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Cationic Dinuclear Platinum and Palladium Complexes with Bridging Hydrogermylene and Hydrido Ligands

Norio Nakata, Noriko Sekizawa, and Akihiko Ishii*

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama, 338-8570, Japan

Experimental Section

General Procedure. All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a UNICO 650-F Glovebox under an inert atmosphere of argon. Solvents were dried by standard methods and freshly distilled prior to use. Deuterated chloroform ($CDCl_3$) was dried over CaH_2 and degassed by a freeze-thaw cycle prior to use. Melting points were determined on a Mel–Temp capillary tube apparatus and are uncorrected. ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker or AVANCE500T and AVANCE500 (500, 471, and 202 MHz, respectively) spectrometers, and ^{13}C NMR spectra were recorded on a Bruker AVANCE400 (101 MHz) spectrometer using $CDCl_3$ as the solvent at room temperature. IR spectra (solid, KBr) were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. High-resolution mass spectrometry (HRMS) data were recorded by using a Hitachi-Hitec NanoFrontier eLD. [PtH(GeH_2Trip)(dcpe)] **1**[1] and [PdH(GeH_2Trip)(dcpe)] **4**[2] were prepared according to the reported procedures.

Synthesis of [{Pt(dcpe)}$_2$(μ-H)(μ-GeHTrip)]$^+$·[HB(C_6F_5)$_3$]$^-$ (3$^+$·[HB(C_6F_5)$_3$]$^-$). A solution of 0.5 eq. of B(C_6F_5)$_3$ (169.5 mg, 0.331 mmol) in toluene (10 mL) was added to a solution of [PtH(GeH_2Trip)(dcpe)] **1** (617.7 mg, 0.653 mmol) in toluene (10 mL) at room temperature to form a yellow solution. The reaction mixture was stirred at same temperature for 30 min. After the removal of the solvent in vacuo, the residue was purified by SiO_2 column chromatography (CH_2Cl_2/hexane = 4/1, R_f = 0.65) to give [{Pt(dcpe)}$_2$(μ-H)(μ-GeHTrip)]$^+$·[HB(C_6F_5)$_3$]$^-$ (**3**$^+$·[HB(C_6F_5)$_3$]$^-$) (366.9 mg, 54%) as yellow crystals and $TripGeH_3$ (78.0 mg, 72%). **3**$^+$·[HB(C_6F_5)$_3$]$^-$: Mp 189–190 ºC (dec.). ^1H NMR (500 Hz, $CDCl_3$): δ –1.79 (tt, $^2J_{P–H}$ = 67, 10, $^1J_{Pt–H}$ = 452 Hz, 2H), –1.07–(–1.04) (m, 2H), 0.10–0.15 (m, 2H), 0.35–0.40 (m, 2H), 0.41–0.46 (m, 2H), 0.53–0.58 (m, 2H), 0.86–0.91 (m, 6H), 1.01 (br, 2H), 1.18–1.95 (m, 68H), 2.36 (s, 8H), 2.66 (br, 2H), 3.44–3.95 (m, br, 1H), 5.32 (s, 1H),

6.78 (t, $^{3}J_{H–H}$ = 8 Hz, 3H), 6.95 (t, $^{3}J_{H–H}$ = 8 Hz, 3H), 7.34 (d, $^{3}J_{H–H}$ = 8 Hz, 3H), 7.76 (d, $^{3}J_{H–H}$ = 7 Hz, 3H), 8.00 (t, $^{2}J_{P–H}$ = 10, $^{2}J_{Pt–H}$ = 135 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 20.2 (br, m, dcpe), 22.8 (m, dcpe), 25.2 (dcpe), 25.75 (dcpe), 25.79 (dcpe), 26.1 (dcpe), 25.3–28.0 (m, dcpe), 26.9 (dcpe), 27.1–27.3 (m, dcpe), 27.8 (dcpe), 29.1 (d, *J* = 17 Hz, dcpe), 29.3 (d, *J* = 16 Hz, dcpe), 30.3 (dcpe), 30.7 (dcpe), 31.6 (dcpe), 33.6 (dcpe), 37.1–37.4 (m, dcpe), 37.8–38.4 (m, dcpe), 55.3 (Trip_CH), 60.4 (br, Trip_C), 123.5 (Trip), 123.6 (Trip), 125.4 (Trip), 127.2 (Trip), 136.5 (br, d, $^{1}J_{C–F}$ = 253 Hz, $HB(C_6F_5)_3$), 137.8 (br, d, $^{1}J_{C–F}$ = 245 Hz, $HB(C_6F_5)_3$), 148.0 (Trip), 148.3 (br, d, $^{1}J_{C–F}$ = 230 Hz, $HB(C_6F_5)_3$), 149.3 (Trip). The ipso carbon atom in the $[HB(C_6F_5)_3]$ was not observed, probably due to coupling with the ^{11}B nucleus, leading to broadening of the peak. $^{11}B\{^{1}H\}$ NMR (99.4 Hz, $CDCl_3$): δ –25.4. $^{19}F\{^{1}H\}$ NMR (471 Hz, $CDCl_3$): δ –133.2 (d, $^{3}J_{F–F}$ = 20 Hz), –164.5 (t, $^{3}J_{F–F}$ = 20 Hz), –167.2 (m). $^{31}P\{^{1}H\}$ NMR (202 Hz, $CDCl_3$): δ 61.4 (s, $^{1}J_{Pt–H}$ = 2232 Hz), 70.8 (s, $^{1}J_{Pt–P}$ = 3848, $^{2}J_{Pt–P}$ = 279, $^{3}J_{P–P}$ = 35 Hz). IR (KBr) (ν, cm^{-1}): 1941 (Ge–H). HRMS (ESI, positive mode) Calcd. for $[C_{72}H_{111}P_4GePt_2]^+$ 1563.6138; Found 1563.6165.

Synthesis of $[\{Pd(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeHTrip)]^+\cdot[HB(C_6F_5)_3]^-$ ($\mathbf{5}^+\cdot[HB(C_6F_5)_3]^-$). A solution of 0.5 eq. of $B(C_6F_5)_3$ (44.2 mg, 0.088 mmol) in toluene (5 mL) was added to a solution of [PdH(GeH_2Trip)(dcpe)] **4** (137.6 mg, 0.160 mmol) in toluene (5 mL) at room temperature to form a yellow solution. The reaction mixture was stirred at same temperature for 30 min. After the removal of the solvent in vacuo, the residue was purified by SiO_2 column chromatography (CH_2Cl_2/hexane = 4/1, R_f = 0.65) to give $[\{Pd(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeHTrip)]^+\cdot[HB(C_6F_5)_3]^-$ ($\mathbf{5}^+\cdot[HB(C_6F_5)_3]^-$) (129.8 mg, 85%) as yellow crystals and $TripGeH_3$ (31.0 mg, 99%). $\mathbf{5}^+\cdot[HB(C_6F_5)_3]^-$: Mp 183–184 ºC (dec.). ^{1}H NMR (500 Hz, $CDCl_3$): δ –5.02 (tt, $^{2}J_{P(\textit{trans})–H}$ = 82, $^{2}J_{P(\textit{cis})–H}$ = 7 Hz, 1H, PtH), (– 0.74)–(–0.66) (m, 2H), 0.33–0.40 (m, 2H), 0.43–0.50 (m, 2H), 0.53–0.64 (m, 4H), 0.82–0.88 (br, 2H), 0.94–1.00 (m, 4H), 1.10–1.52 (m, 32H), 1.63–1.92 (m, 32H), 2.28–2.35 (br, 8H), 2.38–2.42 (br, 2H), 3.44–3.95

(m, br, 1H), 5.32 (s, 1H), 6.79 (t, J = 7 Hz, 3H), 6.95 (t, $^{3}J_{H–H}$ = 7 Hz, 3H), 7.34 (d, $^{3}J_{H–H}$ = 7 Hz, 3H), 7.70 (d, $^{3}J_{H–H}$ =7 Hz, 3H), 8.42 (t, $^{2}J_{P–H}$ = 14 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 19.3 (br, m, dcpe), 22.8 (m, dcpe), 25.3 (dcpe), 25.6 (dcpe), 25.8 (dcpe), 25.9 (dcpe), 26.5 (d, J = 46 Hz, dcpe), 27.2 (d, J = 55 Hz, dcpe), 27.0–28.0 (m, dcpe), 28.7 (dcpe), 28.9 (dcpe), 29.4 (dcpe), 30.5 (d, J = 33 Hz, dcpe), 30.8 (d, J = 34 Hz, dcpe), 32.0 (dcpe), 33.2 (dcpe), 36.0–36.3 (m, dcpe), 37.2–37.8 (m, dcpe), 55.0 (Trip_CH), 61.0 (t, J = 6 Hz, Trip_C), 123.59 (Trip), 123.60 (Trip), 124.9 (Trip), 126.4 (Trip), 136.4 (br, d, $^{1}J_{C–F}$ = 244 Hz, $HB(C_6F_5)_3$), 137.7 (br, d, $^{1}J_{C–F}$ = 248 Hz, $HB(C_6F_5)_3$), 147.8 (Trip), 148.7 (br, d, $^{1}J_{C–F}$ = 250 Hz, $HB(C_6F_5)_3$), 148.7 (Trip). The ipso carbon atom in the $[HB(C_6F_5)_3]$ was not observed, probably due to coupling with the ^{11}B nucleus, leading to broadening of the peak. $^{11}B\{^{1}H\}$ NMR (99.4 Hz, $CDCl_3$): δ –25.4. $^{19}F\{^{1}H\}$ NMR (471 Hz, $CDCl_3$): δ –133.2 (d, $^{3}J_{F–F}$ = 20 Hz), –164.5 (t, $^{3}J_{F–F}$ = 20 Hz), –167.2 (m). $^{31}P\{^{1}H\}$ NMR (202 Hz, $CDCl_3$): δ 58.0 (d, $^{2}J_{P–P}$ = 21 Hz), 72.9 (d, $^{2}J_{P–P}$ = 21 Hz). IR (KBr) (ν, cm^{-1}): 1924 (Ge–H). HRMS (ESI, positive mode) Calcd. for $[C_{72}H_{111}P_4GePd_2]^+$ 1385.4912; Found. 1385.4950.

Synthesis of $[\{Pt(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeClTrip)]^+\cdot[HB(C_6F_5)_3]^-$ ($\mathbf{7}^+\cdot[HB(C_6F_5)_3]^-$). $\mathbf{3}^+\cdot[HB(C_6F_5)_3]^-$ (24.2 mg, 0.012 mmol) was dissolved in $CHCl_3$ (2.5 mL) and the pale yellow solution was stirred at 60 °C. After 2 days, the solvent was evaporated to give almost pure $[\{Pt(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeClTrip)]^+\cdot[HB(C_6F_5)_3]^-$ ($\mathbf{7}^+\cdot[HB(C_6F_5)_3]^-$) in quantitative yield as yellow crystals. $\mathbf{7}^+\cdot[HB(C_6F_5)_3]^-$: Mp 237–238 ˚C (dec.). ^{1}H NMR (500 Hz, $CDCl_3$): δ –2.34 (tt, $^{2}J_{P(trans)–H}$ = 66, $^{2}J_{P(cis)–H}$ = 10Hz, $^{1}J_{Pt–H}$ = 449 Hz, 1H), (–1.00)–(–0.92) (m, 2H), 0.19–0.28 (m, 2H), 0.30–0.35 (m, 4H), 0.44–0.52 (m, 2H), 0.84–0.91 (m, 4H), 0.98–1.09 (m, 4H), 1.17–2.02 (m, 68H), 2.26–2.29 (m, br, 4H), 2.35–2.38 (br, 4H), 2.95–3.00 (m, 2H), 3.45–3.96 (br, 1H), 5.31 (s, 1H), 6.37 (t, $^{3}J_{H–H}$ = 7 Hz, 1H), 6.92 (t, $^{3}J_{H–H}$ = 7 Hz, 1H), 6.99–7.05 (m, 4H), 7.21 (d, $^{3}J_{H–H}$ = 8 Hz, 1H), 7.36–7.39 (m, 3H), 8.50 (d, $^{3}J_{H–H}$ = 7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 19.9 (m, dcpe), 22.9 (m, dcpe), 25.0

(dcpe), 25.9 (dcpe), 26.1 (dcpe), 26.3–27.6 (m, dcpe), 26.86 (dcpe), 26.88 (dcpe), 27.2–27.4 (m, dcpe), 29.2 (d, J = 55 Hz, dcpe), 29.9 (d, J = 55 Hz, dcpe), 30.4 (dcpe), 30.9 (dcpe), 31.8 (dcpe), 32.2 (dcpe), 37.2–37.6 (m, dcpe), 37.6–38.2 (m, dcpe), 55.0 (Trip_CH), 62.9 (t, J = 12 Hz, Trip_C), 123.3 (Trip), 123.4 (Trip), 123.8 (Trip), 123.9 (Trip), 124.2 (Trip), 125.2 (Trip), 126.0 (Trip), 126.8 (Trip), 127.0 (Trip), 136.4 (br, d, $^{1}J_{C–F}$ = 246 Hz, $HB(C_6F_5)_3$), 137.7 (br, d, $^{1}J_{C–F}$ = 244 Hz, $HB(C_6F_5)_3$), 144.1 (Trip), 146.9 (Trip), 148.2 (br, d, $^{1}J_{C–F}$ = 240 Hz, $HB(C_6F_5)_3$), 148.4 (Trip), 148.7 (Trip). $^{11}B\{^{1}H\}$ NMR (99.4 Hz, $CDCl_3$): δ –25.4. $^{19}F\{^{1}H\}$ NMR (471 Hz, $CDCl_3$): δ –133.2 (d, $^{3}J_{F–F}$ = 20 Hz), –164.5 (t, $^{3}J_{F–F}$ = 20 Hz), –167.2 (m). $^{31}P\{^{1}H\}$ NMR (202 Hz, $CDCl_3$): δ 61.9 (s, $^{1}J_{Pt–P}$ = 2256 Hz), 66.8 (d, J = 6, $^{1}J_{Pt–P}$ = 3913, $^{2}J_{Pt–P}$ = 242, $^{2}J_{P–P}$ = 44 Hz). HRMS (ESI, positive mode) Calcd. for $[C_{72}H_{110}P_4ClGePt_2]^+$ 1597.5749; Found. 1597.5755.

Synthesis of $[\{Pd(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeClTrip)]^+\cdot[HB(C_6F_5)_3]^-$ ($\mathbf{8}^+\cdot[HB(C_6F_5)_3]^-$). $\mathbf{5}^+\cdot[HB(C_6F_5)_3]^-$ (16.8 mg, 0.009 mmol) was dissolved in $CHCl_3$ (2.5 mL) and the pale yellow solution was stirred at 60 °C. After 15 min, the solvent was evaporated to give almost pure $[\{Pd(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeClTrip)]^+\cdot[HB(C_6F_5)_3]^-$ ($\mathbf{8}^+\cdot[HB(C_6F_5)_3]^-$) in quantitative yield as yellow crystals. $\mathbf{8}^+\cdot[HB(C_6F_5)_3]^-$: Mp 203–205 ˚C (dec.). ^{1}H NMR (500 Hz, $CDCl_3$): δ –5.57 (tt, $^{2}J_{P(trans)–H}$ = 81, $^{2}J_{P(cis)–H}$ = 5 Hz, 1H), (–0.95)–(–0.89) (m, 2H), 0.24–0.38 (m, 6H), 0.44–0.51 (m, 2H), 0.68–0.75 (br, 2H), 0.84–0.91 (m, 2H), 1.01–1.11 (m, 4H), 1.17–1.59 (m, 38H), 1.77–2.22 (m, 38H), 2.78–2.83 (br, m, 2H), 3.45–3.96 (br, 1 H), 5.32 (s, 1H), 6.40 (br, m, 1H), 6.94 (br, m, 1H), 7.02 (br, m, 4H), 7.23 (d, $^{3}J_{H–H}$ = 7 Hz, 1H), 7.34 (br, m, 3H), 8.41 (br, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 19.4 (m, dcpe), 21.8 (m, dcpe), 25.0 (dcpe), 25.8 (2C, dcpe), 26.0 (dcpe), 26.2 (dcpe), 26.9 (d, J = 4 Hz, dcpe), 27.3–27.5 (m, dcpe), 25.6–27.8 (m, dcpe), 29.2 (d, J = 23 Hz, dcpe), 29.5 (d, J = 21 Hz, dcpe), 30.9 (dcpe), 31.3 (dcpe), 32.2 (dcpe), 32.6 (dcpe), 36.4–36.8 (m, dcpe), 36.8–37.5 (m, dcpe), 54.8 (Trip_CH), 63.3 (t , J = 12 Hz, Trip_C), 123.0 (Trip), 123.7 (Trip), 123.95 (Trip), 123.99 (Trip), 125.2 (Trip), 125.3 (Trip), 126.0 (Trip), 126.7 (Trip), 136.4 (br, d, $^{1}J_{C–F}$ = 251 Hz, $HB(C_6F_5)_3$), 137.7

(br, d, $^{1}J_{C-F}$ = 245 Hz, $HB(C_6F_5)_3$), 144.7 (Trip), 147.2 (Trip), 148.3 (br, d, $^{1}J_{C-F}$ = 245 Hz, $HB(C_6F_5)_3$), 148.2 (Trip), 148.3 (Trip). $^{11}B\{^{1}H\}$ NMR (99.4 Hz, $CDCl_3$): δ –25.4. $^{19}F\{^{1}H\}$ NMR (471 Hz, $CDCl_3$): δ –133.2 (d, $^{3}J_{F-F}$ = 20 Hz), –164.5 (t, $^{3}J_{F-F}$ = 20 Hz), –167.2 (m). $^{31}P\{^{1}H\}$ NMR (202 Hz, $CDCl_3$): δ 62.5 (d, $^{3}J_{P-P}$ = 26 Hz), 70.6 (d , $^{3}J_{P-P}$ = 26 Hz). HRMS (ESI, positive mode) Calcd. for $[C_{72}H_{110}P_4ClGePd_2]^+$ 1419.4522; Found. 1419.4562.

X-Ray Crystallographic Analyses of $3^+\cdot[HB(C_6F_5)_3]^-$, $7^+\cdot[HB(C_6F_5)_3]^-$, and 8^+ $[HB(C_6F_5)_3]^-$. Yellow single crystals of $\mathbf{3}^+\cdot[HB(C_6F_5)_3]^-$ and $\mathbf{8}^+\cdot[HB(C_6F_5)_3]^-$ were grown by slow evaporation of their saturated CH_2Cl_2 solution at room temperature. Yellow single crystals of $\mathbf{7}^+\cdot[HB(C_6F_5)_3]^-$ were grown by slow evaporation of its saturated C_6H_5F solution at room temperature. The intensity data were collected at 100 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX–97)[3]. Hydrogen atoms except the GeH hydrogen of $\mathbf{3}^+\cdot[HB(C_6F_5)_3]^-$ were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystallographic data and details of refinement for $\mathbf{3}^+\cdot[HB(C_6F_5)_3]^-$, $\mathbf{7}^+\cdot[HB(C_6F_5)_3]^-$, and $\mathbf{8}^+$ $[HB(C_6F_5)_3]^-$ are summarized in Table S1.

Table S1. Crystallographic Data and Details of Refinement for $\mathbf{3}^{+}\cdot[HB(C_6F_5)_3]^{-}$, $\mathbf{7}^{+}\cdot[HB(C_6F_5)_3]^{-}$, and $\mathbf{8}^{+}$ $[HB(C_6F_5)_3]^{-}$.

	$\mathbf{3}^{+}\cdot[HB(C_6F_5)_3]^{-}$	$\mathbf{7}^{+}\cdot[HB(C_6F_5)_3]^{-}$	$\mathbf{8}^{+}\cdot[HB(C_6F_5)_3]^{-}$
Formula	$C_{90}H_{112}BF_{15}GeP_4Pt_2$	$C_{90}H_{111}BClF_{15}GeP_4Pt_2$	$C_{96}H_{116}BClF_{16}GeP_4Pd_2$
Formula weight	2076.26	2110.70	2029.42
Color	Yellow	Yellow	Yellow
Crystal size/mm	0.07 × 0.07 × 0.03	0.09 × 0.09 × 0.08	0.10 × 0.08 × 0.08
Temperature / K	100	100	100
Crystal system	triclinic	triclinic	orthorhombic
Space group	*P*-1	*P*-1	$Pna2_1$
a / Å	13.4478(11)	13.4568(16)	24.942(3)
b / Å	18.2478(15)	18.179(2)	32.139(4)
c / Å	18.4257(16)	18.421(2)	11.1842(15)
α / deg.	92.5150(10)	92.6870(10)	90
β / deg.	106.0260(10)	105.9720(10)	90
γ / deg.	97.2910(10)	96.8460(10)	90
V / Å^3	4295.9(6)	4286.5(9)	8966(2)
Z	2	2	4
D_{calcd} / g cm^{-3}	1.605	1.635	1.503
no. of unique data	15657	16406	15938
no. of parameters	1026	1035	1149
no. of restraints	2	2	181
R_1 ($I > 2\sigma(I)$)	0.0335	0.0383	0.0537
wR_2 (all data)	0.0780	0.1019	0.1288
GOF	1.021	1.018	1.014

References

1. N. Nakata, S. Fukazawa, and A. Ishii, *Organometallics*, 2009, **28**, 534.
2. N. Nakata, S. Fukazawa, N. Kato, and A. Ishii, *Organometallics*, 2011, **30**, 4490.
3. G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

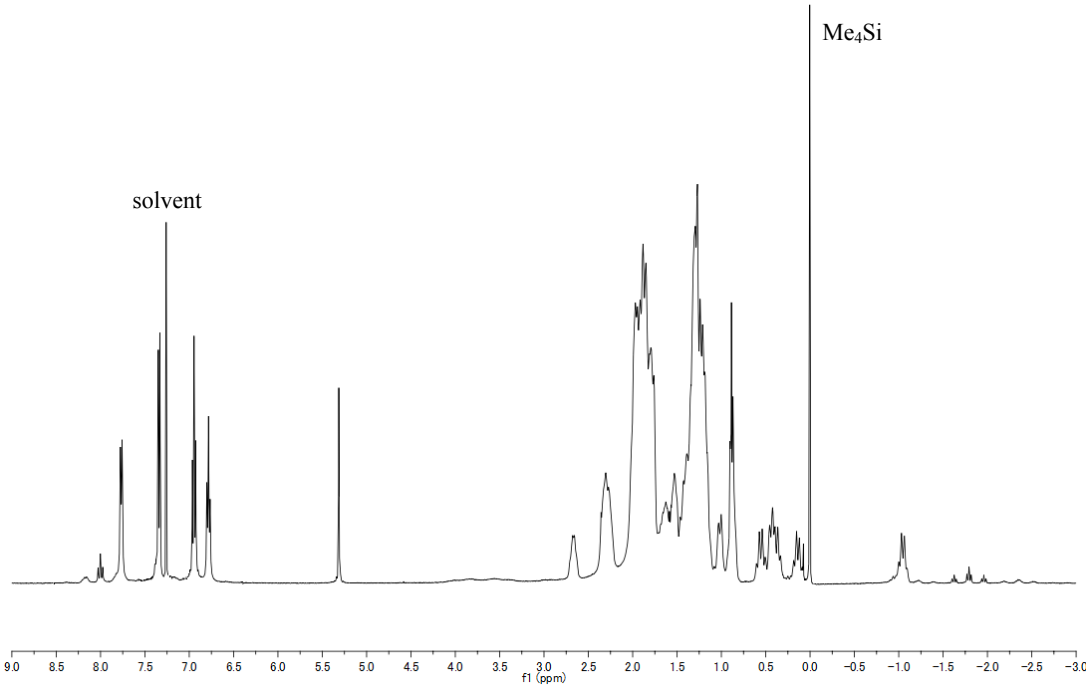


Fig. S1 ^{1}H NMR chart of [{Pt(dcpe)}$_2$(μ-H)(μ-GeHTrip)]$^+$ (**3**$^+$) in $CDCl_3$.

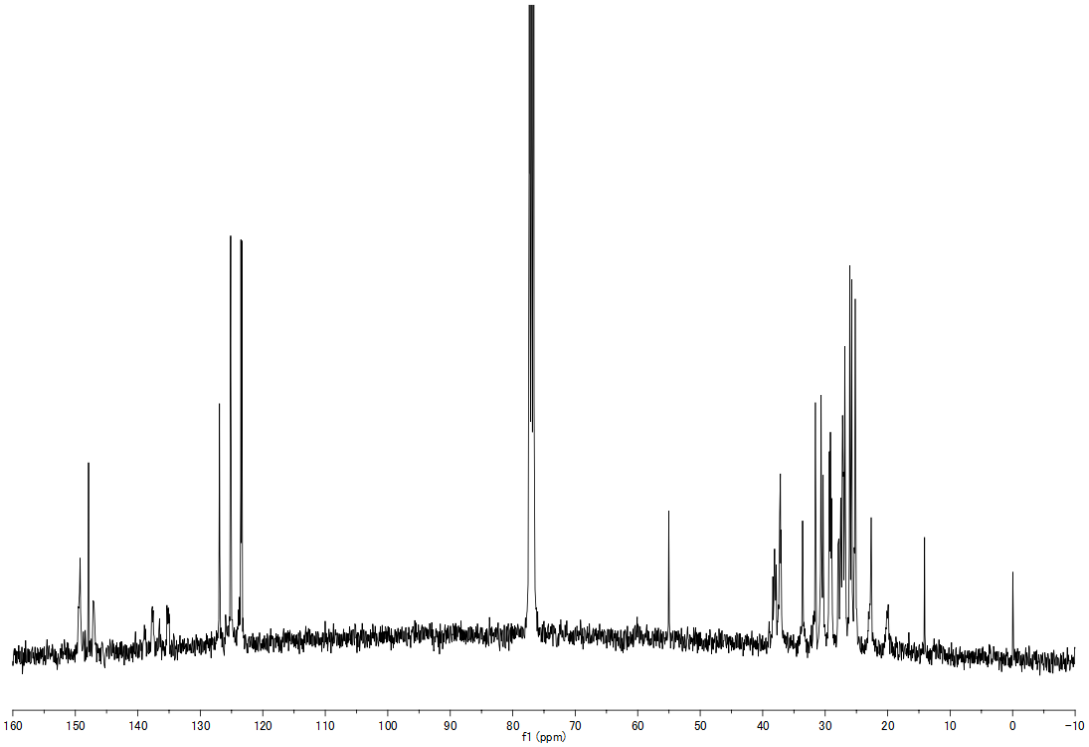


Fig. S2 ^{13}C{^{1}H} NMR chart of [{Pt(dcpe)}$_2$(μ-H)(μ-GeHTrip)]$^+$ (**3**$^+$) in $CDCl_3$.

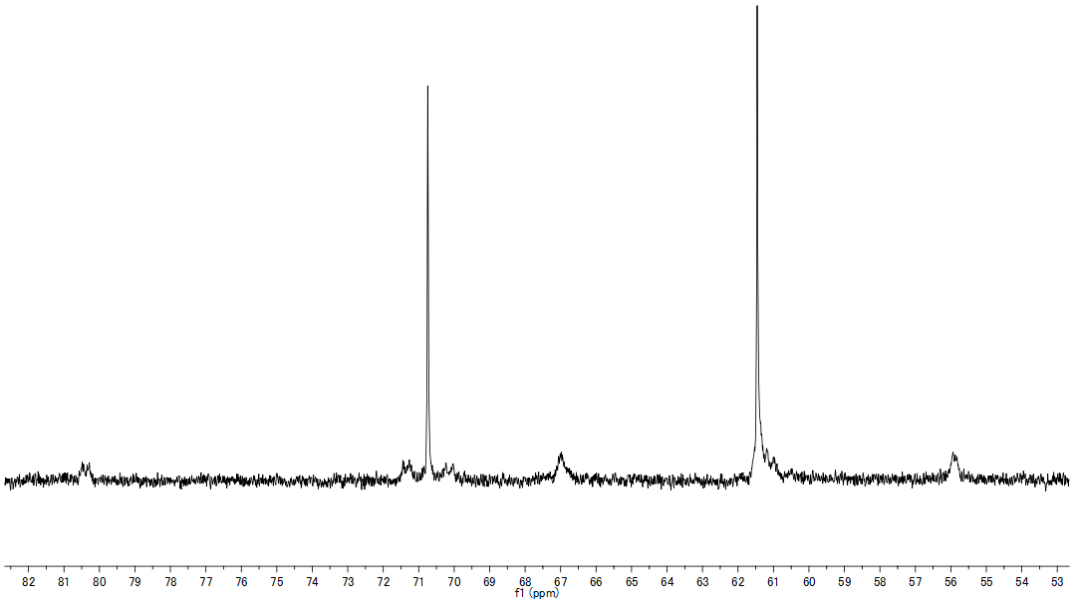


Fig. S3 $^{31}P\{^{1}H\}$ NMR chart of $[\{Pt(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeHTrip)]^+$ (**3**$^+$) in $CDCl_3$.

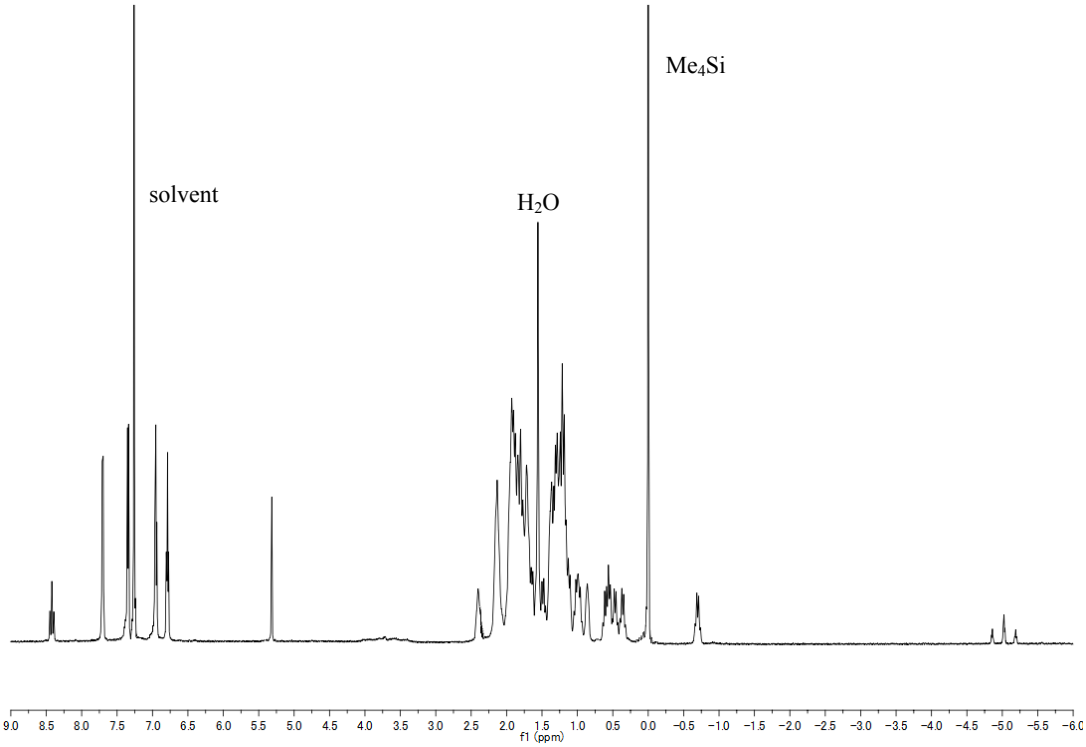


Fig. S4 ^{1}H NMR chart of $[\{Pd(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeHTrip)]^+$ (**5**$^+$) in $CDCl_3$.

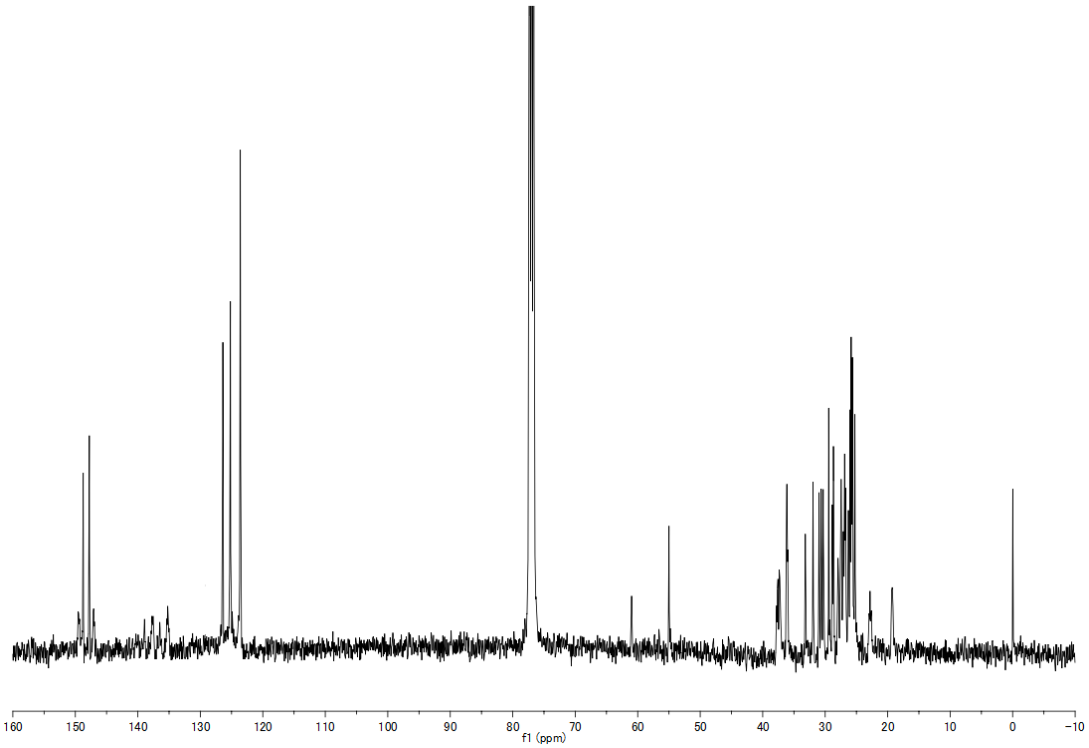


Fig. S5 $^{13}C\{^{1}H\}$ NMR chart of $[\{Pd(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeHTrip)]^+$ (**5**$^+$) in $CDCl_3$.

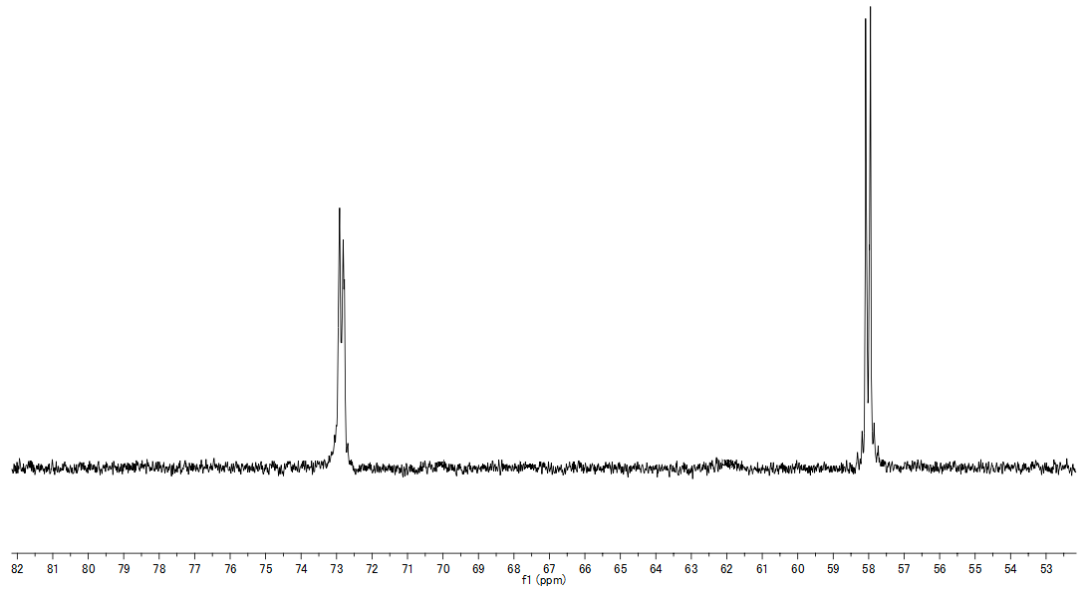


Fig. S6 $^{31}P\{^{1}H\}$ NMR chart of $[\{Pd(dcpe)\}_2(\mu\text{-}H)(\mu\text{-}GeHTrip)]^+$ (**5**$^+$) in $CDCl_3$.

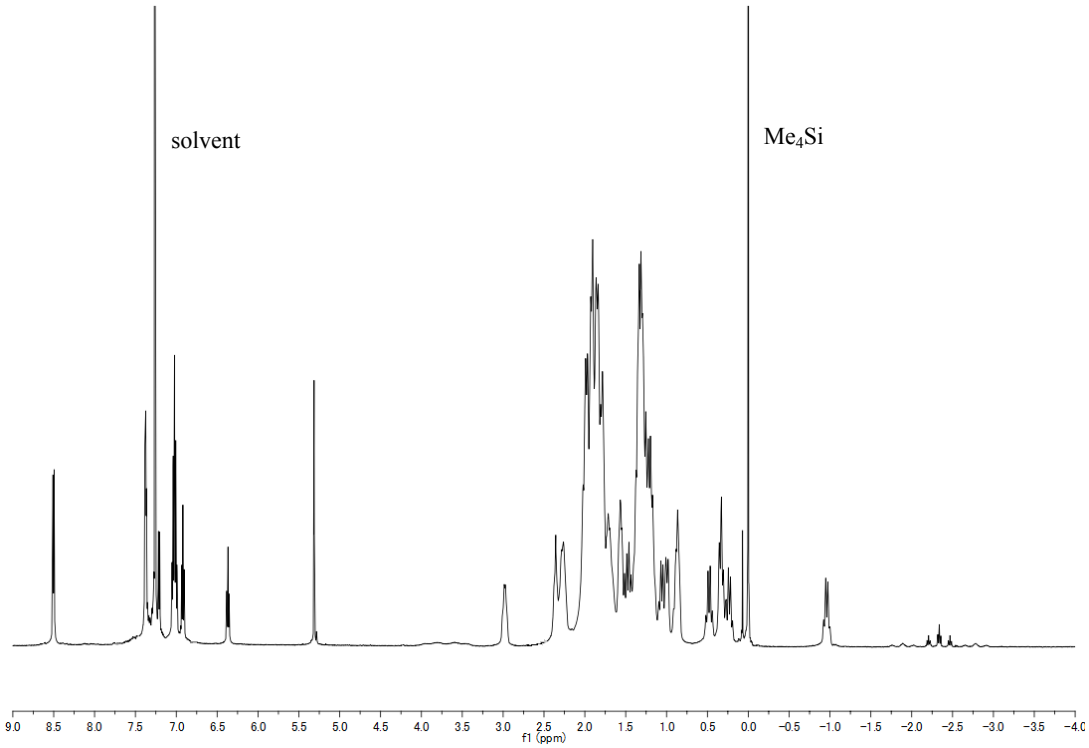


Fig. S7 ^{1}H NMR chart of [{Pt(dcpe)}$_2$(μ-Cl)(μ-GeHTrip)]$^+$ (**7**$^+$) in $CDCl_3$.

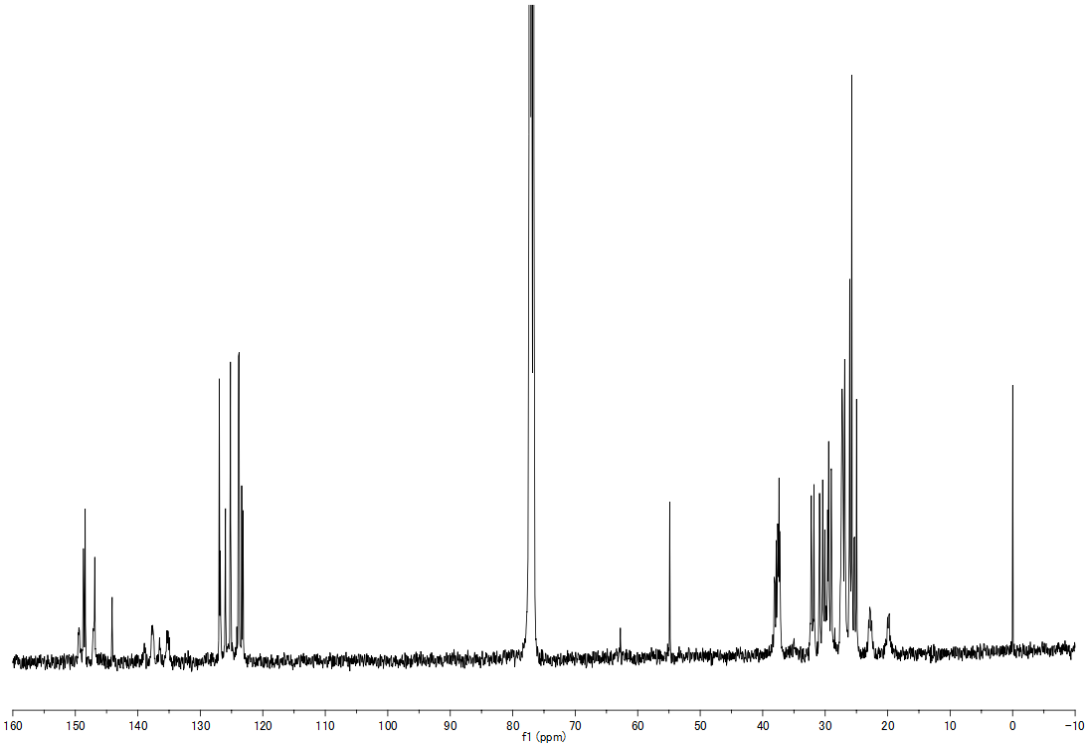


Fig. S8 ^{13}C{^{1}H} NMR chart of [{Pt(dcpe)}$_2$(μ-Cl)(μ-GeHTrip)]$^+$ (**7**$^+$) in $CDCl_3$.

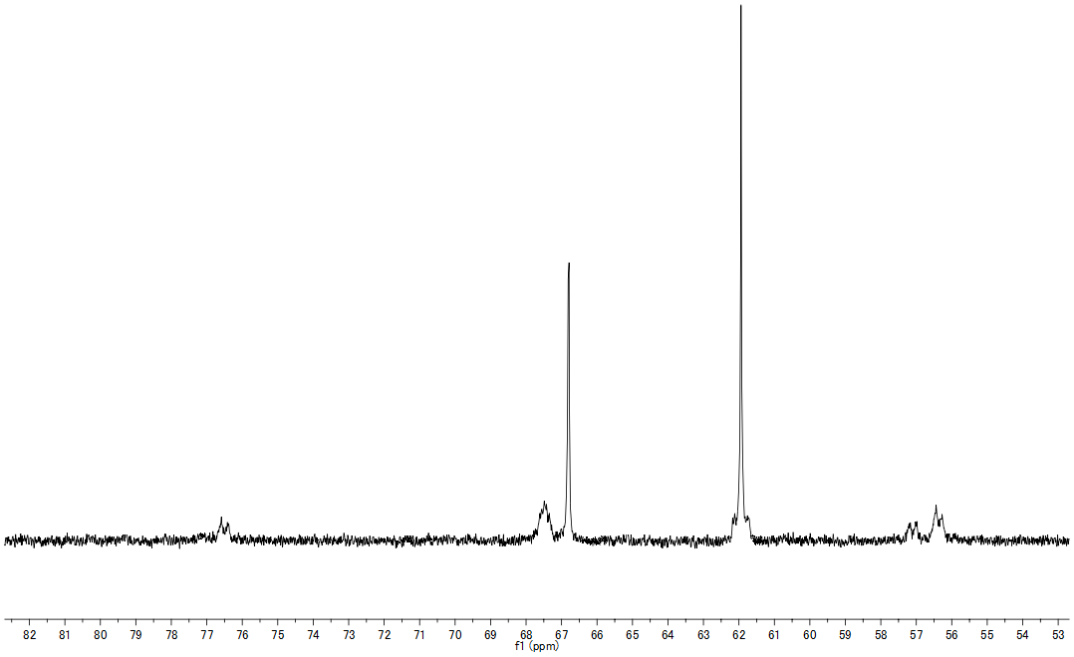


Fig. S9 $^{31}P\{^{1}H\}$ NMR chart of $[\{Pt(dcpe)\}_2(\mu\text{-}Cl)(\mu\text{-}GeHTrip)]^+$ (**7**$^+$) in $CDCl_3$.

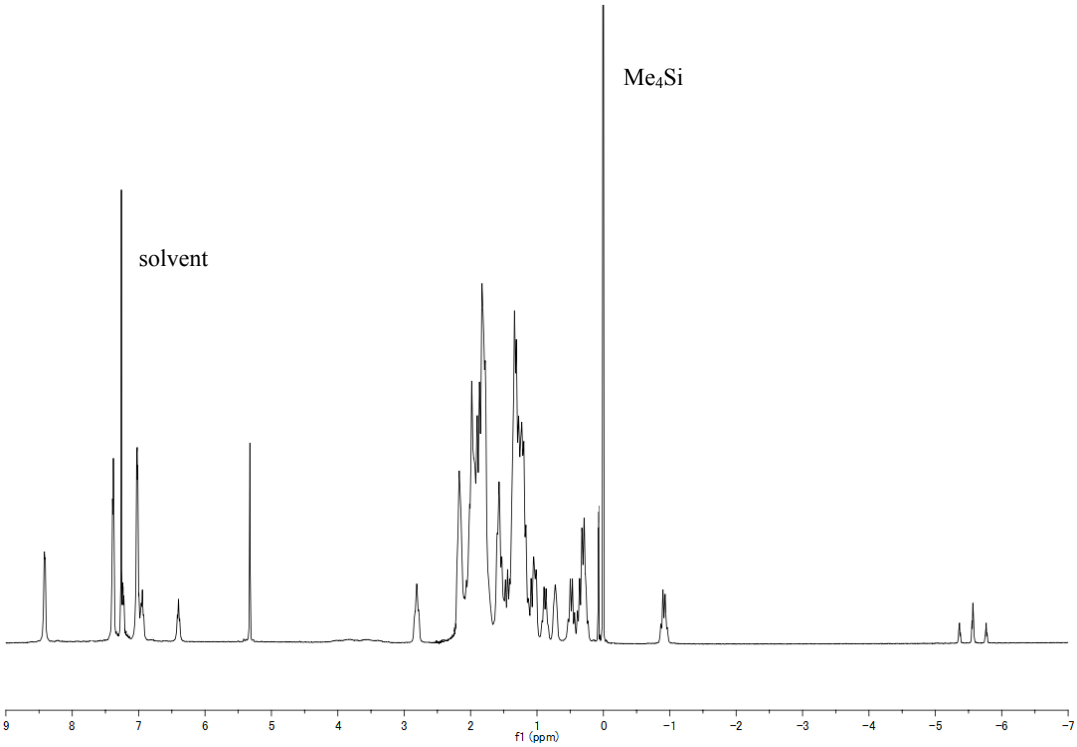


Fig. S10 ^{1}H NMR chart of $[\{Pd(dcpe)\}_2(\mu\text{-}Cl)(\mu\text{-}GeHTrip)]^+$ (**8**$^+$) in $CDCl_3$.

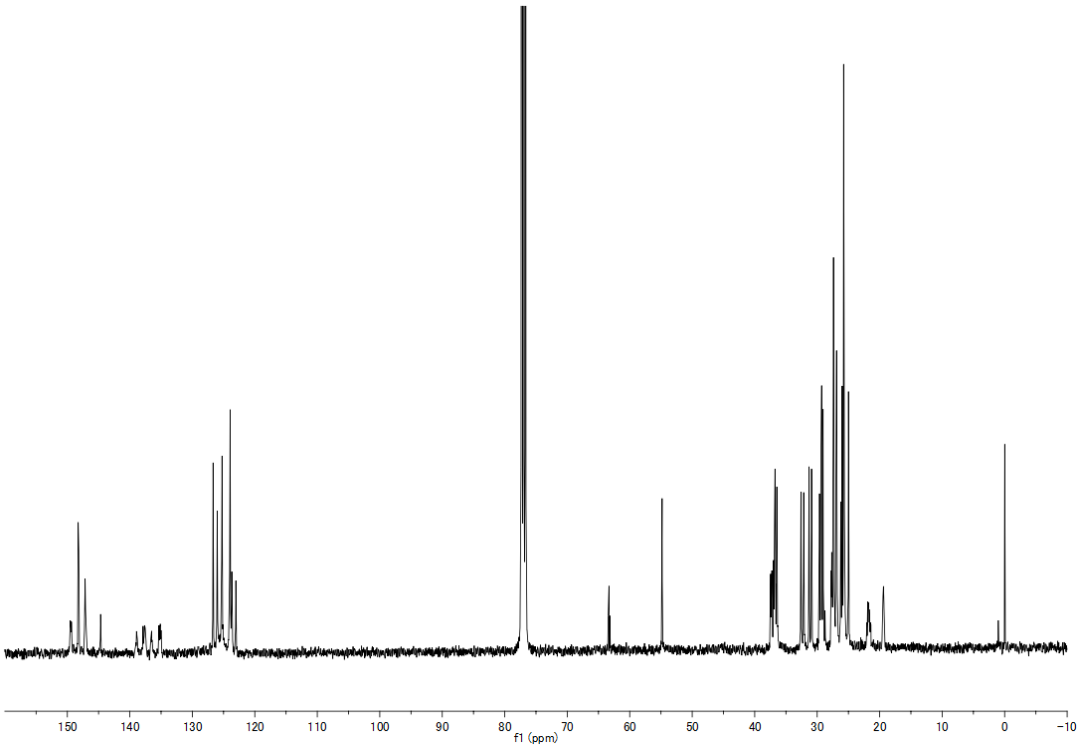


Fig. S11 $^{13}C\{^{1}H\}$ NMR chart of $[\{Pd(dcpe)\}_2(\mu\text{-}Cl)(\mu\text{-}GeHTrip)]^+$ (**8**$^+$) in $CDCl_3$.

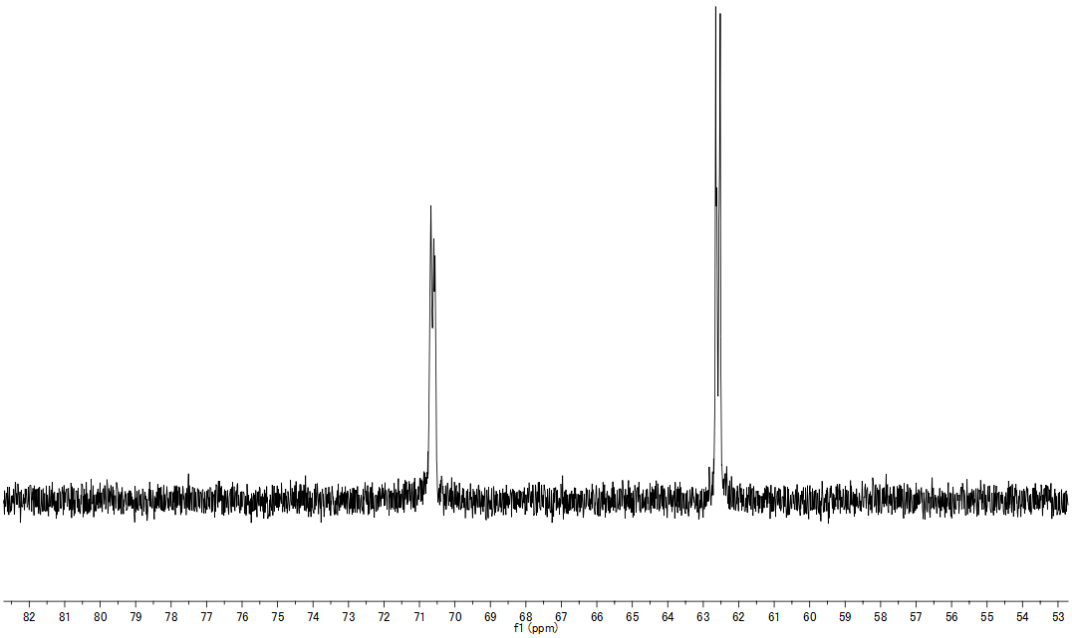
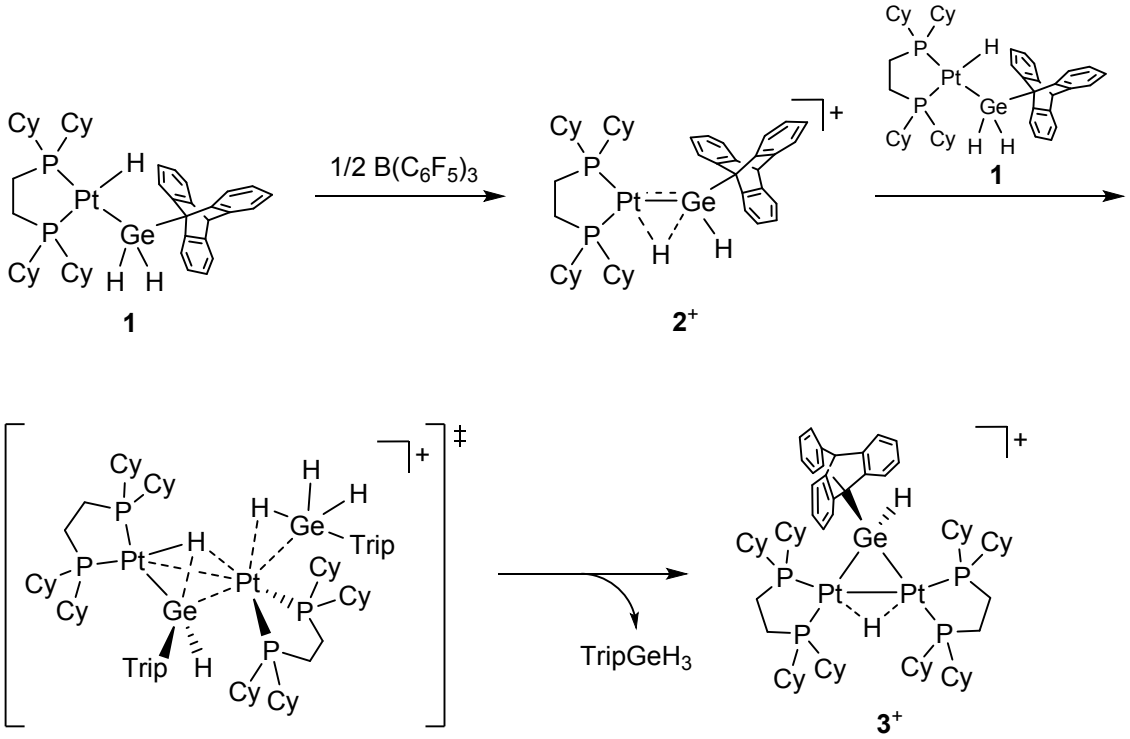


Fig. S12 $^{31}P\{^{1}H\}$ NMR chart of $[\{Pd(dcpe)\}_2(\mu\text{-}Cl)(\mu\text{-}GeHTrip)]^+$ (**8**$^+$) in $CDCl_3$.

Plausible formation mechanism for 3^+



Computational details

Atomic Coordinates for [{Pt($Me_2PCH_2CH_2PMe_2$)}$_2$(μ-H)(μ-GeH^{t}Bu)]$^+$ (**6**$^+$).

Total Energy: –903.722880528 hartree

Pt	0	1.471886	-0.200977	0.073814
Pt	0	-1.447451	-0.182934	0.020144
Ge	0	0.035764	1.780184	-0.211509
P	0	-2.724674	-2.108658	0.552837
P	0	2.587993	-2.293915	0.159701
P	0	-3.321783	0.659898	-0.965002
P	0	3.450460	0.710178	-0.615309
C	0	2.650195	-3.341060	1.670485
C	0	-2.224202	-3.840102	0.180281
C	0	2.135289	-3.490967	-1.163455
C	0	-0.049284	3.248456	1.185956
C	0	-4.021237	2.332310	-0.689882
C	0	4.498314	1.553921	0.634730
C	0	3.509514	1.832421	-2.063927
C	0	-4.317595	-1.919631	-0.395623
C	0	-3.254577	-2.206141	2.312462
C	0	-3.250625	0.532716	-2.795856
C	0	-4.740428	-0.449544	-0.480338
C	0	4.378660	-1.913744	-0.189333
C	0	-0.498995	2.658734	2.527000
C	0	1.348021	3.862649	1.335560
C	0	-1.027695	4.336600	0.731135
C	0	4.502783	-0.731541	-1.156712
H	0	-0.004581	-1.040506	0.621458
H	0	0.130036	2.521147	-1.608026

H	0	3.327515	-4.193936	1.544603
H	0	1.647940	-3.718635	1.896883
H	0	2.983602	-2.742221	2.523848
H	0	-3.036328	-4.546151	0.390005
H	0	-1.359758	-4.111170	0.794688
H	0	-1.939556	-3.928153	-0.872891
H	0	2.786328	-4.372796	-1.148251
H	0	2.208214	-3.007753	-2.142841
H	0	1.097650	-3.811275	-1.028444
H	0	-5.003495	2.414950	-1.169961
H	0	-3.356631	3.089903	-1.114722
H	0	-4.131502	2.527156	0.380726
H	0	5.495211	1.756404	0.226288
H	0	4.596598	0.933442	1.530419
H	0	4.039050	2.501076	0.929250
H	0	4.544916	2.012396	-2.376074
H	0	3.038880	2.787998	-1.814473
H	0	2.953192	1.390257	-2.895853
H	0	-4.141277	-2.324599	-1.400938
H	0	-5.110895	-2.528255	0.056811
H	0	-3.975960	-3.016332	2.470298
H	0	-3.705283	-1.258266	2.621914
H	0	-2.380184	-2.378518	2.948369
H	0	-4.212279	0.806529	-3.245485
H	0	-2.990490	-0.487059	-3.095055
H	0	-2.472335	1.202220	-3.174635
H	0	-5.097746	-0.097767	0.496673
H	0	-5.571592	-0.319498	-1.185543
H	0	4.855324	-1.675548	0.770514
H	0	4.891856	-2.798949	-0.585812
H	0	-0.527941	3.444349	3.297457
H	0	0.183846	1.875585	2.878564

H	0	-1.502160	2.219957	2.461202
H	0	1.316665	4.703546	2.045507
H	0	1.733411	4.258440	0.386338
H	0	2.065627	3.133563	1.728604
H	0	-1.034046	5.164325	1.456889
H	0	-2.055118	3.962852	0.663891
H	0	-0.753358	4.759944	-0.243282
H	0	4.159023	-1.018866	-2.159192
H	0	5.548503	-0.413676	-1.258478

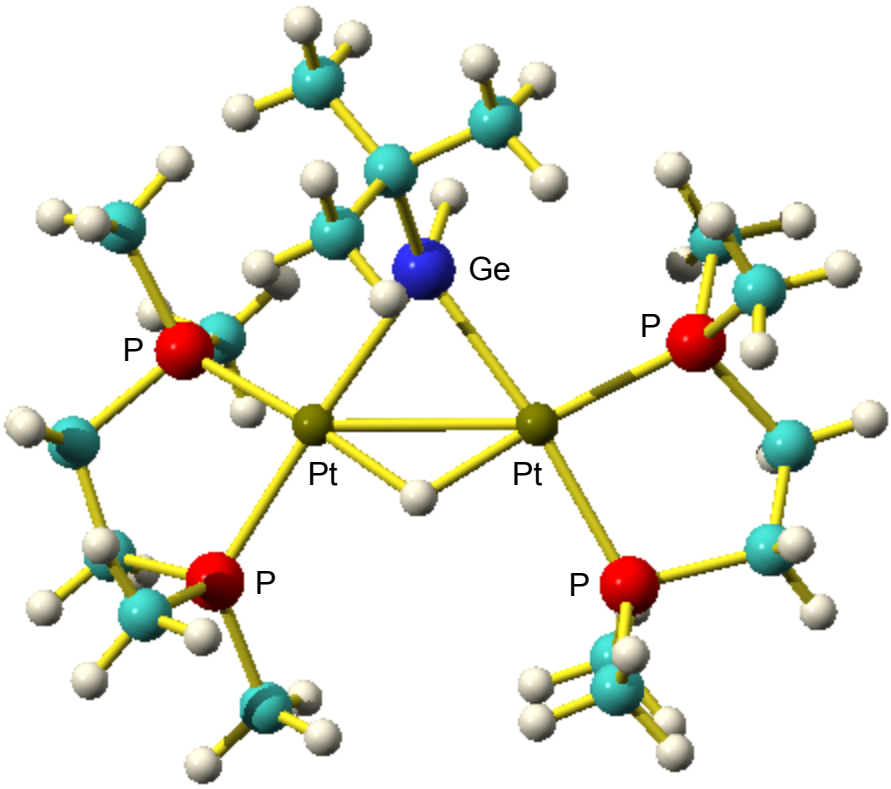


Fig. S13 Optimized geometry of [{Pt($Me_2PCH_2CH_2PMe_2$)}$_2$(μ-H)(μ-GeH^{t}Bu)]$^+$ **6**$^+$ [B3PW91 level with the 6-31G(d) (for H, C, P and Ge) and LANL2DZ (for Pt) basis sets].