

Supporting Information

**(Thio)(silyl)carbene and (Seleno)(silyl)carbene Gold(I)
Complexes from the Reaction of Bis(methylene)- λ^4 -
sulfane and Bis(methylene)- λ^4 -selane with
Chloro(dimethylsulfide)gold(I)**

Koh Sugamata, Yukiko Urao, and Mao Minoura

*College of Science, Department of Chemistry, Rikkyo University, 3-34-1 Nishi-
Ikebukuro, Toshima-ku, Tokyo, 171-8501 (Japan)*

Table of Contents

General Procedure	2
NMR Spectroscopic Analysis	3
UV-vis Spectroscopic Analysis	7
X-ray Crystallographic Analysis of 1 and 2	8
Computational Details	10
References	16

General Procedure

Unless otherwise noted, all experiments were performed under an argon atmosphere. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in CDCl_3 on a JEOL JNM ECS-400SS spectrometer. A signal arising from residual CHCl_3 (7.26 ppm) in CDCl_3 was used as an internal standard for the ^1H NMR spectra and that of CDCl_3 (77.16 ppm) for the ^{13}C NMR spectra. ^{29}Si NMR (79 MHz) spectra were measured in CDCl_3 using $\text{Si}(\text{CH}_3)_4$ (0 ppm) as an external standard. ^{77}Se NMR (76 MHz) spectra were measured in CDCl_3 using Me_2Se (0 ppm) as an external standard. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-T100LP (ESI) mass spectrometer. All melting points were measured on a SMP-300CT capillary melting point apparatus and are uncorrected.

Synthesis of (thio)(silyl)carbene gold(I) complex (1): A C_6H_6 solution (3 mL) of bis(methylene)- λ^4 -sulfane **3** (31 mg, 0.037 mmol) at room temperature was treated with $\text{AuCl}(\text{Me}_2\text{S})$ (23 mg, 0.077 mmol). After stirring over 3 hours, all volatiles were removed in vacuo, and the residue was recrystallized from CH_2Cl_2 and Hexane to afford **1** as a red solid (35 mg, 0.031 mmol, 84 %). mp. 166 °C (dec.); ^1H NMR (400 MHz, CDCl_3 , 298 K) δ 0.31 (s, 6H), 0.76 (s, 3H), 2.62 (s, 6H), 7.20–7.43 (m, 22H), 7.46–7.48 (m, 4H), 7.65–7.68 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 , 298 K), δ -1.99, 0.43, 23.8, 71.8, 127.8, 127.9, 128.1, 129.3, 129.4, 130.0, 133.8, 135.4, 135.7, 136.2, 137.2, 138.1, 309.6; ^{29}Si NMR (79 MHz, CDCl_3 , 298 K), δ -11.7, -12.7; Anal. (%) calcd. for $\text{C}_{43}\text{H}_{45}\text{Au}_2\text{Cl}_2\text{Si}_3$: C, 45.32; H, 3.98; found: C, 45.24; H, 4.02. HRMS (ESI) Calcd. for $\text{C}_{41}\text{H}_{39}\text{Au}_2^{35}\text{Cl}_2\text{SSi}_3$ 1111.0788 ($[\text{M}-\text{Me}_2\text{S}+\text{Cl}]^-$); found: m/z = 1111.0763 ($[\text{M}-\text{Me}_2\text{S}+\text{Cl}]^-$). UV-vis (CHCl_3): λ = 345 nm (ϵ 5800), 490 nm (ϵ 160).

Synthesis of (seleno)(silyl)carbene gold(I) complex (2): The above procedure was followed using bis(methylene)- λ^4 -selane (89 mg, 0.10 mmol) **4** instead of **3** and $\text{AuCl}(\text{Me}_2\text{S})$ (59 mg, 0.20 mmol). The mixture was recrystallized from CH_2Cl_2 and Hexane to afford **2** as a brown solid (109 mg, 0.092 mmol, 92 %). mp. 150 °C (dec.); ^1H NMR (400 MHz, CDCl_3 , 298 K) δ 0.33 (s, 6H), 0.74 (s, 3H), 2.53 (s, 6H), 7.18–7.39 (m, 22H), 7.53–7.55 (m, 4H), 7.64–7.66 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 , 298 K), δ -1.92, 1.28, 24.0, 73.0, 127.8, 127.9, 128.1, 129.2, 129.3, 130.1, 133.6, 135.5, 135.7, 136.1, 138.2, 138.7, 344.8; ^{29}Si NMR (79 MHz, CDCl_3 , 298 K), δ -10.5, -11.5; ^{77}Se NMR (76 MHz, CDCl_3 , 298 K), δ 1494; Anal. (%) Calcd. for $\text{C}_{43}\text{H}_{45}\text{Au}_2\text{ClSSeSi}_3$: C, 43.53; H, 3.82; found: C, 43.31; H, 3.82. HRMS (ESI) Calcd. for $\text{C}_{41}\text{H}_{39}\text{Au}_2^{35}\text{Cl}_2\text{Si}_3^{80}\text{Se}$ 1159.0233 ($[\text{M}-\text{Me}_2\text{S}+\text{Cl}]^-$); found: m/z = 1159.0205 ($[\text{M}-\text{Me}_2\text{S}+\text{Cl}]^-$). UV-vis (CHCl_3): λ = 369 nm (ϵ 6700), 541 nm (ϵ 200).

NMR Spectroscopic Analysis

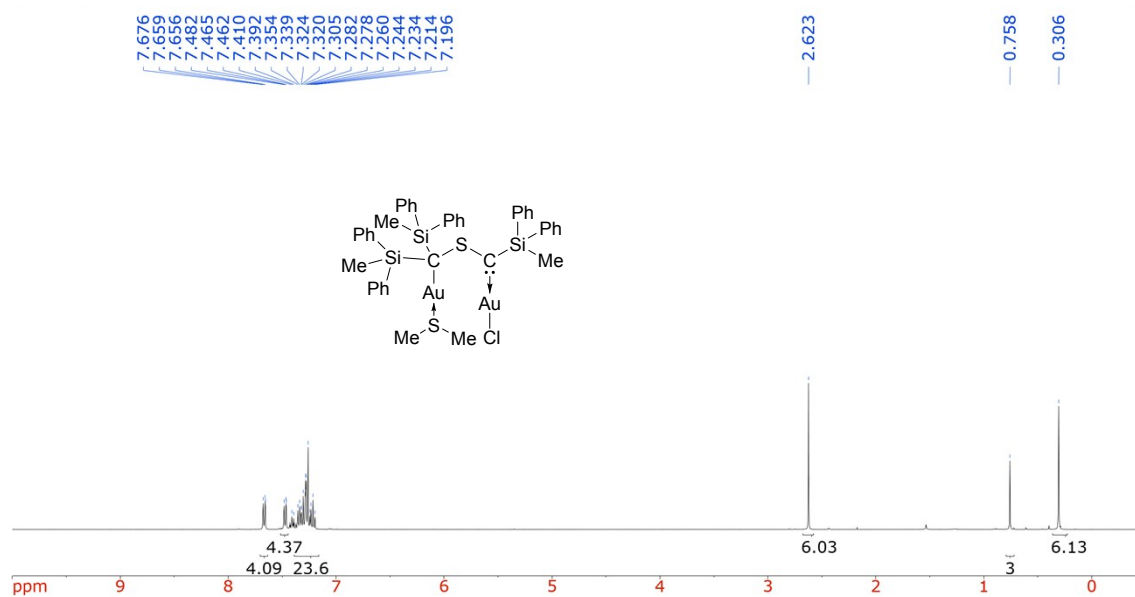


Figure S1. ¹H NMR spectrum of **1** (400 MHz, CDCl₃, 298 K)

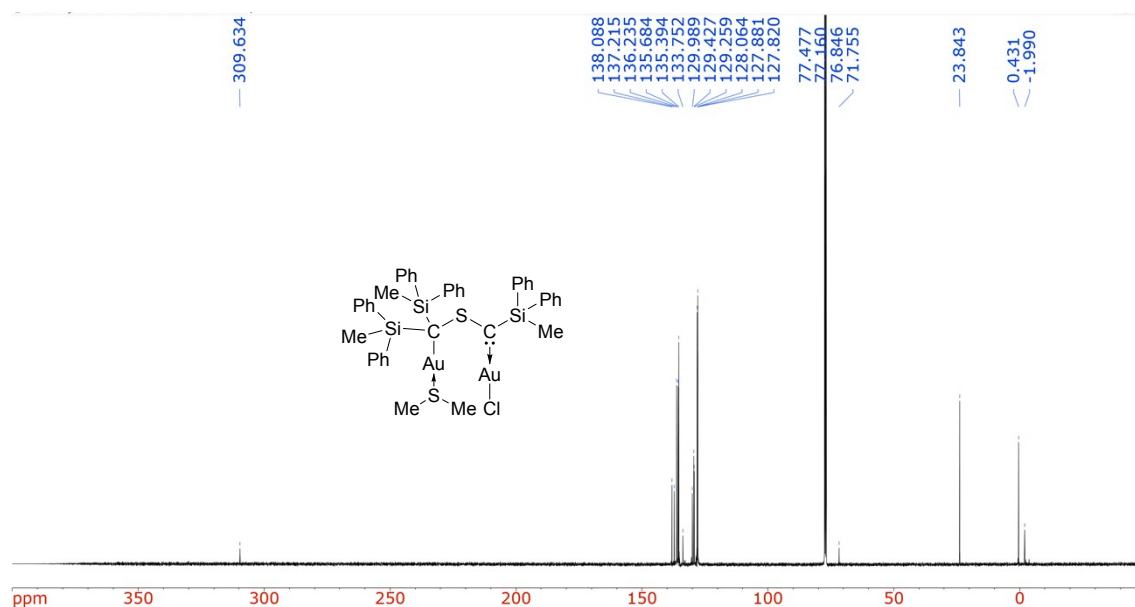


Figure S2. ¹³C NMR spectrum of **1** (100 MHz, CDCl₃, 298 K)

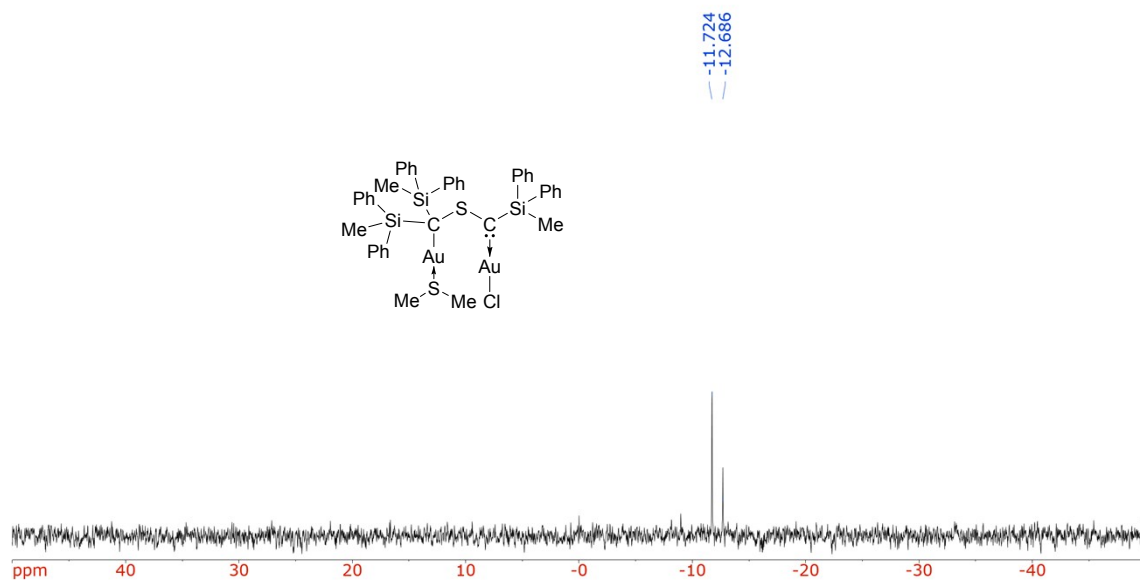


Figure S3. ^{29}Si NMR spectrum of **1** (79 MHz, CDCl_3 , 298 K)

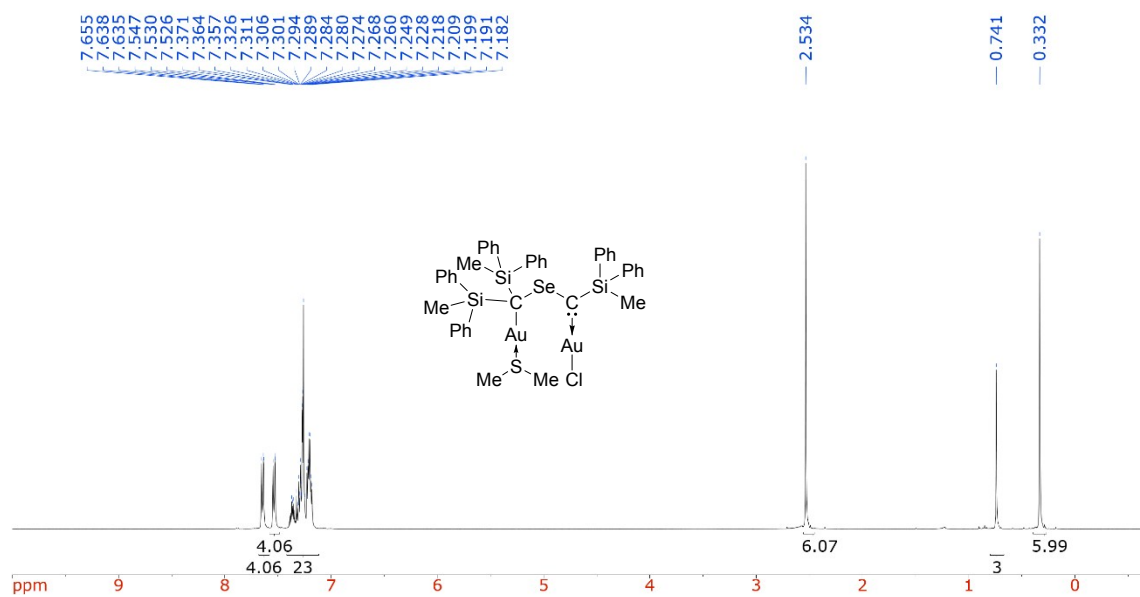


Figure S4. ^1H NMR spectrum of **2** (400 MHz, CDCl_3 , 298 K)

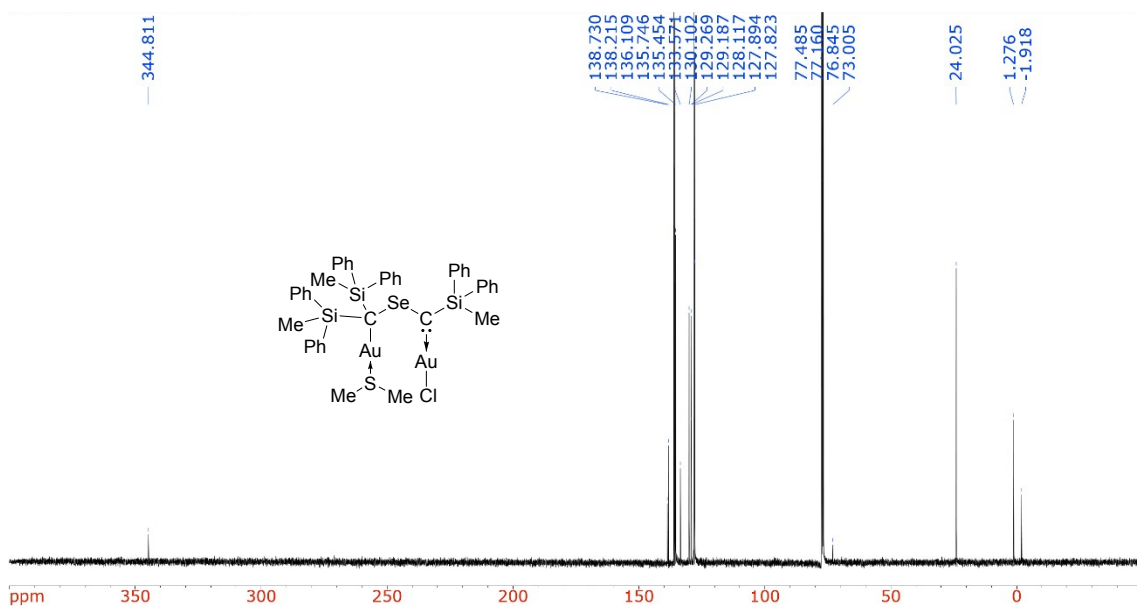


Figure S5. ^{13}C NMR spectrum of **2** (100 MHz, CDCl_3 , 298 K)

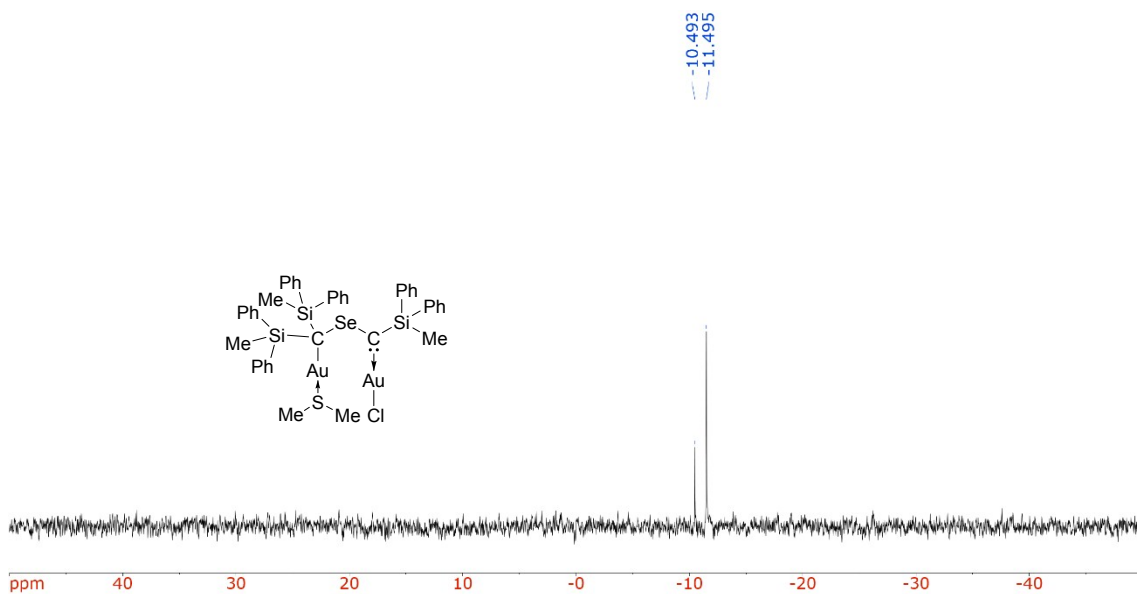


Figure S6. ^{29}Si NMR spectrum of **2** (79 MHz, CDCl_3 , 298 K)

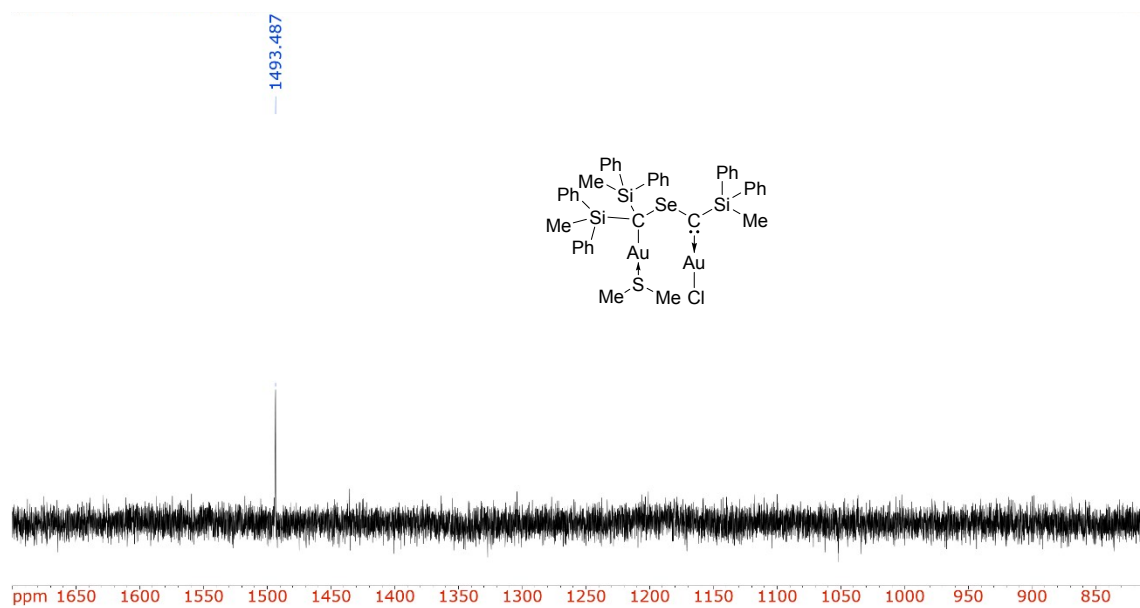


Figure S7. ^{77}Se NMR spectrum of **2** (76 MHz, CDCl_3 , 298 K)

UV-vis Spectroscopic Analysis

UV-vis spectrum of complexes **1** and **2** are shown in Figure S8. Complex **2** exhibited the longest absorption maximum at $\lambda_{\text{max}} = 541$ nm, which is bathochromically shifted compared to that of complex **1** ($\lambda_{\text{max}} = 490$ nm). TD-DFT calculations on **1** and **2** (**1**: $\lambda_{\text{calcd}} = 498$ nm, $f = 0.0003$; **2**: $\lambda_{\text{calcd}} = 527$ nm, $f = 0.0001$), indicating that the HOMO-LUMO energy gap of **2** should slightly decrease compared to that of **1**. The HOMOs of **1** and **2** are dominantly composed of the d_z orbitals in Au, while the LUMOs should be formed by the π^* orbitals of C-Ch bonds as shown in Figure S13.

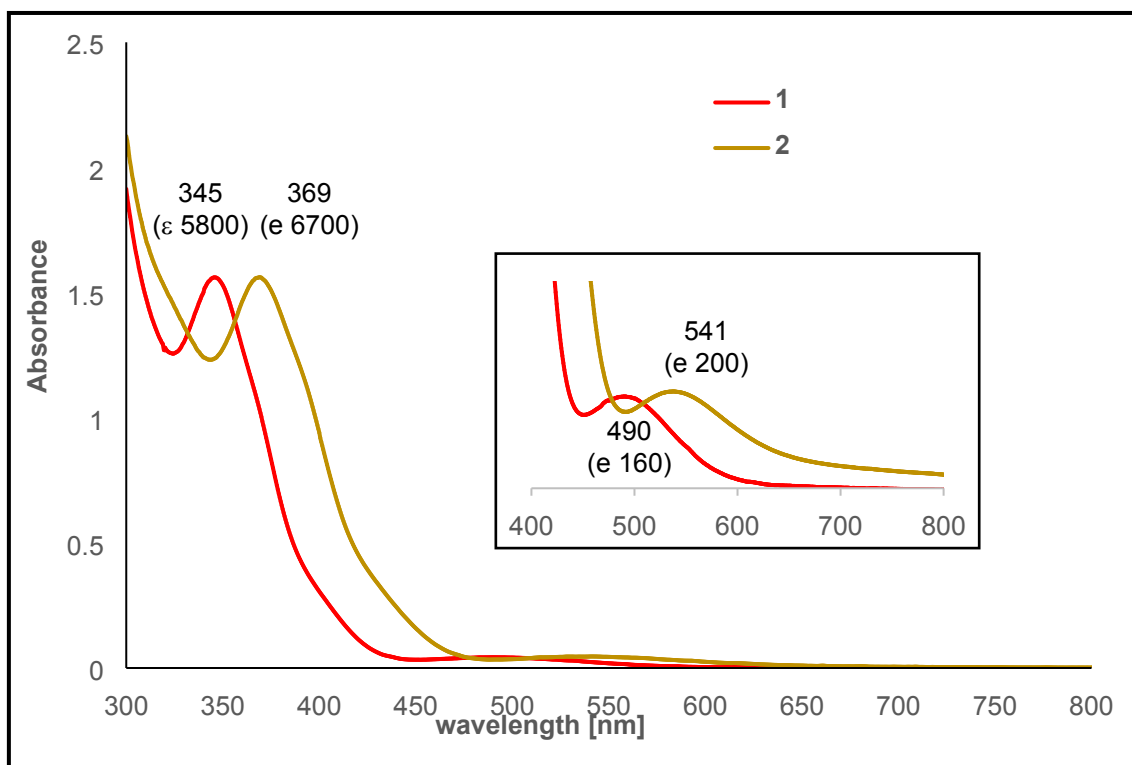


Figure S8. UV-Vis spectra of **1** and **2** in CHCl_3 (1.0×10^{-5} M).

X-ray Crystallographic Analysis of **1** and **2**

Single crystals of **1** and **2** were grown by slow recrystallization of the Hexane and CH₂Cl₂ solutions at room temperature. The structures were solved by a direct method (SHELXT)^[S1] and refined by full-matrix least square method on F² for all reflections (SHELXL-2016).^[S2] All hydrogen atoms were placed using AFIX instructions, while the other atoms were refined anisotropically. The supplementary crystallographic information for this paper has been deposited at The Cambridge Crystallographic Data Centre (CCDC) under the reference numbers CCDC-1985438 (**1**) and CCDC-1985439 (**2**).

Table S1 Crystal data and data collections of **1** and **2**.

	1	2
empirical formula	C ₄₃ H ₄₅ Au ₂ ClSi ₂ Si ₃	C ₄₃ H ₄₅ Au ₂ ClSSeSi ₃
formula weight	1139.56	1186.46
color	red	brown
crystal system	Triclinic	Triclinic
space group	<i>P</i> -1(#2)	<i>P</i> -1(#2)
unit-cell dimensions		
<i>a</i> (Å)	10.5587(1)	10.7306(2)
<i>b</i> (Å)	12.7258(1)	12.7719(3)
<i>c</i> (Å)	16.3375(2)	16.3141(3)
α (°)	96.606(1)	96.455(2)
β (°)	107.201(1)	107.896(2)
κ (°)	93.562(1)	93.832(2)
<i>V</i> (Å ³)	2072.41(4)	2101.99(8)
<i>Z</i>	2	2
<i>D</i> (g/cm ³)	1.826	1.875
independent reflections	9492	9612
parameters	465	465
<i>R</i> 1, <i>wR</i> 2	0.0208, 0.0562	0.0191, 0.0550
goodness-of-fit on <i>F</i> ²	1.068	1.053
CCDC	1985438	1985439

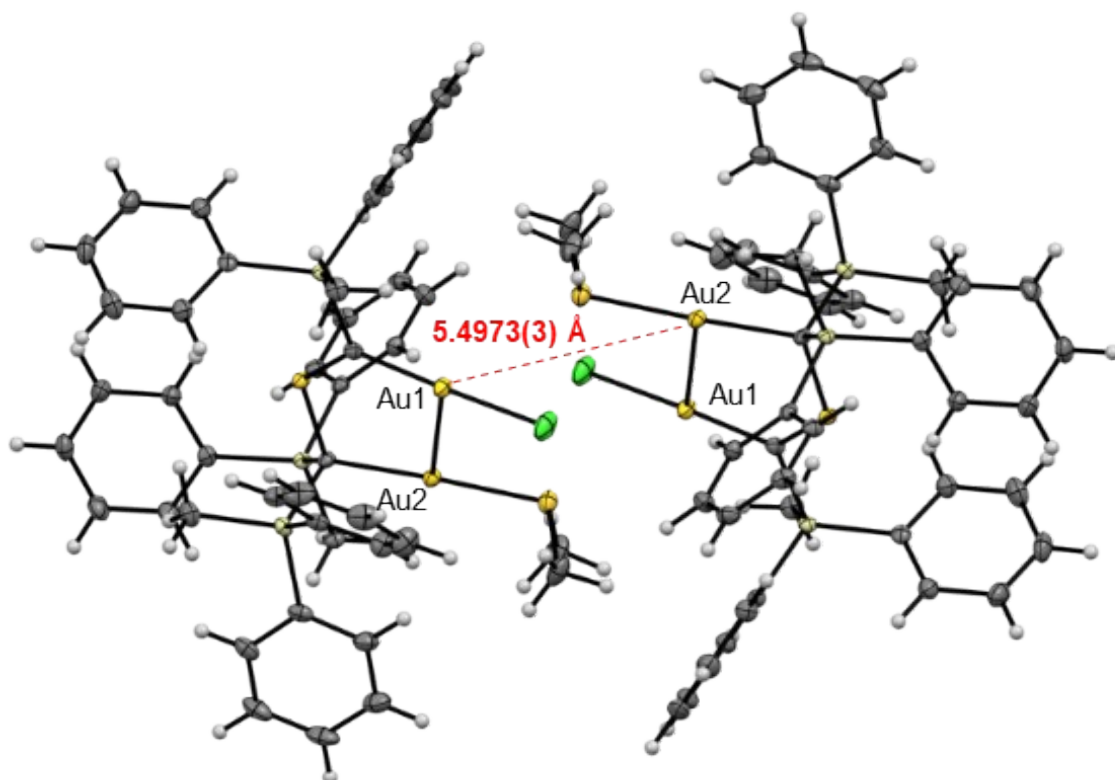


Figure S9. Shortest intermolecular interaction of **1**.

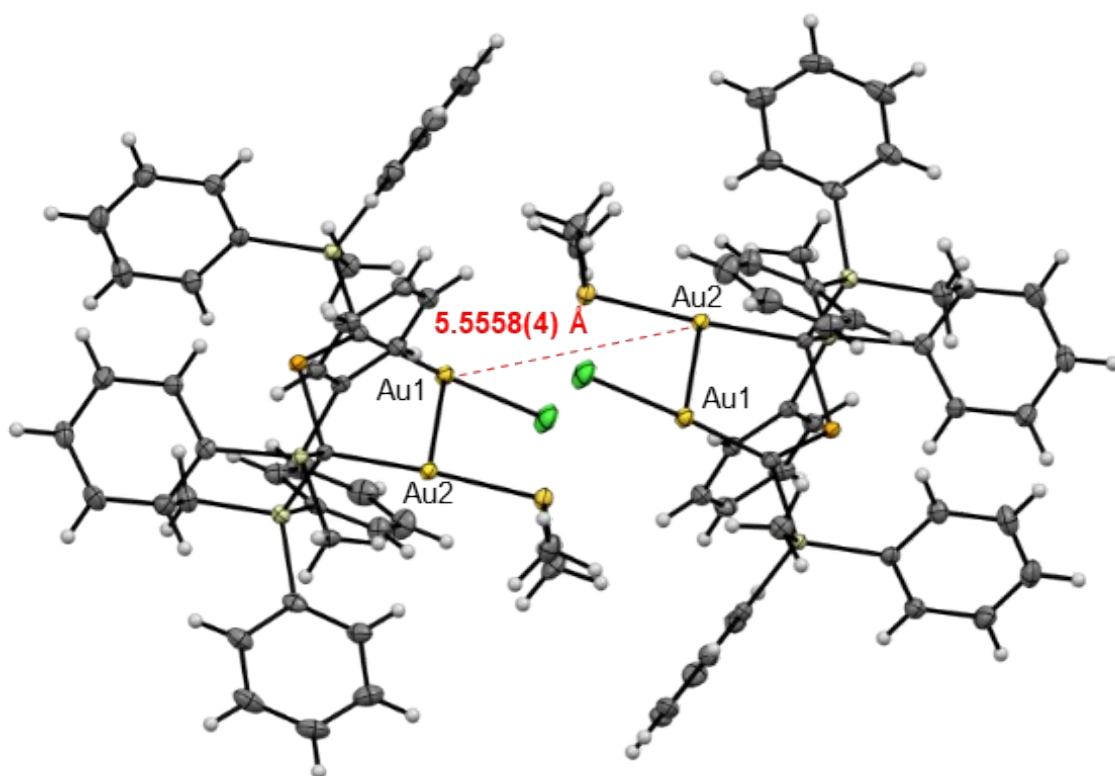


Figure S10. Shortest intermolecular interaction of **2**.

Computational Details

All calculations were performed using the Gaussian 09 suite of programs, revision E 01.^[S3] The geometry optimization and harmonic vibration frequency calculations of **1** and **2** were performed in DFT method at B3PW91/6-311G(2d,p) level of theory. The frequency calculations confirmed minimum energies for the optimized structures. The optimized geometries of **1** and **2** are shown in Figure S11 and S12, respectively, and the selected optimized structural parameters are given in Table S1. Optimized structures are provided as a xyz file.

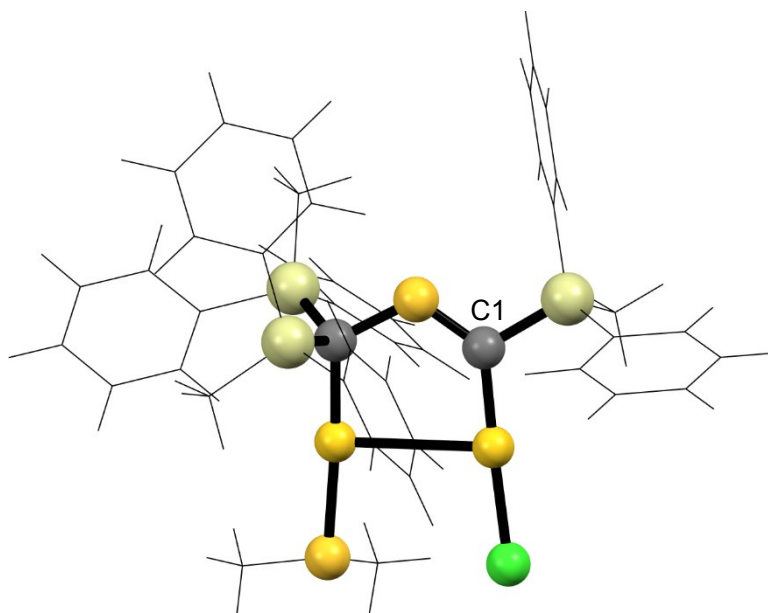


Figure S11. Calculated geometry for **1** at B3PW91/6-311G(2d,p) level. For the comparison of the structural parameters obtained experimentally with those calculated, see Table S2.

Table S2. The bond parameters of the experimental and calculated values for **1**.

	Experimental values (Å, deg)	Calculated values (Å, deg)
C1-S	1.627(3)	1.633
C2-S	1.775(3)	1.800
C1-Si1	1.893(3)	1.913
C2-Si2	1.898(3)	1.921
C2-Si3	1.898(3)	1.929
Au1-C1	1.973(3)	1.981

Au1-Cl	2.2889(7)	2.338
Au2-C2	2.090(3)	2.093
S-C1-Si	114.5(2)	113.81
C1-Au1-Cl	176.29(8)	177.96
C2-Au2-S2	176.05(7)	176.00
Au1-Au2	2.9795(1)	3.153

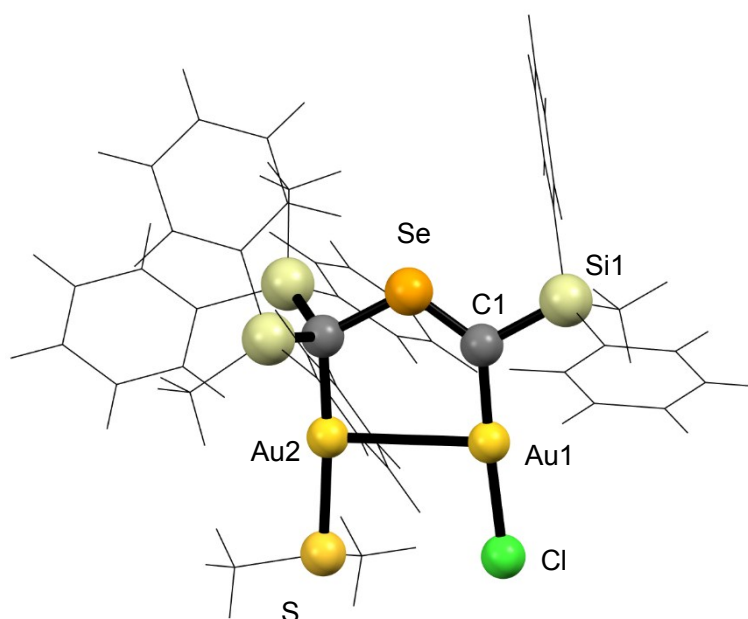


Figure S12. Calculated geometry for **2** at B3PW91/6-311G(2d,p) level. For the comparison of the structural parameters obtained experimentally with those calculated, see Table S3.

Table S3. The bond parameters of the experimental and calculated values for **2**.

	Experimental values (Å, deg)	Calculated values(Å, deg)
C1-Se	1.782(2)	1.783
C2-Se	1.944(2)	1.964
C1-Si1	1.902(2)	1.910
C2-Si2	1.891(2)	1.913
C2-Si3	1.895(2)	1.920
Au1-C1	1.955(2)	1.973
Au1-Cl	2.2933(6)	2.336
Au2-C2	2.083(2)	2.085

Se-C1-Si	113.2(1)	113.93
C1-Au1-Cl	175.52(6)	177.16
C2-Au2-S	174.40(6)	175.00
Au1-Au2	3.0194(1)	3.203

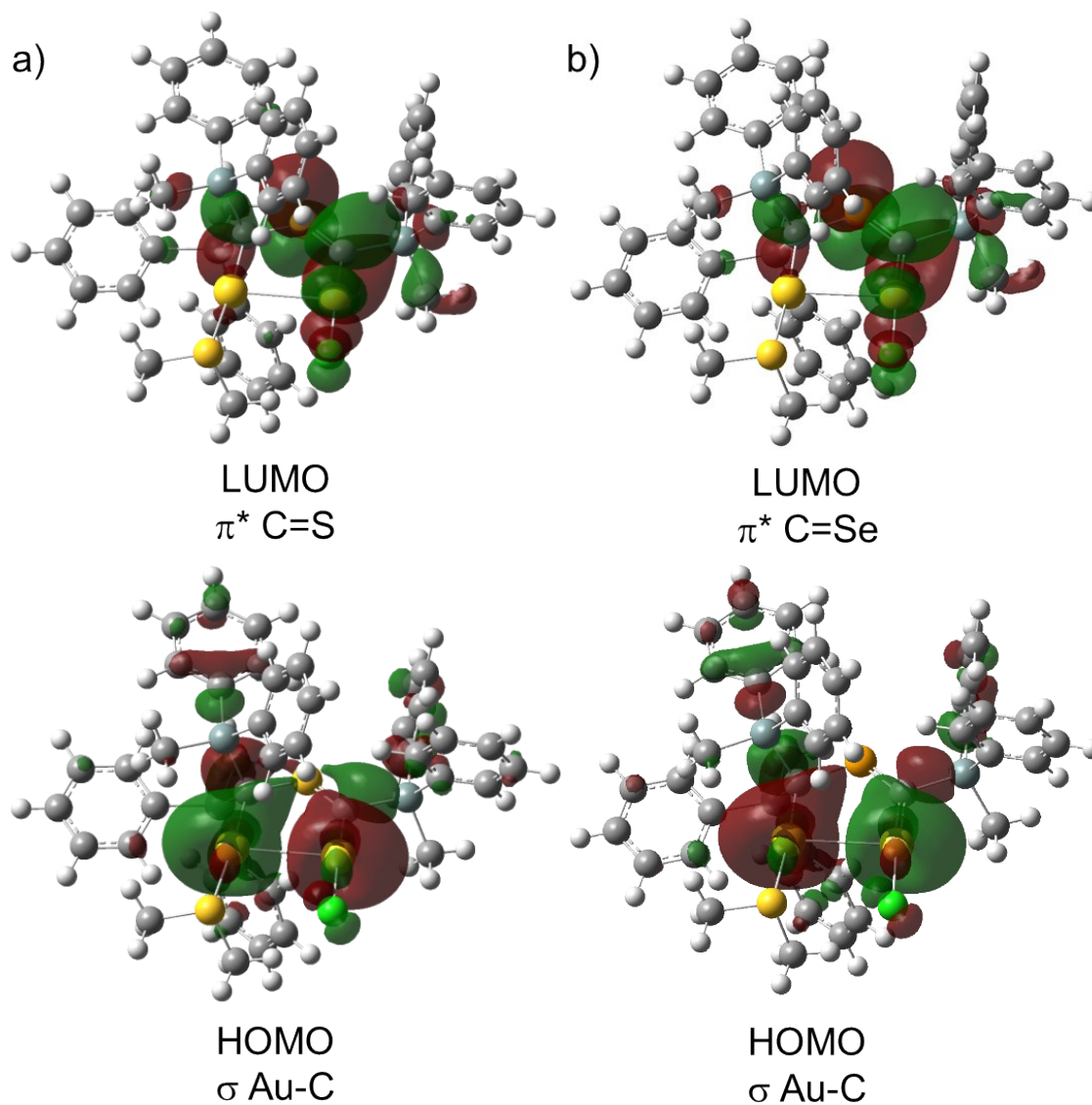


Figure S13. Frontier molecular orbitals of a) **1** and b) **2**.

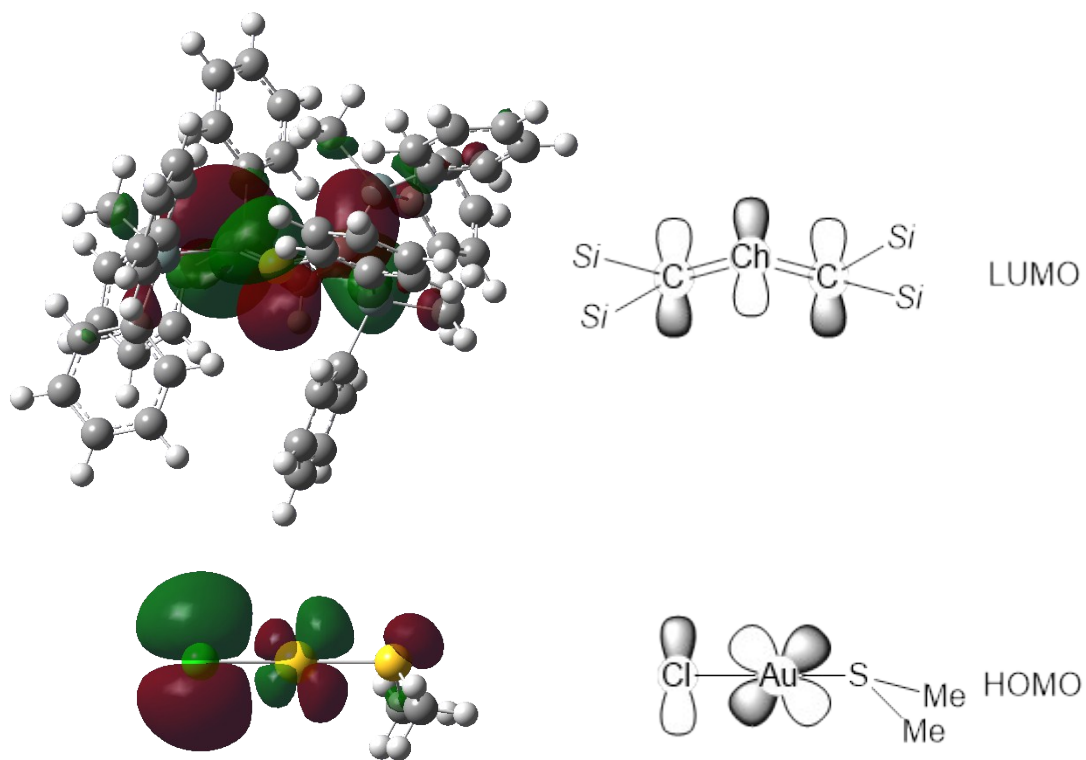
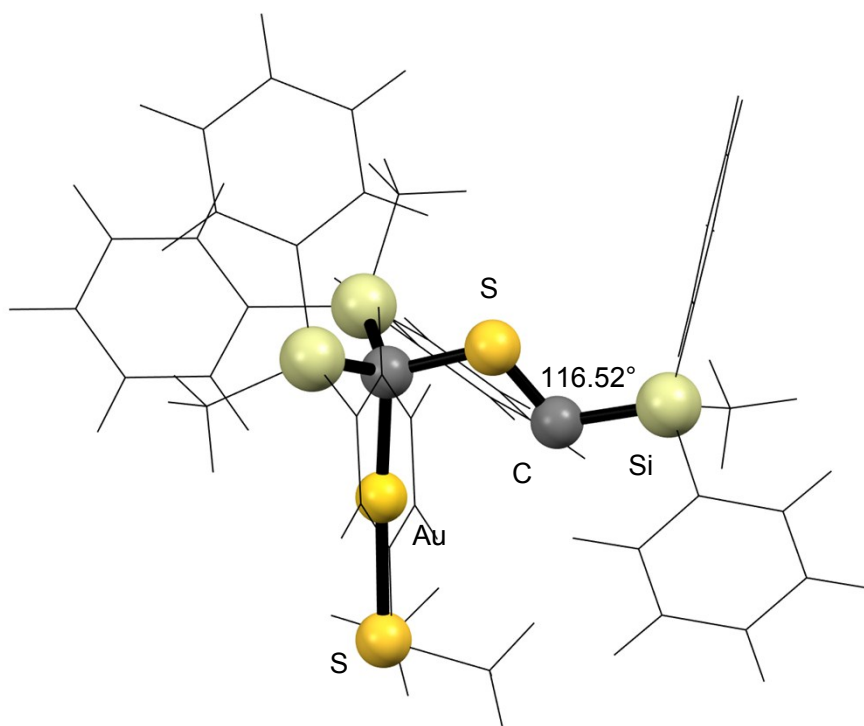


Figure S14. HOMO (AuCl(SMe₂)) – LUMO (C=Ch=C) interactions of C=Ch=C and AuCl(SMe₂)

a)



b)

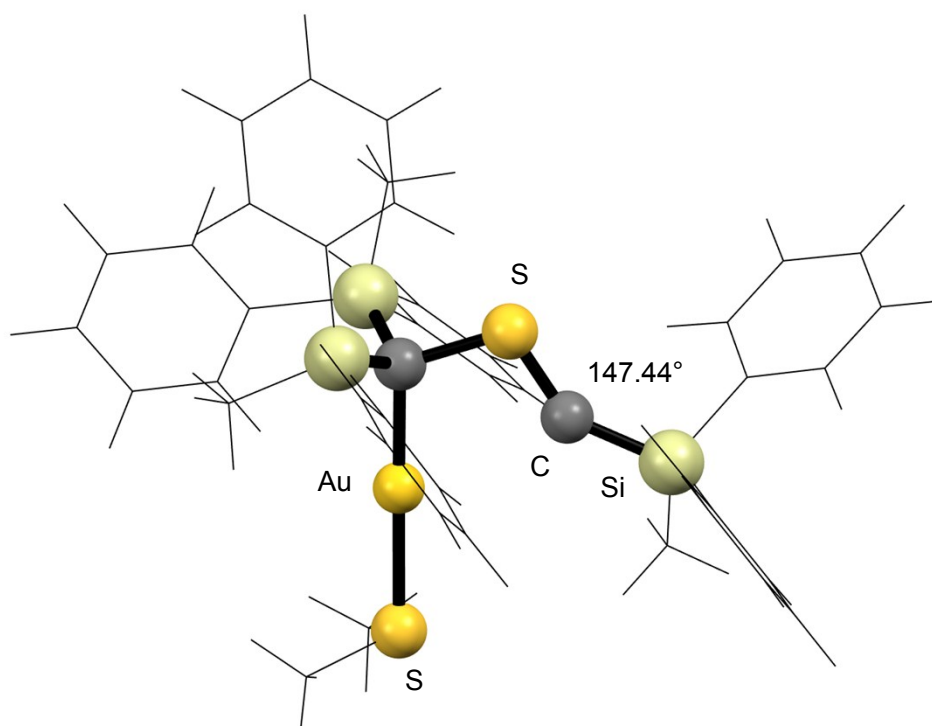
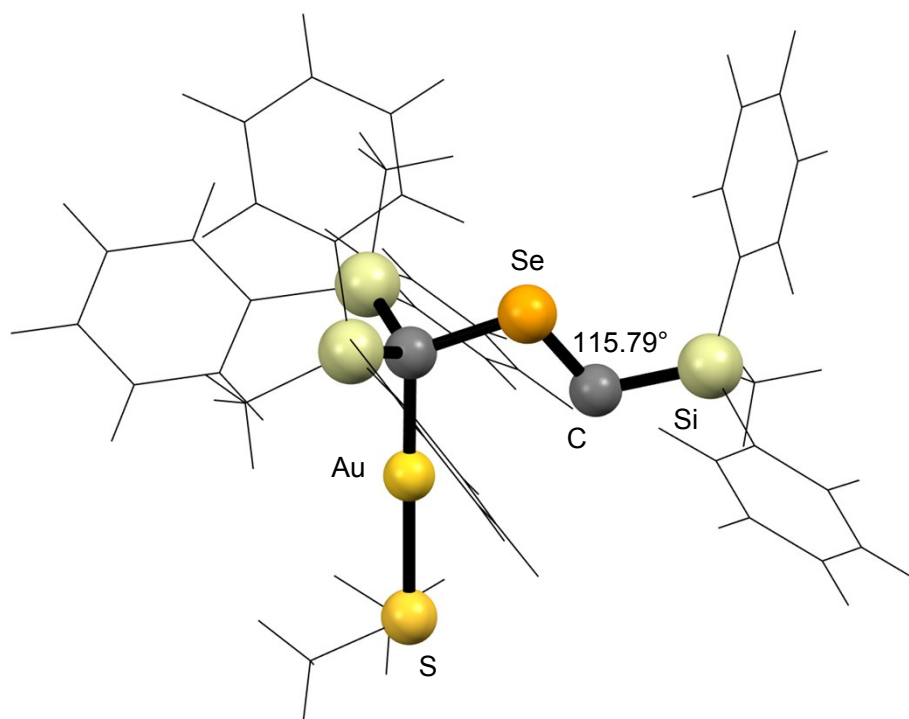


Figure S15. Calculated geometry for 5_s a) Singlet state b) triplet state at B3PW91/6-311G(2d,p) level.

a)



b)

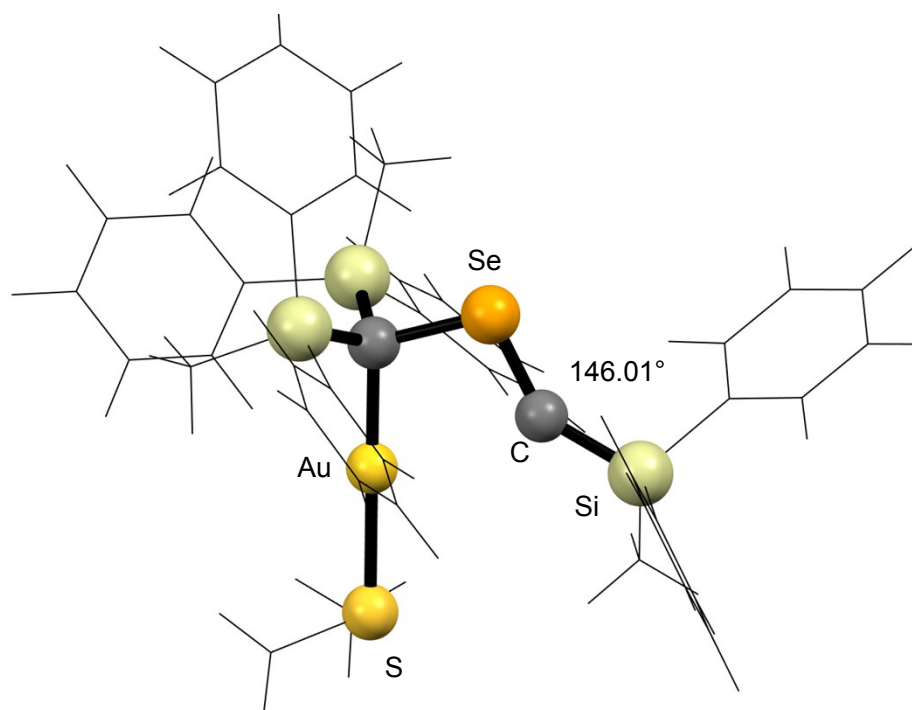


Figure S16. Calculated geometry for $5s$ a) Singlet state b) triplet state at B3PW91/6-311G(2d,p) level.

References

- [S1] Sheldrick, G. M. *Acta Crystallogr. Sect. A*, 2015, 71, 3-8.
- [S2] Sheldrick, G. M. *Acta Crystallogr. Sect. C*, 2015, 71, 3-8.
- [S3] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.