Electronic Supplementary Information

Facile Reactions of Gold (I) Complexes with Tri(*tert*-butyl)azadiboriridine

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Experimental Section

General considerations

All syntheses were carried out under inert atmosphere with standard Schlenk and glovebox techniques unless otherwise stated. Tetrahydrofuran (THF), diethyl ether (Et_2O), hexane and toluene were freshly distilled from Na/benzophenone prior to use. C_6D_6 and Tol-d_8 were distilled from sodium and degassed three times using freeze-pump-thaw cycling and stored in an argon-filled glovebox. The gold(I) complexes AuCl(L), L = SMe_2,[1] PPh_3[2], PMe_3[3] and tri(*tert*-butyl)azadiboriridine [4] were prepared according to the literature procedures. The isonitrile CNtBu was purchased from Sigma-Aldridge and used without further purification. Other chemicals were used as supplied. ^{1}H NMR (400 MHz) ^{11}B{^{1}H} NMR (128 MHz), and ^{31}P{^{1}H} NMR (162 MHz) were recorded using a JEOL AL - 400 spectrometer or JEOL JNM-ECA 600 NMR spectrometer [^{1}H NMR (600 MHz) ^{11}B{^{1}H} NMR (193 MHz), and ^{31}P{^{1}H} NMR (243 MHz)]. Chemical shift (δ) are given in ppm with reference against external $SiMe_4$ (^{1}H, ^{13}C{^{1}H}), $BF_3{\cdot}Et_2O$ (^{11}B) and 85% H_3PO_4 (^{31}P).

Preparation of 2

AuCl(SMe_2) (45.7 mg, 0.155 mmol) was added to a toluene (3.5 mL) solution of tri(*tert*-butyl)azadiboriridine (32.4 mg, 0.157 mmol). The reaction was stirred for 5 minutes at room temperature before filtered through a cotton plug. The collected filtrate was stored at –30 ˚C to afford **2** as dark brown crystals (47.6 mg, 0.108 mmol, Yield: 70%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.12 (BC(CH_3)$_3$, s, 18H), 0.94 (NC(CH_3)$_3$, s, 9H); ^{13}C{^{1}H} NMR (150 MHz, Tol-d_8): 57.6 (s, N*C*(CH$_3$)$_3$), 31.2 (s, NC(*C*H$_3$)$_3$), 29.8 (s, BC(*C*H$_3$)$_3$), 25.3 (br, B*C*(CH$_3$)$_3$); ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ 41.0 (s); ESI: [M+NCCH$_2$]$^-$: found. 479.18964, calcd. 479.18764.

Preparation of 3

AuCl(PPh_3) (33.4 mg, 67.5 μmol) was added to a hexane/Et_2O (1:1) (8 mL) solution of tri(*tert*-butyl)azadiboriridine (14.7 mg, 71.0 μmol). The reaction mixture was stirred for 10 minutes at room temperature before filtered through a cotton plug. The filtrate was concentrated and stored at –30 ˚C to afford pale pink crystals of **3** (30.5 mg, 43.5 μmol, 64 %). ^{1}H NMR (400 MHz, C_6D_6): δ 1.65 (NC(CH_3)$_3$, s, 9H), 1.43 (BC(CH_3)$_3$, s, 18H); ^{13}C{^{1}H} NMR (150 MHz, Tol-d_8): 134.4 (d, $^2J_{C\text{-}P}$= 14.1 Hz), 131.1 (s), 130.3 (d, $^1J_{C\text{-}P}$= 44.3 Hz), 129.1 (d, $^3J_{C\text{-}P}$= 10.7 Hz), 56.7 (dbr, $^4J_{C\text{-}P}$= 12.8 Hz, N*C*(CH$_3$)$_3$), 32.9 (s, BC(*C*H$_3$)$_3$), 32.8 (s, BC(*C*H$_3$)$_3$), 32.5 (s, NC(*C*H$_3$)$_3$), 27.0 (br, B*C*(CH$_3$)$_3$), 26.8 (br, B*C*(CH$_3$)$_3$); ^{11}B NMR (128 MHz, C_6D_6): δ 41.6 (s), 7.3 (s). ^{31}P{^{1}H} NMR (160 Hz, C_6D_6): δ 56.0 (s). ESI: [M–AuPPh$_3$+NCCH$_2$]$^-$: found. 301.24051, calcd. 301.23948.

Alternative synthesis: One equivalent of PPh_3 (3.34 g, 12.7 μmol) was added to a C_6D_6 solution of **2** (5.6 mg, 12.7 μmol). After shaking at room temperature for ten minutes, **3** was observed in quantitative yield by ^{1}H, ^{11}B{^{1}H}, and ^{31}P{^{1}H} NMR measurements.

Preparation of 4

AuCl(PMe_3) (51.5 mg, 0.167 mmol) was added to a benzene solution (0.6 mL) of tri(*tert*-butyl)azadiboriridine (34.7 mg, 0.168 mmol). The reaction mixture was stirred for 10 minutes at room temperature before filtered through a cotton plug. The cotton plug was then washed with

hexane. The combined filtrate was concentrated and stored at –30 ˚C to afford pink crystals of **4** (68.6 mg, 0.133 mmol, 80 %). ^{1}H NMR (400 MHz, C_6D_6): δ 1.63 (NC(CH_3)$_3$, s, 9H), 1.47 (BC(CH_3)$_3$, s, 18H), 0.59 (PMe_3, d, J = 8.3 Hz, 9H). ^{13}C{^{1}H} NMR (150 MHz, Tol-d_8): 56.4 (d, $^{2}J_{C\text{-}P}$= 13.0 Hz, NC(CH$_3$)$_3$), 33.0 (s, BC(CH$_3$)$_3$), 32.4 (s, NC(CH$_3$)$_3$), 27.2 (br, BC(CH$_3$)$_3$), 14.0 (d, $^{2}J_{C\text{-}P}$= 26.7 Hz, P(CH$_3$)$_3$); ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): 41.5 (s), 6.5 (s). ^{31}P{^{1}H} NMR (160 Hz, C_6D_6): δ 18.7 (s). ESI: [M–PMe_3+H]$^{-}$: found. 440.17704, calcd. 440.17674.

Compound **4** can be also obtained in quantitative yield from **2** using a similar procedure to the alternative sythesis of **3** described above.

Preparation of 5

DMAP (1.9 mg, 15.6 μmol) was added to a C_6D_6 (0.6 mL) solution of **2** (6.9 mg, 15.7 μmol) at room temperature. After 10 mins of shaking, colorless crystals of **5** formed in the NMR tube. Compound **5** was sparingly soluable in benzene at room temperature. ^{11}B{^{1}H} NMR signal was observed at high temperatures. ^{1}H NMR (400 MHz, C_6D_6): δ 8.16 (d, J = 6.8 Hz, 2H), 5.46 (d, J = 6.8 Hz, 2H), 2.09 (N(CH_3)$_2$, s, 6H), 1.65 (BC(CH_3)$_3$, s, 9H), 1.53 (BC(CH_3)$_3$, s, 9H), 1.11 (NC(CH_3)$_3$, s, 9H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): 153.8 (s, *C*H), 150.1 (s, *C*H), 106.6 (s, N(*C*H$_3$)$_2$), 54.2 (s, N*C*(CH$_3$)$_3$), 38.0 (s, N(*C*H$_3$)$_2$), 33.4 (br, B*C*(CH$_3$)$_3$), 32.4 (s, BC(*C*H$_3$)$_3$), 29.9 (s, BC(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, 40 °C): δ 35.5, –0.6 (s). ESI: [M–DMAP+OMe]$^{-}$: found. 470.18783, calcd. 470.18621, [DMAP+H]$^{+}$:found. 123.09172, calcd. 123.09167.

Compound **5** can be also obtained in quantitative yield from **2** using a similar procedure to the alternative sythesis of **3** described above.

Preparation of 6

Hexane (2.0 mL) solution of *t*BuNC (4.3 mg, 51.7 μmol) was added to a hexane (4.0 mL) solution of **3** (16.8 mg, 23.9 μmol) at *ca.* –30 °C. The reaction mixture was stirred for 5 minutes at room temperature and turned to a white suspension. The reaction mixture was then stored at –30 ˚C for the white precipitate to settle. After decantation, the residue solid was dried under vacuum to afford a white solid of **6** (14.1 mg, 18.0 μmol, 75 %).^{1}H NMR (400 MHz, C_6D_6): δ 7.38 (br, 6H), 6.97 (br, 9H), 2.21 (N(CH_3)$_2$, s, 6H), 1.86 (BC(CH_3)$_3$, s, 9H), 1.83 (BC(CH_3)$_3$, s, 9H), 1.37 (NC(CH_3)$_3$, s, 9H). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): 133.9 (d, $^{2}J_{CP}$= 14.3 Hz), 131.1 (d, $^{4}J_{CP}$= 16.8 Hz), 130.3 (d, $^{1}J_{CP}$= 35.4 Hz), 129.0 (d, $^{3}J_{CP}$= 9.2 Hz), 63.9 (s, N*C*(CH$_3$)$_3$), 54.2(s, N*C*(CH$_3$)$_3$), 37.3 (s), 34.8 (s), 33.6 (s), 32.7 (s);^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ 40.4 (s), 12.4 (s). ^{31}P{^{1}H} NMR (160 Hz, Tol-d_8): δ 41.1 (br). ESI: [M–Cl]$^{+}$: found. 749.36378, calcd. 749.36360.

In the solution of **6**, signals of a minor species (**6'**) is always observed in the NMR spectra. This can be seen more easily in the ^{31}P{^{1}H} NMR spectra (Figure A17 in Appendix 2). So far we have not been able to isolate this minor species. Its signal diminishes as the temperature decreases, which suggests it is in equilibrium with **6**, possiblly an isomer of **6** due to halide migration or dissociation. Currently we are investigating the nature of this species.

Variable Temperature NMR Spectra

Although at lower temperatures the two boron-bound tBu groups in **3** splitted into two, no coalescence was observed.

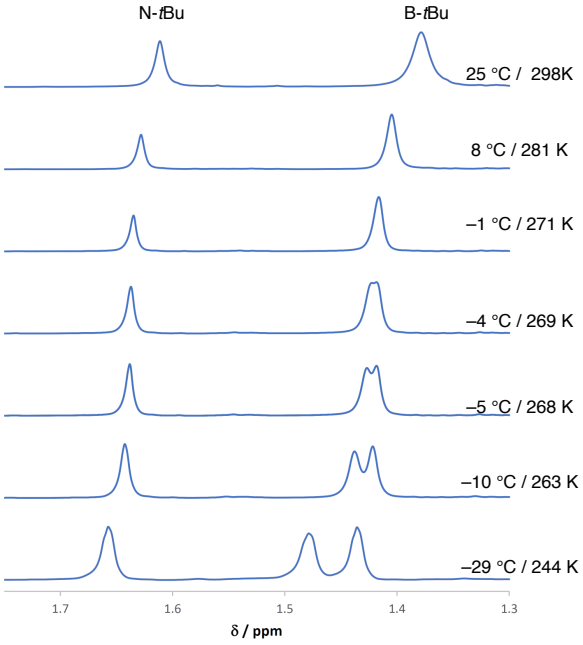


Figure S1. Excerpt of the variable-temperature ^{1}H NMR spectra (600 MHz, Tol-d_8) of 3. Spectra were recorded in the range between –40 and 20 °C.

The lability of PMe_3 was further confirmed by solution $^{31}P\{^{1}H\}$ NMR experiments of **4** with free PMe_3 at room temperature. A single averaged signal between the free PMe_3 and coordinated PMe_3 in **4** was observed at –24.0 ppm (*cf.* **4**: 18.7, free PMe_3 (1 eq.): –62.1 ppm), showing significant broadening ($\nu_{1/2}$ *ca.* 1670 Hz). This suggests a rapid exchange of free and coordinated PMe_3 in solution. By contrast, a solution mixture of **3** and free PPh_3 at room temperature showed two distinct resonances corresponding to **3** and free PPh_3 with slight broadening ($\nu_{1/2}$ 68.4 Hz), consistent to the absence of coalescence in the ^{1}H VTNMR spectra of **3** in solution at room temperature (Figure S1).

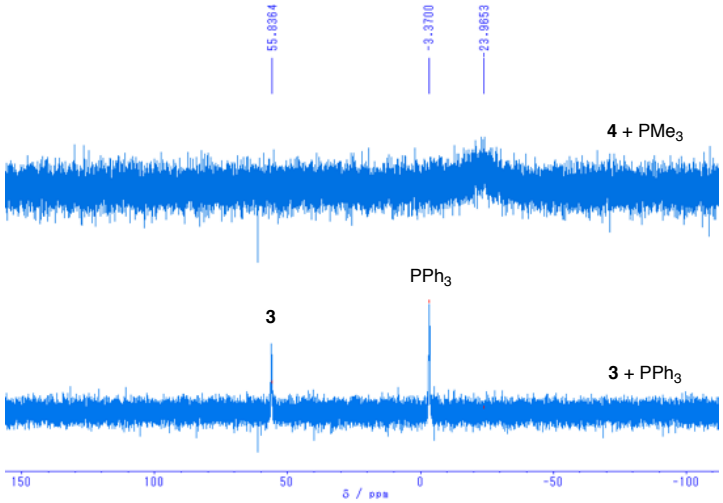


Figure S2. $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, C_6D_6) of a) 4 and PMe_3 in 1 : 1 ratio; b) 3 and PPh_3 in 1:1 ratio.

When one equivalent of PPh_3 was added into a solution of **4**, the $^{31}P\{^1H\}$ NMR spectrum obtained at room temperature showed two very broad singlets, indicating a dynamic competition in solution. The chemical shift of 14.6 ($\nu_{1/2}$ 864.7 Hz, *cf.* **4**, 18.7 ppm) and –4.9 ppm $\nu_{1/2}$ 203.9 Hz; *cf.* free PPh_3: –4.9) suggested that **4** and free PPh_3 were the major species. Both signals sharpened as the solution was cooled, however, the singlet assigned to PPh_3 started to broaden again from –50 °C, accompanied by detection of **3** (56 ppm). At –70 °C, *ca.* 17.5% of **3** with respect to **4** (72.5%, estimated from integration) was generated. These data indicate that **3** is kinetically favored and **4** is thermodynamically more stable than **3**, consistent to the previous findings.

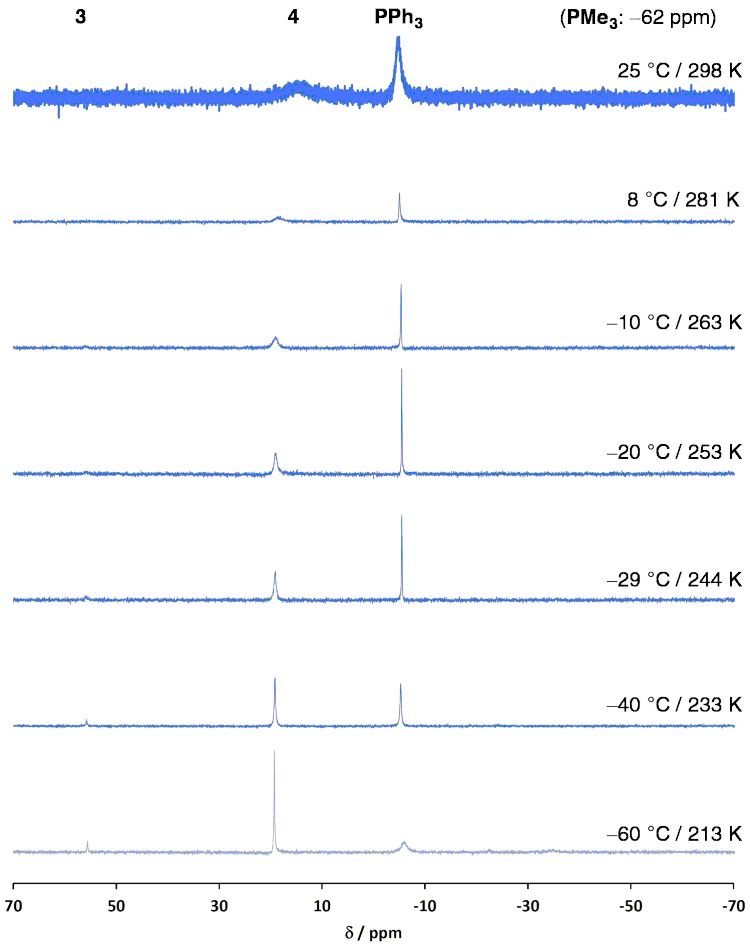


Figure S3. Excerpt of the variable-temperature $^{31}P\{^1H\}$ NMR spectra (243 MHz, Tol-d_8) of 4 and PPh_3 in 1:1 ratio.

Kinetic Studies

A JEOL JNM-ECA 600 NMR spectrometer was used for Variable Temperature (VT)-NMR studies of the solution behaviour of **4**. The probe temperature was calibrated using standard methanol solution purchused from Sigma-Aldridge. The spectra were recorded at set temperatures, the corresponding probe temperatures from calibration curve were used for calculations. The gNMR Spectral Simulation Program (*version 4.1*) was used to simulate the obtained spectra.

From the calibration curve of our instrument, the real probe temperatures were calculated using the calibration equation: $y = -0.0014x^2 + 1.6451\ x - 63.72$

where x = Set Temperature, y = real probe temperatures.

Table S1. Temperature calibration: correlations between the set and real probe temperatures.

Set Temp. / °C	Set Temp. / K	Real Probe Temp / K
0	273	281
–10	263	272
–20	253	263
–30	243	253
–40	233	243
–50	223	234

The hydrogen resonances corresponding to tertiary butyl groups of **4** are shifting depending on the temperature. We ploted chemical shifts against temperatures, and used the best approximation curve to assist the modeling of the chemical shifts (Hz) and half-width (Hz) of the resonances using gNMR. The simulated values for δ1, δ2 (in ppm) and half widthes of signals (in Hz) as well as the rate constant k are listed below (the observed and simulated signals are attached at the end of this section).

Table S2. Simulated parameters from gNMR for an Eyring plot.

Temp. Calibration		gNMR Simulation					Eyring Plot	
Set Temp. / °C	**Real Probe Temp** / K	**δ1** / ppm	**$\nu_{1/2}$ (δ1)** / Hz	**δ2** / ppm	**$\nu_{1/2}$ (δ2)** / Hz	**k** / s^{-1}	**1/T**	**ln(k/T)**
0	281	1.420	4.00	1.455	4.00	77.000	0.00356	–1.29
–10	272	1.420	0.20	1.510	0.20	18.000	0.00368	–2.72
–20	263	1.435	2.50	1.515	2.40	4.670	0.00380	–3.03
–30	253	1.455	2.10	1.520	2.03	0.850	0.00395	–5.70
–40	243	1.475	1.22	1.523	1.10	0.145	0.00411	–7.43
–50	234	1.500	0.90	1.528	0.65	0.020	0.00428	–9.37

With the simulated k values at different temperatures, an Eyring plot (ln(k/T) *v.s.*1/T) was created to estimate the ΔG, ΔS and ΔH values according to the equation:

$$\ln\left(\frac{k}{T}\right) = -\left(\frac{\Delta H^{\neq}}{R}\right)\frac{1}{T} + \frac{\Delta S^{\neq}}{R} + \ln\left(\frac{k_B}{h}\right)$$

where the slope of the plot = $-\left(\frac{\Delta H^{\neq}}{R}\right)$, and the intercept = $\frac{\Delta S^{\neq}}{R} + \ln\left(\frac{k_B}{h}\right)$

From the Eyring plot:

Slope = –11103, y-intercept = 38.16

$\therefore \Delta S^{\ddagger} = 28.6(7)$ cal mol^{-1}, $\Delta H^{\ddagger} = 22.1(2)$ kcal mol^{-1}

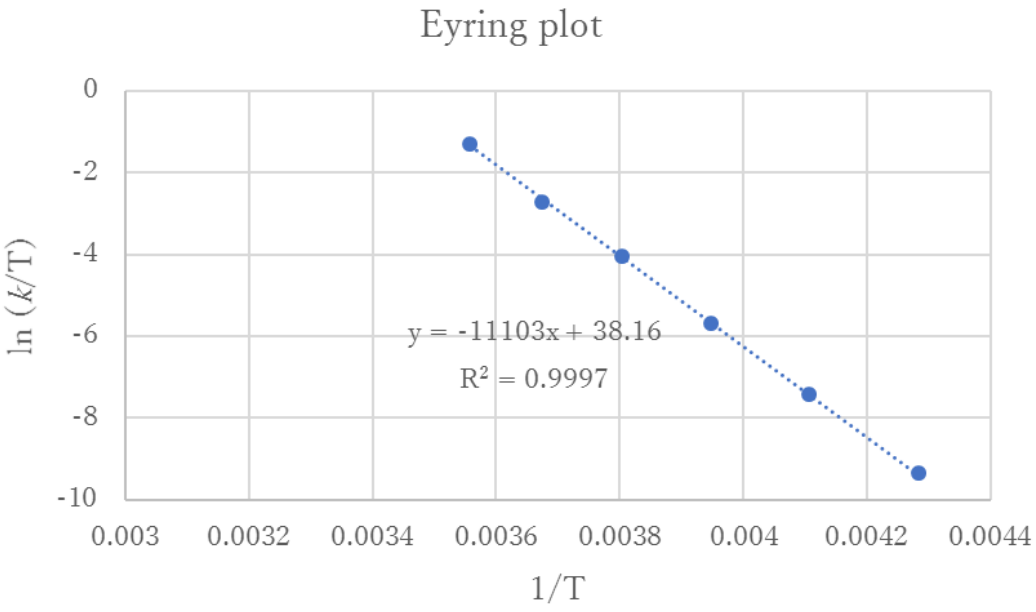


Figure S4. Eyring plot.

To verify our simulation, the $\Delta G^{\ddagger}$ value at each temperature was calculated from the obtained ΔS and ΔH values, from which the corresponding k is also calculated according to the rearranged equation:

$$k = exp^{-\{\frac{\Delta G^{\ddagger}}{RT} - \ln\left(\frac{h}{k_B T}\right)\}}$$

The difference between the calculated k from the Eyring plot and the initial simulated k is within 7%.

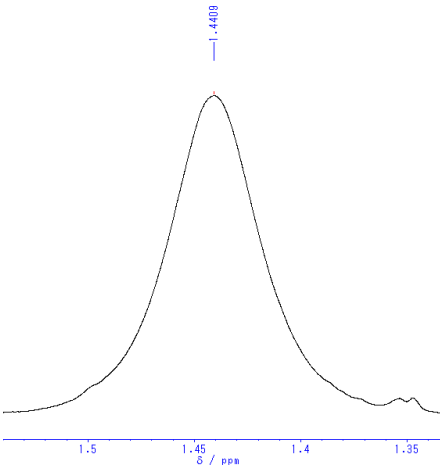
Table S3. Calculated and simulated parameters for k at different temperatures.

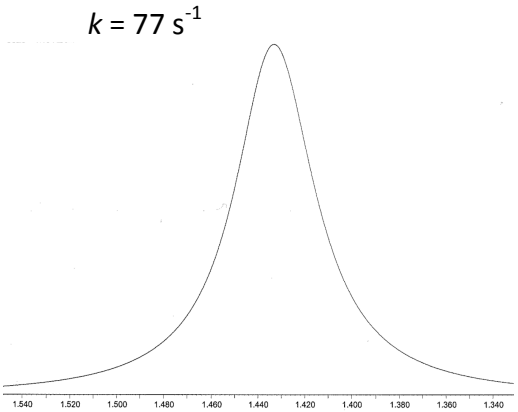
Set Temp. / °C	Real Probe Temp / K	$\Delta G^{\ddagger}$ / kcal/mol	calculated k (Erying plot) / s^{-1}	simulated k (gNMR) / s^{-1}
0	281	14.0(9)	73.211	77.000
–10	272	14.3(9)	19.337	18.000
–20	263	14.5(9)	4.461	4.670
–30	253	14.8(9)	0.881	0.850
–40	243	15.1(9)	0.146	0.145
–50	234	15.4(9)	0.020	0.020

gNMR simulation:

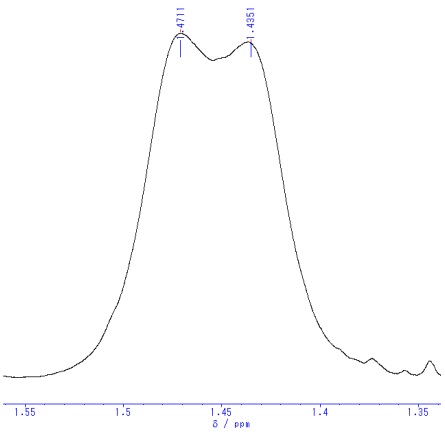
Meausured NMR Spectra **Simulated Spectra (gNMR)**

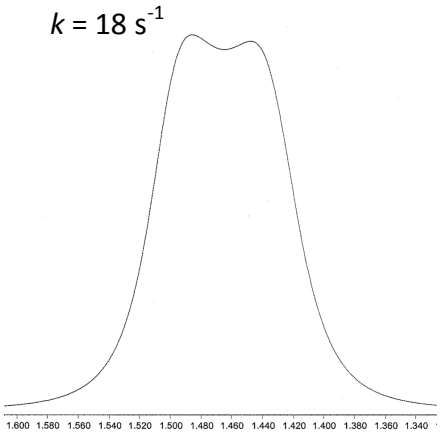
0 °C (Set temperature)



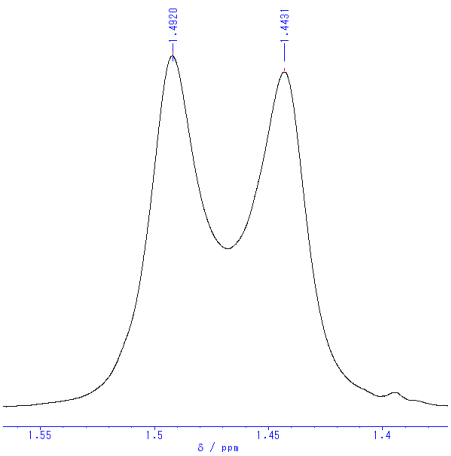


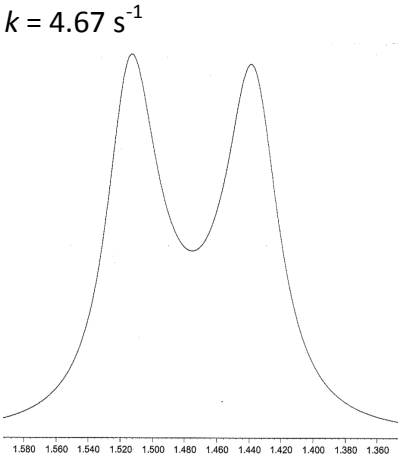
–10 °C





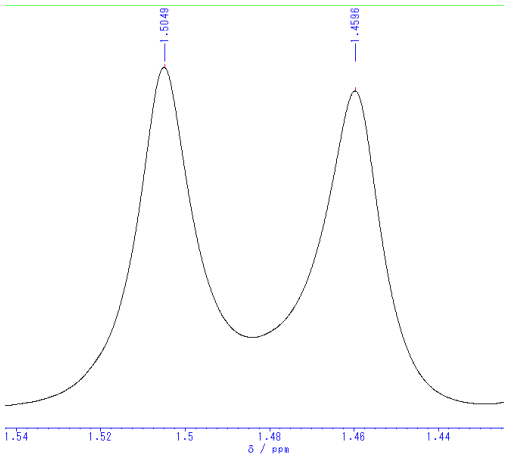
–20 °C

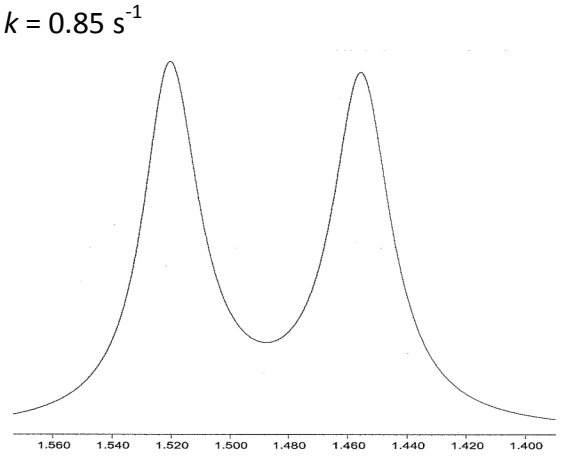




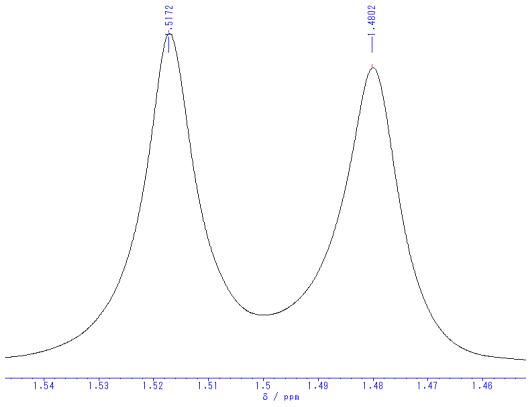
Meausured NMR Spectra **Simulated Spectra (gNMR)**

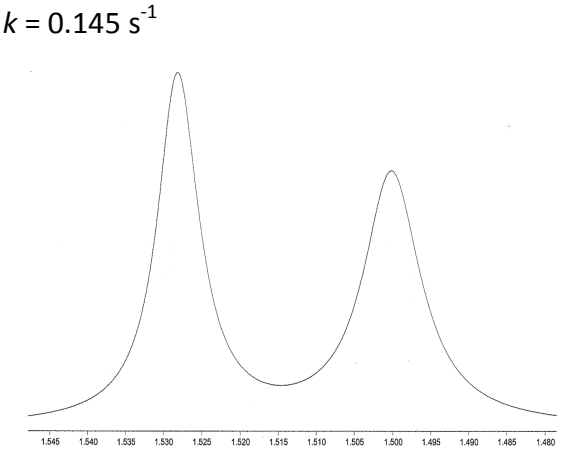
–30 °C



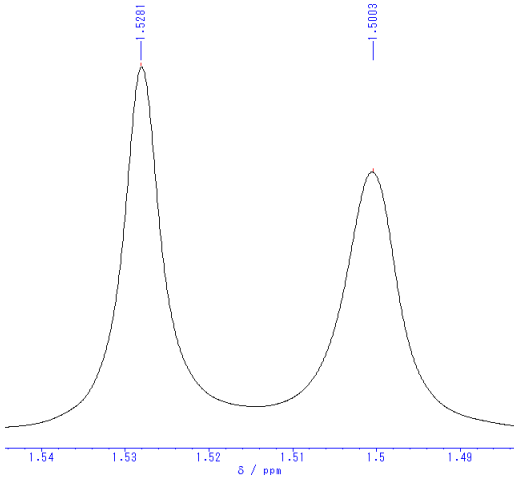


–40 °C





–50 °C



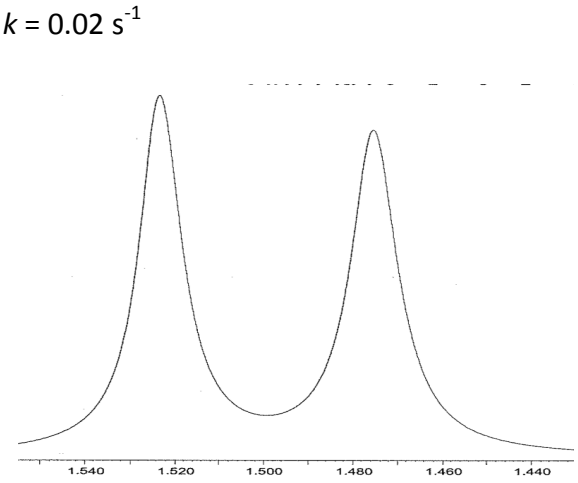


Figure S5. Comparison between measured and simulated spectra.

X-Ray Crystallographic Studies

Crystals suitable for the X-ray structural determination were mounted on a Bruker SMART APEXII CCD diffractometer and irradiated with graphite monochromated Mo-Kα radiation (l = 0.71073 Å) for data collection. The data were processed using the APEX program suite. All structures were solved by the *SHELXT* program (*ver.* 2014/5). Refinement on *F*2 was carried out using full-matrix least-squares with the *SHELXL* software package[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations. The *SHELX* was interfaced with *SHELXLE* GUI for most of refinement steps.[6] The pictures of molecules were prepared using *POV-RAY* 3.6.[7] Crystallographic data (CCDC 1578039-043) can be obtained from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S4. X-ray diffraction analysis parameters of complexes 2-6.

Name	2	3	4	5	6
CCDC No.	CCDC 1578039	CCDC 1578040	CCDC 1578041	CCDC 1578042	CCDC 1578043
Chemical formula	$C_{12}H_{27}AuB_2ClN$	$C_{30}H_{42}AuB_2ClNP$	$C_{15}H_{36}AuB_2ClNP$	$C_{19}H_{37}AuB_2ClN_3$	$C_{35}H_{51}AuB_2ClN_2P$
M_r	439.38	701.65	515.45	561.55	784.78
Crystal system, space group	Orthorhombic, *Pnma*	Triclinic, *P*	Orthorhombic, $Pca2_1$	Monoclinic, $P2_1/c$	Orthorhombic, *Pbca*
Temperature (K)	173	173	173	173	173
a, *b*, *c* (Å)	16.861 (3), 15.985 (3), 6.186 (1)	8.9905 (8), 9.4769 (8), 20.3831 (17)	14.701 (9), 11.511 (9), 12.330 (9)	15.7867 (13), 8.9815 (7), 16.7502 (13)	24.120 (2), 11.1958 (10), 25.776 (2)
α, β, γ (°)	90, 90, 90	82.518 (1), 85.780 (1), 62.071 (1)	90, 90, 90	90, 93.856 (1), 90	90, 90, 90
V (Å^3)	1667.3 (5)	1521.2 (2)	2087 (3)	2369.6 (3)	6960.6 (11)
Z	4	2	4	4	8
μ (mm^{-1})	8.96	5	7.25	6.33	4.38
Crystal size (mm)	0.12 × 0.07 × 0.06	0.08 × 0.07 × 0.03	0.03 × 0.01 × 0.002	0.08 × 0.04 × 0.01	0.02 × 0.004 × 0.002
T_{min}, T_{max}	0.324, 0.615	0.753, 0.857	0.315, 0.986	0.580, 0.945	0.853, 0.991
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667	0.656	0.625	0.659	0.66
$R[F^2 > 2\sigma(F^2)]$	0.026	0.029	0.031	0.016	0.042
$wR(F^2)$	0.055	0.059	0.076	0.04	0.095
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.22, −0.97	1.18, −0.56	2.28, −1.97	0.88, −0.94	3.25, −0.95

Computational Methodology

All the DFT calculations were done using the Gaussian09 software package.[8] We first performed gas-phase geometry optimizations with the M05-2X density-functional in combination mixed triple-ζ quality basis sets: LANL2TZ(f) for Au atom,[9] Pople's 6-311G(2d) for P atoms (with two polarization functions) and 6-311G(d) for the remaining atoms. A subsequent harmonic frequency calculation, for each optimized geometry, was executed to corroborate the character of each critical point in the potential energy surface (PES): reactants, intermediates and products must present all the frequencies as positive (eigenvalues of the Hessian matrix should be real) whereas transition states must have one and just one negative frequency (one eigenvalue of the Hessian matrix has an imaginary value). Thermal and entropy corrections to the total energy were taken from the thermochemistry analyses in the output file at 298K and 1 atm.

Also, we performed calculations for including the solvent effect through the PCM model[10] using the SMD parameters[11] according to the Truhlar's model using benzene as solvent. These energies were added to the gas-phase calculations reported as our final energy values.

Moreover, we have utilized the NBO program[12] for analyzing the bonding mechanism of the chemical structures obtained at the laboratory and the IBO program[13] for visualizing intrinsic molecular orbitals. In addition, we also conducted a gas-phase geometry optimization of compound **1** at the B3LYP/def2-svp level for a better description of its frontier molecular orbitals (shown in Figure 5 of our manuscript).

Selected bonding parameters of the optimised structures of complexes 2-5

For the coordinates of all the structures, please see Table S6 at the end of the SI.

Table S5. Calculated (black) and observed (grey) bond distances (Å) of complexes 2-5.

L =	-		PPh_3		PMe_3		DMAP	
Bond distance	**2**	Observ.	**3**	Observ.	**4**	Observ.	**5**	Observ.
B1-B2	1.906	1.889(8)	2.025	1.991(6)	2.040	2.050(1)	2.046	2.068(3)
B1-N1	1.417	1.420(5)	1.379	1.376(5)	1.382	1.363(9)	1.387	1.381(3)
B2-N1	-	-	1.495	1.495(5)	1.524	1.540(9)	1.512	1.518(3)
B1-Au	2.075	2.118(2)	2.161	2.183(4)	2.097	2.137(7)	2.095	2.117(2)
B2-Au	-	-	2.271	2.301(4)	2.174	2.227(6)	2.178	2.230(2)

Wiberg Bond indices and NBO charges of complexes 2-5

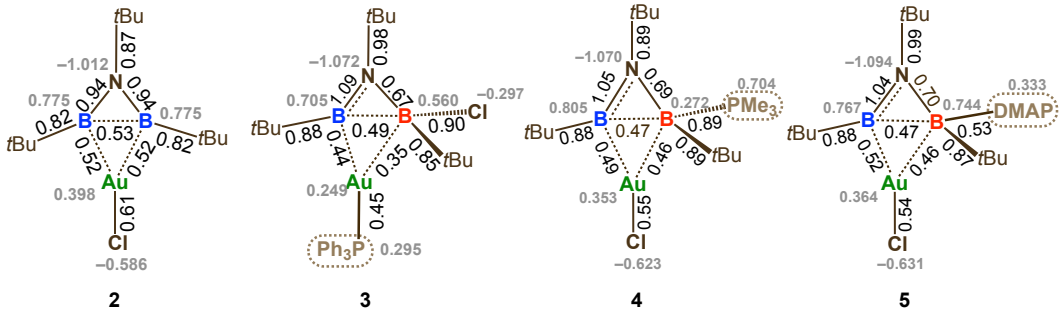


Figure S6. Wiberg bond indices (black) and NBO charges (grey) of complexes **2-5**.

Selected Kohn-Sham Molecular Orbitals of 1-5

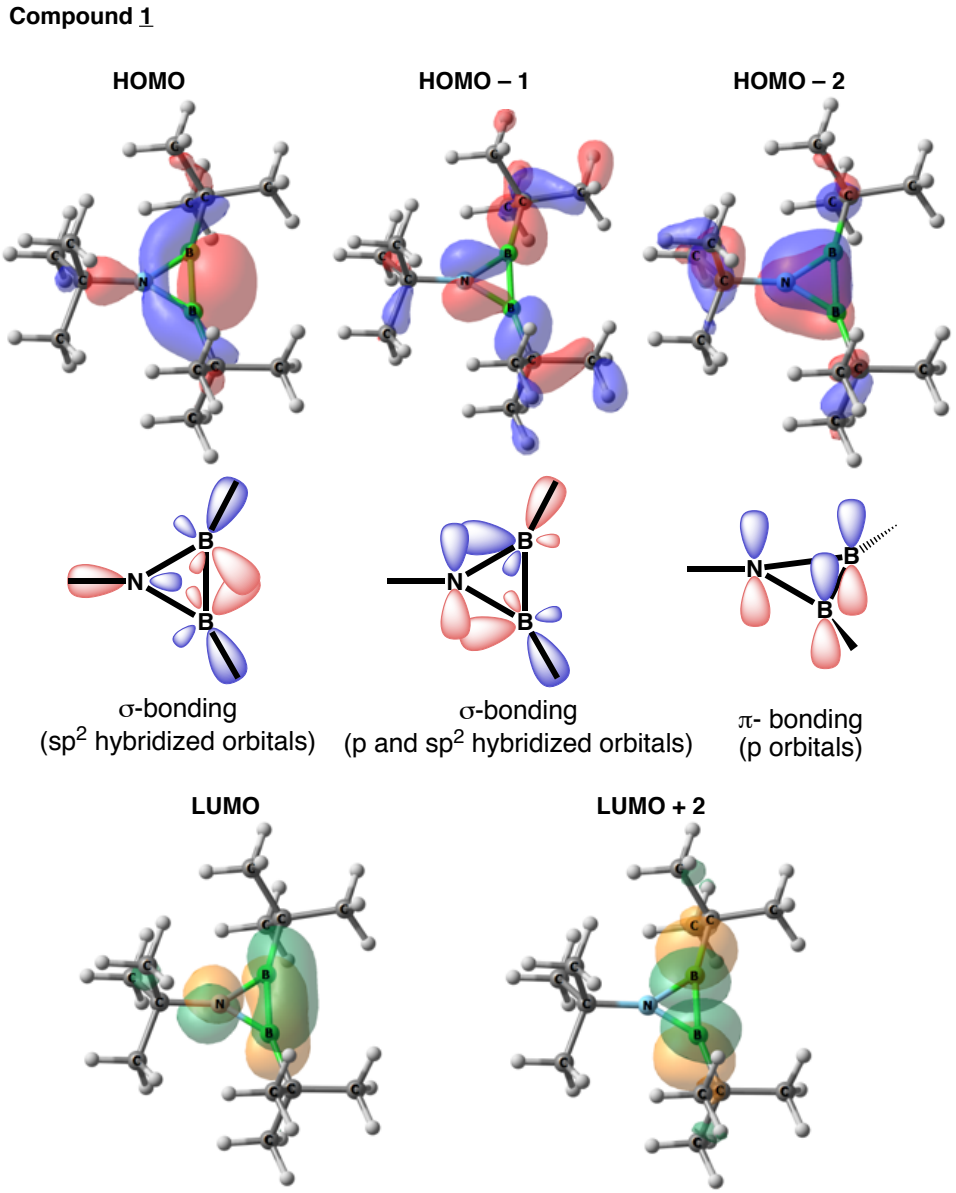


Figure S7. Frontier orbitals of **1** and cartoon illustrations of HOMO, HOMO-1 and HOMO-2 from atomic orbitals of nitrogen and boron atoms.

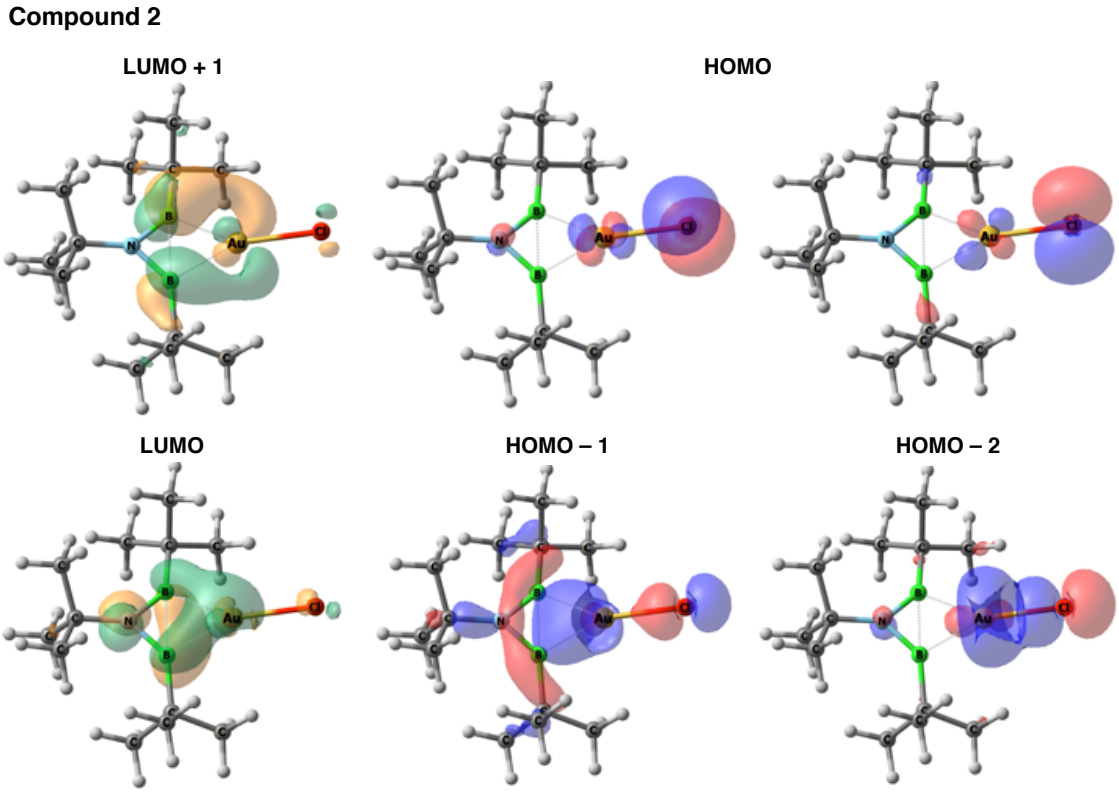


Figure S8. Selected frontier molecular orbitals of **2** (isosurface=0.03 a.u).

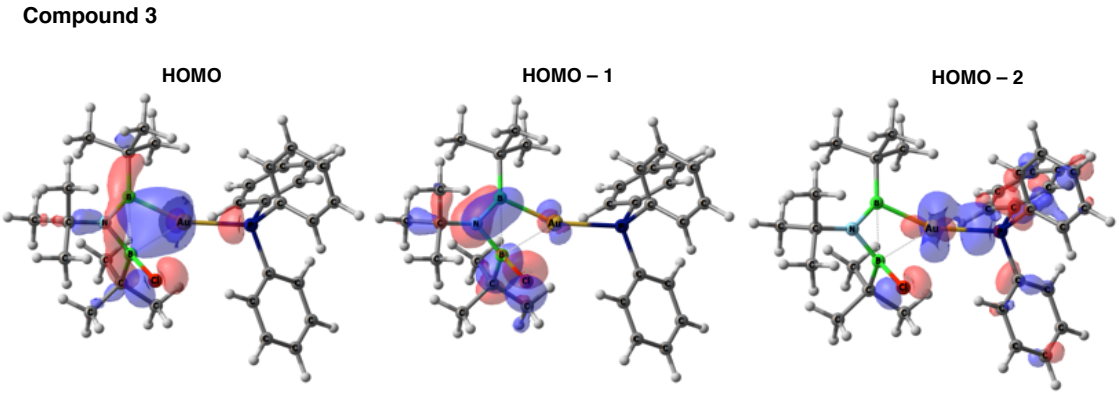


Figure S9. Frontier orbitals of **3** (isosurface=0.03 a.u).

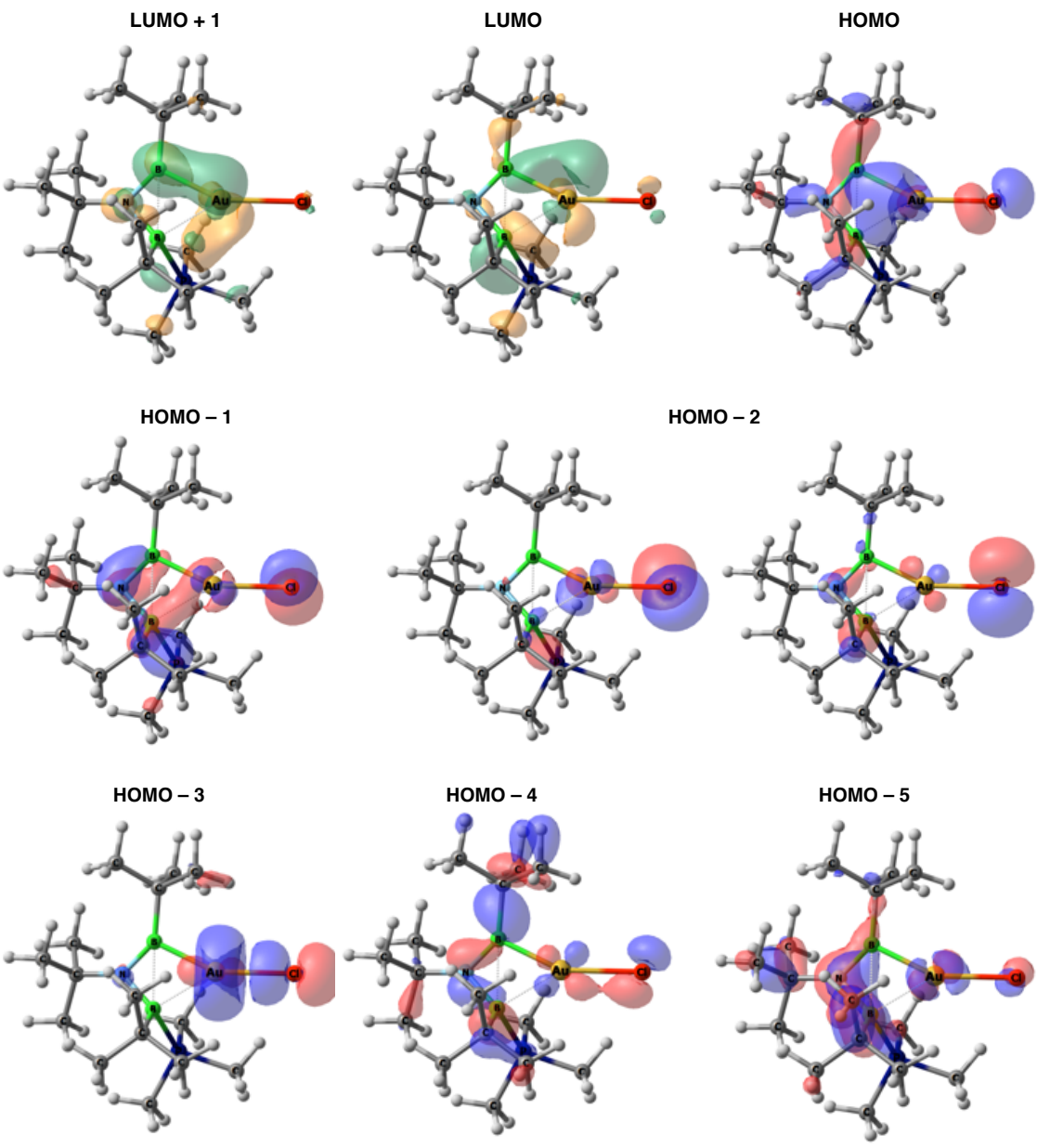


Figure S10. Frontier orbital of **4** (isosurface=0.03 a.u).

Compound 5

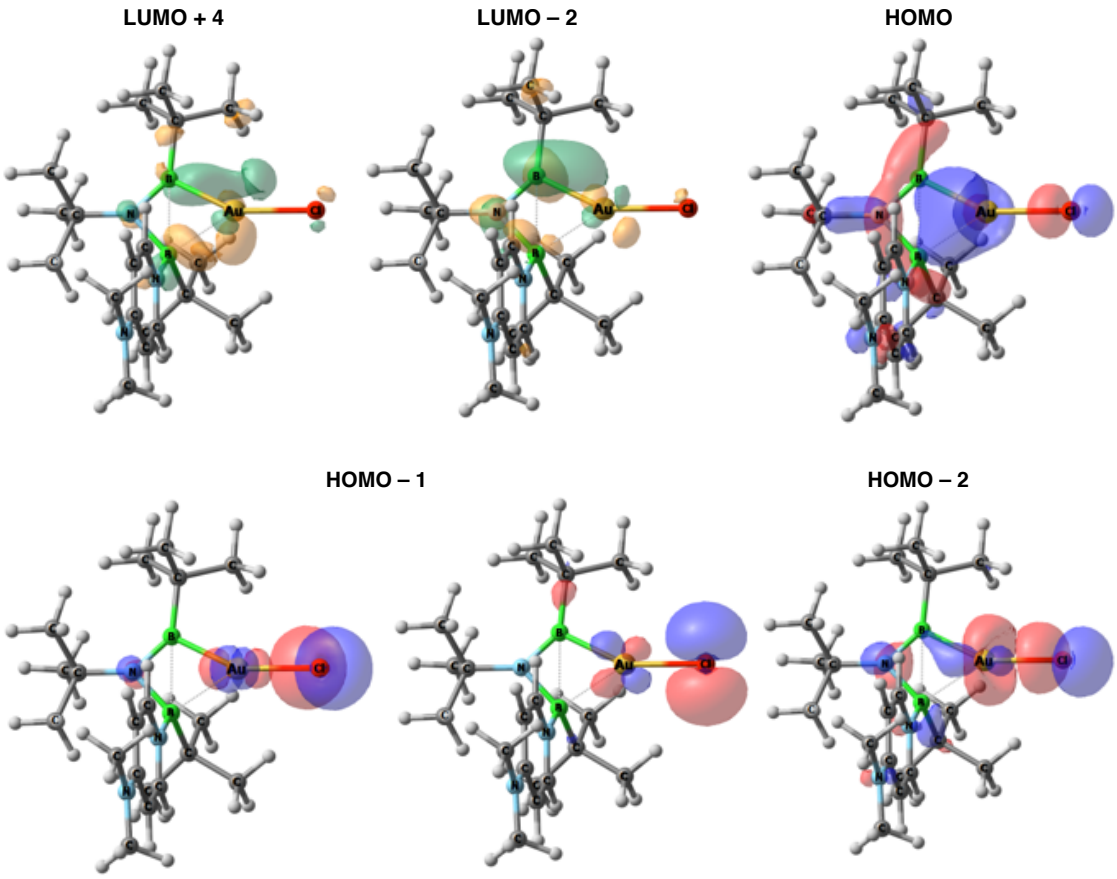
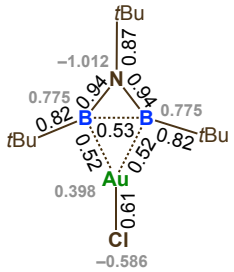


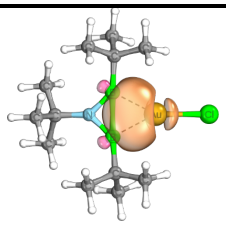
Figure S11. Frontier orbitals of **5** (isosurface=0.03 a.u).

Intrinsic Bonding Orbitals (IBO)

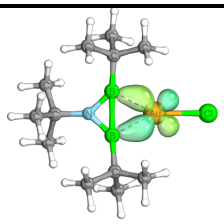
The IBO method uses simple mathematical criterion to creat computed Kohn-Sham wave function as chemical bonding without any approximation, pre-defined bonding motives or empirical input. The electrons in the doubly occupied IBOs are assigned proportionally to the individual atoms, allowing direct quantitative interpretation of chemical bonding. Selected Intrinsic Molecular Orbitals of complexes **2-5** are shown below, along with the fractions of electrons of the doubly occupied orbitals assigned to each atom involved in bonding.



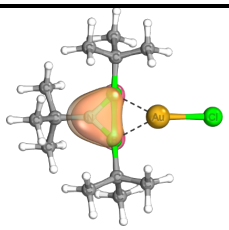
2



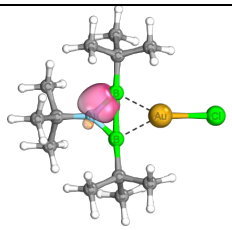
3c-2e bond
Au: 25%,
B1: 37.5%,
B2: 37.5%



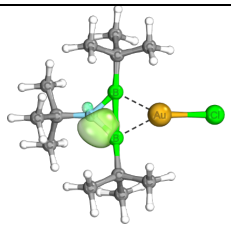
Au---B interactions
Au: 88%,
B1: 6%,
B2: 6%



Delocalized π-bond
N: 68.5%;
B1: 15.75%
B2: 15.75%

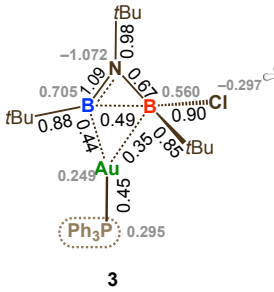


N-B single bond
N: 67%
B1: 33%

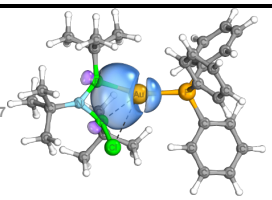


N-B single bond
N: 67%,
B2: 33%

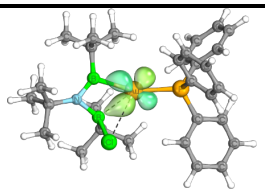
Figure S12. Most important Intrinsic Molecular Orbitals of compound **2**.



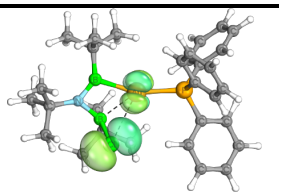
3



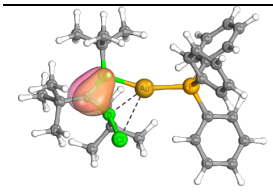
3c-2e bond
B1: 42%
B2: 27%
Au: 31%



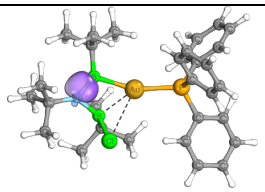
Au---B interactions
B1: 2%
B2: 4%
Au: 94%



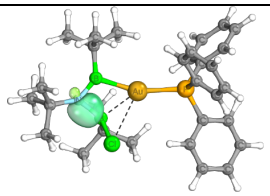
Au---Cl interaction
B2: 1%
Au: 50%
Cl: 49%



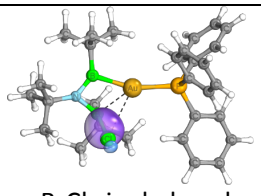
N-B double bond
B1: 23.6%
B2: 0.4%
N: 76%



N-B single bond
B1: 34%
B2: 1%
N: 65%

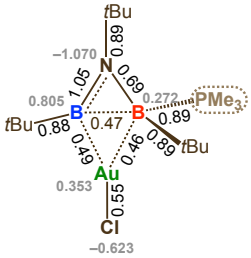


N-B single bond
B1: 1.5%
B2: 32.5%
N: 66%



B-Cl single bond
B2: 30%
Cl: 70%

Figure S13. Most important Intrinsic Molecular Orbitals of compound **3**.



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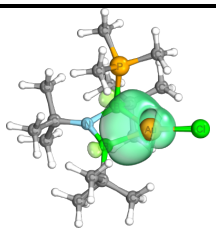
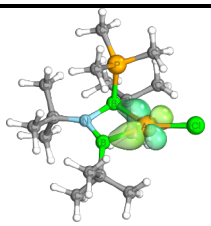
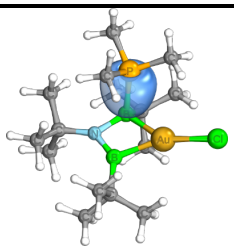


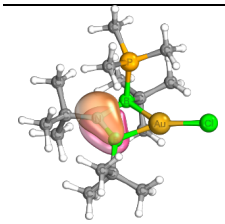
3c-2e bond
B1: 38%
B2: 34.5%
Au: 27.5%



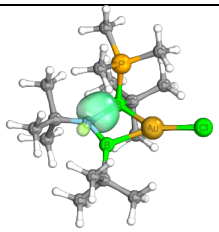
Au---B interactions
B1: 4.5%
B2: 5.5%
Au: 90%



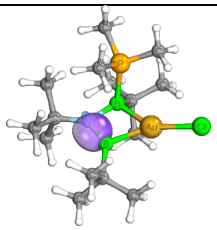
P → B bond
B2: 35.5%
P: 64.5%



N-B double bond
B1: 21%
B2: 3%
N: 76%

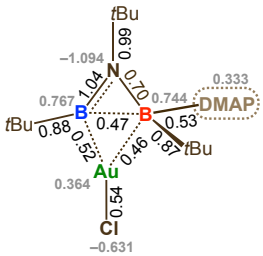


N-B single bond
B1: 1.5%
B2: 33%
N: 65.5%

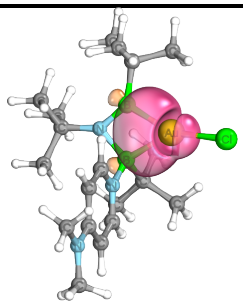


N-B single bond
B1: 34%
N: 66%

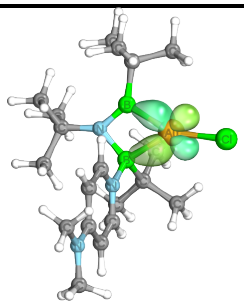
Figure S14. Most important Intrinsic Molecular Orbitals of compound **4**.



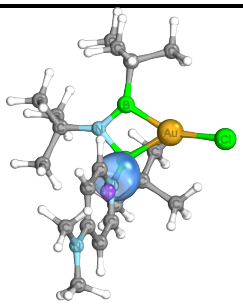
5



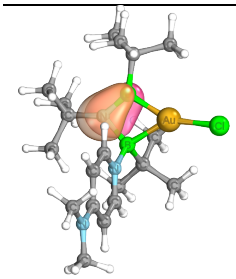
3c-2e bond
B1: 32%
B2: 40%
Au: 28%



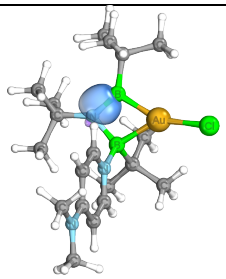
Au---B interactions
B1: 6%
B2: 4%
Au: 90%



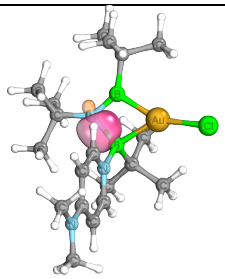
N → B bond
B1: 27%
N2: 73%



N-B double bond
B1: 20.5%
B2: 3.5%
N1: 76%



N-B single bond
B1: 34%
N1: 66%



N-B single bond
B1: 1.5%
B2: 32%
N1: 66.5%

Figure S15. Most important Intrinsic Molecular Orbitals of compound **5**.

Mechanistic pathways of interconversions among complexes 2-5, including transition states and intermediates (*c.f.* Fig. 3)

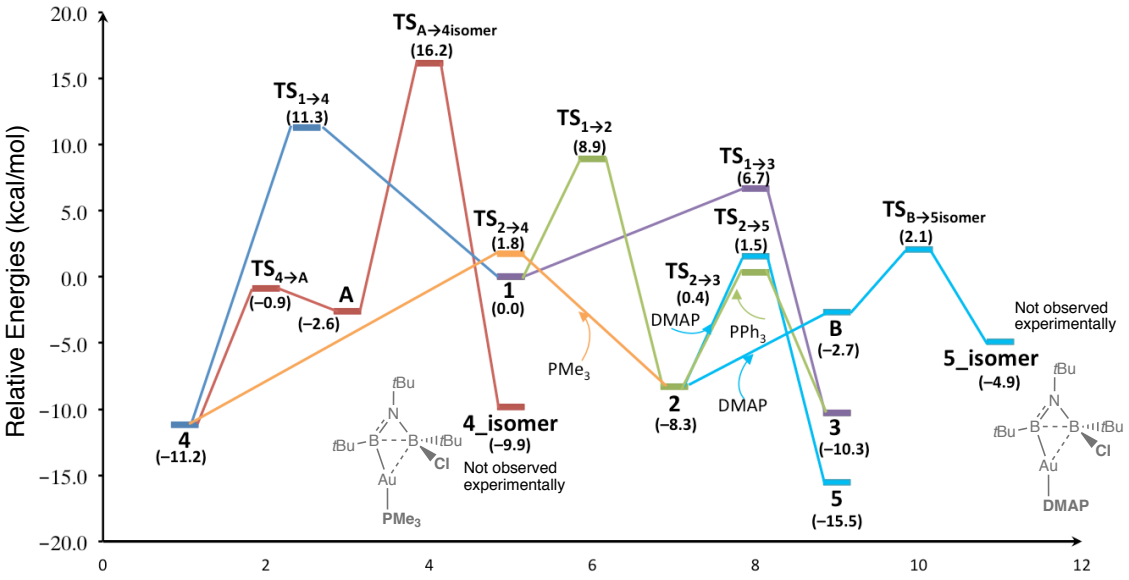
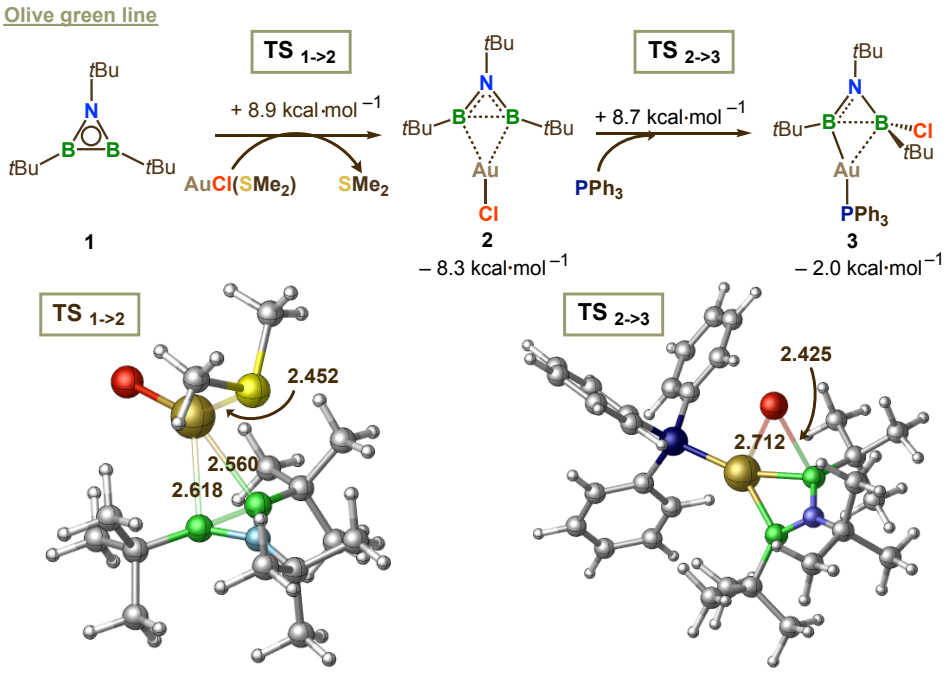
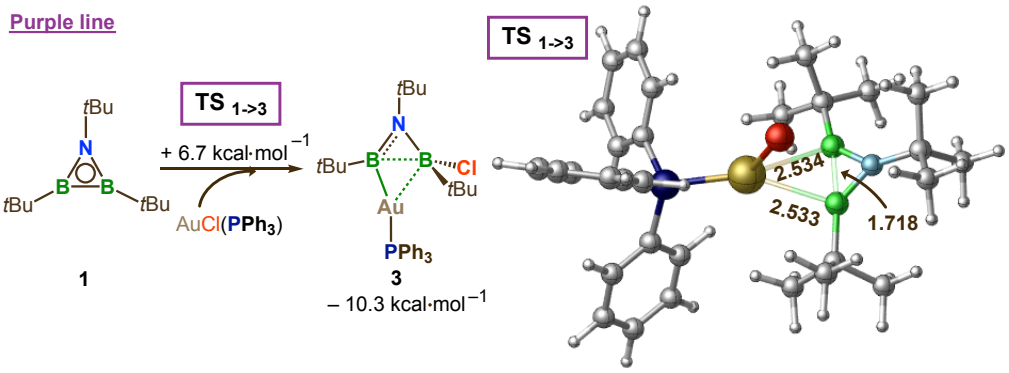


Figure S16. Summary of reaction mechanisms calculated at the SMD(benzene):M05-2X/(LANL2TZ(f), 6-311G(d)) level (298 K) for the formation of **2**-**5**. Energies are given as Gibbs free energies. The geometry of **3_isomer** (isostructural to **4**) could not be optimised.

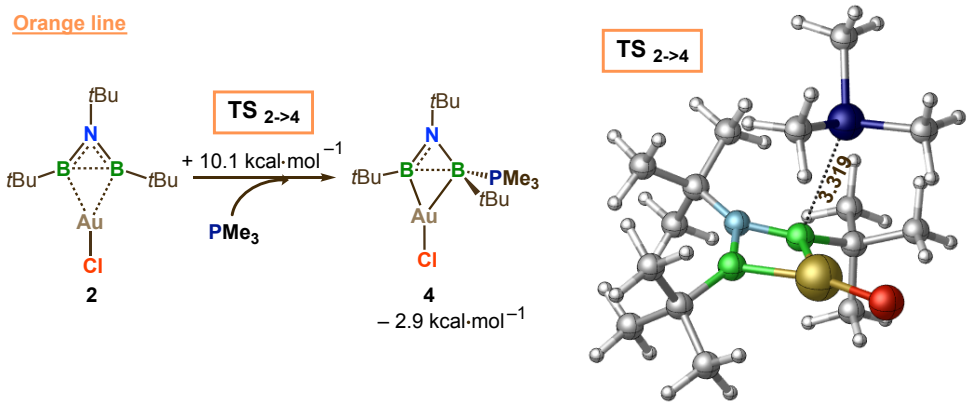
Each pathway is shown below with the corresponding transition states:



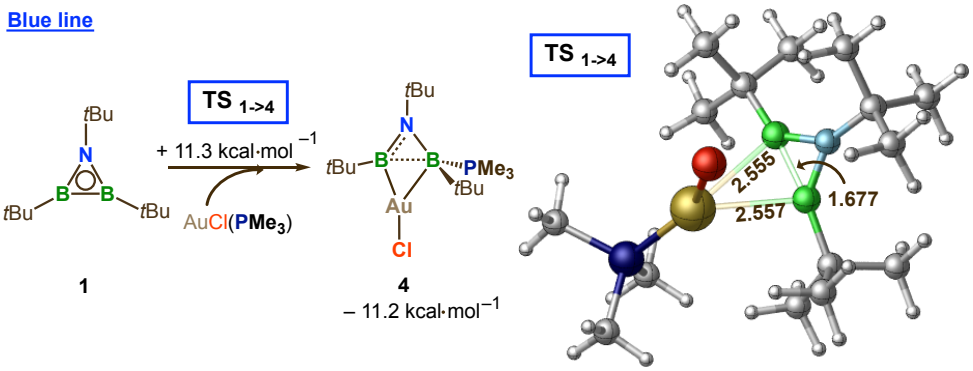
Scheme S1. Reaction mechanism for the interconversion from **1** to **2** and **3**. Calculated transition states show selected bond distances [Å].



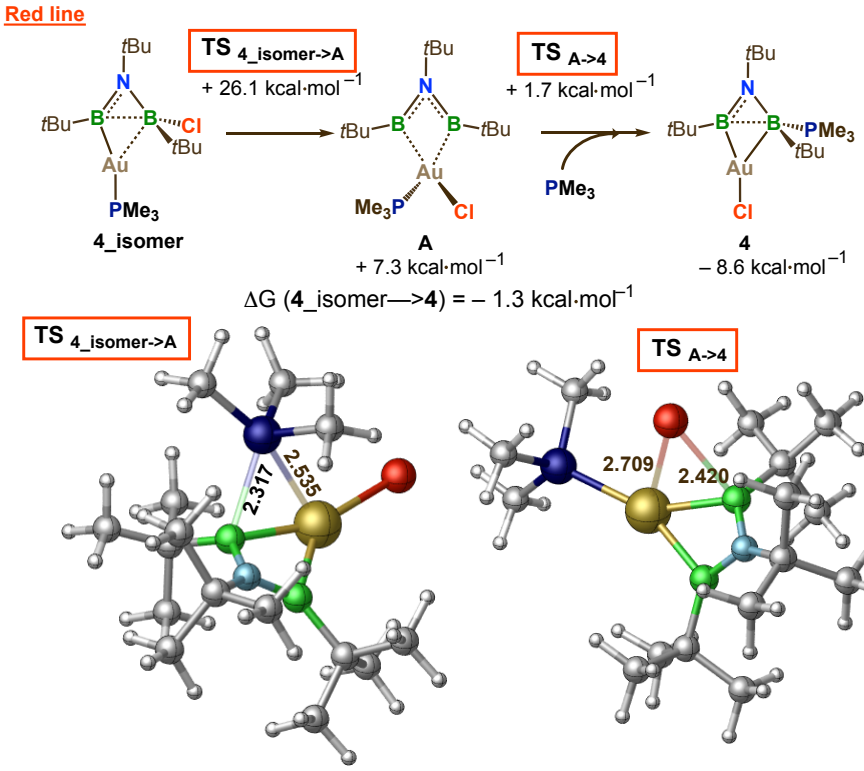
Scheme S2. Reaction mechanism for the direct conversion from **1** to **3**. Calculated transition state shows selected bond distances [Å].



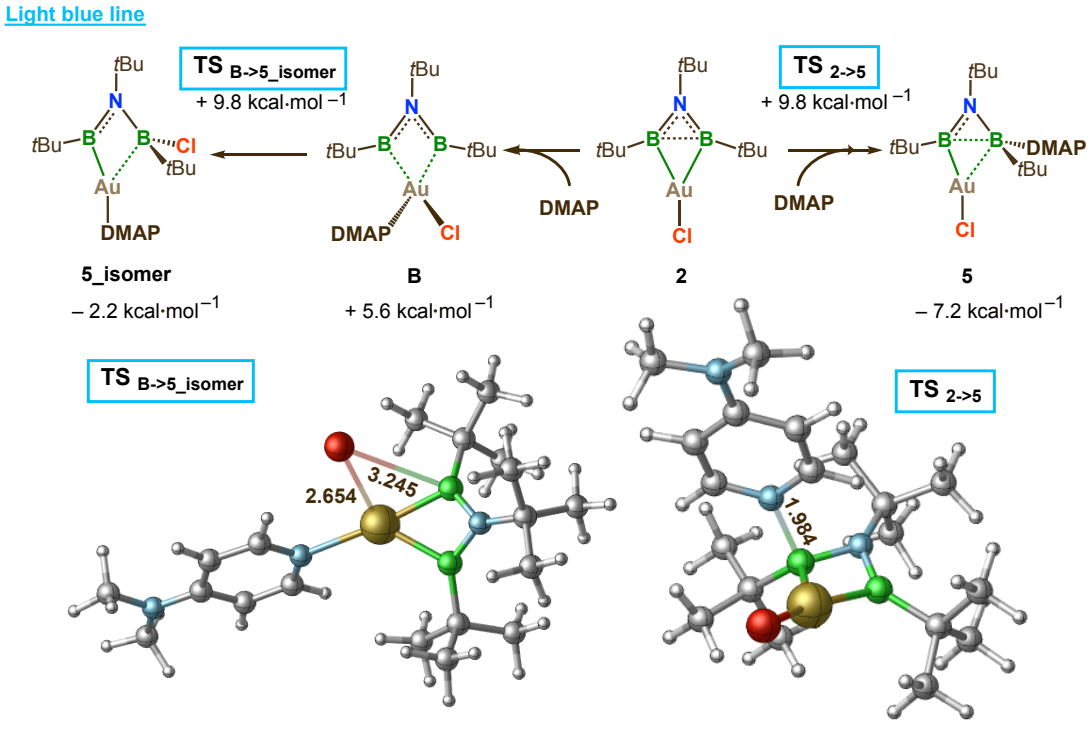
Scheme S3. Reaction mechanism for the conversion from **2** to **4**. Calculated transition state shows the key bond distance [Å].



Scheme S4. Reaction mechanism for the conversion from **1** to **4**. Calculated transition state shows selected bond distances [Å].



Scheme S5. Reaction mechanism for the interconversion from **4_isomer** to **4**. Calculated transition states show selected bond distances [Å].



Scheme S6. Reaction mechanisms about the reactivity of **2** in front of DMAP ligand. Calculated transition states show selected bond distances [Å].

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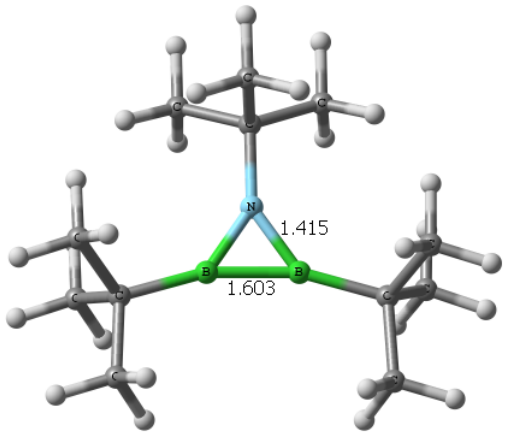
Appendix 1

Cartesian coordinates of the optimized geometries calculated at the M05-2X/(LANL2TZ(f),6-311G(d)) level, unless otherwise stated, for all the studied molecules reported in this work. Selected bond distances are shown in Angstroms.

1

E(scf) = -578.071023054 a.u.



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C	-2.375896	-2.584664	0.234842
H	-1.848164	-3.131400	-0.547216
H	-3.417484	-2.919347	0.245510
H	-1.922656	-2.856552	1.189114
C	-2.961438	-0.755786	-1.354061
H	-2.443716	-1.250325	-2.177912
H	-2.978898	0.313979	-1.560316
H	-3.994569	-1.114476	-1.350115
C	-3.062505	-0.356177	1.118154
H	-3.091583	0.723102	0.968519
H	-2.611819	-0.547913	2.093862
H	-4.095050	-0.714571	1.155391
C	-0.026691	2.019323	-0.004394
C	-0.147267	2.435222	1.461715
H	-0.176389	3.522460	1.545517
H	-1.058582	2.028076	1.899428
C	-1.223649	2.529932	-0.799801
H	-1.164651	2.193564	-1.835169
H	-1.241985	3.620197	-0.791294
H	-2.157831	2.170798	-0.372402
B	0.813291	-0.606321	-0.053609
C	2.327902	-1.033812	-0.009237
C	2.421549	-2.563690	0.060201
H	1.961833	-3.023866	-0.815039
H	3.467012	-2.883222	0.105126

$AuClSMe_2$

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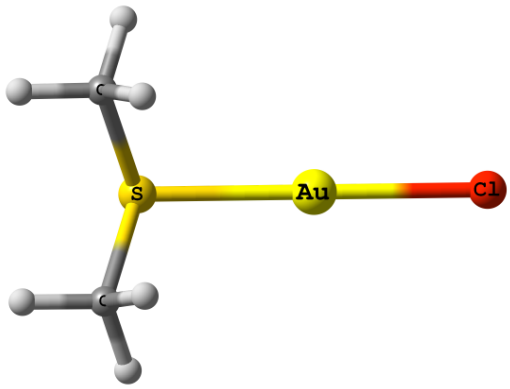

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C	2.512081	-1.382930	0.504218
H	2.136453	-2.298402	0.057955
H	3.598190	-1.375475	0.466859
H	2.158350	-1.304322	1.527292
C	2.511700	1.383275	0.504008
H	3.597809	1.376186	0.466548
H	2.135725	2.298569	0.057657
H	2.158097	1.304693	1.527126

DMAP

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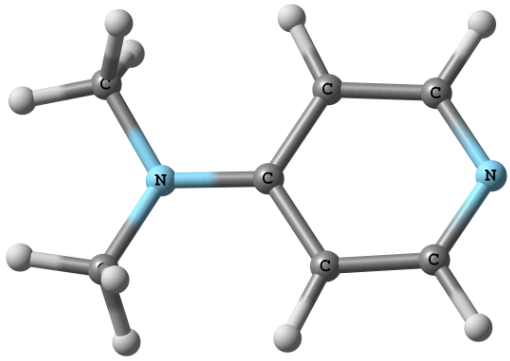

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C	0.562994	1.192487	-0.023338
H	0.087370	2.160343	-0.028028

H	1.908442	-2.949508	0.941843
C	3.076012	-0.556813	-1.262490
H	2.617153	-0.945845	-2.173231
H	3.102715	0.529452	-1.335399
H	4.108653	-0.916188	-1.234912
C	2.999347	-0.445618	1.240944
H	3.008288	0.644525	1.225609
H	2.492365	-0.764277	2.153735
H	4.036485	-0.786851	1.303307
H	0.704938	2.065251	2.032098
C	1.260145	2.572773	-0.604636
H	1.368229	2.249984	-1.640112
H	1.245584	3.662859	-0.582428
H	2.128246	2.232383	-0.042963

1 (B3LYP/def2-svp level)

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H	-2.573956	-0.708644	2.169188
H	-4.111181	-0.763375	1.279752
C	-3.064585	-0.577626	-1.296389
H	-2.572855	-0.985663	-2.195330
H	-3.090490	0.517840	-1.397592
H	-4.109698	-0.936114	-1.305100
C	-2.435148	-2.568805	0.095694
H	-1.941492	-3.052132	-0.762567
H	-3.486820	-2.908018	0.116748
H	-1.941847	-2.941993	1.007582
C	0.290227	2.480071	1.455489
H	0.337701	3.578573	1.524873
H	-0.524269	2.129938	2.108420
C	-1.277997	2.621542	-0.510617
H	-1.475244	2.301753	-1.545172
H	-1.244896	3.722074	-0.494605
H	-2.121941	2.299834	0.116000
C	0.049234	2.042556	-0.001704
B	0.782123	-0.622214	-0.009952
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C	3.148306	-0.301085	1.014163
H	3.192654	0.771246	0.767122
H	2.753782	-0.390224	2.040261
H	4.187300	-0.676391	1.030416
C	2.875151	-0.917844	-1.419580
C	-0.182912	0.000017	-0.052955
C	0.562964	-1.192459	-0.023296
H	0.087309	-2.160303	-0.027946
C	1.944693	-1.125194	0.013469
H	2.515646	-2.046591	0.033378
C	-2.264415	-1.250511	0.042882
H	-2.060668	-1.728024	1.006085
H	-1.999798	-1.948088	-0.752199
H	-3.330465	-1.058654	-0.027546
C	-2.264521	1.250471	0.042927
H	-2.060856	1.727989	1.006160
H	-3.330544	1.058507	-0.027505
H	-1.999947	1.948128	-0.752091

PPh3

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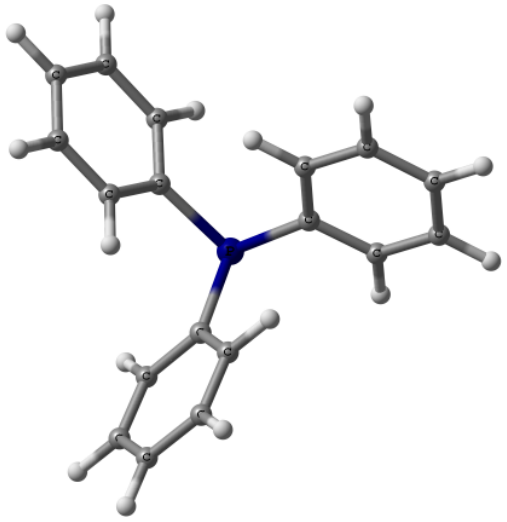

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C	3.157229	-2.447547	-0.418634
H	3.579379	-3.340757	-0.858876
C	3.732544	-1.889808	0.717414
H	4.603852	-2.348458	1.164828
C	3.189520	-0.737572	1.271826
H	3.636587	-0.298045	2.153323
C	2.069970	-0.144468	0.699217
H	1.650662	0.750154	1.139169
C	-1.346212	-0.943835	-0.447316
C	-2.628025	-0.803766	-0.984475
H	-2.774048	-0.182357	-1.859972
C	-3.712386	-1.449149	-0.406848
H	-4.700601	-1.326595	-0.829554

H	2.290398	-1.474514	-2.170595
H	2.895437	0.139176	-1.728286
H	3.912039	-1.296938	-1.463764
C	2.355222	-2.596620	0.375869
H	1.770808	-3.208046	-0.329651
H	3.396539	-2.966787	0.366605
H	1.945250	-2.778613	1.382861
H	1.237090	2.070794	1.838884
C	1.197391	2.532168	-0.898796
H	1.052274	2.199123	-1.938254
H	1.242240	3.632522	-0.895583
H	2.168309	2.153533	-0.549517
C	-3.523957	-2.261651	0.705571
H	-4.365734	-2.773024	1.152651
C	-2.250214	-2.420011	1.236255
H	-2.097939	-3.055359	2.098527
C	-1.165411	-1.761894	0.666822
H	-0.178196	-1.886128	1.091123
C	-0.143194	1.627732	-0.450310
C	-0.960152	1.881449	0.650502
H	-1.570656	1.090279	1.064087
C	-0.992753	3.149232	1.221298
H	-1.632440	3.336494	2.073465
C	-0.206530	4.171022	0.704574
H	-0.233396	5.155433	1.151805
C	0.609529	3.926464	-0.394257
H	1.219574	4.719247	-0.805628
C	0.632017	2.665270	-0.973077
H	1.258251	2.478783	-1.837393

$TS_{1\rightarrow 2}$

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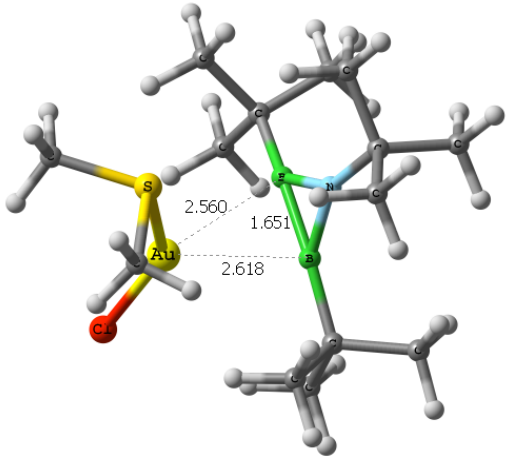

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H	0.038366	-0.920452	-3.453421
H	0.374642	-2.657566	-3.414892
H	1.268871	-1.544484	-2.371241
C	-2.101330	-2.317565	-2.423196
H	-2.901337	-2.542901	-1.719506
H	-1.953910	-3.199305	-3.052312
H	-2.439632	-1.505789	-3.069783
C	-0.354708	-3.121346	-0.811606
H	-1.067445	-3.304543	-0.007301
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2

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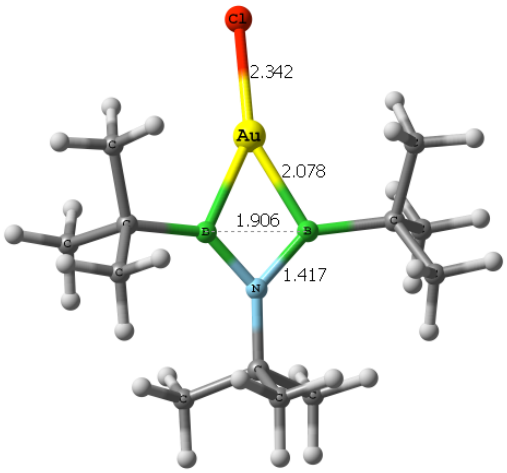

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B	0.569671	0.950688	0.105466
C	0.455997	2.496676	0.467622
C	-0.818780	2.768245	1.289634
H	-1.728496	2.553818	0.728198
H	-0.848950	3.823899	1.570617
H	-0.842895	2.177645	2.206777
C	0.337778	3.291877	-0.846091
H	-0.518173	2.956650	-1.434389
H	1.228531	3.212281	-1.467762
H	0.184563	4.348535	-0.613572
C	1.635668	3.019875	1.301086

H	-0.269270	-4.037090	-1.402609
C	-3.202464	-0.294963	0.719533
C	-3.191759	0.605055	1.952634
H	-4.083504	0.427030	2.553892
H	-2.315617	0.387565	2.565870
C	-3.230493	-1.751280	1.171907
H	-3.265856	-2.429925	0.323144
H	-4.114942	-1.930177	1.784133
H	-2.347088	-1.982568	1.766872
B	-1.092920	0.971501	-0.487658
C	-0.989659	2.546740	-0.508378
C	-0.430623	3.072228	0.822973
H	0.582026	2.703441	1.000597
H	-0.380141	4.163792	0.793296
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C	-0.058390	2.994934	-1.644271
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H	-0.427906	2.651917	-2.612163
H	-0.003609	4.087081	-1.672588
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S	0.681411	-0.911893	2.111630
C	1.061114	0.454149	3.245204
H	0.317077	1.228243	3.084786
H	1.002486	0.096466	4.270165
H	2.048814	0.851308	3.030168
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H	2.030644	-2.327722	3.511683
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H	3.025019	-1.444415	2.310788
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H	1.454565	4.066258	1.557650
C	3.036010	0.031349	-0.481989
C	3.837502	0.117119	0.815720
H	4.904599	0.127176	0.591044
H	3.594810	1.023332	1.366352
C	3.327192	1.230294	-1.382285
H	2.737473	1.168132	-2.297230
H	4.382635	1.233156	-1.654071
H	3.106078	2.172287	-0.893016
B	0.580489	-0.955552	0.091885
C	0.508983	-2.501625	0.462248
C	-0.828708	-2.846483	1.141785
H	-1.680106	-2.698942	0.476463
H	-0.822268	-3.898358	1.438405
H	-0.995671	-2.247988	2.038566
C	0.597337	-3.344309	-0.823072
H	-0.200038	-3.079636	-1.519752
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H	0.473562	-4.399811	-0.568620
C	1.622495	-2.897296	1.444941
H	2.622381	-2.769623	1.039040
H	1.557838	-2.319116	2.368689
H	1.510658	-3.951143	1.710539
H	3.629703	-0.739160	1.455545
C	3.419019	-1.223124	-1.262220
H	2.804593	-1.316518	-2.157754
H	4.461465	-1.148024	-1.570803
H	3.314370	-2.125870	-0.669942

SMe_2

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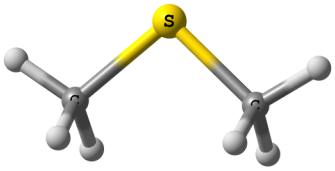

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H	-1.336712	1.143813	0.890508
H	-1.336827	1.144003	-0.890368
C	1.366881	0.519498	-0.000023
H	1.336473	1.143867	0.890466
H	2.293664	-0.047946	0.000267
H	1.337006	1.143962	-0.890466

3

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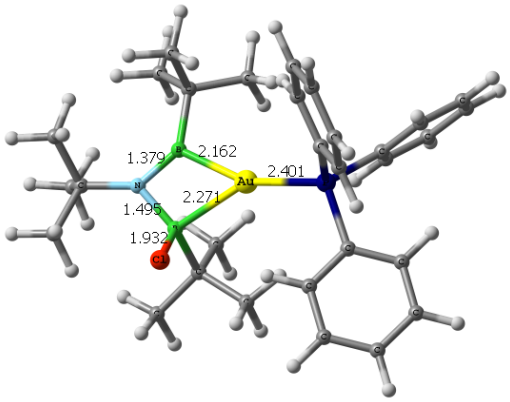

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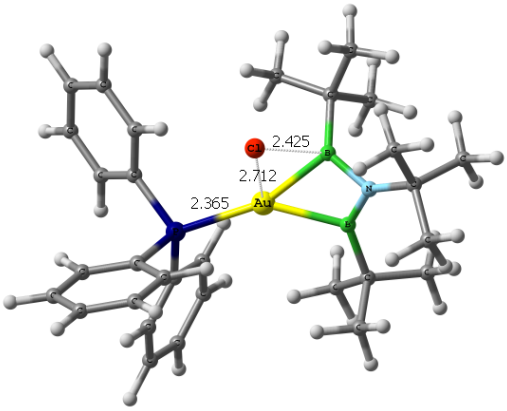
C	-2.390777	1.993790	1.224332
N	-3.326285	-0.096143	-0.286496
B	-2.347893	1.013478	-0.073075
Cl	-1.856171	1.970069	-1.677961
P	2.010014	0.001790	-0.062311
B	-2.355922	-1.005978	0.076857
C	-2.624761	1.166595	2.494337
H	-1.799751	0.471340	2.672124
H	-3.542556	0.580270	2.431340
H	-2.703039	1.822533	3.366234
C	-4.736417	-0.114554	-0.723907
C	-3.526721	3.021839	1.108270
H	-3.444659	3.603291	0.188983
H	-3.482722	3.718419	1.950917
H	-4.508723	2.550938	1.133107
C	-1.090830	2.789277	1.404647
H	-0.887115	3.420886	0.540273
H	-0.225471	2.137095	1.553573
H	-1.165885	3.434398	2.285182
C	-5.673906	-0.229259	0.480557
H	-5.591434	0.649096	1.118815
H	-5.440157	-1.106958	1.079150
H	-6.709100	-0.305709	0.143249
C	-5.063509	1.163704	-1.497454
H	-4.479010	1.221852	-2.412756
H	-4.861105	2.057635	-0.914859
H	-6.123047	1.158089	-1.758298
C	-4.961058	-1.281816	-1.686077
H	-4.254323	-1.217045	-2.513407
H	-5.972689	-1.233065	-2.091338
H	-4.842853	-2.247063	-1.203804

$TS_{2\rightarrow 3}$

E(scf) = -2210.13826407 a.u.

ν_{min} = -120.03 cm^{-1}



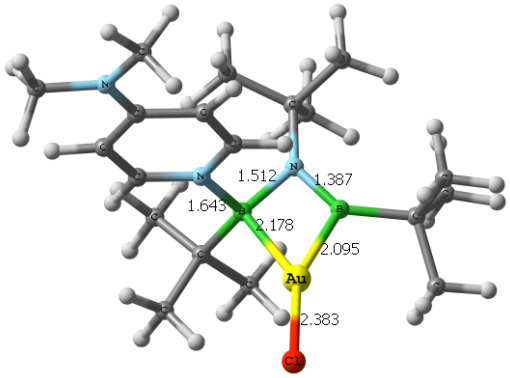
Au	-0.396210	-0.034031	-0.104355
C	-2.595571	-1.897788	-1.419860
N	-3.282973	0.155754	0.319592
B	-2.395294	-0.831699	-0.253625
Cl	-1.252606	-2.032024	1.516678
B	-2.294662	1.054734	-0.071853
C	-3.095865	-1.090969	-2.638379
H	-2.367322	-0.339413	-2.923082
H	-4.045075	-0.594931	-2.427629
H	-3.250048	-1.760932	-3.482698
C	-4.629073	0.120912	0.925820
C	-3.606266	-3.003206	-1.090004
H	-3.313524	-3.545932	-0.194256
H	-3.659421	-3.720893	-1.921088
H	-4.619474	-2.615942	-0.947219
C	-1.292047	-2.589710	-1.829647
H	-0.891294	-3.194259	-1.018023
H	-0.526268	-1.869865	-2.132246
H	-1.478394	-3.248426	-2.685778
C	-5.703541	0.167675	-0.157363
H	-5.663116	-0.718070	-0.793659
H	-5.597216	1.045568	-0.789748
H	-6.693506	0.198670	0.310508
C	-4.742965	-1.161980	1.746784
H	-3.997563	-1.167554	2.539389
H	-4.570978	-2.047891	1.134912
H	-5.744978	-1.225356	2.181562
C	-4.797430	1.299791	1.881446
H	-3.987755	1.311655	2.608184
H	-5.739386	1.202121	2.413196
H	-4.807549	2.256507	1.357058

C	-2.283669	-2.580200	0.411048	C	-2.199820	2.628266	-0.345907
C	-3.543822	-3.096566	1.120838	C	-3.480312	3.117599	-1.041993
H	-3.712825	-2.560273	2.056577	H	-3.638798	2.592747	-1.992078
H	-3.418789	-4.155230	1.365704	H	-3.389523	4.178849	-1.269787
H	-4.443266	-3.009682	0.519011	H	-4.379815	2.988804	-0.434219
C	-2.057438	-3.360076	-0.893543	C	-1.999486	3.389849	0.978390
H	-1.157904	-3.011147	-1.406325	H	-1.091637	3.043640	1.494813
H	-2.890811	-3.259893	-1.586835	H	-2.832302	3.269862	1.667644
H	-1.926696	-4.423799	-0.673076	H	-1.877867	4.454596	0.776763
C	-1.108805	-2.900780	1.353280	C	-1.018023	2.973907	-1.258494
H	-0.140828	-2.712534	0.885709	H	-0.060894	2.774930	-0.785555
H	-1.138760	-3.957295	1.635470	H	-1.053501	4.046286	-1.518887
H	-1.154067	-2.306386	2.267865	H	-1.043502	2.406425	-2.189008
C	2.843965	-0.871308	1.299074	P	1.959104	0.055507	0.086190
C	2.237521	-0.841783	2.555458	C	2.708469	1.487763	-0.740777
H	1.287722	-0.335819	2.681805	C	2.324760	1.713919	-2.070411
C	2.843869	-1.468279	3.635298	H	1.608846	1.043265	-2.545002
H	2.370286	-1.443360	4.606789	C	2.840283	2.789694	-2.772680
C	4.049741	-2.137839	3.461489	H	2.543004	2.954895	-3.797154
H	4.517513	-2.633632	4.301160	C	3.726712	3.669406	-2.147869
C	4.650288	-2.179445	2.209021	H	4.115148	4.517930	-2.689600
H	5.584577	-2.706556	2.072667	C	4.094893	3.467389	-0.823391
C	4.050778	-1.547808	1.126376	H	4.776496	4.153652	-0.324517
H	4.514896	-1.586717	0.149761	C	3.589690	2.371821	-0.116912
C	2.651090	1.700282	-0.021261	H	3.873335	2.218580	0.911814
C	1.906008	2.686615	-0.669473	C	2.732448	-1.391363	-0.691366
H	0.959227	2.438138	-1.134632	C	2.183699	-2.641498	-0.387029
C	2.373840	3.993430	-0.701960	H	1.321591	-2.707149	0.265213
H	1.792524	4.756193	-1.201142	C	2.744597	-3.793235	-0.930095
C	3.573934	4.319141	-0.080787	H	2.311727	-4.759936	-0.693598
H	3.931825	5.339608	-0.099824	C	3.844194	-3.701640	-1.780197
C	4.309928	3.339548	0.575861	H	4.270798	-4.602718	-2.200030
H	5.238110	3.595896	1.067785	C	4.387373	-2.457827	-2.086260
C	3.851637	2.028697	0.607314	H	5.242612	-2.389500	-2.742499
H	4.420310	1.267192	1.124393	C	3.844781	-1.309391	-1.542053
C	2.704176	-0.738450	-1.571122	H	4.262026	-0.340887	-1.785925
C	3.677375	-0.105573	-2.339867	C	2.601381	0.026643	1.783728
H	4.037408	0.874718	-2.058660	C	3.949885	-0.196713	2.042386
C	4.177116	-0.733993	-3.475464	H	4.638798	-0.375620	1.216698
H	4.928517	-0.238405	-4.074652	C	4.418784	-0.225780	3.343277
C	3.711461	-1.989986	-3.840657	H	5.470095	-0.409674	3.541278
H	4.100941	-2.473852	-4.725788	C	3.532932	-0.033463	4.400070
C	2.737015	-2.622567	-3.075075	H	3.894312	-0.066779	5.422663
H	2.366189	-3.596246	-3.363719	C	2.180518	0.169317	4.156059
C	2.228653	-1.996131	-1.947415	H	1.483931	0.293700	4.978818
H	1.458742	-2.479954	-1.357910	C	1.705003	0.202625	2.842224

H	0.646863	0.331804	2.643701

5

E(scf) = -1556.06330417 a.u.

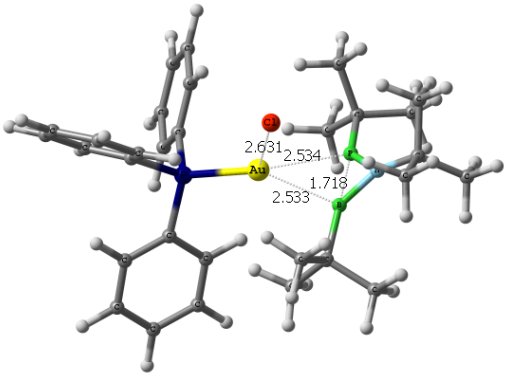


Au	-0.984607	-1.311764	0.018046
Cl	-0.807863	-3.686369	-0.085652
N	-0.835126	1.565761	-0.064810
B	-1.658932	0.577906	-0.583478
B	-0.196052	0.541597	0.846100
C	-2.914993	0.496751	-1.580946
C	-3.764361	-0.756263	-1.301401
H	-4.119093	-0.778215	-0.269419
H	-3.213274	-1.679714	-1.482413
H	-4.639939	-0.760252	-1.957099
C	-3.866138	1.696822	-1.474086
H	-4.713651	1.549743	-2.149209
H	-3.403952	2.643218	-1.741901
H	-4.266677	1.790831	-0.462816
C	-2.374230	0.378359	-3.016145
H	-1.726089	-0.495384	-3.115460
H	-1.809674	1.259394	-3.322320
H	-3.204745	0.252985	-3.716739
C	-0.615034	3.012214	-0.242741
C	-1.685545	3.824164	0.490753
H	-1.554652	4.889390	0.292428
H	-1.620785	3.670724	1.566383
H	-2.681668	3.531966	0.167598
C	0.765183	3.404347	0.294064
H	0.902206	3.097801	1.327313
H	0.873648	4.488669	0.247927
H	1.563006	2.965187	-0.305144
C	-0.626378	3.361140	-1.732262
H	0.120858	2.768905	-2.262613
H	-0.384573	4.416210	-1.868760
H	-1.593146	3.176684	-2.188868
C	-0.524909	0.514429	2.457236
C	-0.124489	-0.803916	3.150662

$TS_{1\rightarrow 3}$

E(scf) = -2210.11959183 a.u.

ν_{min} = -56.74 cm^{-1}



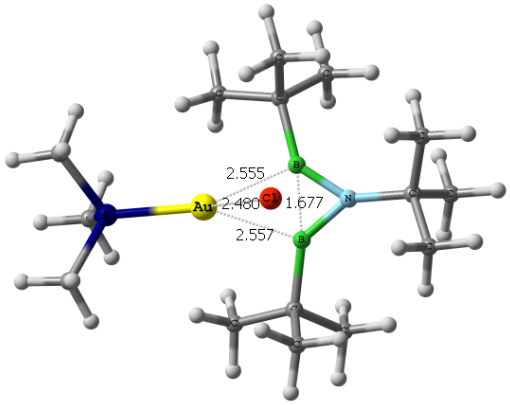
N	3.626007	0.017331	-0.121797
B	2.593799	-0.889410	-0.394774
C	2.418588	-2.439076	-0.678327
C	1.164951	-2.724462	-1.519333
H	0.248537	-2.530915	-0.961103
H	1.154118	-3.775726	-1.820886
H	1.137733	-2.111198	-2.421821
C	2.313768	-3.238659	0.629311
H	1.477568	-2.895550	1.238063
H	3.212391	-3.152524	1.237157
H	2.161490	-4.295562	0.392468
C	3.629491	-2.927309	-1.493780
H	4.567808	-2.813254	-0.956399
H	3.716797	-2.388092	-2.439464
H	3.508757	-3.988056	-1.728123
C	4.989994	0.085382	0.442521
C	6.011114	0.098367	-0.691379
H	7.020359	0.152306	-0.281537
H	5.930713	-0.807244	-1.292272
C	5.198341	-1.117715	1.357763
H	4.407951	-1.149993	2.107851
H	6.160203	-1.026626	1.863156
H	5.200335	-2.052491	0.803071
B	2.550575	0.824445	-0.508470
C	2.289982	2.326980	-0.938421
C	1.076110	2.453141	-1.872464
H	0.144051	2.208860	-1.364344
H	0.996844	3.481878	-2.235054
H	1.167095	1.795267	-2.738964
C	2.041701	3.196437	0.304990
H	1.200357	2.823704	0.890120
H	2.905537	3.221952	0.967262

H	-0.443577	-0.776556	4.196701
H	0.946029	-1.008564	3.150902
H	-0.606366	-1.664477	2.686025
C	0.040736	1.688089	3.282788
H	-0.389462	2.638550	2.970903
H	1.125626	1.796633	3.245461
H	-0.225287	1.550220	4.334382
C	-2.054971	0.615778	2.607080
H	-2.557262	-0.239413	2.153190
H	-2.448494	1.520172	2.143197
H	-2.323638	0.635435	3.666979
N	1.382624	0.367263	0.424070
N	5.320165	-0.104381	-0.863136
C	1.692629	0.295978	-0.885344
H	0.856400	0.355837	-1.563746
C	2.968541	0.151792	-1.354599
H	3.116216	0.089763	-2.419983
C	4.049966	0.060498	-0.446178
C	3.711894	0.148322	0.920445
H	4.457608	0.091178	1.695950
C	2.397909	0.293298	1.294288
H	2.138326	0.353000	2.334395
C	6.389222	-0.238376	0.112552
H	6.233873	-1.109359	0.751449
H	6.461220	0.651905	0.738443
H	7.331127	-0.361158	-0.410024
C	5.607757	-0.240592	-2.282229
H	5.097861	-1.106022	-2.707787
H	6.675465	-0.375823	-2.413522
H	5.308741	0.653108	-2.830946
H	1.819627	4.220576	-0.008688
C	3.509377	2.860227	-1.710291
H	4.415951	2.861900	-1.110112
H	3.701986	2.269806	-2.608543
H	3.320951	3.889566	-2.026283
H	5.856254	0.958543	-1.341826
C	5.092978	1.346007	1.297103
H	4.298493	1.347037	2.043381
H	6.056526	1.362740	1.806989
H	5.017035	2.249288	0.697253
Au	0.271197	-0.050024	0.168780
Cl	1.484673	-0.037050	2.503089
P	-1.976415	-0.052468	0.013221
C	-2.856546	-0.435643	1.554322
C	-2.153594	-0.987855	2.622120
H	-1.086204	-1.155155	2.545155
C	-2.821692	-1.279122	3.807288
H	-2.271514	-1.696702	4.638670
C	-4.179149	-1.017425	3.925487
H	-4.693130	-1.240522	4.850671
C	-4.879248	-0.449612	2.863883
H	-5.933316	-0.229514	2.963983
C	-4.219641	-0.152980	1.681726
H	-4.755003	0.309888	0.861967
C	-2.629982	-1.179559	-1.257372
C	-2.023317	-1.139013	-2.515518
H	-1.194702	-0.461494	-2.684324
C	-2.467426	-1.971223	-3.531073
H	-1.994844	-1.933812	-4.502851
C	-3.507517	-2.864801	-3.292147
H	-3.846428	-3.522631	-4.080886
C	-4.100351	-2.920450	-2.038790
H	-4.900131	-3.622632	-1.847635
C	-3.666705	-2.078170	-1.019821
H	-4.127449	-2.134905	-0.043931
C	-2.610323	1.596138	-0.433278
C	-3.471595	1.823599	-1.501978
H	-3.807128	0.999598	-2.117052
C	-3.900175	3.118236	-1.780104
H	-4.567784	3.293731	-2.612555
C	-3.474786	4.179112	-0.993305
H	-3.808654	5.183620	-1.214398
C	-2.617286	3.951561	0.079346
H	-2.283040	4.776273	0.693697
C	-2.182238	2.665478	0.357572
H	-1.506777	2.484759	1.186206

$TS_{1\rightarrow 4}$

E(scf) = -1634.83507326 a.u.

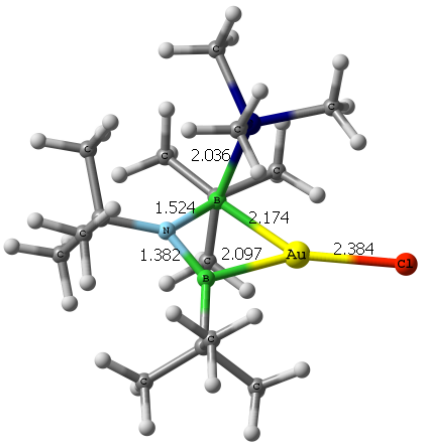
ν_{min} = -77.36 cm^{-1}



N	2.310597	0.005898	0.266409
B	1.217504	0.842145	0.540988
C	0.960978	2.373287	0.861994
C	-0.346733	2.576040	1.642837
H	-1.213110	2.351344	1.019857
H	-0.428942	3.616071	1.970896
H	-0.389731	1.934765	2.525431
C	0.885739	3.201251	-0.430123
H	0.089316	2.846011	-1.084844
H	1.812697	3.156371	-0.998612
H	0.688240	4.248032	-0.180650
C	2.103191	2.896634	1.749125
H	3.068964	2.846866	1.251527
H	2.176170	2.331251	2.680622
H	1.918249	3.942255	2.009500
C	3.712145	0.008461	-0.192860
C	4.640895	0.029084	1.018711
H	5.680782	0.031359	0.689619
H	4.467218	0.919322	1.622586
C	3.933960	1.234845	-1.073780
H	3.212457	1.238796	-1.890674
H	4.940236	1.206344	-1.492899
H	3.832861	2.158527	-0.509094
B	1.220730	-0.834439	0.543601
C	0.971995	-2.363868	0.879609
C	-0.345861	-2.569188	1.642604
H	-1.204526	-2.366623	1.001374
H	-0.421004	-3.604388	1.987182
H	-0.410666	-1.913127	2.512850
C	0.925988	-3.213832	-0.399335
H	0.136660	-2.877001	-1.071976

4

E(scf) = -1634.87180189 a.u.



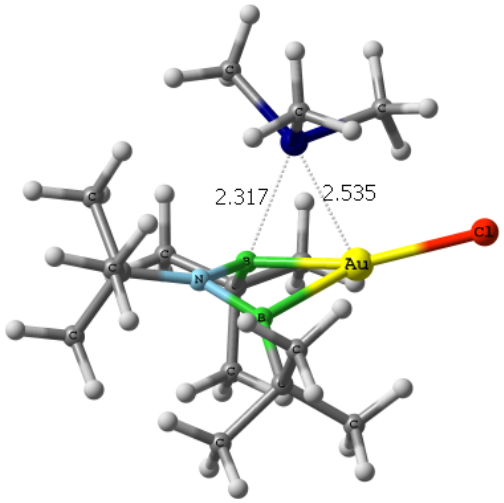
Au	0.892837	0.284648	0.056334
C	-3.430324	-0.212727	-0.710117
Cl	-0.326751	-1.944940	-1.686913
C	-1.172163	3.320514	-0.892691
H	-1.174005	4.393286	-0.676788
H	-1.992379	3.114045	-1.577841
H	-0.239136	3.086498	-1.410551
P	3.249235	0.050208	-0.270159
C	4.021288	1.244702	-1.413836
H	3.495950	1.212223	-2.366353
H	5.073611	1.009634	-1.572605
H	3.933119	2.250434	-1.007313
N	-2.025444	-0.065859	-0.278984
C	-0.847871	-2.043173	1.215285
B	-1.162703	0.951857	0.084015
B	-0.931157	-1.058025	-0.076266
C	-1.285964	2.522444	0.415813
C	-1.191509	-1.262471	2.489515
H	-1.172948	-1.925234	3.359511
H	-2.183311	-0.812984	2.430143
H	-0.473398	-0.457206	2.665501
C	-0.143279	2.985361	1.337310
H	-0.099207	2.392095	2.252514
H	-0.294455	4.031809	1.618279
H	0.828112	2.913107	0.844784
C	0.544563	-2.665170	1.398228
H	0.534230	-3.362557	2.241054
H	1.299905	-1.904865	1.618815
H	0.854253	-3.212113	0.507609
C	-1.839928	-3.209480	1.084086
H	-1.717180	-3.897943	1.925501

H	1.861388	-3.169535	-0.953522
H	0.734513	-4.258158	-0.135272
C	2.105636	-2.859532	1.793867
H	3.079405	-2.804676	1.312371
H	2.155426	-2.279422	2.717872
H	1.929193	-3.903425	2.066673
H	4.477897	-0.848444	1.643937
C	3.950356	-1.236599	-1.042381
H	3.230523	-1.270413	-1.860077
H	4.956878	-1.205979	-1.460745
H	3.860085	-2.146752	-0.454309
Au	-0.984560	-0.004857	-0.443554
Cl	0.391086	-0.032240	-2.506772
P	-3.119419	0.003669	0.247120
C	-3.403684	0.003327	2.047826
C	-4.102754	-1.422927	-0.321008
C	-4.093644	1.436874	-0.320185
H	-3.640656	2.354117	0.051854
H	-5.121628	1.370998	0.036875
H	-4.082408	1.465940	-1.407660
H	-4.092313	-1.451045	-1.408509
H	-5.130075	-1.351659	0.036911
H	-3.654528	-2.343039	0.049768
H	-2.944669	-0.882022	2.483286
H	-4.470606	0.008276	2.272093
H	-2.935786	0.882818	2.485669
H	-1.673889	-3.771458	0.164234
H	-2.874203	-2.867696	1.099094
C	-4.369895	-0.228514	0.497751
H	-4.173166	-1.094426	1.128002
H	-5.407248	-0.282598	0.163001
H	-4.248328	0.667362	1.102770
C	-3.802723	0.927805	-1.658612
H	-4.801325	0.756520	-2.063038
H	-3.096431	0.961886	-2.488156
H	-3.806413	1.895161	-1.166632
C	-3.601394	-1.512613	-1.498708
H	-3.287592	-2.382055	-0.928099
H	-3.018135	-1.488272	-2.416589
H	-4.654412	-1.635544	-1.756375
C	4.331288	0.095239	1.198857
H	4.260702	1.071839	1.673947
H	5.368438	-0.103323	0.928568
H	3.994439	-0.656253	1.910899
C	3.612545	-1.567532	-1.026120
H	3.284070	-2.356542	-0.352066
H	4.677489	-1.677987	-1.231068
H	3.040706	-1.661702	-1.947214
C	-2.588446	2.880939	1.145049
H	-2.673427	2.330948	2.084413
H	-3.479476	2.679528	0.558785
H	-2.592590	3.947959	1.386091

$TS_{4\rightarrow A}$

E(scf) = -1634.85720866 a.u.

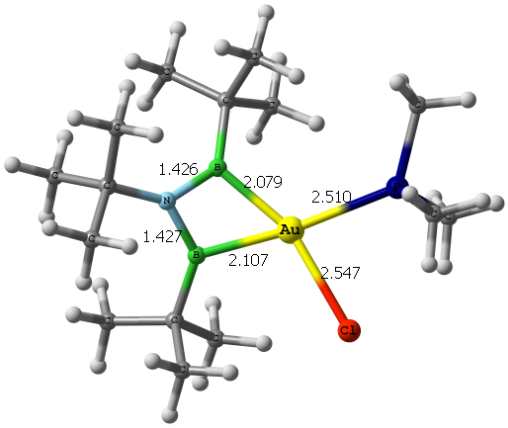
ν_{min} = -115.12 cm^{-1}



Au	0.855854	0.178314	-0.145458
C	-1.066712	-2.061131	-1.278434
N	-2.008329	-0.003426	0.344243

A

E(scf) = -1634.86189452 a.u.



N	2.001561	-0.397017	0.347510
B	0.873290	-1.072296	-0.203499
C	0.634317	-2.511775	-0.848474
C	-0.346140	-2.365279	-2.025141
H	-1.299478	-1.946425	-1.707671
H	-0.533835	-3.343637	-2.476305

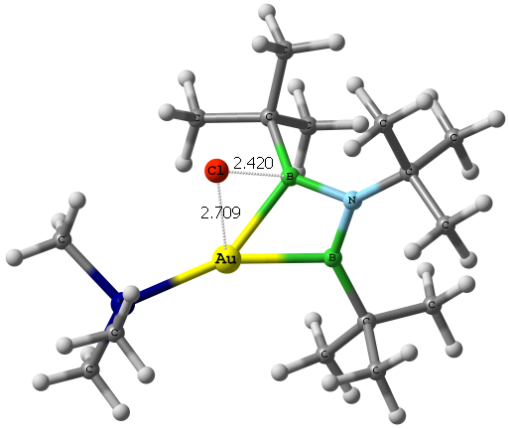
B	-1.004956	-0.892679	-0.187317	H	0.056708	-1.709488	-2.798846
Cl	0.322736	-1.809609	1.616256	C	0.000251	-3.438999	0.199136
B	-1.167215	0.994995	-0.142502	H	-0.892493	-2.988271	0.630222
C	-1.720655	-1.433449	-2.523439	H	0.685464	-3.667584	1.015070
H	-1.131774	-0.589818	-2.892287	H	-0.290837	-4.384193	-0.267710
H	-2.729022	-1.073030	-2.318797	C	1.899766	-3.167930	-1.417330
H	-1.784476	-2.174871	-3.324468	H	2.622336	-3.437655	-0.651242
C	-3.314196	-0.183983	1.006884	H	2.395359	-2.517233	-2.139663
C	-1.887033	-3.278822	-0.836821	H	1.628395	-4.089253	-1.939058
H	-1.489380	-3.700114	0.086683	C	3.271955	-0.768897	1.011851
H	-1.843358	-4.051031	-1.610237	C	4.401107	-1.024805	0.014750
H	-2.938453	-3.035757	-0.685897	H	5.307832	-1.296317	0.557214
C	0.323342	-2.565445	-1.687225	H	4.153074	-1.839605	-0.660310
H	0.838311	-3.022554	-0.843893	C	3.019065	-2.017745	1.855517
H	0.945592	-1.755075	-2.078255	H	2.200345	-1.841296	2.553853
H	0.223603	-3.313237	-2.479110	H	3.913703	-2.261179	2.428738
C	-4.429187	-0.350501	-0.024333	H	2.770170	-2.878082	1.241863
H	-4.277943	-1.250902	-0.616934	B	1.397296	0.801405	-0.136349
H	-4.468873	0.503657	-0.699307	C	1.923777	2.202372	-0.669066
H	-5.391580	-0.437473	0.481893	C	1.044772	2.630733	-1.859333
C	-3.222940	-1.421104	1.899461	H	0.008356	2.772656	-1.564147
H	-2.443309	-1.290866	2.647766	H	1.416511	3.577142	-2.261529
H	-2.979810	-2.311525	1.326781	H	1.078569	1.891636	-2.663611
H	-4.178448	-1.581044	2.401002	C	1.796183	3.267114	0.434344
C	-3.599047	1.015353	1.908056	H	0.766924	3.357852	0.777214
H	-2.771918	1.164965	2.601921	H	2.431394	3.047085	1.293725
H	-4.502403	0.824112	2.487974	H	2.104648	4.236547	0.033319
H	-3.754446	1.931026	1.344468	C	3.370712	2.164689	-1.182665
C	-1.307057	2.539507	-0.516890	H	4.102056	1.993401	-0.396054
C	-2.675312	2.823496	-1.155595	H	3.505155	1.399808	-1.950181
H	-2.814900	2.229857	-2.061429	H	3.612448	3.128398	-1.637514
H	-2.738909	3.877872	-1.438098	H	4.612344	-0.138842	-0.577203
H	-3.506579	2.612581	-0.488541	C	3.651143	0.361568	1.968009
C	-1.120151	3.398441	0.743155	H	2.840700	0.545806	2.673759
H	-0.151067	3.203827	1.207684	H	4.542782	0.084022	2.530576
H	-1.891712	3.216002	1.489126	H	3.860059	1.286473	1.440100
H	-1.154013	4.458411	0.475237	Au	-0.652807	0.327922	-0.019729
C	-0.242308	2.964784	-1.539094	Cl	-1.838235	2.549350	0.366936
H	0.761855	2.897342	-1.121306	P	-2.993557	-0.509662	0.323048
H	-0.417150	4.000124	-1.845915	C	-4.077618	0.167495	-0.979747
H	-0.269557	2.335356	-2.430024	C	-3.745532	0.093613	1.873261
P	3.181491	0.159333	0.286471	C	-3.496628	-2.276313	0.350401
C	3.833501	-1.513513	-0.022442	H	-3.151685	-2.793711	-0.542278
H	3.222870	-2.218683	0.539877	H	-4.583523	-2.346347	0.403297
H	4.875334	-1.590615	0.288843	H	-3.072893	-2.770269	1.222553
H	3.749590	-1.751767	-1.081234	H	-3.242414	-0.368232	2.721504

C	4.341583	1.265955	-0.582688
H	4.256458	1.104402	-1.655428
H	5.368049	1.078162	-0.267806
H	4.082636	2.301623	-0.370742
C	3.528350	0.428258	2.052699
H	3.267429	1.448580	2.327340
H	4.579696	0.247609	2.276006
H	2.902449	-0.255253	2.624508
H	-4.806304	-0.156350	1.903610
H	-3.610491	1.170438	1.927164
H	-3.948556	1.246901	-1.003884
H	-5.120618	-0.081983	-0.783259
H	-3.783730	-0.243582	-1.944784

$TS_{A \rightarrow 4\_isomer}$

E(scf) = -1634.83291311 a.u.

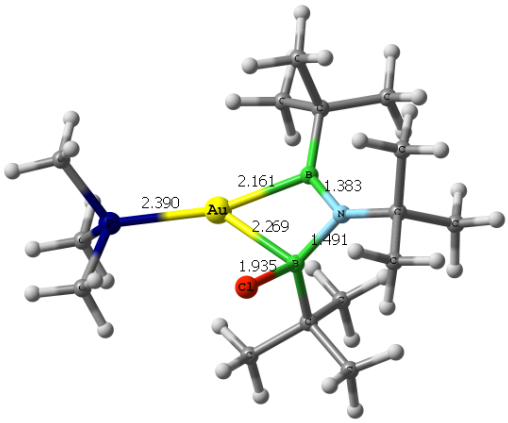
ν_{min} = -121.39 cm^{-1}



Au	1.053911	0.582782	0.179887
C	-2.922421	-0.726768	-0.829105
Cl	3.243079	1.457923	-0.199923
C	-1.197429	3.123548	-1.415385
H	-1.394046	4.198784	-1.395805
H	-1.868382	2.674339	-2.147753
H	-0.171079	2.981037	-1.758968
P	1.071407	-1.699537	-0.923624
C	1.007792	-0.906610	-2.573733
H	-0.023233	-0.628287	-2.803027
H	1.372306	-1.598591	-3.338401
H	1.623437	-0.005196	-2.575948
N	-1.647680	-0.225981	-0.287882
C	-0.568824	-1.563957	1.908787
B	-1.032882	0.988921	-0.051454
B	-0.525856	-0.802755	0.495857
C	-1.392602	2.540548	-0.004995
C	-1.261147	-0.619019	2.904928
H	-1.344869	-1.094154	3.886240
H	-2.266455	-0.343592	2.577087
H	-0.683323	0.303895	3.032848
C	-0.459856	3.302299	0.952318
H	-0.498360	2.890583	1.962348

4_isomer

E(scf) = -1634.87062166 a.u.



Au	1.304437	0.284335	0.066526
C	-3.039062	0.381966	-0.257229
Cl	3.673810	0.118673	-0.143347
C	-0.246710	3.196061	-1.673610
H	-0.048788	4.265156	-1.790437
H	-1.159149	2.962576	-2.221751
H	0.579102	2.655912	-2.141608
P	-0.224313	-2.086406	-1.092218
C	-0.492406	-1.308240	-2.715170
H	-1.536683	-1.043888	-2.850502
H	-0.182737	-1.990516	-3.505494
H	0.107046	-0.400596	-2.764855
N	-1.577153	0.334522	-0.074253
C	-0.589800	-1.363519	1.890655
B	-0.548538	1.257036	-0.064530
B	-0.590241	-0.732921	0.384471
C	-0.351906	2.848292	-0.178190
C	-0.510579	-0.214392	2.906922
H	-0.607348	-0.600074	3.925751
H	-1.305191	0.517119	2.748813
H	0.444176	0.309893	2.837820
C	0.956299	3.305175	0.495681
H	0.993818	3.010032	1.545933
H	1.025572	4.395614	0.453358

H	-0.770030	4.349360	1.005824	H	1.843680	2.906258	0.002819
H	0.578028	3.279870	0.619429	C	0.614689	-2.287597	2.125021
C	0.838211	-1.868658	2.445104	H	0.659113	-2.582420	3.176960
H	0.769132	-2.274461	3.456362	H	1.565733	-1.814142	1.875252
H	1.460270	-0.968477	2.492421	H	0.530372	-3.212722	1.547418
H	1.345893	-2.610771	1.825855	C	-1.839288	-2.192622	2.229175
C	-1.330583	-2.896074	1.883621	H	-1.724417	-2.639317	3.220813
H	-1.275443	-3.373667	2.865774	H	-1.998668	-3.013019	1.526024
H	-0.903479	-3.583665	1.157627	H	-2.743407	-1.587457	2.256408
H	-2.385607	-2.761848	1.648147	C	-3.733581	0.931617	0.991684
C	-4.028171	-0.688439	0.226508	H	-3.581150	0.274841	1.845744
H	-3.798441	-1.348929	1.059711	H	-4.807462	1.017124	0.817387
H	-4.972036	-1.014356	-0.212919	H	-3.348655	1.914759	1.249036
H	-4.168121	0.318766	0.616685	C	-3.377822	1.255466	-1.466831
C	-3.325406	0.131333	-2.027669	H	-4.451338	1.225304	-1.657444
H	-4.216739	-0.285371	-2.497403	H	-2.859990	0.892145	-2.355001
H	-2.523638	0.149497	-2.766621	H	-3.095221	2.291062	-1.313652
H	-3.545575	1.154274	-1.737900	C	-3.579584	-1.016379	-0.551573
C	-2.709778	-2.152224	-1.330813	H	-3.304459	-1.727187	0.221571
H	-2.340200	-2.800007	-0.539370	H	-3.219595	-1.379624	-1.514035
H	-1.995361	-2.151633	-2.153739	H	-4.668020	-0.982565	-0.605061
H	-3.651693	-2.559511	-1.697935	C	1.468627	-2.750904	-1.248599
C	2.873453	-1.860120	-0.540877	H	2.159037	-1.958668	-1.528802
H	3.034431	-1.735283	0.584933	H	1.467866	-3.527364	-2.013966
H	3.436336	-0.988354	-1.073776	H	1.808705	-3.170818	-0.306216
H	3.245786	-2.885754	-0.905382	C	-1.218796	-3.624243	-1.139552
C	0.711773	-3.462065	-1.376880	H	-0.935669	-4.254851	-0.298453
H	0.867682	-4.090446	-0.488907	H	-1.010086	-4.161094	-2.064497
H	1.388790	-3.800293	-2.166183	H	-2.281931	-3.414051	-1.077936
H	-0.315212	-3.579833	-1.705990	C	-1.473080	3.669349	0.474797
C	-2.829073	2.792721	0.476355	H	-1.552867	3.447542	1.540602
H	-2.988815	2.379838	1.474339	H	-2.449014	3.515447	0.023053
H	-3.581985	2.373902	-0.186818	H	-1.240991	4.733385	0.380510
H	-3.010600	3.868876	0.533372				

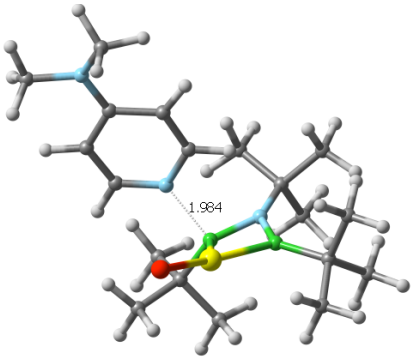
$TS_{2\rightarrow 5}$

E(scf) = -1556.03681123 a.u.

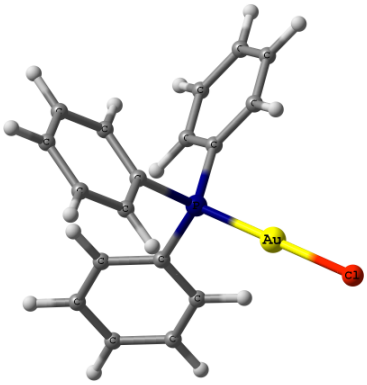
ν_{min} = -114.30 cm^{-1}

$AuClPPh_3$

E(scf) = -1632.03535668 a.u.



Au	-0.366258	-1.292496	0.265751
Cl	1.174998	-3.091216	0.451605
N	-1.524609	1.245564	-0.348540
B	-1.825017	-0.083165	-0.652080
B	-0.781375	0.698564	0.797046
C	-2.892963	-0.847624	-1.567879
C	-3.123451	-2.279057	-1.055555
H	-3.458749	-2.282872	-0.016983
H	-2.217333	-2.882572	-1.104989
H	-3.892249	-2.767612	-1.660920
C	-4.260790	-0.150101	-1.562814
H	-4.970680	-0.735234	-2.153654
H	-4.232990	0.850260	-1.987253
H	-4.661788	-0.073237	-0.550062
C	-2.342819	-0.949405	-3.000365
H	-1.379897	-1.464830	-3.010534
H	-2.212415	0.025768	-3.461535
H	-3.032539	-1.528705	-3.620501
C	-1.843066	2.608138	-0.810216
C	-3.132586	3.128922	-0.172009
H	-3.408085	4.084745	-0.620332
H	-3.004865	3.287946	0.897296
H	-3.959478	2.428640	-0.321036
C	-0.685649	3.536354	-0.452940
H	-0.460235	3.508712	0.609800
H	-0.941852	4.560758	-0.719523
H	0.217837	3.265456	-0.998184
C	-1.982491	2.615105	-2.332239
H	-1.087448	2.194684	-2.798339
H	-2.105906	3.639733	-2.684495
H	-2.840509	2.041158	-2.667841
C	-1.070165	0.905805	2.370333
C	-0.382146	-0.149488	3.260441
H	-0.646488	0.034857	4.303975
H	0.697190	-0.162871	3.190579
H	-0.726529	-1.155040	3.014292
C	-0.739913	2.304455	2.910350

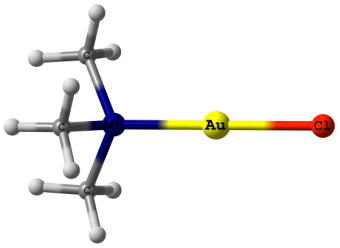


Au	0.000000	0.000000	1.824870
Cl	0.000000	0.000000	4.134709
P	0.000000	0.000000	-0.395747
C	0.630617	1.540127	-1.124347
C	0.295035	2.744880	-0.505566
H	-0.282713	2.737490	0.410049
C	0.711944	3.947545	-1.057397
H	0.453090	4.878473	-0.572817
C	1.471687	3.951664	-2.221819
H	1.803558	4.889514	-2.645827
C	1.815250	2.753092	-2.834411
H	2.414547	2.756020	-3.734425
C	1.395187	1.545628	-2.289679
H	1.672299	0.613980	-2.763846
C	-1.649097	-0.223933	-1.124347
C	-2.524654	-1.116932	-0.505566
H	-2.229379	-1.613582	0.410049
C	-3.774646	-1.357211	-1.057397
H	-4.451427	-2.046849	-0.572817
C	-4.158085	-0.701314	-2.221819
H	-5.136222	-0.882830	-2.645827
C	-3.291873	0.195507	-2.834411
H	-3.594057	0.713050	-3.734425
C	-2.036147	0.435453	-2.289679
H	-1.367872	1.141264	-2.763846
C	1.018481	-1.316194	-1.124347
C	0.640960	-1.981082	-2.289679
H	-0.304428	-1.755244	-2.763846
C	1.476623	-2.948599	-2.834411
H	1.179509	-3.469069	-3.734425
C	2.686398	-3.250351	-2.221819
H	3.332664	-4.006684	-2.645827
C	3.062702	-2.590334	-1.057397
H	3.998337	-2.831624	-0.572817
C	2.229618	-1.627948	-0.505566
H	2.512092	-1.123908	0.410049

H	-1.374526	3.068827	2.463001
H	0.297836	2.591781	2.738059
H	-0.913980	2.331525	3.988148
C	-2.577516	0.674000	2.541576
H	-2.861885	-0.328250	2.207945
H	-3.175578	1.390247	1.974860
H	-2.853933	0.763544	3.595709
N	1.140607	0.894652	0.343891
N	5.131807	0.736424	-0.910354
C	1.459178	0.799486	-0.955471
H	0.625629	0.751162	-1.635825
C	2.745735	0.741226	-1.421473
H	2.885301	0.647067	-2.486545
C	3.834750	0.791286	-0.518325
C	3.480390	0.938272	0.837933
H	4.221212	0.978109	1.619123
C	2.153926	0.988449	1.209082
H	1.899114	1.088394	2.249025
C	6.168302	0.692433	0.105653
H	6.097680	-0.212505	0.727257
H	6.121983	1.572922	0.742718
H	7.140391	0.690407	-0.391275
C	5.531591	0.174224	-2.191321
H	4.766003	0.468584	-2.992864
H	5.609255	-0.982378	-2.128621
H	6.555378	0.620335	-2.470443

$AuClPMe_3$

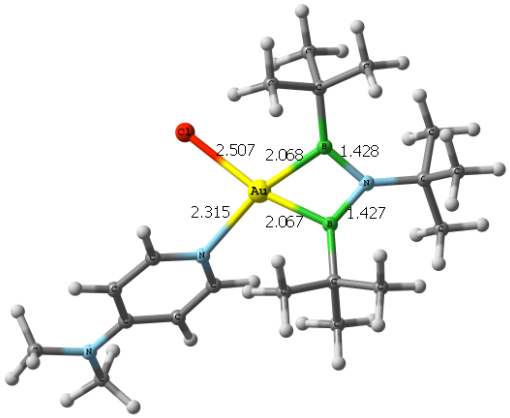
E(scf) = -1056.75467759 a.u.



Au	-0.547907	-0.000855	0.000156
Cl	-2.856355	0.001465	-0.000320
P	1.666845	0.000212	-0.000081
C	2.424232	1.653827	-0.019158
C	2.428260	-0.841211	-1.421392
C	2.428727	-0.808358	1.439915
H	2.104382	-0.307119	2.349518
H	3.515766	-0.770247	1.370338
H	2.103044	-1.845515	1.485786
H	3.515282	-0.801773	-1.352574
H	2.102307	-1.879058	-1.443529
H	2.104136	-0.360769	-2.342233
H	2.097766	2.190874	-0.907330
H	3.511398	1.576956	-0.018844
H	2.098622	2.210586	0.857021

B

E(scf) = -1556.04309195 a.u.

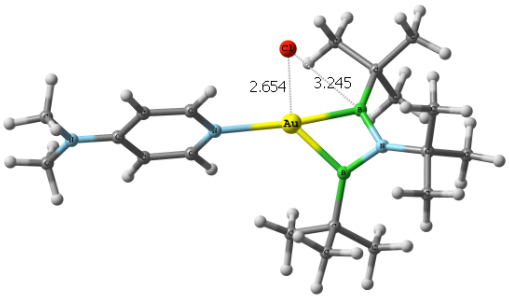


Au	-0.211015	-0.570218	0.107327
Cl	0.723770	-2.857985	-0.314213
N	-2.559924	0.768211	-0.382700
B	-2.273005	-0.590539	-0.051525
B	-1.371951	1.126230	0.322641
C	-3.110918	-1.911717	0.198827
C	-2.515402	-2.654172	1.407652

$TS_{B\rightarrow 5isomer}$

E(scf) = -1556.03445045 a.u.

ν_{min} = -33.16 cm^{-1}



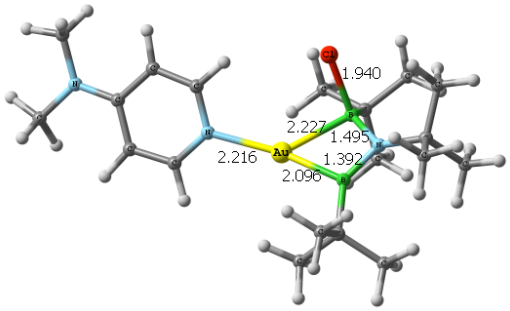
Au	0.067825	-0.282285	0.100076
C	2.530540	-1.854707	1.270106
N	2.717520	0.388840	-0.391749
B	2.068051	-0.685394	0.294348
Cl	-0.027658	-2.408281	-1.485845
B	1.592466	1.154769	0.002174
C	3.090954	-1.108046	2.500820
H	2.335275	-0.454207	2.942410
H	3.962653	-0.500196	2.260973

H	-2.549673	-2.028777	2.310676	H	3.384725	-1.836643	3.261018
H	-1.479102	-2.950454	1.232205	C	4.021620	0.553796	-1.068820
H	-3.096821	-3.553084	1.609341	C	3.594592	-2.815104	0.727268
C	-4.596096	-1.683509	0.519140	H	3.241503	-3.321003	-0.171693
H	-5.060123	-2.647859	0.760025	H	3.803059	-3.580290	1.479660
H	-5.165769	-1.262677	-0.305150	H	4.538358	-2.319488	0.504492
H	-4.725705	-1.037695	1.388848	C	1.346530	-2.704768	1.753062
C	-2.983254	-2.823243	-1.040000	H	0.895972	-3.261835	0.934892
H	-1.940887	-3.056975	-1.249556	H	0.569360	-2.086754	2.209492
H	-3.429135	-2.379479	-1.924228	H	1.694514	-3.410340	2.512994
H	-3.505596	-3.769860	-0.844466	C	5.164151	0.632862	-0.058435
C	-3.662795	1.483809	-1.075494	H	5.268612	-0.297257	0.494820
C	-4.832078	1.797160	-0.139796	H	4.997804	1.441799	0.652795
H	-5.602746	2.330402	-0.692594	H	6.102977	0.820618	-0.580749
H	-4.514927	2.419987	0.688756	C	4.197092	-0.647907	-1.998898
H	-5.270854	0.883311	0.259639	H	3.387981	-0.676903	-2.728143
C	-3.099593	2.778153	-1.667363	H	4.182229	-1.584311	-1.450067
H	-2.791857	3.480051	-0.900464	H	5.147491	-0.572257	-2.528542
H	-3.866612	3.262578	-2.273343	C	4.010016	1.809144	-1.934640
H	-2.244970	2.554371	-2.303850	H	3.154108	1.796406	-2.608839
C	-4.123639	0.610290	-2.243528	H	4.917460	1.833041	-2.538236
H	-3.287632	0.412817	-2.917171	H	3.983222	2.719619	-1.342490
H	-4.905704	1.122151	-2.798968	C	1.315997	2.700904	0.274726
H	-4.518959	-0.338433	-1.901972	C	2.491004	3.299499	1.065241
C	-0.903843	2.398601	1.169950	H	2.642702	2.767607	2.007014
C	-0.046252	3.337793	0.315310	H	2.280432	4.344990	1.305891
H	0.290063	4.180004	0.925176	H	3.427783	3.270305	0.513977
H	-0.589184	3.746439	-0.538672	C	1.089536	3.483422	-1.028553
H	0.843515	2.828913	-0.057087	H	0.279259	3.043598	-1.613121
C	-2.076753	3.170517	1.784647	H	1.974613	3.525462	-1.657310
H	-2.727881	2.510019	2.370177	H	0.803327	4.511102	-0.788545
H	-2.691387	3.683497	1.045233	C	0.053125	2.878694	1.129254
H	-1.695301	3.936134	2.466832	H	-0.833209	2.555633	0.583594
C	-0.037333	1.906265	2.340673	H	-0.073361	3.933664	1.388235
H	0.866990	1.412258	1.987209	H	0.110585	2.302851	2.054321
H	-0.580435	1.199590	2.975111	N	-2.152780	-0.065086	0.004146
H	0.265914	2.760001	2.963916	N	-6.317288	0.202538	-0.119306
N	2.034870	-0.010817	0.081246	C	-2.858233	-0.622109	-0.991536
N	6.165691	0.428679	-0.382679	H	-2.278553	-1.160599	-1.728569
C	2.553329	0.764865	-0.875685	C	-4.230178	-0.555208	-1.076802
H	1.844909	1.255037	-1.529210	H	-4.713998	-1.037269	-1.910589
C	3.901522	0.942127	-1.070988	C	-4.965917	0.114762	-0.077828
H	4.229722	1.582920	-1.879845	C	-4.213281	0.684676	0.971574
C	4.821003	0.286776	-0.227257	H	-4.682184	1.209156	1.788277
C	4.263866	-0.534354	0.777402	C	-2.842436	0.570323	0.960689
H	4.888111	-1.095610	1.451134	H	-2.256234	1.006234	1.757811

C	2.895010	-0.657162	0.875339
H	2.464208	-1.316903	1.610277
C	7.069012	-0.360544	0.442848
H	6.927302	-1.431517	0.288098
H	6.917852	-0.134279	1.498610
H	8.090811	-0.096224	0.192657
C	6.687445	1.167891	-1.521283
H	6.346805	0.730775	-2.463894
H	7.775219	1.134536	-1.495933
H	6.376868	2.208738	-1.473706
C	-7.033542	0.849367	0.963859
H	-6.738416	1.895209	1.062658
H	-6.859292	0.344822	1.916521
H	-8.096957	0.818699	0.752483
C	-7.049238	-0.439768	-1.195921
H	-6.747838	-0.043367	-2.166348
H	-8.108673	-0.246187	-1.067043
H	-6.894002	-1.520520	-1.195979

5_isomer

E(scf) = -1556.05192484 a.u.

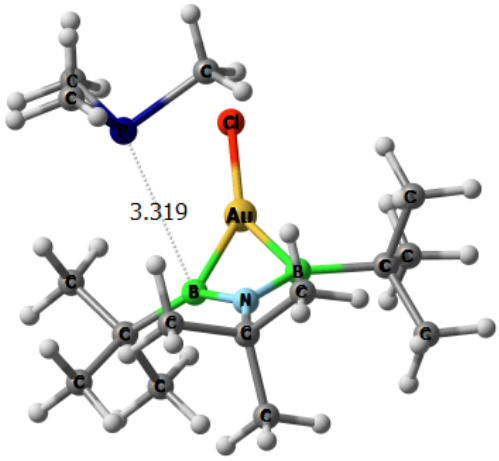


Au	-0.042460	0.432799	0.044083
Cl	0.849800	-2.131869	-1.475721
N	2.724660	-0.251201	-0.310930
B	1.994729	0.910275	-0.076755
B	1.554309	-1.120005	0.021828
C	2.314458	2.479754	0.061899
C	1.230376	3.187141	0.903625
H	1.125068	2.720020	1.888507
H	0.259946	3.163092	0.410998
H	1.501808	4.232348	1.051886
C	3.647088	2.777618	0.754381
H	3.773947	3.859659	0.869632
H	4.507811	2.413070	0.202018
H	3.675037	2.341308	1.754709
C	2.281221	3.125117	-1.335763
H	1.323943	2.937778	-1.831383
H	3.068255	2.752249	-1.988121
H	2.405654	4.209996	-1.245037
C	4.098868	-0.583321	-0.730833
C	5.053546	-0.562864	0.466659
H	6.076300	-0.737033	0.134448
H	4.794470	-1.338035	1.188601
H	5.016354	0.398478	0.981149
C	4.132543	-1.976563	-1.362387
H	3.739038	-2.739953	-0.700480

$TS_{2\rightarrow 4}$

E(scf) = -1634.85091793 a.u.

ν_{min} = -36.55 cm^{-1}



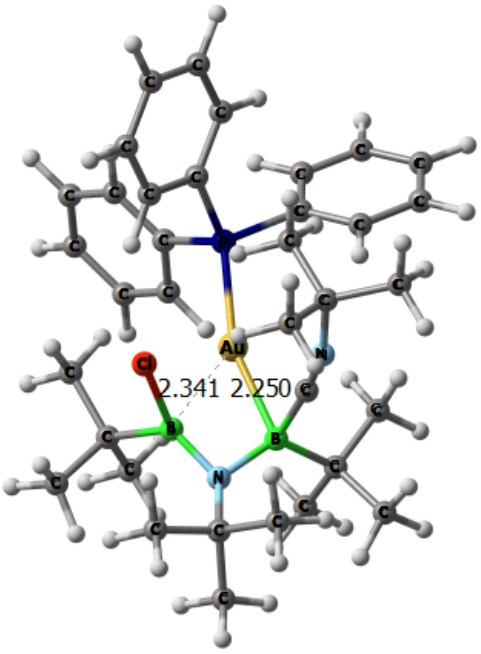
Au	-0.631729	-1.017111	0.342556
C	2.638311	1.705392	-0.403600
Cl	-2.646019	-2.234099	0.181287
C	1.848625	-1.956237	-2.340529
H	2.294271	-2.864695	-2.753410
H	2.283318	-1.104369	-2.861027
H	0.780583	-1.982311	-2.565667
P	-1.823951	1.776928	-1.272744
C	-1.665540	0.601400	-2.688809
H	-0.678523	0.694183	-3.142968
H	-2.425529	0.794285	-3.447250
H	-1.785042	-0.418468	-2.325291
N	1.596085	0.729332	-0.012828
C	0.005369	1.317249	2.245750
B	1.336747	-0.640917	-0.226820
B	0.471648	0.680905	0.859120
C	2.091401	-1.914344	-0.820441
C	0.527966	0.304518	3.292818

H	5.165424	-2.228945	-1.608147
H	3.547758	-1.994729	-2.281539
C	4.573241	0.395402	-1.804864
H	3.859417	0.413362	-2.622507
H	5.538744	0.075846	-2.192809
H	4.687225	1.406812	-1.422245
C	1.411186	-1.938546	1.412963
C	-0.024600	-2.403197	1.676937
H	-0.074433	-2.974647	2.606515
H	-0.387358	-3.042771	0.871045
H	-0.716482	-1.563514	1.776508
C	2.289420	-3.203014	1.405700
H	3.350438	-2.965232	1.377233
H	2.054638	-3.851214	0.560454
H	2.115050	-3.780956	2.323712
C	1.853732	-1.059320	2.591022
H	1.210099	-0.187889	2.696004
H	2.873575	-0.703466	2.466139
H	1.806613	-1.628814	3.528377
N	-2.255132	0.350562	-0.051489
N	-6.387588	-0.196649	-0.172253
C	-2.806104	-0.681961	-0.700713
H	-2.111120	-1.370623	-1.169301
C	-4.163375	-0.895822	-0.790780
H	-4.510789	-1.753043	-1.335989
C	-5.051654	-0.000228	-0.155033
C	-4.459239	1.106897	0.501151
H	-5.052764	1.876824	0.973282
C	-3.088423	1.224545	0.530075
H	-2.624345	2.058934	1.042972
C	-7.267820	0.785274	0.449763
H	-7.346519	1.744667	-0.174900
H	-6.886065	1.037034	1.492127
H	-8.292938	0.300534	0.549715
C	-6.949572	-1.237269	-1.017796
H	-6.711431	-1.085453	-2.074390
H	-8.031864	-1.228975	-0.902108
H	-6.590900	-2.224259	-0.711060
H	0.285316	0.667742	4.294185
H	1.612722	0.184968	3.235905
H	0.071662	-0.677912	3.170981
C	1.518303	-3.216023	-0.227945
H	1.582938	-3.227946	0.861155
H	2.088351	-4.067846	-0.607203
H	0.474665	-3.371764	-0.502751
C	-1.522077	1.411531	2.381560
H	-1.774734	1.717851	3.400017
H	-2.026993	0.465023	2.185741
H	-1.919513	2.156993	1.694146
C	0.576936	2.690265	2.610216
H	0.271807	2.941750	3.629007
H	0.192976	3.471473	1.954920
H	1.666228	2.709774	2.586984
C	3.815918	1.618484	0.564889
H	3.493719	1.841129	1.581519
H	4.586297	2.337770	0.284835
H	4.254196	0.622392	0.556622
C	3.084569	1.409485	-1.833549
H	3.793306	2.171319	-2.157753
H	2.226191	1.432994	-2.505987
H	3.568826	0.443954	-1.925281
C	2.047967	3.111985	-0.403184
H	1.751271	3.431162	0.587163
H	1.181219	3.155813	-1.063553
H	2.798262	3.809772	-0.776029
C	-3.572455	1.444141	-0.795680
H	-3.637315	0.467400	-0.318602
H	-4.227444	1.458256	-1.667776
H	-3.909106	2.199822	-0.086758
C	-2.068100	3.350235	-2.218194
H	-2.370550	4.141523	-1.533157
H	-2.835756	3.235178	-2.984674
H	-1.139357	3.655395	-2.697554
C	3.597396	-1.923671	-0.515830
H	3.781633	-1.900180	0.559786
H	4.140985	-1.099034	-0.968169
H	4.035197	-2.847583	-0.901331

SECOND PART (Reaction mechanism from **3** to **6**)

3a

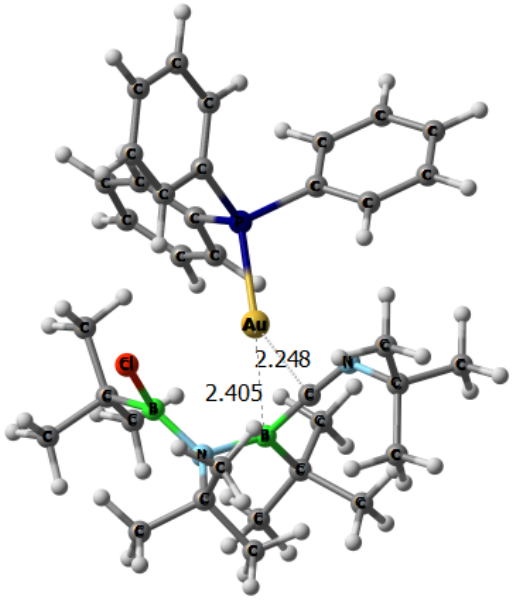
E(scf) = -2460.85347415 a.u.



Au	0.154887	0.297389	0.294823
Cl	1.827101	-0.009290	-2.425233
P	-2.201516	0.070892	0.048962
C	2.250369	0.125980	2.664013
N	3.160329	0.791631	0.089581
B	2.265739	0.028718	1.024903
C	2.208610	1.590036	3.103290
H	2.245055	1.663967	4.195196
H	1.292603	2.073240	2.761363
H	3.049414	2.151372	2.696056
N	2.057805	-2.567863	0.082546
B	2.062649	1.184027	-0.732571
C	3.489175	-0.529548	3.295163
H	3.428320	-0.468879	4.386386
H	4.415148	-0.042919	2.997057
H	3.563161	-1.588803	3.033174
C	4.610868	0.661082	-0.139393
C	1.035976	-0.591177	3.273297
H	1.109913	-0.604142	4.365268
H	0.972020	-1.632413	2.940998
H	0.097266	-0.098576	3.013392
C	4.996470	0.947003	-1.592903
H	6.071710	0.797095	-1.707152
H	4.775680	1.970166	-1.878874
H	4.478009	0.279816	-2.276542

3b

E(scf) = -2460.84365975 a.u.



Au	0.053175	0.203406	-0.192781
Cl	1.673281	-2.001670	2.400534
P	-2.241929	0.143012	0.064927
C	2.520059	0.332435	-2.443150
N	2.924025	-1.148719	-0.014228
B	2.371751	0.046061	-0.811370
C	3.084994	-0.861506	-3.230040
H	3.547593	-0.509964	-4.156614
H	2.299510	-1.557594	-3.513203
H	3.832616	-1.420675	-2.670050
N	1.723342	2.334913	0.533694
B	1.910050	-1.977972	0.539705
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C	4.263812	-1.031301	0.642629
C	1.184649	0.716854	-3.102649
H	1.340654	0.935927	-4.164275
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H	0.456448	-0.092935	-3.036197
C	4.822104	-2.438573	0.861544
H	5.807983	-2.378918	1.326121
H	4.918127	-2.958081	-0.092633
H	4.181361	-3.026466	1.518649
C	5.214970	-0.301544	-0.303231
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C	5.355676	1.658567	0.754716	H	4.927112	0.739329	-0.418497
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H	5.154546	1.473924	1.807990	C	4.256725	-0.273254	1.985063
H	5.027800	2.672878	0.524048	H	5.238037	0.172635	2.161898
C	5.083406	-0.764679	0.158296	H	4.030503	-0.926702	2.821580
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H	4.641663	-1.459832	-0.557079	C	1.056378	-3.138740	-0.155734
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H	2.870523	2.804156	-2.848944	C	2.624863	3.440881	0.924787
H	3.545612	3.535882	-1.379184	C	2.019762	1.278661	-0.021207
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H	0.014937	3.807179	-2.127245	H	-0.374591	-3.514312	1.457239
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H	0.552090	3.144121	0.780099	H	2.685607	5.554891	0.478783
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H	-3.478342	-2.835886	-4.659135	H	-5.520326	0.225661	3.772228
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C	-3.724876	-1.778966	-1.449742	C	-3.068584	-1.091378	-0.981676
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C	-3.332046	-2.018009	-3.190981
H	-3.104696	-1.997443	-4.247876
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3c

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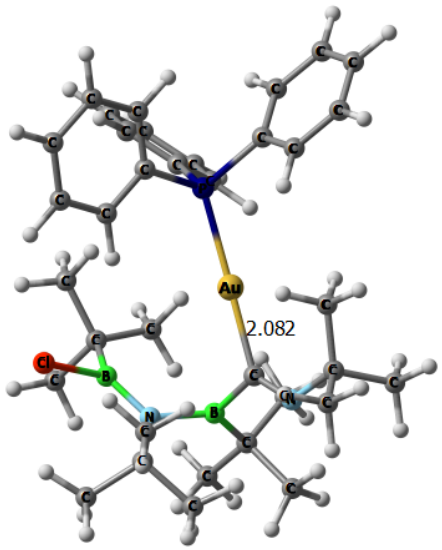

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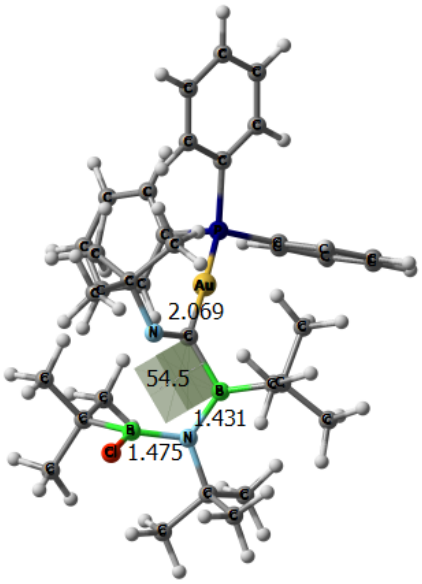

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H	-4.957307	0.708686	-3.440700	B	-2.489321	1.058378	-0.515570
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H	-5.063543	1.294502	-1.780377	H	-2.500442	4.265923	-2.331622
N	-2.456533	-2.476970	0.097837	H	-1.813930	4.171061	-0.720275
B	-2.099811	2.059533	0.498924	H	-3.544176	3.966387	-0.967584
C	-4.543289	-1.444046	-2.086735	N	-2.220246	-1.222998	-1.260909
H	-4.788720	-1.692121	-3.122586	B	-3.917166	-0.601198	0.636009
H	-5.477253	-1.208312	-1.583050	C	-3.261001	1.740973	-2.736996
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C	-3.960893	0.576073	1.479859	H	-4.305478	1.767292	-2.435503
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H	-1.853242	4.764314	-1.638267	C	-3.353447	-1.580790	1.772887
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C	-2.437201	-4.214086	1.734416	H	-2.175511	-0.034816	2.776312
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H	-3.510688	-4.280012	1.563176	C	-2.670096	-3.296628	-2.394588
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C	-1.995028	-4.683888	-0.679566	H	-0.999580	-4.161320	-0.727115
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H	0.626892	1.214434	2.046680	C	3.826235	-0.589939	-0.981444
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C	4.262918	1.192273	3.352110	C	5.522088	-1.808010	-2.823834
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C	2.334968	1.090444	-2.539049	C	2.238510	-1.420327	3.969232
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C	3.448758	-1.339938	-0.269112	C	2.020181	-0.771633	2.761410
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H	6.268834	-2.190101	-1.942385	H	4.254158	1.431087	2.401297
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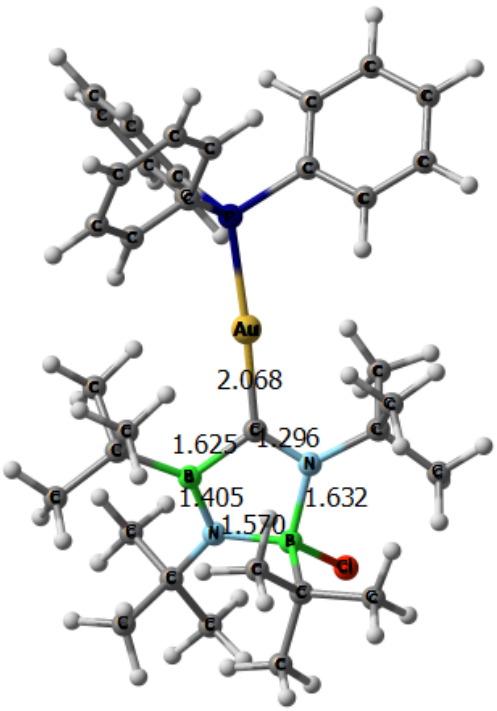

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C	-1.017618	2.220906	1.884969
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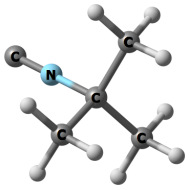

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C	-3.971572	2.553248	-2.047120
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H	-6.093166	0.583701	1.161842
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H	-0.388213	-3.921100	0.809962
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H	5.234340	-0.811038	-1.540874

C	3.557995	0.706012	1.476682
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C	3.493980	2.433631	3.155027
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C	4.912508	2.706679	-2.300067
H	5.763454	3.363873	-2.185512
C	4.236645	2.646523	-3.512439
H	4.562420	3.257527	-4.343118
C	3.134702	1.811065	-3.656572
H	2.600846	1.771608	-4.595742
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Appendix 2. NMR Spectra of Complexes **2-6**

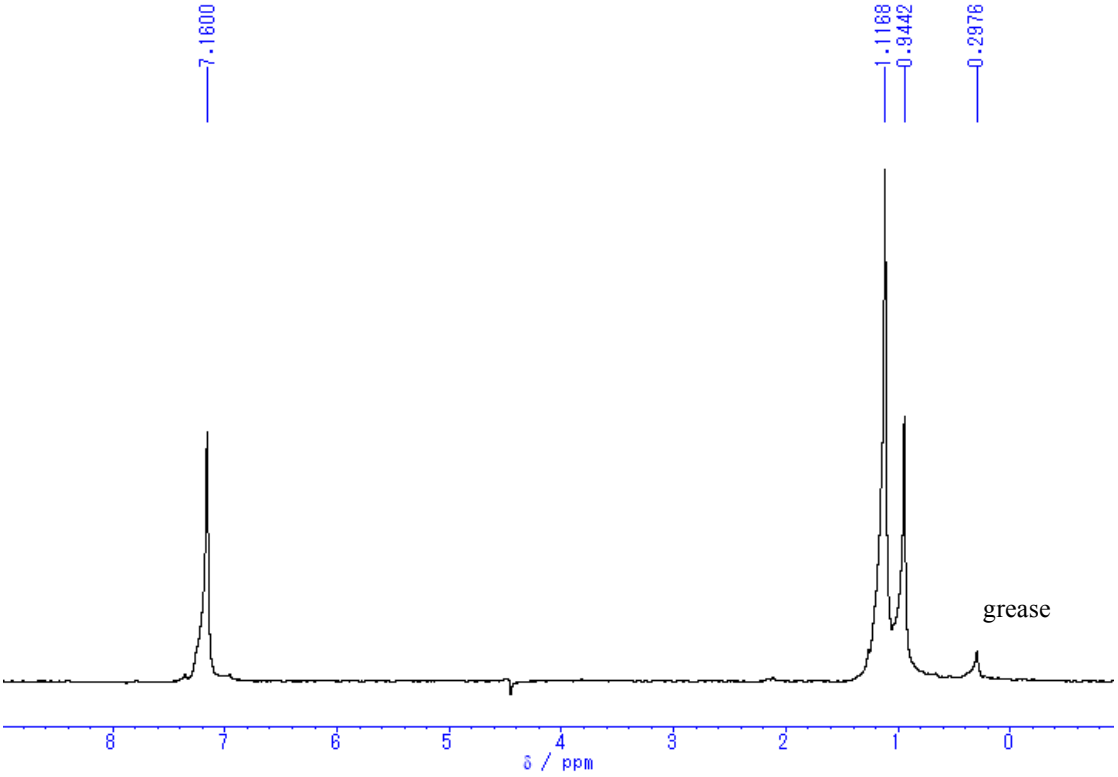

Figure A1. ^{1}H NMR spectrum (400 MHz) of **2** in C_6D_6 at room temperature.

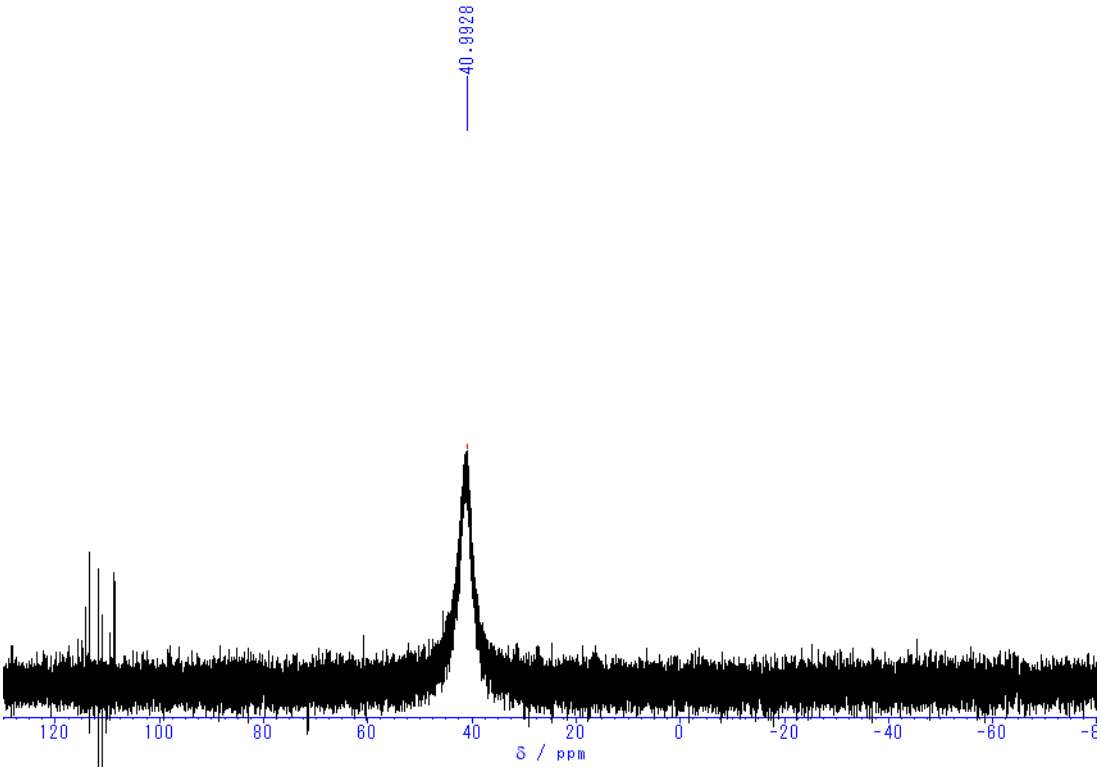

Figure A2. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz) of **2** in C_6D_6 at room temperature.

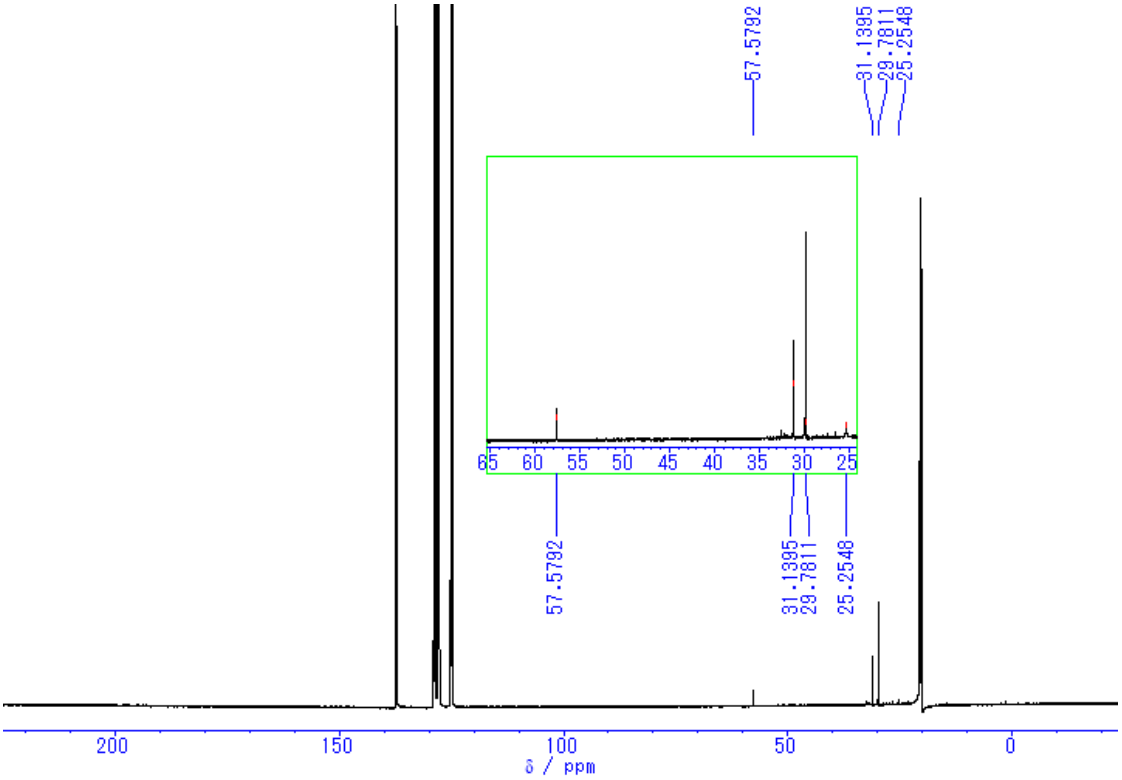

Figure A3. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of **2** in toluene-d_8 at –50 °C.

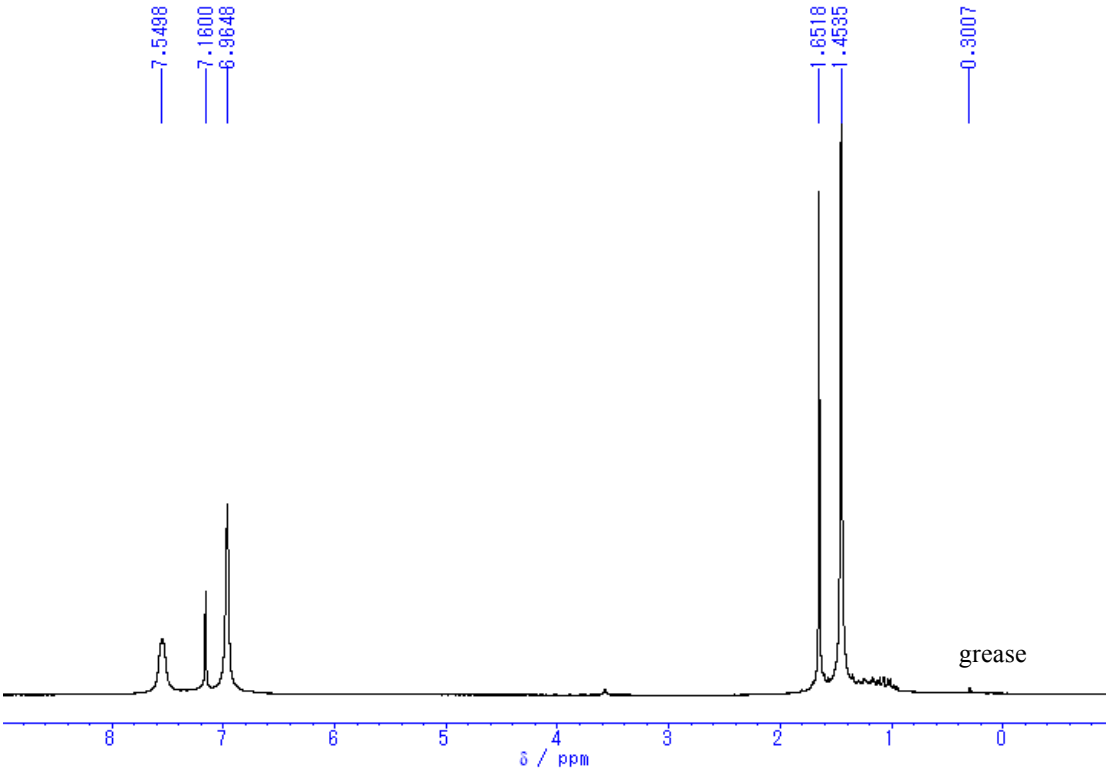

Figure A4. ^{1}H NMR spectrum (400 MHz) of **3** in C_6D_6 at room temperature.

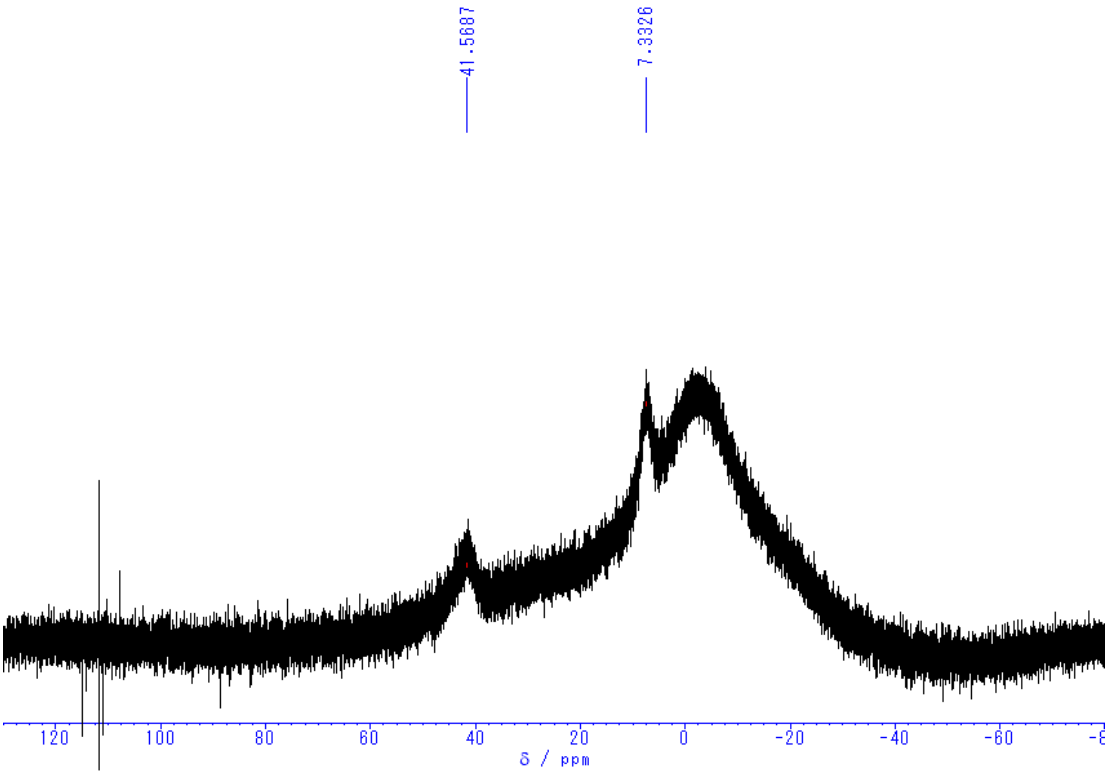

Figure A5. ^{11}B{^{1}H} NMR spectrum (128 MHz) of **3** in C_6D_6 at room temperature.

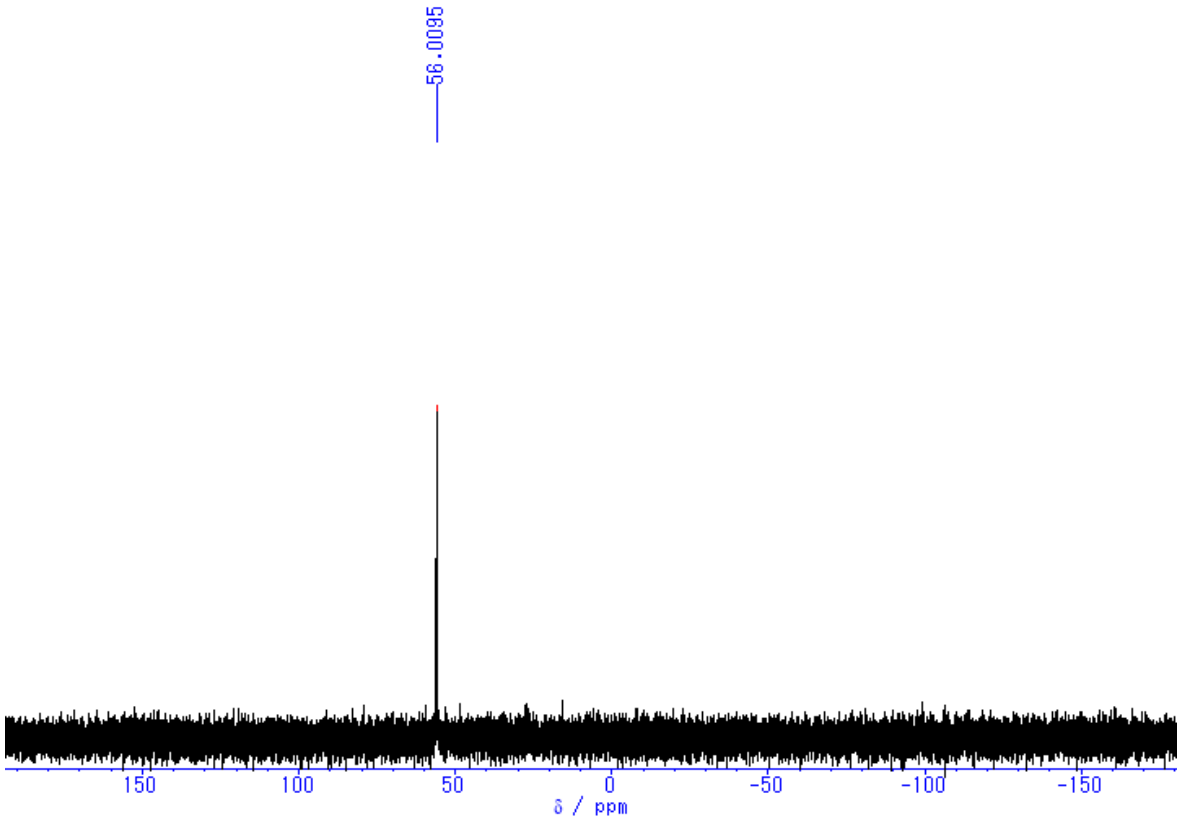

Figure A6. $^{31}P\{^{1}H\}$ NMR spectrum (160 MHz) of **3** in C_6D_6 at room temperature.

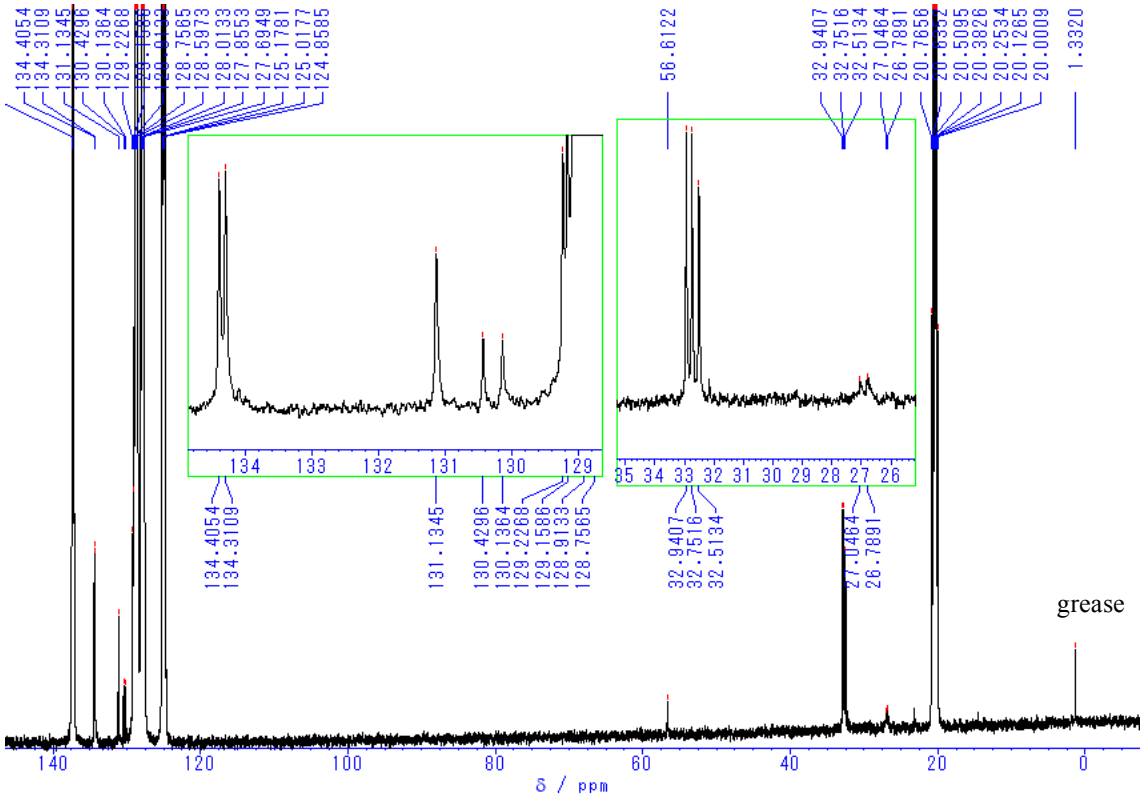

Figure A7. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of **3** in toluene-d_8 at –50 °C.

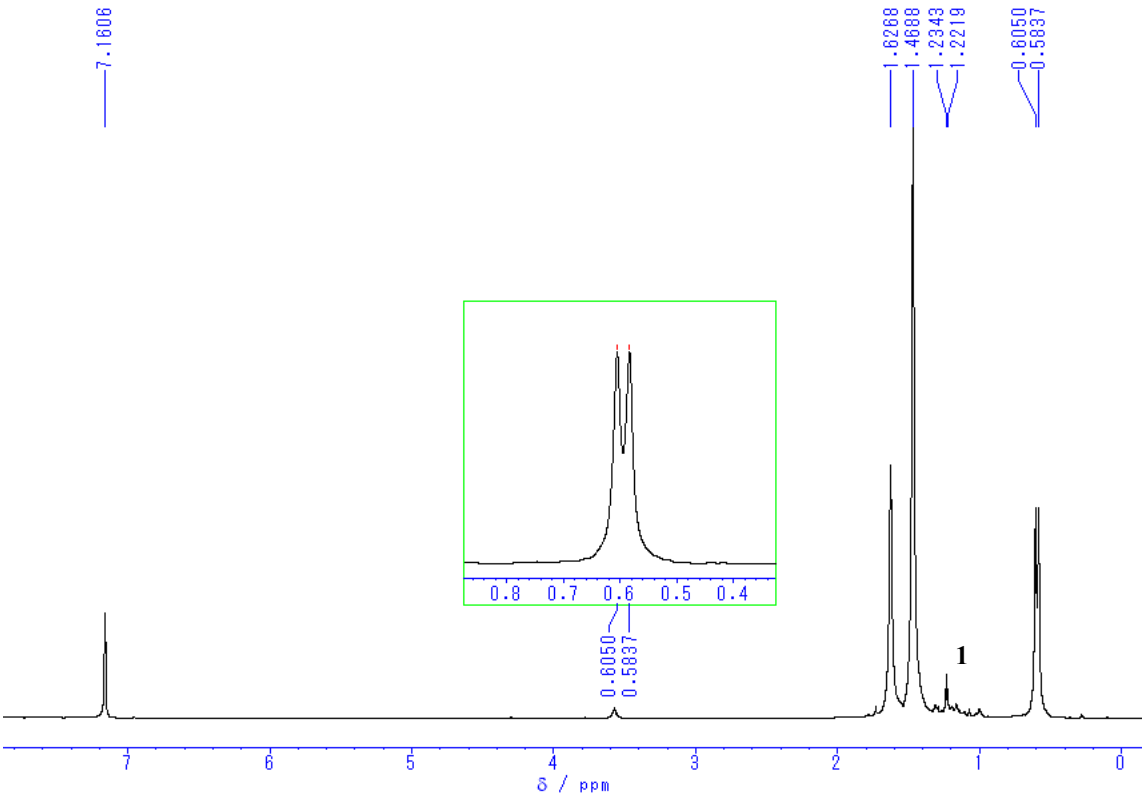

Figure A8. ^{1}H NMR spectrum (400 MHz) of **4** in C_6D_6 at room temperature. Signals at 1.23 and 1.22 correspond to a small residue of ligand precursor **1**.

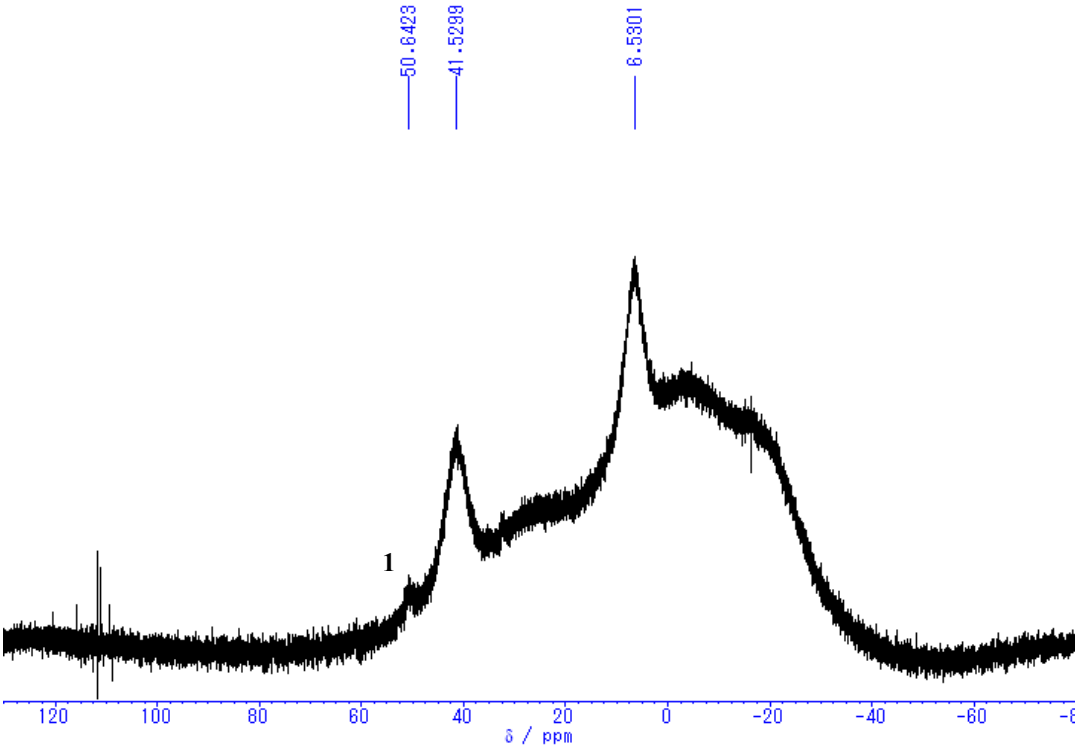

Figure A9. ^{11}B{^{1}H} NMR spectrum (128 MHz) of **4** in C_6D_6 at room temperature. The small singlet at 50.6 corresponds to the ligand precursor **1**.

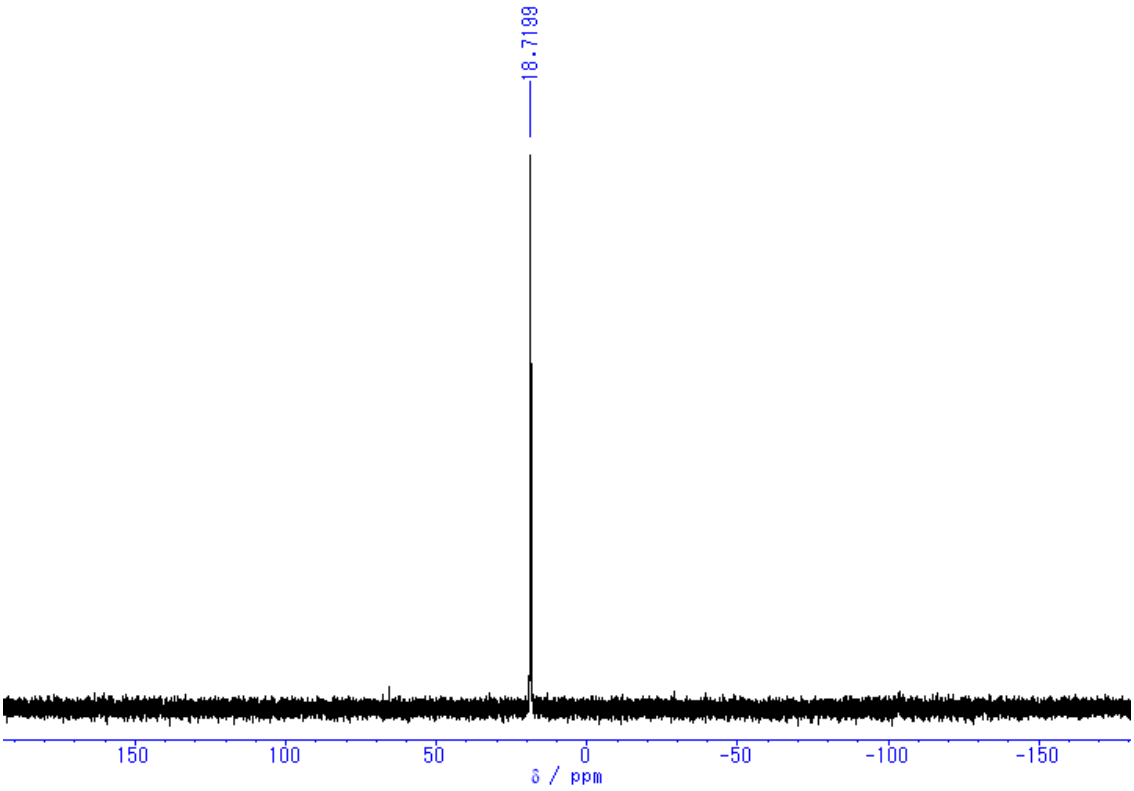

Figure A10. $^{31}P\{^{1}H\}$ NMR spectrum (160 MHz) of **4** in C_6D_6 at room temperature.

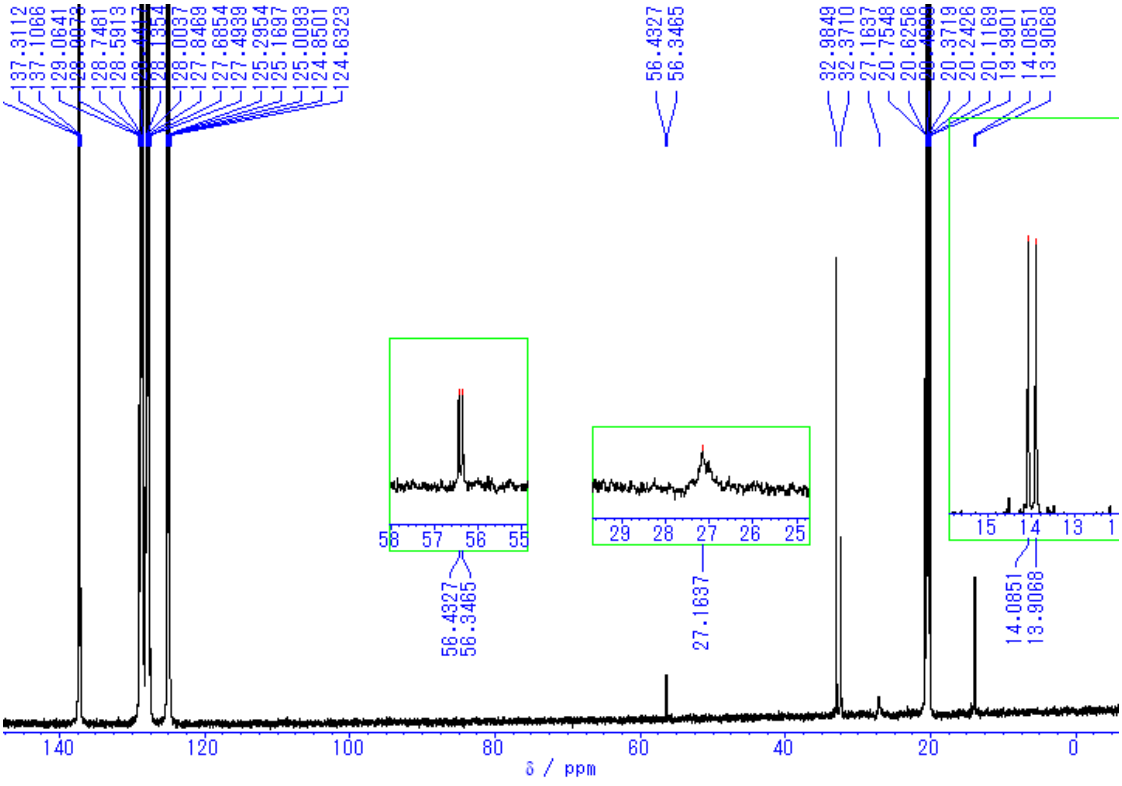

Figure A11. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of **4** in toluene-d_8 at –50 °C.

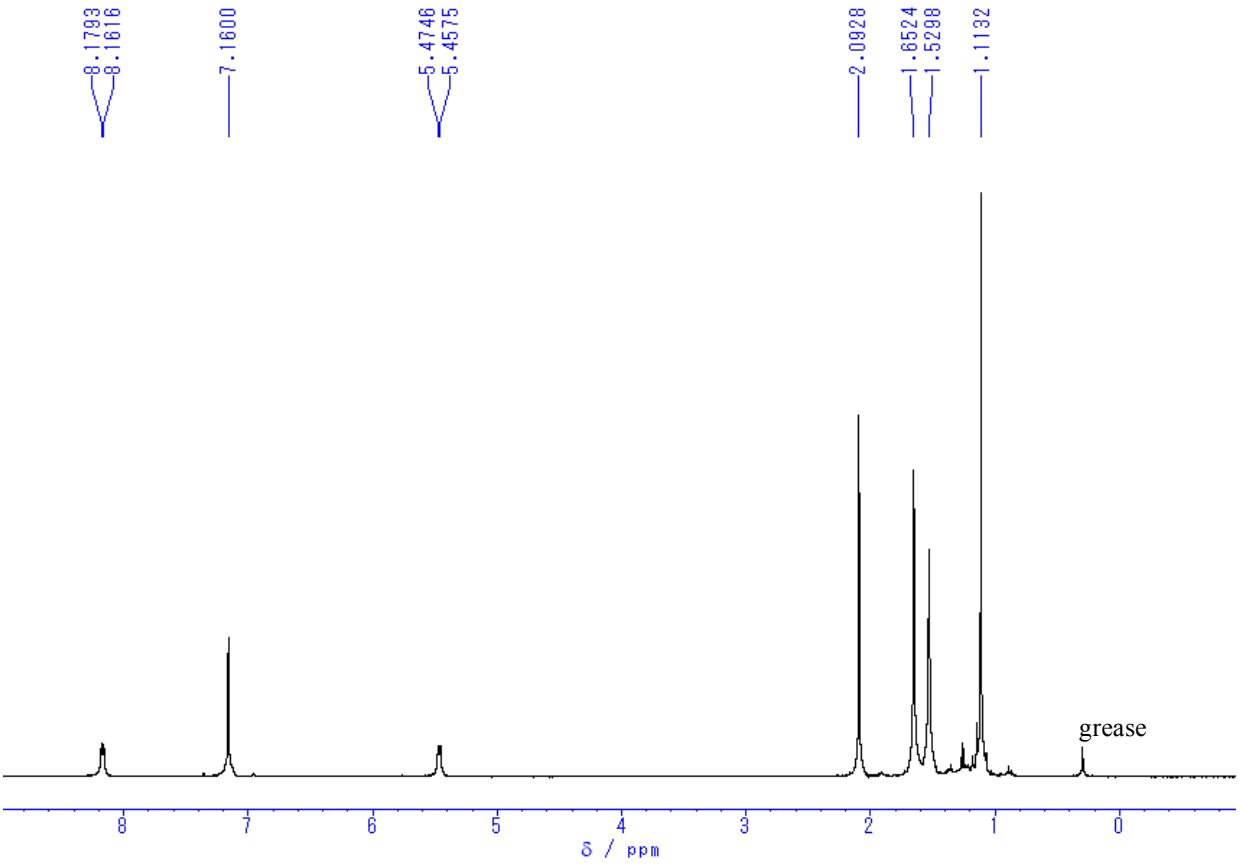

Figure A12. ^{1}H NMR spectrum (400 MHz) of **5** in C_6D_6 at room temperature.

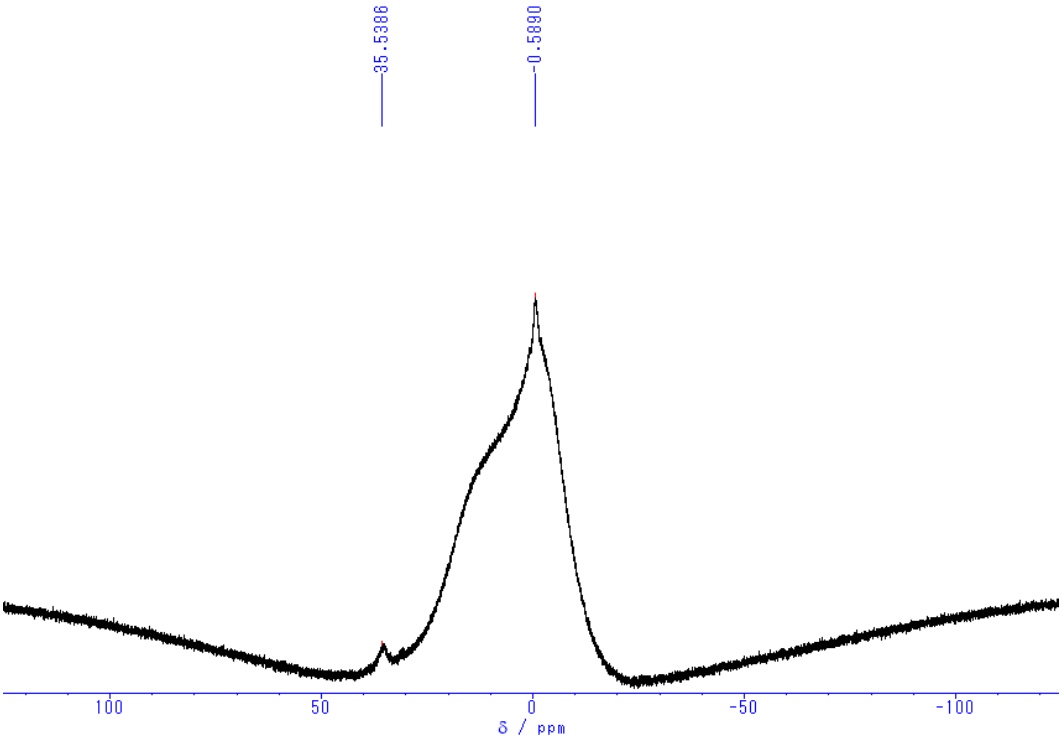

Figure A13. ^{11}B{^{1}H} NMR spectrum (128 MHz) of **5** in C_6D_6 at 40 °C.

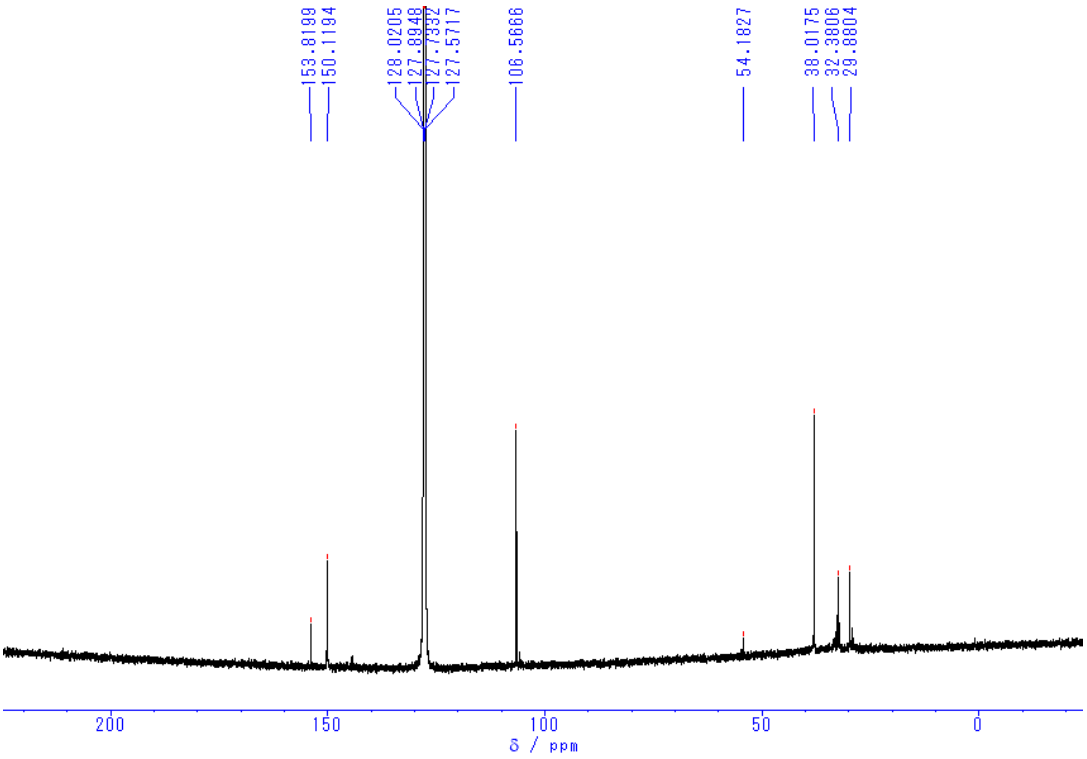

Figure A14. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of **5** in toluene-d_8 at room temperature.

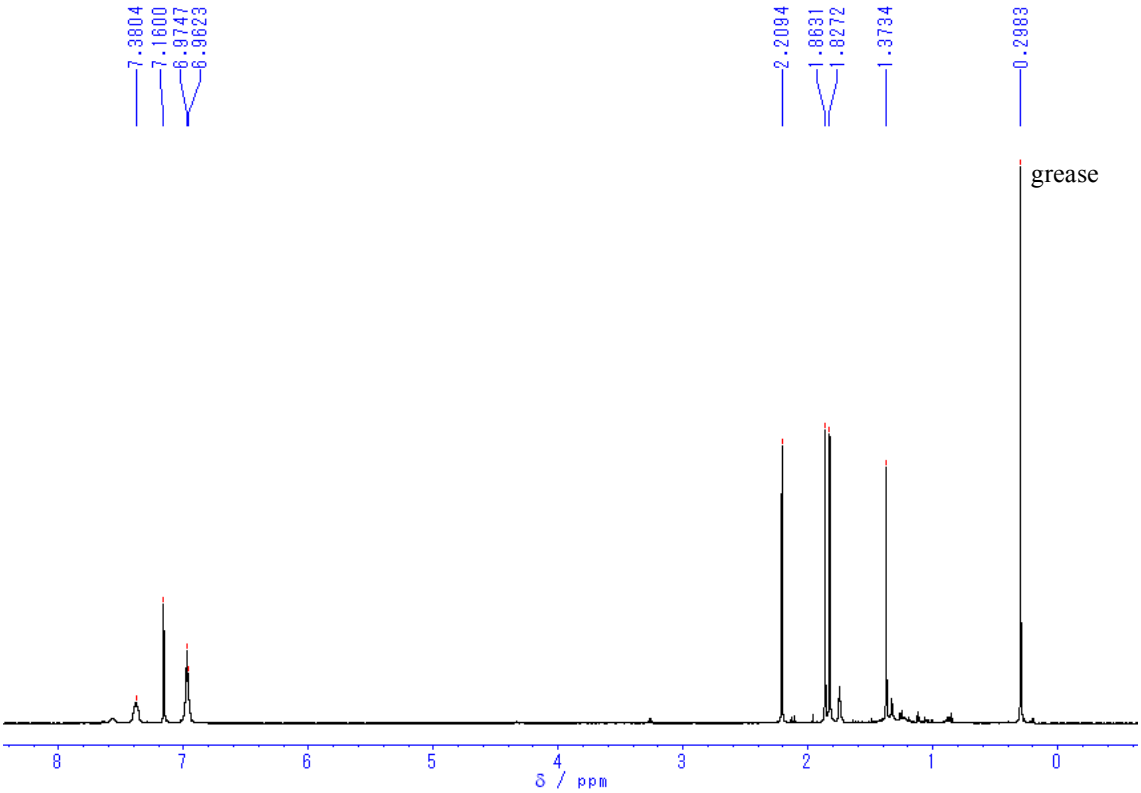

Figure A15. ^{1}H NMR spectrum (600 MHz) of **6** in C_6D_6 at room temperature.

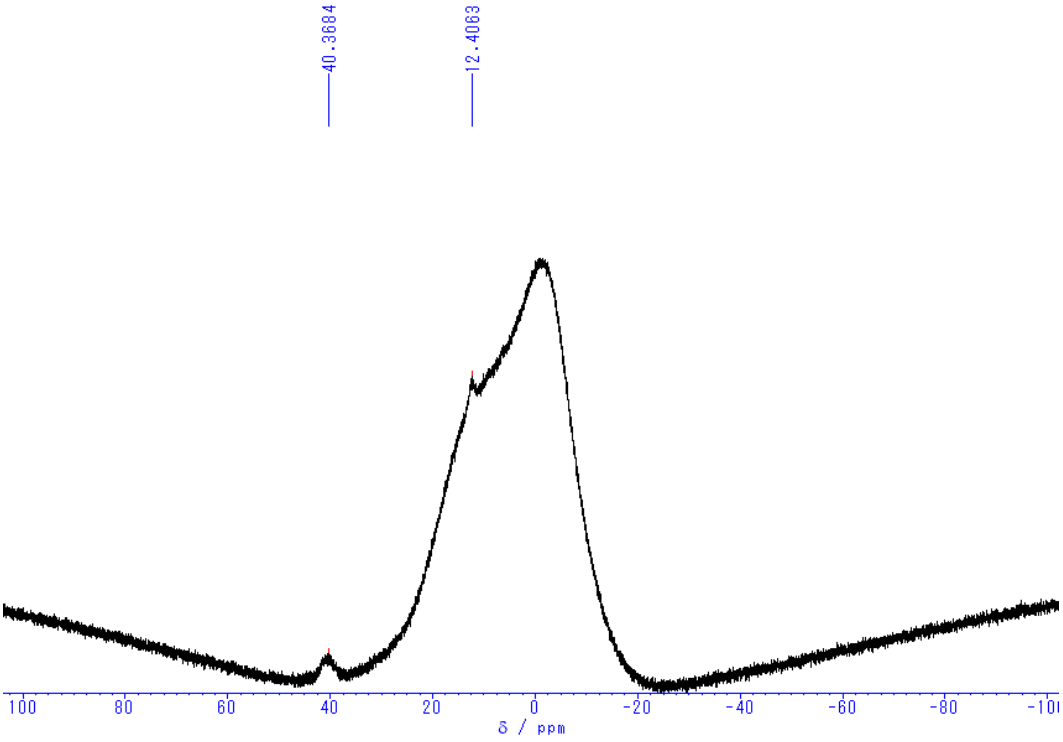

Figure A16. $^{11}B\{^{1}H\}$ NMR spectrum (192 MHz) of **6** in C_6D_6 at room temperature.

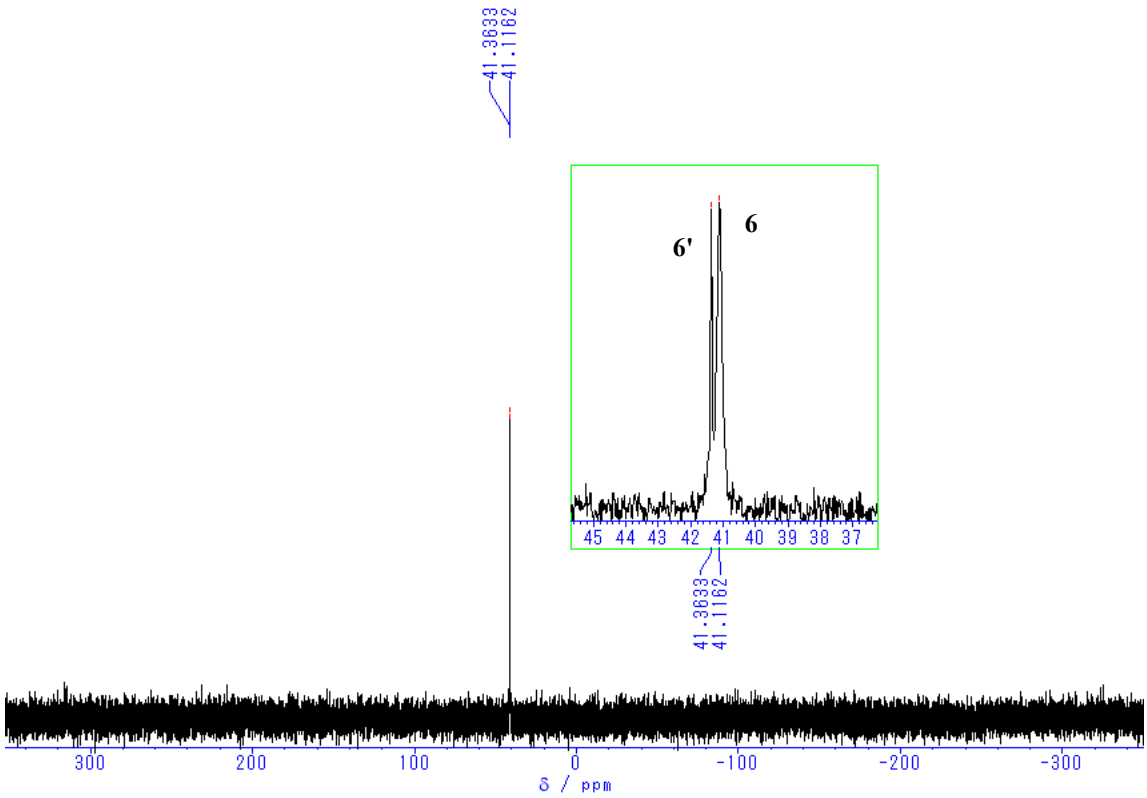

Figure A17. $^{31}P\{^{1}H\}$ NMR spectrum (160 MHz) of **6** in toluene-d_8 at room temperature. A small amount of **6'** is always present even crystals of **6** was used. The integration of **6'** with respect to **6** diminishes with decreasing temperatures. The nature of **6'** is currently under investigation.

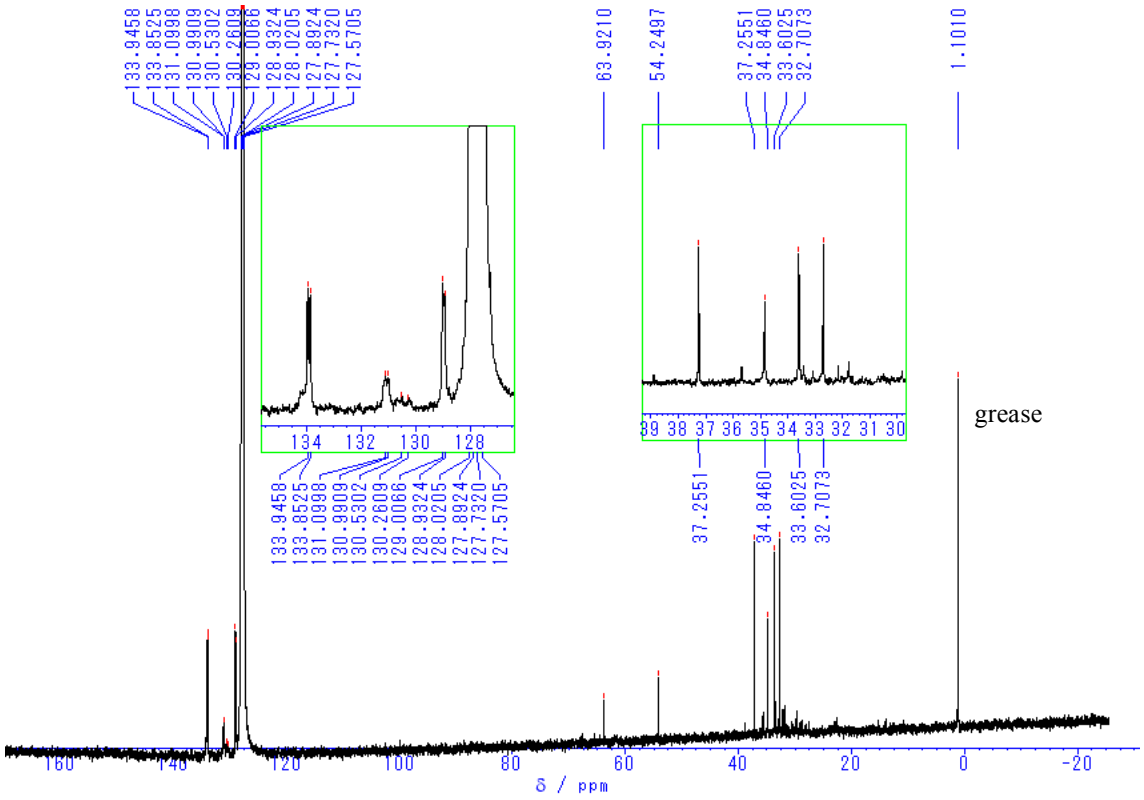

Figure A18. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of **6** in C_6D_6 at room temperature.