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Supporting Information

Stepwise isolation of an unprecedented silylene supported dinuclear gold(I) cation with aurophilic interaction

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Supporting Information

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1. Experimental Section

All manipulations were carried out in an inert gas atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen filled glove box. The solvents used were purified by a MBRAUN solvent purification system MB SPS-800. Compound **1**[1] and $LiN(PPh_2)(2,6\text{-}i Pr_2C_6H_3)$[2] were prepared by literature methods. All chemicals purchased from Aldrich were used without further purification. ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded in C_6D_6, and CD_2Cl_2 using Bruker 400 MHz spectrometer. NMR spectra were referenced to external $SiMe_4$ (^{1}H, ^{13}C, and ^{29}Si) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded using AB Sciex, 4800 plus MALDI TOF/TOF.

Synthesis of 2: Toluene (30 mL) was added to the mixture of chlorosilylene **1** (0.295 g, 1mmol) and $LiN(PPh_2)(2,6\text{-}i Pr_2C_6H_3)$ (0.367 g, 1mmol) at room temperature and stirred for overnight. The resulting solution was filtered off and solvent was removed to yield pale yellow solid. Single crystals suitable for X-ray analysis were grown in toluene at -30 ˚C. M. P.: 121-123˚C. Yield: 80% (0.486 g). **^{1}H NMR** (C_6D_6, 400 MHz, TMS): δ 0.43 (d, 6H, $(CH_3)_2CH$, J = 6.7 Hz), 1.32 (d, 6H, $(CH_3)_2CH$, J = 6.7 Hz), 1.44 (s, 18H, $(CH_3)_3N$), 3.57-3.63 (sept, 2H, $(CH_3)_2CH$), 6.88-7.57 (m, 18H, Ph) ppm; **^{13}C NMR** (C_6D_6, 100.61 MHz): δ 22.58, 27.44, 28.6, 32.31, 53.81, 124.53, 126.92, 132.04, 135.08, 135.32, 141.38, 144.06, 144.17, 148.72, 166.54 ppm ; **^{31}P NMR** (C_6D_6, 161.97 MHz) : δ 54.09 (s) ppm ; **^{29}Si NMR** (C_6D_6, 79.49 MHz): δ 10.72 ppm (d, $^{2}J_{Si\text{-}P}$ = 10.6 Hz). Elemental analysis ($C_{39}H_{50}N_3PSi$): calculated C, 75.44; H, 8.28; N, 6.77; obtained C, 74.89; H, 7.97; N, 6.54. Mass spectrum could not be obtained due to the decomposition of the compound.

Synthesis of 3: 20 mL of toluene was added to the flask containing mixture of **2** (0.620 g, 1mmol) and $AuCl(SMe_2)$ (0.3 g, 1 mmol). It was left for stirring overnight at ambient temperature. The solvent was removed under vacuum to afford **3** as colorless solid**.** Single crystals suitable for X-ray analysis were grown from the CH_2Cl_2/*n*-pentane mixture (1:1). Yield 78% (0.664 g); M. P.: 128-130 ˚C (decomposition). **^{1}H NMR** (CD_2Cl_2, 400 MHz, TMS): δ 0.91-1.36 (m, 12H, $(CH_3)_2CH$), 1.53 (s, 18H, $(CH_3)_2C$), 3.07-3.10 (m, 2H, $(CH_3)_2CH$), 7.07 (d, 2H, Ph, J = 7.6 Hz), 7.22-7.32 (m, 9H, Ph), 7.38 (t, 2H, Ph, J = 7.1 Hz), 7.55-7.66 (m, 5H, Ph) ppm; **^{13}C NMR** (CD_2Cl_2, 100.61 MHz): δ 21.48, 28.29, 28.77, 34.44, 56.13, 126.98, 127.65, 128.41, 128.48, 130.33, 131.63, 135.72, 137.21, 148.32, 178.28 ppm; **^{31}P{H}NMR** (CD_2Cl_2, 161.97 MHz) : δ 55.74 (s) ppm; **^{29}Si NMR** (CD_2Cl_2, 79.49 MHz): δ 24.73 (d, $^2J_{Si\text{-}P}$ = 18.4 Hz) ppm: Elemental analysis ($C_{39}H_{50}AuClN_3PSi$) (dried overnight to remove the solvent): calculated C, 54.96; H, 5.91; N, 4.93; obtained C, 54.64; H, 5.23; N, 4.35. **MS (Positive ESI)** *m/z* for $C_{39}H_{50}N_3PSi$ (851.2866): 815.32 $[M\text{-}Cl]^+$ (10%), 632.43 $[M\text{-}(Cl+PPh_2)]^+$ (30%).

Synthesis of 4: 25 mL of DCM was added to the flask containing **3** (0.430 g, 0.5 mmol) and $AgSbF_6$ (0.172 g, 0.5 mmol), and stirred overnight under the dark. The solution was filtered through a pad of celite and concentrated to dryness to afford **4** as a beige solid. Single crystals suitable for X-ray analysis were grown in CH_2Cl_2/*n*-pentane (1:1) mixture. Yield: 62% (0.331 g). M. P.: ~140 ˚C. **^{1}H NMR** (CD_2Cl_2, 400 MHz, TMS): δ 0.98 (s, 36H, $(CH_3)_3C$), 1.62-1.66 (m, 24H, $(CH_3)_2CH$), 3.48-3.55 (m, 4H, $(CH_3)_2CH$), 7.28-7.85 (m, 36H, Ph) ; **^{13}C NMR** (CD_2Cl_2, 100.61 MHz): δ 24.66, 27.68, 32.08, 48.40, 57.19, 126.91, 128.03, 128.73, 129.74, 129.86, 132.56, 133.20, 133.60, 134.68, 139.44, 146.59 ppm; **^{31}P{H}NMR** (CD_2Cl_2, 161.97 MHz) : δ 97.10 (s) ppm ; **^{29}Si NMR** (CD_2Cl_2, 79.49 MHz): δ 78.05-78.36 (m) ppm; **^{19}F NMR** (CD_2Cl_2,

376.49 MHz) δ **:** -192.66 to -161.96 (br) ppm ; **MS (Positive ESI) for** $[C_{78}H_{100}Au_2N_6P_2Si_2]^{2+}$ (1632.6354): m/z = 815.41.

2. Crystallographic details

	2	**3**	**4**
Formula	$C_{39}H_{50}N_3PSi$	$C_{40}H_{52}AuCl_3N_3PSi$	$C_{80}H_{104}Au_2Cl_4F_{12}N_6P_2Sb_2Si_2$
Formula weight	619.88	937.22	2275.07
T, K	150(2)	150(2)	150(2)
Color, habit	Pale yellow, block	colorless, block	colorless, plate
Crystal system	triclinic	Triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a, Å	9.8573(12)	11.933(11)	12.058(6)
b, Å	10.9843(13)	12.334(13)	14.762(9)
c, Å	19.208(2)	17.499(16)	15.001(9)
α, deg	93.409(3)	81.27(3)	116.997(14)
β, deg	98.295(3)	82.82(2)	104.713(14)
γ, deg	115.316(3)	65.87(2)	95.716(14)
V, Å^3	1843.2(4)	2318(4)	2228(2)
Z	2	2	2
d_{calcd}, g cm^{-3}	1.117	1.343	1.695
Wavelength	0.71073	0.71073	0.71073
Absorption coefficient	0.137	3.435	4.133
Theta range [°]	2.31° to 25.25°	2.15° to 27.5°	2.31° to 24.25°

Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17
Reflections collected	43905	38188	89255
Independent reflections	6666[*R*(int)= 0.0868]	10080[$R_{(int)}$=0.0812]	7185 [$R_{(int)}$= 0.2448]
Completeness	1.000	0.947	0.999
Absorption correction	multi-scan	multi-scan	multi-scan
Parameters	407	452	494
R1 (*R1* all data)[a]	0.0541(0.1082)	0.0752 (0.0982)	0.0571 (0.0985)
wR2 (*wR2* all data)[b]	0.1205(0.1462)	0.2087 (0.2296)	0.1046 (0.1210)
GOF	0.950	1.047	1.028
max., min. peaks [eÅ^{-3}]	0.343, -0.204	3.306, -1.545	1.321, -1.030,

[a] $R1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$. [b] $wR2 = \{\Sigma[w-(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

A crystal of suitable size, coated with paraffin oil was mounted for **2**, **3** and **4**. Data collection for all the crystals were done on Bruker Smart Apex Duo diffractometer at 150 K using Mo Kα radiation (λ = 0.71073 Å). Collected data were integrated by using SAINT and then absorption correction was done by multi-scan method using SADABS program. All the structures were solved by directs methods and refined by full-matrix least-squares methods against F^2 *(SHELXL-2014/6)*. Crystallographic Information File (CIF) for the structures has been deposited to the Cambridge Crystallographic Data Centre as supplementary publication nos. 1437075 (**2**), 1437076 (**3**), 1437077 (**4**). These CIF can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Luminescence Studies

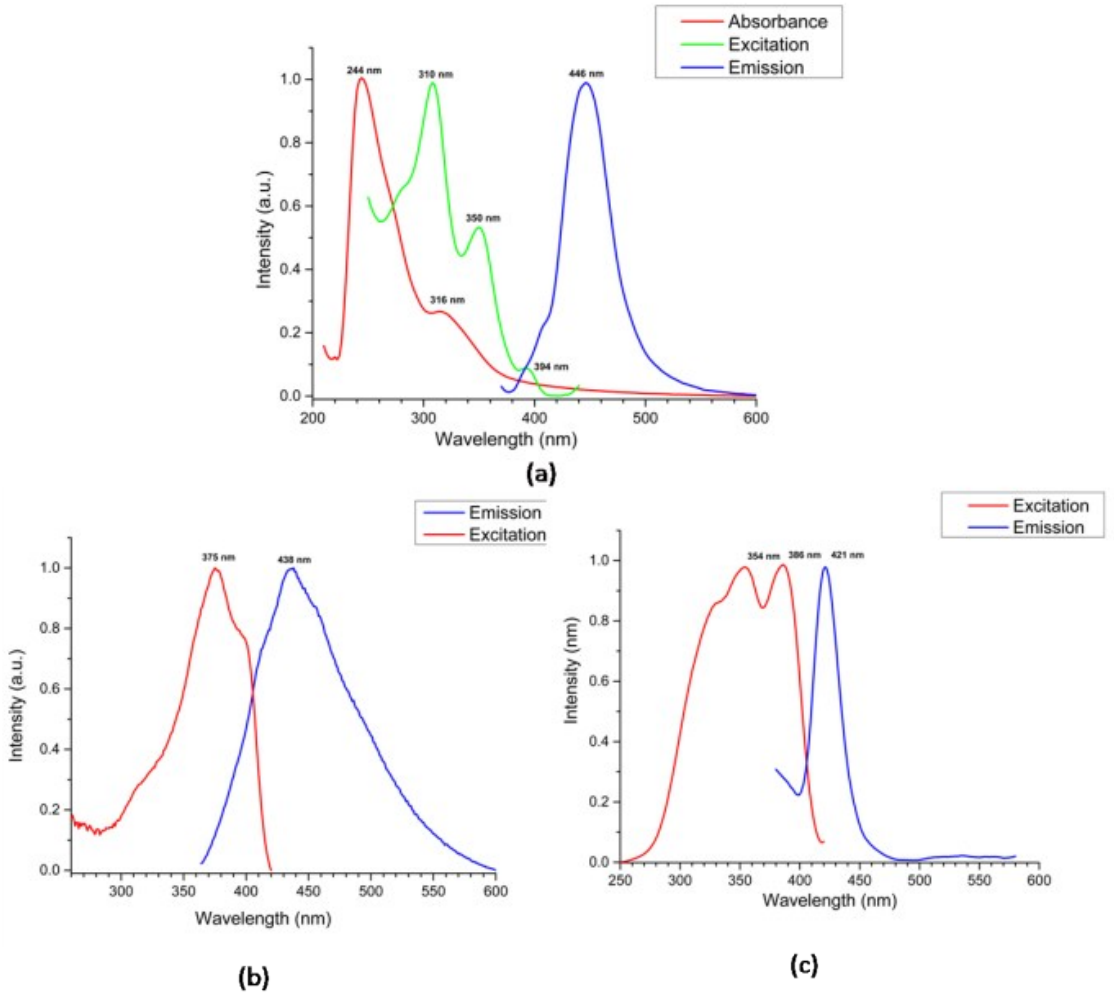


Figure S1. Normalized absorption, excitation and emission (λ_{ex} = 315 nm spectra of **4**. (a) solution state (CH_2Cl_2, 1.56 X 10^{-5} M) spectrum; (b) solid state spectrum at room temperature; (c) solid state spectrum at 77 K.

To get more insight luminescence studies of **4** were performed. A weak greenish blue luminescence was observed under irradiation of UV light at ambient temperature. The absorption spectrum of 4 was recorded in CH_2Cl_2 at room temperature (Figure 5). Two bands were observed in the absorption spectrum of **4**, (a) 244 nm (related to the aromatic systems; ε = 3.1 X 10^4 $Lmol^{-1}cm^{-1}$); (b) 316 nm (presumably due to the charge transfer; ε = 7.1 X 10^3 $Lmol^{-1}cm^{-1}$). The solution state spectrum at ambient temperature shows only one peak around 446 nm while solid state spectrum displays a broad band around 438 nm without any significant shift if compared to the solution state. The low temperature (77 K) solid state emission spectrum reveals a band around 421 nm which is slightly shifted towards higher energy. This emission wavelength range normally corresponds to the fluorescence between two singlet states. We tried several times but could not obtain the life time and quantum yield of **4** due to the weak emission.

4. ^{29}Si NMR and ^{31}P NMR Spectra

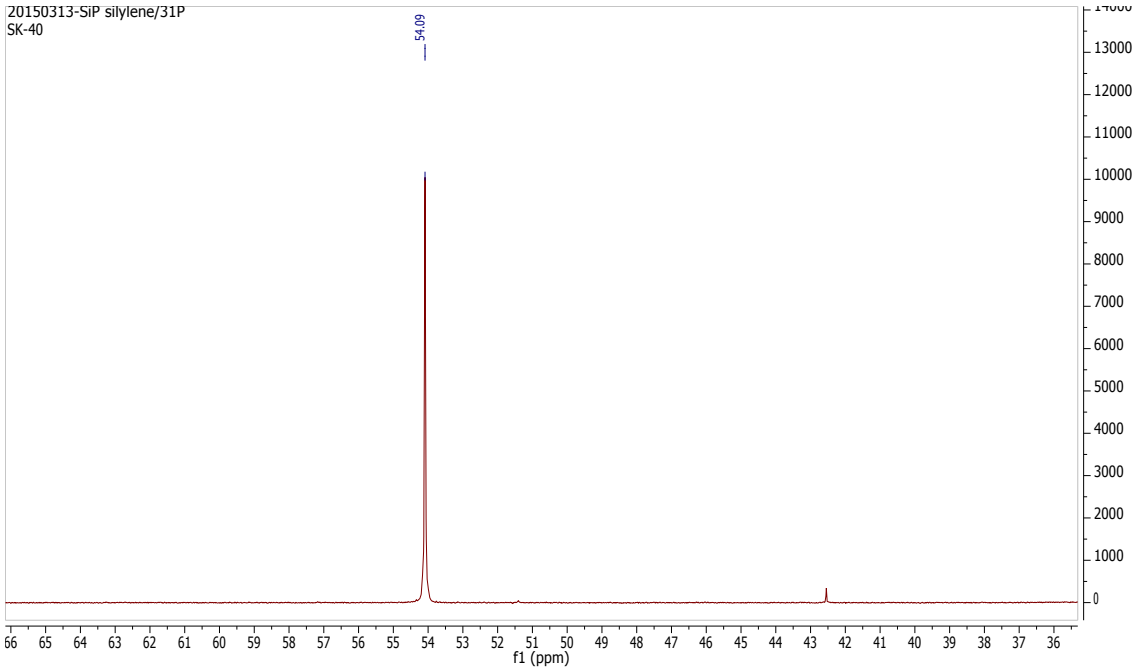


Figure 1. ^{31}P NMR (C_6D_6) of **2**

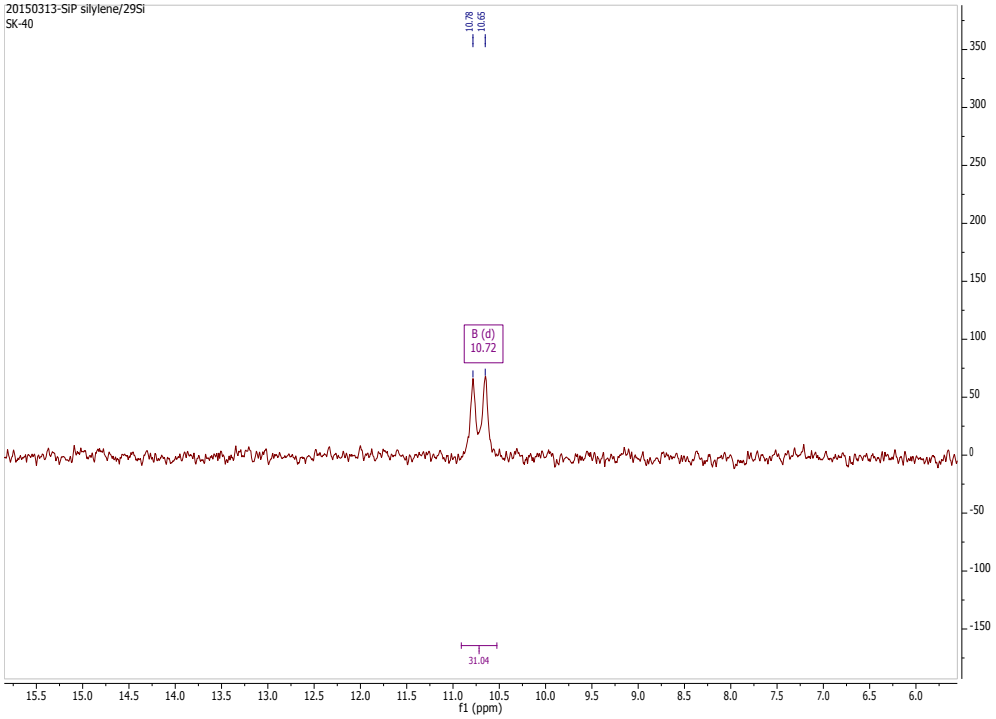


Figure 2. ^{29}Si NMR (C_6D_6) of **2**

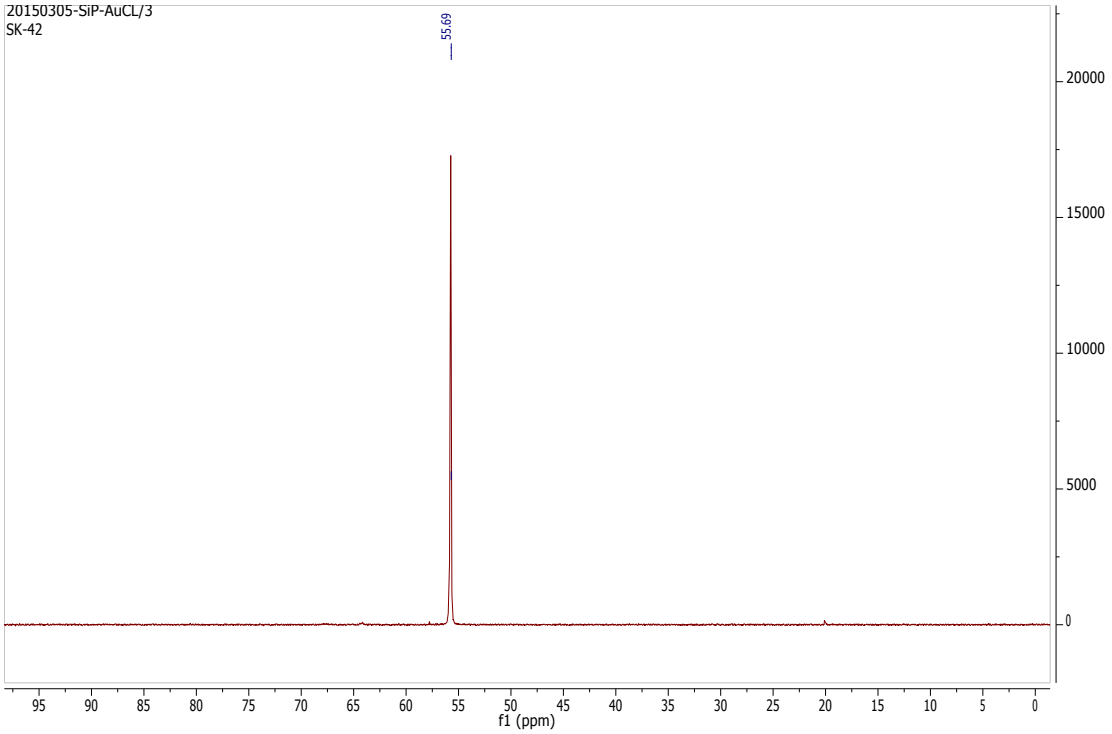


Figure 3. ^{31}P NMR (CD_2Cl_2) of **3**

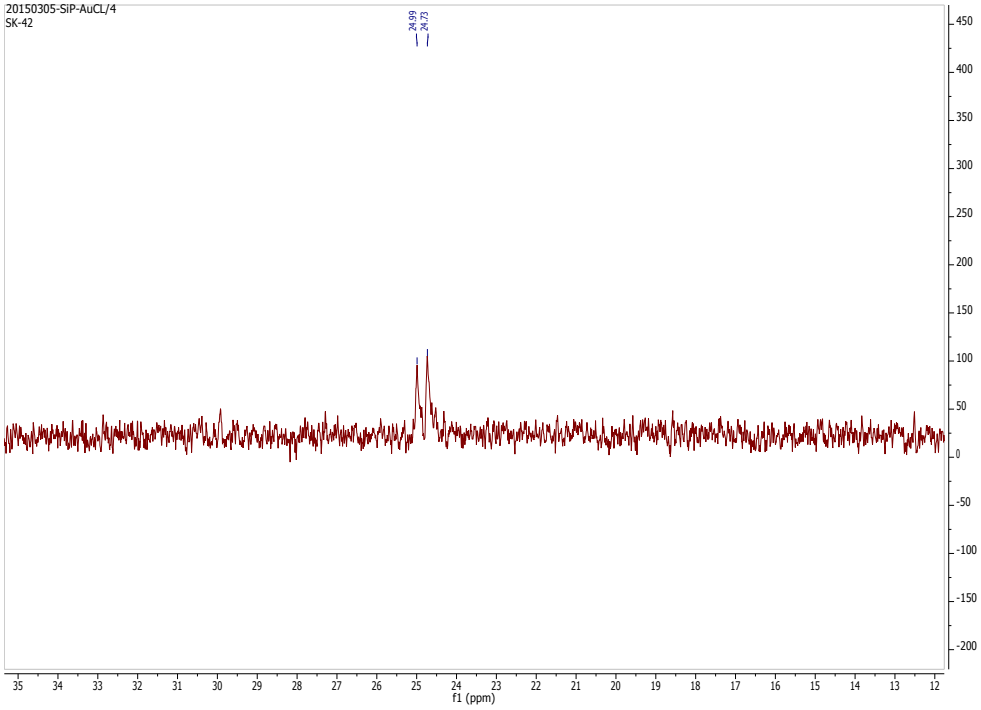


Figure 4. ^{29}Si NMR (CD_2Cl_2) of **3**

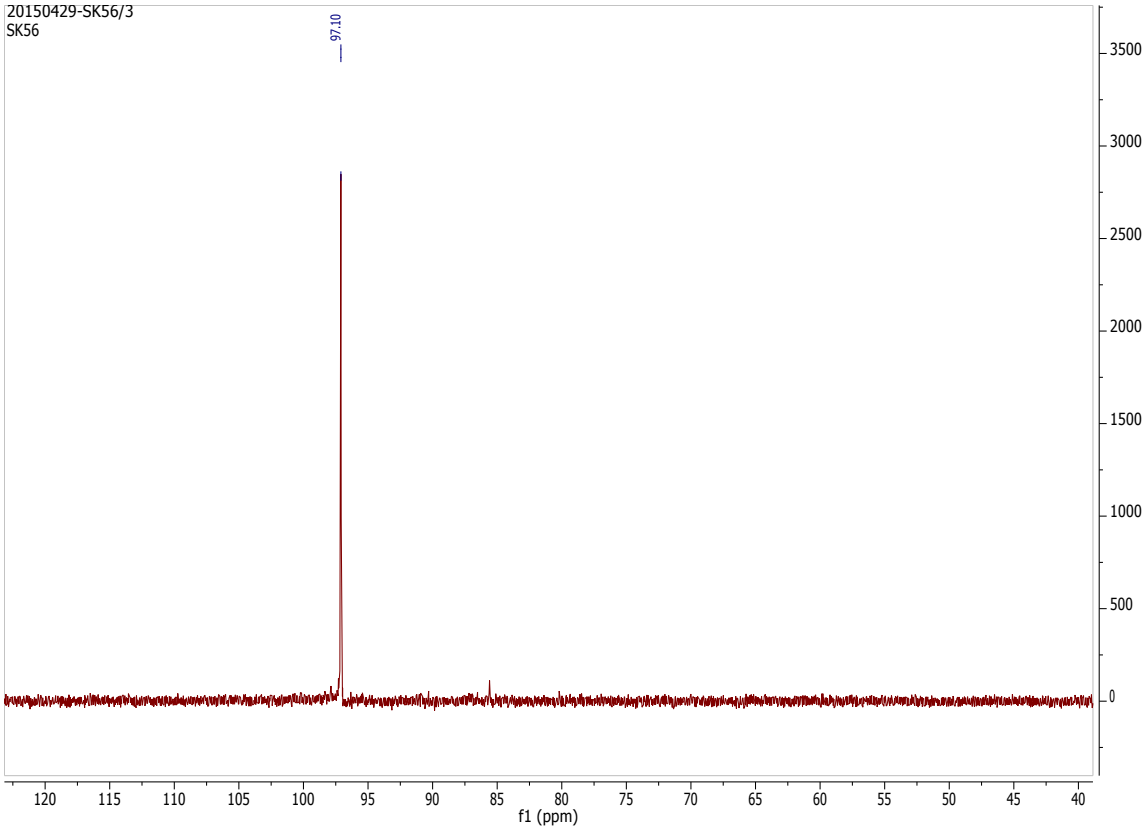


Figure 5. ^{31}P NMR (CD_2Cl_2) of **4**

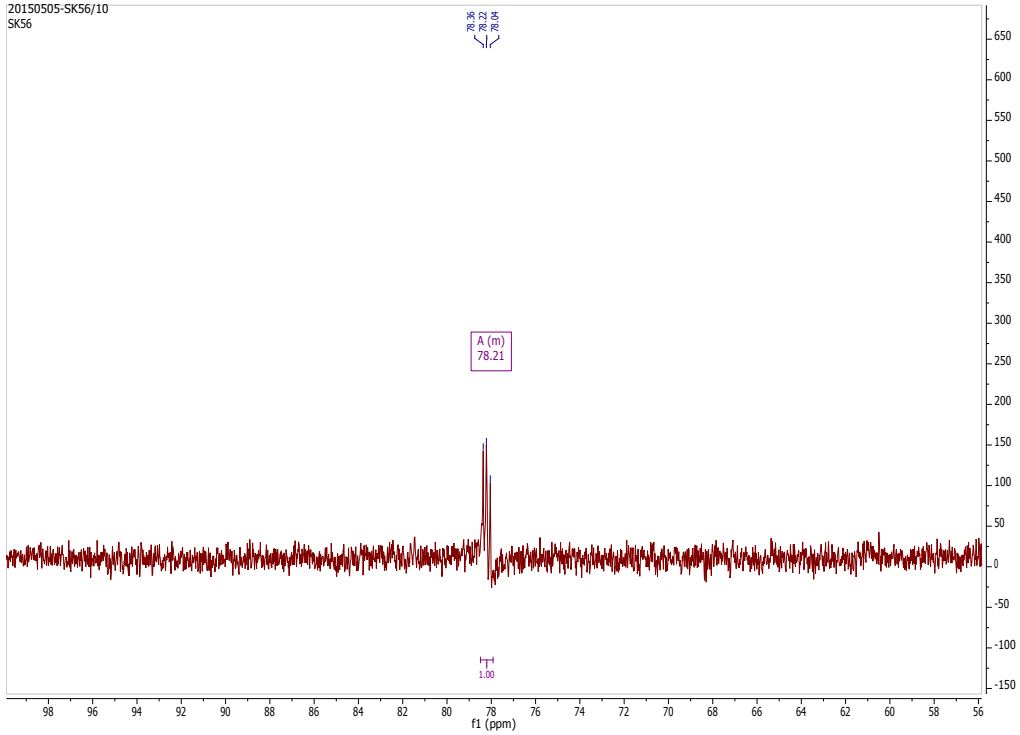


Figure 6. ^{29}Si NMR (CD_2Cl_2) of **4**

4. Computational Data

Computational Methodology

All the geometry optimizations were performed with Gaussian 09 program[3] using BP86[4]/def2-SVP basis set.[5] Meta-GGA exchange correlation functional M06[6] with def2-TZVPP basis set[5] was used for the single point calculations on the optimized geometries and the energies were corrected by adding the zero point energies from the BP86/def2-SVP level of theory. Natural Bond Order (NBO)[7] analysis and the quantitative analysis of electrostatic potential (ESP) on the van der Waals surface of molecules using Multiwfn program[8] were done at the same level of theory. Quantum theory of atoms in molecules (QTAIM)[9] method implemented in AIMALL program package[10] was used for the topological analysis of electron density. Wave function for this analysis was generated at M06/def2-TZVPP//BP86/def2-SVP level of theory using Gaussian 09 program.

The nature of Si–Au bond was studied using EDA-NOCV method at the BP86/TZ2P level of theory using ADF 2013.01 program.[11] Scalar relativistic effects were incorporated using Zeroth Order Regular Approximation (ZORA).[12] The core electrons were treated by the frozen-core approximations. Energy Decomposition Analysis (EDA)[13] gives the instantaneous interaction energy (ΔE_{int}) between two fragents in the frozen geometry of the compound. The interaction energy can be divided into three parts:

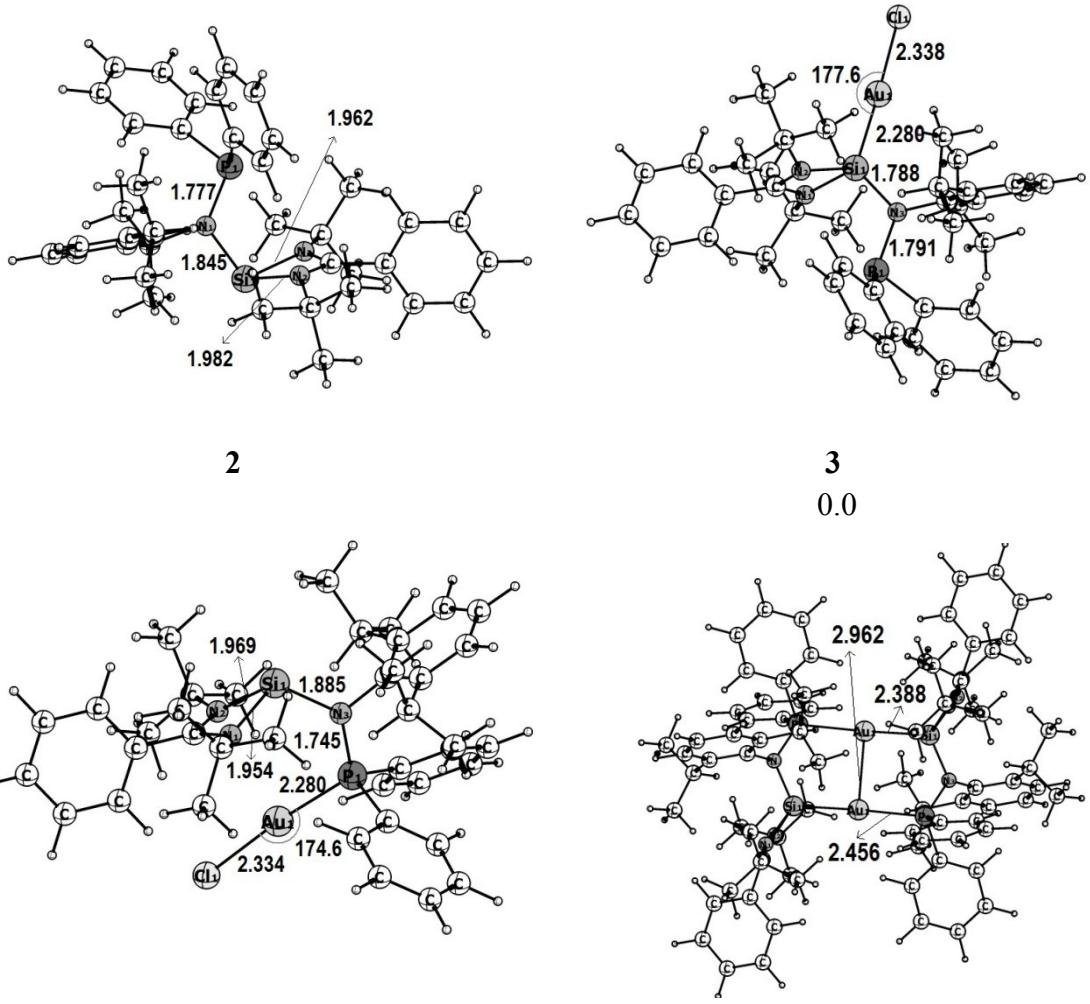
$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

ΔE_{elstat} gives the electrostatic interaction energy between the frozen charge densities of the two fragents. ΔE_{Pauli} is the result of repulsive interaction between two fragents, which are caused by the electrons of same spin. ΔE_{orb} is the lowering in energy due to the overlap of

orbitals of the two fragents. Sum of ΔE_{int} and ΔE_{prep} (energy necessary to promote the fragents from their ground state geometry to the geometry in the compound) gives –De (dissociation energy).

$$-De = \Delta E_{int} + \Delta E_{prep}$$

In the EDA-NOCV analysis method, ΔE_{orb} term is decomposed into the contributions from different natural orbitals of chemical valence (NOCV).[14] It provides the energy contributions for each specific orbital interaction between fragents to the total bond energy.



2 **3**

0.0

3' **4**

14.5

Figure S7: Optimized geometries and important geometrical parameters of **2**, **3**, **3'** and **4** at the M06/def2-TZVPP//BP86/def2-SVP level of theory. Relative energies of **3** and **3'** are in kcal/mol.

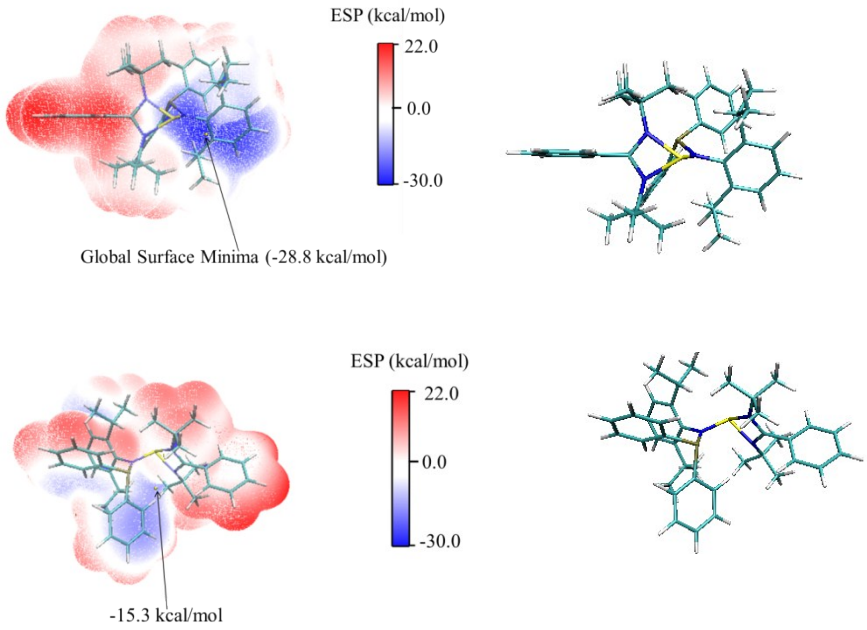


Figure S8: Plot of electrostatic potential on the molecular van der Waals surface of Silylene **2** at the M06/Def2-TZVPP//BP86/Def2-SVP level of theory. The minima at the direction of lone pair on Si- and P-atoms are indicated.

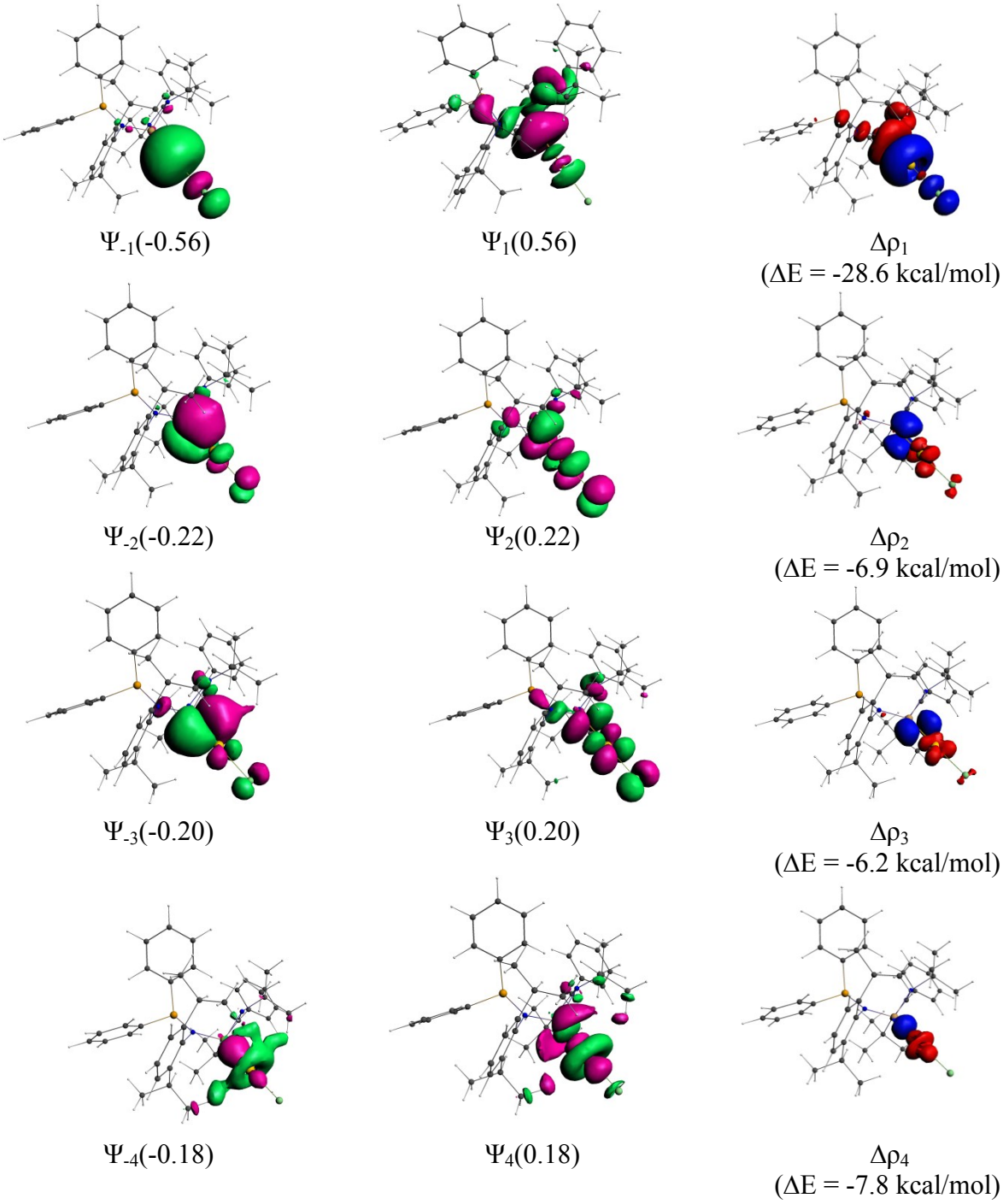
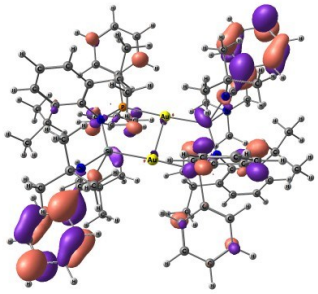
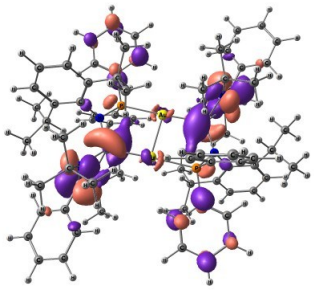


Figure S9: NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots (Δρ) and orbital stabilization energies ΔE for Si–Au bond of **3** at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot Δρ is from red → blue. Isosurface value for NOCV pair orbitals is 0.03 and that for deformation density is 0.001.



LUMO+6
-2.43



LUMO+5
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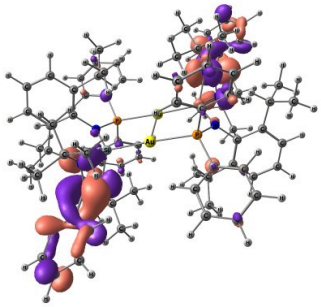
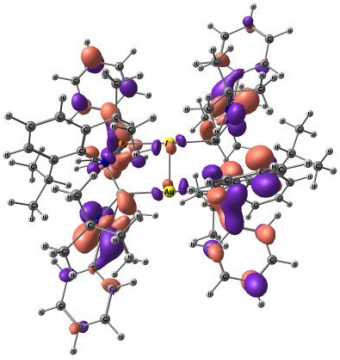
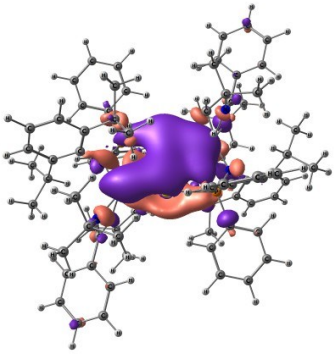


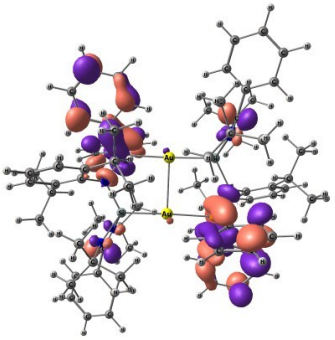
LUMO+4
-2.72



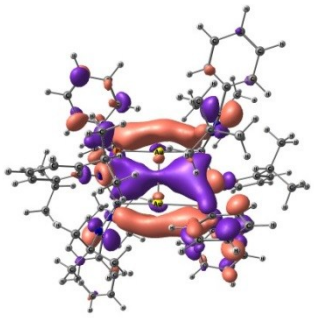
LUMO+3
-2.88



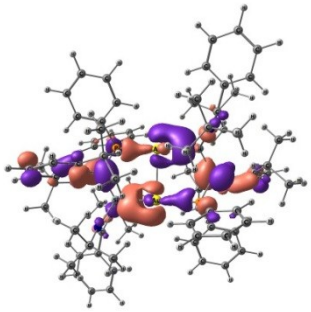
LUMO+2
-2.94



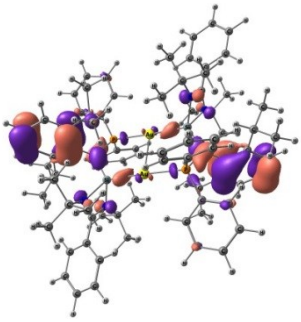
LUMO+1
-3.01



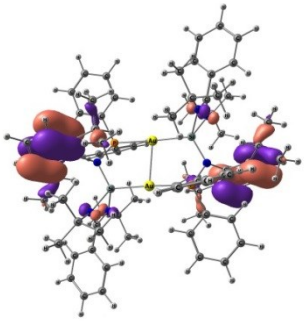
LUMO
-3.27



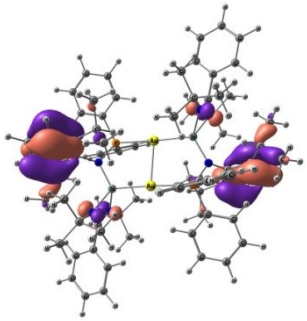
HOMO
-6.22



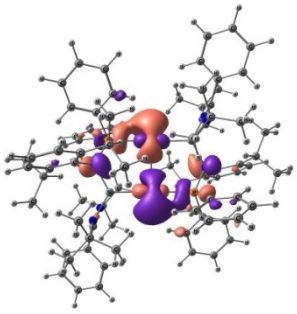
HOMO-1
-6.50



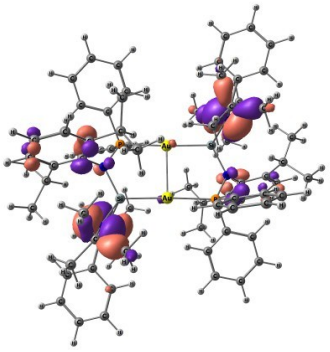
HOMO-2
-6.54



HOMO-3
-6.55



HOMO-4
-6.62



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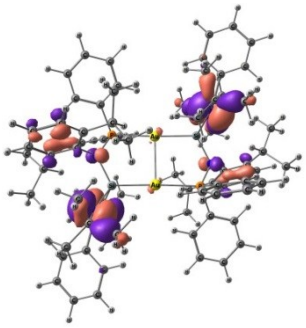

HOMO-6
-6.74

Figure S10: Plot of important molecular orbitals of **4** at the BP86/def2-SVP level of theory including implicit solvent model.

Table S1: EDA-NOCV results for the Si–Au bond of **3** at the BP86/TZ2P level of theory. Energies are in kcal/mol.

ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat} [a]	ΔE_{orb} [a]	ΔE_1 [b]	ΔE_2 [b]	ΔE_3 [b]	ΔE_4 [b]	ΔE_{rest} [b,c]	ΔE_{prep}	ΔE(-De)
-63.7	219.5	-214.6 (75.8%)	-68.5 (24.2%)	-28.6 (41.7%)	-6.9 (10.1%)	-6.2 (9.1%)	-7.8 (11.4%)	-19.0 (27.7%)	1.5	-62.2

[a]Values in parenthesis give the percentage contribution to the total attractive interactions $\Delta E_{Elstat}+\Delta E_{Orb}$. [b]Values in parenthesis give the percentage contribution to orbital interaction ΔE_{Orb}. [c]$\Delta E_{rest} = \Delta E_{Orb} - (\Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4)$.

Table S2: Topological analysis of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), total energy density (H), potential energy density (V) and kinetic energy density (G) of **4** at the selected bond critical points (BCPs) at the M06/def2-TZVPP//BP86/ def2-SVP level of theory.

Atoms	ρ(e Å^{-3})	$\nabla^2\rho$(e Å^{-5})	H(hartree Å^{-3})	V(hartree Å^{-3})	G(hartree Å^{-3})
Au1-Au2	0.2207	2.0098	-0.0216	-0.1842	0.1626
Au1-Si1	0.6344	-1.1471	-0.3057	-0.5311	0.2254
Au1-P1	0.5811	2.4774	-0.1950	-0.5635	0.3685
Au2-Si2	0.6344	-1.1471	-0.3057	-0.5311	0.2254
Au2-P2	0.5811	2.4774	-0.1950	-0.5635	0.3685

Table S3: Charge distribution given by the Natural Bond Orbital Analysis for **2**, **3** and **4** complex at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

2		**3**		**4**	
Atom	Charge	Atom	Charge	Atom	Charge
P	1.03	P	1.03	P1	1.18
Si	1.18	Si	1.47	P2	1.18
N1	-1.20	Au	0.11	Si1	1.57
N2	-0.73	Cl	-0.58	Si2	1.57
N3	-0.71	N1	-1.22	Au1	-0.05
		N2	-0.72	Au2	-0.05
		N3	-0.76	N1	-1.23
				N2	-1.23

Table S4: Theoretical data for absorption for **4** at the TDBP86/def2-SVP level of theory using polarizable continuum model for the solvent CH_2Cl_2.

Wavelength(λ) nm	Transition	%	Oscillator Frequency(f)
410	HOMO→LUMO	100	0.0398
367.8	HOMO-4→LUMO HOMO→LUMO+3	10.3 89.7	0.0407
357.3	HOMO-4→LUMO HOMO→LUMO+3	89.6 10.4	0.1143
352.8	HOMO-1→LUMO+1	100	0.0381
349.3	HOMO-3→LUMO+1	100	0.0115
331.2	HOMO-6→LUMO+1 HOMO-5→LUMO+3 HOMO→LUMO+5	61.8 4.6 33.6	0.0145
329.1	HOMO-4→LUMO+3 HOMO→LUMO+5 HOMO→LUMO+6	84.8 2.6 12.6	0.0456
324.4	HOMO-6→LUMO+2 HOMO-5→LUMO+3 HOMO-4→LUMO+3 HOMO-3→LUMO+4 HOMO→LUMO+6	44.6 10.9 3.3 12.9 28.3	0.0385
323.0	HOMO-9→LUMO HOMO-8→LUMO+1 HOMO-4→LUMO+3 HOMO-3→LUMO+4 HOMO-9→LUMO+1	58.5 2.3 5.0 18.6 15.6	0.0295
312.5	HOMO-9→LUMO+8	100	0.0216
308.2	HOMO-18→LUMO HOMO-7→LUMO+3 HOMO-6→LUMO+4 HOMO-2→LUMO+5	10.3 69.9 9.8 10.0	0.0239

Table S5. Optimized Cartesian coordinates and total energies (in a.u.) including zero point energy correction of all the calculated molecules at the BP86/def2-SVP level of theory (E1) and total energy at M06/def2-TZVPP level of theory including zero point energy correction from the BP86/def2-SVP level of theory (E2) using G09 program package. Symmetry of the structures is mentioned in the parenthesis. The number of imaginary frequencies is abbreviated as Nimag.

2 (C1)
E1 = -2309.239689 a.u.
E2 = -2309.9420349 a.u.
Nimag = nil

15	0.814883000	-0.167363000	1.194221000
14	-0.660425000	-0.610600000	-1.539109000
7	0.831541000	-0.098931000	-0.581470000
7	-2.150554000	0.569285000	-0.977431000
7	-1.830575000	-1.449439000	-0.206972000
6	4.940267000	-1.824236000	2.704797000
1	5.890361000	-2.231603000	3.086442000
6	3.719658000	-2.412352000	3.076842000
1	3.706285000	-3.281588000	3.753882000
6	2.510732000	-1.890694000	2.581530000
1	1.554428000	-2.353405000	2.876750000
6	2.498251000	-0.771911000	1.715741000
6	-2.731307000	-0.454852000	-0.305308000
6	-4.138896000	-0.461777000	0.219393000
6	-5.212482000	-1.027151000	-0.504076000
1	-5.024790000	-1.501976000	-1.479176000
6	-6.519311000	-0.986178000	0.012104000
1	-7.347139000	-1.427568000	-0.565221000
6	-6.769163000	-0.387066000	1.259021000
1	-7.793518000	-0.357337000	1.662848000
6	0.487091000	4.105635000	3.112388000
1	0.355099000	5.088673000	3.592061000
6	-0.395131000	3.684762000	2.099248000
1	-1.224643000	4.338903000	1.783715000
6	-0.232570000	2.426629000	1.497947000
1	-0.947525000	2.085781000	0.729592000
6	0.834676000	1.572606000	1.869609000
6	-5.705597000	0.174041000	1.988101000
1	-5.892914000	0.644360000	2.966380000
6	-4.399845000	0.140639000	1.471791000
1	-3.568664000	0.586844000	2.039885000
6	-1.969823000	-2.774994000	0.455631000
6	-0.626178000	-3.509816000	0.303884000
1	-0.366793000	-3.650254000	-0.764929000
1	-0.688409000	-4.511468000	0.775269000
1	0.187708000	-2.944236000	0.798452000
6	-3.062284000	-3.635624000	-0.224858000
1	-4.077580000	-3.229550000	-0.056198000
1	-3.042693000	-4.665132000	0.190046000
1	-2.882419000	-3.703326000	-1.317830000
6	-2.271843000	-2.604241000	1.961676000
1	-1.509477000	-1.946442000	2.426587000
1	-2.243887000	-3.592991000	2.465635000
1	-3.274101000	-2.167555000	2.137190000
6	-2.832657000	1.647172000	-1.750509000
6	-3.764406000	2.509313000	-0.868910000
1	-4.671360000	1.964323000	-0.545782000
1	-4.095456000	3.397676000	-1.446260000
1	-3.234050000	2.869842000	0.036264000
6	-1.716342000	2.546038000	-2.309239000
1	-1.157704000	3.043075000	-1.492441000
1	-2.143056000	3.330772000	-2.966326000
1	-0.998809000	1.948290000	-2.907877000
6	-3.625669000	1.052775000	-2.940665000
1	-2.962661000	0.426526000	-3.572781000
1	-4.042676000	1.865245000	-3.572519000
1	-4.474415000	0.430363000	-2.594935000
6	2.059369000	0.064854000	-1.352716000
6	2.554508000	1.362072000	-1.710148000
6	3.766444000	1.466023000	-2.427177000
1	4.143590000	2.467747000	-2.689569000
6	4.489825000	0.337880000	-2.826108000
1	5.430325000	0.445523000	-3.390094000
6	3.991384000	-0.928815000	-2.506168000
1	4.546214000	-1.825176000	-2.826628000
6	2.797477000	-1.093364000	-1.774109000
6	2.342581000	-2.523378000	-1.490546000
1	1.509780000	-2.454461000	-0.767137000
6	1.797807000	-3.195635000	-2.770826000
1	0.948966000	-2.619875000	-3.195002000
1	1.445361000	-4.227634000	-2.555069000
1	2.585919000	-3.268072000	-3.551213000
6	3.443084000	-3.389493000	-0.843951000
1	4.282571000	-3.584879000	-1.545275000
1	3.030400000	-4.378163000	-0.550297000
1	3.862906000	-2.910505000	0.063036000
6	1.837163000	2.670062000	-1.378741000
1	0.877571000	2.400425000	-0.895278000
6	2.639232000	3.541579000	-0.389736000
1	2.841868000	3.008119000	0.559503000
1	2.076778000	4.465000000	-0.136862000
1	3.614162000	3.850770000	-0.824758000
6	1.526818000	3.479941000	-2.657612000
1	2.454896000	3.871151000	-3.126176000
1	0.886294000	4.356088000	-2.421714000
1	1.005428000	2.867311000	-3.419920000

6	4.944535000	-0.711385000	1.843378000
1	5.898261000	-0.245342000	1.548121000
6	3.735923000	-0.185431000	1.356181000
1	3.758032000	0.690789000	0.691793000
6	1.706134000	2.001760000	2.897889000
1	2.532872000	1.352512000	3.224996000
6	1.531244000	3.255371000	3.513209000
1	2.224298000	3.570293000	4.310414000

3 (C1)
E1 = -2905.338977 a.u.
E2 = -2906.032672 a.u.
Nimag = nil

6	2.368203000	1.120731000	-0.440579000
6	-1.726038000	2.782238000	0.939375000
6	-2.088370000	-0.883739000	0.400464000
6	1.710881000	0.633816000	-2.874385000
6	-2.715354000	-1.706685000	-0.594530000
6	-2.266063000	-1.765845000	-2.051977000
1	-1.556407000	-0.932683000	-2.199339000
6	-3.054945000	1.665098000	-1.345701000
6	4.811092000	1.629522000	-0.982275000
1	5.024082000	0.553943000	-1.073260000
6	3.507315000	2.067095000	-0.663735000
6	-3.784856000	-2.544901000	-0.217949000
1	-4.259122000	-3.176956000	-0.985279000
6	-2.537076000	-0.968718000	1.756581000
6	-1.870016000	-0.247414000	2.925403000
1	-1.039292000	0.355013000	2.508442000
6	-1.274631000	-1.273929000	3.915924000
1	-0.611470000	-2.000724000	3.404074000
1	-2.075284000	-1.856008000	4.419616000
1	-0.688843000	-0.764643000	4.709940000
6	3.251531000	3.452410000	-0.539839000
1	2.235208000	3.795077000	-0.291217000
6	3.199452000	2.001896000	2.526762000
1	2.373884000	2.739056000	2.599144000
1	3.982521000	2.420091000	1.867057000
1	3.641591000	1.887094000	3.537768000
6	-4.246553000	1.227420000	-0.717236000
1	-4.215490000	0.820595000	0.304463000
6	2.685758000	0.626370000	2.045698000
6	-0.668099000	2.963717000	1.862905000
1	0.260288000	2.383724000	1.732322000
6	-3.133991000	2.190890000	-2.656276000
1	-2.214391000	2.541779000	-3.153389000
6	-2.827191000	0.715234000	3.657620000
1	-3.679541000	0.169527000	4.115757000
1	-3.241614000	1.483475000	2.974805000
1	-2.295750000	1.244938000	4.476027000
6	-4.257528000	-2.592190000	1.096753000
1	-5.101832000	-3.246804000	1.365698000
6	-5.477764000	1.315657000	-1.388645000
1	-6.395457000	0.967619000	-0.888335000
6	-0.780407000	3.873359000	2.925774000
1	0.051463000	3.985838000	3.640171000
6	2.957292000	-0.156139000	-3.339941000
1	2.938445000	-1.186678000	-2.929391000
1	3.897824000	0.335585000	-3.025893000
1	2.969670000	-0.223843000	-4.447432000
6	-3.624895000	-1.812563000	2.069157000
1	-3.969384000	-1.869794000	3.113986000
6	-2.884354000	3.580074000	1.088815000
1	-3.715953000	3.486965000	0.374960000
6	5.842871000	2.565067000	-1.172986000
1	6.857532000	2.212745000	-1.416117000
6	-1.944931000	4.650180000	3.071602000
1	-2.032211000	5.371303000	3.899792000
6	-1.519848000	-3.087462000	-2.341504000
1	-1.151513000	-3.111472000	-3.389594000
1	-2.190193000	-3.962311000	-2.203065000
1	-0.650906000	-3.227061000	-1.663037000
6	1.761339000	2.095269000	-3.371051000
1	2.695983000	2.610761000	-3.080451000
1	0.899900000	2.669186000	-2.972688000
1	1.705406000	2.106085000	-4.479109000
6	-3.418017000	-1.571496000	-3.059530000
1	-4.133779000	-2.420837000	-3.038121000
1	-3.014419000	-1.518091000	-4.092922000
1	-3.988196000	-0.642150000	-2.865904000
6	-2.989584000	4.505212000	2.144311000
1	-3.902885000	5.114168000	2.241941000
6	0.465041000	-0.043966000	-3.465414000
1	-0.457718000	0.493630000	-3.170755000
1	0.391805000	-1.098538000	-3.133146000
1	0.527768000	-0.041186000	-4.571997000
6	-4.367832000	2.283974000	-3.325315000
1	-4.409837000	2.700687000	-4.344239000
6	-5.542219000	1.845252000	-2.691065000
1	-6.510879000	1.914368000	-3.211463000
6	5.582240000	3.940987000	-1.054218000
1	6.392273000	4.671474000	-1.206687000
6	4.284172000	4.382079000	-0.739061000
1	4.072942000	5.458856000	-0.644949000
79	1.230547000	-2.675065000	0.202769000
14	0.671119000	-0.482841000	-0.080871000
15	-1.377136000	1.718829000	-0.555247000
7	-1.030932000	0.055592000	0.013265000
7	1.595622000	0.560459000	-1.387919000
7	1.894432000	0.735348000	0.772108000
17	1.890894000	-4.893964000	0.532738000
6	1.741158000	0.048992000	3.111426000
1	1.340024000	-0.933779000	2.791008000
1	0.893836000	0.732247000	3.315273000
1	2.294145000	-0.106474000	4.059261000
6	3.870271000	-0.350750000	1.856900000
1	4.614369000	0.042331000	1.136476000

1	3.509583000	-1.337088000	1.496198000
1	4.392634000	-0.506459000	2.823494000

3' (C1)
E1 = -2905.314283 a.u.
E2 = -2906.0095589 a.u.
Nimag = nil

6	2.645168000	0.413031000	0.874667000
6	-1.843579000	1.028939000	-1.949690000
6	-2.338970000	0.655355000	1.632769000
6	2.282292000	-1.962713000	1.766618000
6	-2.873087000	-0.368922000	2.484799000
6	-2.136396000	-1.670923000	2.780258000
1	-1.358678000	-1.774691000	1.999524000
6	-2.629407000	-1.503267000	-0.744267000
6	4.987404000	0.565624000	1.821069000
1	4.552788000	0.768590000	2.812209000
6	4.137483000	0.371057000	0.708306000
6	-4.105716000	-0.156085000	3.135331000
1	-4.509396000	-0.949838000	3.783103000
6	-3.042806000	1.898122000	1.523816000
6	-2.483061000	3.133621000	0.822107000
1	-1.560613000	2.820218000	0.297344000
6	-2.103226000	4.195337000	1.880316000
1	-1.418095000	3.781098000	2.648115000
1	-3.006014000	4.567182000	2.410203000
1	-1.609914000	5.069818000	1.406203000
6	4.704710000	0.111664000	-0.559028000
1	4.052254000	-0.100999000	-1.421743000
6	2.936894000	3.069488000	-0.889739000
1	2.262340000	2.679243000	-1.679014000
1	3.897949000	2.526497000	-0.965566000
1	3.135697000	4.141335000	-1.098974000
6	-3.972657000	-1.179556000	-0.430450000
1	-4.241416000	-0.162794000	-0.108318000
6	2.297489000	2.917956000	0.509044000
6	-0.934086000	2.070554000	-2.248383000
1	0.025826000	2.115461000	-1.709864000
6	-2.322210000	-2.821141000	-1.153562000
1	-1.281401000	-3.076968000	-1.413432000
6	-3.441074000	3.740284000	-0.220859000
1	-4.370300000	4.127078000	0.249384000
1	-3.731730000	3.001301000	-0.992857000
1	-2.957108000	4.595266000	-0.737609000
6	-4.828088000	1.029989000	2.971443000
1	-5.798243000	1.169743000	3.474717000
6	-4.978815000	-2.155081000	-0.535189000
1	-6.018924000	-1.888326000	-0.289757000
6	-1.225718000	3.018687000	-3.239711000
1	-0.504156000	3.822516000	-3.455737000
6	2.672731000	-1.909339000	3.263236000
1	1.845395000	-1.495294000	3.875270000
1	3.572081000	-1.280740000	3.420627000
1	2.903883000	-2.929280000	3.636337000
6	-4.284302000	2.046855000	2.181381000
1	-4.826301000	3.001078000	2.083433000
6	-3.035782000	0.934619000	-2.700603000
1	-3.741830000	0.110789000	-2.523480000
6	6.382694000	0.507331000	1.668538000
1	7.034359000	0.660365000	2.543441000
6	-2.424647000	2.927118000	-3.970995000
1	-2.650681000	3.662917000	-4.758953000
6	-1.434309000	-1.577554000	4.155212000
1	-0.859532000	-2.503644000	4.371160000
1	-2.180265000	-1.447912000	4.968292000
1	-0.736495000	-0.714811000	4.196431000
6	3.444169000	-2.557875000	0.938083000
1	4.416308000	-2.078741000	1.153029000
1	3.246468000	-2.491921000	-0.151606000
1	3.541928000	-3.630974000	1.203147000
6	-3.020469000	-2.931407000	2.714627000
1	-3.771959000	-2.956809000	3.532465000
1	-2.392032000	-3.839728000	2.828269000
1	-3.560776000	-3.009357000	1.750918000
6	-3.320753000	1.879786000	-3.704299000
1	-4.252587000	1.787955000	-4.284779000
6	1.068670000	-2.894830000	1.594902000
1	0.722367000	-2.894902000	0.540662000
1	0.230796000	-2.580527000	2.241908000
1	1.341968000	-3.931280000	1.877795000
6	-3.331760000	-3.794210000	-1.253133000
1	-3.073768000	-4.814432000	-1.578114000
6	-4.662410000	-3.462289000	-0.947193000
1	-5.455403000	-4.222676000	-1.029334000
6	6.943130000	0.254007000	0.403794000
1	8.037251000	0.206132000	0.284310000
6	6.101470000	0.055325000	-0.704338000
1	6.531845000	-0.159475000	-1.695213000
79	0.653931000	-1.070944000	-1.645744000
14	0.483930000	0.690902000	1.857054000
15	-1.266581000	-0.252500000	-0.729343000
7	-1.101746000	0.412617000	0.875578000
7	1.866323000	-0.599628000	1.309599000
7	1.856689000	1.508831000	0.731692000
17	2.537523000	-1.855751000	-2.779145000
6	1.040957000	3.800385000	0.585764000
1	0.552568000	3.696867000	1.574550000
1	0.305148000	3.536235000	-0.197135000
1	1.316266000	4.865648000	0.449821000
6	3.273474000	3.415031000	1.604253000
1	4.261672000	2.923074000	1.544341000
1	2.846700000	3.237380000	2.613277000
1	3.437700000	4.506932000	1.490380000

4 (Ci)
E1 = -4889.995071 a.u.
E2 = -4891.221072 a.u.
Nimag = nil

7	0.969312000	1.752195000	2.558158000
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6	-2.983911000	0.312228000	-3.178668000
6	-2.033910000	-2.699785000	-2.913097000
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1	-1.711007000	-4.538746000	-0.644591000
1	-1.524582000	-5.568044000	-2.097391000
1	-1.620172000	-6.311566000	-0.466750000
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1	5.691952000	-6.199853000	-0.369804000
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1	-5.241971000	-0.336654000	-5.685746000
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6	0.022210000	-4.752647000	-5.168831000
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1	-0.373048000	-2.855054000	-7.166267000
6	0.876554000	-6.689532000	-1.490357000
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1	0.321711000	-7.541659000	-1.049383000
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6	5.323897000	-6.649031000	-2.469154000
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6	-4.059661000	-4.576161000	-3.529002000
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6	4.508733000	-6.397834000	-3.586366000
1	4.714128000	-6.899777000	-4.544420000
6	2.857940000	-0.323772000	-2.744231000
1	2.926989000	-0.158219000	-1.649679000
1	3.593734000	0.337699000	-3.242715000
1	1.853127000	-0.010971000	-3.086668000
6	3.113764000	-1.971325000	-4.635867000
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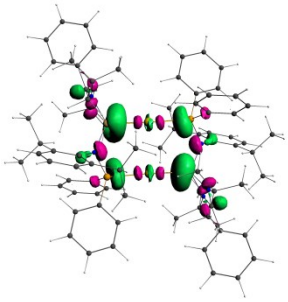
1	3.901460000	-1.351070000	-5.109732000
1	3.299573000	-3.026160000	-4.919158000
6	4.546320000	-2.149758000	-2.554207000
1	5.269288000	-1.389439000	-2.913319000
1	4.560859000	-2.132850000	-1.445311000
1	4.908251000	-3.136071000	-2.896751000
79	0.790586000	-1.147856000	0.500342000
14	0.443115000	-2.301427000	-1.561176000
15	-1.258989000	-0.004048000	-2.617717000
7	0.784762000	-4.154136000	-1.606034000
7	2.047937000	-2.601614000	-2.490436000

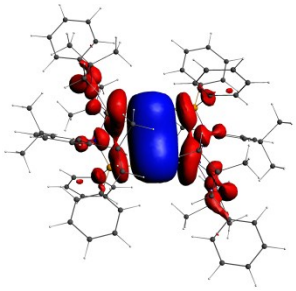
Table S6: EDA-NOCV results for the Si–Au and P–Au bonds of 4 at the BP86/TZ2P level of theory. Energies are in kcal/mol**.**

ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat} [a]	ΔE_{orb} [a]	$\Delta E_{\sigma(L\rightarrow Au)}$ [b]	$\Delta E_{\sigma(Au\rightarrow L)}$ [b]	ΔE_{rest} [b,c]	ΔE_{prep}	ΔE ($-D_e$)
-516.2	510.7	-536.2 (52.2%)	-490.7 (47.8%)	-248.2 (50.6%)	-51.6 (10.5%)	-190.9 (38.9%)	140.7	-375.5

[a]Values in parenthesis give the percentage contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [b]Values in parenthesis give the percentage contribution to orbital interaction ΔE_{orb}. [c]$\Delta E_{rest} = \Delta E_{orb} - (\Delta E_{\sigma(L\rightarrow Au)} + \Delta E_{\sigma(Au\rightarrow L)} + \Delta E_{\sigma_3} + \Delta E_{\sigma_4} + \Delta E_p + \Delta E_b)$. $\Delta E_{\sigma(L\rightarrow Au)}$ is the energy corresponding to σ donation from ligand to Au and $\Delta E_{\sigma(Au\rightarrow L)}$ is the energy corresponding to back donation from Au to ligand.

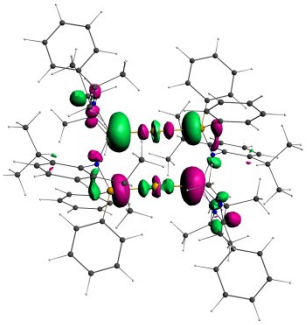


$\Psi_{-1}(-1.00)$

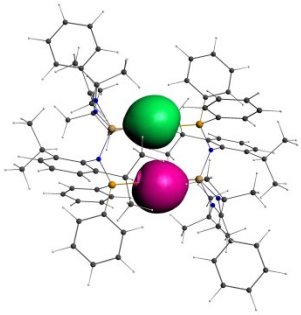


$\Psi_1(1.00)$

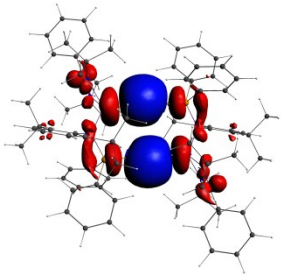
$\Delta\rho_1$
($\Delta E_{\sigma_{1(L\rightarrow Au)}}$ = -102.4 kcal/mol)



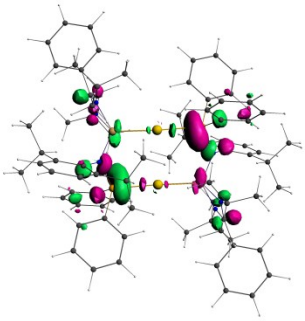
$\Psi_{-2}(-0.89)$

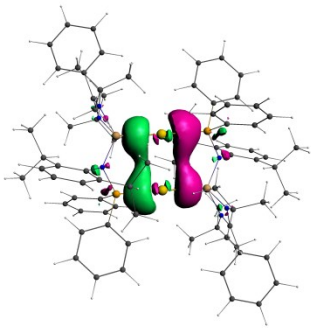


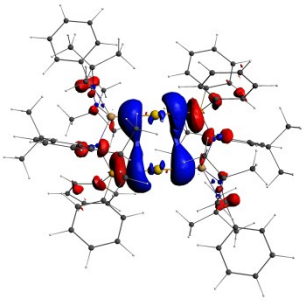
$\Psi_2(0.89)$



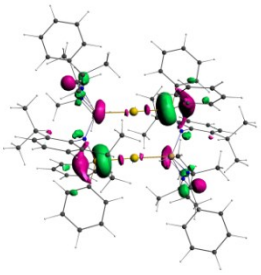
$\Delta\rho_2$
($\Delta E_{\sigma_{2(L\rightarrow Au)}}$ = -77.5 kcal/mol)





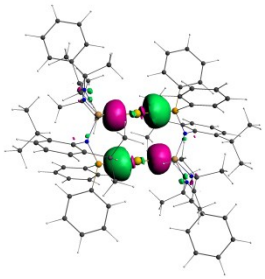


Ψ_{-3}(-0.51)



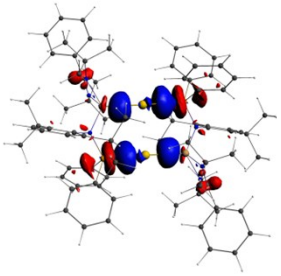
Ψ_{-4}(-0.49)

Ψ_3(0.51)

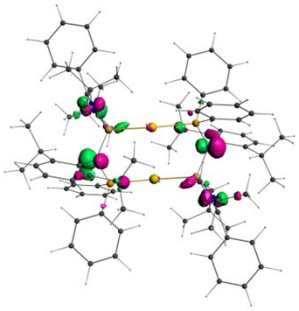


Ψ_4(0.49)

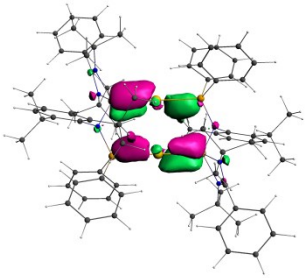
$\Delta\rho_3$
($\Delta E_{\sigma_{3(L\rightarrow Au)}}$= -34.3 kcal/mol)



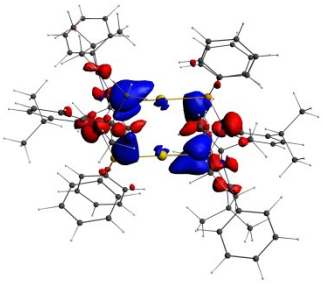
$\Delta\rho_4$
($\Delta E_{\sigma_{4(L\rightarrow Au)}}$=-34.0 kcal/mol)



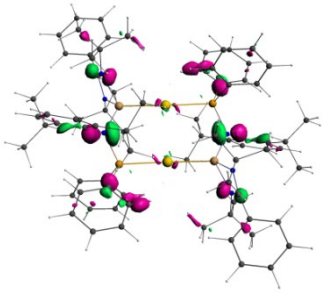
$\Psi_{-5}(-0.35)$



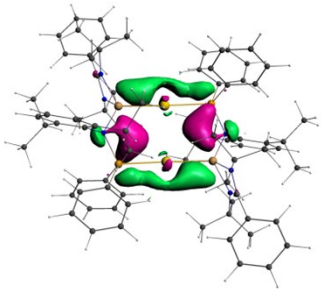
$\Psi_{5}(0.35)$



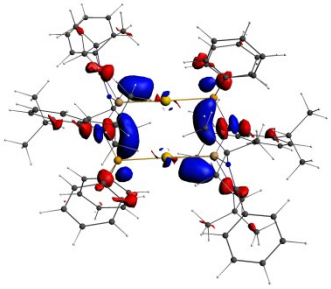
$\Delta\rho_5$
($\Delta E_{5(L\rightarrow L)}$=-12.3 kcal/mol)



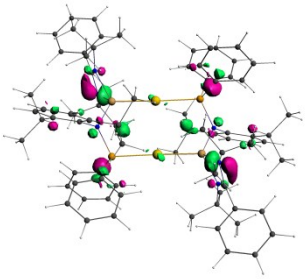
$\Psi_{-6}(-0.30)$



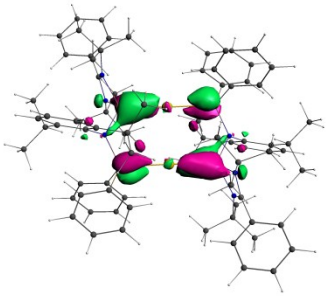
$\Psi_{6}(0.30)$



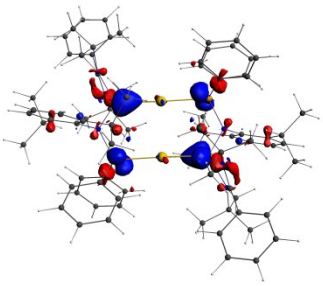
$\Delta\rho_6$
($\Delta E_{6(L\rightarrow L)}$=-9.9 kcal/mol)



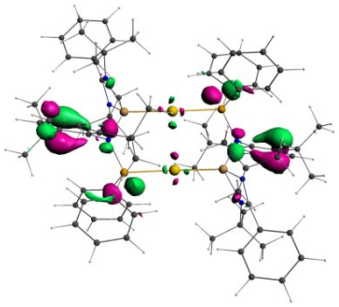
$\Psi_{-7}(-0.26)$



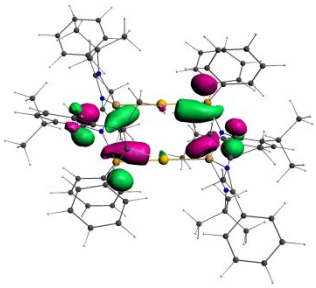
$\Psi_{7}(0.26)$



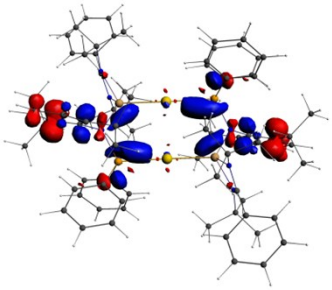
$\Delta\rho_7$
($\Delta E_{7(L\rightarrow L)}$=-8.5 kcal/mol)



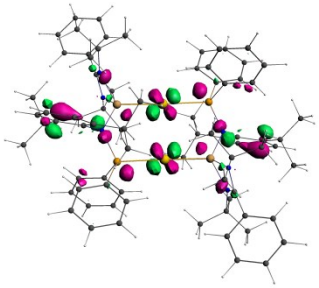
$\Psi_{-8}(-0.25)$



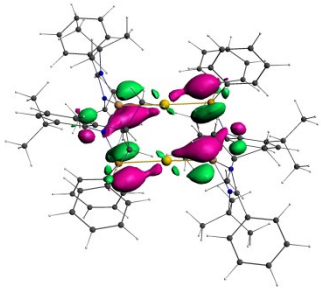
$\Psi_{8}(0.25)$



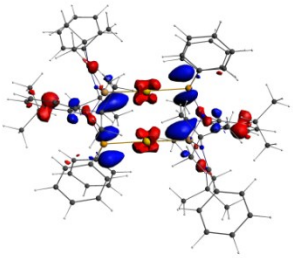
$\Delta\rho_8$
($\Delta E_{7(L\rightarrow L)}$= -8.1 kcal/mol)



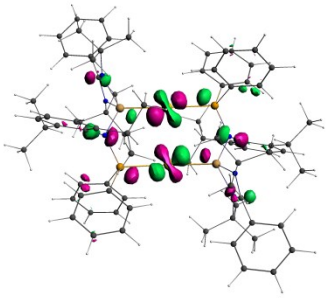
Ψ_{-9}(-0.24)



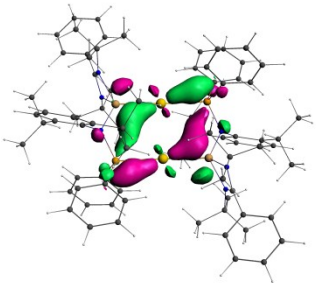
Ψ_{9}(0.24)



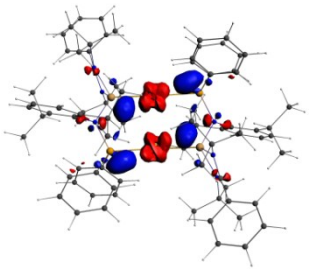
$\Delta\rho_{9}$
($\Delta E_{\sigma_{9(Au\rightarrow L)}}$=-8.2 kcal/mol)



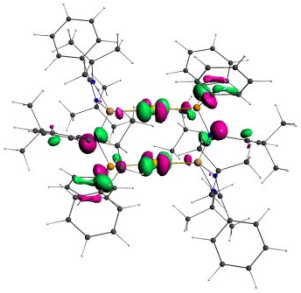
Ψ_{-10}(-0.22)



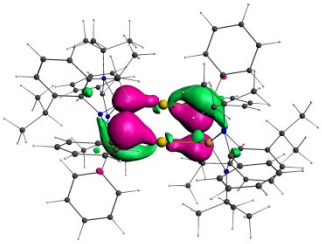
Ψ_{10}(0.22)



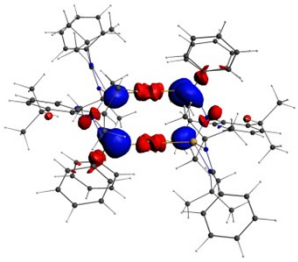
$\Delta\rho_{10}$
($\Delta E_{\sigma_{10(Au\rightarrow L)}}$=-9.1 kcal/mol)



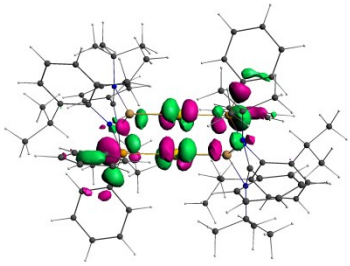
Ψ_{-11}(-0.22)



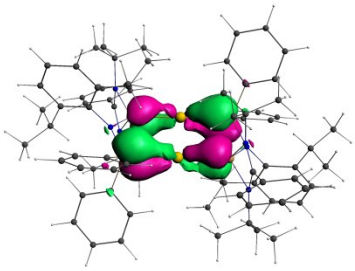
Ψ_{11}(0.22)



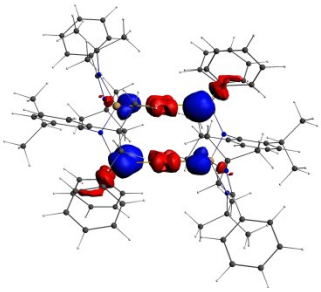
$\Delta\rho_{11}$
($\Delta E_{\sigma_{11(Au\rightarrow L)}}$=-8.7 kcal/mol)



Ψ_{-12}(-0.21)



Ψ_{12}(0.21)



$\Delta\rho_{12}$
($\Delta E_{\sigma_{12(Au\rightarrow L)}}$=-8.6 kcal/mol)

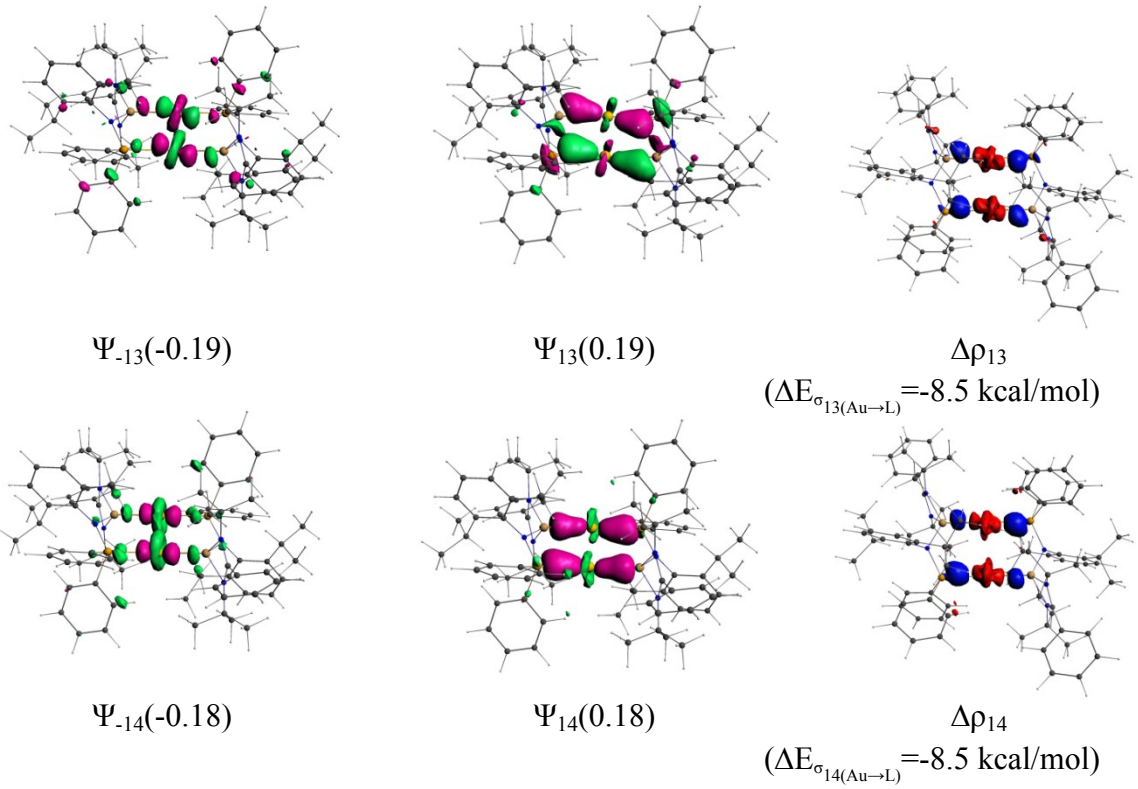


Figure S11: NOCV pair of orbitals with their eigen values in parenthesis, the associated deformation density plots Δρ and orbital stabilization energies ΔE of **4** at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot Δρ is from red → blue. Isosurface value for NOCV pair orbitals is 0.03 and that for deformation density is 0.001 up to $\Delta\rho_4$ and 0.0005 for $\Delta\rho_5$-$\Delta\rho_{14}$. $\Delta\rho_5$-$\Delta\rho_8$ corresponds to the polarization of electron density within the fragments.

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