

# Supporting Information for:

## $\sigma$ -SiH Complexes of Copper: Experimental Evidence and Computational Analysis

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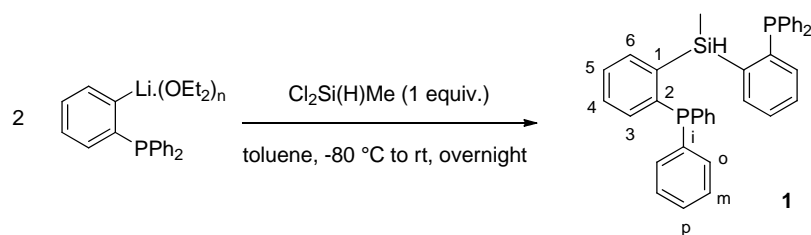
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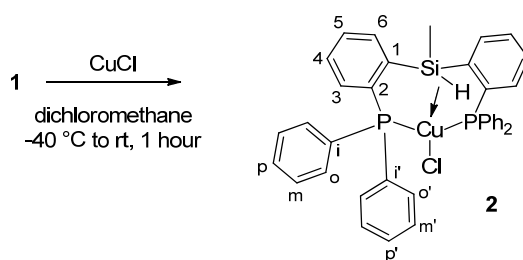
## Materials and methods

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or in a glovebox under inert atmosphere. Dry, oxygen-free solvents were employed. Melting points were determined with a Stuart SMP40 apparatus and are uncorrected. Solution  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR spectra were recorded on Bruker Avance 300, 400 or 500 spectrometers at 298 K. Chemical shifts ( $\delta$ ) are expressed with a positive sign, in parts per million.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts reported are referenced internally to residual protio- ( $^1\text{H}$ ) or deuterio- ( $^{13}\text{C}$ ) solvent, while  $^{29}\text{Si}$  and  $^{31}\text{P}$  chemical shifts are relative to  $\text{SiMe}_4$  and 85%  $\text{H}_3\text{PO}_4$  external references, respectively. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. The  $^1\text{H}$  and  $^{13}\text{C}$  resonance signals were attributed by means of 2D HSQC and HMBC experiments. The  $N$  values corresponding to  $\frac{1}{2} [J(\text{AX})+J(\text{A}'\text{X})]$  are provided when second-order  $\text{AA}'\text{X}$  and  $\text{AA}'\text{XX}'$  systems are observed in the  $^{13}\text{C}$  NMR spectra.<sup>1</sup> IR spectra were recorded on a PerkinElmer Spectrum One FT-IR ATR spectrometer. Mass spectra were recorded on a Waters LCT apparatus. Elemental analyses were performed by the in-house service at the *Laboratoire de Chimie de Coordination* (205, Route de Narbonne, 31077, Toulouse, France) on a PerkinElmer 2400 Series II system. *o*-Lithiated triphenylphosphine was prepared following a described procedure.<sup>2</sup> All starting materials were purchased from Aldrich. Dichloro(methyl)silane was distilled prior to use.



### Synthesis of the diphosphine-hydrosilane ligand **1**

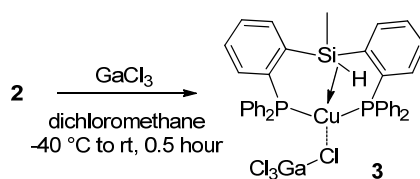
A solution of dichloro(methyl)silane (229  $\mu\text{l}$ , 2.2 mmol) in toluene (2 mL) was added dropwise to a solution of the *o*-lithiated triphenylphosphine (1.765 g, 4.65 mmol) in toluene (13 mL) at  $-80\text{ }^{\circ}\text{C}$ . The solution was allowed to warm to room temperature overnight, after which volatiles were removed under vacuum. The resulting orange oil was purified by column chromatography (eluent: pentane/dichloromethane 9:1) to give the desired product as a white solid. Yield: 1.020 g (61 %). **Mp**:  $151\text{ }^{\circ}\text{C}$ ;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.75 – 7.57 (m, 2H,  $\text{H}_{\text{ar}}$ ), 7.43 – 7.20 (m, 16H,  $\text{H}_{\text{ar}}$ ), 7.19 – 6.96 (m, 10H,  $\text{H}_{\text{ar}}$ ), 5.48 (tq,  $^4J_{\text{HP}} = 5.6\text{ Hz}$ ,  $^3J_{\text{HH}} = 3.85\text{ Hz}$ ,  $^1J_{\text{HSi}} = 204\text{ Hz}$ , 1H, SiH), 0.73 (dt,  $^3J_{\text{HH}} = 3.85\text{ Hz}$ ,  $^5J_{\text{HP}} = 0.9\text{ Hz}$ , 3H,  $\text{SiCH}_3$ );  **$^{31}\text{P}\{^1\text{H}\}\text{NMR}$**  (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-13.2$  (s);  **$^{29}\text{Si}\{^1\text{H}\}\text{NMR}$**  (60 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$   $-24$  (t,  $^3J_{\text{SiP}} = 20\text{ Hz}$ );  **$^{13}\text{C}\{^1\text{H}\}\text{NMR}$**  (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  145.0 (dd,  $^2J_{\text{CP}} = 46.8\text{ Hz}$ ,  $^4J_{\text{CP}} = 3.5\text{ Hz}$ ,  $\text{C}^1$ ), 144.4 (d,  $^1J_{\text{CP}} = 11.2\text{ Hz}$ ,  $\text{C}^2$ ), 138.4 (d,  $^1J_{\text{CP}} = 12.4\text{ Hz}$ ,  $\text{C}^i$ ), 137.3 (dd,  $^3J_{\text{CP}} = 15.4\text{ Hz}$ ,  $^5J_{\text{CP}} = 2.4\text{ Hz}$ ,  $\text{C}^3$ ), 134.6 (s,  $\text{C}^p$ ), 133.9 (m,  $\text{C}^o$ ,  $\text{C}^m$ ), 129.9 (s,  $\text{C}^5$ ),  $-2.3$  (t,  $^4J_{\text{CP}} = 8.7\text{ Hz}$ ,  $\text{SiCH}_3$ ), signals of  $\text{C}^4$  and  $\text{C}^6$  overlap with the solvent signal; **IR**:  $\nu(\text{SiH})$ :  $2142\text{ cm}^{-1}$ ; **HRMS (ESI+)**: calcd for  $[\text{M}+\text{H}]^+ = \text{C}_{37}\text{H}_{33}\text{P}_2\text{Si}^+$ : 567.1827. Found: 567.1827.



\*\*\* The same atom labeling scheme was used for the NMR assignments of all complexes. \*\*\*

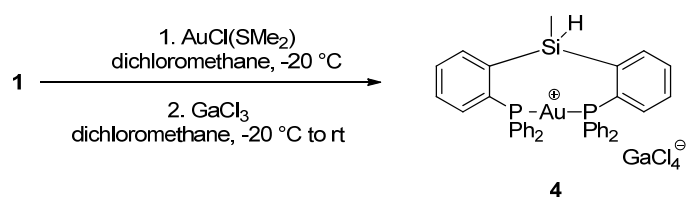
### Coordination of the diphosphine-hydrosilane **1** to copper chloride

A solution of diphosphine-hydrosilane ligand **1** (100 mg, 0.18 mmol) in dichloromethane (3 mL) was added at  $-40^\circ\text{C}$  to a dispersion of copper chloride (17.5 mg, 0.18 mmol) in dichloromethane (1 mL). The reaction mixture was stirred for 60 minutes while warming up to room temperature. The colorless solution was concentrated to a volume of about 1 mL. Upon addition of pentane (5 mL), **2** precipitates as a white solid which was separated by filtration and dried under vacuum. Yield: 80 mg (68 %). Crystals suitable for X-ray diffraction analysis were grown at  $-30^\circ\text{C}$  from a saturated solution of **2** in dichloromethane layered with pentane. **Mp**:  $215^\circ\text{C}$  (decomposition);  **$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.85 – 6.86 (m, 28H,  $\text{H}_{\text{ar}}$ ), 6.63 (qt,  $^3J_{\text{HH}} = 3.4$  Hz,  $^4J_{\text{HP}} = 6.7$  Hz,  $^1J_{\text{HSi}} = 180$  Hz, 1H, SiH), 0.46 (d,  $^3J_{\text{HH}} = 3.4$  Hz, 3H,  $\text{SiCH}_3$ );  **$^{31}\text{P}\{^1\text{H}\}$  NMR** (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-7.6$  (s);  **$^{29}\text{Si}\{^1\text{H}\}$  NMR** (79 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-30$  (t,  $^3J_{\text{SiP}} = 23$  Hz);  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  141.5 (*virtual t*, AA'X,  $N = 19.2$  Hz,  $\text{C}^1$ ), 139.6 (*virtual t*, AA'X,  $N = 16.1$  Hz,  $\text{C}^2$ ), 135.3 (*virtual t*, AA'X,  $N = 7.5$  Hz,  $\text{C}^3$ ), 134.5 (*virtual t*, AA'X,  $N = 7.8$  Hz,  $\text{C}^{\text{o}}$  or  $\text{C}^{\text{m}}$ ), 133.5 (*virtual t*, AA'X,  $N = 18.4$  Hz,  $\text{C}^{\text{i}}$ ), 133.0 (*virtual t*, AA'X,  $N = 7.4$  Hz,  $\text{C}^{\text{o}}$  or  $\text{C}^{\text{m}}$ ), 132.7 (s,  $\text{C}^4$ ), 131.7 (*virtual t*, AA'X,  $N = 15.6$  Hz,  $\text{C}^{\text{i}}$ ), 130.2 (s,  $\text{C}^5$ ), 129.7 (*virtual t*, AA'X,  $N = 2.6$  Hz,  $\text{C}^6$ ), 129.4 (s,  $\text{C}^{\text{p}}$ ), 129.3 (s,  $\text{C}^{\text{p}'}$ ), 128.7 (*virtual t*, AA'X,  $N = 4.9$  Hz,  $\text{C}^{\text{o}}$  or  $\text{C}^{\text{m}}$ ), 128.3 (*virtual t*, AA'X,  $N = 4.6$  Hz,  $\text{C}^{\text{o}}$  or  $\text{C}^{\text{m}}$ ),  $-4.1$  (t,  $^4J_{\text{PC}} = 3.7$  Hz,  $\text{SiCH}_3$ ); **IR**:  $\nu(\text{SiH})$ :  $1996\text{ cm}^{-1}$  (br); **HRMS (ESI+)**: calcd for  $[\text{M}(\text{Cl})]^+ = \text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCu}^+$ : 629.1045. Found: 629.1054. **Elt. Anal.**: calcd for  $\text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCuCl} + \text{CH}_2\text{Cl}_2$ : C, 60.80; H, 4.57. Found: C, 61.28; H, 4.54.



### Reaction of the diphosphine-hydrosilane copper chloride complex **2** with $\text{GaCl}_3$

A solution of  $\text{GaCl}_3$  (13.2 mg, 0.08 mmol) in dichloromethane (1 mL) was added to a solution of **2** (50 mg, 0.08 mmol) in dichloromethane (2 mL) at  $-40\text{ }^\circ\text{C}$ . The mixture was stirred for 30 minutes while warming up to room temperature, then concentrated to a volume of about 1 mL. Complex **3** precipitated upon addition of pentane (3 mL). The colorless solid was separated from the supernatant by filtration and dried under vacuum. Yield: 51 mg (80 %). Crystals suitable for X-ray diffraction analysis were grown at  $-60\text{ }^\circ\text{C}$  from a saturated solution in dichloromethane layered with pentane. **Mp**:  $119\text{ }^\circ\text{C}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.15 – 6.60 (m, 28H,  $\text{H}_{\text{ar}}$ ), 6.44 (mbr,  $^1J_{\text{HSi}} = 170\text{ Hz}$ , 1H, SiH), 0.32 (ml, 3H, SiCH<sub>3</sub>);  **$^{31}\text{P}\{^1\text{H}\}$  NMR** (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  - 5.0 (sbr);  **$^{29}\text{Si}\{^1\text{H}\}$  NMR** (79 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  - 30 (t,  $^3J_{\text{SiP}} = 23\text{ Hz}$ );  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  140.7 (*virtual t*, AA'X,  $N = 18.7\text{ Hz}$ , C<sup>1</sup>), 139.1 (*virtual t*, AA'X,  $N = 16.1\text{ Hz}$ , C<sup>2</sup>), 134.2 (*virtual t*, AA'X,  $N = 7.6\text{ Hz}$ , C<sup>3</sup>), 133.9 (*virtual t*, AA'X,  $N = 7.9\text{ Hz}$ , C<sup>0</sup> or C<sup>m</sup>), 132.3 (*virtual t*, AA'X,  $N = 18.1\text{ Hz}$ , C<sup>1</sup>), 132.1 (*virtual t*, AA'X,  $N = 7.3\text{ Hz}$ , C<sup>0</sup> or C<sup>m</sup>), 131.9 (s, C<sup>4</sup>), 130.9 (*virtual t*, AA'X,  $N = 15.6\text{ Hz}$ , C<sup>1</sup>), 129.3 (s, C<sup>5</sup>), 128.8 (*virtual t*, AA'X,  $N = 2.6\text{ Hz}$ , C<sup>6</sup>), 128.3 (s, C<sup>p</sup>), 128.2 (s, C<sup>p</sup>), 127.9 (*virtual t*, AA'X,  $N = 5.1\text{ Hz}$ , C<sup>0</sup> or C<sup>m</sup>), 127.3 (*virtual t*, AA'X,  $N = 4.6\text{ Hz}$ , C<sup>0</sup> or C<sup>m</sup>), - 4.8 (t,  $^4J_{\text{PC}} = 3.9\text{ Hz}$ , SiCH<sub>3</sub>); **IR**:  $\nu(\text{SiH})$ :  $1973\text{ cm}^{-1}$  (br); **HRMS (ESI+)**: calcd for  $[\text{M}-(\text{GaCl}_4)]^+ = \text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCu}^+$ : 629.1045. Found: 629.1054. **Elt. Anal.**: calcd for  $\text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCuGaCl}_4 + \text{C}_5\text{H}_{12}$ : C, 55.20; H, 4.85. Found: C, 54.87; H, 4.52.



### Coordination of the diphosphine-hydrosilane **1** to gold

A solution of the diphosphine-hydrosilane ligand **1** (100 mg, 0.18 mmol) in dichloromethane (3 mL) was added at  $-20\text{ }^\circ\text{C}$  to a solution of chloro(dimethylsulfide)gold (52 mg, 0.18 mmol) in dichloromethane (1 mL). The reaction mixture was stirred for 20 minutes before a solution of  $\text{GaCl}_3$  (31 mg, 0.18 mmol) in dichloromethane (1 mL) was slowly added at  $-20\text{ }^\circ\text{C}$ . The mixture was allowed to warm up to room temperature under stirring for 30 minutes. The solution was then concentrated under vacuum to a volume of about 2 mL, filtered and layered with pentane (5 mL) to give **4** as yellowish crystals upon crystallization at  $-60\text{ }^\circ\text{C}$  over 3 days. Yield: 149 mg (85 %). **Mp**:  $194\text{ }^\circ\text{C}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.15 – 8.05 (m, 2H,  $\text{H}_{\text{ar}}$ ), 7.73 – 7.38 (m, 24H,  $\text{H}_{\text{ar}}$ ), 7.00 – 7.15 (m, 2H,  $\text{H}_{\text{ar}}$ ), 6.88 (q,  $^3J_{\text{HH}} = 3.6\text{ Hz}$ ,  $^1J_{\text{HSi}} = 204\text{ Hz}$ , 1H, SiH), 0.52 (d,  $^3J_{\text{HH}} = 3.6\text{ Hz}$ , 3H, SiCH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  45.4 (s);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -37 (t,  $^3J_{\text{SiP}} = 15\text{ Hz}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  141.4 (*virtual t*, AA'X,  $N = 14.6\text{ Hz}$ ,  $\text{C}^1$ ), 137.1 (*virtual t*, AA'X,  $N = 7.7\text{ Hz}$ ,  $\text{C}^3$ ), 134.5 (*virtual t*, AA'X,  $N = 8.2\text{ Hz}$ ,  $\text{C}^0$  or  $\text{C}^m$ ), 133.9 (*virtual t*, AA'X,  $N = 4.4\text{ Hz}$ ,  $\text{C}^4$  or  $\text{C}^6$ ), 133.2 (*virtual t*, AA'X,  $N = 14.6\text{ Hz}$ ,  $\text{C}^0$  or  $\text{C}^m$ ), 132.7 (s,  $\text{C}^p$ ), 132.4 (s,  $N = 14.6\text{ Hz}$ ,  $\text{C}^p$ ), 132.3 (*virtual t*, AA'X,  $N = 29.1\text{ Hz}$ ,  $\text{C}^2$ ), 131.4 (s,  $\text{C}^5$ ), 130.6 (*virtual t*, AA'X,  $N = 4.4\text{ Hz}$ ,  $\text{C}^4$  or  $\text{C}^6$ ), 129.7 (*virtual t*, AA'X,  $N = 5.3\text{ Hz}$ ,  $\text{C}^0$  or  $\text{C}^m$ ), 129.6 (*virtual t*, AA'X,  $N = 5.3\text{ Hz}$ ,  $\text{C}^0$  or  $\text{C}^m$ ), 127.1 (*virtual t*, AA'X,  $N = 29.7\text{ Hz}$ ,  $\text{C}^i$ ), 126.3 (*virtual t*, AA'X,  $N = 30.3\text{ Hz}$ ,  $\text{C}^i$ ), -0.9 (t,  $^4J_{\text{CP}} = 2.3\text{ Hz}$ , SiCH<sub>3</sub>); **IR**:  $\nu(\text{SiH})$ :  $2141\text{ cm}^{-1}$ ; **HRMS (ESI+)**: calcd for  $[\text{M}]^+ = \text{C}_{37}\text{H}_{32}\text{P}_2\text{SiAu}^+$ : 763.1414. Found: 763.1423. **Elt. Anal.**: calcd for  $\text{C}_{37}\text{H}_{32}\text{P}_2\text{SiAuGaCl}_4$ : C, 45.52; H, 3.41. Found: C, 45.38; H, 3.11.

## NMR spectra of complexes 2, 3 and 4

Figure S1.  $^1\text{H}$  NMR spectrum of complex 2

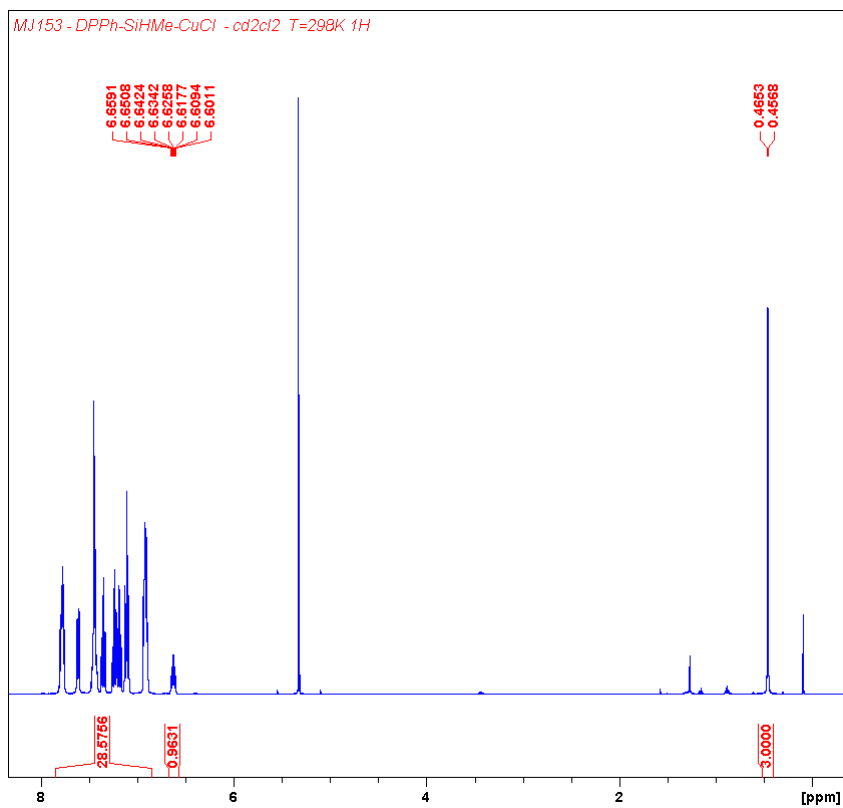
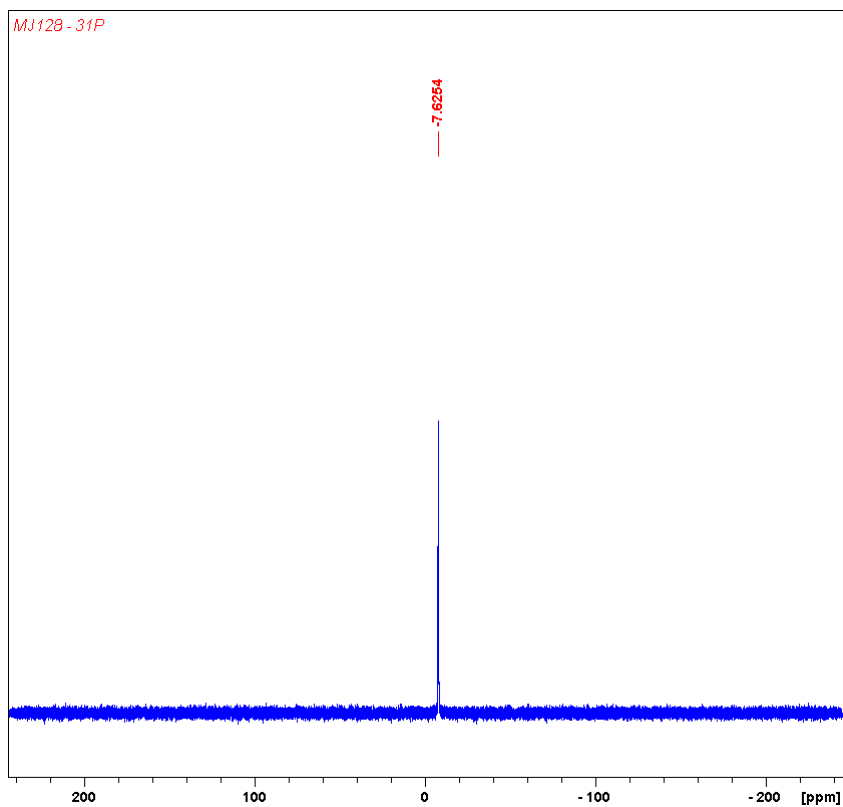
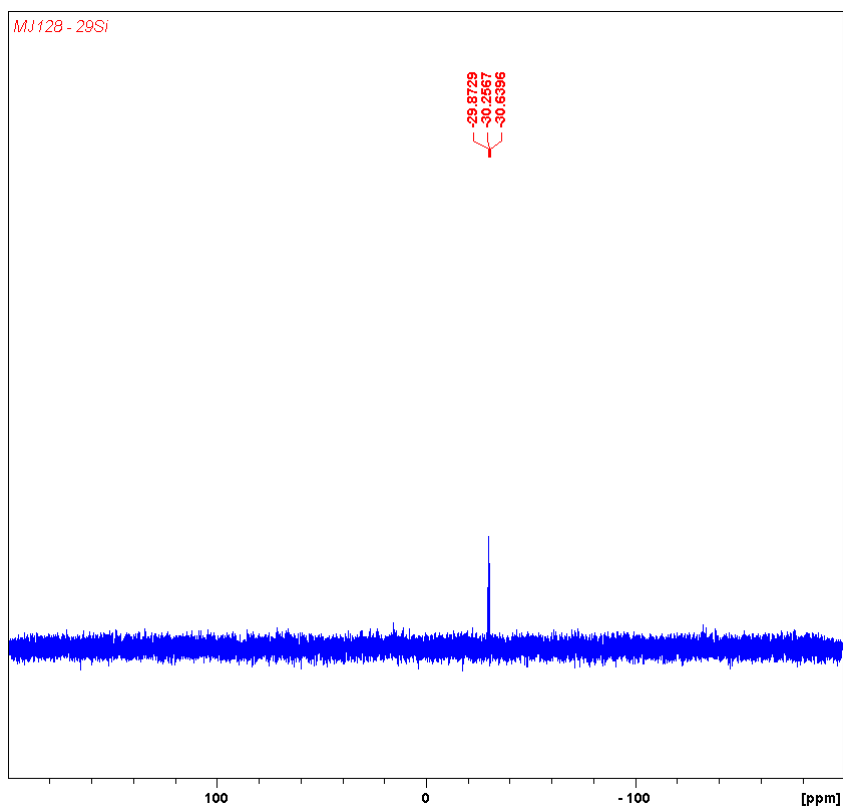


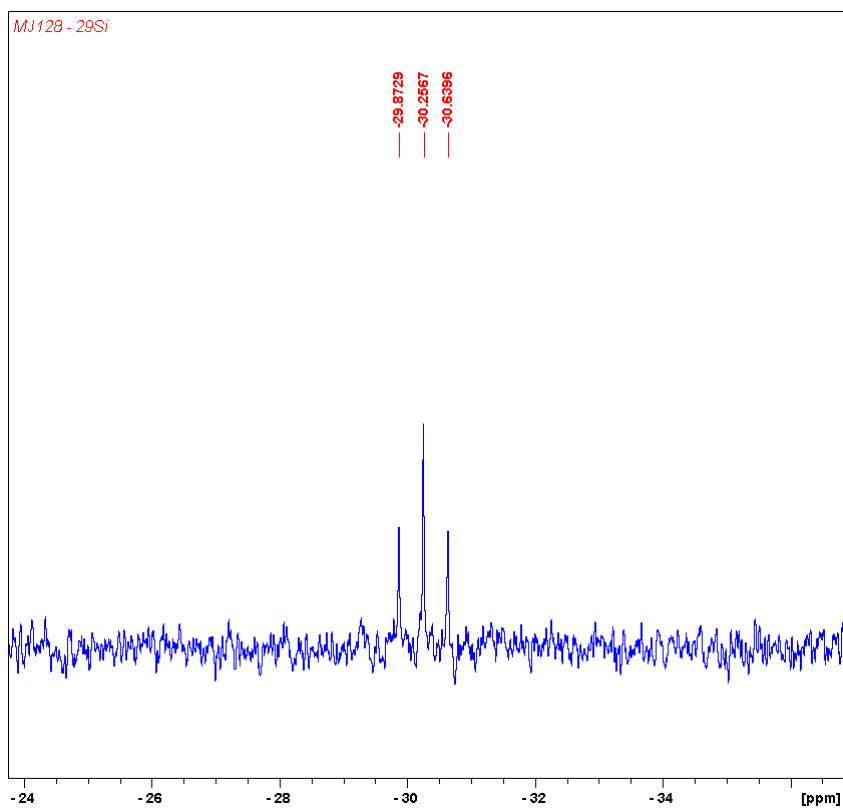
Figure S2.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex 2



**Figure S3.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of complex **2**

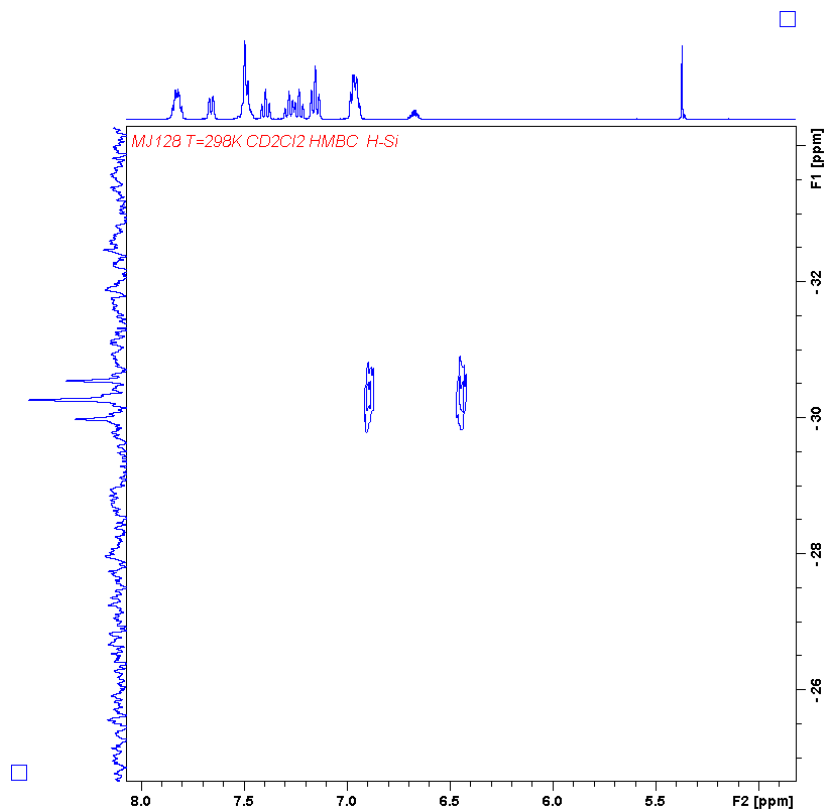


**Figure S4.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of complex **2** (enlarged view):

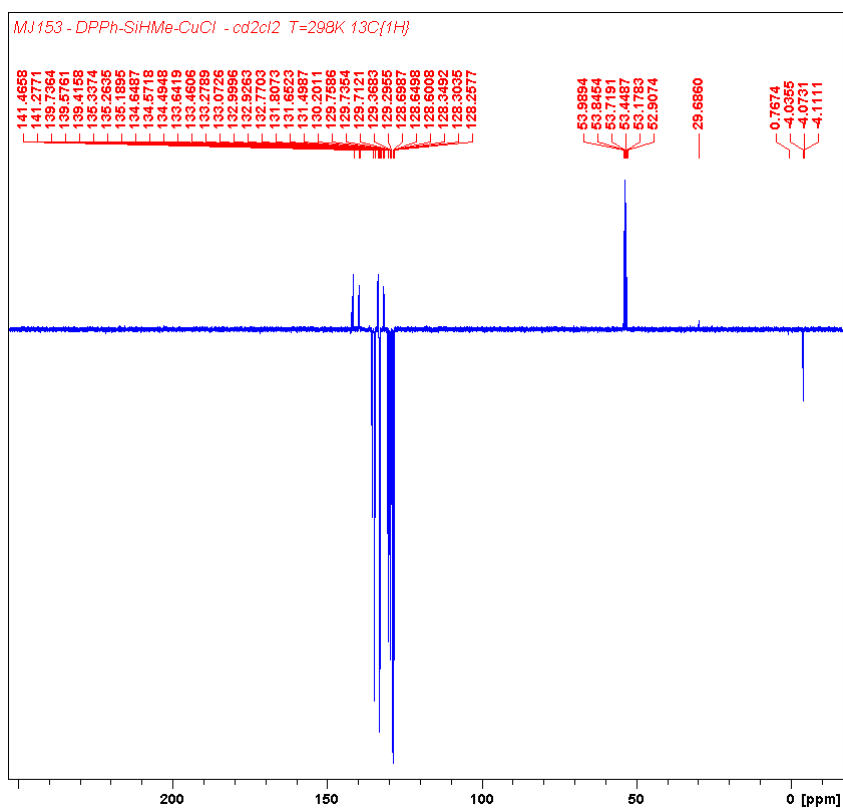




**Figure S5.**  $^{29}\text{Si}\{^1\text{H}\}$ - $^1\text{H}$  HMBC NMR spectrum (F1:  $^{29}\text{Si}\{^1\text{H}\}$ , F2:  $^1\text{H}$ ) of complex **2**

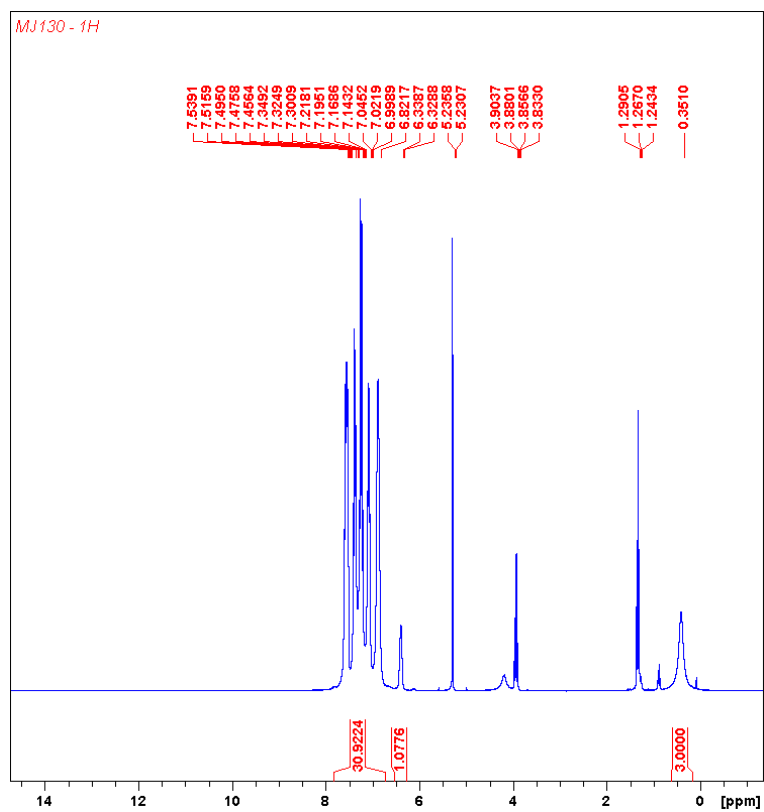


**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **2**

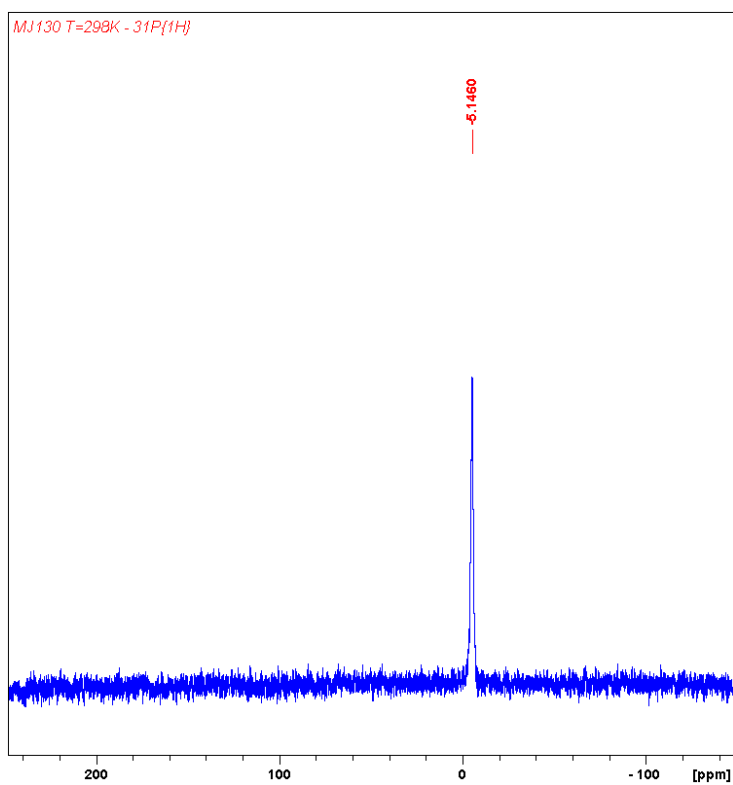


**Figure S7.**  $^1\text{H}$  NMR spectrum of complex **3**

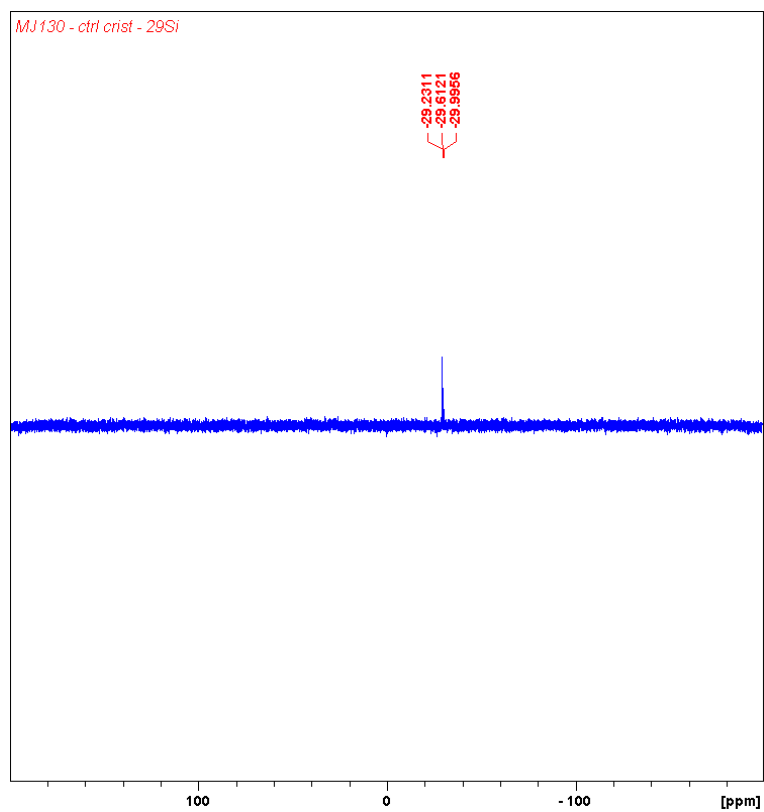
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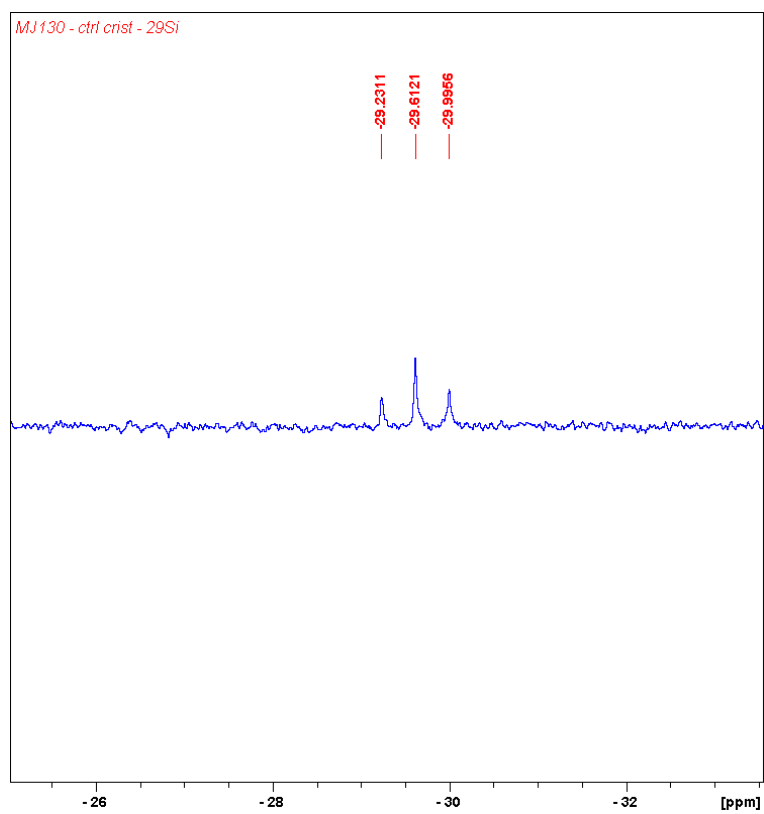
**Figure S8.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **3**



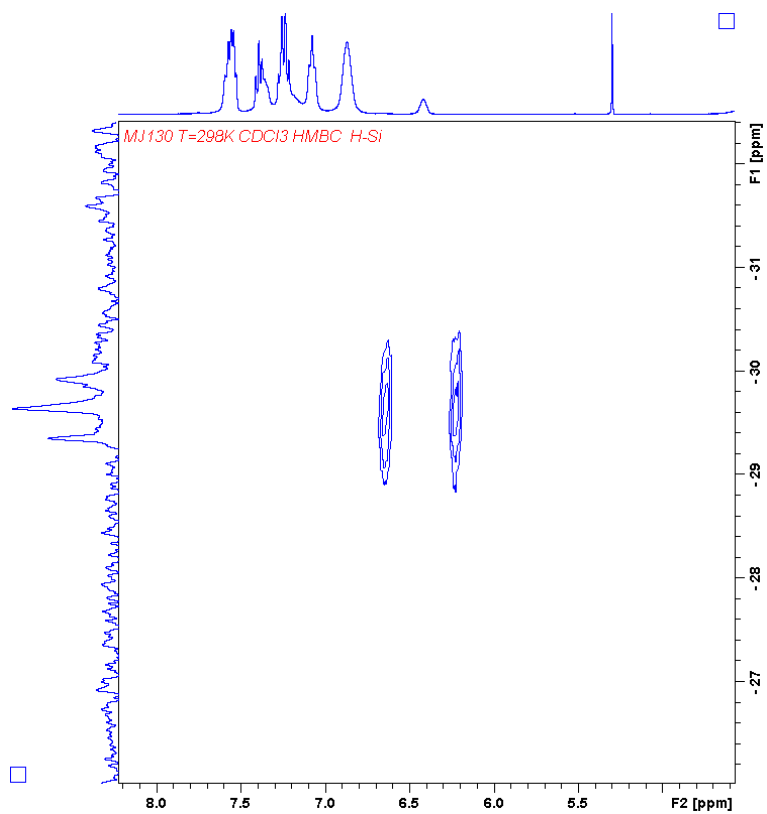
**Figure S9.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of complex **3**



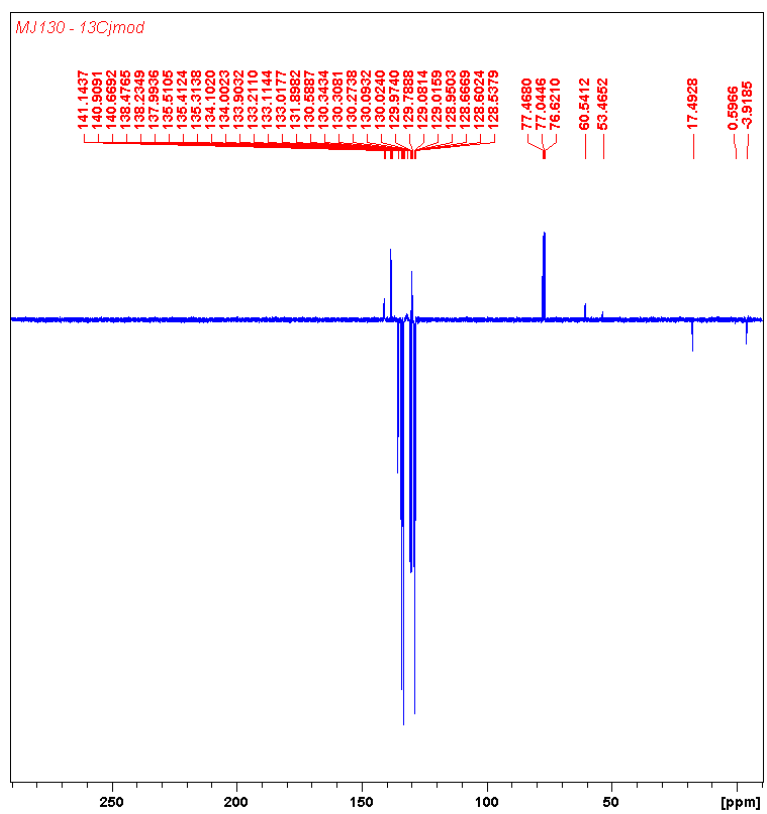
**Figure S10.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of complex **3** (enlarged view):



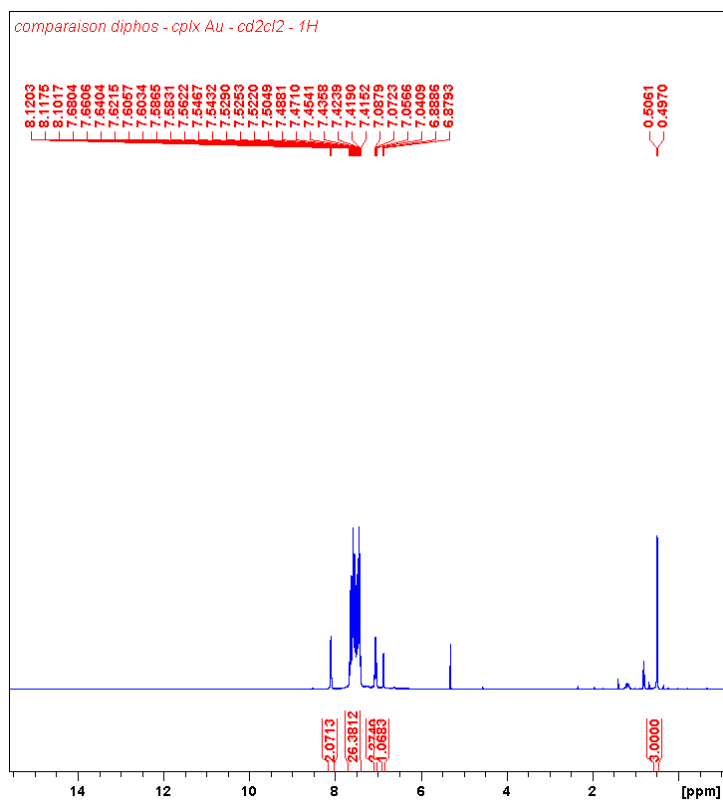
**Figure S11.**  $^{29}\text{Si}\{^1\text{H}\}$ - $^1\text{H}$  HMBC NMR spectrum (F1:  $^{29}\text{Si}\{^1\text{H}\}$ , F2:  $^1\text{H}$ ) of complex **3**



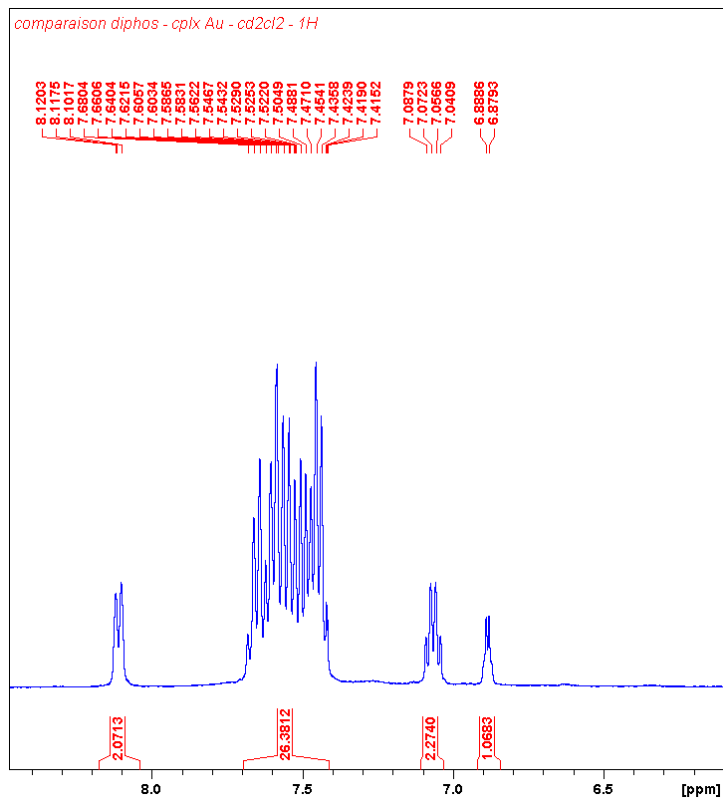
**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **3**



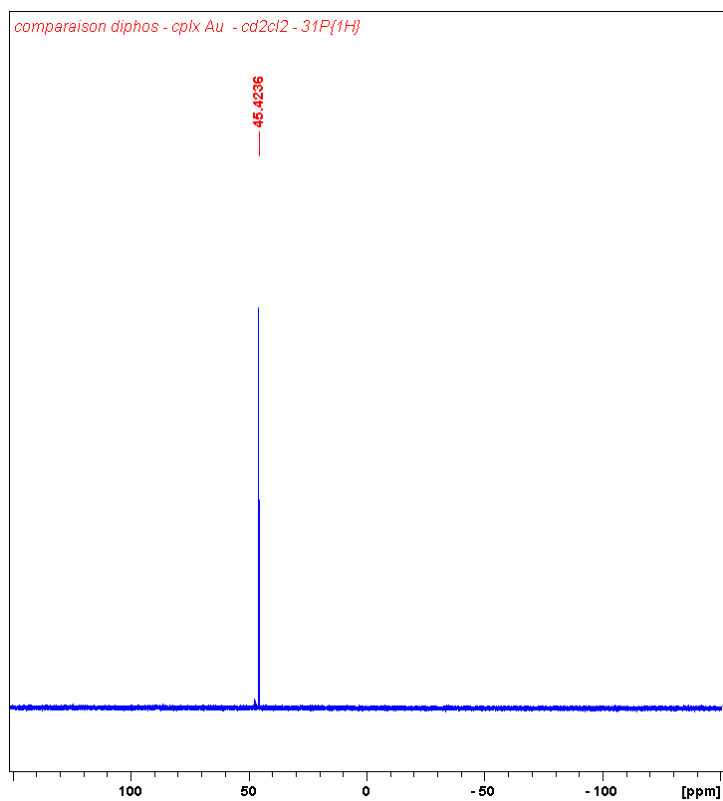
**Figure S13.**  $^1\text{H}$  NMR spectrum of complex **4**



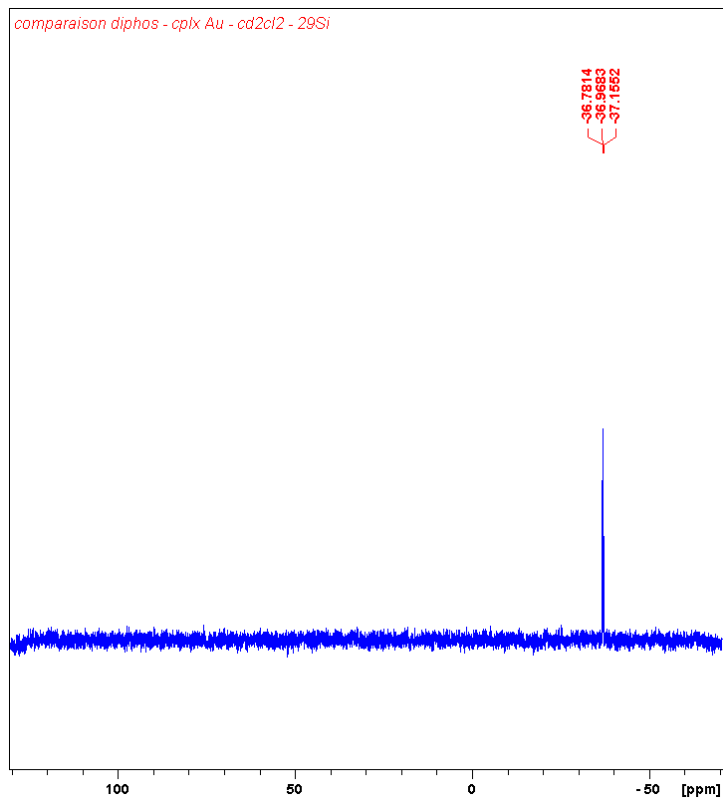
**Figure S14.**  $^1\text{H}$  NMR spectrum of complex **4** (enlarged view):



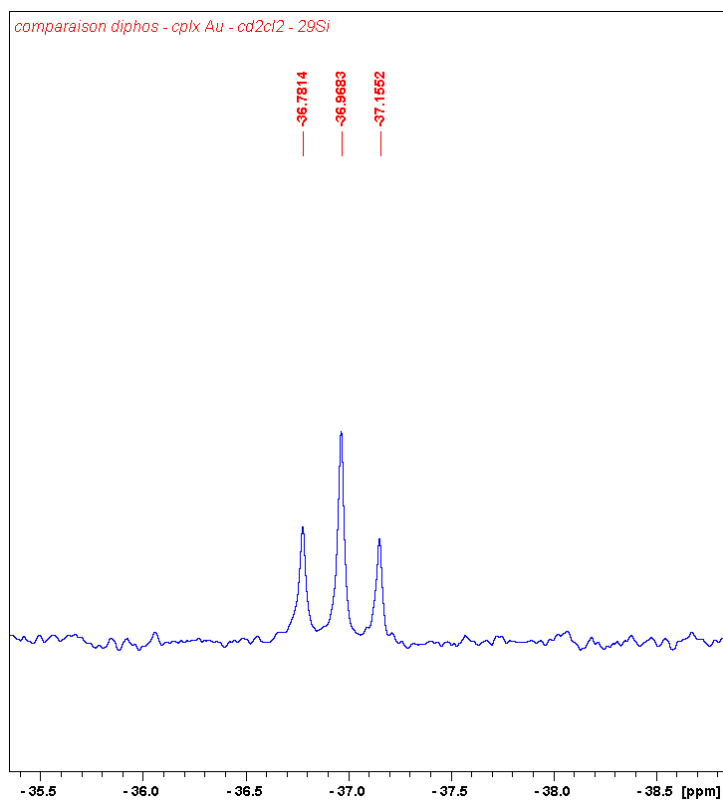
**Figure S15.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex 4



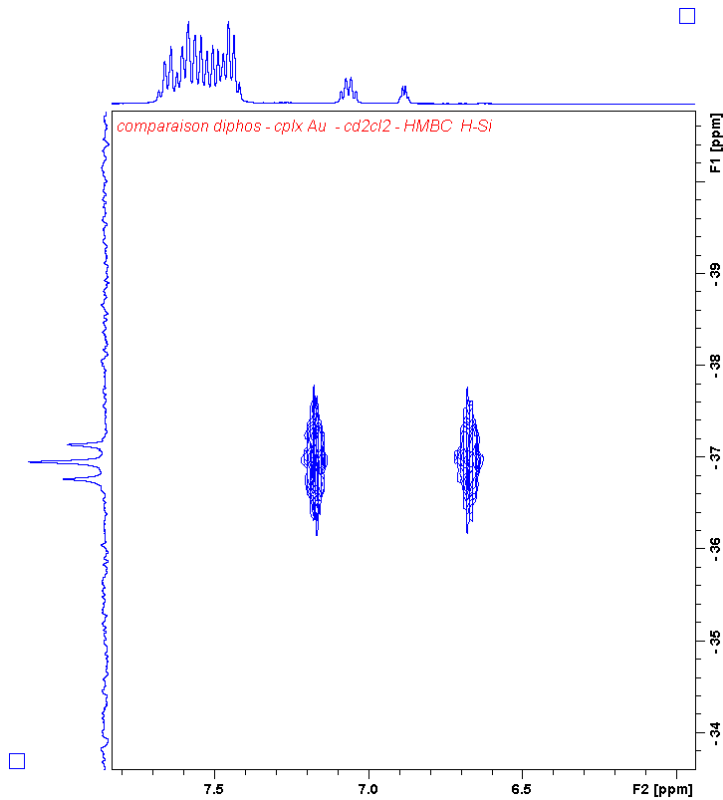
**Figure S16.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of complex 4



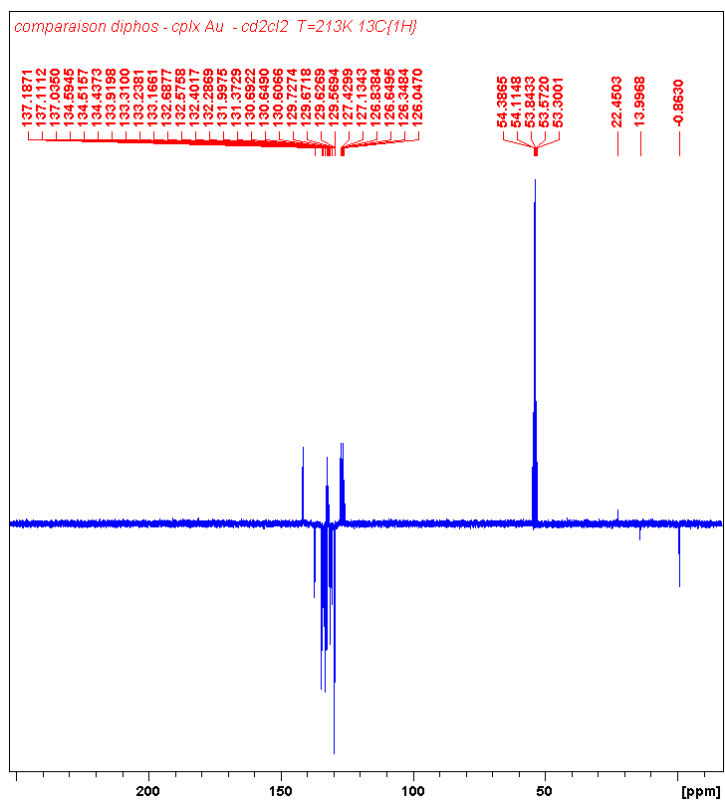
**Figure S17.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of complex 4 : (enlarged view):



**Figure S18.**  $^{29}\text{Si}\{^1\text{H}\}$ - $^1\text{H}$  HMBC NMR spectrum (F1:  $^{29}\text{Si}\{^1\text{H}\}$ , F2:  $^1\text{H}$ ) of complex 4



**Figure S19.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex 4





## Selected crystal data

Crystallographic data were collected at 193(2) K on a Bruker-AXS Kappa APEXII Quazar diffractometer (for **2** and **3**) or on a Bruker-AXS SMART APEX II (for **4**), with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using an oil-coated shock-cooled crystal. Phi- and omega- scans were used. Semi-empirical absorption correction was employed.<sup>3</sup> The structures were solved by direct methods (SHELXS-97)<sup>4</sup> and refined using the least-squares method on  $F^2$ . All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp<sup>3</sup> carbon and 1.2 times for all other carbon atoms.

**Table S1.** Crystal Data, Data Collection, and Structure Refinement for **2**, **3** and **4**

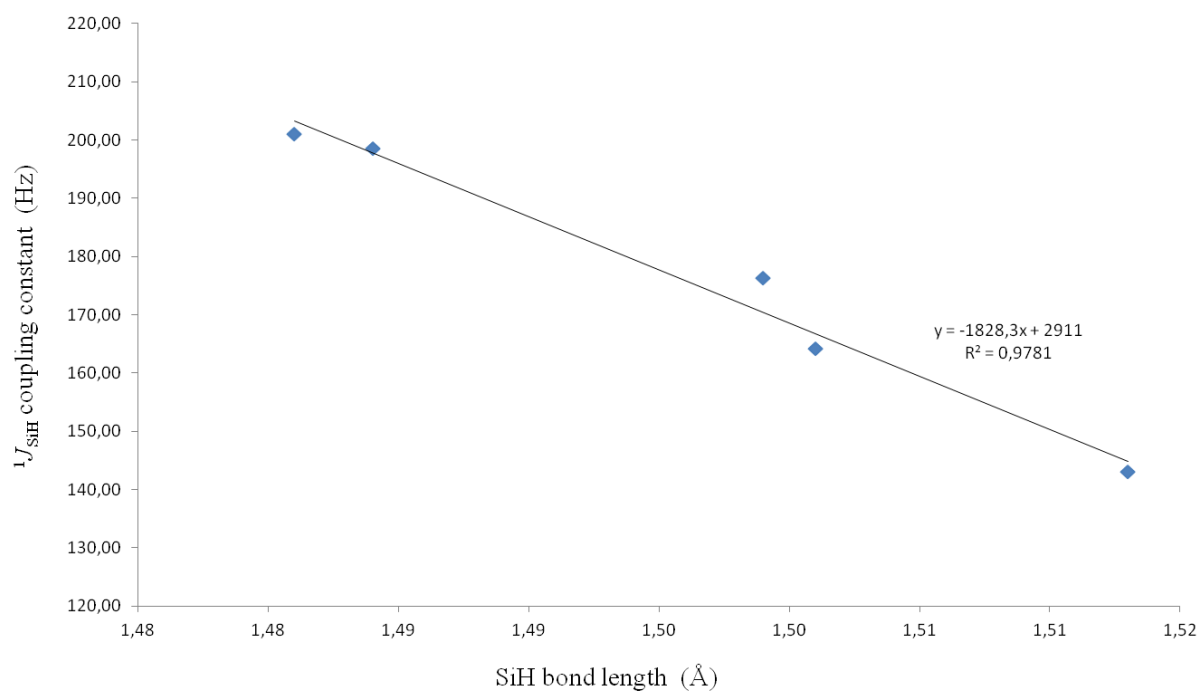
	<b>2</b>	<b>3</b>	<b>4</b>
<b>Crystal data</b>			
formula	C <sub>37</sub> H <sub>32</sub> ClCu P <sub>2</sub> Si, CH <sub>2</sub> Cl <sub>2</sub>	C <sub>37</sub> H <sub>32</sub> Cl <sub>4</sub> CuGaP <sub>2</sub> Si, CH <sub>2</sub> Cl <sub>2</sub>	C <sub>37</sub> H <sub>32</sub> AuP <sub>2</sub> Si, 0.45(C <sub>4</sub> H <sub>10</sub> O), Cl <sub>4</sub> Ga, 0.55(CH <sub>2</sub> Cl <sub>2</sub> )
$M_r$	750.58	926.65	1055.21
crystal system	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
$a$ (Å)	11.4211(6)	10.4670(4)	25.7847(6)
$b$ (Å)	12.7243(6)	12.3178(4)	9.9052(2)
$c$ (Å)	14.0664(7)	16.7001(6)	16.9885(4)
$\alpha$ (°)	113.428(2)	107.352(2)	90
$\beta$ (°)	103.894(2)	91.413(2)	90
$\gamma$ (°)	92.722(2)	99.282(2)	90
$V$ (Å <sup>3</sup> )	1797.20(16)	2022.19(13)	4338.91(17)
$Z$	2	2	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.387	1.522	1.615
$\mu$ (mm <sup>-1</sup> )	0.980	1.724	4.442
$F(000)$	772	936	2072
crystal size (mm <sup>3</sup> )	0.48 x 0.4 x 0.4	0.16 x 0.14 x 0.14	0.20 x 0.14 x 0.14
$T/K$	193(2)	193(2)	193(2)
measd reflns	38474	64292	48551
Unique reflns (Rint)	7274 (0.02)	12287 (0.0311)	9816 (0.0346)
reflns used for refinement	7274	12287	9816
refined parameters	438	476	493
GOF on $F^2$	1.037	1.026	1.005
$R_1^a$	0.0281	0.0342	0.027
$[I > 2\sigma(I)]$			
$wR_2^b$ [all data]	0.0768	0.0937	0.0582

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

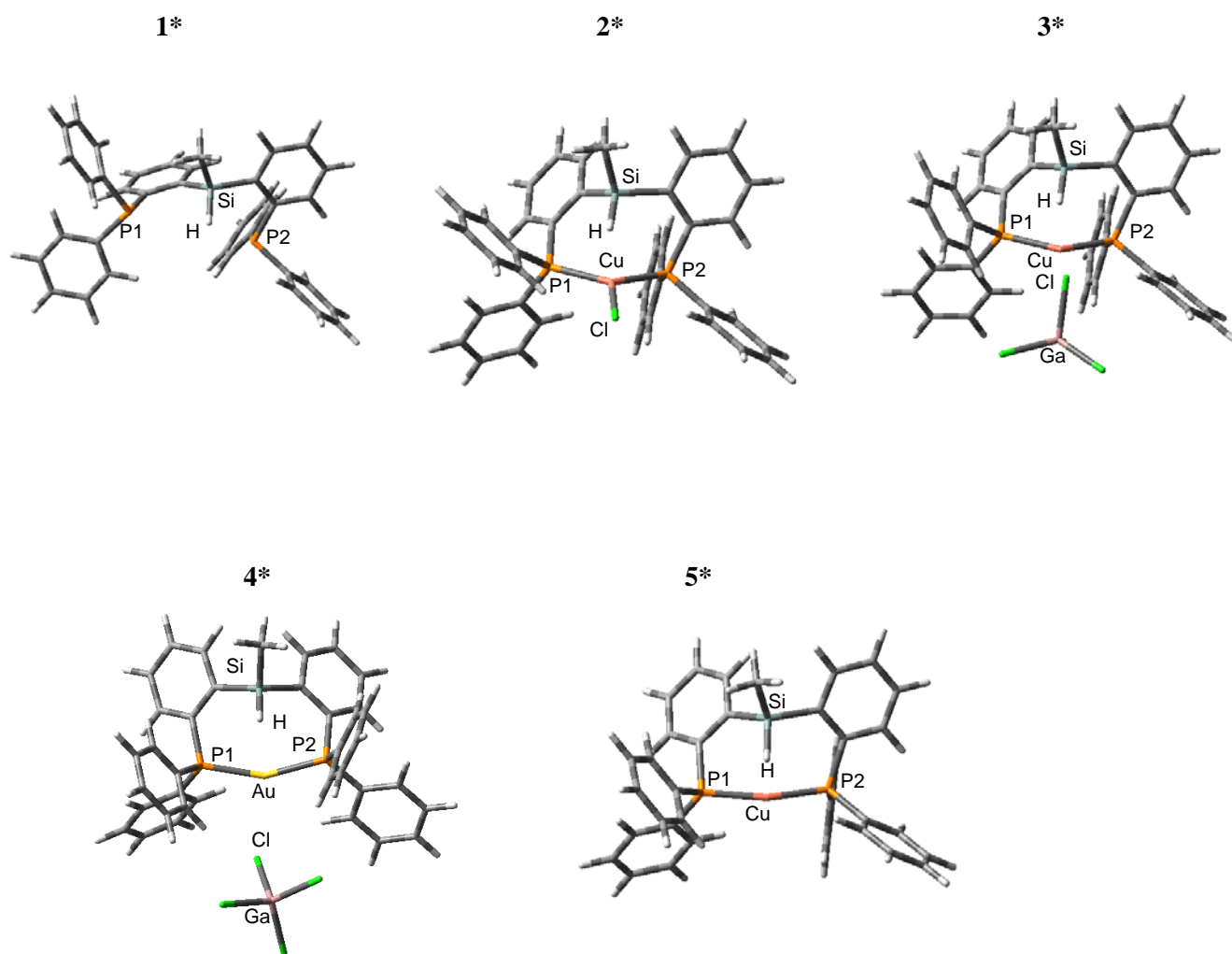
## Computational details

Calculations were carried out with the Gaussian 09 program<sup>5</sup> on the ligand **1\*** and complexes **2\***, **3\***, **4\*** and **5\*** at the DFT level of theory using the hybrid functional B3PW91.<sup>6</sup> B3PW91 is Becke's three parameter functional, with the non-local correlation provided by the Perdew 91 expression. Cu, Au and Ga were treated with the Stuttgart-Dresden set-RECP (relativistic effective core potential) in combination with its adapted basis set.<sup>7</sup> This latter has been augmented by a set of polarization function<sup>8</sup> (f for the metal atoms and d for the Ga atom). All the other atoms (C, H, Si, P, Cl) have been described with a 6-31G(d,p) double- $\zeta$  basis set.<sup>9</sup> Geometry optimizations were carried out without any symmetry restrictions, the nature of the *extrema* was verified with analytical frequency calculations. The bonding situation in all complexes was studied using Natural Bond Orbital analysis (NBO-5 program).<sup>10</sup>  $J_{\text{SiH}}$  coupling constants were evaluated by employing the direct implementation of the Gauge Including Atomic Orbitals (GIAO) method<sup>11</sup> at the B3PW91 density functional level of theory. IGLOO II basis set was used for Si and P atoms.<sup>12</sup>

**Figure S1'.** Plot of computed  $^1J_{\text{SiH}}$  coupling constant (using the GIAO method with IGLOO II basis set) versus Si-H bond length predicted computationally using B3PW91/SDD+f(Cu,Au),6-31G\*\*(other atoms) level of theory.



**Figure S2<sup>7</sup>**. Plot of the geometrical structures of the ligand **1\*** and the complexes **2\*-5\***.



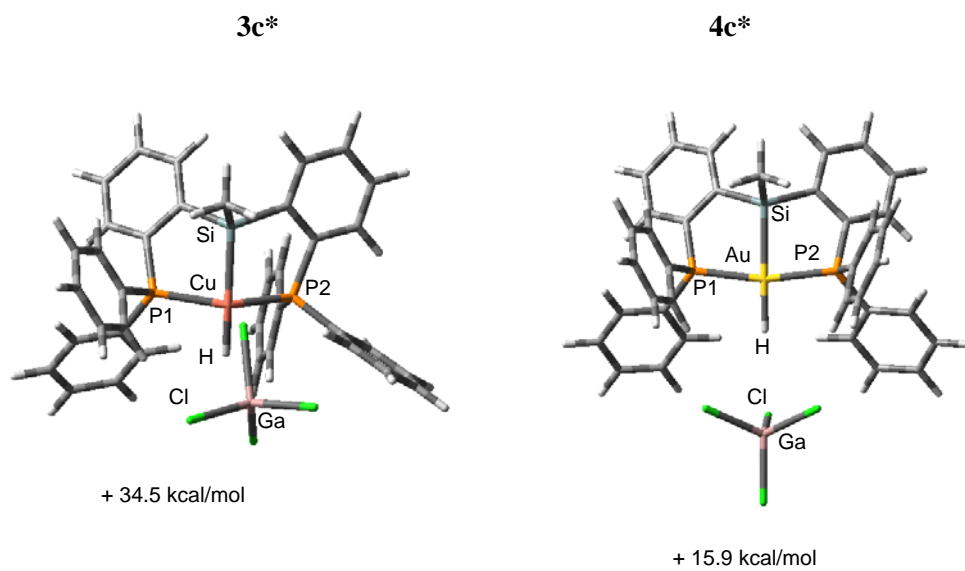
**Table S2.** NBO analyses for ligand **1\*** and complexes **2\*-5\*** at the B3PW91/SDD+f(M), 6-31G\*\*(other atoms) level of theory.

	<b>Ligand 1*</b>	<b>CuCl Complex 2*</b>	<b>CuClGaCl<sub>3</sub> Complex 3*</b>	<b>Cu<sup>+</sup> Complex 5*</b>	<b>Au<sup>+</sup>GaCl<sub>4</sub><sup>-</sup> Complex 4*</b>
<b>NBO</b>					
$\sigma_{\text{SiH}} \rightarrow \text{Lp}^*(\text{M})^{\text{a}}$	–	8.4	12.4	14.3	–
$\text{d}(\text{M}) \rightarrow \sigma^*_{\text{SiH}}^{\text{b}}$	–	0.9	1.1	1.3	0.2
<b>hybridization of Lp*(M)<sup>c</sup></b>	–	98.8%	99%	97.6%	92.9%
<b>NLMO</b>					
$\sigma_{\text{SiH}}^{\text{d}}$	–	0.985 $\sigma_{\text{SiH}} +$ 0.063 Lp*(Cu)	0.984 $\sigma_{\text{SiH}} +$ 0.079 Lp*(Cu)	0.982 $\sigma_{\text{SiH}} +$ 0.081 Lp*(Cu)	0.990 $\sigma_{\text{SiH}} +$ 0.013 Lp*(Au)
<b>Atoms % in <math>\sigma_{\text{SiH}}^{\text{e}}</math></b>	41.1 % Si 57.5 % H	39.9% Si 57.7 % H 0.53% Cu	36.8% Si 60.4% H 0.86 %Cu	36.2% Si 60.9 %H 0.91 % Cu	41.0 % Si 57.7 %H 0.11 % Au

<sup>a</sup> main  $\sigma_{\text{SiH}} \rightarrow \text{M}$  donation in kcal/mol ( $\Delta E_{\text{NBO}}$ ), Lp\*(M) : strong s character; <sup>b</sup> main  $\text{M} \rightarrow \sigma^*_{\text{SiH}}$  back-donation in kcal/mol ( $\Delta E_{\text{NBO}}$ ); <sup>c</sup> % of s character in the Lp\*(M) NBO orbital involved in the main  $\sigma_{\text{SiH}} \rightarrow \text{M}$  donation; <sup>d</sup> composition of the  $\sigma_{\text{SiH}}$  NLMO; <sup>e</sup> participation (%) of the Si, H and M atoms in the  $\sigma_{\text{SiH}}$  NLMO;

For the Cu complexes, a Natural Localized Molecular Orbital (NLMO) involving the  $\sigma_{\text{SiH}} \rightarrow \text{Cu}$  donation with a global stabilizing interaction was found by Second order perturbation theory analysis. The NLMO displays a strong participation of the  $\sigma_{\text{SiH}}$  donor orbital and a weak participation of the Lp\*(Cu) acceptor orbital (mainly s orbital).

**Figure S3'.** Plot of the geometrical structures of the oxidative addition products **3c\*** and **4c\*** deriving from the complexes **3\*** and **4\*** respectively. Relative energy ( $\Delta G$  in kcal/mol) compared with the most stable form **3\*** and **4\***.



## Z-matrices :

1\*

C	-0.81316600	-0.70004900	0.85809100	C	-2.75023900	2.80118700	-1.37036400
C	-0.12923900	-0.70183600	2.08494200	C	-5.36149900	3.45599600	-0.66933900
H	0.77005700	-1.30259800	2.19227400	H	-5.60428000	1.37078900	-0.20243600
C	-0.55623300	0.06603900	3.16588800	C	-3.18710600	4.11872700	-1.46963700
H	0.00513800	0.05131800	4.09589000	H	-1.73312400	2.54762100	-1.66010900
C	-1.68682700	0.86757800	3.03914800	C	-4.49663500	4.44993000	-1.12136200
H	-2.02124700	1.48305200	3.87020000	H	-6.38424000	3.70547500	-0.39895200
C	-2.39002500	0.88146300	1.83703700	H	-2.50775700	4.88654400	-1.82996400
H	-3.26841400	1.51318600	1.73625900	H	-4.84173000	5.47653800	-1.20799200
C	-1.97853700	0.09686900	0.75131100	C	4.06110400	0.65814200	-1.46855900
C	1.62557900	-2.38355000	-0.14270700	C	5.21828300	1.26166100	-0.96079100
C	1.81281000	-3.75404800	0.10779200	C	3.99897400	0.37316700	-2.84145000
H	0.95033800	-4.41413500	0.14261500	C	6.28949300	1.56127600	-1.80271200
C	3.07855900	-4.30473600	0.29578600	H	5.28162600	1.50170800	0.09642700
H	3.18512200	-5.36990100	0.48358500	C	5.07292100	0.66146600	-3.67818200
C	4.20394400	-3.48901400	0.22036200	H	3.09951600	-0.07643800	-3.25583300
H	5.19837100	-3.90976500	0.34419900	C	6.22227800	1.25911500	-3.16068500
C	4.04950800	-2.12612200	-0.01910800	H	7.17982000	2.03081800	-1.39259500
H	4.92898700	-1.49176400	-0.09126900	H	5.00899200	0.42886000	-4.73775300
C	2.77728600	-1.55955400	-0.17929600	H	7.05771200	1.49319400	-3.81471700
Si	-0.13138200	-1.77042100	-0.55730000	C	2.97918700	1.00764500	1.17119600
P	-2.92180700	0.08159700	-0.83874800	C	2.64279900	2.36016200	1.33584500
P	2.56261300	0.25774700	-0.46402300	C	3.56591900	0.32974700	2.24712500
H	-0.05566700	-1.00215900	-1.82510900	C	2.90716100	3.02257800	2.53129400
C	-4.41100000	-0.93442700	-0.44083000	H	2.16201300	2.89441500	0.51978100
C	-5.25309600	-1.26726900	-1.51464100	C	3.81752800	0.98949400	3.45006600
C	-4.71787200	-1.43773200	0.82944500	H	3.82482700	-0.72010500	2.14836900
C	-6.38152700	-2.05835700	-1.31912600	C	3.49431200	2.33707000	3.59420100
H	-5.01880400	-0.90282600	-2.51237000	H	2.64267700	4.07113600	2.63734700
C	-5.84044300	-2.24296000	1.02166300	H	4.27128700	0.44708700	4.27550900
H	-4.07579700	-1.20205600	1.67250800	H	3.69278300	2.84934600	4.53166000
C	-6.67694200	-2.55187800	-0.04842200	C	-1.23564700	-3.27884500	-0.83224900
H	-7.02430400	-2.29936800	-2.16150200	H	-0.81699000	-3.93632600	-1.60152200
H	-6.06124100	-2.62772500	2.01384600	H	-1.37613700	-3.86303300	0.08306200
H	-7.55108500	-3.17884900	0.10417500	H	-2.22567100	-2.95824400	-1.16970600
C	-3.60797600	1.79392200	-0.90181900				
C	-4.92122200	2.13713400	-0.55692900				

2\*

Sum of electronic and zero-point Energies= -3057.858982  
Sum of electronic and thermal Free Energies= -3057.935105

C	-1.05161100	-1.65925700	1.57839000
C	-0.93855700	-2.24406000	2.84965600
H	-0.31209800	-3.12460300	2.98241100
C	-1.59531500	-1.72154200	3.96168500
H	-1.47910100	-2.19296400	4.93378200
C	-2.39601800	-0.59247900	3.81865600
H	-2.91438000	-0.17397900	4.67707700
C	-2.53220000	0.00554600	2.56768600
H	-3.15323100	0.89003500	2.46020400
C	-1.86881900	-0.51286800	1.44914400
C	1.75141600	-2.56687700	0.53328900
C	2.29727900	-3.77372900	1.00355300
H	1.64796700	-4.63233900	1.15316600
C	3.65698900	-3.91551400	1.26834100
H	4.04515000	-4.86572600	1.62493000
C	4.51359800	-2.83976000	1.05741100
H	5.57897200	-2.93779900	1.24646900
C	4.00086500	-1.63226500	0.59241900
H	4.67795400	-0.80275200	0.41413900
C	2.63217100	-1.47835900	0.33680400
Si	-0.11112600	-2.53052100	0.17392500
P	-2.00552100	0.28133500	-0.20934700
P	1.99559900	0.15836300	-0.25145900
Cl	-0.07977100	0.22838500	-3.55331900
Cu	-0.01317800	0.09165200	-1.32329300
H	-0.34336500	-1.89518100	-1.16408400
C	-3.37509000	-0.64421500	-1.01238200
C	-3.38688000	-0.71612000	-2.41263300
C	-4.39706300	-1.26586100	-0.28057800
C	-4.41830500	-1.38932900	-3.06585900
H	-2.57611300	-0.26665400	-2.98361000
C	-5.42134700	-1.94085200	-0.94058300
H	-4.38940200	-1.22722700	0.80511500
C	-5.43457800	-2.00052800	-2.33414900
H	-4.41751900	-1.44264900	-4.15085100
H	-6.20826700	-2.42169400	-0.36571800
H	-6.23329400	-2.52936100	-2.84733000
C	-2.71459900	1.94013600	0.13354800
C	-4.03467200	2.28307500	-0.18126300
C	-1.87364100	2.91269100	0.69459600
C	-4.50487300	3.57239000	0.06639400
H	-4.69513700	1.54463600	-0.62461500
C	-2.35067600	4.19391000	0.95196400
H	-0.84285300	2.66505300	0.93368000
C	-3.66753500	4.52843700	0.63556600
H	-5.53008000	3.82693400	-0.18790100
H	-1.68953000	4.93533100	1.39189600
H	-4.03639000	5.53225500	0.82698900
C	3.37436900	0.82664700	-1.26948900
C	4.45729500	1.52908800	-0.72021700
C	3.33323300	0.59791400	-2.65135800
C	5.48928400	1.98104900	-1.53910800
H	4.48851700	1.73492100	0.34598100
C	4.37236800	1.04882600	-3.46370300
H	2.47057400	0.10417200	-3.09329000
C	5.45042800	1.73714600	-2.91166300
H	6.32226500	2.52681900	-1.10418400
H	4.32617400	0.87269600	-4.53452400
H	6.25451800	2.09358600	-3.54977300
C	2.05584600	1.21398500	1.25642800
C	1.88745100	2.59970200	1.10036000

C	2.20125600	0.69291000	2.54640800
C	1.88295300	3.44114000	2.20924400
H	1.77437700	3.02211700	0.10473800
C	2.18311500	1.53815600	3.65612700
H	2.33316200	-0.37498400	2.68813300
C	2.02808700	2.91181800	3.49225900
H	1.76731300	4.51259600	2.07013100
H	2.29684600	1.11710800	4.65124000
H	2.02130400	3.56856000	4.35754400
C	-0.76929300	-4.29499100	0.04974600
H	-0.21650500	-4.86837200	-0.70098600
H	-0.72855300	-4.83706900	1.00016400
H	-1.81799500	-4.25783300	-0.26196700



## 3\*

Sum of electronic and zero-point Energies= -4440.586505  
 Sum of electronic and thermal Free Energies= -4440.676759

C	0.13573000	-3.29156700	-0.61193100
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H	1.54033300	-4.83979800	-1.15552300
C	0.35493200	-5.44977200	0.51680800
H	0.84779900	-6.41455500	0.59867200
C	-0.65977800	-5.10020100	1.40220900
H	-0.97014200	-5.78948800	2.18248800
C	-1.27864200	-3.85724600	1.29072200
H	-2.06530700	-3.58614900	1.98793200
C	-0.89277000	-2.95025800	0.29682900
C	2.62396000	-1.91213800	-1.89511800
C	3.47857500	-2.67787300	-2.70735500
H	3.05479400	-3.40742700	-3.39248400
C	4.86166600	-2.51968500	-2.67804100
H	5.49195000	-3.12514200	-3.32349600
C	5.42738300	-1.57258100	-1.83029900
H	6.50387200	-1.42911400	-1.80444200
C	4.60553900	-0.79671000	-1.01824000
H	5.05171900	-0.04533200	-0.37386400
C	3.21407600	-0.95955200	-1.03267100
Si	0.76318500	-2.23077000	-2.05511400
P	-1.68154100	-1.28627600	0.18260000
P	2.18355200	0.09713200	0.08333300
Cl	-0.76835800	1.94175700	-1.88071800
Cl	-3.61187500	3.50901800	-0.31735900
Cl	-0.55584600	5.44792900	-0.99647600
Cl	-0.56009300	2.81198600	1.56823900
Cu	-0.02464200	0.15068900	-0.46160700
Ga	-1.41586400	3.54525300	-0.34414500
H	0.04158300	-0.91659600	-2.13581900
C	-3.00664400	-1.50305500	-1.07010900
C	-3.70188100	-0.35968000	-1.49163800
C	-3.33485800	-2.74812900	-1.62130300
C	-4.71274800	-0.46684400	-2.44241500
H	-3.45825200	0.61604200	-1.08106600
C	-4.34207900	-2.84698600	-2.58109900
H	-2.80815600	-3.64159000	-1.29939000
C	-5.03201100	-1.70847300	-2.99175100
H	-5.24371700	0.42639200	-2.75763400
H	-4.58897500	-3.81749000	-3.00284200
H	-5.81632200	-1.78731800	-3.73936100
C	-2.58687500	-1.07625700	1.76038400
C	-3.90602100	-1.51799800	1.92827700
C	-1.92870100	-0.45426000	2.82867000
C	-4.55062200	-1.34687300	3.15115000
H	-4.43114400	-1.98590800	1.10097200
C	-2.57553700	-0.29096800	4.05070400
H	-0.91635600	-0.08484400	2.69756800
C	-3.88611800	-0.73600900	4.21343300
H	-5.57579600	-1.68577300	3.27079000
H	-2.06004500	0.20063700	4.87041500
H	-4.39368700	-0.59665900	5.16375500
C	3.07525500	1.70142500	0.10926400
C	4.07837300	1.99438600	1.04322700
C	2.74246400	2.65476400	-0.86149900
C	4.73975800	3.21967800	0.99892700
H	4.33394500	1.27292800	1.81361300
C	3.40714500	3.87797200	-0.90168600
H	1.94847800	2.45121800	-1.57366400
C	4.40588200	4.16180100	0.02753500
H	5.51242400	3.43975900	1.73035800

H	3.12469400	4.61508700	-1.64679100
H	4.91525700	5.12089700	0.00237400
C	2.47147600	-0.59510200	1.76143200
C	1.99184000	0.13023400	2.86419200
C	3.09073400	-1.83094000	1.97438500
C	2.14662400	-0.37007800	4.15353400
H	1.50782100	1.09174700	2.71190900
C	3.23247700	-2.33218900	3.26848500
H	3.46439800	-2.40404800	1.13193100
C	2.76514000	-1.60386500	4.35901000
H	1.78211700	0.20600700	4.99938100
H	3.71493000	-3.29366500	3.42053900
H	2.88181800	-1.99388600	5.36616500
C	0.39532500	-3.13533700	-3.66710500
H	0.79140400	-2.58492400	-4.52609900
H	0.80272500	-4.15125100	-3.68737400
H	-0.68977900	-3.21225500	-3.78751200

### 3\*c: (oxidative addition)

Sum of electronic and zero-point Energies= -4440.534093  
Sum of electronic and thermal Free Energies= -4440.621812

C	-2.98846600	-0.95693400	-1.50138400
C	-3.97642500	-1.78426800	-2.05215800
H	-3.71680000	-2.49112100	-2.83673800
C	-5.29135200	-1.73659500	-1.59148400
H	-6.04016300	-2.39666000	-2.02111300
C	-5.64602400	-0.85265500	-0.57284800
H	-6.66864300	-0.82248900	-0.20761400
C	-4.68521600	-0.01311200	-0.01348200
H	-4.95642900	0.66760500	0.78842700
C	-3.36654900	-0.06782700	-0.47575300
C	-0.50238100	-2.68202900	-2.30383600
C	-0.81423200	-3.46753700	-3.42458300
H	-1.48135200	-3.08046400	-4.19137400
C	-0.26085800	-4.73508900	-3.58831100
H	-0.50749400	-5.32528200	-4.46671900
C	0.62583700	-5.24117600	-2.63684600
H	1.07016800	-6.22304800	-2.77267100
C	0.95589600	-4.47949000	-1.52007600
H	1.66449400	-4.86246900	-0.79104900
C	0.38820900	-3.21035700	-1.35468200
Si	-1.15572700	-0.91993200	-2.02253800
P	-2.02821700	1.00870800	0.17873500
P	0.76670300	-2.14210200	0.09314500
Cl	1.47480600	1.45179400	-1.28382400
Cl	2.41832600	4.70239800	-0.03818300
Cl	4.95490600	2.22274100	-1.01007100
Cl	2.98239900	1.76865600	2.04638500
Cu	-0.10608100	-0.10892300	-0.09032300
Ga	3.03550700	2.58648700	0.00545600
H	0.38805800	0.14029800	1.32002200
C	-2.15919300	2.58785500	-0.73004800
C	-1.20627400	3.58482600	-0.47792000
C	-3.16832000	2.81600200	-1.67432700
C	-1.26782300	4.79580100	-1.16039000
H	-0.40783200	3.41987900	0.23870300
C	-3.22331100	4.03180700	-2.35380800
H	-3.90871600	2.04887500	-1.87911000
C	-2.27475900	5.02023900	-2.09869900
H	-0.51178600	5.54953300	-0.96579600
H	-4.00876000	4.20270900	-3.08467000
H	-2.31593200	5.96391500	-2.63525700
C	-2.52626500	1.41265300	1.89484200
C	-3.32003100	2.53325800	2.17162800
C	-2.15160100	0.55762600	2.93697300
C	-3.73524600	2.78894500	3.47725700
H	-3.60158100	3.21254400	1.37281100
C	-2.57658000	0.81334100	4.23734500
H	-1.51246300	-0.29565100	2.72959400
C	-3.36686200	1.92936300	4.50994200
H	-4.34087400	3.66621600	3.68578500
H	-2.27763400	0.14661300	5.04080800
H	-3.68617300	2.13443200	5.52779100
C	2.56306700	-2.32002800	0.36856600
C	3.07584800	-3.33639200	1.18741500
C	3.44140400	-1.46189700	-0.30332700
C	4.45323300	-3.48716900	1.32707600
H	2.40530700	-4.00034400	1.72457600
C	4.81732700	-1.61588300	-0.15449100
H	3.05526200	-0.66247300	-0.92721500
C	5.32373700	-2.62740400	0.65883100
H	4.84455000	-4.27298600	1.96710600

H	5.48390500	-0.92505300	-0.66045400
H	6.39729900	-2.73977900	0.78045400
C	-0.02508500	-2.96504700	1.52830600
C	0.28414500	-2.50940000	2.81958600
C	-0.94604500	-4.00563800	1.36872600
C	-0.30591700	-3.10481800	3.93000100
H	0.98914100	-1.69287500	2.95079100
C	-1.54569200	-4.58773600	2.48601900
H	-1.19377500	-4.36690000	0.37572700
C	-1.22451200	-4.14313400	3.76540000
H	-0.04885600	-2.75507300	4.92580500
H	-2.26108900	-5.39386700	2.35114900
H	-1.68783200	-4.60235000	4.63400300
C	-0.95250600	0.07187100	-3.61432200
H	0.10136300	0.12226300	-3.90200500
H	-1.51540800	-0.39006800	-4.43430000
H	-1.31591300	1.09486300	-3.48393300

## 4\*

Sum of electronic and zero-point Energies= -2535.931353  
 Sum of electronic and thermal Free Energies= -2536.008032

C	-4.60491900	1.26446800	2.17511300
H	-5.55598200	1.56021500	1.72300400
H	-4.22358200	2.12899000	2.72845300
H	-4.80392900	0.46737100	2.89870800
C	-3.85999100	-0.92780600	0.15010400
C	-5.25519900	-1.03797400	0.01357800
H	-5.89065800	-0.23217400	0.37032200
C	-5.87348400	-2.14830500	-0.55732100
H	-6.95564000	-2.17917300	-0.64791600
C	-5.09737400	-3.21007400	-1.00298800
H	-5.55811800	-4.08578100	-1.45070800
C	-3.71331300	-3.14676900	-0.86782600
H	-3.10960700	-3.97999800	-1.21369400
C	-3.08692000	-2.02749800	-0.30263200
C	-0.89848800	-2.84361000	1.47524700
C	-1.89999600	-3.41378600	2.26990800
H	-2.93066300	-3.42264900	1.92885200
C	-1.57131100	-3.97046200	3.50495500
H	-2.35129600	-4.40968500	4.12052000
C	-0.24965100	-3.96360000	3.94719400
H	0.00180800	-4.39726600	4.91100500
C	0.75046600	-3.39892700	3.15544600
H	1.78424500	-3.38616900	3.48626000
C	0.43068900	-2.83433100	1.92444600
H	1.22002100	-2.39748300	1.31781400
C	-0.68465700	-3.28650100	-1.40711400
C	-0.42790000	-4.62489200	-1.08895300
H	-0.54936800	-4.97523400	-0.06845200
C	0.00137400	-5.50528500	-2.08028000
H	0.20975800	-6.54029100	-1.82570600
C	0.17394300	-5.05723100	-3.38794400
H	0.51766700	-5.74374100	-4.15619800
C	-0.07729100	-3.72317600	-3.70770100
H	0.07395500	-3.36678000	-4.72221700
C	-0.49847300	-2.83763800	-2.72114000
H	-0.66703300	-1.79210900	-2.96645300
C	-3.16393800	2.09738300	-0.38143700
C	-4.39614600	2.45014600	-0.95429900
H	-5.29788600	1.92280400	-0.65185200
C	-4.51679500	3.45081600	-1.91723700
H	-5.49002900	3.67987700	-2.34205500
C	-3.38732900	4.14761100	-2.32722700
H	-3.46164600	4.93133100	-3.07552500
C	-2.14765400	3.83154400	-1.77523700
H	-1.26464200	4.37024800	-2.10403500
C	-2.02367400	2.81937600	-0.81719000
C	-0.25301200	3.04124400	1.50624400
C	-1.19068500	3.95705400	1.99872600
H	-2.01550200	4.28442500	1.37245400
C	-1.06593000	4.44930200	3.29730300
H	-1.79527200	5.16034000	3.67520600
C	-0.00926500	4.03274100	4.10464600
H	0.08505900	4.41699900	5.11636100
C	0.92771000	3.12365600	3.61359200
H	1.75683300	2.79893700	4.23493900
C	0.80907400	2.62341600	2.32008500
H	1.55295300	1.92480800	1.94456400
C	0.87689100	3.31129100	-1.16272700
C	1.10362200	4.67555500	-0.92909400
H	0.55331800	5.19491700	-0.14933400
C	2.05020700	5.36075800	-1.68426400

H	2.22795600	6.41576500	-1.49712400
C	2.78073300	4.68966500	-2.66553800
H	3.52911800	5.22408200	-3.24357700
C	2.56953800	3.33132200	-2.88902700
H	3.15779500	2.79996400	-3.63072000
C	1.62177800	2.63883600	-2.13848000
H	1.49018100	1.57031000	-2.28353500
Si	-3.27934500	0.71628600	0.94204600
H	-2.04771100	0.54892700	1.74710700
P	-1.25043800	-2.09067500	-0.14946600
P	-0.34965000	2.37786200	-0.19296900
Au	-0.33310200	0.04703800	-0.30580300
Cl	4.21556500	-2.32507000	1.71939600
Cl	6.03053800	-0.81975200	-1.10118000
Cl	4.09558200	1.26879800	1.19512500
Cl	2.41711900	-0.98125800	-1.09778800
Ga	4.26708500	-0.70966700	0.20160900

#### 4\*c : (oxidative addition)

Sum of electronic and zero-point Energies= -4378.989030  
Sum of electronic and thermal Free Energies= -4379.078820

C	3.92032500	0.00157600	1.79979500
H	5.01073100	0.00213400	1.68813900
H	3.63614700	-0.88456500	2.37510300
H	3.63524500	0.88737900	2.37517600
C	3.51104800	1.60590100	-0.81197700
C	4.76762500	1.87184200	-1.37415900
H	5.56093000	1.13277500	-1.30081700
C	5.02976100	3.06526700	-2.04491600
H	6.00834400	3.23571900	-2.48517800
C	4.03504500	4.03328300	-2.15995600
H	4.22956300	4.95926100	-2.69306800
C	2.78277300	3.81045400	-1.59297100
H	2.00426600	4.56100800	-1.68986900
C	2.52277900	2.61128000	-0.92047500
C	0.99051900	2.98388400	1.57774900
C	2.14499000	3.60437100	2.06864900
H	3.01671000	3.72208300	1.43180800
C	2.17134100	4.07745600	3.38007500
H	3.06680500	4.56215800	3.75843100
C	1.05363000	3.93138300	4.19900500
H	1.07803900	4.30013200	5.22049500
C	-0.09801600	3.31532500	3.70793200
H	-0.97353200	3.20397000	4.34039000
C	-0.13701800	2.83889900	2.40097700
H	-1.04298000	2.36869300	2.02338800
C	-0.35763900	3.31505000	-0.97838900
C	-0.44512300	4.69379100	-0.72858100
H	0.19963700	5.16114500	0.01087400
C	-1.38532900	5.46009600	-1.40961200
H	-1.45776600	6.52520500	-1.20976600
C	-2.24837100	4.85678500	-2.32505700
H	-2.99491800	5.45497600	-2.83938200
C	-2.17685600	3.48570600	-2.55646200
H	-2.87586200	3.00045100	-3.22949100
C	-1.23305500	2.71195000	-1.88536800
H	-1.21952900	1.63665800	-2.03128100
C	3.51232000	-1.60321000	-0.81195100
C	4.76914600	-1.86812200	-1.37406900
H	5.56191800	-1.12850700	-1.30047700
C	5.03220700	-3.06121300	-2.04505700
H	6.01094600	-3.23086700	-2.48527700
C	4.03819800	-4.02992200	-2.16038400
H	4.23342600	-4.95563600	-2.69369600
C	2.78573400	-3.80815000	-1.59340900
H	2.00780400	-4.55928000	-1.69047200
C	2.52481000	-2.60930500	-0.92068700
C	0.99309500	-2.98318400	1.57767500
C	2.14802700	-3.60297800	2.06836300
H	3.01971700	-3.72011400	1.43137600
C	2.17488100	-4.07611400	3.37975900
H	3.07070600	-4.56027700	3.75795000
C	1.05721100	-3.93077300	4.19887500
H	1.08201100	-4.29956100	5.22034200
C	-0.09489200	-3.31539900	3.70801800
H	-0.97037400	-3.20461600	4.34062300
C	-0.13439800	-2.83893600	2.40109200
H	-1.04071000	-2.36927500	2.02367000
C	-0.35503700	-3.31560200	-0.97822300
C	-0.44101400	-4.69444700	-0.72842700
H	0.20444800	-5.16115400	0.01082300
C	-1.38062300	-5.46172000	-1.40918500
H	-1.45187600	-6.52691100	-1.20934600
C	-2.24458600	-4.85929200	-2.32434500
H	-2.99066600	-5.45825000	-2.83845600
C	-2.17456800	-3.48813600	-2.55573600
H	-2.87428000	-3.00358600	-3.22854100
C	-1.23136500	-2.71340200	-1.88492400
H	-1.21901000	-1.63809700	-2.03084800
Si	3.05785800	0.00117700	0.11874900

H	-0.99126800	-0.00052800	-0.34026700
P	0.89309600	2.31893800	-0.11758900
P	0.89494100	-2.31831900	-0.11766200
Au	0.61901500	0.00018200	-0.06806700
Cl	-3.58753200	1.81144600	1.11662400
Cl	-6.60353100	-0.00228100	0.16836200
Cl	-3.58591000	-1.81342700	1.11683300
Cl	-3.72292600	-0.00134200	-2.04335500
Ga	-4.40434000	-0.00141200	0.09920800

## 5\*

Sum of electronic and zero-point Energies= -2597.487944 ua  
 Sum of electronic and thermal Free Energies= -2597.563065 ua

C	1.18976400	-1.48297700	-1.67766500
C	1.11919400	-1.94230100	-3.00278100
H	0.39755900	-2.71284900	-3.26770400
C	1.94459100	-1.43578000	-4.00468400
H	1.85947500	-1.81257300	-5.01961800
C	2.87377900	-0.44676500	-3.69831600
H	3.52422400	-0.04554000	-4.46973200
C	2.96301000	0.03835300	-2.39548400
H	3.67485200	0.82510000	-2.16423500
C	2.13524700	-0.46689400	-1.38631700
C	-1.77805800	-2.31513200	-0.91143700
C	-2.29398900	-3.42585500	-1.60299600
H	-1.63642200	-4.25185600	-1.86053000
C	-3.63750200	-3.51902600	-1.95784300
H	-3.99710100	-4.39382400	-2.49148600
C	-4.51690300	-2.49842100	-1.60967400
H	-5.56974200	-2.56589100	-1.86641800
C	-4.03971600	-1.38947200	-0.91825500
H	-4.73235600	-0.60180400	-0.63542200
C	-2.68453800	-1.27993300	-0.57913100
Si	0.06178900	-2.39905600	-0.45048000
P	2.19424000	0.26717200	0.30035200
P	-2.15186500	0.23075100	0.32562200
H	0.23086600	-1.82389400	0.93816000
C	3.30799000	-0.78017300	1.29832200
C	3.26965800	-0.64876700	2.69438500
C	4.18915100	-1.69894700	0.71473800
C	4.10915200	-1.41982500	3.49283400
H	2.58715400	0.06088900	3.15646100
C	5.02316600	-2.47320700	1.52053800
H	4.22423700	-1.81069300	-0.36508200
C	4.98504000	-2.33386300	2.90648500
H	4.07731200	-1.31034600	4.57269400
H	5.70503700	-3.18362700	1.06262100
H	5.63608500	-2.93816600	3.53105900

C	3.01588800	1.88794700	0.14284300
C	4.38882600	2.04530300	0.37097000
C	2.24094200	2.99874100	-0.21996500
C	4.97806900	3.30022600	0.23000300
H	4.99423000	1.19311100	0.66473700
C	2.83743500	4.24747900	-0.36680700
H	1.17234600	2.88635100	-0.38754200
C	4.20541500	4.39936400	-0.14017600
H	6.04203000	3.41796500	0.41226000
H	2.23320700	5.10419100	-0.64979500
H	4.66752800	5.37628900	-0.24641200
C	-3.28537700	0.38495600	1.75176500
C	-4.48481800	1.10572300	1.68929300
C	-2.94020200	-0.27920500	2.93711500
C	-5.32685200	1.15311800	2.79818300
H	-4.75644400	1.64051900	0.78392200
C	-3.78797900	-0.23318000	4.04005200
H	-2.00857000	-0.83752300	2.99709400
C	-4.98186400	0.48368100	3.97115200
H	-6.25389100	1.71612900	2.74485000
H	-3.51385600	-0.75118000	4.95411700
H	-5.64063100	0.52507800	4.83333600
C	-2.51167800	1.64980500	-0.77293700
C	-2.40872500	2.94319800	-0.23544200
C	-2.79588900	1.49251900	-2.13401600
C	-2.61005300	4.05642500	-1.04514900
H	-2.18536300	3.08056400	0.81975300
C	-2.98683700	2.61349600	-2.94180300
H	-2.87328300	0.50027100	-2.56652200
C	-2.89837300	3.89334100	-2.40084200
H	-2.54244600	5.05215900	-0.61695700
H	-3.21041400	2.48126500	-3.99619000
H	-3.05399700	4.76312100	-3.03195800
C	0.62474300	-4.18934800	-0.33565600
H	-0.03136600	-4.76913200	0.32039700
H	0.65768600	-4.67995400	-1.31359900
H	1.63684700	-4.22087200	0.07939600
Cu	0.02049400	0.12403600	0.78164300

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