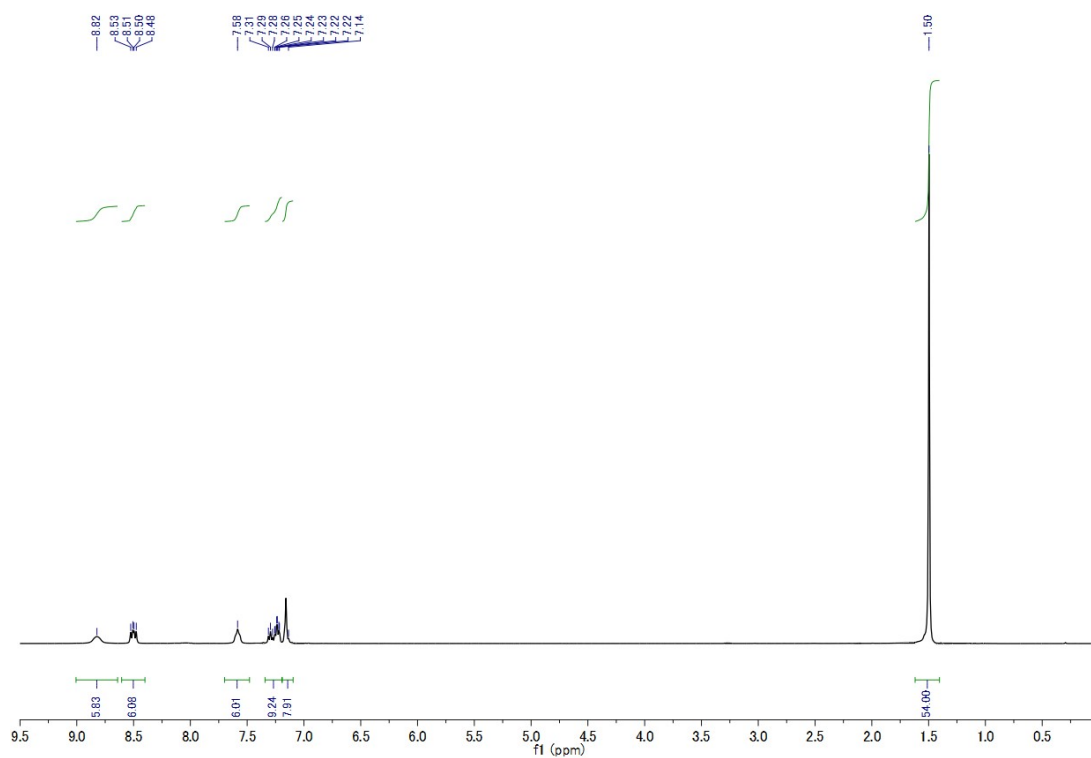


Figure S1. 1H NMR spectrum (400 MHz, 25 °C, C_6D_6) of **2**.

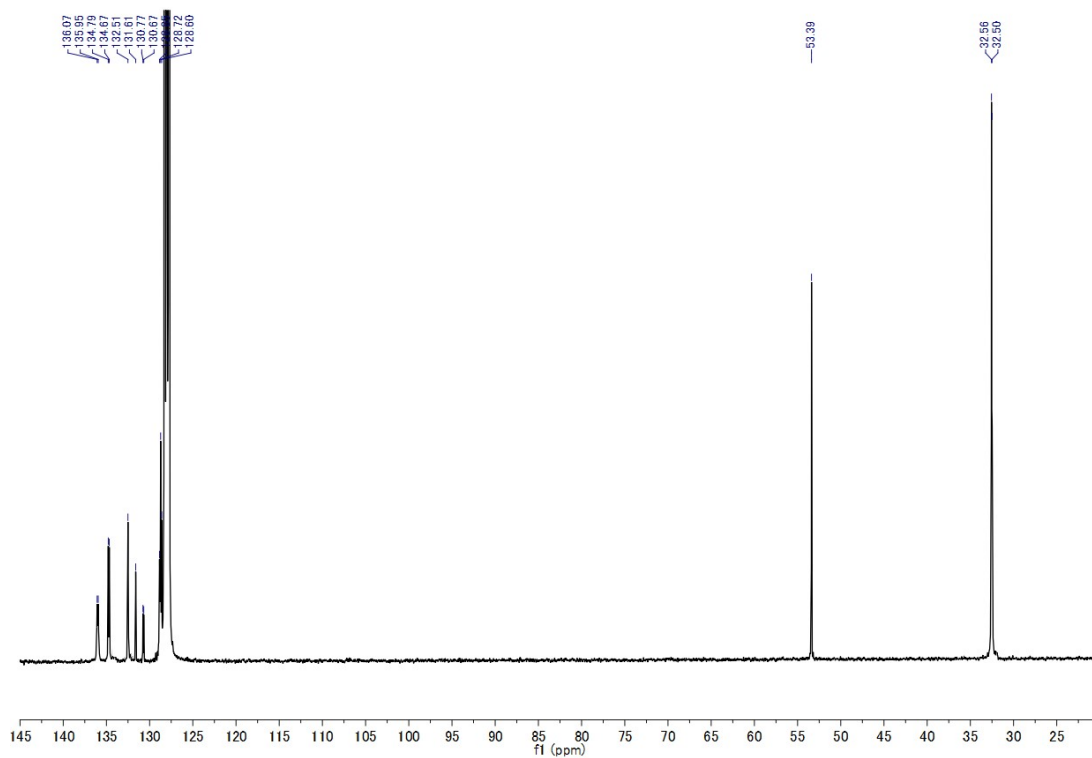


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, 25 °C, C_6D_6) of **2**.

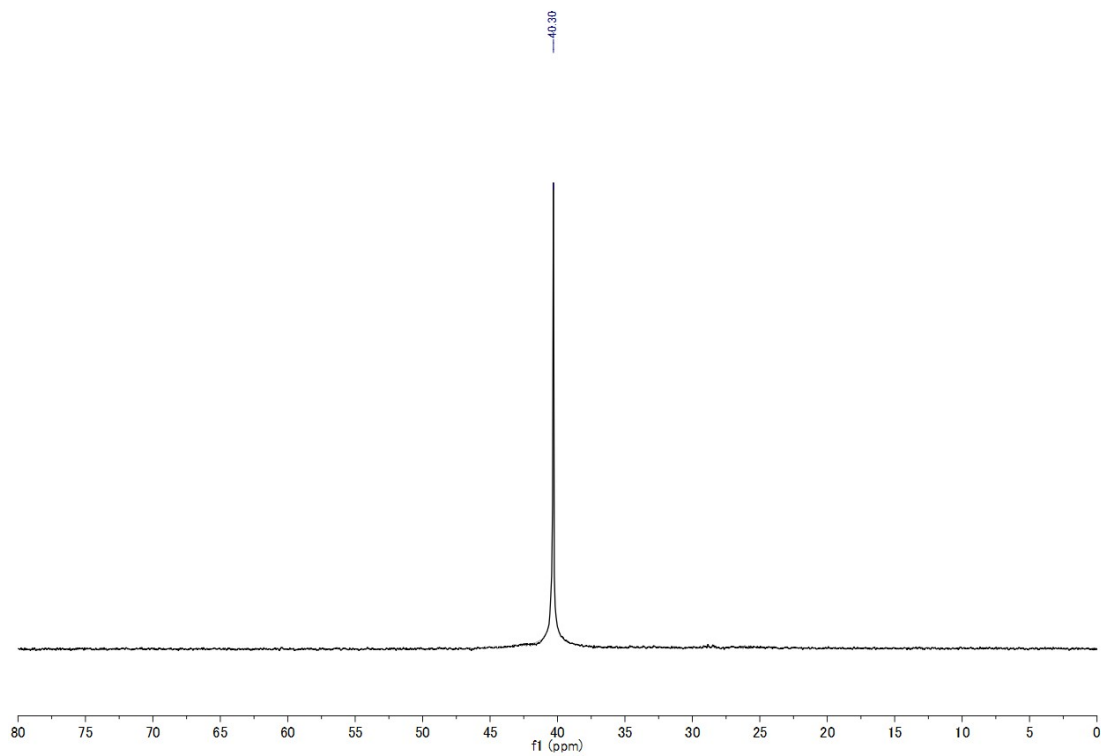


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, 25 °C, C_6D_6) of **2**.

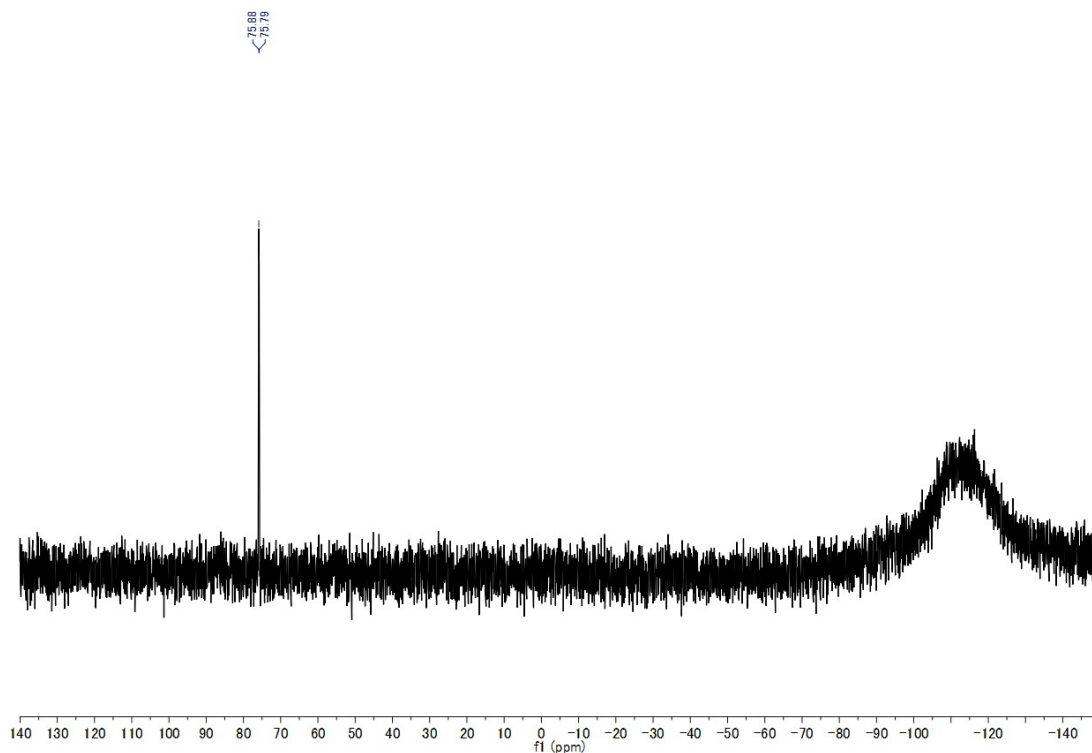


Figure S4. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (99 MHz, 25 °C, C_6D_6) of **2**.

2-2 Reaction of $[\text{PdMe}_2(\text{tmeda})]$ with **1**

In a J. Young NMR tube, $[\text{PdMe}_2(\text{tmeda})]$ (62.0 mg, 0.24 mmol) and **1** (72.2 mg, 0.18 mmol) were dissolved into C_6D_6 (0.5 mL) at ambient temperature. The resulting brown solution was kept for 12 h at the temperature. The reaction mixture was filtered, and all volatiles of the filtrate were removed under reduced pressure. The obtained residue was recrystallized from C_6D_6 at room temperature to give tetranuclear palladium cluster **3** (35.4 mg, 37%) as orange crystals. Mp. 275–277 °C (decomp.). ^1H NMR (CD_2Cl_2 , 400 MHz): δ 1.11 (s, 54H, CH_3), 7.76–7.81 (m, 18H, Ar), 8.69–8.74 (m, 12H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz): δ 33.1 (d, $J_{\text{CP}} = 5$ Hz, CH_3), 54.9 (C), 125.9 (d, $J_{\text{CP}} = 96$ Hz, C_{Ar}), 129.8 (d, $J_{\text{CP}} = 20$ Hz, CH_{Ar}), 134.6 (d, $J_{\text{CP}} = 3$ Hz, CH_{Ar}), 136.7 (d, $J_{\text{CP}} = 13$ Hz, CH_{Ar}). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 99 MHz): δ 184.2

(d, $J_{\text{SiP}} = 9$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz): δ 48.2 (s). Anal. Calcd for $\text{C}_{60}\text{H}_{84}\text{N}_6\text{Si}_3\text{P}_3\text{Cl}_3\text{Pd}_4$: C, 45.08; H, 5.30; N, 5.26. Found: C, 45.40; H, 5.38; N, 5.02.

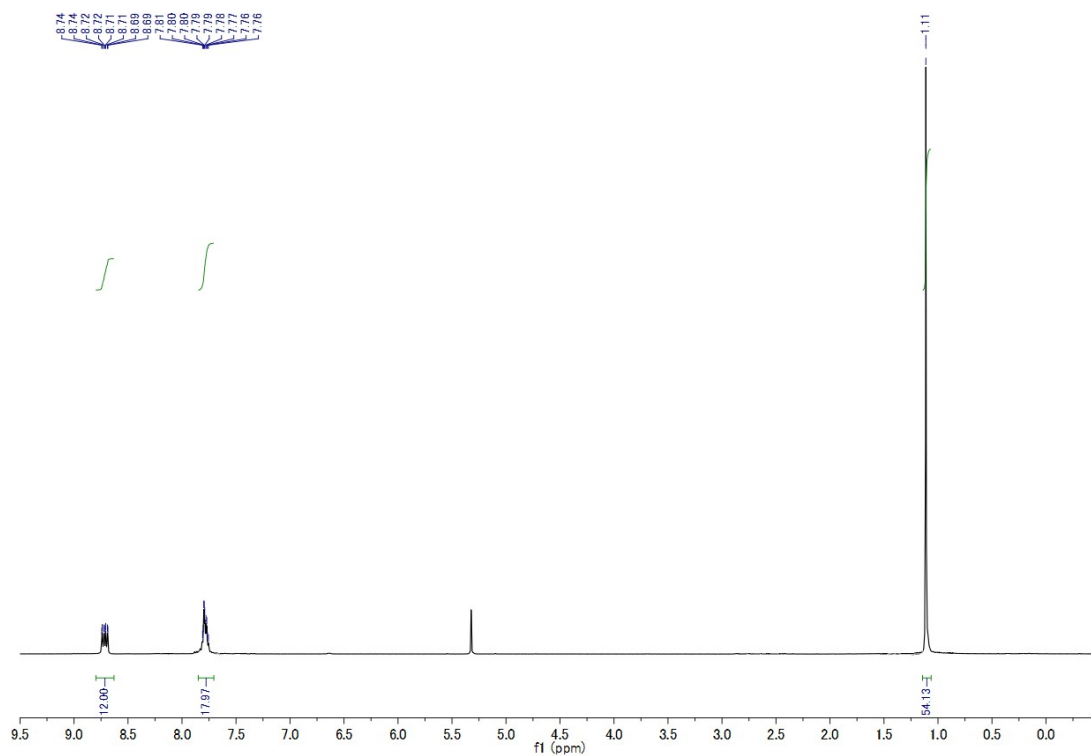


Figure S5. ^1H NMR spectrum (400 MHz, 25 °C, CD_2Cl_2) of **3**.

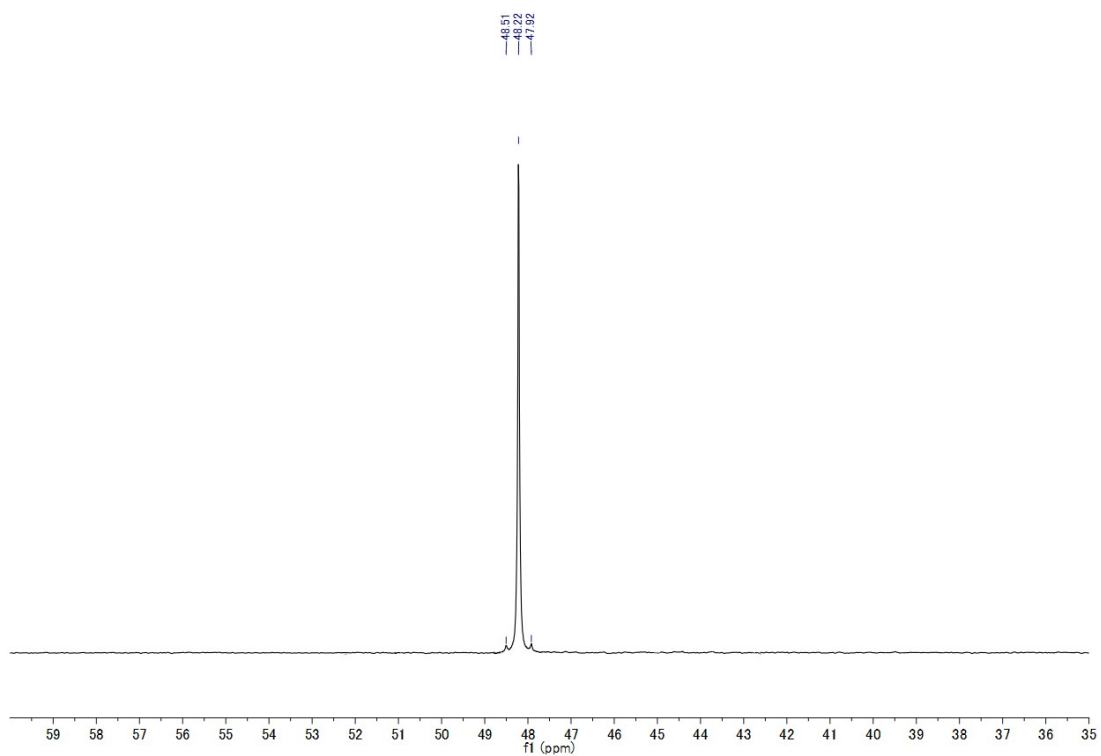
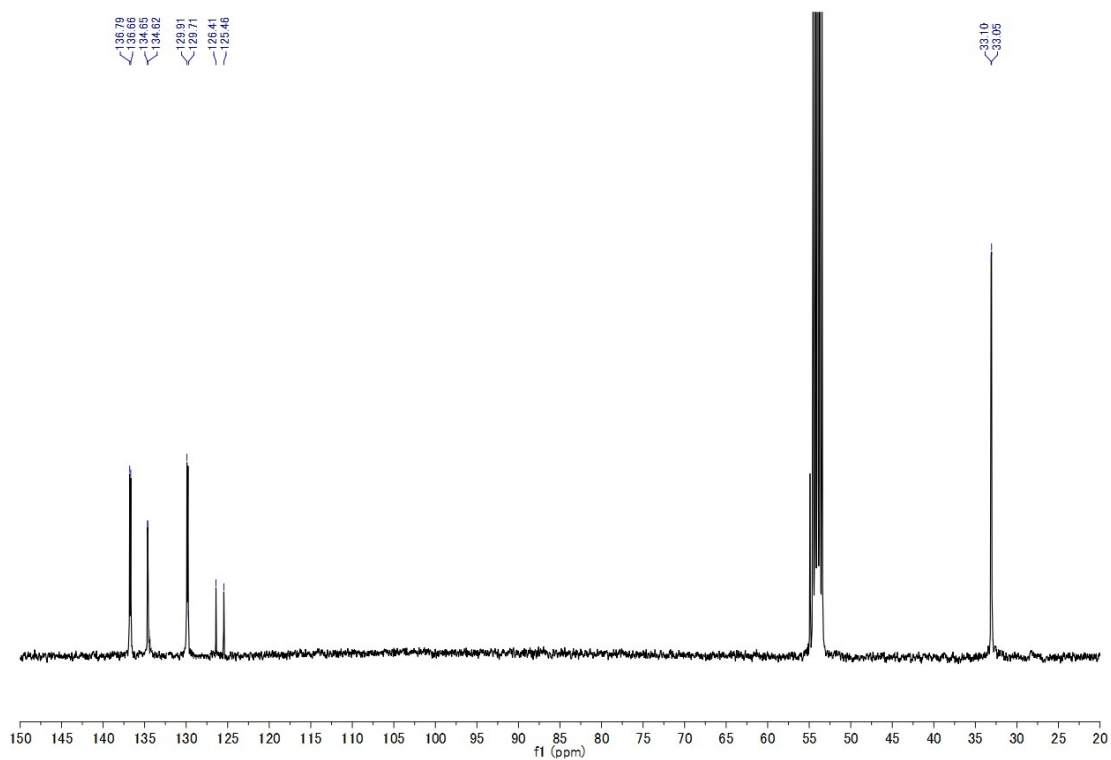


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, 25 °C, CD_2Cl_2) of **3**.

Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, 25 °C, CD_2Cl_2) of **3**.

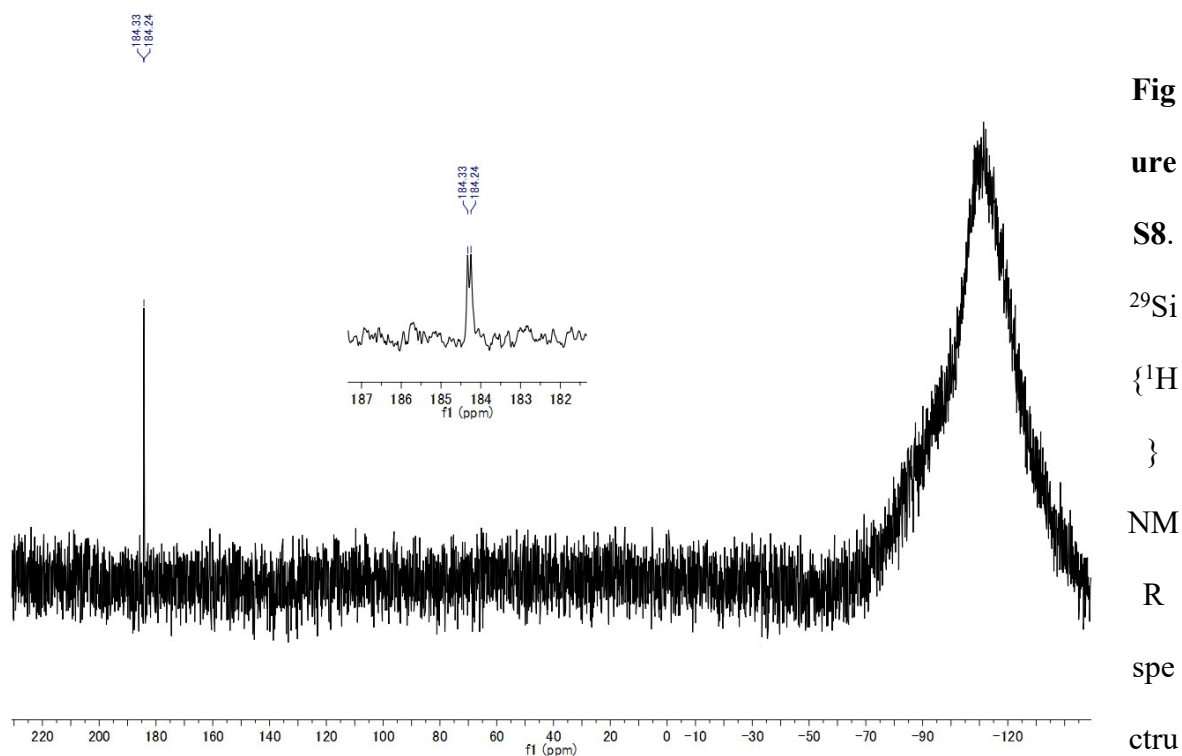


Figure S8. ^{29}Si { ^1H } NMR spectrum

m (99 MHz, 25 °C, CD_2Cl_2) of **3**.

3- Crystallographic data collection and structure determination

Brown single crystals of **2** were grown from saturated THF solution at room temperature. Orange single crystals of **3** were obtained from saturated C_6D_6 solution at room temperature. The intensity data were collected at 120 or 150 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved by direct methods (SHELXT)^{S4} and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL).^{S5} Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without the further refinement of the parameters. The crystallographic data for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication nos. 2259953 (**2**) and 2259954 (**3**).

Table S1. Crystallographic data and details of refinement for **2** and **3**.

| | 2 | 3 |
|---|---|--|
| Formula | C ₆₀ H ₈₄ Cl ₃ N ₆ P ₃ PdSi ₃ | C ₆₀ H ₈₄ Cl ₃ N ₆ P ₃ Pd ₄ Si _{3,2} (C ₆ H ₆) |
| Formula weight | 1279.26 | 1754.67 |
| Color | brown | orange |
| Crystal size / mm | 0.11 × 0.09 × 0.04 | 0.19 × 0.17 × 0.14 |
| Temperature / K | 150 | 120 |
| Crystal system | triclinic | triclinic |
| Space group | <i>P</i> -1 | <i>P</i> -1 |
| <i>a</i> / Å | 15.160(3) | 14.9430(12) |
| <i>b</i> / Å | 15.382(3) | 15.0116(12) |
| <i>c</i> / Å | 15.980(3) | 18.1731(14) |
| <i>a</i> / deg. | 108.610(3) | 80.8930(10) |
| <i>b</i> / deg. | 104.396(3) | 76.3520(10) |
| <i>g</i> / deg. | 100.007(3) | 76.1360(10) |
| <i>V</i> / Å ³ | 3288.2(11) | 3823.6(5) |
| <i>Z</i> | 2 | 2 |
| <i>D</i> _{calcd} / g cm ⁻³ | 1.292 | 1.524 |
| No. of unique data | 11884 | 13903 |
| No. of parameters | 703 | 891 |
| No. of restraints | 0 | 246 |
| <i>R</i> ₁ (<i>I</i> > 2 <i>s</i> (<i>I</i>)) | 0.0709 | 0.0385 |
| <i>wR</i> ₂ (all data) | 0.1495 | 0.1129 |
| GOF | 1.829 | 1.034 |

4- Computational details

The geometry has been optimized with the Gaussian-09 program^{S6} using B3PW91/LANL2DZ for Pd and 6-31G(d,p) for the others level of theory on **3**. Harmonic vibrational frequencies were calculated in order to verify that these structures correspond to energy minima (all frequencies are real) or to transition states (only one imaginary frequency corresponding to the transition vector). The optimized structures were subjected to natural bond orbital (NBO) analysis at the same level of theory using the NBO method^{S7} with the NBO 6.0 program.^{S8}

Atomic Coordinates for **3** at B3LYP-D3/6-31+G(d,p) level of theory.

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | -0.008057 | -0.016528 | 0.182537 | C | 3.293708 | -5.188302 | 0.026722 |
| Pd | 2.516452 | 0.643964 | -0.402591 | C | 3.950020 | 4.543030 | -0.628207 |
| Pd | -0.740635 | -2.590262 | -0.066066 | C | 3.289700 | 6.531072 | 0.597496 |
| Pd | -1.869398 | 1.905118 | 0.292820 | C | -5.298347 | -2.954133 | -0.014367 |
| P | 1.265364 | 4.659549 | 0.008464 | C | 1.405343 | 3.464481 | 2.605112 |
| P | -4.686102 | -1.249981 | -0.030510 | C | 0.125572 | 6.063505 | 0.070407 |
| Cl | -3.558909 | 3.469283 | 1.018702 | C | -6.124068 | -0.155287 | -0.143991 |
| P | 3.445261 | -3.387373 | 0.092782 | C | -1.123766 | 5.877116 | 0.675061 |
| Cl | 4.566127 | 1.265540 | -1.540318 | C | 2.603461 | -2.807029 | -2.586437 |
| Cl | -1.143461 | -4.930083 | -0.391298 | C | 0.590001 | 3.697860 | -2.600943 |
| Si | 0.667999 | 2.153775 | -0.003012 | C | -5.080366 | -0.869168 | 3.188136 |
| Si | -2.226778 | -0.492121 | 0.082502 | C | 4.288239 | -5.993392 | -0.553161 |
| Si | 1.501112 | -1.705638 | 0.003561 | C | 2.621154 | -2.495799 | 2.685097 |
| N | -3.623969 | -0.878336 | 1.190439 | C | 6.082181 | -3.837393 | 0.967607 |
| N | 2.468519 | -2.662285 | 1.221490 | C | 5.206405 | -2.995472 | 0.260910 |
| N | 1.010400 | 3.508343 | 1.177021 | C | 2.086284 | -5.763698 | 0.443892 |
| N | 2.645750 | -2.576136 | -1.118152 | C | -6.000672 | 1.147889 | 0.355240 |
| N | 0.935782 | 3.535615 | -1.168210 | C | 1.851202 | -1.622566 | -3.198208 |
| N | -3.495870 | -0.952398 | -1.151260 | C | 5.665099 | -1.760354 | -0.214186 |
| C | -3.675565 | -1.155396 | 2.646283 | C | 0.517077 | 2.416728 | 3.283892 |
| C | 2.948615 | 5.326823 | -0.040439 | C | -6.525489 | -3.290862 | 0.581769 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | 1.236493 | -2.154329 | 3.245092 | C | -8.211806 | 1.671159 | -0.465945 |
| C | -4.459927 | -3.968102 | -0.494678 | C | -6.078309 | -5.629330 | 0.177205 |
| C | 4.083618 | -7.363959 | -0.681655 | C | -4.007379 | 0.763082 | -2.862841 |
| C | -3.287235 | -2.614688 | 2.922406 | C | -4.576917 | -1.654960 | -3.262516 |
| C | -7.293809 | -0.533533 | -0.824452 | H | 3.715451 | 3.587301 | -1.090658 |
| C | -2.676261 | -0.211416 | 3.322261 | H | 2.525854 | 7.140251 | 1.070849 |
| C | 5.275140 | 4.970223 | -0.593603 | H | -1.384843 | 4.929380 | 1.136376 |
| C | 4.616660 | 6.950806 | 0.625413 | H | -5.367907 | 0.171418 | 3.016343 |
| C | -0.874194 | 4.135712 | -2.747864 | H | -5.103979 | -1.058720 | 4.265932 |
| C | -2.188886 | -0.935817 | -3.193199 | H | -5.830716 | -1.521971 | 2.729096 |
| C | 1.167696 | 4.826381 | 3.265847 | H | 5.215425 | -5.553587 | -0.907794 |
| C | 6.987487 | -1.380034 | 0.000953 | H | 5.738653 | -4.792597 | 1.352820 |
| C | 0.412899 | 7.278311 | -0.574968 | H | 1.284966 | -5.141787 | 0.830585 |
| C | 0.796959 | 2.336297 | -3.270616 | H | -5.085392 | 1.479796 | 0.839193 |
| C | 2.887198 | -7.935294 | -0.245506 | H | 0.819852 | -1.587841 | -2.831128 |
| C | -8.333467 | 0.379005 | -0.978951 | H | 1.820185 | -1.731640 | -4.287091 |
| C | 1.861472 | -4.109878 | -2.914191 | H | 2.342994 | -0.676718 | -2.948910 |
| C | 2.882629 | 3.065603 | 2.734657 | H | 5.003127 | -1.076737 | -0.739458 |
| C | -3.582365 | -0.690063 | -2.608114 | H | -0.540493 | 2.679342 | 3.187927 |
| C | 4.028595 | -2.843612 | -3.148289 | H | 0.772975 | 2.344097 | 4.346115 |
| C | 1.889463 | -7.135251 | 0.308189 | H | 0.658748 | 1.430601 | 2.829462 |
| C | -6.912549 | -4.624725 | 0.670311 | H | -7.176924 | -2.517215 | 0.976422 |
| C | 1.519320 | 4.724982 | -3.256625 | H | 0.858009 | -1.220396 | 2.815671 |
| C | -0.535230 | 8.297042 | -0.591550 | H | 1.293410 | -2.033679 | 4.331837 |
| C | 5.608927 | 6.173027 | 0.026821 | H | 0.517322 | -2.944433 | 3.009762 |
| C | -1.774251 | 8.109530 | 0.023510 | H | -3.485571 | -3.735553 | -0.913513 |
| C | 7.856430 | -2.221930 | 0.692859 | H | 4.855810 | -7.984111 | -1.127852 |
| C | 3.109300 | -3.800526 | 3.323788 | H | -4.014896 | -3.310222 | 2.495010 |
| C | 7.402156 | -3.448991 | 1.178368 | H | -3.235734 | -2.796578 | 4.001717 |
| C | -7.045430 | 2.054438 | 0.193814 | H | -2.310122 | -2.840007 | 2.482126 |
| C | -2.068791 | 6.899514 | 0.648919 | H | -7.395231 | -1.534002 | -1.233900 |
| C | 3.604117 | -1.355801 | 2.987974 | H | -1.656447 | -0.406001 | 2.974321 |
| C | -4.851973 | -5.300692 | -0.397155 | H | -2.699181 | -0.366057 | 4.406088 |

| | | | | | | | |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | -2.916630 | 0.833396 | 3.103919 | H | 0.942065 | -7.565172 | 0.617114 |
| H | 6.037705 | 4.344887 | -1.047572 | H | -7.863893 | -4.879114 | 1.129009 |
| H | 4.875194 | 7.884291 | 1.117254 | H | 1.413165 | 5.715197 | -2.800299 |
| H | -1.532731 | 3.443929 | -2.211742 | H | 1.262437 | 4.828465 | -4.315557 |
| H | -1.162917 | 4.147256 | -3.804693 | H | 2.565170 | 4.415386 | -3.185888 |
| H | -1.038269 | 5.137874 | -2.341710 | H | -0.307446 | 9.235592 | -1.088876 |
| H | -1.850932 | -1.954363 | -2.979345 | H | 6.643794 | 6.503821 | 0.052099 |
| H | -2.208993 | -0.785740 | -4.277486 | H | -2.513376 | 8.905920 | 0.004567 |
| H | -1.457778 | -0.240793 | -2.768899 | H | 8.887698 | -1.922550 | 0.859485 |
| H | 1.791683 | 5.606577 | 2.817444 | H | 2.419976 | -4.624344 | 3.120038 |
| H | 1.432888 | 4.770563 | 4.326331 | H | 3.182376 | -3.674007 | 4.408627 |
| H | 0.119678 | 5.127946 | 3.190349 | H | 4.104596 | -4.080171 | 2.963344 |
| H | 7.320451 | -0.417454 | -0.374966 | H | 8.074781 | -4.105287 | 1.723263 |
| H | 1.370602 | 7.430686 | -1.063305 | H | -6.925751 | 3.063045 | 0.577146 |
| H | 1.829524 | 1.994973 | -3.151442 | H | -3.038248 | 6.726195 | 1.105087 |
| H | 0.565204 | 2.410945 | -4.338035 | H | 4.615174 | -1.602965 | 2.652012 |
| H | 0.134737 | 1.582197 | -2.833017 | H | 3.641684 | -1.156923 | 4.064790 |
| H | 2.728781 | -9.005044 | -0.351739 | H | 3.291683 | -0.442104 | 2.471783 |
| H | -9.236949 | 0.080809 | -1.503136 | H | -4.177002 | -6.070939 | -0.756039 |
| H | 2.414540 | -4.988064 | -2.569720 | H | -9.025062 | 2.381103 | -0.590411 |
| H | 1.736191 | -4.199647 | -3.999040 | H | -6.382068 | -6.669975 | 0.252377 |
| H | 0.873519 | -4.126567 | -2.443883 | H | -3.965727 | 0.990364 | -3.933842 |
| H | 3.071556 | 2.125741 | 2.204754 | H | -5.027864 | 0.946793 | -2.515768 |
| H | 3.151968 | 2.935605 | 3.788705 | H | -3.342269 | 1.451965 | -2.331536 |
| H | 3.538825 | 3.829073 | 2.307119 | H | -4.277105 | -2.696184 | -3.116707 |
| H | 4.546786 | -1.898168 | -2.966949 | H | -5.589098 | -1.522257 | -2.866234 |
| H | 3.992320 | -3.014906 | -4.228956 | H | -4.623228 | -1.459174 | -4.338372 |
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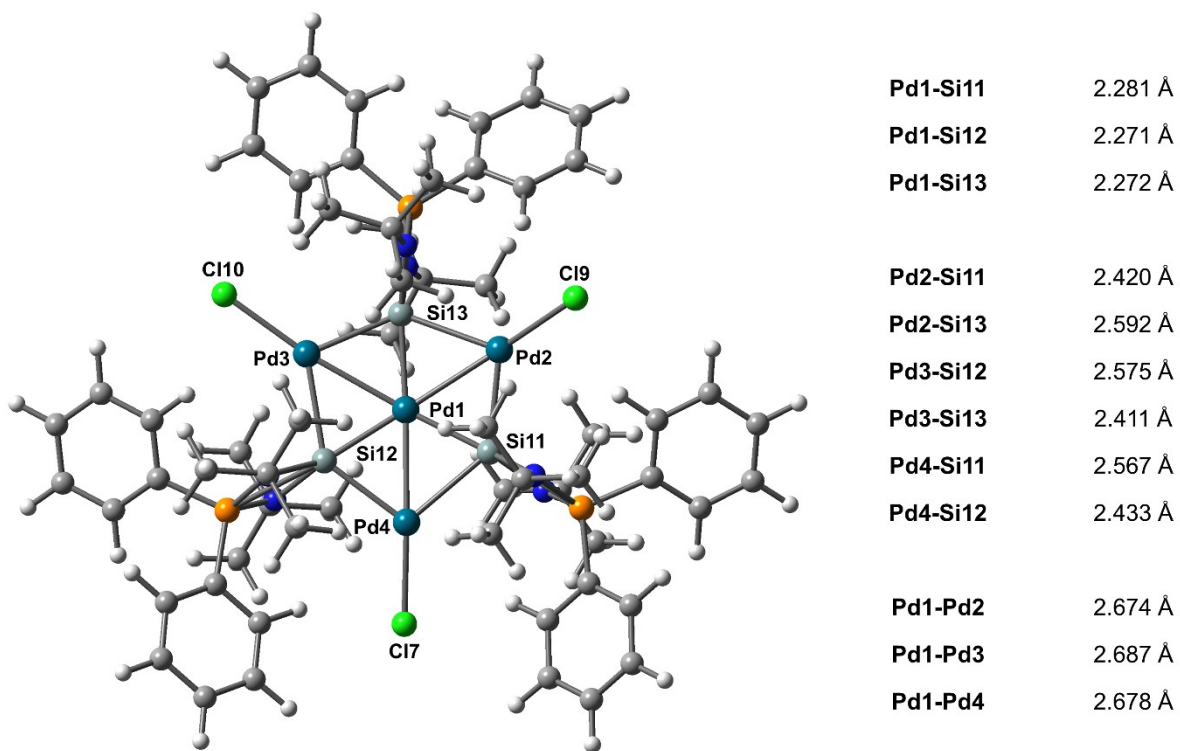


Figure S9. Optimized geometry and selected bond lengths of **2**.

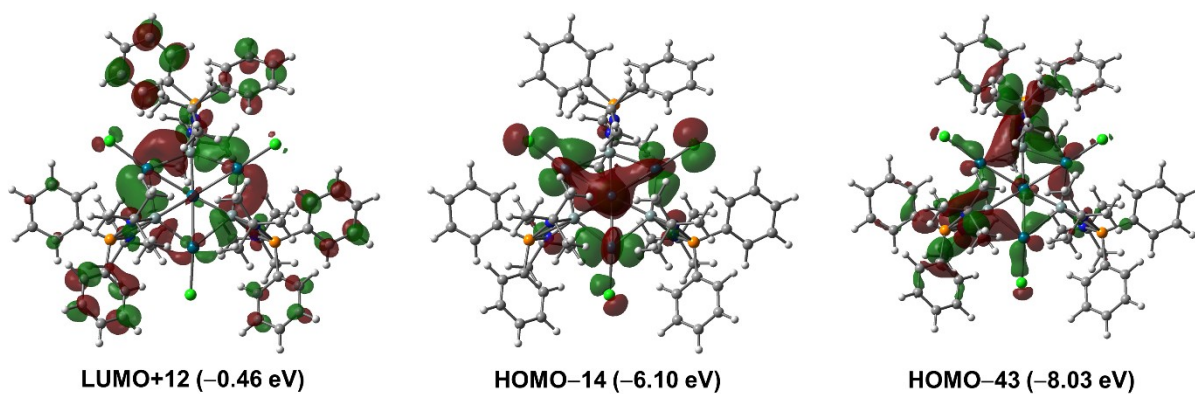


Figure S10. Selected Kohn-Sham orbitals of **3** (isovalue = 0.023 au).

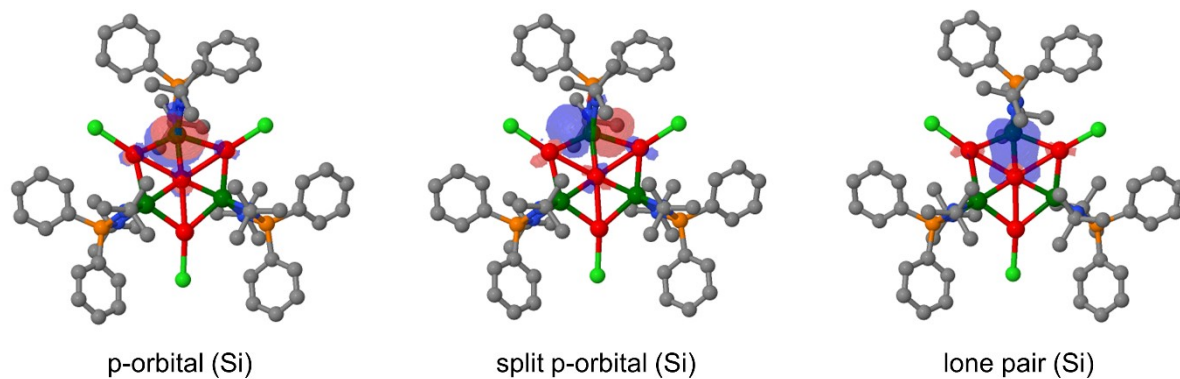


Figure S11. NBO orbitals of cluster **3**.

5- Plausible formation mechanism for **3**

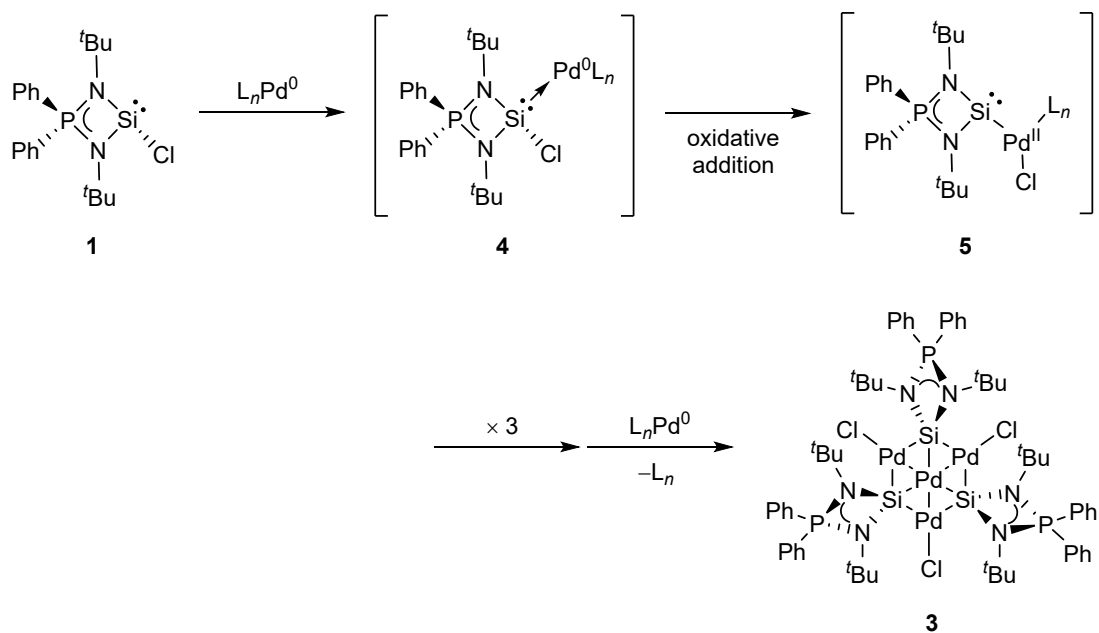


Figure S12. Plausible formation mechanism for **3**.

6- XPS study for 3

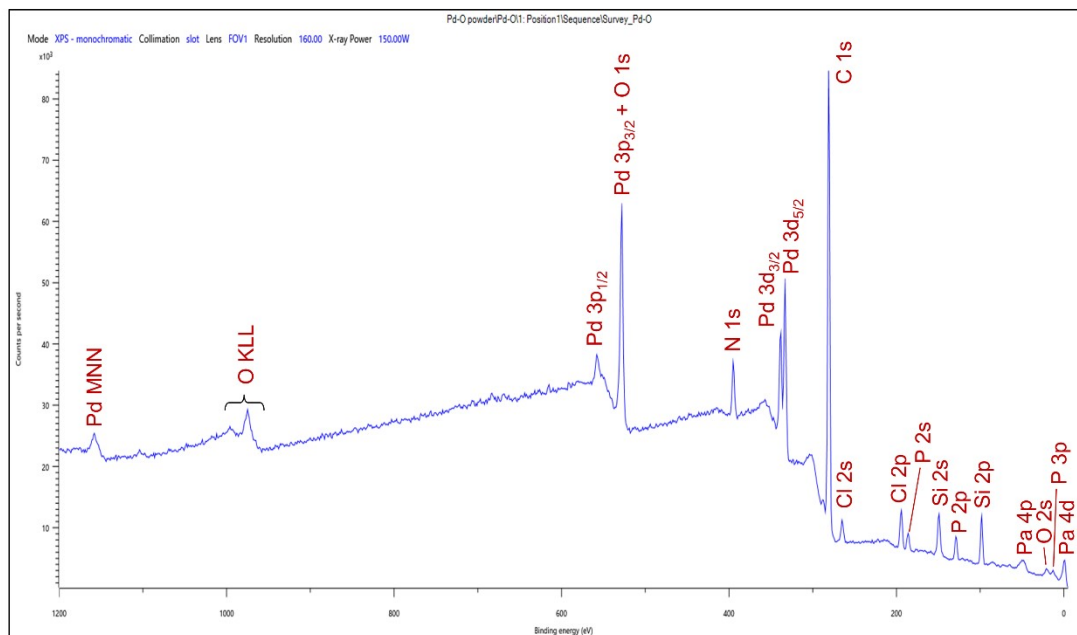


Figure S13. Survey spectrum of **3**.

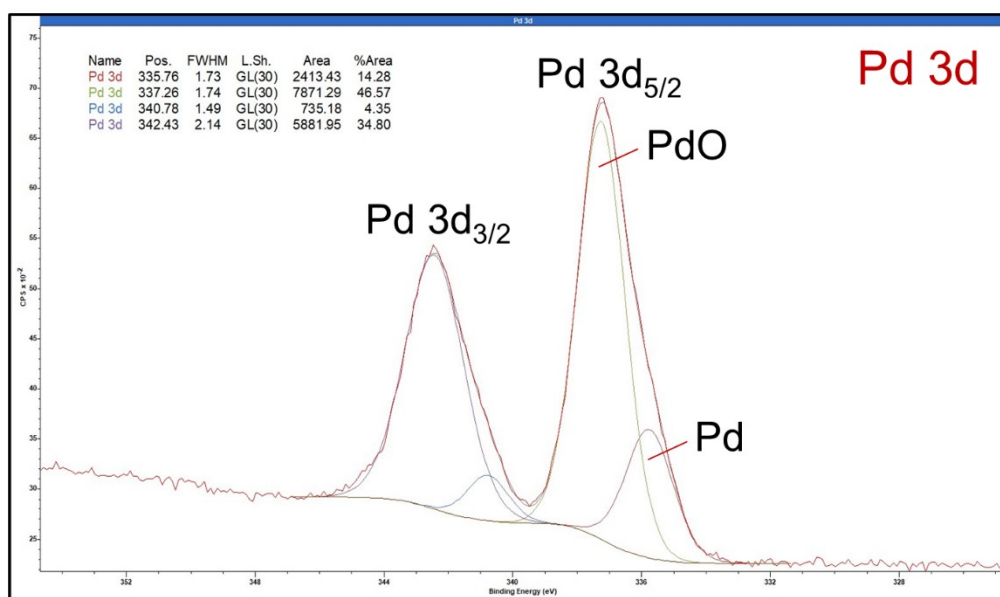


Figure S14. XPS spectrum of **3** in the Pd 3d region.

7- References

- S1 S. Takahashi, J. Sekiguchi, A. Ishii and N. Nakata, *Angew. Chem., Int. Ed.*, 2020, **60**, 4055–4059.
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