ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis and initial transition metal chemistry of the first PGeP pincer-type germylene

Lucía Álvarez-Rodríguez,^a Javier Brugos,^a Javier A. Cabeza,^{a,*} Pablo García-Álvarez,^{a,*} Enrique Pérez-Carreño^b and Diego Polo^a

^aCentro de Innovación en Química Avanzada (ORFEO-CINQA) and Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain.

^bDepartamento de Química Física y Analítica, Universidad de Oviedo, E-33071 Oviedo, Spain.

Experimental Details

General Procedures. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) or CaH₂ (dichloromethane) and distilled under argon before use. The reactions were carried out under argon in an MBraun glovebox or using Schlenk-vacuum line techniques. The reagent *o*- $\{N(H)CH_2P'Bu_2\}_2C_6H_4$ was prepared following a published procedure.¹ All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run on Bruker NAV-400 instrument, using as standards the residual protic solvent resonance for ¹H [$\delta(C_6HD_5) = 7.16$ ppm] and the solvent resonance for ¹³C [$\delta(C_6D_6) = 128.10$ ppm]. 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 having the greatest mass.

Ge(**NCH₂P'Bu₂)₂C₆H₄ (1).** LiBu (3.8 mL, 6.1 mmol, 1.6 M in hexanes) was added to a solution of *o*-{N(H)CH₂P'Bu₂}₂C₆H₄ (1.27 g, 3.0 mmol) in diethyl ether (20 mL) at -78 °C. The resulting grey suspension was allowed to reach the room temperature and was stirred for 2 h. Then, GeCl₂(dioxane) (695 mg, 3.0 mmol) was added and the resulting yellow suspension was stirred for 18 h. Solvents were evaporated under reduced pressure and the residue was washed with hexane (20 mL). The hexane-insoluble solid was extracted into toluene (2 x 15 mL). The solution was decanted to separate a white solid (LiCl) and was evaporated to dryness to give **1** as a yellow solid (995 mg, 67%). Anal. (%) Calcd. for C₂4H₄4GeN₂P₂ (M_w = 495.18 amu): C, 58.21; H, 8.96; N, 5.66; found: C, 58.25; H, 9.02; N, 5.58. ¹H NMR (C₆D₆, 400.1 MHz, 293 K): δ 7.31 (m, 2 H, 2 CH of C₆H₄), 7.24 (m, 2 H, 2 CH of C₆H₄), 4.11 (s, 4 H, 4 CH of 2 PCH₂), 1.09 (d, *J*_{H-P} = 11.5 Hz, 36 H, 12 CH₃ of 4 ^{*i*}Bu) ppm. ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 293 K): δ 145.0 (s, 2 C of C₆H₄),

118.7 (s, 2 *C*H of C₆H₄), 109.2 (s, 2 *C*H of C₆H₄), 42.1 (d, $J_{C-P} = 13.5$ Hz, 2 *C*H₂ of 2 P*C*H₂), 32.5 (d, $J_{C-P} = 23.1$ Hz, 4 *C* of 4 ^{*t*}Bu), 29.8 (d, $J_{C-P} = 14.1$ Hz, 12 *C*H₃ of 4 ^{*t*}Bu) ppm. ³¹P{¹H} NMR (C₆D₆, 162.0 MHz, 293 K): δ 25.6 (s) ppm.

[Co₂{ μ -κ³*P*,*Ge*,*P*-Ge(NCH₂*P*'Bu₂)₂C₆H₄}(CO)₆] (2). Toluene (6 mL) was added to a mixture of 1 (35 mg, 0.070 mmol) and [Co₂(CO)₈] (24 mg, 0.071 mmol). The resulting solution was stirred at room temperature for 1 h. The initial dark red color did not change. Purification by flash chromatography (2 x 5 cm silica gel column packed in hexane) eluting with hexane/CH₂Cl₂ (1:1) furnished compound **2** as a light red solid (33 mg, 60%). Anal. (%) Calcd. for C₃₀H₄₄Co₂GeN₂O₆P₂ (M_W = 781.10 amu): C, 46.13; H, 5.68; N, 3.59; found: C, 46.64; H, 6.47; N, 3.95. (+)-ESI HRMS: m/z = 782.0581 [M]⁺. IR (toluene), v_{CO} 2039 (vs), 2021 (s), 1967 (s), 1945 (s) cm⁻¹. ¹H NMR (C₆D₆, 300.1 MHz, 300 K): δ 6.81 (m, 2 H, 2 CH of C₆H₄), 6.67 (m, 2 H, 2 CH of C₆H₄), 4.29 (dd, J_{H-H} = 14.1 Hz, J_{H-P} = 8.3 Hz, 2 H, 2 CH of PCH₂), 3.17 (t, J_{H-H} = 14.1 Hz, $J_{H,P}$ = 14.1 Hz, 2 H, 2 CH of PCH₂), 1.11 (d, J_{H-P} = 11.8 Hz, 18 H, 6 CH₃ of 2 'Bu), 0.75 (d, J_{H-P} = 12.7 Hz, 18 H, 6 CH₃ of 2 'Bu) ppm. ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 300 K): 205.5 (br, COs), 144.1 (s, 2 C of C₆H₄), 117.9 (s, 2 CH of C₆H₄), 111.5 (s, 2 CH of C₆H₄), 41.9 (d, J_{C-P} = 8.5 Hz, 2 CH₂ of 2 PCH₂), 37.4 (d, J_{C-P} = 8.1 Hz, 2 C of 2 'Bu), 35.2 (d, J_{C-P} = 4.1 Hz, 2 C of 2 'Bu), 30.5 (s, 6 CH₃ of 2 'Bu), 29.8 (d, J_{C-P} = 5.6 Hz, 6 CH₃ of 2 'Bu) ppm. ³¹P{¹H} NMR (C₆D₆, 121.5 MHz, 300 K): δ 149.7 (s) ppm.

 $[Rh{\kappa^2 P,Ge-GeCl(NCH_2P'Bu_2)_2C_6H_4}(cod)]$ (3). Toluene (3 mL) was added to a mixture of 1 (69) mg, 0.140 mmol) and [Rh₂(µ-Cl)₂(cod)₂] (35 mg, 0.070 mmol). The initial orange color changed immediately to dark orange. The solution was stirred at room temperature for 30 min and was evaporated to dryness to give **3** as an orange solid (101 mg, 97%). Anal. (%) Calcd. for $C_{32}H_{56}ClGeN_2P_2Rh$ ($M_W = 741.72$ amu): C, 51.82; H, 7.61; N, 3.78; found: C, 51.86; H, 7.66; N, 3.73. (+)-ESI HRMS: m/z = 738.2365 [M + MeOH – Cl]⁺. ¹H NMR (C₆D₆, 400.5 MHz, 298 K): δ 7.13–7.03 (m, 3 H, 3 CH of C₆H₄), 6.80 (d, J_{H-H} = 7.2 Hz, 1 H, 1 CH of C₆H₄), 6.50–5.00 (m, br, 4 H, 4 CH of cod), 3.95 (dd, $J_{H-H} = 13.2$ Hz, $J_{H-P} = 6.5$ Hz, 1 H, 1 CH of PCH₂), 3.61 (dd, $J_{\text{H-H}} = 13.2$ Hz, $J_{\text{H-P}} = 4.9$ Hz, 1 H, 1 CH of PCH₂), 3.51 (t, $J_{\text{H-H}} = 12.4$ Hz, $J_{\text{H-P}} = 12.4$ Hz 12.4 Hz, 1 H, 1 CH of PCH₂), 2.92 (dd, J_{H-H} = 12.4 Hz, J_{H-P} = 7.9 Hz, 1 H, 1 CH of PCH₂), 2.30–2.10 (m, 2 H of CH_2 of cod), 2.10–1.95 (m, 4 H of 2 CH_2 of cod), 1.95–1.80 (m, 2 H of CH_2 of cod), 1.26 (d, $J_{\text{H-P}}$ = 11.3 Hz, 9 H, 3 CH₃ of 'Bu), 1.15 (d, $J_{H-P} = 10.4$ Hz, 9 H, 3 CH₃ of 'Bu), 0.96 (d, $J_{H-P} = 12.1$ Hz, 9 H, 3 CH₃ of 'Bu), 0.93 (d, $J_{\text{H-P}} = 12.0 \text{ Hz}$, 9 H, 3 C H_3 of 'Bu) ppm. ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 143.9 (d, $J_{C-Rh} = 14.2$ Hz, C of C₆H₄), 140.7 (d, $J_{C-Rh} = 12.8$, C of C₆H₄), 117.4 (s, CH of C₆H₄), 117.1 (s, CH of C₆H₄), 108.9 (s, CH of C₆H₄), 108.9 (s, CH of C₆H₄), 92.8 (m, br, 2 CH of cod), 68.4 (m, br, 2 CH of cod), 39.5 (d, $J_{C-P} = 9.0$ Hz, C of ^tBu), 38.7 (d, $J_{C-P} = 4.2$ Hz, CH₂ of PCH₂), 35.4 (d, $J_{C-P} = 9.7$ Hz, C of ^tBu), 33.8 (d, $J_{C-P} = 29.2$ Hz, CH_2 of PCH₂), 32.5 (d, $J_{C-P} = 23.1$ Hz, C of ^tBu), 32.0 (d, $J_{C-P} = 17.1$ Hz, C of ^tBu), 31.5 (m, 3 CH₃ of ^tBu), 31.3 (s, 2 CH₂ of cod), 30.3 (d, $J_{C-P} = 12.3$ Hz, 3 CH₃ of ^tBu), 30.0 (d, $J_{C-P} = 11.4$ Hz, 3 CH_3 of ^tBu), 29.8 (s, 2 CH_2 of cod), 29.6 (m, 3 CH_3 of ^tBu) ppm. ³¹P{¹H} NMR (C₆D₆, 162.0 MHz, 293 K): δ 84.7 (d, J_{P-Rh} = 147 Hz), 31.6 (s) ppm.

[**Rh**{κ³*P*,*Ge*,*P*-GeCl(NCH₂*P*'Bu₂)₂C₆H₄}(CO)₂] (4). In an NMR tube, a solution of complex **3** (4 mg, 0.006 mmol) in toluene (1 mL) or in C₆D₆ (0.3 mL) was bubbled with carbon monoxide (1 atm) for 10 min. The color changed from dark orange to yellow. The following data of **4** were obtained from solutions maintained under an atmosphere of CO. IR (toluene): v_{CO} 2012 (vs), 1971 (vs) cm⁻¹. ¹H NMR (C₆D₆, 400.1 MHz, 298 K): δ 6.94 (m, 2 H, 2 CH of C₆H₄), 6.83 (m, 2 H, 2 CH of C₆H₄), 3.58 (m, 2 H, 2 CH of PCH₂), 2.99 (m, 2 H, 2 CH of PCH₂), 1.24 (m, 18 H, 6 CH₃ of 2 ^{*t*}Bu), 0.79 (m, 18 H, 6 CH₃ of 2 ^{*t*}Bu) ppm. ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 146.6 (s, 2 C of C₆H₄), 119.6 (s, 2 C H of C₆H₄), 114.7 (s, 2 C H of C₆H₄), 47.2 (br, 2 CH₂ of 2 PCH₂), 37.4 (br, 2 C of 2 ^{*t*}Bu), 36.2 (br, 2 C of 2 ^{*t*}Bu), 30.4 (br, 6 CH₃ of 2 ^{*t*}Bu), 30.0 (br, 6 CH₃ of 2 ^{*t*}Bu) ppm; the Rh(CO)₂ resonance(s) was(were) not observed. ³¹P{¹H} NMR (C₆D₆, 162.0 MHz, 293 K): δ 142.4 (d, *J*_{P-Rh} = 126 Hz) ppm.

[**Rh**{κ³*P*,*Ge*,*P*-GeCl(NCH₂*P*'Bu₂)₂C₆H₄}(CO)] (5). Carbon monoxide was bubbled for 10 min through a solution of complex **3** (37 mg, 0.05 mmol) in toluene (4 mL). The color changed from dark orange to yellow. The solvent was removed under reduced pressure to give **5** as an orange solid (32 mg, 97 %). Anal. (%) Calcd. for C₂₅H₄₄ClGeN₂OP₂Rh (M_W = 661.55 amu): C, 45.39; H, 6.70; N, 4.24; found: C, 45.66; H, 6.76; N, 4.36. (+)-ESI HRMS: $m/z = 659.1338 [M + MeOH - Cl]^+$. IR (toluene): v_{CO} 1963 (vs) cm⁻¹. ¹H NMR (C₆D₆, 400.1 MHz, 298 K): δ 6.92 (m, 2 H, 2 C*H* of C₆H₄), 6.79 (m, 2 H, 2 C*H* of C₆H₄), 3.70 (m, br, 2 H, 2 C*H* of PC*H*₂), 3.42 (m, br, 2 H, 2 C*H* of PC*H*₂), 1.23 (m, 18 H, 6 C*H*₃ of 2 ¹Bu), 0.89 (s, br, 18 H, 6 C*H*₃ of 2 ¹Bu) ppm. ¹³C {¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 146.2 (s, br, 2 C of Ph), 119.2 (s, br, 2 CH of Ph), 114.0 (s, br, 2 CH of Ph), 47.4 (s, br, 2 CH₂ of 2 PCH₂), 37.3 (s, br, 2 C of 2 ¹Bu), 36.0 (s, br, 2 C of 2 ¹Bu), 30.7–29.3 (m, 12 CH₃ of 4 ¹Bu) ppm; the Rh(CO) resonance was not observed. ³¹P {¹H} NMR (C₆D₆, 162.0 MHz, 293 K): δ 126.6 (d, J_{P-Rh} = 144 Hz) ppm.

[PdCl{κ³*P*,*Ge*,*P*-GeCl(NCH₂P'Bu₂)₂C₆H₄] (6). Toluene (4 mL) was added to a mixture of compound 1 (29 mg, 0.060 mmol) and [PdCl₂(MeCN)₂] (15 mg, 0.060 mmol). The resulting orange solution was stirred at room temperature for 1 h. The reaction mixture was vacuum-dried to give **6** as an orange solid (37 mg, 93 %). Anal. (%) Calcd. for C₂₄H₄₄Cl₂GeN₂P₂Pd (M_W = 672.50 amu): C, 42.86; H, 6.59; N, 4.17; found: C, 42.92; H, 6.62; N, 4.15. ¹H NMR (C₆D₆, 400.5 MHz, 293 K): δ 6.90 (m, 2 H, 2 CH of C₆H₄), 6.72 (m, 2 H, 2 CH of C₆H₄), 3.48–3.38 (m, 4 H, 4 CH of PCH₂), 1.28 (m, 18 H, 6 CH₃ of 2 ^{*i*}Bu), 1.14 (m, 18 H, 6 CH₃ of 2 ^{*i*}Bu) ppm. ¹³C {¹H} NMR (C₆D₆, 100.7 MHz, 293 K): δ 144.0 (s, 2 C of C₆H₄), 119.6 (s, 2 CH of C₆H₄), 113.0 (s, 2 CH of C₆H₄), 46.2 (s, 2 CH₂ of PCH₂), 37.9 (s, 2 C of 2 ^{*i*}Bu), 36.8 (s, 2 C of 2 ^{*i*}Bu), 30.5 (s, 6 CH₃ of 2 ^{*i*}Bu), 29.8 (s, 6 CH₃ of 2 ^{*i*}Bu) ppm. ³¹P {¹H} NMR (C₆D₆, 162.1 MHz, 293 K): δ 122.3 (s) ppm.

X-Ray Diffraction Analyses. Crystals of **2**, **3**, **5** and $6 \cdot (C_7H_8)_{1.25}$ were studied by XRD. A selection of crystal, measurement, and refinement data is given in Table S1. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer using CuK α radiation. Empirical absorption corrections were applied using *XABS2*² (for **2**) or the *SCALE3 ABSPACK* algorithm, as

implemented in *CrysAlisPro RED*³ (for **3**, **5** and **6**·(C₇H₈)_{1.25}). The structures were solved with SIR-97.⁴ Isotropic and full matrix anisotropic least square refinements were carried out using *SHELXL*.⁵ The data of **2** were of poor quality [R_1 (on F, $I > 2\sigma(I)$) = 0.093], probably due to twining that could not be satisfactorily treated. Restraints were applied on the thermal parameters of the carbonyl C atoms of **2** due to their tendency to give nonpositive definite ellipsoids. One of the five solvent molecules present in the unit cell of **6**·(C₇H₈)_{1.25} was disordered about a symmetry centre. All non-H atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The *WINGX* program system⁶ was used throughout the structure determinations. The molecular plots were made with *MERCURY*.⁷ CCDC deposition numbers: 1516697 (**2**), 1516698 (**3**), 1516699 (**5**) and 1516700 (**6**·(C₇H₈)_{1.25}).

DFT Calculations. The molecular structure of germylene **1** was optimized using the wB97XD functional,⁸ which includes the second generation of Grimme's dispersion interaction correction⁹ as well as long-range interactions effects. The Stuttgart-Dresden relativistic effective core potential and the associated basis sets (SDD) were used for the Ge atom.¹⁰ The basis set used for the remaining atoms was the cc-pVDZ.¹¹ The stationary point was fully optimized in gas phase and confirmed as energy minimum by analytical calculation of frequencies. The orbital analysis was carried out within the NBO framework.¹² All calculations were carried out with the Gaussian09 package.¹³

References

- 1 Y. Segawa, M. Yamashita and K. Nozaki, J. Am. Chem. Soc., 2009, 131, 9201.
- 2 S. Parkin, B. Moezzi and H. Hope, J. Appl. Crystallogr., 1995, 28, 53.
- 3 CrysAlisPro RED, version 1.171.38.43; Rigaku Oxford Diffraction Ltd., Oxford, UK, 2015.
- 4 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. C. Moliterni,
 G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
- 5 SHELXL-2014: G. M. Sheldrick, Acta Cryst., 2008, A64, 112.
- 6 WINGX, version 2013.3: L. J. Farrugia, J. Appl. Cryst., 2012, 45, 849.
- 7 MERCURY: CSD 3.8 (build RC2), Cambridge Crystallographic Data Centre, Cambridge, UK, 2016.
- 8 J.-D. Chai and M. Head-Gordon, Phys. Chem. Chem. Phys., 2008, 10, 6615.
- 9 (a) S. Ehrlich, J. Moellmann and S. Grimme, *Acc. Chem. Res.*, 2013, 46, 916; (b) S. Grimme, *Comp. Mol. Sci.*, 2011, 1, 211; (c) T. Schwabe and S. Grimme, *Acc. Chem. Res.*, 2008, 41, 569.
- 10 B. Metz, H. Stoll and M. Dolg, J. Chem. Phys., 2000, 113, 2563.
- 11 T. H. Dunning, J. Chem. Phys., 1989, 90, 1007.
- 12 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, NBO 6.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.
- 13 M. J. Frisch, et al., Gaussian 09, revision A.01, Gaussian Inc., Wallingford, CT, 2009.



Figure S1. ¹H (top), ¹³C{¹H} (middle) and ³¹P{¹H} (bottom) NMR spectra (C_6D_6 , 293 K) of $Ge(NCH_2P^tBu_2)_2C_6H_4$ (1).



Figure S2. ¹H (top), ¹³C{¹H} (middle) and ³¹P{¹H} (bottom) NMR spectra (C_6D_6 , 300 K) of [$Co_2{\mu-\kappa^3P,Ge,P-Ge(NCH_2P^tBu_2)_2C_6H_4}(CO)_6$] (**2**).



Figure S3. ¹H (top), ¹³C{¹H} (middle) and ³¹P{¹H} (bottom) NMR spectra (C₆D₆, 298 K) of [Rh{ $\kappa^{2}Ge,P-GeCl(NCH_{2}P'Bu_{2})_{2}C_{6}H_{4}$ }(cod)] (**3**).



Figure S4. ¹H (top), ¹³C{¹H} (middle) and ³¹P{¹H} (bottom) NMR spectra (C_6D_6 , 298 K) of [Rh{ κ^3P , Ge, P-GeCl(NCH₂P^tBu₂)₂C₆H₄}(CO)₂] (**4**).



Figure S5. ¹H (top), ¹³C{¹H} (middle) and ³¹P{¹H} (bottom) NMR spectra (C_6D_6 , 298 K) of [Rh{ κ^3P , Ge, P-GeCl(NCH₂P^tBu₂)₂C₆H₄](CO)] (**5**).



Figure S6. ¹H (top), ¹³C{¹H} (middle) and ³¹P{¹H} (bottom) NMR spectra (C₆D₆, 293 K) of [PdCl{ $\kappa^{3}P,Ge,P-GeCl(NCH_{2}P^{t}Bu_{2})_{2}C_{6}H_{4}$] (6).



Figure S7. Two views of the DFT-optimized molecular structure of germylene **1**. Selected interatomic distances (Å) and angles (°): Ge1–N1 1.901, N1–C1 1.386, N1–C2 1.453, C2–P1 1.875, C1–C1' 1.420, Ge1…P1 3.362, N1–Ge1–N1' 83.34, Ge1–N1–C2 126.71.



NBO Atomic Charges

Wiberg Bond Indices

Figure S8. NBO atomic charges for selected atoms (left) and Wiberg Bond Indices between selected atoms (right) of germylene **1** (the molecule has an idealized twofold symmetry).



Figure S9. P lone pair (left) to $\sigma^*(Ge-N)$ (right) donor-acceptor orbital interactions responsible for the weak P…Ge interaction found in germylene **1**.



Figure S10. Molecular structure of compound **2** (20% displacement ellipsoids, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Co1–Ge1 2.413(3), Co1–P1 2.261(4), Co2–Ge1 2.439(3), Co2–P2 2.258(5), Ge1–N1 1.84(1), Ge1–N2 1.89(1), P1–C4 1.89(1), P1–C8 1.89(1), P1–C9 1.85(2), P2–C16 1.87(1), P2–C20 1.90(1), P2–C24 1.91(2), N1–C9 1.46(2), N1–C10 1.40(2), N2–C15 1.40(2), N2–C16 1.46(2), C10–C15 1.42(2), N1–Ge1–N2 86.5(5), N1–Ge1–Co1 102.7(4), N2–Ge1–Co1 123.8(4), N1–Ge1–Co2 123.3(4), N2–Ge1–Co2 102.7(3), Co1–Ge1–Co2 116.0(1).



Figure S11. Molecular structure of compound **3** (30% displacement ellipsoids, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Rh1–C25 2.210(3), Rh1–C26 2.202(3), Rh1–C29 2.213(3), Rh1–C30 2.219(3), Rh1–P1 2.3757(7), Rh1–Ge1 2.4144(3), Ge1–N1 1.856(2), Ge1–N2 1.869(2), Ge1–Cl1 2.2931(8), P1–C4 1.886(3), P1–C8 1.896(3), P1–C9 1.867(3), P2–C16 1.855(3), P2–C20 1.892(3), P2–C24 1.888(3), N1–C9 1.434(4), N1–C10 1.380(4), N2–C15 1.396(3), N2–C16 1.456(4), C10–C15 1.419(4), C26–C25 1.376(5), C30–C29 1.381(5), P1–Rh1–Ge1 82.05(2), N1–Ge1–N2 85.5(1), N1–Ge1–Cl1 104.55(8), N2–Ge1–Cl1 98.68(8), N1–Ge1–Rh1 106.59(7), N2–Ge1–Rh1 142.98(7), Cl1–Ge1–Rh1 111.23(2).



Figure S12. Molecular structure of compound **5** (30% displacement ellipsoids, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Rh1–C101 1.883(3), Rh1–P1 2.3420(6), Rh1–P2 2.3327(6), Rh1–Ge1 2.3596(3), Ge1–N1 1.853(2), Ge1–N2 1.864(2), Ge1–Cl1 2.2213(7), P1–C4 1.883(3), P1–C8 1.886(3), P1–C9 1.902(3), P2–C16 1.899(3), P2–C24 1.887(3), P2–C20 1.883(3), O101–C101 1.139(4), N1–C9 1.460(3), N1–C10 1.404(3), N2–C15 1.404(3), N2–C16 1.460(3), C10–C15 1.423(4), C101–Rh1–P1 99.37(8), C101–Rh1–P2 99.58(8), P1–Rh1–Ge1 80.46(2), P2–Rh1–Ge1 80.91(2), P1–Rh1–P2 151.46(2), C101–Rh1–Ge1 179.11(9), N1–Ge1–N2 91.15(9), N1–Ge1–Cl1 104.24(7), N2–Ge1–Cl1 105.42(7), N1–Ge1–Rh1 108.25(7), N2–Ge1–Rh1 108.28(7), C11–Ge1–Rh1 131.95(2).



Figure S13. Molecular structure of compound **6** (20% displacement ellipsoids, H atoms omitted for clarity). Only one of the two analogous molecules contained in the asymmetric unit is shown. Selected bond distances (Å) and angles (°): Pd1–Cl2 2.3946(7), Pd1–P1 2.3689(6), Pd1–P2 2.3936(6), Pd1–Ge1 2.2777(3), Ge1–N1 1.843(2), Ge1–N2 1.834(2), Ge1–Cl1 2.1604(8), P1–C4 1.881(3), P1–C8 1.888(3), P1–C9 1.898(3), P2–C16 1.898(3), P2–C24 1.877(3), P2–C20 1.867(3), N1–C9 1.462(3), N1–C10 1.419(3), N2–C15 1.407(4), N2–C16 1.457(3), C10–C15 1.418(4), Cl2–Pd1–P1 101.04(2), Cl2–Pd1–P2 102.75(2), P1–Pd1–Ge1 80.60(2), P2–Pd1–Ge1 79.79(2), P1–Pd1–P2 149.36(2), Cl2–Pd1–Ge1 168.84(2), N1–Ge1–N2 92.47(9), N1–Ge1–Cl1 112.18(7), N2–Ge1–Cl1 106.14(8), N1–Ge1–Pd1 111.75(7), N2–Ge1–Pd1 113.06(7), Cl1–Ge1–Pd1 118.20(3).

	2	3	5	6 ⋅ (C ₇ H ₈) _{1.25}
formula	C ₃₀ H ₄₄ Co ₂ GeN ₂ O ₆ P ₂	C ₃₂ H ₅₆ ClGeN ₂ P ₂ Rh	C ₂₅ H ₄₄ ClGeN ₂ OP ₂ Rh	C ₂₄ H ₄₄ Cl ₂ GeN ₂ P ₂ Pd·1.25(C ₇ H ₈)
fw	781.06	741.67	661.51	787.61
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic
space group	<i>P</i> bca	<i>P</i> 21/c	<i>P</i> 21/c	<i>P</i> –1
<i>a</i> , Å	17.295(1)	14.5188(2)	9.9709(1)	11.7387(6)
b, Å	17.5482(8)	17.9914(2)	20.7798(3)	17.267(1)
<i>c</i> , Å	22.8262(9)	13.3164(2)	14.2744(2)	18.697(1)
α , deg	90	90	90	74.296(5)
β , deg	90	92.922(1)	98.872(1)	80.993(4)
γ, deg	90	90	90	80.308(4)
V, Å ³	6927.5(7)	3473.90(8)	2922.17(7)	3571.6(4)
Z	8	4	4	4
<i>F</i> (000)	3216	1544	1360	1626
$D_{\text{calcd}}, \text{ g cm}^{-3}$	1.498	1.418	1.504	1.465
μ, mm ⁻¹ (Cu Kα)	9.660	6.650	7.859	7.499
cryst size, mm	0.13 x 0.10 x 0.06	0.13 x 0.05 x 0.05	0.11 x 0.08 x 0.05	0.15 x 0.15 x 0.10
<i>Т</i> , К	145(2)	151(2)	152(2)	149(2)
θ range, deg	3.87 to 69.71	3.05 to 68.62	3.79 to 69.67	3.85 to 69.81
min./max. h, k, l	–15/15, –20/16, –27/18	–17/17, –21/21, –16/12	–11/11, –24/23, –14/17	-14/14, -20/20, -22/21
no. collected refins	10802	18304	14287	43518
no. unique reflns	4632	6419	5396	13241
no. refins with $l > 2\sigma(l)$	3180	5805	4857	11788
no. params/restraints	376/0	364/0	310/0	757/99
GOF (on F^2)	1.058	1.040	1.020	1.020
R_1 (on F, $I > 2\sigma(I)$)	0.093	0.031	0.027	0.027
wR_2 (on F^2 , all data)	0.353	0.079	0.067	0.067
min./max. $\Delta \rho$, e Å ⁻³	-1.897/1.517	-0.553/1.478	-0.706/1.099	-0.691/0.601

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

 Table S2. DFT-optimized atomic coordinates for compound 1.

Ge	0.000200	-0.560500	-0.000600
Р	3.337200	-0.962000	-0.065200
Ν	1.246200	0.859800	-0.212400
С	0.696900	2.129900	-0.136500
С	2.665900	0.734700	-0.495100
Н	3.233500	1.500000	0.062200
Н	2.858800	0.923800	-1.565100
С	0.680000	4.549400	-0.153100
Н	1.212000	5.493800	-0.279000
С	4.776800	-1.069900	-1.312600
С	4.008300	-0.670700	1.697900
С	1.369900	3.347300	-0.300000
Н	2.431900	3.362400	-0.545700
С	5.735700	-2.189000	-0.885400
Н	6.434700	-2.412900	-1.709100
Н	5.196900	-3.118400	-0.641600
Н	6.340900	-1.902300	-0.012800
C	4.387000	-2.039100	2.288100
Н	4.642200	-1.924100	3.355400
Н	5.256200	-2.487600	1.787800
H	3.549800	-2.750200	2.214900
C	2.829800	-0.117100	2.519900
Н	1.955700	-0.786400	2.478600
н	2.509300	0.880200	2.184300
H	3.134300	-0.033000	3.576800
C II	4.101300	-1.490600	-2.631400
н	4.862100	-1.594400	-3.423800
п	3.303700	-0.747000	-2.977400
п С	5.301000	-2.454500	-2.323200
L L	5.195100	0.291000	1.820000
п u	1 096900	1 272400	2.094000
п	6 106000	_0 116100	1 371000
п С	5 576100	-0.110100	1.571000
ц	6 092500	0.218700	-0.655600
н	4 944300	1 037600	-0.033000
н	6 345400	0 029800	-2 325500
P	-3 337100	-0 962300	0 065200
N	-1 246000	0.302500	0.003200
C	-0.696900	2.129800	0.136700
c C	-2 665600	0 734200	0 495000
H	-3.233400	1.499600	-0.062100
Н	-2.858300	0.923300	1.565100
C	-0.680500	4.549200	0.153800
H	-1.212800	5,493500	0.279800
С	-4.776600	-1.070000	1.312700
С	-4.008600	-0.670500	-1.697700
С	-1.370200	3.346900	0.300500
Н	-2.432300	3.361800	0.545900
С	-5.735900	-2.188900	0.885500
Н	-6.434900	-2.412600	1.709000
Н	-5.197500	-3.118300	0.641300
Н	-6.341100	-1.901600	0.012900
С	-4.387700	-2.038600	-2.288200
Н	-4.642900	-1.923300	-3.355600
Н	-5.257000	-2.487000	-1.788100
Н	-3.550700	-2.750000	-2.215200
С	-2.830100	-0.117000	-2.519800
Н	-1.956300	-0.786500	-2.479000
Н	-2.509200	0.880200	-2.184000
Н	-3.134900	-0.032400	-3.576600
С	-4.101100	-1.491500	2.631400
Н	-4.861700	-1.595100	3.423800
Н	-3.365100	-0.748200	2.977400

Table S2 (continued). DFT-optimized atomic	С
coordinates for compound 1.	

Н	-3.581000	-2.455200	2.524900
С	-5.193200	0.292100	-1.825700
Н	-5.411800	0.468800	-2.893000
Н	-4.986500	1.272800	-1.369700
Н	-6.106900	-0.115500	-1.369900
С	-5.575400	0.218500	1.557500
Н	-6.091600	0.572800	0.656200
Н	-4.943500	1.037100	1.931500
Н	-6.345000	0.029700	2.325900

Energy= -2027.70392355 hartree