

## ELECTRONIC SUPPLEMENTARY INFORMATION

### A Z-type PGeP pincer germylene ligand in a T-shaped palladium(0) complex

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## General experimental data

All reactions and product manipulations were carried out at room temperature in an argon-filled drybox. Solvents were dried over appropriate desiccating reagents and were distilled under argon before use. Compounds  $\text{Ge}(\text{pyrm}^i\text{Pr}_2)_2\text{CMe}_2$  (**D**),<sup>1</sup>  $[\text{AuCl}(\text{tht})]_2$  and  $[\text{PdCl}_2(\text{MeCN})_2]$ <sup>3</sup> were prepared following published procedures. All remaining reagents were purchased from commercial sources and were stored under argon in a drybox. All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. NMR spectra were run on a NAV-400 instrument, using as standards the residual protic solvent resonance for  $^1\text{H}$  [ $\delta(\text{C}_6\text{HD}_5)$  7.16 ppm], the solvent resonance for  $^{13}\text{C}$  [ $\delta(\text{C}_6\text{D}_6)$  128.10 ppm] and external 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  ( $\delta$  0.00 ppm). Microanalyses were obtained with a Thermo-Finnigan FlashEA112 microanalyzer. High-resolution mass spectra (HRMS) were obtained with a Bruker Impact II mass spectrometer operating in the ESI-Q-ToF positive mode; data given refer to the most abundant isotopomer of the species with the greatest mass. CHN microanalysis and mass spectra were not obtained for the products that were very unstable towards air and/or moisture.

## Synthetic procedures and characterization data

**Synthesis of  $[\text{Pd}\{\kappa^3\text{P,Ge,P-Ge}(\text{pyrm}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**1**):** Toluene 4 (mL) was added to a mixture of germylene **D** (0.12 g, 0.24 mmol) and  $[\text{Pd}(\text{PPh}_3)_4]$  (0.23 g, 0.20 mmol) and the resulting dark green solution was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the oily residue was triturated and washed with hexane (4 x 3 mL) to give complex **1** as a dark green solid (0.097 g, 79 %).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400.5 MHz, 298 K):  $\delta$  6.35 (d,  $J_{\text{H-H}} = 2.5$  Hz, 2 H, 2 CH of 2 pyrrole), 6.14 (s, 2 H, 2 CH of 2 pyrrole), 3.21 (d,  $J_{\text{H-H}} = 14.1$  Hz, 2 CH of 2  $\text{CH}_2\text{P}$ ), 2.88 (d,  $J_{\text{H-H}} = 14.1$  Hz, 2 H, 2 CH of 2  $\text{CH}_2\text{P}$ ), 1.95 (s, 3 H, 1  $\text{CH}_3$  of  $\text{CMe}_2$ ), 1.75 (s, 3 H, 1  $\text{CH}_3$  of  $\text{CMe}_2$ ), 1.85–1.75 (m, 4 H, 4 CH of 4  $\text{CHMe}_2$ ), 1.04–0.82 (m, 24 H, 8  $\text{CH}_3$  of 4  $\text{CHMe}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 100.6 MHz, 298 K):  $\delta$  143.9 (s, 2 C of 2 pyrrole), 129.1 (s, 2 C of 2 pyrrole), 108.6 (s, 2 CH of 2 pyrrole), 102.8 (s, 2 CH of 2 pyrrole), 40.6 (s,  $\text{CH}_3$  de  $\text{CMe}_2$ ), 37.1 (s,  $\text{CMe}_2$ ), 26.1 (s,  $\text{CH}_3$  de  $\text{CMe}_2$ ), 25.2 (vt,  $J_{\text{C-P}} = 5.8$  Hz, 2 CH of 2  $\text{CHMe}_2$ ), 24.1 (vt,  $J_{\text{C-P}} = 9.2$  Hz, 2  $\text{CH}_2\text{P}$ ), 20.6 (vt,  $J_{\text{C-P}} = 5.8$  Hz, 2 CH of 2  $\text{CHMe}_2$ ), 19.5 (s, 2  $\text{CH}_3$  of 2  $\text{CHMe}_2$ ), 19.4 (s, 2  $\text{CH}_3$  of 2  $\text{CHMe}_2$ ), 18.9 (s, 2  $\text{CH}_3$  of 2  $\text{CHMe}_2$ ), 18.8 (s, 2  $\text{CH}_3$  of 2  $\text{CHMe}_2$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 162.1 MHz, 298 K):  $\delta$  45.2 (s) ppm.

**Synthesis of  $\text{Ge}\{(\text{pyrm}^i\text{Pr}_2)_2\text{CMe}_2\}(\text{dmap})$  (**D-dmap**):** Germylene **D** (0.041 g, 0.08 mmol) was added to a solution of dmap (0.011 g, 0.09 mmol) in toluene (2 mL). The resulting pale orange solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give **D-dmap** as an orange oil (0.050 g, 100%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400.5 MHz, 298 K):  $\delta$  7.95 (d,  $J_{\text{H-H}} = 8.0$  Hz, 2 CH of py), 6.40 (s, 2 CH of 2 pyrrole), 5.77 (d,  $J_{\text{H-H}} = 8.0$  Hz, 2 CH of py), 3.12 (s, 4 H, 2  $\text{CH}_2\text{P}$ ), 2.00 (s, 6 H,  $\text{NMe}_2$ ), 1.85–1.75 (m, 4 H, 4  $\text{CHMe}_2$ ), 1.75 (s, 6 H,  $\text{CMe}_2$ ), 1.14–1.07 (m, 24 H, 4  $\text{CHMe}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.6 MHz, 298 K):  $\delta$  155.1 (s, C of py), 147.0 (s, 2 CH of py), 143.5 (s, 2 C of 2 pyrrole), 133.4 (d,  $J_{\text{C-P}} = 9.9$  Hz, 2 C of 2 pyrrole), 108.9 (d,  $J_{\text{C-P}} = 7.1$  Hz, 2 CH of 2 pyrrole), 106.7 (s, 2 CH of py), 103.9 (s, 2 CH of 2 pyrrole), 38.3 (s,  $\text{NMe}_2$ ), 37.3 (s,  $\text{CMe}_2$ ), 33.8 (s,  $\text{CMe}_2$ ), 24.2 (d,  $J_{\text{C-P}} = 16.0$  Hz, 4  $\text{CHMe}_2$ ), 23.5 (d,  $J_{\text{C-P}} = 18.8$  Hz, 2  $\text{CH}_2\text{P}$ ), 20.1 (d,  $J_{\text{C-P}} = 12.0$  Hz, 4  $\text{CH}_3$  of 2  $\text{CHMe}_2$ ), 19.7 (d,  $J_{\text{C-P}} = 12.0$  Hz, 4  $\text{CH}_3$  of 2  $\text{CHMe}_2$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 162.1 MHz, 298 K):  $\delta$  1.33 (s) ppm.

**Reaction of  $[\text{Pd}(\text{PPh}_3)_4]$  with **D-dmap**:** Germylene **D** (0.041 g, 0.08 mmol) was added to a solution of dmap (0.011 g, 0.09 mmol) in toluene (2 mL). After stirring at room temperature for 2 h, the solution was added to a suspension of  $[\text{Pd}(\text{PPh}_3)_4]$  (0.092 g, 0.08 mmol) in toluene (1 mL). The resulting green solution was stirred for 12 h. The reaction mixture was vacuum-dried to give a sticky precipitate that contained a mixture of complex **1**, dmap and  $\text{PPh}_3$  (NMR analysis). The precipitate was washed with hexane (4 x 3 mL) to give complex **1** as a dark green solid (0.030 g, 60 %).

**Reaction of complex **1** with  $[\text{AuCl}(\text{tht})]$ . Synthesis of  $[\text{PdCl}\{\kappa^3\text{P,Ge,P-GeCl}(\text{pyrm}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**2**):** THF (4 mL) was added to a mixture of complex **1** (0.034 g, 0.056 mmol) and  $[\text{AuCl}(\text{tht})]$  (0.036 g, 0.110 mmol). After

stirring at room temperature for 12 h, the solvent was removed under reduced pressure. Extraction of the residue with C<sub>6</sub>D<sub>6</sub> allowed the separation of an orange solution from an insoluble violet solid (metallic gold). NMR analyses of the orange solution confirmed that it contained complex **2** (the corresponding analytical data are given below).

**Direct synthesis of [PdCl{κ<sup>3</sup>P,Ge,P-GeCl(pyrmP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>CMe<sub>2</sub>}] (2):** Toluene (4 mL) was added to a mixture of germylene **D** (0.037 g, 0.073) and [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] (0.019 g, 0.073 mmol). The resulting orange solution was stirred at room temperature for 4 h. Solvent removal under reduced pressure afforded complex **2** as an orange solid (0.047 g, 94 %). Anal. (%) Calcd. for C<sub>25</sub>H<sub>42</sub>Cl<sub>2</sub>GeN<sub>2</sub>P<sub>2</sub>Pd (*M* = 682.52 amu): C, 43.99; H, 6.20; N, 4.10; found: C, 44.04; H, 6.26; N 4.06. (+)-ESI HRMS: *m/z* 647.0635, calcd. for C<sub>25</sub>H<sub>42</sub>ClGeN<sub>2</sub>P<sub>2</sub>Pd [*M* – Cl]<sup>+</sup>: 647.0771. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.5 MHz, 298 K): δ 6.22 (s, 2 H, 2 CH of 2 pyrrole), 6.05 (s, 2 H, 2 CH of 2 pyrrole), 3.00 (d, *J*<sub>H-H</sub> = 14.8 Hz, 2 CH of 2 CH<sub>2</sub>P), 2.89 (d, *J*<sub>H-H</sub> = 14.8 Hz, 2 H, 2 CH of 2 CH<sub>2</sub>P), 2.45 (m, 2 H, 2 CH of 2 CHMe<sub>2</sub>), 2.20 (m, 2 H, 2 CH of 2 CHMe<sub>2</sub>), 1.83 (s, 3 H, 1 CH<sub>3</sub> of CMe<sub>2</sub>), 1.78 (s, 3 H, 1 CH<sub>3</sub> of CMe<sub>2</sub>), 1.37 (dd, *J*<sub>H-H</sub> = 6.0 Hz, *J*<sub>H-P</sub> = 14.0 Hz, 6 H, 2 CH<sub>3</sub> of 2 CHMe<sub>2</sub>), 1.03 (dd, *J*<sub>H-H</sub> = 6.0 Hz, *J*<sub>H-P</sub> = 14.0 Hz, 6 H, 2 CH<sub>3</sub> of 2 CHMe<sub>2</sub>), 0.89 (m, 6 H, 2 CH<sub>3</sub> of 2 CHMe<sub>2</sub>), 0.72 (dd, *J*<sub>H-H</sub> = 6.0 Hz, *J*<sub>H-P</sub> = 14.0 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 298 K): δ 146.1 (s, 2 C of 2 pyrrole), 129.4 (s, 2 C of 2 pyrrole), 109.7 (s, 2 CH of 2 pyrrole), 104.7 (s, 2 CH of 2 pyrrole), 38.7 (s, CH<sub>3</sub> of CMe<sub>2</sub>), 37.0 (s, CMe<sub>2</sub>), 27.1 (vt, *J*<sub>C-P</sub> = 11.6 Hz, 2 CH<sub>2</sub>P), 25.3 (2 CH of 2 CHMe<sub>2</sub>), 25.2 (s, CH<sub>3</sub> of CMe<sub>2</sub>), 19.8 (s, 2 CH<sub>3</sub> of 2 CHMe<sub>2</sub>), 19.5 (s, 2 CH<sub>3</sub> of 2 CHMe<sub>2</sub>), 19.3 (vt, *J*<sub>C-P</sub> = 11.5 Hz, 2 CH of 2 CHMe<sub>2</sub>), 18.0 (s, 2 CH<sub>3</sub> of 2 CHMe<sub>2</sub>), 17.9 (s, 2 CH<sub>3</sub> of 2 CHMe<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162.1 MHz, 298 K): δ 38.9 (s) ppm.

**Reaction of complex 1 with HCl. Synthesis of [PdH{κ<sup>3</sup>P,Ge,P-GeCl(pyrmP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>CMe<sub>2</sub>}] (3):** A diethyl ether solution of HCl (70 μL, 1.0 M, 0.07 mmol) was dropwise added to a cold (–78 °C) Schlenk tube containing a solution of **1** (0.042 g, 0.07 mmol) in toluene (2 mL). The resulting orange solution was allowed to reach room temperature and was stirred for 2 h. Solvents were removed under vacuum and the residue was washed with hexane (2 x 1 mL) to give **3** as a pale orange solid (0.029 g, 63 %). Anal. (%) Calcd. for C<sub>25</sub>H<sub>43</sub>ClGeN<sub>2</sub>P<sub>2</sub>Pd (*M* = 648.05 amu): C, 46.33; H, 6.69; N, 4.32; found: C, 46.28; H, 6.62; N, 4.28. (+)-ESI HRMS: *m/z* 613.1271; calcd. for C<sub>25</sub>H<sub>43</sub>GeN<sub>2</sub>P<sub>2</sub>Pd [*M* – Cl]<sup>+</sup>: 613.1200. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.5 MHz, 298 K): δ 6.34 (d, *J*<sub>H-H</sub> = 2.9 Hz, 2 CH of 2 pyrrole), 6.15 (d, *J*<sub>H-H</sub> = 2.9 Hz, 2 CH of 2 pyrrole), 2.93 (m, 2 H of 2 CH<sub>2</sub>P), 2.51–2.42 (m, 4 H, 2 H of 2 CH<sub>2</sub>P and 2 H of 2 CHMe<sub>2</sub>), 2.27 (m, 2 H of 2 CHMe<sub>2</sub>), 1.89 (s, 3 H of CMe<sub>2</sub>), 1.67 (s, 3 H of CMe<sub>2</sub>), 1.32 (dd, *J*<sub>H-H</sub> = 7.4 Hz, *J*<sub>H-P</sub> = 15.7 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>), 1.09 (dd, *J*<sub>H-H</sub> = 7.4 Hz, *J*<sub>H-P</sub> = 15.7 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>), 0.88 (dd, *J*<sub>H-H</sub> = 7.4 Hz, *J*<sub>H-P</sub> = 15.7 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>), 0.75 (dd, *J*<sub>H-H</sub> = 7.4 Hz, *J*<sub>H-P</sub> = 15.7 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>), –5.09 (t, *J*<sub>H-P</sub> = 7.8 Hz, 1 H, PdH) ppm. <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 298 K): δ 144.7 (s, 2 C of 2 pyrrole), 109.2 (s, 2 CH of 2 pyrrole), 104.6 (s, 2 CH of 2 pyrrole), 40.1 (s, CMe<sub>2</sub>), 36.8 (s, CMe<sub>2</sub>), 27.0 (vt, *J*<sub>C-P</sub> = 11.6 Hz, 2 CHMe<sub>2</sub>), 25.4 (s, CMe<sub>2</sub>), 25.1 (vt, *J*<sub>C-P</sub> = 11.6 Hz, 2 CHMe<sub>2</sub>), 20.2 (vt, *J*<sub>C-P</sub> = 11.1 Hz, 2 CH<sub>2</sub>P), 19.8 (m, 4 CHMe<sub>2</sub>), 18.0 (s, 2 CHMe<sub>2</sub>), 17.9 (s, 2 CHMe<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162.1 MHz, 298 K): δ 42.7 (s) ppm.

**Reaction of complex 1 with Ph<sub>2</sub>S<sub>2</sub>. Synthesis of [Pd(SPh){κ<sup>3</sup>P,Ge,P-Ge(SPh)(pyrmP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>CMe<sub>2</sub>}] (4):** Toluene (3 mL) was added to a mixture of complex **1** (0.040 g, 0.07 mmol) and diphenyl disulphide (0.014 g, 0.07 mmol). The initial dark green colour changed to orange. The solution was stirred at room temperature for 2 h. The solvent was evaporated to dryness and the residue was washed with hexane (2 x 1 mL) to give **4** as an orange solid (0.053 g, 91 %). Anal. (%) Calcd. for C<sub>37</sub>H<sub>52</sub>GeN<sub>2</sub>P<sub>2</sub>PdS<sub>2</sub> (*M* = 829.23 amu): C, 53.55; H, 6.32; N, 3.38; found: C, 53.72; H, 6.40; N, 3.32. (+)-ESI HRMS: *m/z* 721.1325; calcd. for C<sub>31</sub>H<sub>47</sub>GeN<sub>2</sub>P<sub>2</sub>PdS [*M* – SPh]<sup>+</sup>: 721.1234. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.5 MHz, 298 K): δ 7.64 (dd, *J*<sub>H-H</sub> = 8.0, 1.5 Hz, 2 H of 2 Ph), 7.40 (dd, *J*<sub>H-H</sub> = 8.0, 1.5 Hz, 2 H of 2 Ph), 6.98–6.88 (m, 6 H of 2 Ph), 6.28 (d, *J*<sub>H-H</sub> = 3.2 Hz, 2 CH of 2 pyrrole), 6.14 (m, 2 CH of 2 pyrrole), 3.32 (d, *J*<sub>H-H</sub> = 14.4 Hz, 2 H of 2 CH<sub>2</sub>P), 3.05 (dvt, *J*<sub>H-H</sub> = 14.4 Hz, *J*<sub>H-P</sub> = 5.8 Hz, 2 H of 2 CH<sub>2</sub>P), 2.46 (m, 2 H of 2 CHMe<sub>2</sub>), 2.02 (m, 2 H of 2 CHMe<sub>2</sub>), 1.77 (s, 3 H of CMe<sub>2</sub>), 1.40 (s, 3 H of CMe<sub>2</sub>), 1.26 (dd, *J*<sub>H-H</sub> = 7.3 Hz, *J*<sub>H-P</sub> = 16.0 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>), 1.00 (dd, *J*<sub>H-H</sub> = 7.3 Hz, *J*<sub>H-P</sub> = 16.0 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>), 0.89 (dd, *J*<sub>H-H</sub> = 7.3 Hz, *J*<sub>H-P</sub> = 16.0 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>), 0.75 (dd, *J*<sub>H-H</sub> = 7.3 Hz, *J*<sub>H-P</sub> = 16.0 Hz, 6 H, 2 CH<sub>3</sub> of CHMe<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 298 K): δ 147.9 (s, C of Ph), 145.4 (s, 2 C of 2 pyrrole), 136.0 (s, 2 CH

of Ph), 134.3 (s, 2 CH of Ph), 122.8 (s, 2 CH of Ph), 109.6 (s, 2 CH of 2 pyrrole), 104.9 (s, 2 CH of 2 pyrrole), 37.7 (s, CMe<sub>2</sub>), 36.9 (s, CMe<sub>2</sub>), 29.9 (s, CMe<sub>2</sub>), 27.1 (vt,  $J_{C-P} = 11.5$  Hz, 2 CHMe<sub>2</sub>), 25.4 (vt,  $J_{C-P} = 11.5$  Hz, 2 CHMe<sub>2</sub>), 20.4 (s, 2 CHMe<sub>2</sub>), 20.3 (s, 2 CHMe<sub>2</sub>), 19.8 (vt,  $J_{C-P} = 10.4$  Hz, 2 CH<sub>2</sub>P), 17.8 (s, 2 CHMe<sub>2</sub>), 17.7 (s, 2 CHMe<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162.1 MHz, 298 K): δ 36.9 (s) ppm.

### X-Ray diffraction analyses

Crystals of **2** and **4** were analyzed by X-ray diffraction. A selection of crystal, measurement and refinement data is given in Table S1. Diffraction data were collected on Oxford Diffraction Xcalibur Onyx Nova (for **2**) and Bruker D8 Venture Photon III-14 (for **4**) single crystal diffractometers, using CuK $\alpha$  radiation. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm (as implemented in CrysAlisPro RED<sup>4a</sup>) (for **2**) and SADABS-2016/2<sup>4b</sup> (for **4**) The structures were solved using SIR-97.<sup>5</sup> Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.<sup>6</sup> H atoms were set in calculated positions and were refined riding on their parent atoms. The WINGX program system<sup>7</sup> was used throughout the structure determinations. The molecular plots were made with MERCURY.<sup>8</sup> CCDC deposition numbers: 2035174 (**2**) and 2035175 (**4**).

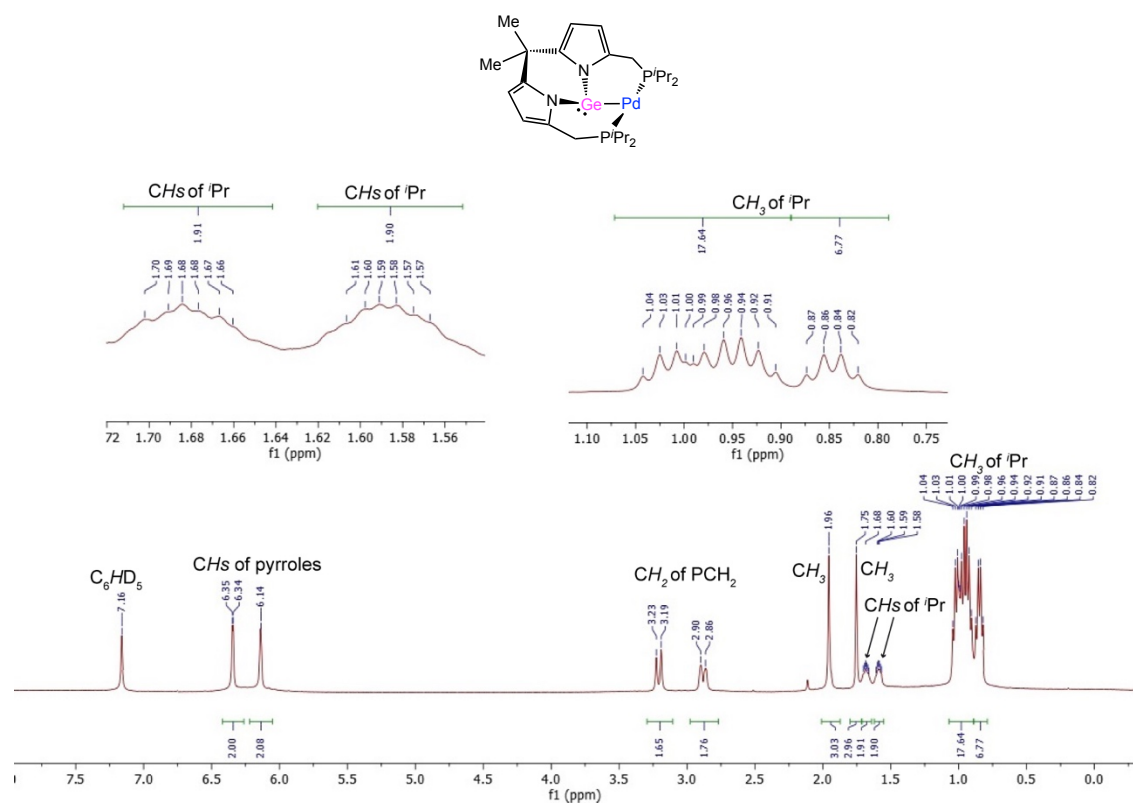
### Computational details

Structure optimizations were performed with the Gaussian09 suite of programs,<sup>9</sup> using the wb97XD functional,<sup>10</sup> which includes the second generation of Grimme's dispersion interaction correction.<sup>11</sup> The Stuttgart-Dresden relativistic effective core potentials and the associated basis sets (SDD) was used for the Pd atoms.<sup>12</sup> The basis set used for the remaining atoms was the cc-pVDZ.<sup>13</sup> This level of theory is indicated as wb97XD/SDD/cc-pVDZ. Frequency calculations confirmed the optimized structures as energy minima (zero imaginary eigenvalues). All Gibbs energies were computed at 298.15 K and 1.0 atm. Orbital calculations were performed with the NBO package.<sup>14</sup>

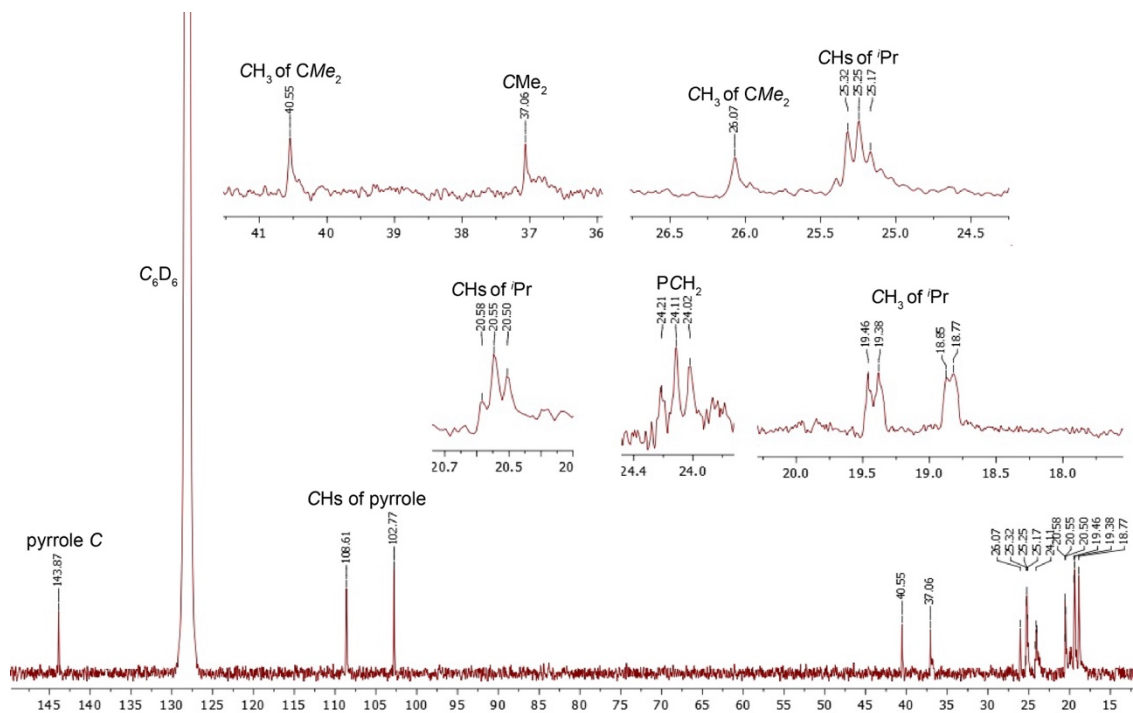
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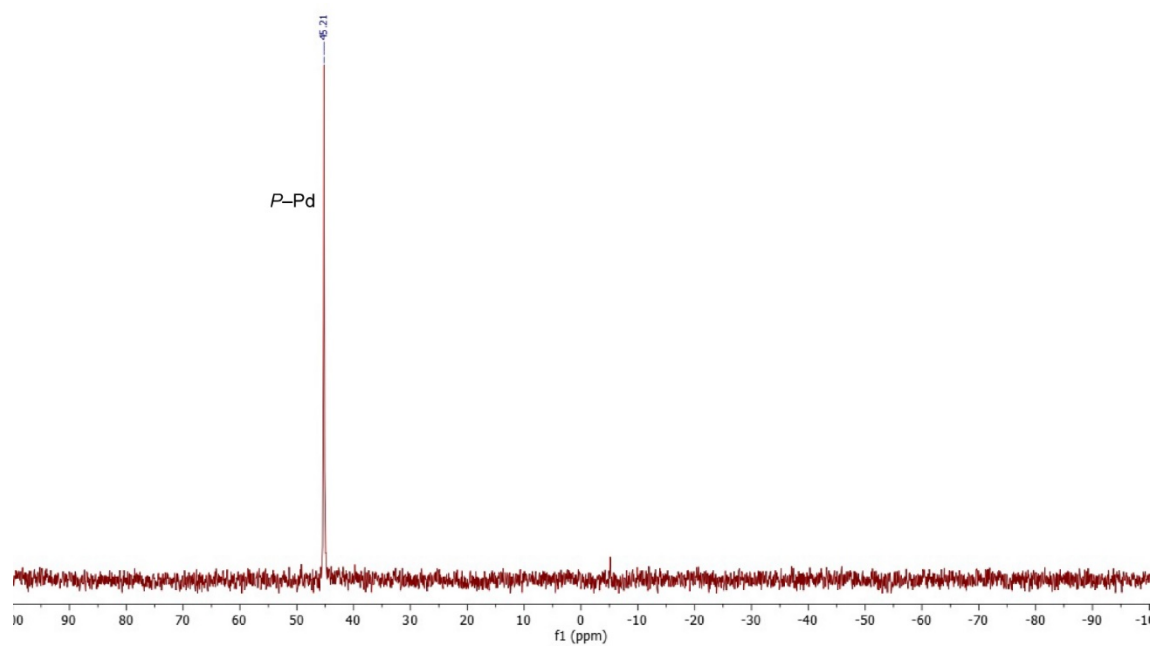
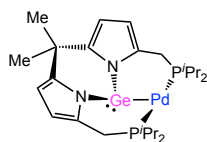
## NMR spectra



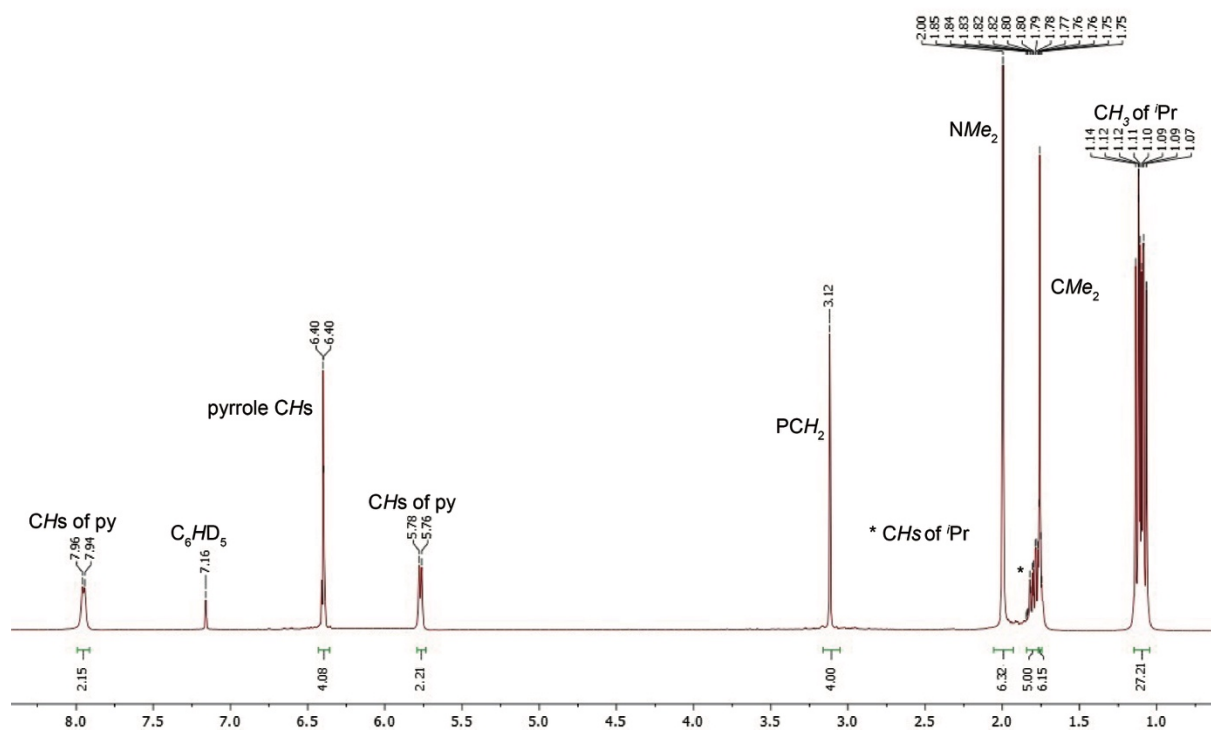
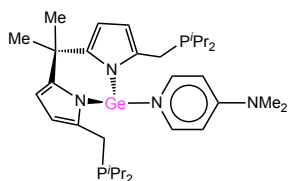
**Fig. S1**  $^1H$  NMR spectrum (400.5 MHz,  $C_6D_6$ , 298 K) of  $[Pd\{\kappa^3P,Ge,P-Ge(pyrmP'Pr_2)_2CMe_2\}]$  (1).



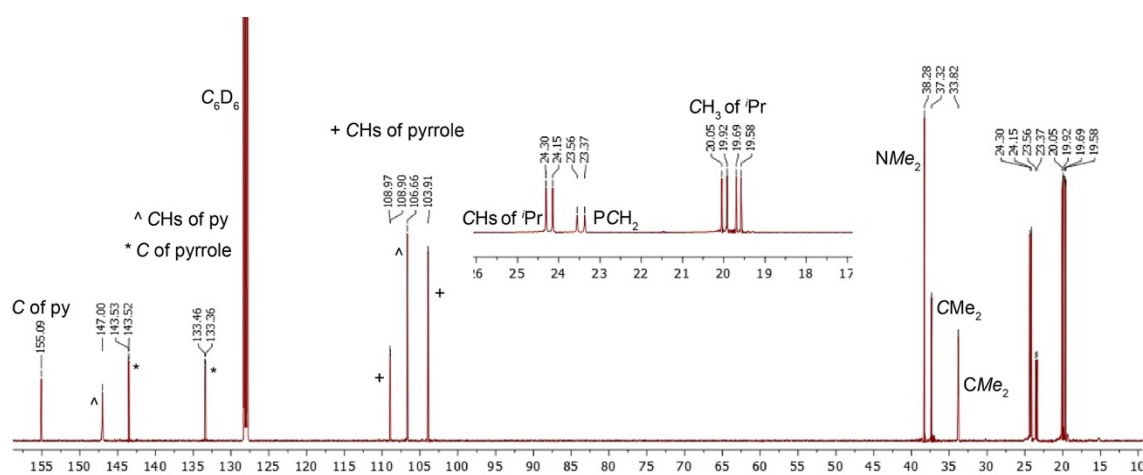
**Fig. S2**  $^{13}C\{^1H\}$  NMR spectrum (100.6 MHz,  $C_6D_6$ , 298 K) of  $[Pd\{\kappa^3P,Ge,P-Ge(pyrmP'Pr_2)_2CMe_2\}]$  (1).



**Fig. S3**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$  298 K) of  $[\text{Pd}\{\kappa^3\text{P,Ge,P-Ge}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**1**).

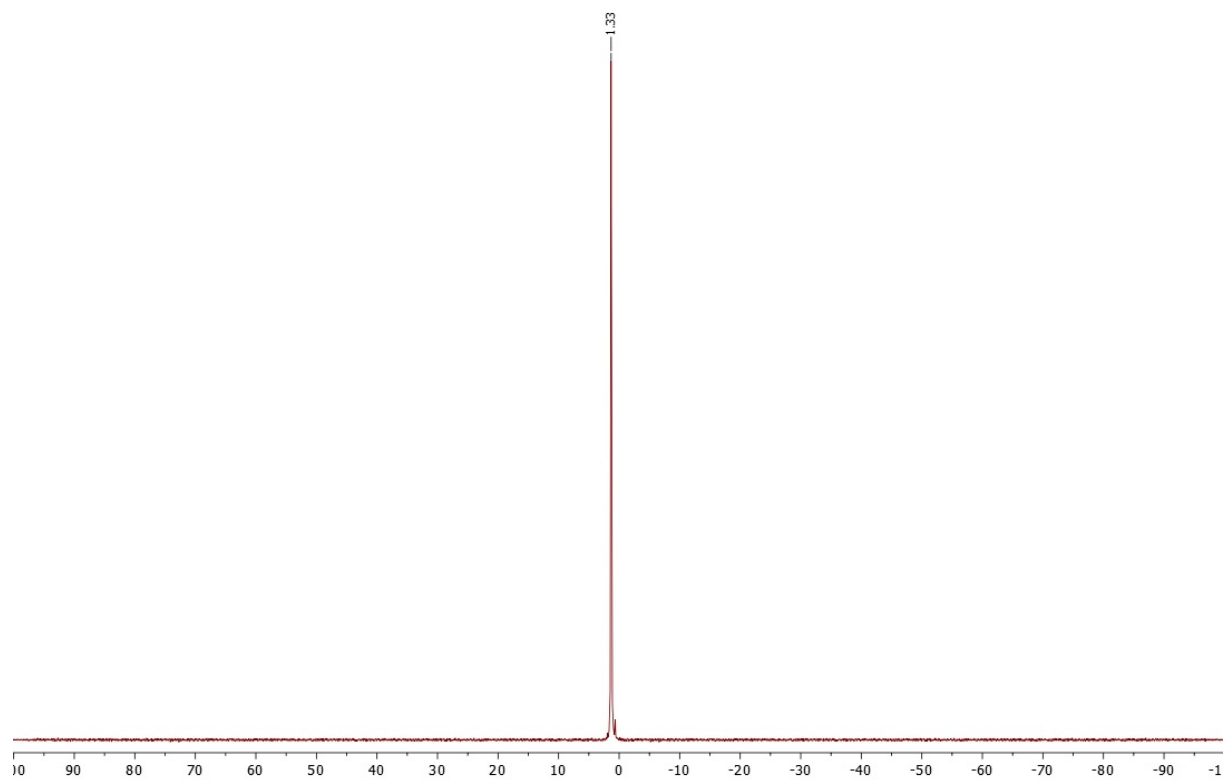
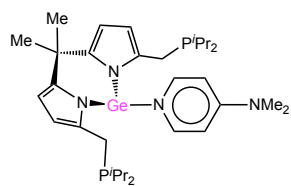


**Fig. S4**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $\text{Ge}\{(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}(\text{dmap})$  (**D-dmap**).

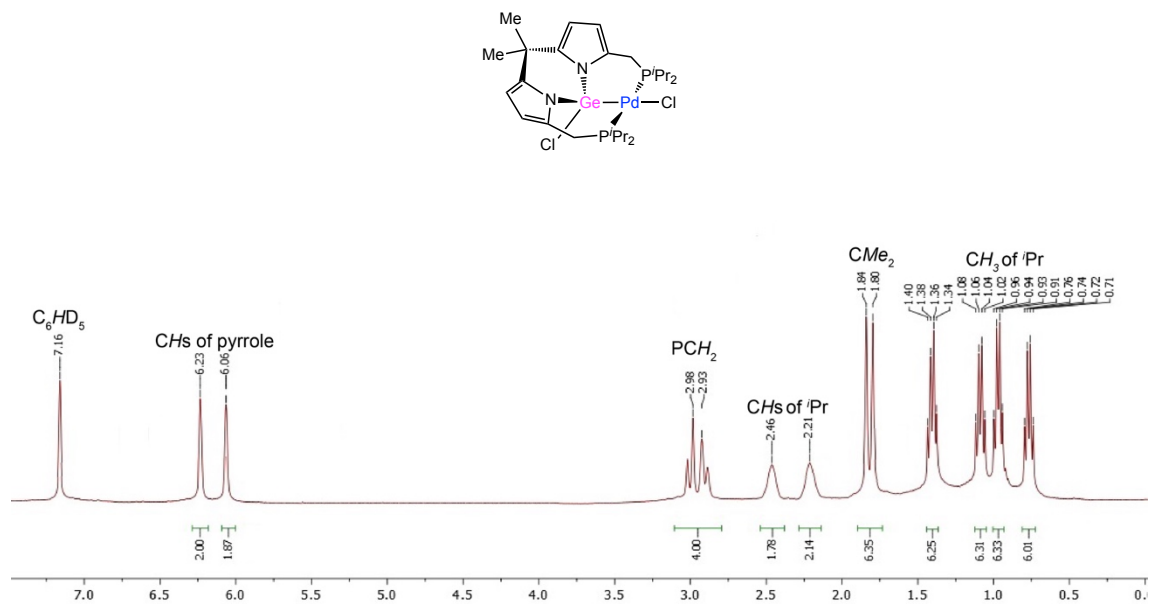


**Fig. S5**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $\text{Ge}\{(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}(\text{dmap})$  (**D-dmap**).

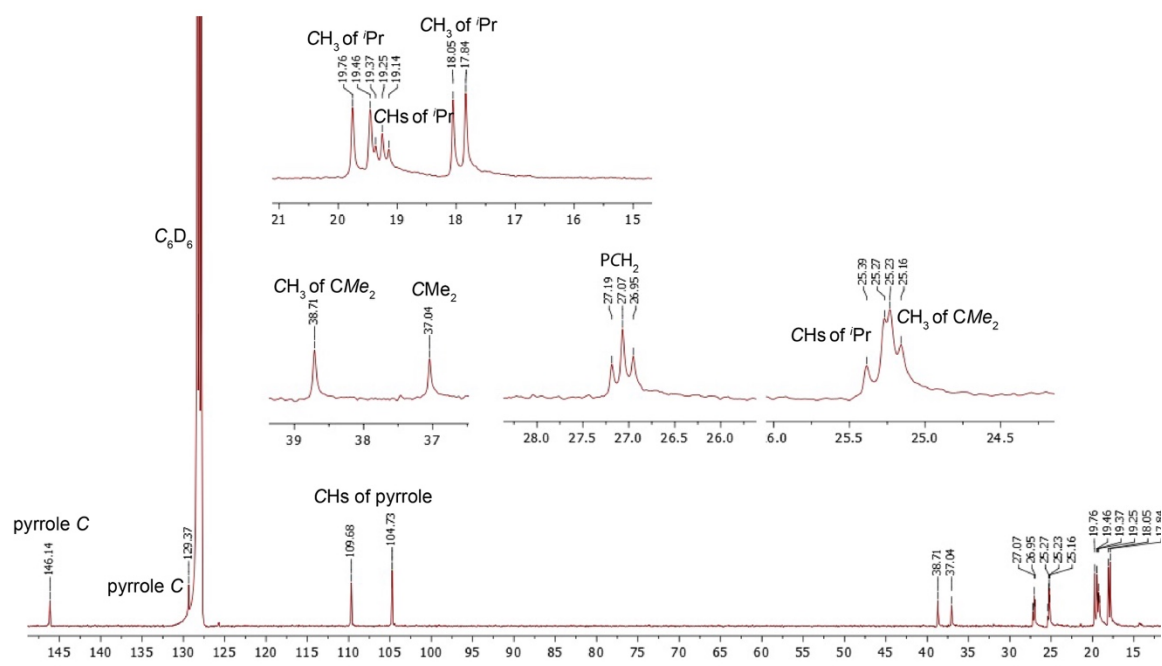




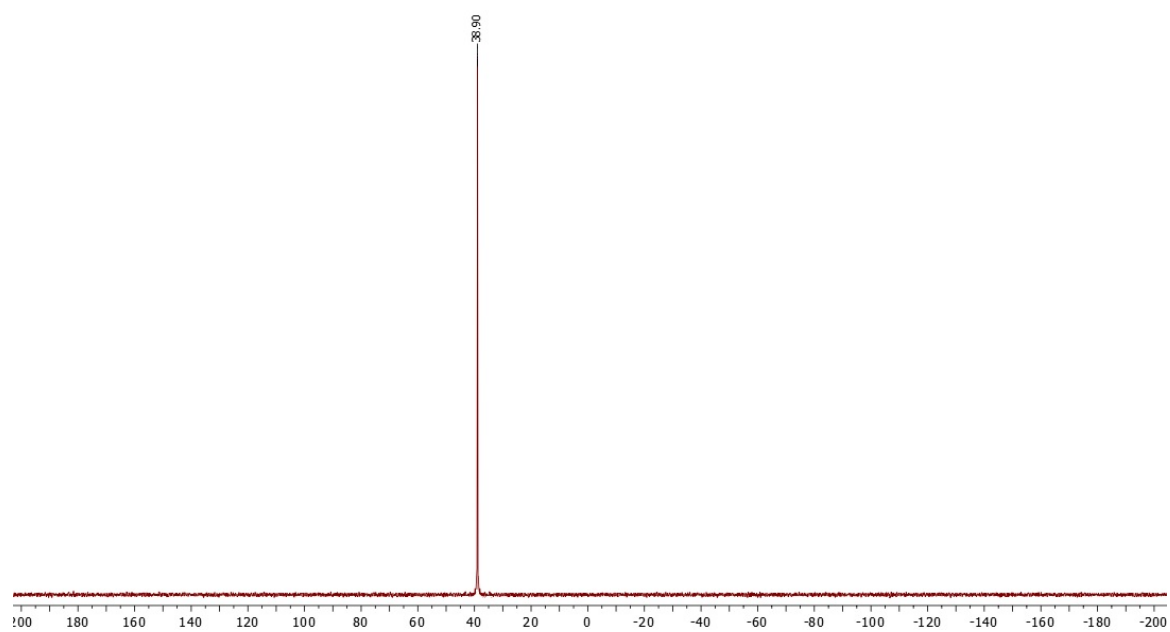
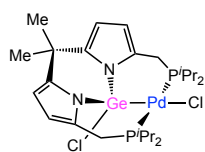
**Fig. S6** <sup>31</sup>P{<sup>1</sup>H}NMR spectrum (162.1 MHz, C<sub>6</sub>D<sub>6</sub> 298 K) of Ge{(pyrmP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>CMe<sub>2</sub>}(dmap) (**D**·dmap).



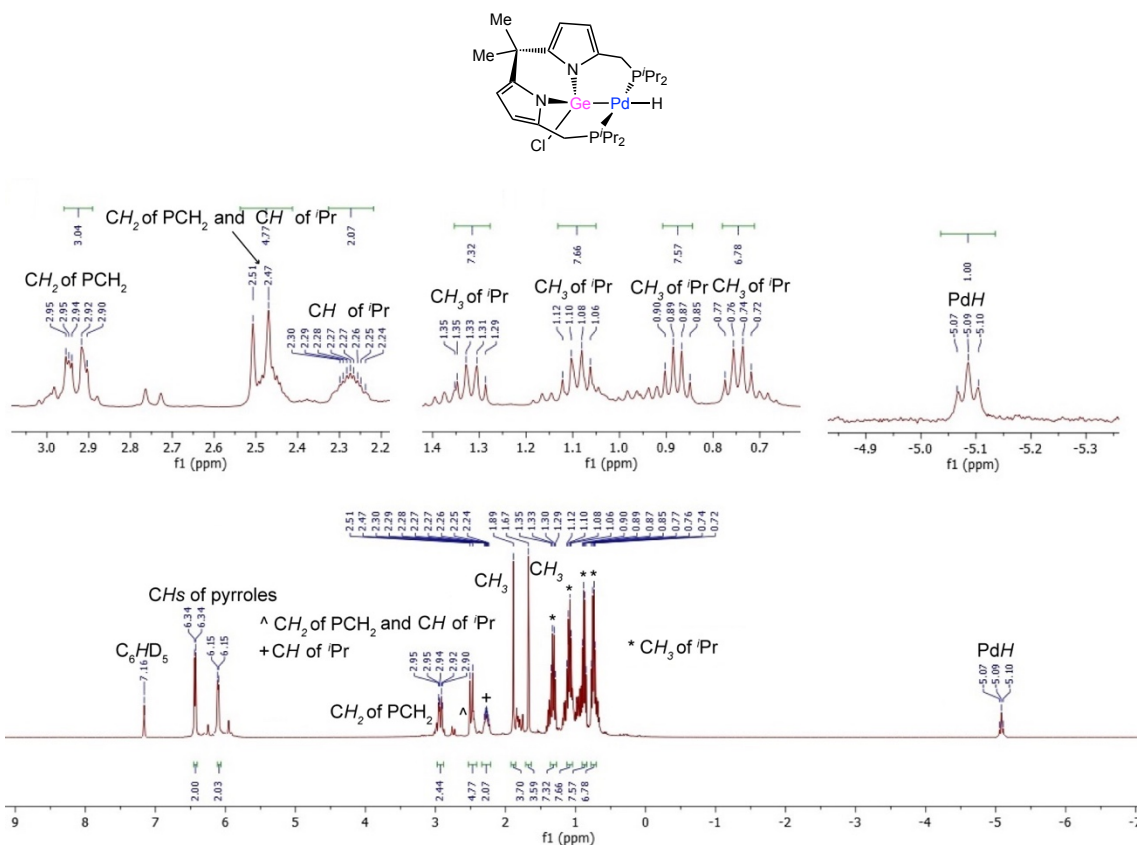
**Fig. S7**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdCl}\{\kappa^3\text{P,Ge,P-GeCl}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (2).



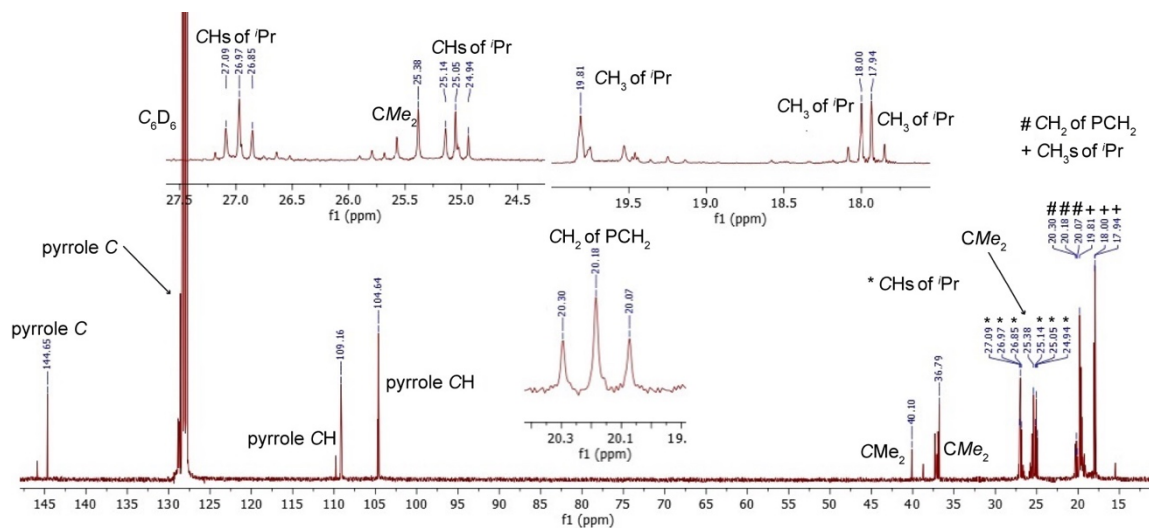
**Fig. S8**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdCl}\{\kappa^3\text{P,Ge,P-GeCl}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (2).



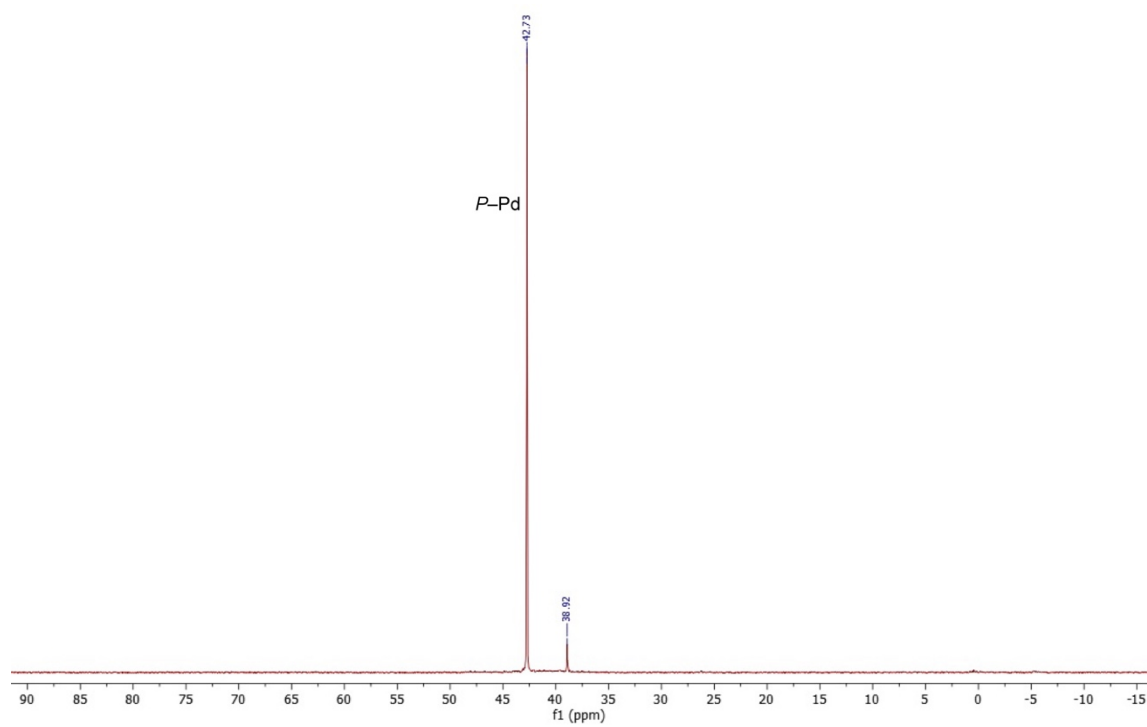
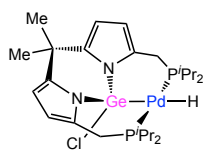
**Fig. S9**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdCl}\{\kappa^3\text{P,Ge,P-GeCl}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**2**).



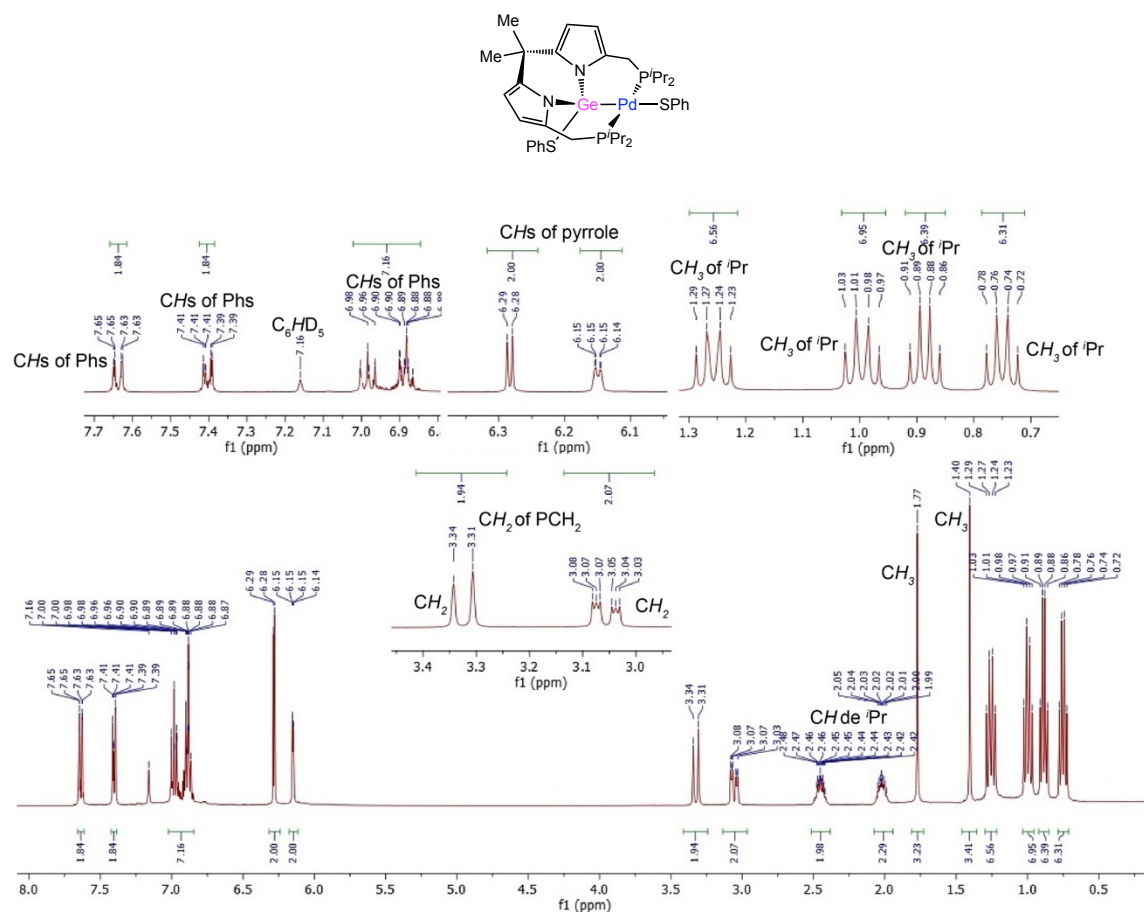
**Fig. S10**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdH}\{\kappa^3\text{P,Ge,P-GeCl}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**3**). The sample contains a small amount of complex **2**.



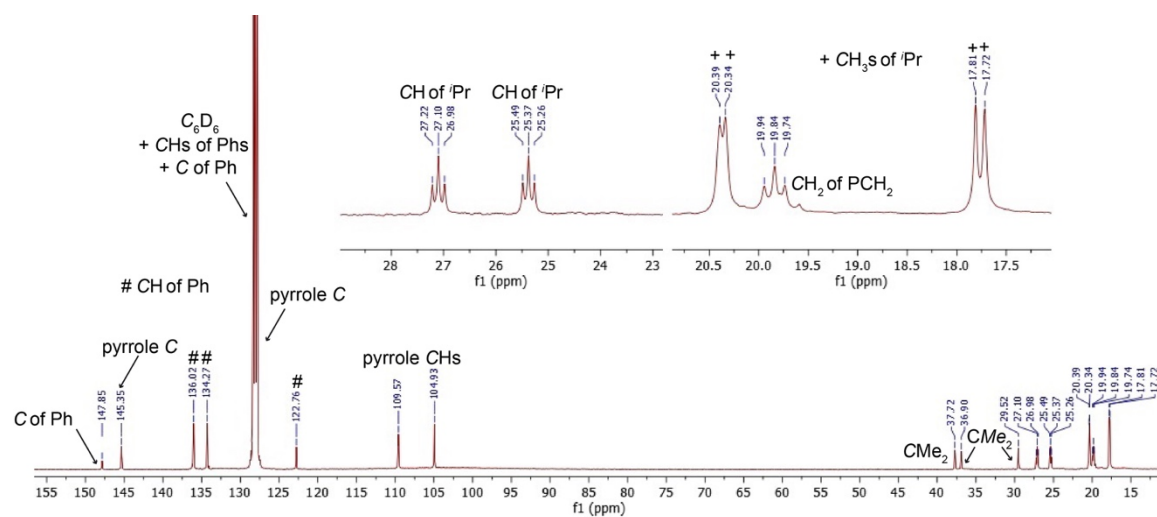
**Fig. S11**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdH}\{\kappa^3\text{P,Ge,P-GeCl}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**3**). The sample contains a small amount of complex **2**.



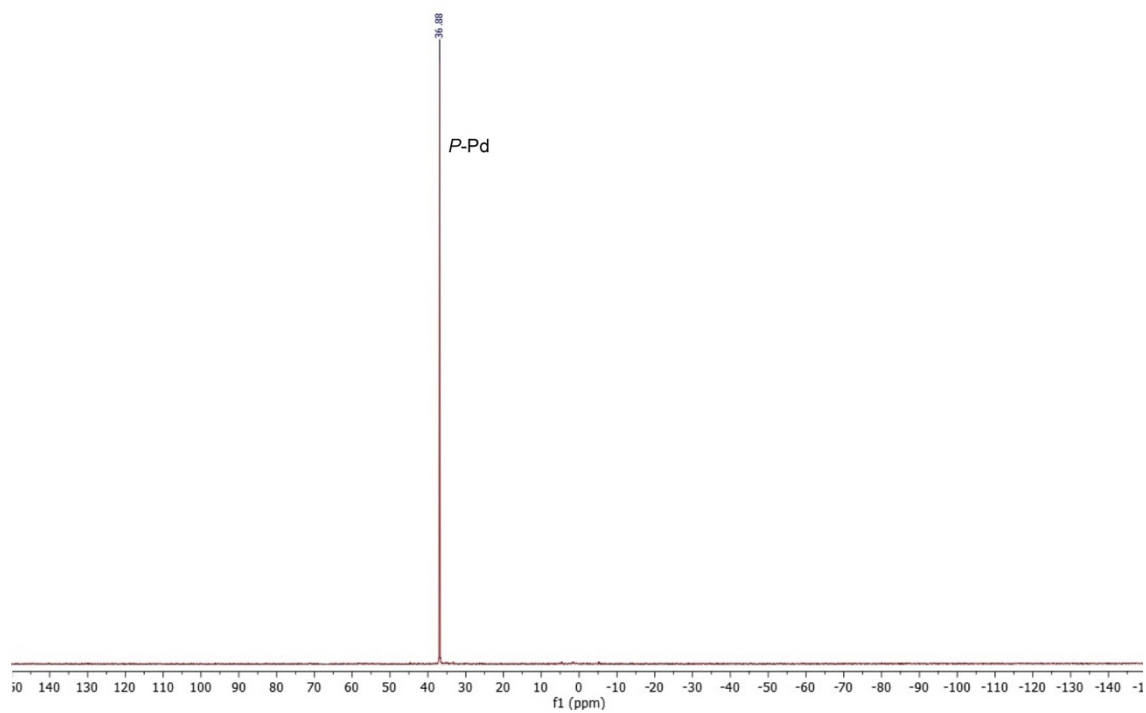
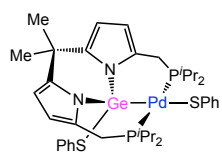
**Fig. S12**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdH}\{\kappa^3\text{P,Ge,P-GeCl}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**3**). The sample contains a small amount of complex **2**.



**Fig. S13**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pd}(\text{SPh})\{\kappa^3\text{P, Ge, P-Ge}(\text{SPh})(\text{pyrmP}'\text{Pr}_2)_2\text{CMe}_2\}]$  (**4**).

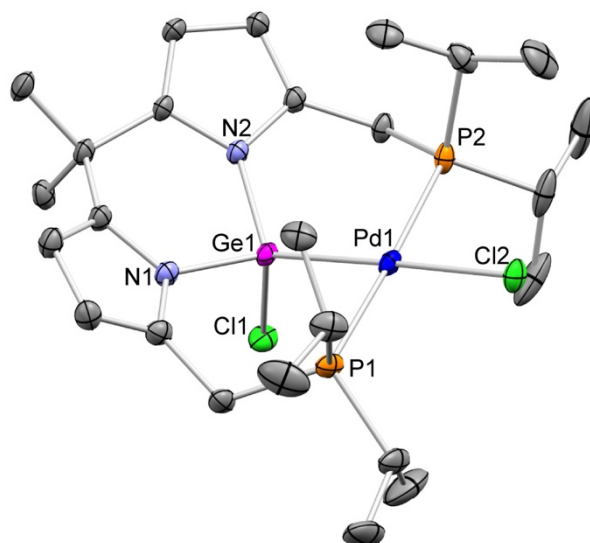


**Fig. S14**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pd}(\text{SPh})\{\kappa^3\text{P, Ge, P-Ge}(\text{SPh})(\text{pyrmP}'\text{Pr}_2)_2\text{CMe}_2\}]$  (**4**).

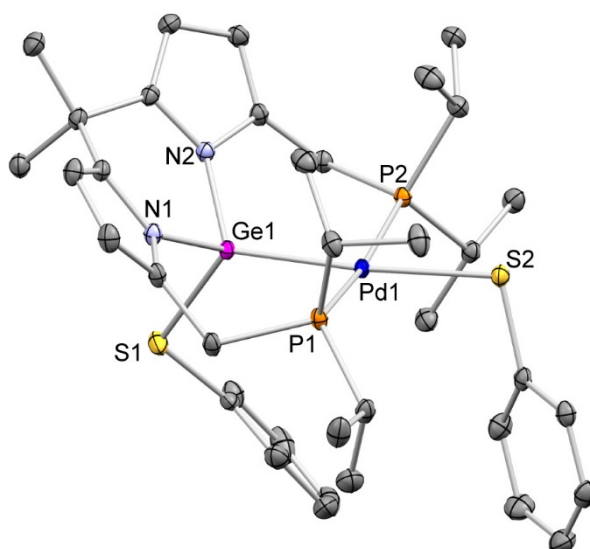


**Fig. S15**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pd}(\text{SPh})\{\kappa^3\text{P,Ge,P-Ge}(\text{SPh})(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$  (**4**).

## Figures of X-ray diffraction structures



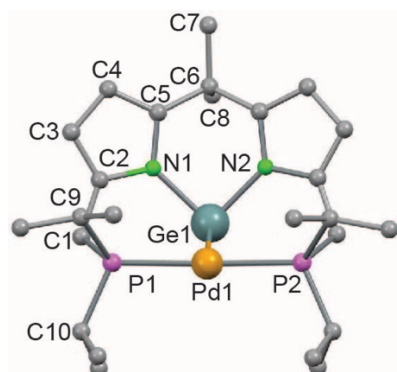
**Fig. S16** Molecular structure of compound **2** (20% displacement ellipsoids; H atoms have been omitted for clarity). Selected bond distances (Å) and angles (°): Pd1–Ge1 2.3001(4), Pd1–Cl2 2.3707(7), Pd1–P1 2.3138(9), Pd1–P2 2.3197(9), Ge1–Cl1 2.2070(8), Ge1–N1 1.851(3), Ge1–N2 1.851(2), P1–Pd1–P2 177.51(3), P1–Pd1–Ge1 88.85(2), P1–Pd1–Cl2 89.15(3), P2–Pd1–Ge1 88.89(2), P2–Pd1–Cl2 93.12(3), Ge1–Pd1–Cl2 178.00(3), N1–Ge1–N2 97.2(1), N1–Ge1–Pd1 118.56(8), N2–Ge1–Pd1 118.18(8), N1–Ge1–Cl1 104.88(9), N2–Ge1–Cl1 102.57(8), Cl1–Ge1–Pd1 113.07(3).



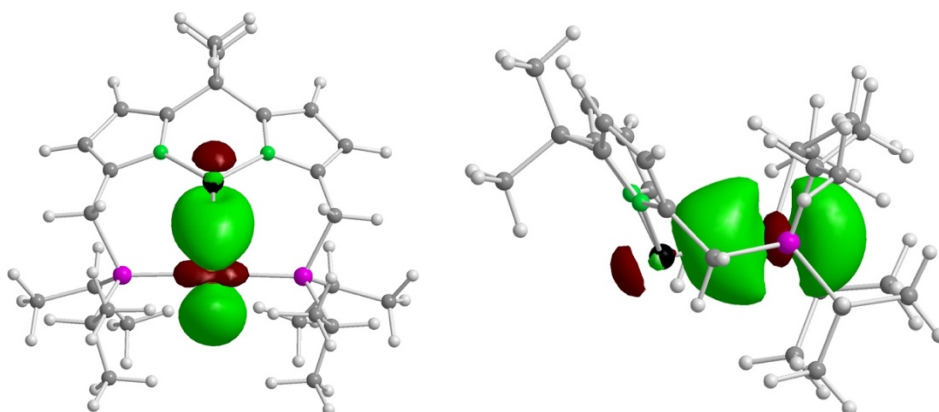
**Fig. S17** Molecular structure of compound **4** (50% displacement ellipsoids; H atoms have been omitted for clarity). Pd1–Ge1 2.3680(2), Pd1–S2 2.4003(4), Pd1–P1 2.3488(4), Pd1–P2 2.3343(4), Ge1–S1 2.2673(4), Ge1–N1 1.887(1), Ge1–N2 1.887(1), P1–Pd1–P2 170.29(1), P1–Pd1–Ge1 88.92(1), P1–Pd1–S2 93.58(1), P2–Pd1–Ge1 90.28(1), P2–Pd1–S2 86.61(1), Ge1–Pd1–S2 175.35(1), N1–Ge1–N2 94.64(5), N1–Ge1–Pd1 117.21(4), N2–Ge1–Pd1 114.58(4), N1–Ge1–S1 97.76(4), N2–Ge1–S1 106.30(4), S1–Ge1–Pd1 121.94(1).



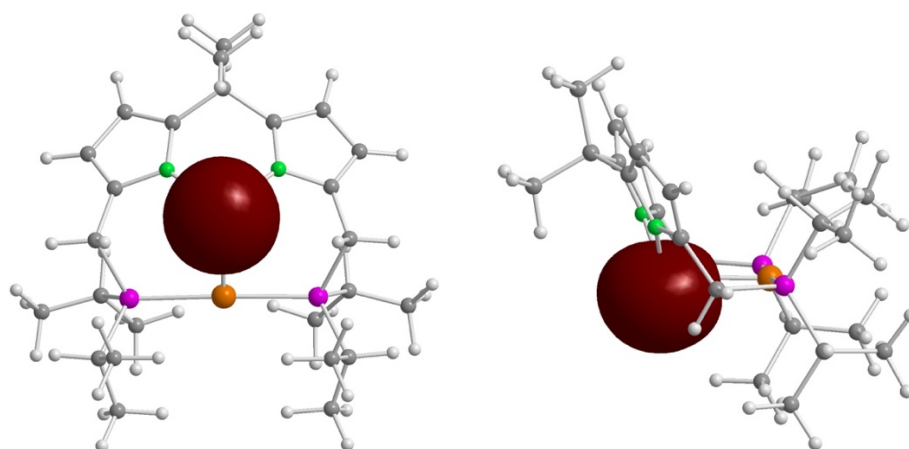
## Figures of DFT/NBO calculations



**Fig. S18** DFT-optimized structure of compound **1** (wB97XD/SDD/cc-pVDZ level of theory; H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Pd1–P1 2.347, Pd1–P2 2.346, Pd1–Ge1 2.507, Ge1–N1 1.957, Ge1–N2 1.957, P1–C1 1.861, P1–C8 1.867, P1–C9 1.866, N1–C2 1.363, N1–C5 1.362, C1–C2 1.494, C2–C3 1.377, C3–C4 1.424, C4–C5 1.380, C5–C6 1.514, C6–C7 1.533, C6–C8 1.550; P1–Pd1–P2 175.35, Ge1–Pd1–P1 91.87, Ge1–Pd1–P2 91.84, N1–Ge1–N2 90.43.



**Fig. S19** Front (left) and side (right) views (NBO) of the HOMO of complex **1**. Composition: 79.49% Pd and 20.51% Ge. Atomic orbital contributions: Pd: 43.12% s, 1.62% p, 55.26% d; Ge: 2.13% s, 97.25% p, 0.61% d.



**Fig. S20** Front (left) and side (right) views (NBO) of the lone pair orbital (HOMO–12) of complex **1**. Composition: 100 % Ge. Atomic orbital contributions: Ge: 84.60% s, 15.37% p, 0.02% d.

**Table S1.** Crystal, measurement and refinement data for the compounds studied by X-ray diffraction.

	<b>2</b>	<b>4</b>
formula	C <sub>25</sub> H <sub>42</sub> Cl <sub>2</sub> GeN <sub>2</sub> P <sub>2</sub> Pd	C <sub>37</sub> H <sub>52</sub> GeN <sub>2</sub> P <sub>2</sub> PdS <sub>2</sub>
fw	682.43	829.85
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 21/ <i>n</i>
<i>a</i> , Å	11.4960(2)	17.5001(4)
<i>b</i> , Å	18.4130(3)	12.1142(2)
<i>c</i> , Å	14.6710(3)	18.9450(4)
$\alpha$ , deg	90	90
$\beta$ , deg	106.665(2)	114.670(1)
$\gamma$ , deg	90	90
<i>V</i> , Å <sup>3</sup>	2975.1(1)	3649.8(1)
<i>Z</i>	4	4
<i>F</i> (000)	1392	1712
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.524	1.510
$\mu$ , mm <sup>-1</sup> (Cu K $\alpha$ )	8.908	7.101
cryst size, mm	0.29 x 0.17 x 0.06	0.14 x 0.09 x 0.05
<i>T</i> , K	140(2)	100.0(1)
$\theta$ range, deg	3.96 to 69.64	2.89 to 74.49
min./max. <i>h</i> , <i>k</i> , <i>l</i>	-12/13, -22/16, -17/17	-21/21, -15/14, -23/23
no. collected reflns	16009	176781
no. unique reflns	5525	7461
no. reflns with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	5074	7173
no. params/restraints	308/0	416/0
GOF (on <i>F</i> <sup>2</sup> )	1.030	1.068
<i>R</i> <sub>1</sub> (on <i>F</i> , <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.036	0.018
<i>wR</i> <sub>2</sub> (on <i>F</i> <sup>2</sup> , all data)	0.100	0.042
min./max. $\Delta\rho$ , e Å <sup>-3</sup>	-0.849/1.080	-0.317/0.422
CCDC dep. no.	2035174	2035175

**Table S2.** Atomic coordinates of the DFT-optimized structure (wB97XD/SDD/cc-pVDZ) of complex 1.  
(E = -3974.62933217 hartree)

Pd	-0.952411	0.176146	-0.351526	C	1.934160	-3.786654	0.253029
Ge	1.130402	-0.227093	-1.686905	H	1.651031	-4.788028	0.572730
P	-1.431205	-2.119216	-0.263966	C	-0.307626	4.686254	1.545465
P	-0.540044	2.484518	-0.261298	H	-1.346555	5.037687	1.441012
C	3.206556	2.834322	0.159461	H	0.302202	5.193644	0.782331
H	3.318301	3.877794	0.448627	H	0.055083	5.022810	2.529507
N	1.870670	-1.772014	-0.741029	C	-3.006486	-2.172896	-2.559778
N	2.386937	0.957211	-0.766140	H	-3.975378	-2.391528	-3.035864
C	-1.437625	-2.861514	1.449948	H	-2.231975	-2.712436	-3.123558
H	-0.355048	-2.980897	1.632394	H	-2.809693	-1.093062	-2.664469
C	3.534810	0.612487	-0.077889	C	-2.051528	3.146893	-2.504026
C	-0.210136	3.163376	1.446684	H	-2.261791	2.070548	-2.618290
H	0.845633	2.873074	1.589556	H	-1.151741	3.378890	-3.091812
C	-0.174320	-3.186730	-1.127078	H	-2.890003	3.707741	-2.946195
H	-0.449766	-4.246731	-1.023276				
H	-0.217964	-2.937482	-2.199479				
C	-2.096762	-4.238599	1.534882				
H	-1.919395	-4.680526	2.528038				
H	-1.696162	-4.941359	0.788348				
H	-3.187636	-4.177381	1.393674				
C	3.061053	-1.852283	-0.043525				
C	3.127438	-3.081305	0.579912				
H	3.948617	-3.449946	1.188582				
C	-1.033538	2.457985	2.526523				
H	-0.717997	2.801711	3.524501				
H	-0.891516	1.368385	2.478518				
H	-2.111273	2.662255	2.429646				
C	-3.211381	3.314455	-0.273000				
H	-4.023041	3.870587	-0.768505				
H	-3.154136	3.664084	0.767752				
H	-3.492709	2.247890	-0.257135				
C	5.183833	-0.969492	0.920021				
H	5.649707	-1.961809	0.834604				
H	5.982969	-0.221856	0.812932				
H	4.743496	-0.871717	1.922684				
C	0.993692	3.011985	-1.174867				
H	0.835041	2.774365	-2.238981				
H	1.122460	4.101721	-1.095465				
C	1.191862	-2.963629	-0.564839				
C	4.060908	1.748022	0.503196				
H	4.970796	1.804117	1.094393				
C	4.806164	-0.930944	-1.552919				
H	5.253620	-1.932101	-1.651764				
H	4.080255	-0.803229	-2.370937				
H	5.591470	-0.168933	-1.675712				
C	-1.893939	3.515783	-1.025483				
H	-1.591110	4.573983	-0.950310				
C	-1.981870	-1.894184	2.503411				
H	-3.058032	-1.700879	2.373494				
H	-1.458690	-0.927854	2.458309				
H	-1.839169	-2.316348	3.510996				
C	4.122964	-0.780038	-0.169659				
C	-4.218956	-1.901295	-0.369483				
H	-4.085494	-0.806587	-0.348482				
H	-4.333594	-2.247475	0.667582				
H	-5.160780	-2.116618	-0.898668				
C	-3.044427	-2.576401	-1.082354				
H	-3.157989	-3.671711	-1.012142				
C	2.198787	2.320037	-0.625939				