# Supplementary Information

# Cumulative 2c-2e vs 3c-2e π-Back Donations: Conformation Preferences in Germylene Gold(I) Complexes

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## 1. Experimental Procedures

General Procedures: All reactions were performed under an atmosphere of nitrogen by using standard Schlenk or dry box techniques. Solvents are used as anhydrous solvents. $^{1}$H, $^{13}$C, and $^{29}$Si NMR spectra were obtained with a Bruker AV 400 instrument at 400 MHz ($^{1}$H NMR), and 101 MHz ($^{13}$C NMR), as well Bruker AV 500 instrument at 500 MHz ($^{1}$H NMR), 126 MHz ($^{13}$C NMR), 99 MHz ($^{29}$Si NMR) and 471 MHz ($^{19}$F NMR) at 298 K. The $^{1}$H and $^{13}$C NMR chemical shifts were referenced to residual $^{1}$H and $^{13}$C of the solvents: $C_6D_6$ ($^{1}$H δ 7.16 and $^{13}$C δ 128.0) and $CDCl_3$ ($^{1}$H δ 7.26 and $^{13}$C δ 77.16). NMR multiplicities are abbreviated as follows: s = singlet, brs = broad singlet, d = doublet, dt = doublet of triplets, t = triplet, and m = multiplet. Coupling constants *J* are given in Hz. **1** was synthesized according to literature procedures.[61] **2a** was synthesized according to literature procedures.[60]

***Synthesis of 2b***

NHCAuCl (312 mg, 0.50 mmol) was added to a 25 mL tetrahydrofuran solution of dialkylgermylene **1** (200 mg, 0.48 mmol) at room temperature. After stirring for 10 hours, the solvent was removed in vacuo, and the residue was washed with *n*-hexane to afford the germylgold **2b** (449 mg) as a white powder in 90% yield.: $^{1}$H NMR (400 MHz, $C_6D_6$): $\delta$= 7.28-7.24 (t, 2H, Ar-*H*), 7.11-7.13 (d, 4H, Ar-*H*), 6.33 (s, 2H, C*H*), 2.61 (m, 4H, C*H*$(CH_3)_2$), 2.35 (m, 2H, C$H_2$), 2.04 (m, 2H, C$H_2$), 1.50 (d, *J* = 1.50 Hz, 12H, CH(C$H_3$)$_2$), 1.05 (d, *J* = 1.05 Hz, 12H, CH(C$H_3$)$_2$), 0.48 (s, 18H, Si(C$H_3$)$_3$), 0.15 (s, 18H, Si(C$H_3$)$_3$); $^{13}$C NMR (126 MHz, $C_6D_6$): $\delta$ = 200.54 ($C^{carbene}$), 145.50 (*C*H), 135.05 (*C*H), 130.81 (*C*H), 124.67 (*C*H), 123.29 (*C*H), 35.57 ($C^{q}$), 29.15 (*C*$H_2$), 25.03 (*C*H), 24.73 (*C*$H_3$), 24.49 (*C*$H_3$), 5.41 (Si(*C*$H_3$)$_3$),4.93 (Si(*C*$H_3$)$_3$); $^{29}$Si NMR (99 MHz, $C_6D_6$): $\delta$ = 3.62, 1.52. HRMS (ESI) m/z: Calcd for $C_{43}H_{76}AuGeN_2Si_4$: 1003.3963 [(M-Cl)]$^{+}$; Found: 1003.3958.

***Synthesis of 3***

**2a** (200 mg, 0.27 mmol) was reacted with an equimolar amount of $AgAl(OC(CF_3)_3)_4$ (290 mg, 0.27 mmol) in chloroform at room temperature for 30 minutes. The reaction mixture gradually changed from colorless to brownish-yellow, forming a brown precipitate. After filtration, concentration, and recrystallization at –35°C, white solid **3** was obtained (160 mg, 31% yield): $^1$H NMR (500 MHz, $C_6D_6$): δ = 2.55 (s, 8H, C$H_2$), 0.31(s, 72H, Si(C$H_3$)$_3$); $^{13}$C NMR (126 MHz, $C_6D_6$): δ = 62.22 ($C^q$), 36.12 ($C$H$_2$), 2.83 (Si($C$H$_3$)$_3$); $^{29}$Si NMR (99 MHz, $C_6D_6$) δ = 0.62; $^{19}$F NMR (471 MHz, $C_6D_6$) δ = –75.38. HRMS (ESI) m/z: Calcd for $C_{32}H_{80}AuGe_2Si_8$: 1033.2503 $[(M+H)]^+$; Found: 1034.2472.

***Synthesis of 4***

$AgAl(OC(CF_3)_3)_4$ (207 mg, 0.19 mmol) was added to a solution of **3b** (200 mg, 0.19 mmol) in $CHCl_3$. The mixture was stirred at room temperature for 30 minutes, turning brownish-yellow with the formation of a gray silver chloride precipitate. After filtration, the filtrate was recrystallized at –35°C to yield white solid **5** (330 mg, 87% yield): $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ = 7.62-7.58 (m, 4H, Ar), 7.45 (d, 2H, $J$ = 8 Hz, Ar), 3.39 (d, 2H, $J$ = 4 Hz, C$H$), 2.67-2.63 (m, 4H, C$H$), 2.40 (s, 4H, C$H_2$), 1.36 (d, $J$ = 1.31 Hz, 12H, CH(C$H_3$)$_2$), 1.26 (d, $J$ = 1.31 Hz, 12H, CH(C$H_3$)$_2$), 0.05 (s, 36H, Si(C$H_3$)$_3$); $^{13}$C NMR (126 MHz, THF-$d_8$): $\delta$ = 189.55 ($C^{carbene}$), 144.44 ($C^q$), 130.09 ($C$H), 124.85 ($C^q$), 123.58 ($C^q$), 121.76 ($C$H) ,118.85 ($C$H), 34.67 ($C^q$), 27.91 ($C$H$_2$), 22.25 ($C$H$_3$), 0.90 (Si($C$H$_3$)$_3$); $^{29}$Si NMR (99 MHz, THF-$d_8$): $\delta$ = 0.04. HRMS (ESI) m/z: Calcd for $C_{43}H_{76}AuGeN_2Si_4$: 1003.3963 $[(M-Al(OR)_4]^+$; Found: 1003.3958.

***Synthesis of 5***

To a solution of NaHMDS (770 mg, 4.1 mmol) in toluene (10 mL) at low temperature, $GeCl_2$·dioxane (500 mg, 2.1 mmol) was added. The reaction mixture was stirred for 2 hours, turning gradually yellow.[65] After filtration and solvent removal

under vacuum, **5** was isolated (793 mg, 96% yield) as ayellow oil; $^{1}$H NMR (400 MHz, $C_6D_6$): $\delta$ = 0.32 (s, 36H, Si (C$H_3$)$_3$).

***Synthesis of 6a***

$PMe_3AuCl$ (157 mg, 0.50 mmol) was added to a solution of **5** (200 mg, 0.50 mmol) in toluene and stirred at room temperature for 12 hours. The resulting solution was filtered, concentrated under reduced pressure, and recrystallized at room temperature to afford colorless solid **6a** (339 mg, 95% yeild); $^{1}$H NMR (400 MHz, $C_6D_6$): $\delta$ = 0.68 (s, 36H, Si(C$H_3$)$_3$), 0.43-0.45 (d, $J$ = 0.44 Hz, 9H, P(C$H_3$)$_3$); $^{13}$C NMR (126 MHz, $C_6D_6$): $\delta$ = 6.90 (Si(*C*H$_3$)$_3$), 14.76 (d, $J$ = 37.8 Hz, P(C$H_3$)$_3$); $^{31}$P NMR (162 MHz, $C_6D_6$): $\delta$ = 7.99. HRMS (ESI) m/z: Calcd for $C_{15}H_{45}AuGeN_2PSi_4Cl$: $[M]^+$ 702.0963; Found: $[C15H45N2AuGeSi4]^+$ 636.1716.

***Synthesis of 6b***

NHCAuCl (316 mg, 0.50 mmol) was slowly added to a toluene solution of **5** (200 mg, 0.50 mmol) and stirred at room temperature for 12 hours. The resulting mixture was filtered, concentrated, and recrystallized at −35 °C to afford colorless solid **6b** (480 mg, 93% yeild): $^{1}$H NMR (400 MHz, $C_6D_6$): $\delta$ = 6.26 (s, 2H, C*H*), 2.62 (m, 4H, C*H*(CH$_3$)$_2$), 1.45 (d, $J$ = 1.44 Hz, 12H, CH(C$H_3$)$_2$), 1.02 (d, $J$ = 1.01 Hz, 12H, CH(C$H_3$)$_2$), 0.44 (s, 36H, Si(C$H_3$)$_3$); $^{13}$C NMR (126 MHz, $C_6D_6$): $\delta$ = 197.12 ($C^{carbene}$), 145.34 (*C*H), 134.97 ($C^q$), 131.05 (*C*H), 124.73 (*C*H), 123.59 ($C^q$), 29.02 (*C*H), 24.70 (*C*H$_3$), 24.26 (*C*H$_3$), 6.93 (Si(*C*H$_3$)$_3$); $^{29}$Si NMR (99 MHz, $CD_3CN$): $\delta$ = 1.30. HRMS (ESI) m/z: Calcd for $C_{12}H_{36}AuClGeN_2Si_4$: 626.0522 $[(M\text{-}NHC)]^+$; Found: 626.2795.

***Synthesis of 7***

An chloroform solution of **6b** (200 mg, 0.19 mmol) was treated with one equivalent of $AgAl(OC(CF_3)_3)_4$ (212 mg, 0.19 mmol) at room temperature for 30 minutes. The reaction mixture turned brown-yellow, accompanied by the formation of a gray silver chloride precipitate. Filtration of the reaction mixture, followed by

recrystallization at -35 °C, afforded colorless crystals of **8** (330 mg, 78% yeild): $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.22 (s, 2H, C*H*), 2.52 (m, 4H, C*H*($CH_3$)$_2$), 1.32 (d, *J* = 1.32 Hz, 12H CH(C*H*$_3$)$_2$), 1.22 (d, *J* = 1.21 Hz, 12H, CH(C*H*$_3$)$_2$), –0.44 (s, 18H, Si(C*H*$_3$)$_3$); $^{13}$C NMR (126MHz, $CDCl_3$): $\delta$ = 187.22 ($C^{carbene}$), 145.36 (*C*H), 133.53 ($C^{q}$), 131.73 (*C*H), 125.10 (*C*H), 122.61 ($C^{q}$), 120.28 (*C*H), 117.95 (*C*H), 31.78 ($C^{q}$), 29.05 (*C*H), 24.73 (*C*H$_3$), 24.11 (*C*H$_3$), 5.25 (Si(*C*H$_3$)$_3$); $^{29}$Si NMR (99 MHz, $CDCl_3$): $\delta$ = 6.77; $^{19}$F NMR (471 MHz, $CDCl_3$): $\delta$ = 75.92. HRMS (ESI) m/z: Calcd for $C_{39}H_{72}AuGeN_4Si_4$: 979.3712 [(M-Al(OR)$_4$)]$^+$; Found: 973.5372; Calcd for $C_{16}O_4AlF_{36}$: 966.9037 [(M-Al(OR)$_4$)]$^-$; Found: 966.9017

***Synthesis of 8***

$AgBF_4$ (72 mg, 0.38 mmol) and **6b** (400 mg, 0.38 mmol) were mixed and stirred in chloroform at room temperature for 30 minutes. The solution turned from colorless to brown-yellow with the formation of a brown precipitate. After filtration to remove AgCl, the filtrate was cooled to –35 °C to afford colorless crystals of **7** (142mg, 42% yeild); $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.48 (m, 2H, C*H*), 7.30-7.26 (m, 4H, C*H*), 7.22 (s, 2H, C*H*), 2.53 (m, 4H, C*H*($CH_3$)$_2$), 1.33 (d, *J* = 1.32 Hz, 12H, CH(C*H*$_3$)$_2$), 1.23 (d, *J* = 1.22 Hz, 12H, CH(C*H*$_3$)$_2$), –0.04 (s, 36H, Si(C*H*$_3$)$_3$); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 195.91 ($C^{carbene}$), 145.64 (*C*H), 133.75 ($C^{q}$), 131.02 (*C*H), 124.48 (*C*H), 123.72 ($C^{q}$), 28.98 (*C*H), 24.80 (*C*H$_3$), 24.23 (*C*H$_3$), 4.89 (Si(*C*H$_3$)$_3$); $^{29}$Si NMR (99 MHz, $CDCl_3$): $\delta$ = 6.77; $^{19}$F NMR (471 MHz, $CDCl_3$): $\delta$ = –109.66. HRMS (ESI) m/z: Calcd for $C_{33}H_{54}AuFGeN_3Si_2$: 837.2718 [(M-F)]$^+$; Found: 837.2608.

## 2. Crystallographic Details

All crystallographic intensity data was collected using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector, and PhotonJet-S microfocus sealed tube X-ray sources for generating Cu Kα radiation (λ = 1.54184 Å). A suitable single crystal identified by microscopy was mounted on a Nylon loop with paratone oil, and then quickly placed onto the instrument. The crystal temperature was held at 173 K using an Oxford Cryosystems CryostreamPlus 800 open-flow $N_2$ cryostat. Reflections were recorded, indexed and corrected for absorption with the *CrysAlis*$^{pro}$ software suit.[68] All structures were solved by intrinsic phasing (ShelXT-2015),[S1, S2] and refined to convergence by full-matrix least squares methods based on $F^2$ (SHELX-2018) [S3] embedded in the Olex2.[S4] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were located at calculated positions or found in the *F*map. CCDC: **2401588, 2401589, 2401590, 2401591, 2401592, 2401593** and **2401594** contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_reCquest/cif.

**Table S1.** X-ray Data for **2b**.

| Parameters | **2b** |
|---|---|
| Empirical formula | $C_{43}H_{76}AuClGeN_2Si_4$ |
| Formula weight | 1038.36 |
| Temperature/K | 170.00 |
| Crystal system | monoclinic |
| space group | $P2_1/c$ |
| a/Å | 28.7462(15) |
| b/Å | 17.8390(8) |
| c/Å | 24.1570(11) |
| α/° | 90 |
| β/° | 101.624(2) |
| γ/° | 90 |
| Volume /Å$^3$ | 12133.7(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.464 |
| μ/mm$^{-1}$ | 6.429 |
| F(000) | 5416.0 |
| Crystal size/mm$^3$ | 0.08 × 0.07 × 0.03 |
| Radiation | GaKα (λ = 1.34139) |
| 2Θ range for data collection/° | 5.398 to 121.714 |
| Index ranges | $-37 \leq h \leq 37$, $-19 \leq k \leq 23$, $-30 \leq l \leq 31$ |
| Reflections collected | 152207 |
| Independent reflections | 27806 [$R_{int}$ = 0.0666, $R_{sigma}$ = 0.0528] |
| Data/restraints/parameters | 27806/76/1199 |
| Goodness-of-fit on $F^2$ | 1.054 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0578, $wR_2$ = 0.1547 |
| Final R indexes [all data] | $R_1$ = 0.0795, $wR_2$ = 0.1683 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.03/-1.31 |

**Table S2.** X-ray Data for **3**.

| Parameters | **3** |
|---|---|
| Empirical formula | $C_{48}H_{80}AlAuF_{36}Ge_2O_4Si_8$ |
| Formula weight | 1998.96 |
| Temperature/K | 170.00 |
| Crystal system | Monoclinic |
| space group | $P2_1/c$ |
| a/Å | 20.9302(13) |
| b/Å | 33.697(2) |
| c/Å | 22.7129(13) |
| α/° | 90 |
| β/° | 94.980(2) |
| γ/° | 90 |
| Volume /Å$^3$ | 15958.6(16) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.664 |
| μ/mm$^{-1}$ | 4.459 |
| F(000) | 7936.0 |
| Crystal size/mm$^3$ | 0.08 × 0.06 × 0.04 |
| Radiation | GaKα (λ = 1.34139) |
| 2Θ range for data collection/° | 4.336 to 121.686 |
| Index ranges | $-27 \leq h \leq 27$, $-43 \leq k \leq 43$, $-29 \leq l \leq 29$ |
| Reflections collected | 280324 |
| Independent reflections | 36620 [$R_{int}$ = 0.0514, $R_{sigma}$ = 0.0333] |
| Data/restraints/parameters | 36620/1643/2230 |
| Goodness-of-fit on F$^2$ | 1.052 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0449, $wR_2$ = 0.1166 |
| Final R indexes [all data] | $R_1$ = 0.0573, $wR_2$ = 0.1245 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.89/-1.15 |

**Table S3**. X-ray Data for **4**.

| Parameters | **4** |
|---|---|
| Empirical formula | $C_{59}H_{76}AlAuF_{36}GeN_2O_4Si_4$ |
| Formula weight | 1970.11 |
| Temperature/K | 170.00 |
| Crystal system | Monoclinic |
| space group | $P2_1/c$ |
| a/Å | 10.6882(6) |
| b/Å | 20.2536(11) |
| c/Å | 36.451(2) |
| α/° | 90 |
| β/° | 90.609(2) |
| γ/° | 90 |
| Volume /Å$^3$ | 7890.3(8) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.658 |
| μ/mm$^{-1}$ | 3.881 |
| F(000) | 3920.0 |
| Crystal size/mm$^3$ | 0.04 × 0.02 × 0.01 |
| Radiation | GaKα (λ = 1.34139) |
| 2Θ range for data collection/° | 4.218 to 107.806 |
| Index ranges | $-12 \leq h \leq 12$, $-24 \leq k \leq 24$, $-43 \leq l \leq 43$ |
| Reflections collected | 63724 |
| Independent reflections | 14393 [$R_{int}$ = 0.1210, $R_{sigma}$ = 0.1367] |
| Data/restraints/parameters | 14393/344/993 |
| Goodness-of-fit on $F^2$ | 1.068 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0782, $wR_2$ = 0.1826 |
| Final R indexes [all data] | $R_1$ = 0.1184, $wR_2$ = 0.2068 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.54/-0.75 |

**Table S4.** X-ray Data for **6a**.

| Parameters | **6a** |
|---|---|
| Empirical formula | $C_{15}H_{45}AuClGeN_2PSi_4$ |
| Formula weight | 701.86 |
| Temperature/K | 170.00 |
| Crystal system | triclinic |
| space group | P-1 |
| a/Å | 10.9157(5) |
| b/Å | 11.3209(5) |
| c/Å | 13.9382(7) |
| α/° | 84.0760(10) |
| β/° | 70.022(2) |
| γ/° | 65.5240(10) |
| Volume /Å$^3$ | 1471.82(12) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.584 |
| μ/mm$^{-1}$ | 9.118 |
| F(000) | 696.0 |
| Crystal size/mm$^3$ | 0.07 × 0.06 × 0.04 |
| Radiation | GaKα (λ = 1.34139) |
| 2Θ range for data collection/° | 5.876 to 121.306 |
| Index ranges | -14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18 |
| Reflections collected | 21905 |
| Independent reflections | 6687 [Rint = 0.0318, Rsigma = 0.0319] |
| Data/restraints/parameters | 6687/65/282 |
| Goodness-of-fit on F$^2$ | 1.067 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0233, wR2 = 0.0567 |
| Final R indexes [all data] | R1 = 0.0258, wR2 = 0.0575 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.22/-0.98 |

**Table S5.** X-ray Data for **6b**.

| Parameters | **6b** |
|---|---|
| Empirical formula | $C_{53}H_{88}AuClGeN_4Si_4$ |
| Formula weight | 1198.64 |
| Temperature/K | 170.00 |
| Crystal system | triclinic |
| space group | P-1 |
| a/Å | 11.4734(4) |
| b/Å | 13.2785(4) |
| c/Å | 19.7989(6) |
| α/° | 86.7530(10) |
| β/° | 81.1060(10) |
| γ/° | 84.3230(10) |
| Volume /Å$^3$ | 2962.84(16) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.344 |
| μ/mm$^{-1}$ | 3.142 |
| F(000) | 1236.0 |
| Crystal size/mm$^3$ | 0.29 × 0.16 × 0.06 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.43 to 50.698 |
| Index ranges | $-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-23 \leq l \leq 22$ |
| Reflections collected | 64553 |
| Independent reflections | 10641 [$R_{int}$ = 0.0325, $R_{sigma}$ = 0.0222] |
| Data/restraints/parameters | 10641/1/599 |
| Goodness-of-fit on F$^2$ | 1.016 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0225, $wR_2$ = 0.0545 |
| Final R indexes [all data] | $R_1$ = 0.0237, $wR_2$ = 0.0553 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.53/-0.88 |

**Table S6.** X-ray Data for **7**.

| Parameters | **7** |
|---|---|
| Empirical formula | $C_{55}H_{72}AlAuF_{36}GeN_4O_4Si_4$ |
| Formula weight | 1946.06 |
| Temperature/K | 250.00 |
| Crystal system | monoclinic |
| space group | $P2_1/n$ |
| a/Å | 17.6176(10) |
| b/Å | 27.1229(15) |
| c/Å | 17.9460(10) |
| α/° | 90 |
| β/° | 109.893(2) |
| γ/° | 90 |
| Volume /Å$^3$ | 8063.6(8) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.603 |
| μ/mm$^{-1}$ | 3.797 |
| F(000) | 3864.0 |
| Crystal size/mm$^3$ | 0.26 × 0.15 × 0.13 |
| Radiation | GaKα (λ = 1.34139) |
| 2Θ range for data collection/° | 5.282 to 121.58 |
| Index ranges | $-22 \leq h \leq 21$, $-35 \leq k \leq 35$, $-23 \leq l \leq 23$ |
| Reflections collected | 118975 |
| Independent reflections | 18565 [$R_{int}$ = 0.0874, $R_{sigma}$ = 0.0730] |
| Data/restraints/parameters | 18565/702/975 |
| Goodness-of-fit on $F^2$ | 1.058 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0651, $wR_2$ = 0.1773 |
| Final R indexes [all data] | $R_1$ = 0.0883, $wR_2$ = 0.1955 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.81/-1.02 |

**Table S7.** X-ray Data for **8**.

| Parameters | **8** |
|---|---|
| Empirical formula | $C_{33}H_{54}AuF_2GeN_3Si_2$ |
| Formula weight | 856.55 |
| Temperature/K | 100.0(2) |
| Crystal system | triclinic |
| space group | P-1 |
| a/Å | 10.6937(12) |
| b/Å | 17.289(2) |
| c/Å | 24.936(3) |
| α/° | 70.706(4) |
| β/° | 78.905(4) |
| γ/° | 81.874(5) |
| Volume /Å$^3$ | 4254.9(9) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.523 |
| μ/mm$^{-1}$ | 6.634 |
| F(000) | 1952.0 |
| Crystal size/mm$^3$ | 0.18 × 0.16 × 0.08 |
| Radiation | GaKα (λ = 1.34138) |
| 2Θ range for data collection/° | 3.306 to 113.964 |
| Index ranges | -13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -31 ≤ l ≤ 30 |
| Reflections collected | 85057 |
| Independent reflections | 17305 [$R_{int}$ = 0.0887, $R_{sigma}$ = 0.0568] |
| Data/restraints/parameters | 17305/58/871 |
| Goodness-of-fit on F$^2$ | 1.058 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0490, w$R_2$ = 0.1275 |
| Final R indexes [all data] | $R_1$ = 0.0599, w$R_2$ = 0.1326 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.66/-2.37 |

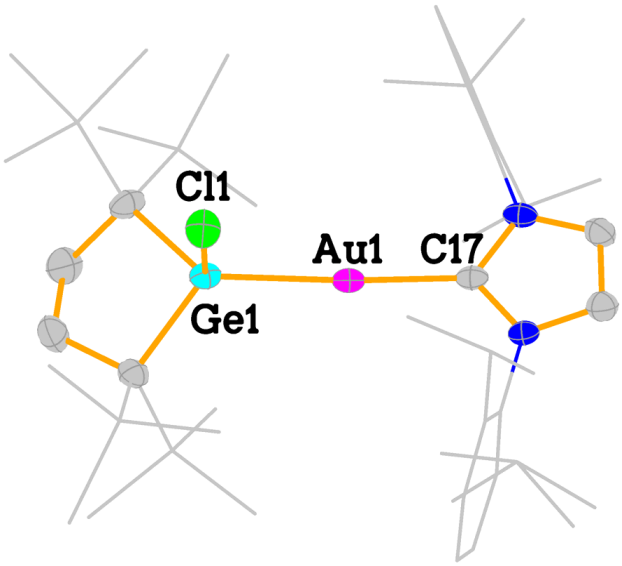


**Fig. S1.** Solid structures of **2b**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

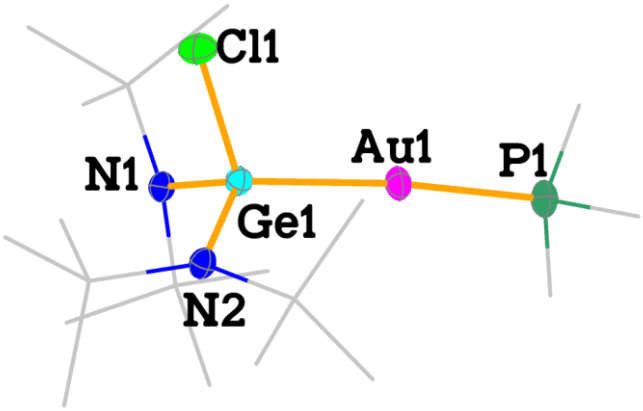


**Fig. S2.** Solid structures of **6a**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

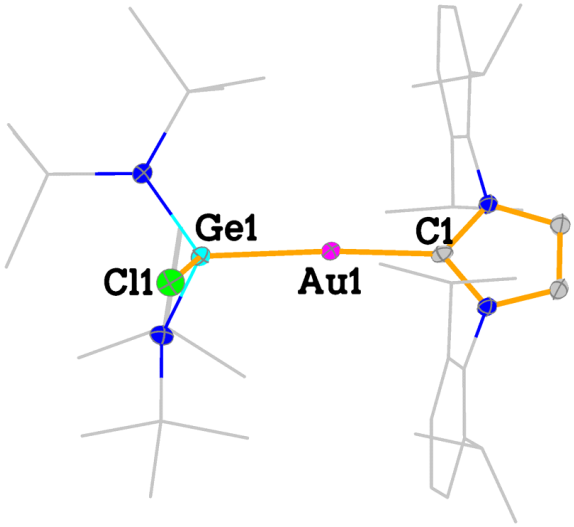


**Fig. S3.** Solid structures of **6b**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

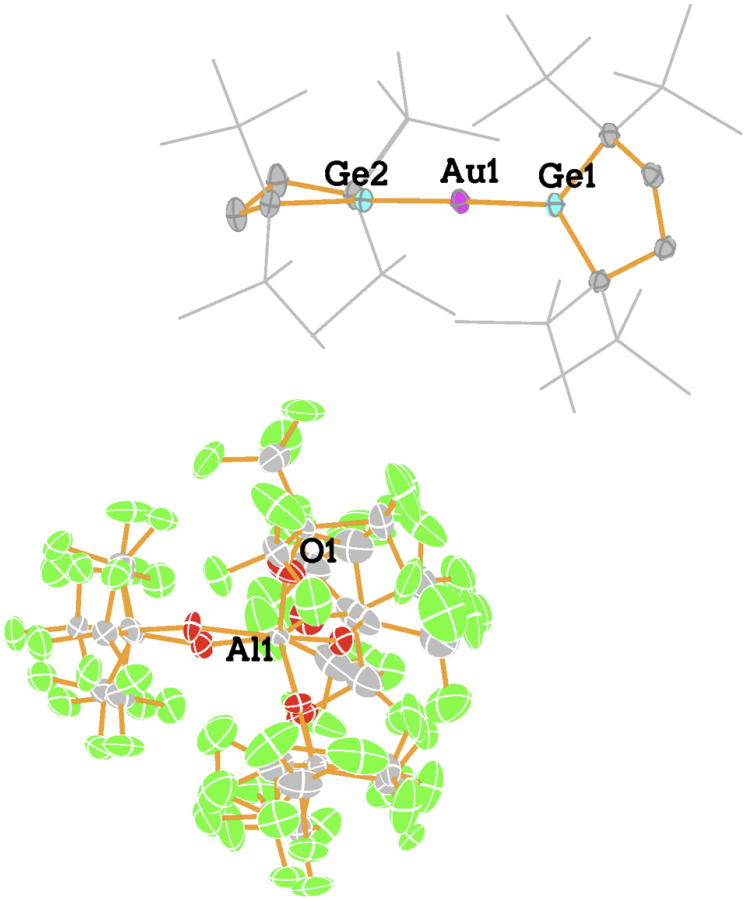


**Fig. S4.** Solid structures of **3**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

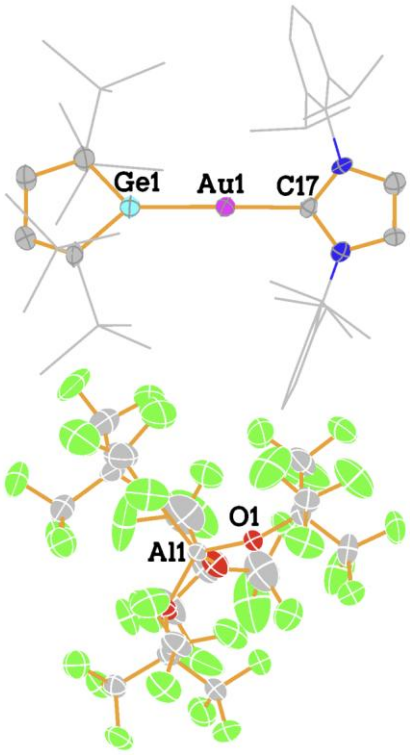


**Fig. S5.** Solid structures of **4**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

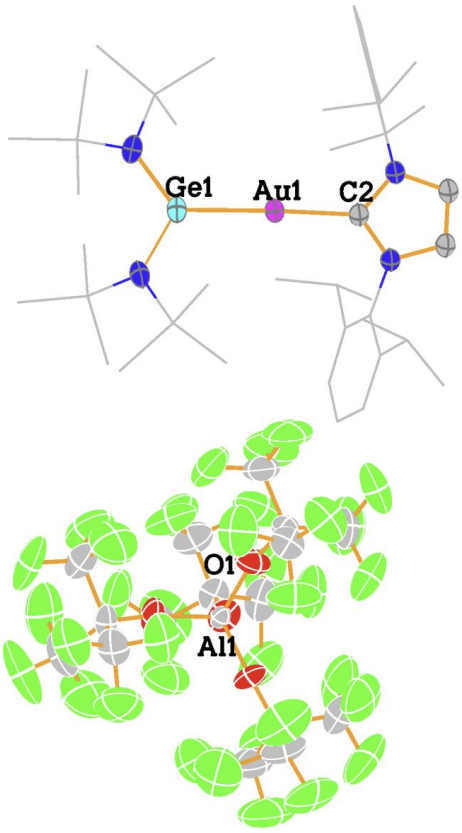


**Fig. S6.** Solid structures of **7**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity.

## 3. Computational Details

All the calculations were performed with the Gaussian 16 program package.[S7] Geometry optimizations and frequency calculations were performed at the level of MN15-D3BJ/def2svp.[S8-S11] Based on the optimized structures, we further carried out the single point calculations to obtain better wavefunctions for the principal interacting orbital (PIO) analysis.[70, 71] In these single-point calculations, all atoms were calculated with def2tzvp basis sets.[S12-13] To compared with the gas phase results, we performed additional PIO analysis in the presence of SMD solvation models.[72] The plots of structures and orbitals were displayed by GaussView 6.0.[S14]

**Workflow for PIO analysis**

First, we carried out single point calculation followed by natural population analysis to obtain the natural atomic orbital (NAO) coefficients and the NAO-based density matrix. [S15]

Second, we divided the complexes into two fragments.

Third, we performed the PIO program to generate a set of orbitals for each fragment that interacts with the other fragment.[70, 71]

**Fragmentation for PIO analysis**

For complex **3**, one of the germylene moieties was treated as one fragment and the remaining part as the other fragment to study the bonding interactions between them.

For complexes **4** and **7**, the Au center was treated as one fragment and the remaining part as the other fragment to study the bonding interactions between them.

**Selected bond lengths for crystal structures and optimized structures**

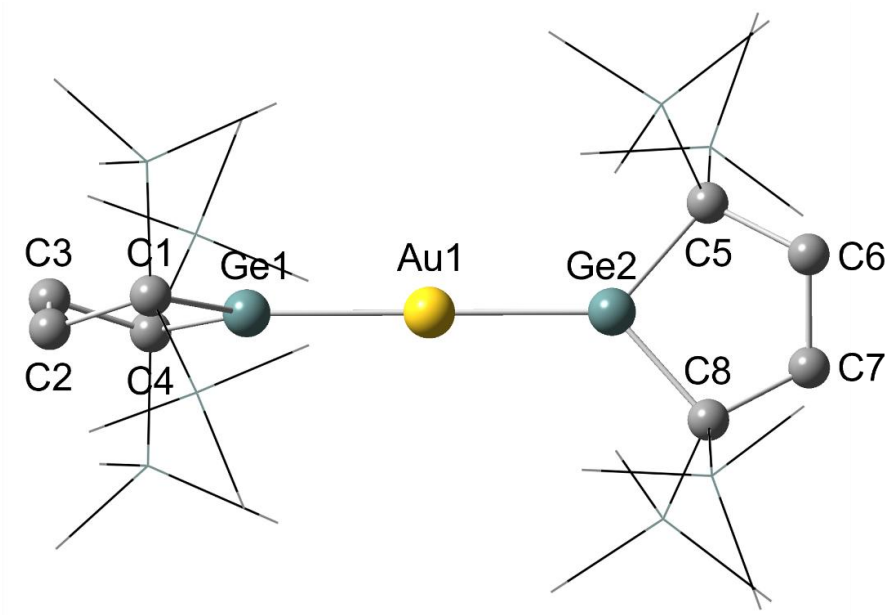


**Fig. S7** Optimized structure of complex **3**. For clarity, the hydrogen atoms are omitted, and the trimethylsilyl moieties are displayed in wireframes.

**Table S9.** Selected bond lengths (Å) for crystal structure and optimized structure (in parentheses, on average) of complex **3**.

| | | | |
|---|---|---|---|
| Au1-Ge1 | 2.41 (2.39) | Au1-Ge2 | 2.41 (2.39) |
| Ge1-C1 | 1.92 (1.93) | C1-C2 | 1.56 (1.57) |
| C2-C3 | 1.54 (1.54) | C3-C4 | 1.56 (1.57) |
| C4-Ge1 | 1.92 (1.93) | Ge2-C5 | 1.92 (1.94) |
| C5-C6 | 1.56 (1.56) | C6-C7 | 1.54 (1.54) |
| C7-C8 | 1.56 (1.56) | C8-Ge2 | 1.92 (1.93) |

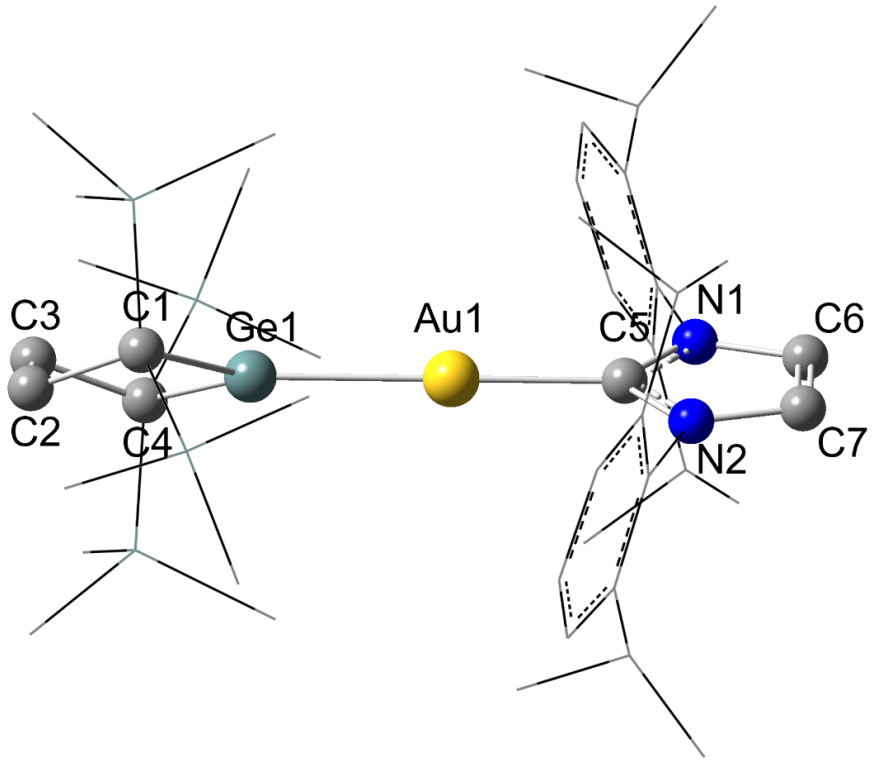


**Fig. S8** Optimized structure of complex **4**. For clarity, the hydrogen atoms are omitted, and the trimethylsilyl moieties as well as the 2,6-diisopropylphenyl moieties are displayed in wireframes.

**Table S10.** Selected bond lengths (Å) for crystal structure and optimized structure (in parentheses) of complex **4**.

| | | | |
|---|---|---|---|
| Au1-Ge1 | 2.40 (2.38) | Au1-C5 | 2.07 (2.07) |
| Ge1-C1 | 1.93 (1.95) | C1-C2 | 1.56 (1.59) |
| C2-C3 | 1.54 (1.53) | C3-C4 | 1.56 (1.57) |
| C4-Ge1 | 1.93 (1.93) | C5-N1 | 1.35 (1.36) |
| N1-C6 | 1.38 (1.39) | C6-C7 | 1.36 (1.33) |
| C7-N2 | 1.38 (1.38) | N2-C5 | 1.35 (1.33) |

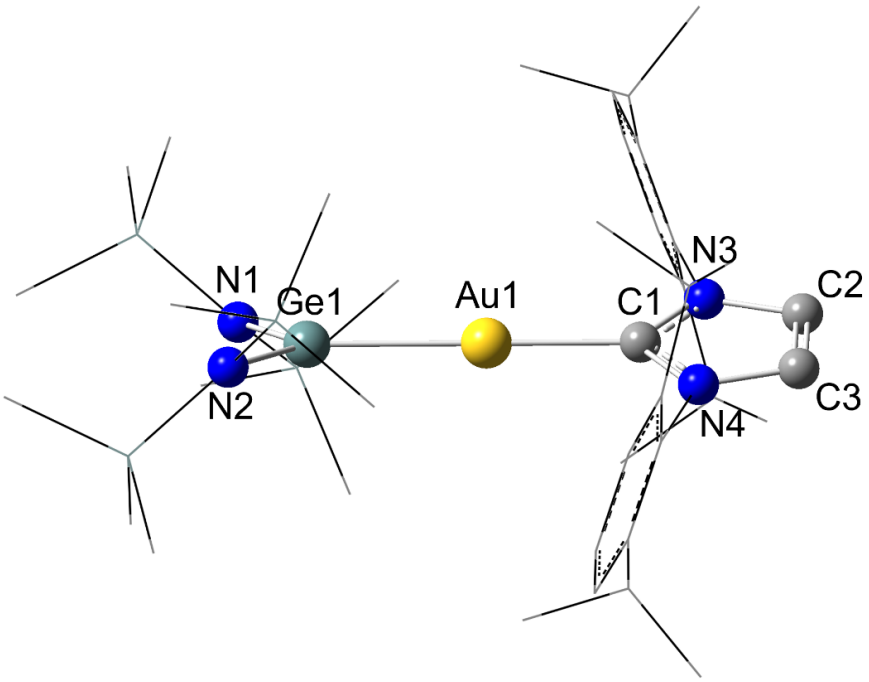


**Fig. S9** Optimized structure of complex **7**. For clarity, the hydrogen atoms are omitted, and the trimethylsilyl moieties as well as the 2,6-diisopropylphenyl moieties are displayed in wireframes.

**Table S10.** Selected bond lengths (Å) for crystal structure and optimized structure (in parentheses) of complex **4**.

| | | | |
|---|---|---|---|
| Au1-Ge1 | 2.40 (2.38) | Au1-C1 | 2.06 (2.05) |
| Ge1-N1 | 1.80 (1.81) | Ge1-N2 | 1.80 (1.81) |
| C1-N3 | 1.35 (1.35) | N3-C2 | 1.39 (1.38) |
| C2-C3 | 1.36 (1.33) | C3-N4 | 1.39 (1.38) |
| N4-C1 | 1.35 (1.35) | | |

**Fragmentation for PIO analysis**

For complex **3**, one of the germylene moieties were treated as one fragment and the remaining part as the other fragment to study the bonding interactions between them.

For complexes **4** and **7**, the Au center was treated as one fragment and the remaining part as the other fragment to study the bonding interactions between them.

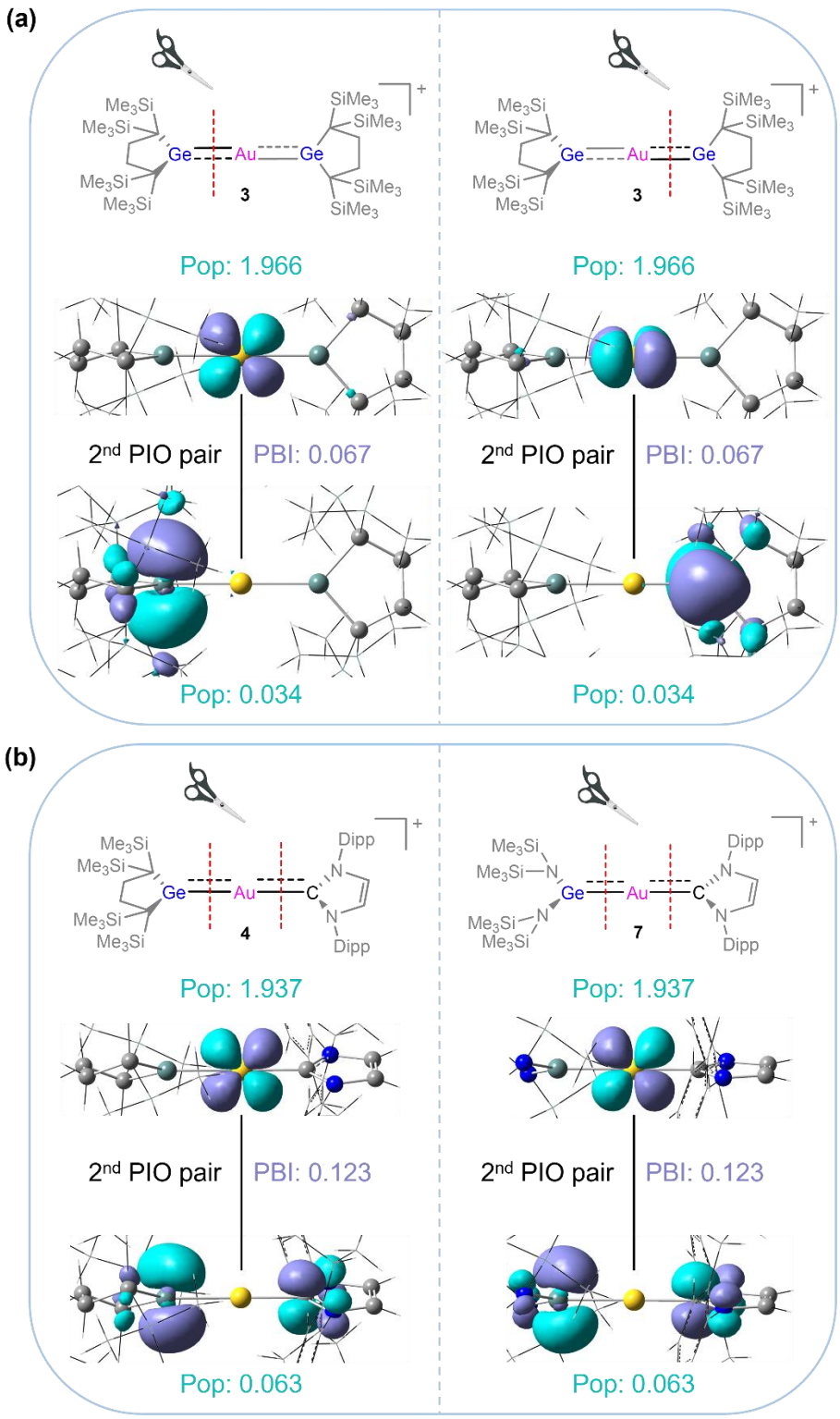


**Fig. S10** Selected principal interacting with orbital (PIO) plots (isovalue =0.05). The results were obtained in the presence of SMD solvation models. (a) PIO pairs representing cumulative 2c-2e π-back donations in complex **3**, with corresponding populations (Pop) and PIO-based bond indices (PBI). (b) PIO pairs representing 3c-2e π-back donations in complexes **4** and **7**, with corresponding populations (Pop) and PIO-based bond indices (PBI).

# 4. $^{1}$H, $^{13}$C, $^{19}$F and $^{29}$Si NMR spectra

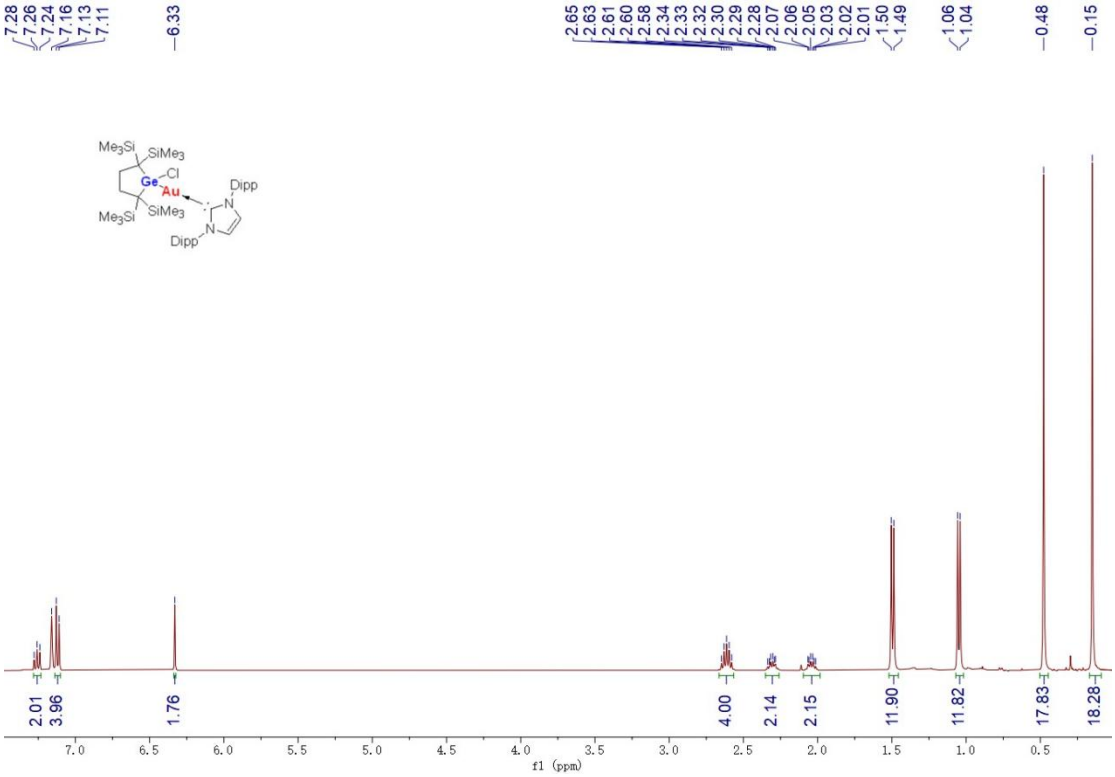


**Fig. S11** $^{1}$H NMR spectrum of **2b** in $C_6D_6$.

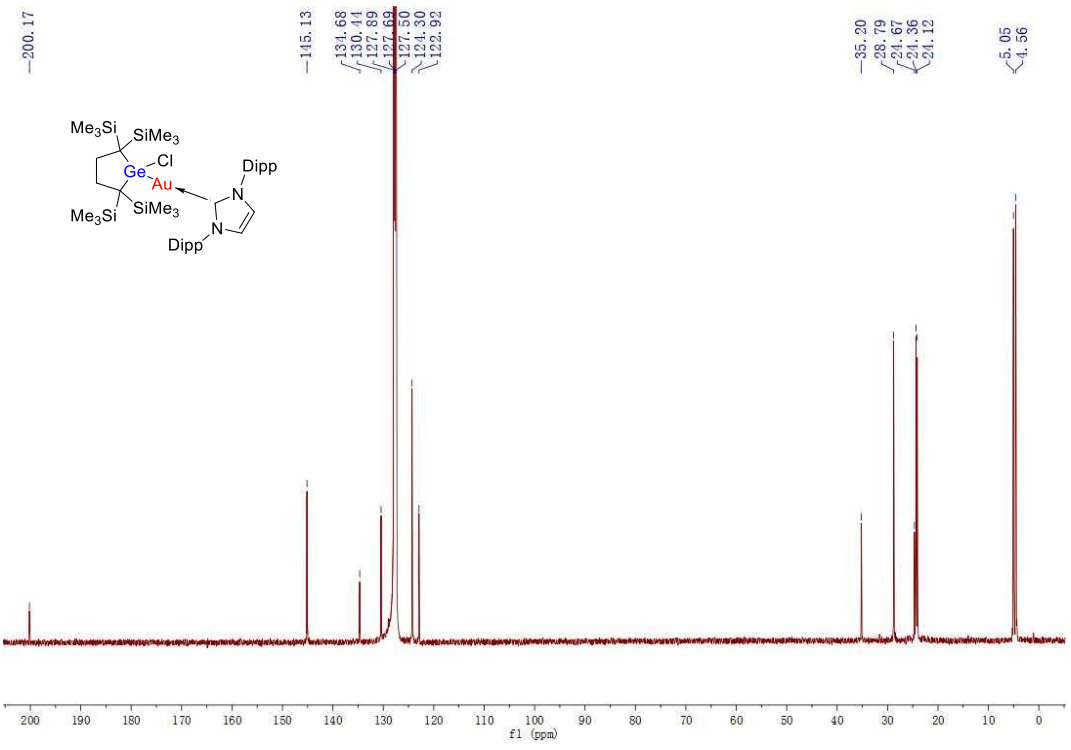


**Fig. S12** $^{13}$C NMR spectrum of **2b** in $C_6D_6$.

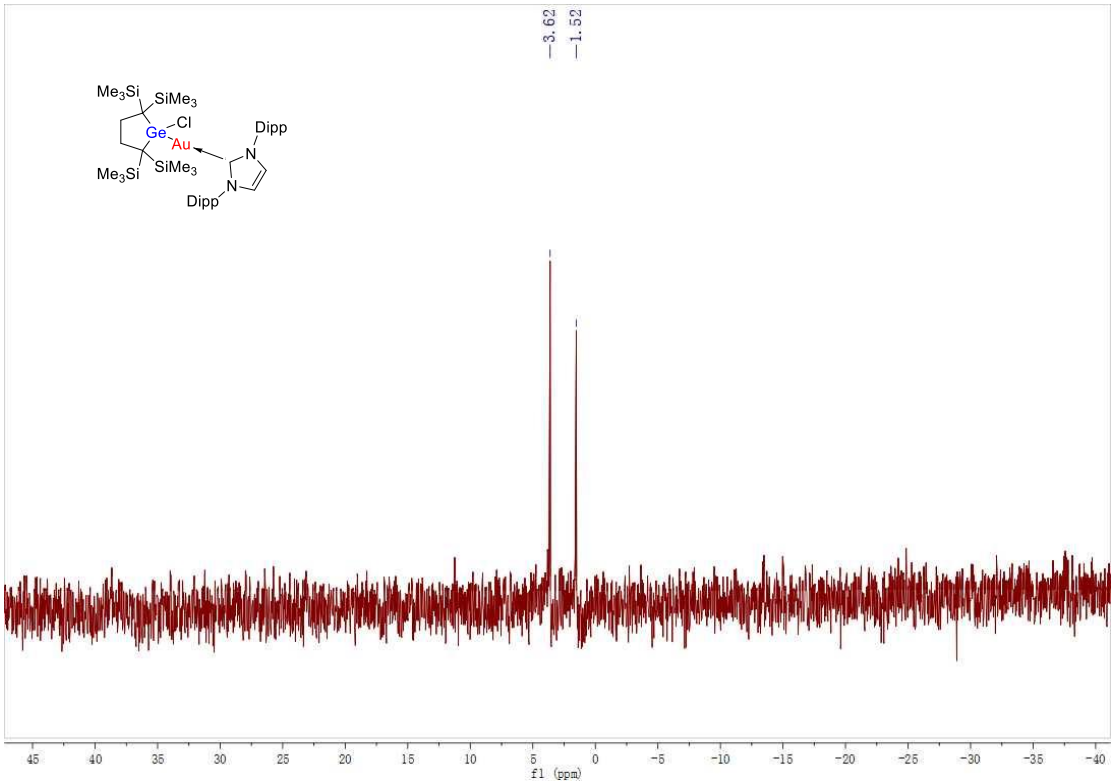


**Fig. S13** $^{29}$Si NMR spectrum of **2b** in $C_6D_6$.

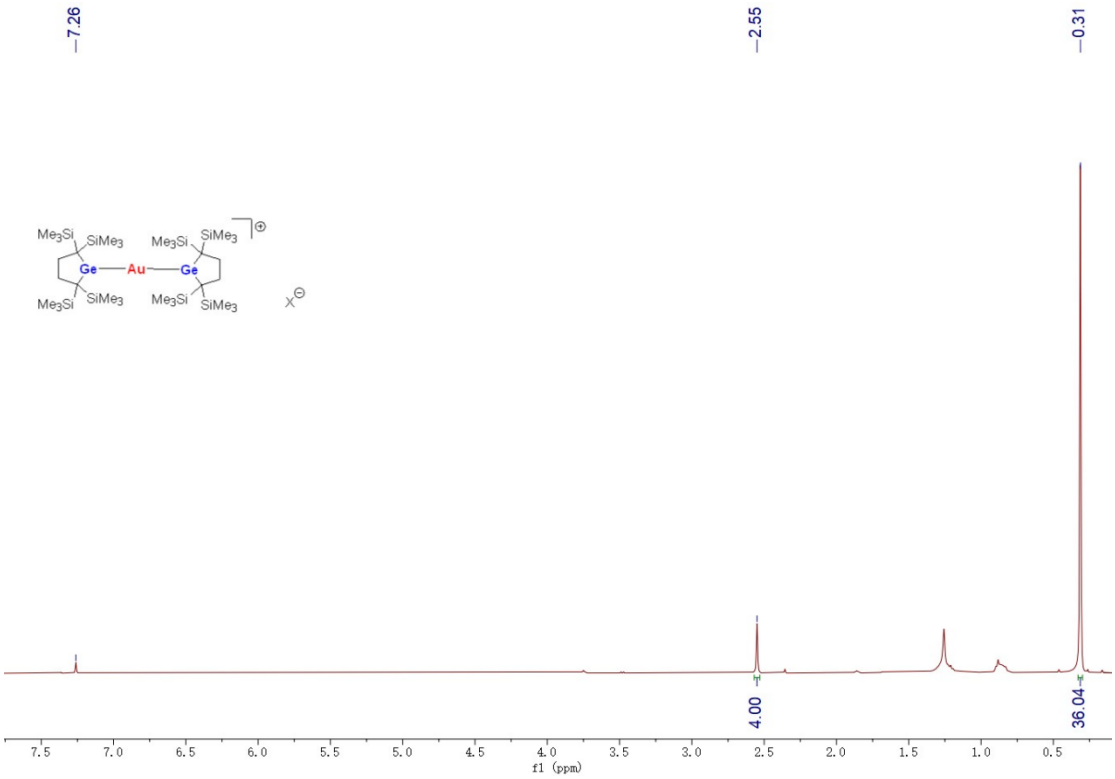


**Fig. S14** $^{1}$H NMR spectrum of **3** in $CDCl_3$.

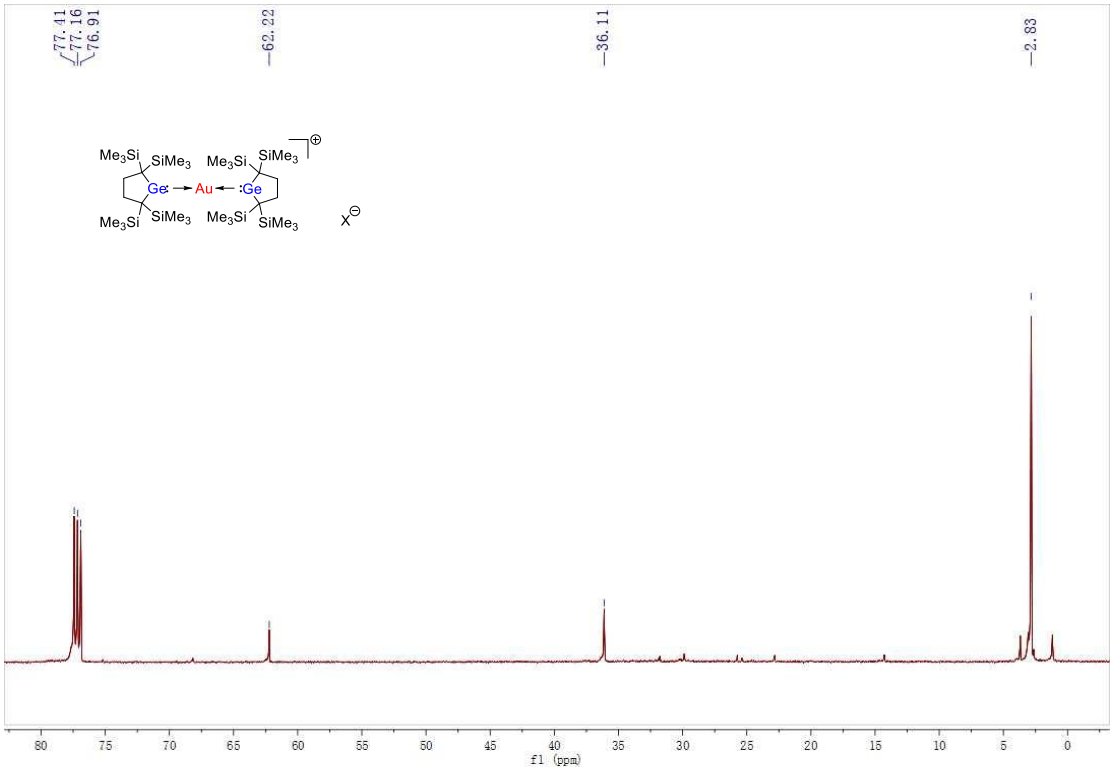


**Fig. S15** $^{13}$C NMR spectrum of **3** in $CDCl_3$.

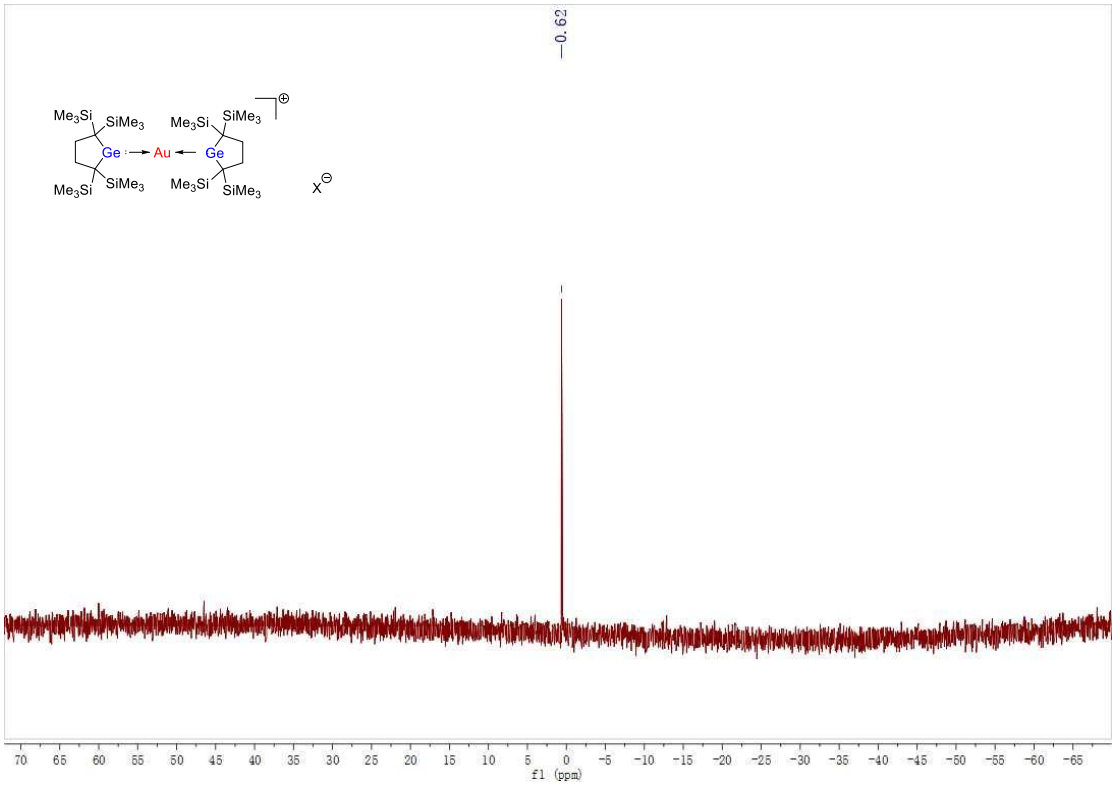


**Fig. S16** $^{29}$Si NMR spectrum of **3** in $CDCl_3$.

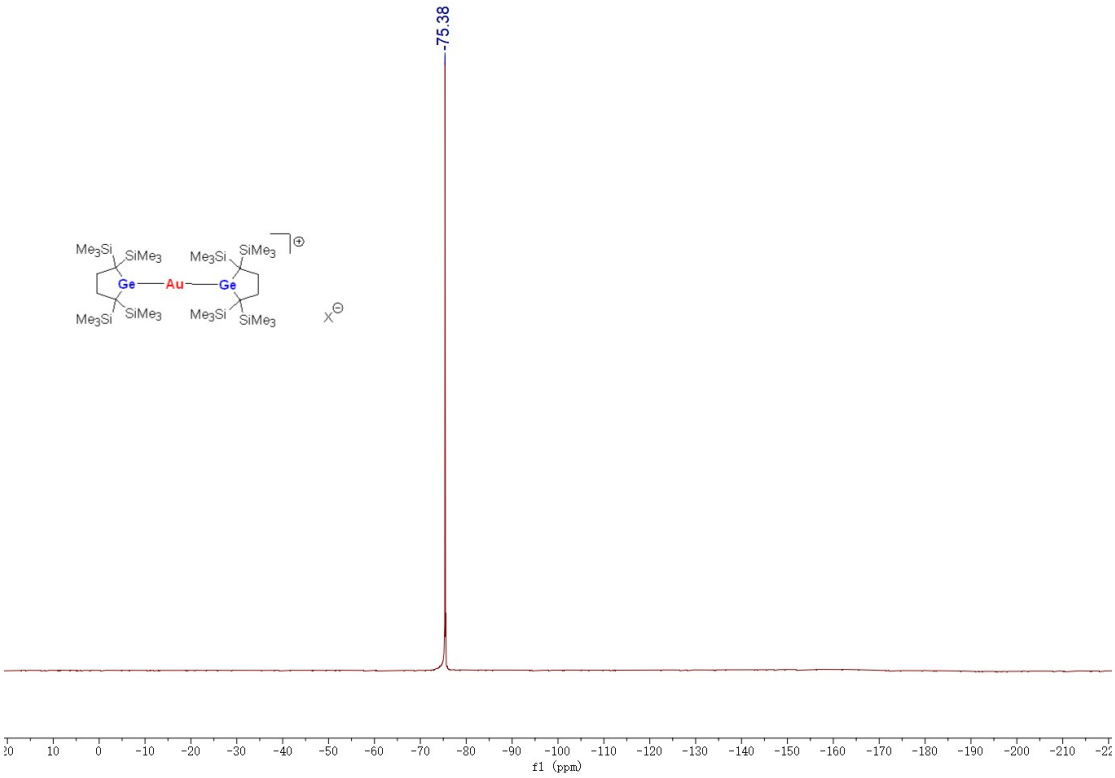


**Fig. S17** $^{19}$F NMR spectrum of **3** in $CDCl_3$.

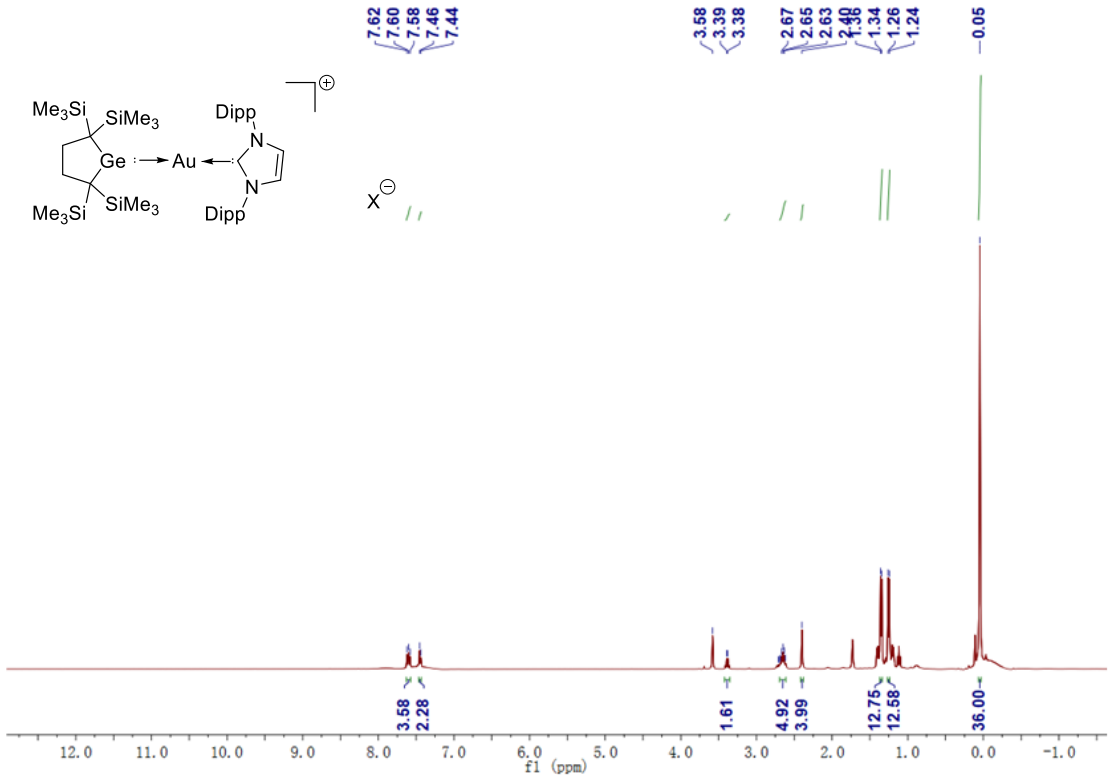


**Fig. S18** $^{1}$H NMR spectrum of **4** in THF-$d_8$.

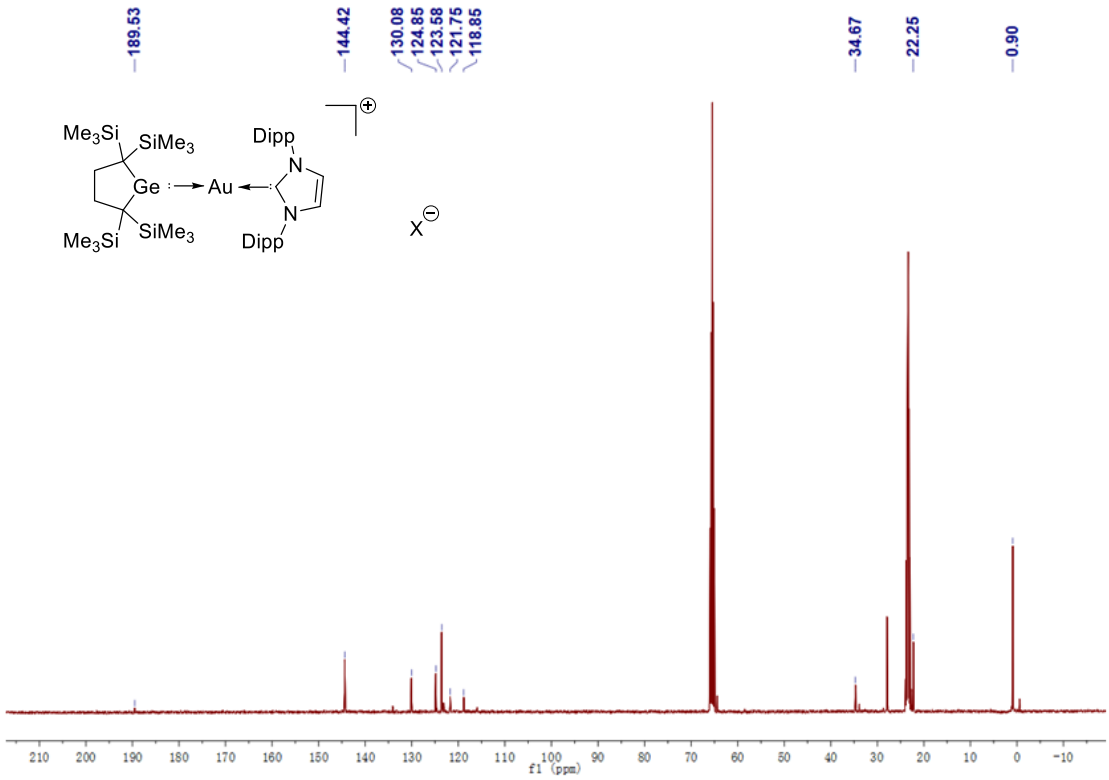


**Fig. S19** $^{13}$C NMR spectrum of **4** in THF-$d_8$.

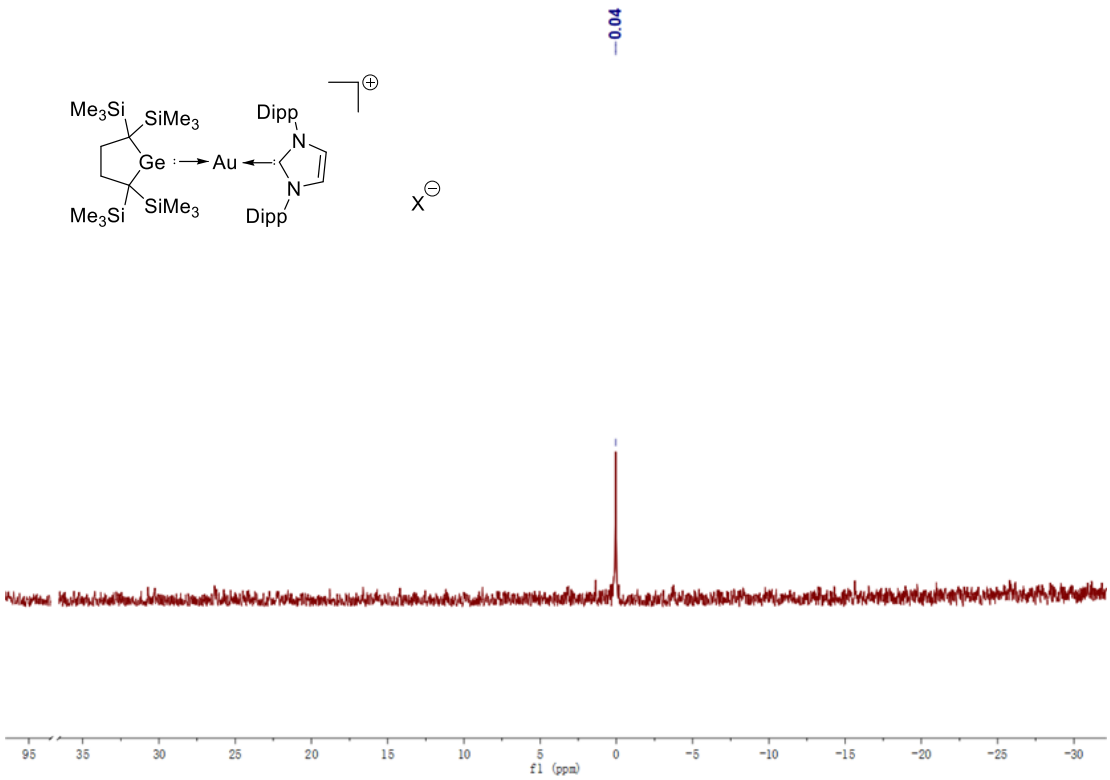


**Fig. S20** $^{29}$Si NMR spectrum of **4** in THF-$d_8$.

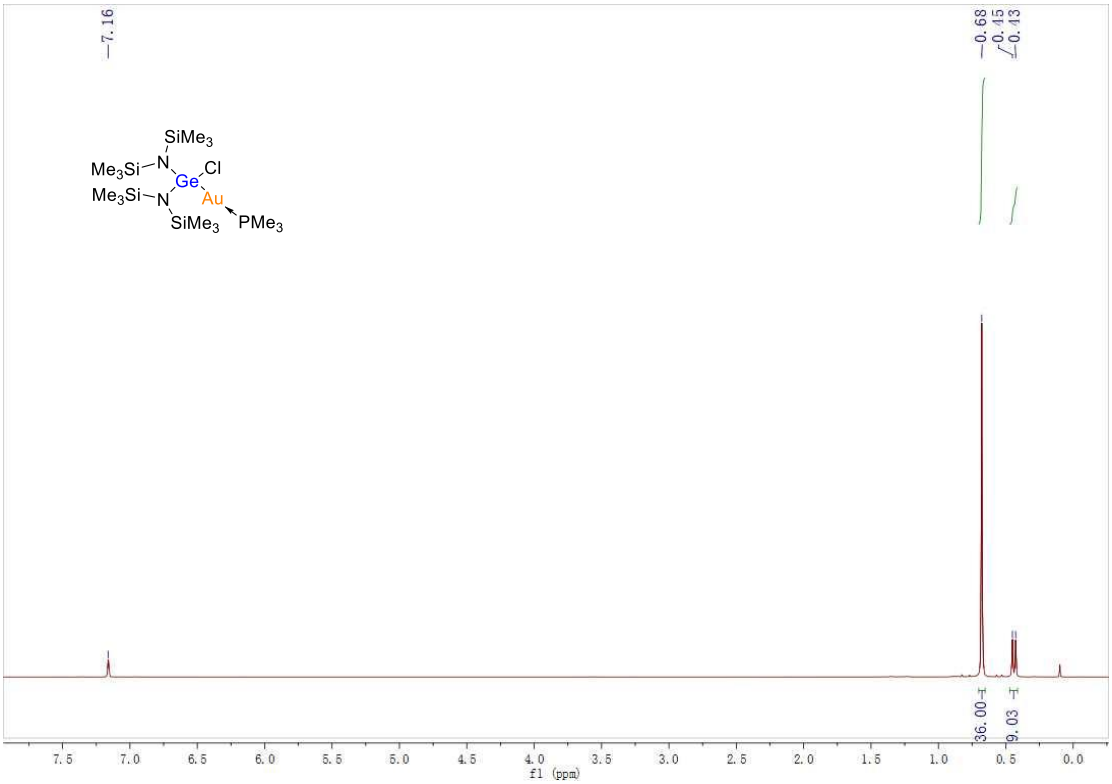


**Fig. S21** $^{1}$H NMR spectrum of **6a** in $C_6D_6$.

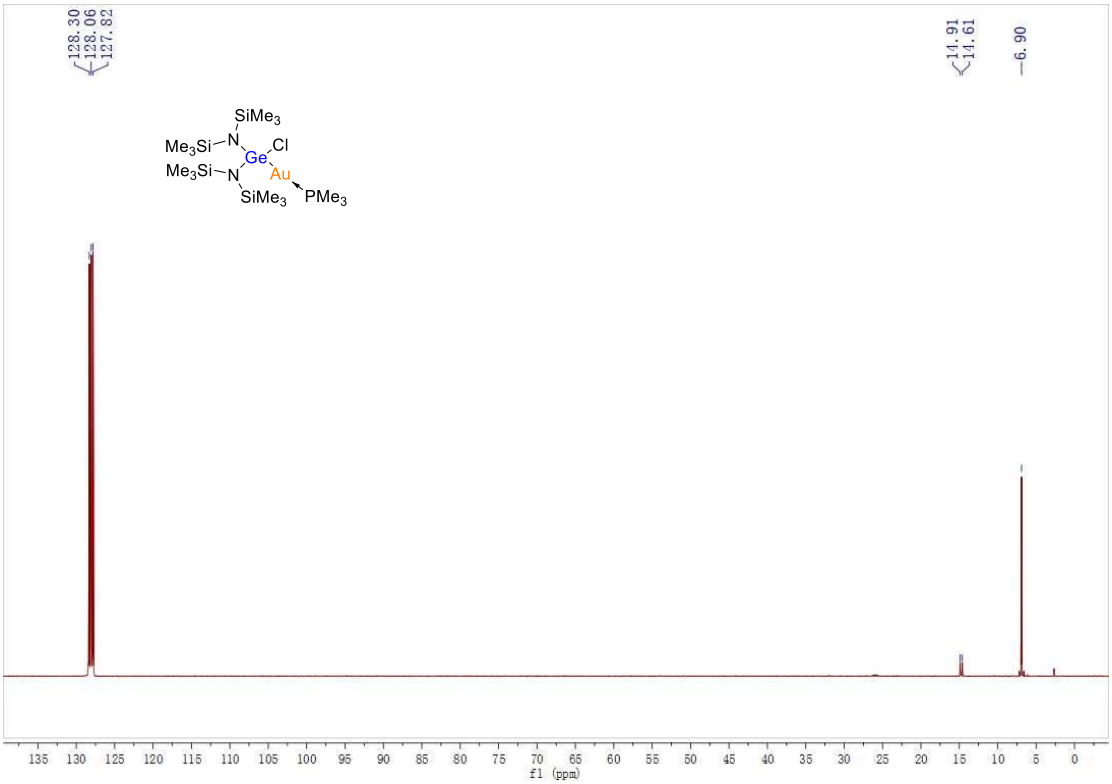


**Fig. S22** $^{13}$C NMR spectrum of **6a** in $C_6D_6$.

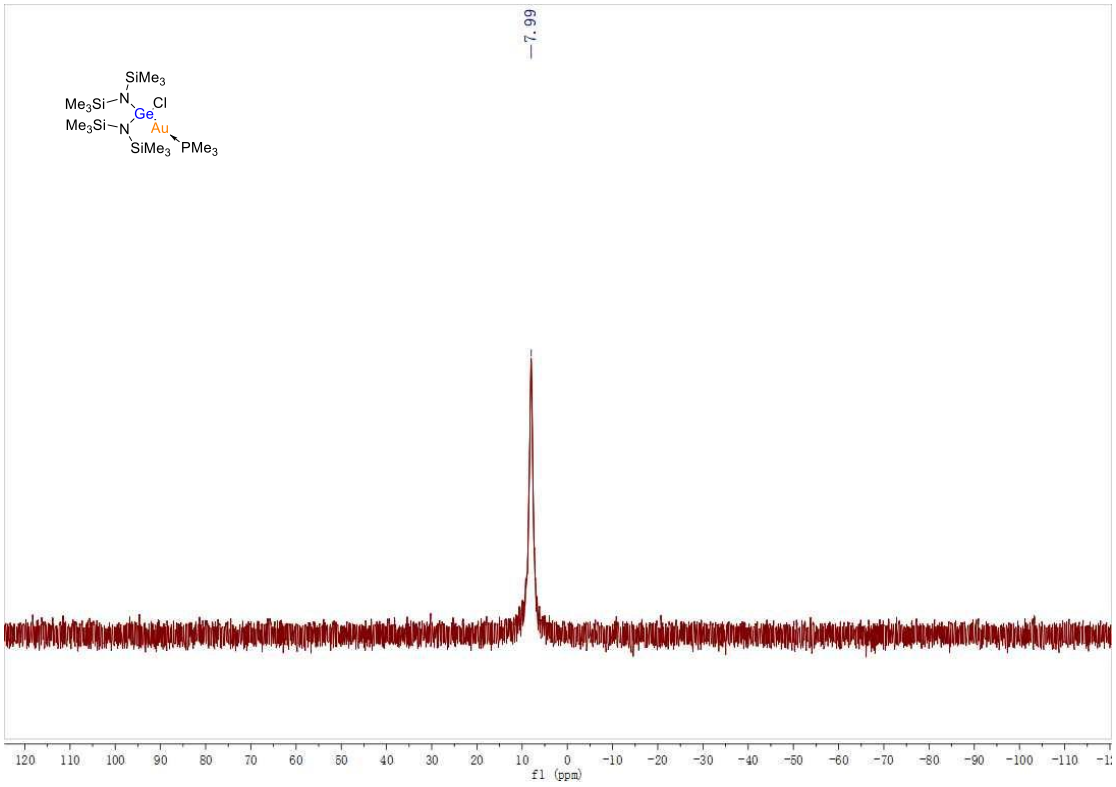


**Fig. S23** $^{31}$P NMR spectrum of **6a** in $C_6D_6$.

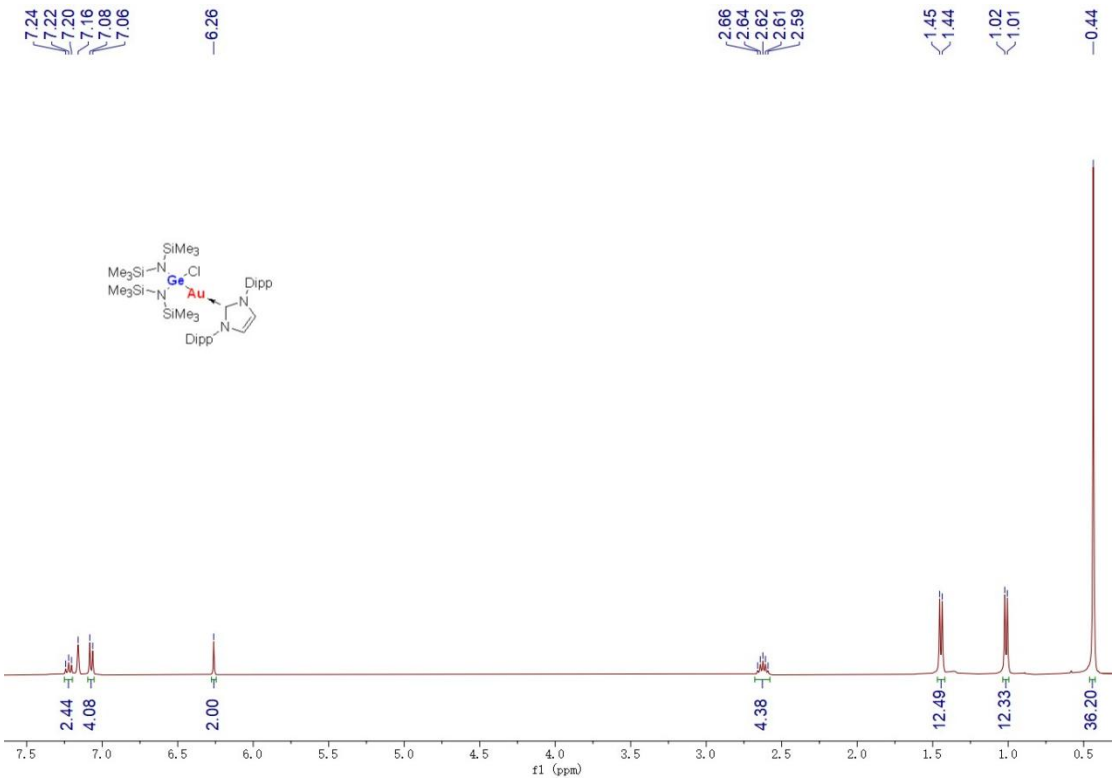


**Fig. S24** $^{1}$H NMR spectrum of **6b** in $C_6D_6$.

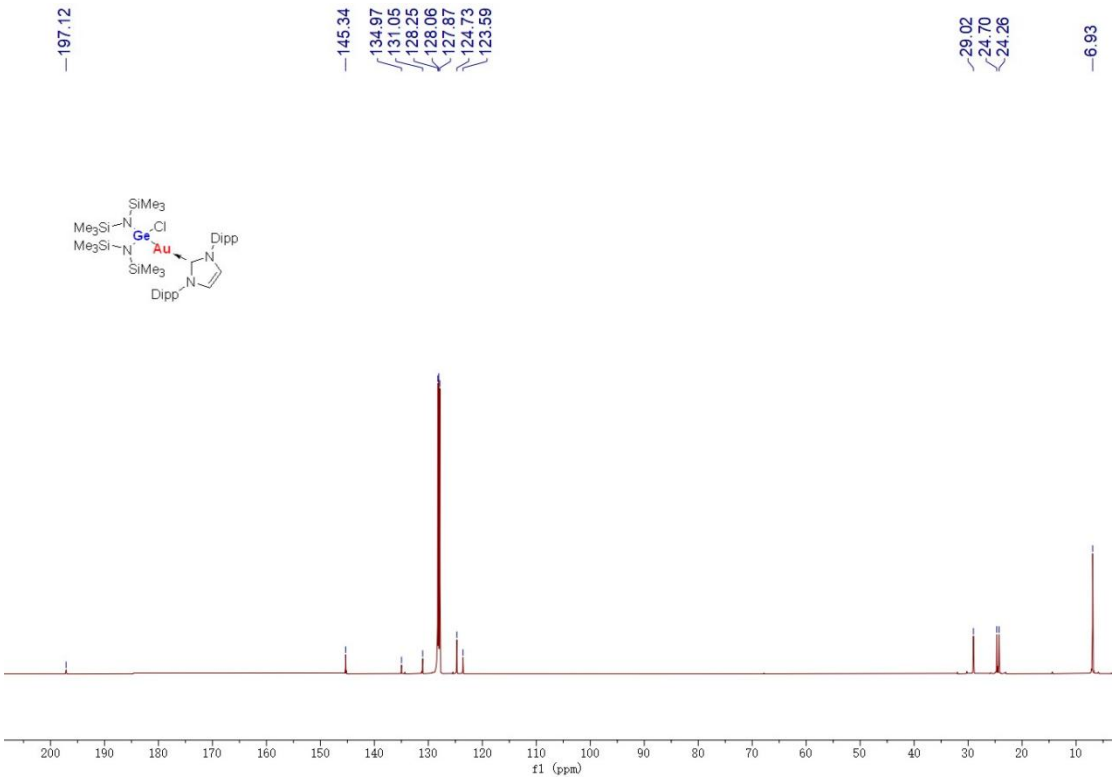


**Fig. S25** $^{13}$C NMR spectrum of **6b** in $C_6D_6$.

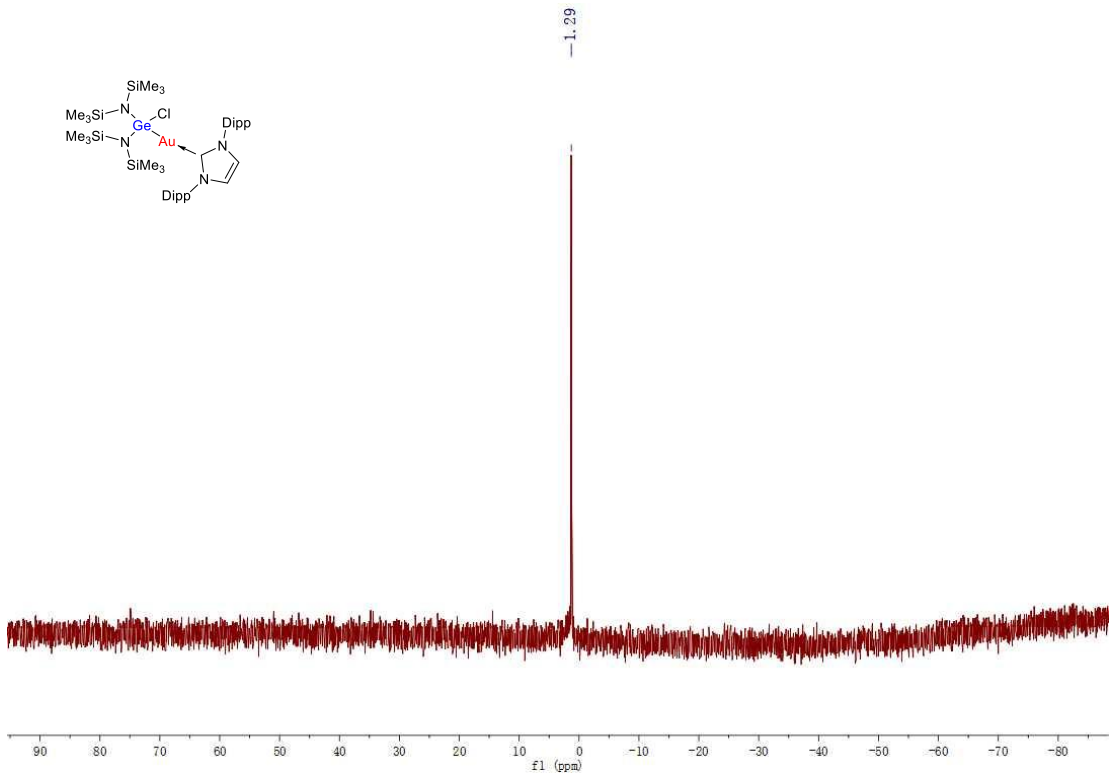


**Fig. S26** $^{29}$Si NMR spectrum of **6b** in $C_6D_6$.

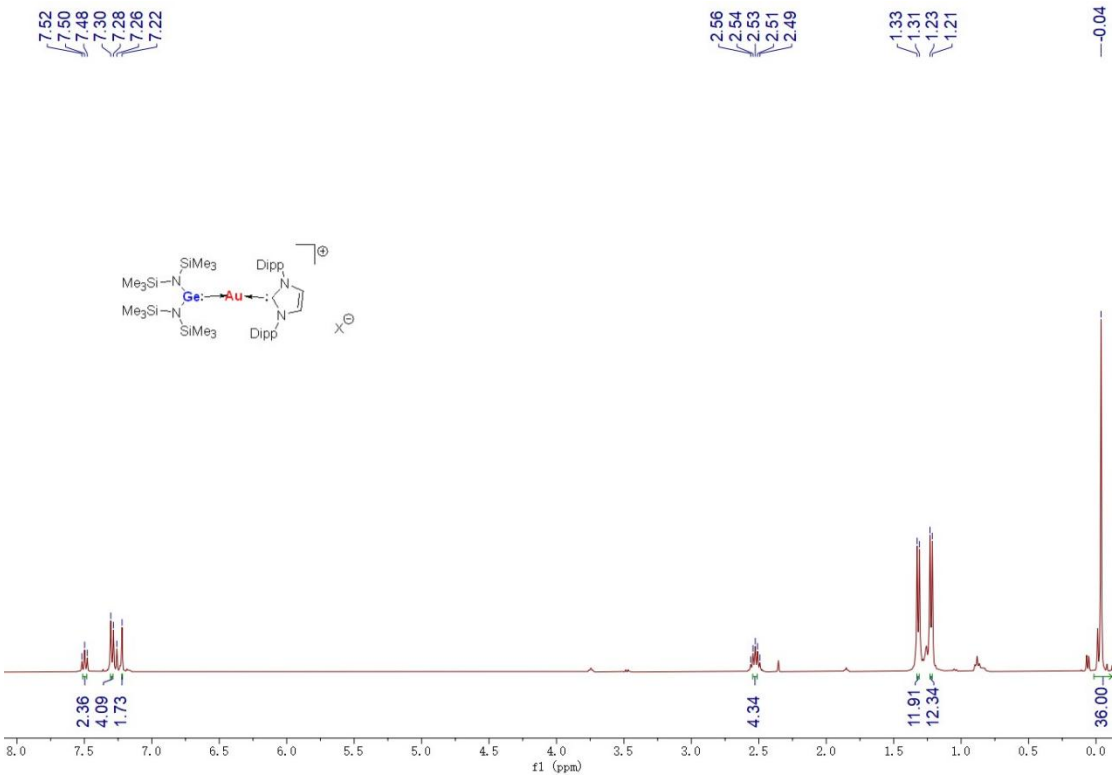


**Fig. S27** $^{1}$H NMR spectrum of **7** in $CDCl_3$.

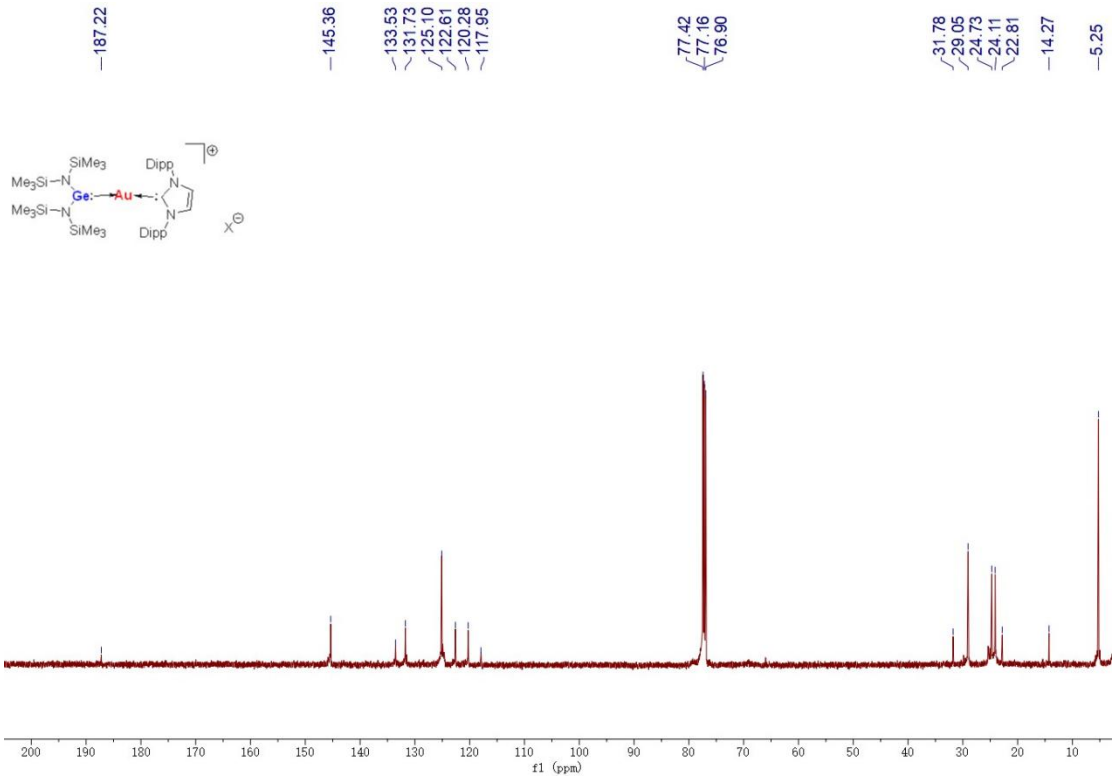


**Fig. S28** $^{13}$C NMR spectrum of **7** in $CDCl_3$.

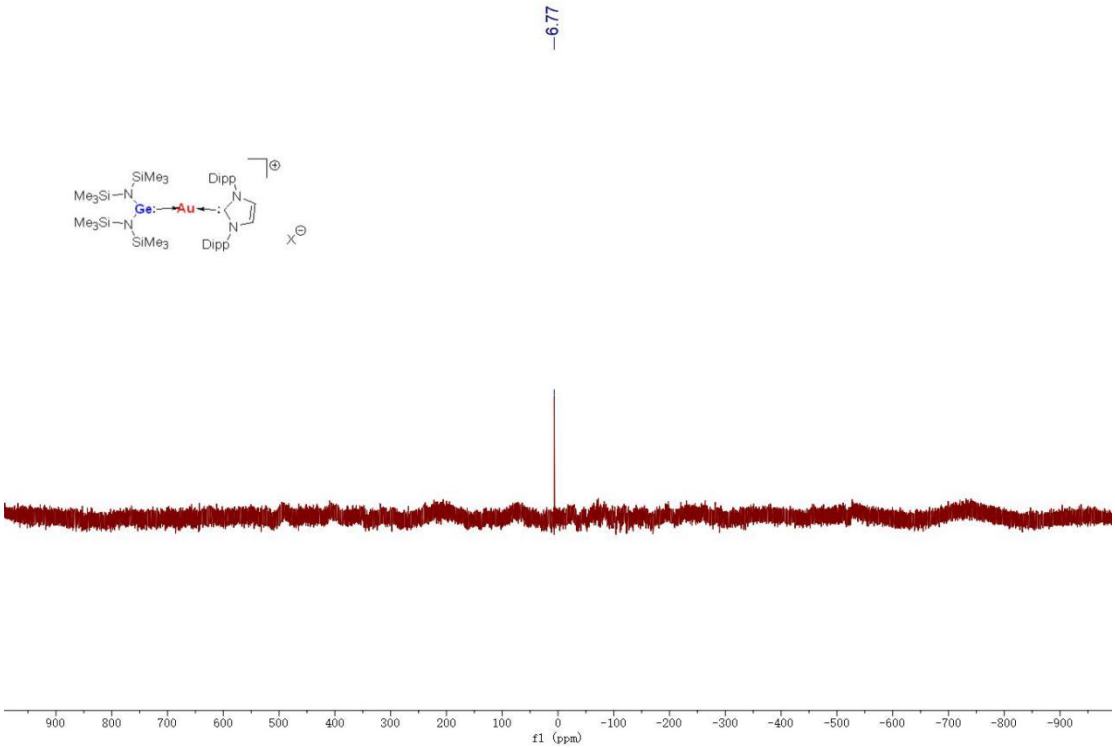


**Fig. S29** $^{29}$Si NMR spectrum of **7** in $CDCl_3$.

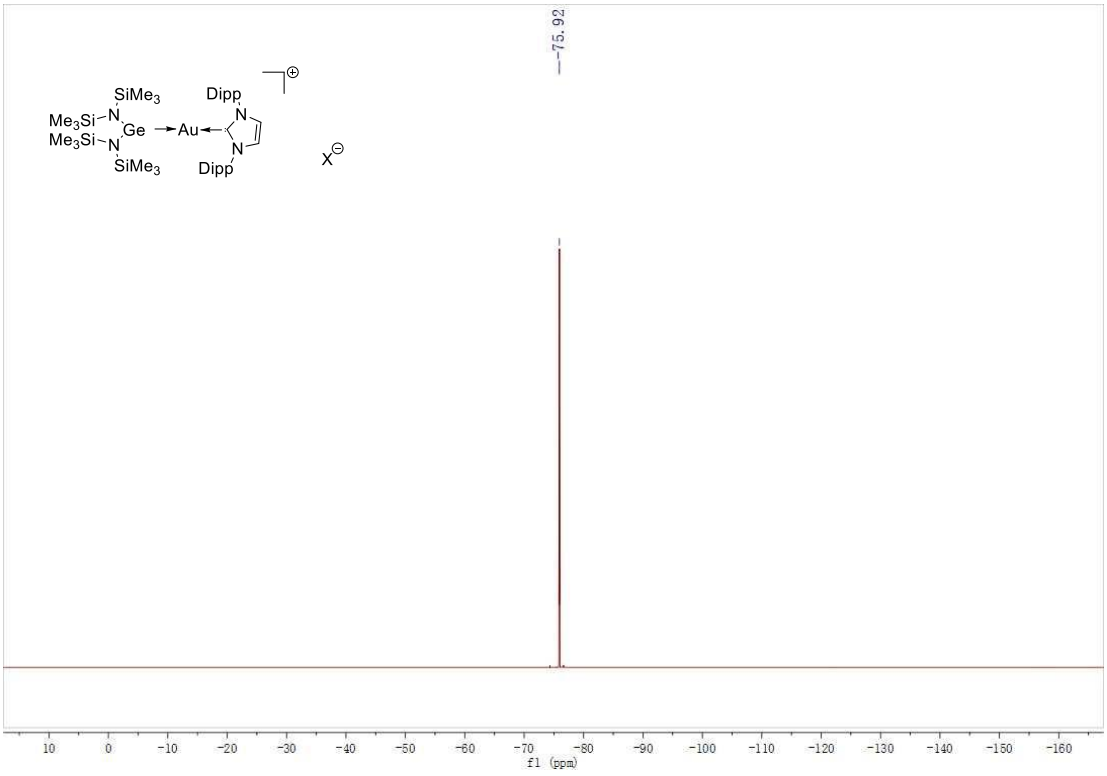


**Fig. S30** $^{19}$F NMR spectrum of **7** in $CDCl_3$.

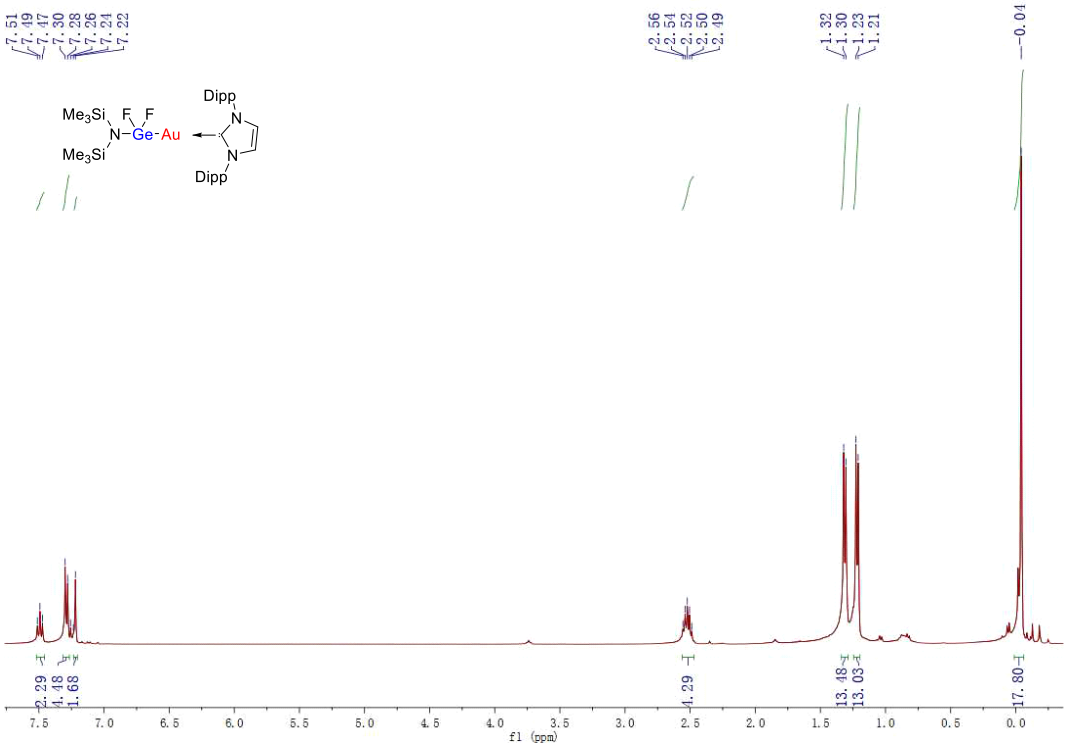


**Fig. S31** $^{1}$H NMR spectrum of **8** in $CDCl_3$.

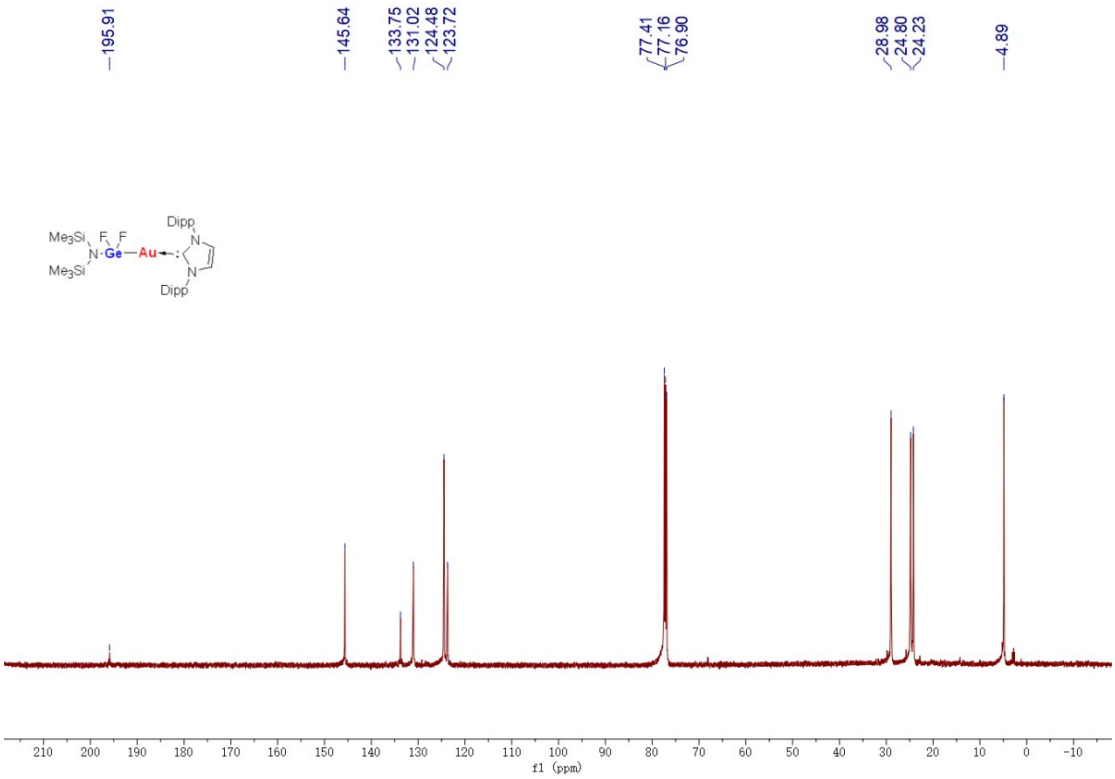


**Fig. S32** $^{13}$C NMR spectrum of **8** in $CDCl_3$

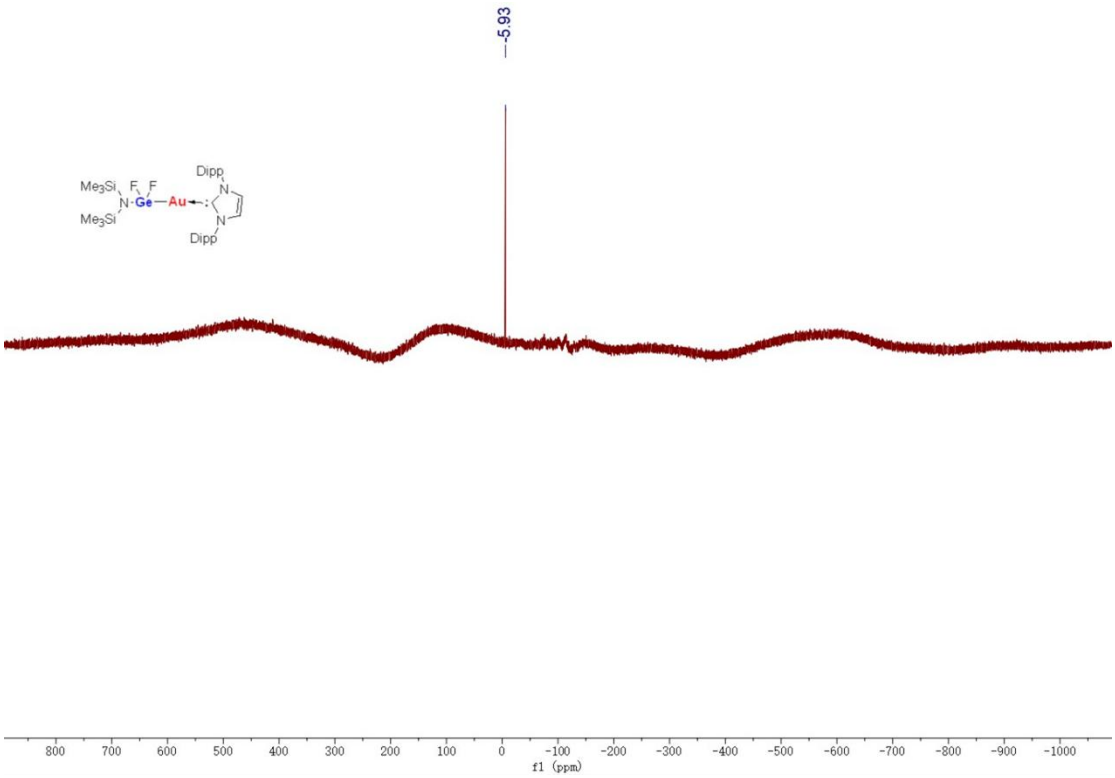


**Fig. S33** $^{29}$Si NMR spectrum of **8** in $CDCl_3$.

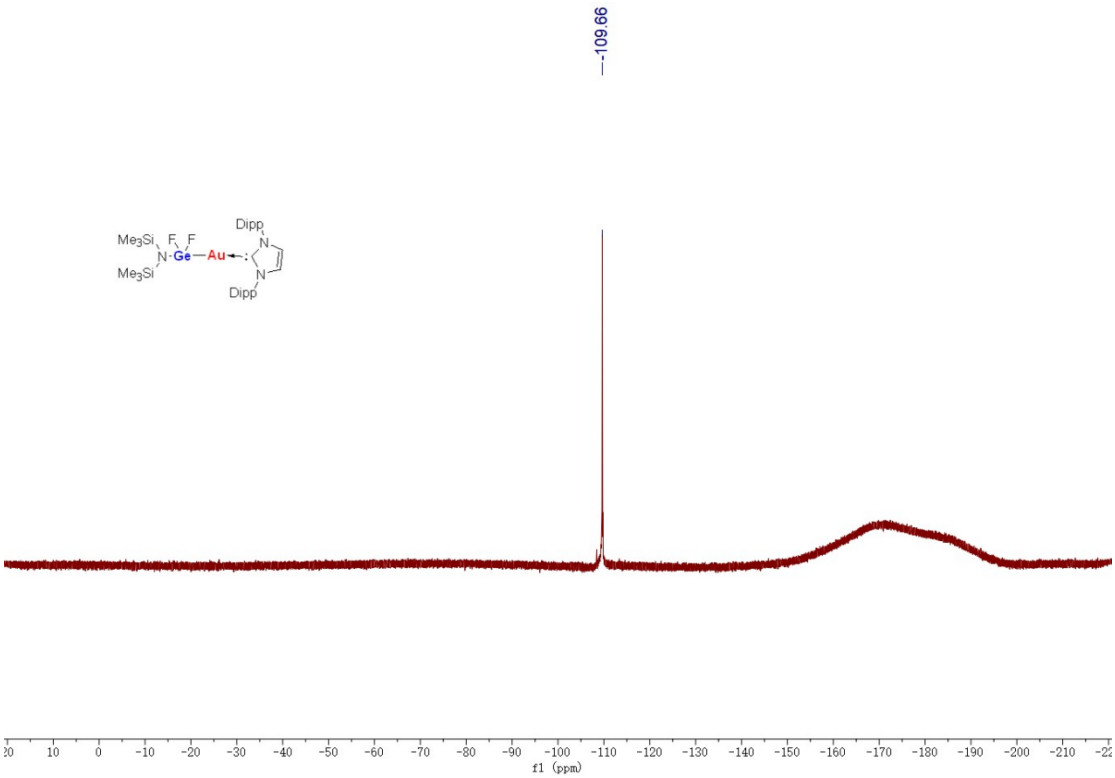


**Fig. S34** $^{19}$F NMR spectrum of **8** in $CDCl_3$.

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## 6. XYZ Coordinates

**$3^+$**

| | | | |
|---|---|---|---|
| Au | -0.00000700 | 0.00000600 | 0.00008000 |
| Ge | 2.40944100 | 0.00002600 | 0.00000700 |
| Si | 3.71801300 | 2.87369800 | 0.66414600 |
| C | 3.67567400 | 0.99947900 | 1.04718000 |
| Ge | -2.40945100 | 0.00002400 | 0.00004200 |
| Si | 3.07499100 | 0.67639900 | 2.84166000 |
| C | 5.00695700 | 0.25593700 | 0.72620400 |
| H | 5.88527800 | 0.89935900 | 0.90903300 |
| H | 5.12808200 | -0.61291200 | 1.39958500 |
| Si | 3.07495000 | -0.67644300 | -2.84169700 |
| C | 5.00693100 | -0.25589300 | -0.72630100 |
| H | 5.88525000 | -0.89931200 | -0.90915400 |
| H | 5.12801700 | 0.61294700 | -1.39970100 |
| Si | 3.71801900 | -2.87365900 | -0.66411000 |
| C | 3.67565100 | -0.99945400 | -1.04721100 |
| Si | -3.07499400 | 2.84191200 | -0.67566300 |
| C | 4.35424200 | 3.84479500 | 2.13366900 |
| H | 3.74511000 | 3.76139600 | 3.04491500 |
| H | 4.39465200 | 4.91084300 | 1.85654400 |
| H | 5.38279200 | 3.53382700 | 2.38015200 |
| Si | -3.71795200 | 0.66488800 | -2.87349300 |
| C | 4.93792700 | 3.26201400 | -0.70633500 |
| H | 5.93990300 | 2.86633200 | -0.47459400 |
| H | 5.03293000 | 4.35829100 | -0.77334200 |
| H | 4.65272600 | 2.89986600 | -1.70411200 |
| Si | -3.71812200 | -0.66501700 | 2.87348400 |
| C | 2.00431500 | 3.45475600 | 0.16402200 |
| H | 1.71576700 | 3.02768700 | -0.81154900 |
| H | 1.98568700 | 4.55157600 | 0.06071300 |
| H | 1.23154500 | 3.17011400 | 0.89612500 |
| Si | -3.07490800 | -2.84181800 | 0.67554600 |
| C | 4.49819400 | 0.86668400 | 4.03163200 |
| H | 5.32414800 | 0.18870800 | 3.76376700 |
| H | 4.16478500 | 0.59617700 | 5.04654100 |
| H | 4.89522400 | 1.89059100 | 4.06716300 |
| C | 2.45267600 | -1.10097000 | 2.95648900 |
| H | 1.44487800 | -1.20828300 | 2.51316800 |
| H | 2.36496800 | -1.39581800 | 4.01518300 |
| H | 3.12296500 | -1.83062800 | 2.47510400 |

| | | | |
|---|---|---|---|
| C | 1.59028300 | 1.72844300 | 3.28649200 |
| H | 1.77335300 | 2.81225500 | 3.29887100 |
| H | 1.24099800 | 1.43320300 | 4.28976900 |
| H | 0.76221500 | 1.52634000 | 2.58322400 |
| C | 2.45306200 | 1.10106100 | -2.95673700 |
| H | 1.44525500 | 1.20864200 | -2.51350600 |
| H | 2.36551500 | 1.39583300 | -4.01546500 |
| H | 3.12347700 | 1.83061200 | -2.47536600 |
| C | 4.49806600 | -0.86724400 | -4.03168700 |
| H | 5.32422200 | -0.18948600 | -3.76389300 |
| H | 4.16472600 | -0.59674200 | -5.04661900 |
| H | 4.89479400 | -1.89127200 | -4.06711800 |
| C | 1.58998100 | -1.72819300 | -3.28635600 |
| H | 1.77278600 | -2.81205200 | -3.29861800 |
| H | 1.24073200 | -1.43297900 | -4.28965300 |
| H | 0.76198800 | -1.52580000 | -2.58308300 |
| C | 4.93805500 | -3.26189400 | 0.70628700 |
| H | 5.94000500 | -2.86621300 | 0.47442600 |
| H | 5.03307500 | -4.35816600 | 0.77334500 |
| H | 4.65294700 | -2.89969400 | 1.70407100 |
| C | 4.35412100 | -3.84479700 | -2.13365700 |
| H | 3.74487900 | -3.76144500 | -3.04483400 |
| H | 4.39460800 | -4.91083400 | -1.85650400 |
| H | 5.38262900 | -3.53379100 | -2.38026900 |
| C | 2.00436700 | -3.45473700 | -0.16384100 |
| H | 1.71585900 | -3.02763700 | 0.81172700 |
| H | 1.98579600 | -4.55155300 | -0.06047300 |
| H | 1.23153800 | -3.17017600 | -0.89591600 |
| C | -3.67564300 | 1.04748300 | -0.99918700 |
| C | -5.00694700 | 0.72632600 | -0.25577300 |
| H | -5.12809400 | 1.39947500 | 0.61325000 |
| H | -5.88524100 | 0.90933700 | -0.89918200 |
| C | -5.00695800 | -0.72632800 | 0.25563600 |
| H | -5.12801800 | -1.39946400 | -0.61341200 |
| H | -5.88530400 | -0.90936800 | 0.89896500 |
| C | -3.67570500 | -1.04747400 | 0.99914600 |
| C | -4.49823600 | 4.03187100 | -0.86573900 |
| H | -4.89518200 | 4.06767400 | -1.88966800 |
| H | -4.16490500 | 5.04672100 | -0.59491400 |
| H | -5.32423100 | 3.76376600 | -0.18790800 |
| C | -2.45277300 | 2.95640100 | 1.10176000 |
| H | -3.12304400 | 2.47479100 | 1.83128600 |
| H | -2.36519200 | 4.01504200 | 1.39683400 |
| H | -1.44493800 | 2.51315800 | 1.20902300 |

| | | | |
|---|---|---|---|
| C | -1.59023500 | 3.28703400 | -1.72751600 |
| H | -0.76215800 | 2.58375500 | -1.52548300 |
| H | -1.24099700 | 4.29026000 | -1.43204400 |
| H | -1.77322200 | 3.29962300 | -2.81133900 |
| C | -4.35406700 | 2.13465600 | -3.84429000 |
| H | -5.38260500 | 2.38114400 | -3.53328500 |
| H | -4.39448800 | 1.85773600 | -4.91039200 |
| H | -3.74487700 | 3.04584500 | -3.76070900 |
| C | -2.00428600 | 0.16474400 | -3.45463100 |
| H | -1.23144500 | 0.89668300 | -3.16977200 |
| H | -1.98563800 | 0.06172800 | -4.55147800 |
| H | -1.71586700 | -0.81098000 | -3.02781600 |
| C | -4.93794400 | -0.70543400 | -3.26210200 |
| H | -4.65281700 | -1.70328700 | -2.90010400 |
| H | -5.03291500 | -0.77225300 | -4.35839300 |
| H | -5.93991600 | -0.47369000 | -2.86640900 |
| C | -4.93791100 | 0.70548300 | 3.26212500 |
| H | -4.65257300 | 1.70331200 | 2.90023000 |
| H | -5.03295100 | 0.77224100 | 4.35841400 |
| H | -5.93989600 | 0.47395800 | 2.86633900 |
| C | -2.00441100 | -0.16523900 | 3.45480300 |
| H | -1.23170600 | -0.89733200 | 3.16996400 |
| H | -1.98583900 | -0.06229100 | 4.55165800 |
| H | -1.71574200 | 0.81044500 | 3.02806900 |
| C | -4.35452600 | -2.13476100 | 3.84411900 |
| H | -5.38307600 | -2.38109800 | 3.53304100 |
| H | -4.39496400 | -1.85792000 | 4.91024100 |
| H | -3.74544400 | -3.04601900 | 3.76049900 |
| C | -1.59008700 | -3.28680800 | 1.72736900 |
| H | -0.76206500 | -2.58346100 | 1.52535300 |
| H | -1.24078300 | -4.29000800 | 1.43188500 |
| H | -1.77306800 | -3.29943300 | 2.81119400 |
| C | -2.45270800 | -2.95611500 | -1.10189800 |
| H | -3.12307000 | -2.47459400 | -1.83140100 |
| H | -2.36493900 | -4.01472900 | -1.39701900 |
| H | -1.44495100 | -2.51269200 | -1.20915300 |
| C | -4.49799600 | -4.03196300 | 0.86562100 |
| H | -4.89488300 | -4.06787400 | 1.88956900 |
| H | -4.16455000 | -5.04675500 | 0.59472100 |
| H | -5.32406400 | -3.76392700 | 0.18785100 |

**4**$^{+}$

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|---|---|---|---|
| Au | -0.52549900 | 0.00019300 | 0.00017100 |
| Ge | 1.87448900 | -0.00047900 | 0.00002400 |
| Si | 2.57583600 | -2.87750000 | 0.54693100 |
| N | -3.41646500 | 1.01793600 | -0.34927600 |
| C | 3.15649500 | -1.36309800 | -0.47603600 |
| Si | 3.25973800 | -1.79591700 | -2.33642900 |
| N | -3.41724000 | -1.01574500 | 0.34894000 |
| C | 4.48515300 | -0.76656800 | 0.07470800 |
| H | 4.59849700 | -1.01076500 | 1.14691500 |
| H | 5.36507600 | -1.20761700 | -0.42585200 |
| Si | 3.26213800 | 1.79359800 | 2.33599400 |
| C | 4.48588600 | 0.76300400 | -0.07553000 |
| H | 4.59916100 | 1.00712800 | -1.14776800 |
| H | 5.36639500 | 1.20315700 | 0.42479000 |
| Si | 2.57842200 | 2.87577700 | -0.54723800 |
| C | 3.15800300 | 1.36087700 | 0.47561800 |
| C | 1.95140100 | -2.27479200 | 2.21996100 |
| H | 2.63982500 | -1.57096700 | 2.71489500 |
| H | 1.82458800 | -3.13554300 | 2.89796000 |
| H | 0.95890600 | -1.79715300 | 2.13207900 |
| C | 1.10203200 | -3.72119700 | -0.23928100 |
| H | 0.23943200 | -3.02888500 | -0.25095500 |
| H | 0.81148400 | -4.58057400 | 0.38693600 |
| H | 1.26476800 | -4.08824900 | -1.26333900 |
| C | 4.01137200 | -4.02699100 | 0.86646700 |
| H | 4.40926300 | -4.49572400 | -0.04363600 |
| H | 3.68496200 | -4.83040200 | 1.54671100 |
| H | 4.83549300 | -3.49064500 | 1.36348900 |
| C | 3.91456700 | -3.53259100 | -2.59214100 |
| H | 4.93329600 | -3.62570600 | -2.18158100 |
| H | 3.98290000 | -3.71728000 | -3.67673100 |
| H | 3.29632000 | -4.33109800 | -2.15749000 |
| C | 4.49173500 | -0.70169200 | -3.23354300 |
| H | 4.18395300 | 0.34929300 | -3.33245500 |
| H | 4.61411900 | -1.10146000 | -4.25370100 |
| H | 5.48496100 | -0.72378000 | -2.75747100 |
| C | 1.57565800 | -1.58124000 | -3.12519800 |
| H | 0.76739700 | -2.04067600 | -2.53466900 |
| H | 1.55307600 | -2.01648500 | -4.13698300 |
| H | 1.35131900 | -0.50609900 | -3.22388800 |
| C | 4.49335300 | 0.69818500 | 3.23273300 |
| H | 4.18467900 | -0.35255900 | 3.33143500 |

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|---|---|---|---|
| H | 4.61621700 | 1.09758800 | 4.25297700 |
| H | 5.48653400 | 0.71953800 | 2.75653300 |
| C | 3.91867200 | 3.52966200 | 2.59142000 |
| H | 4.93716100 | 3.62194600 | 2.18007300 |
| H | 3.98796300 | 3.71424800 | 3.67596400 |
| H | 3.30076700 | 4.32871700 | 2.15728000 |
| C | 4.01477800 | 4.02412500 | -0.86714900 |
| H | 4.41206500 | 4.49381000 | 0.04273000 |
| H | 3.68930600 | 4.82684600 | -1.54865400 |
| H | 4.83911600 | 3.48682600 | -1.36277600 |
| C | 1.10561800 | 3.72072900 | 0.23948600 |
| H | 0.24248900 | 3.02910500 | 0.25170100 |
| H | 0.81543100 | 4.58028300 | -0.38664800 |
| H | 1.26918400 | 4.08773100 | 1.26343800 |
| C | 1.95286000 | 2.27347500 | -2.22000600 |
| H | 2.64088500 | 1.56973500 | -2.71559700 |
| H | 1.82555700 | 3.13442400 | -2.89766700 |
| H | 0.96035900 | 1.79591000 | -2.13159800 |
| C | -2.59902800 | 0.00082100 | -0.00002800 |
| C | -4.74403500 | 0.64332300 | -0.22610300 |
| H | -5.55847800 | 1.32030800 | -0.47006200 |
| C | -4.74452800 | -0.64027200 | 0.22530500 |
| H | -5.55948600 | -1.31665700 | 0.46921500 |
| C | -2.93559400 | 2.27624600 | -0.85748900 |
| C | -2.53866500 | 2.33292300 | -2.20421000 |
| C | -2.00569500 | 3.54598700 | -2.66170700 |
| H | -1.67750500 | 3.62818700 | -3.70132200 |
| C | -1.91816100 | 4.65130800 | -1.81908300 |
| H | -1.51348000 | 5.59213600 | -2.19874000 |
| C | -2.35806200 | 4.57147600 | -0.49692100 |
| H | -2.29145500 | 5.45084700 | 0.14659700 |
| C | -2.87067000 | 3.37676100 | 0.01826500 |
| C | 1.57804900 | 1.58046500 | 3.12521100 |
| H | 0.76994200 | 2.03962800 | 2.53426200 |
| H | 1.55570900 | 2.01679900 | 4.13652800 |
| H | 1.35325200 | 0.50551900 | 3.22501900 |
| C | -2.70719600 | 1.16403800 | -3.16210300 |
| H | -3.19126500 | 0.33455000 | -2.61867400 |
| C | -3.62021700 | 1.54598300 | -4.33072500 |
| H | -4.59690700 | 1.90982500 | -3.97950700 |
| H | -3.79064500 | 0.67795000 | -4.98468200 |
| H | -3.16700300 | 2.33938900 | -4.94513600 |
| C | -1.35544000 | 0.65263700 | -3.65871000 |
| H | -0.80146500 | 1.43941200 | -4.19651600 |

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|---|---|---|---|
| H | -1.48427400 | -0.19954800 | -4.34373800 |
| H | -0.73333900 | 0.31568600 | -2.81470400 |
| C | -3.28018400 | 3.25465600 | 1.47706000 |
| H | -4.04198800 | 2.46044800 | 1.54743500 |
| C | -3.89603100 | 4.53574500 | 2.03719500 |
| H | -4.30213700 | 4.35144300 | 3.04225700 |
| H | -4.71006200 | 4.91188700 | 1.40061300 |
| H | -3.14406300 | 5.33368100 | 2.13720400 |
| C | -2.07881800 | 2.81875700 | 2.32332800 |
| H | -1.29272800 | 3.59116400 | 2.29231900 |
| H | -1.63895000 | 1.87807200 | 1.95219300 |
| H | -2.37083700 | 2.66938500 | 3.37469700 |
| C | -2.93731400 | -2.27424300 | 0.85756900 |
| C | -2.54002300 | -2.33063600 | 2.20419400 |
| C | -2.00812500 | -3.54401100 | 2.66215700 |
| H | -1.67971000 | -3.62598600 | 3.70171900 |
| C | -1.92206600 | -4.64987500 | 1.82011700 |
| H | -1.51825900 | -5.59093200 | 2.20013200 |
| C | -2.36234000 | -4.57028600 | 0.49804800 |
| H | -2.29693700 | -5.45010600 | -0.14496700 |
| C | -2.87376900 | -3.37529700 | -0.01764200 |
| C | -2.70748300 | -1.16129000 | 3.16173200 |
| H | -3.19025800 | -0.33129800 | 2.61791800 |
| C | -1.35540300 | -0.65146400 | 3.65905400 |
| H | -0.80270200 | -1.43882900 | 4.19730700 |
| H | -1.48363600 | 0.20095300 | 4.34390100 |
| H | -0.73236900 | -0.31536500 | 2.81539500 |
| C | -3.62159900 | -1.54193400 | 4.32993200 |
| H | -4.59854200 | -1.90464700 | 3.97824800 |
| H | -3.79131900 | -0.67358900 | 4.98366000 |
| H | -3.16966800 | -2.33579900 | 4.94470000 |
| C | -3.28345300 | -3.25340300 | -1.47640200 |
| H | -4.04540900 | -2.45933900 | -1.54679000 |
| C | -2.08223800 | -2.81740800 | -2.32286600 |
| H | -1.64215000 | -1.87683100 | -1.95172400 |
| H | -2.37448900 | -2.66786500 | -3.37414500 |
| H | -1.29624100 | -3.58991300 | -2.29215300 |
| C | -3.89912400 | -4.53459600 | -2.03645600 |
| H | -3.14701100 | -5.33238300 | -2.13659200 |
| H | -4.30539500 | -4.35033800 | -3.04145700 |
| H | -4.71300600 | -4.91090600 | -1.39978100 |

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| | | | |
|---|---|---|---|
| Au | 0.50690000 | 0.00011400 | 0.00008500 |
| Ge | -1.89252700 | -0.00014000 | 0.00014900 |
| Si | -2.16918600 | -2.74195800 | 1.26164500 |
| Si | -4.22289900 | -1.88468000 | -0.92606700 |
| Si | -4.22372600 | 1.88363100 | 0.92598100 |
| Si | -2.17005200 | 2.74149500 | -1.26150300 |
| N | 3.38192100 | -1.04693300 | -0.24758800 |
| N | 3.38170000 | 1.04772600 | 0.24739900 |
| C | 2.56640500 | 0.00029900 | -0.00005300 |
| N | -2.88087800 | 1.49271200 | -0.18939900 |
| C | 2.93268600 | 2.37167300 | 0.59558200 |
| N | -2.88029800 | -1.49339700 | 0.18947500 |
| C | 2.93319300 | -2.37100100 | -0.59569200 |
| C | 3.38403600 | 3.05028500 | -1.82346300 |
| H | 4.11496800 | 2.22513200 | -1.80270400 |
| C | 4.70965300 | -0.65959800 | -0.16257200 |
| H | 5.52361900 | -1.35824000 | -0.33735100 |
| C | 3.00063400 | -3.37661800 | 0.38932000 |
| C | 2.99968600 | 3.37730200 | -0.38944200 |
| C | 2.40777200 | 1.51598500 | 2.96268100 |
| H | 2.72624400 | 0.56502000 | 2.50639100 |
| C | 4.70951200 | 0.66071400 | 0.16223100 |
| H | 5.52333400 | 1.35956100 | 0.33687300 |
| C | 2.47122600 | 2.60224400 | 1.90251200 |
| C | -5.86266100 | -1.97783900 | -0.04355000 |
| H | -5.87030900 | -2.76975600 | 0.72000200 |
| H | -6.65511900 | -2.21313700 | -0.77269600 |
| H | -6.13326000 | -1.03208600 | 0.44869900 |
| C | 2.47171400 | -2.60173800 | -1.90258700 |
| C | 2.60965900 | -4.66551200 | 0.01545000 |
| H | 2.65474900 | -5.47580700 | 0.74533200 |
| C | 2.60827300 | 4.66606100 | -0.01555000 |
| H | 2.65299400 | 5.47636400 | -0.74544500 |
| C | 3.38505700 | -3.04949500 | 1.82329300 |
| H | 4.11566000 | -2.22405300 | 1.80246200 |
| C | 2.14165600 | 2.55337400 | -2.57381700 |
| H | 1.67195800 | 1.69548700 | -2.06390100 |
| H | 2.39299400 | 2.24831200 | -3.60196900 |
| H | 1.38847500 | 3.35642600 | -2.62636700 |
| C | 2.40783000 | -1.51553900 | -2.96279400 |
| H | 2.72590600 | -0.56442400 | -2.50654000 |
| C | -1.45244000 | -1.89103000 | 2.76854000 |

| | | | |
|---|---|---|---|
| H | -0.69506000 | -1.12473900 | 2.53239500 |
| H | -0.96404300 | -2.63885400 | 3.41520600 |
| H | -2.25241800 | -1.41661600 | 3.35848900 |
| C | -0.82770400 | -3.66288100 | 0.34821500 |
| H | -1.21120300 | -4.14803200 | -0.56268000 |
| H | -0.37957300 | -4.44496600 | 0.98303700 |
| H | -0.01356100 | -2.97847400 | 0.04429900 |
| C | 3.36510900 | 1.81845100 | 4.11847100 |
| H | 4.40187800 | 1.92407000 | 3.76650100 |
| H | 3.33592600 | 1.01121200 | 4.86567900 |
| H | 3.08590400 | 2.75442500 | 4.62725600 |
| C | 2.07195400 | 3.90840000 | 2.21848700 |
| H | 1.71049200 | 4.12672400 | 3.22671800 |
| C | -1.45323100 | 1.89079700 | -2.76848400 |
| H | -0.69594100 | 1.12439500 | -2.53240600 |
| H | -0.96471700 | 2.63866900 | -3.41500100 |
| H | -2.25321400 | 1.41653800 | -3.35855300 |
| C | 0.97491600 | 1.32473200 | 3.46811200 |
| H | 0.63104100 | 2.20580200 | 4.03292300 |
| H | 0.91181600 | 0.45306300 | 4.13842100 |
| H | 0.27303100 | 1.16930300 | 2.63063500 |
| C | 2.15011700 | 4.92965300 | 1.27633500 |
| H | 1.84837900 | 5.94343100 | 1.54770700 |
| C | 4.02772500 | 4.21876400 | -2.56616700 |
| H | 3.29988700 | 5.02152700 | -2.76151200 |
| H | 4.40414700 | 3.88353500 | -3.54325200 |
| H | 4.86848500 | 4.64972800 | -2.00327400 |
| C | 0.97489800 | -1.32492100 | -3.46826900 |
| H | 0.63147300 | -2.20612600 | -4.03314600 |
| H | 0.91141300 | -0.45324400 | -4.13853000 |
| H | 0.27290600 | -1.16988400 | -2.63080900 |
| C | 2.07286600 | -3.90803500 | -2.21853200 |
| H | 1.71140700 | -4.12648100 | -3.22673700 |
| C | -4.27176700 | 0.63351600 | 2.31567500 |
| H | -4.51228800 | -0.39366000 | 2.00768600 |
| H | -5.02622000 | 0.96214500 | 3.04904500 |
| H | -3.29893500 | 0.61699000 | 2.83780000 |
| C | -5.86335000 | 1.97671800 | 0.04319400 |
| H | -5.87147700 | 2.76983300 | -0.71910700 |
| H | -6.65618200 | 2.21022900 | 0.77251100 |
| H | -6.13305600 | 1.03151900 | -0.45060800 |
| C | -0.82877700 | 3.66267100 | -0.34801100 |
| H | -1.21243900 | 4.14771100 | 0.56287800 |
| H | -0.38082600 | 4.44489100 | -0.98279800 |

| | | | |
|---|---|---|---|
| H | -0.01446200 | 2.97847800 | -0.04407700 |
| C | 2.14258400 | -2.55312500 | 2.57385800 |
| H | 1.67247600 | -1.69539800 | 2.06405600 |
| H | 2.39393400 | -2.24802300 | 3.60199400 |
| H | 1.38972400 | -3.35648000 | 2.62646300 |
| C | 2.15147300 | -4.92926400 | -1.27639400 |
| H | 1.85006500 | -5.94314800 | -1.54773500 |
| C | -3.83104300 | 3.51880600 | 1.74525700 |
| H | -2.89391700 | 3.43621500 | 2.31970400 |
| H | -4.63623600 | 3.77155500 | 2.45402900 |
| H | -3.72960200 | 4.36330500 | 1.04827100 |
| C | -4.27090100 | -0.63468100 | -2.31586300 |
| H | -4.51183400 | 0.39242600 | -2.00795200 |
| H | -5.02504000 | -0.96355600 | -3.04944400 |
| H | -3.29791900 | -0.61785500 | -2.83770000 |
| C | 4.02933300 | -4.21773500 | 2.56586500 |
| H | 3.30188100 | -5.02084400 | 2.76121800 |
| H | 4.40567900 | -3.88239600 | 3.54294200 |
| H | 4.87024700 | -4.64827300 | 2.00287900 |
| C | -3.82980100 | -3.51984600 | -1.74516900 |
| H | -2.89270000 | -3.43703900 | -2.31962600 |
| H | -4.63492600 | -3.77282400 | -2.45393600 |
| H | -3.72812900 | -4.36429600 | -1.04816200 |
| C | 3.36529300 | -1.81764700 | -4.11856900 |
| H | 4.40211300 | -1.92279500 | -3.76660800 |
| H | 3.33575000 | -1.01046000 | -4.86582000 |
| H | 3.08649400 | -2.75376700 | -4.62730800 |
| C | -3.51350200 | -3.87113400 | 1.88981700 |
| H | -4.25459200 | -3.29242000 | 2.46483600 |
| H | -3.06061200 | -4.60272100 | 2.57873400 |
| H | -4.04551200 | -4.43585400 | 1.11123300 |
| C | -3.51461700 | 3.87047400 | -1.88947500 |
| H | -4.25587100 | 3.29163800 | -2.46416000 |
| H | -3.06195400 | 4.60194900 | -2.57866000 |
| H | -4.04638500 | 4.43531900 | -1.11081500 |