Supplementary Information for DT-ART-02-2013-050555

Influence of a Thioether Function in Short-Bite Diphosphine Ligands on the Nature of their Silver Complexes: Structure of a Trinuclear Complex and of a Coordination Polymer.

Vitor Rosa,[a,b] Christophe Fliedel,[a,b] Alessio Ghisolfi,[a] Roberto Pattacini,[a] Teresa Avilés[b] and Pierre Braunstein*[a]

[a] Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, F-67081 Strasbourg Cedex, France. E-mail: braunstein@unistra.fr; Fax: +33 3-6885-1322.

[b] REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal.

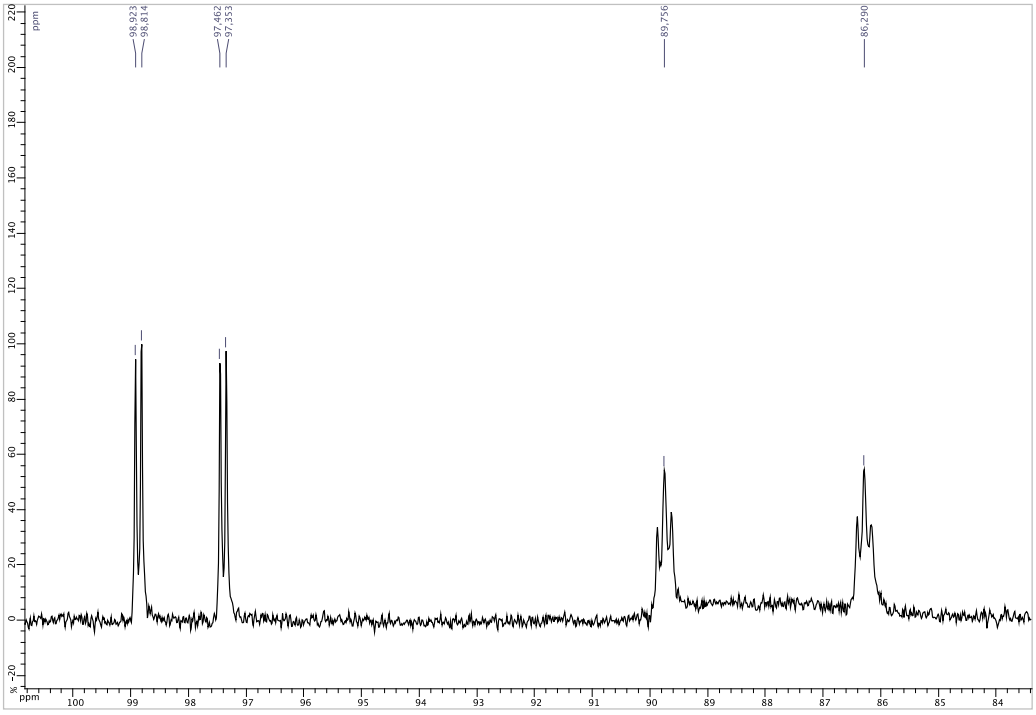


Figure S1. ^{31}P NMR spectrum of the crude reaction mixture of complex **1**·BF_4 after 1 h reaction.

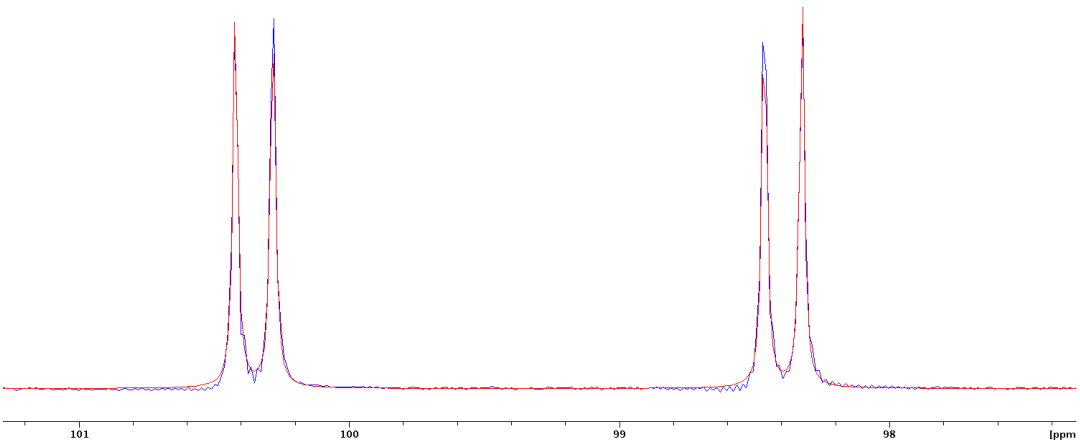


Figure S2. Simulation (red line) and ^{31}P NMR spectrum (blue line) of complex **1**·BF_4.

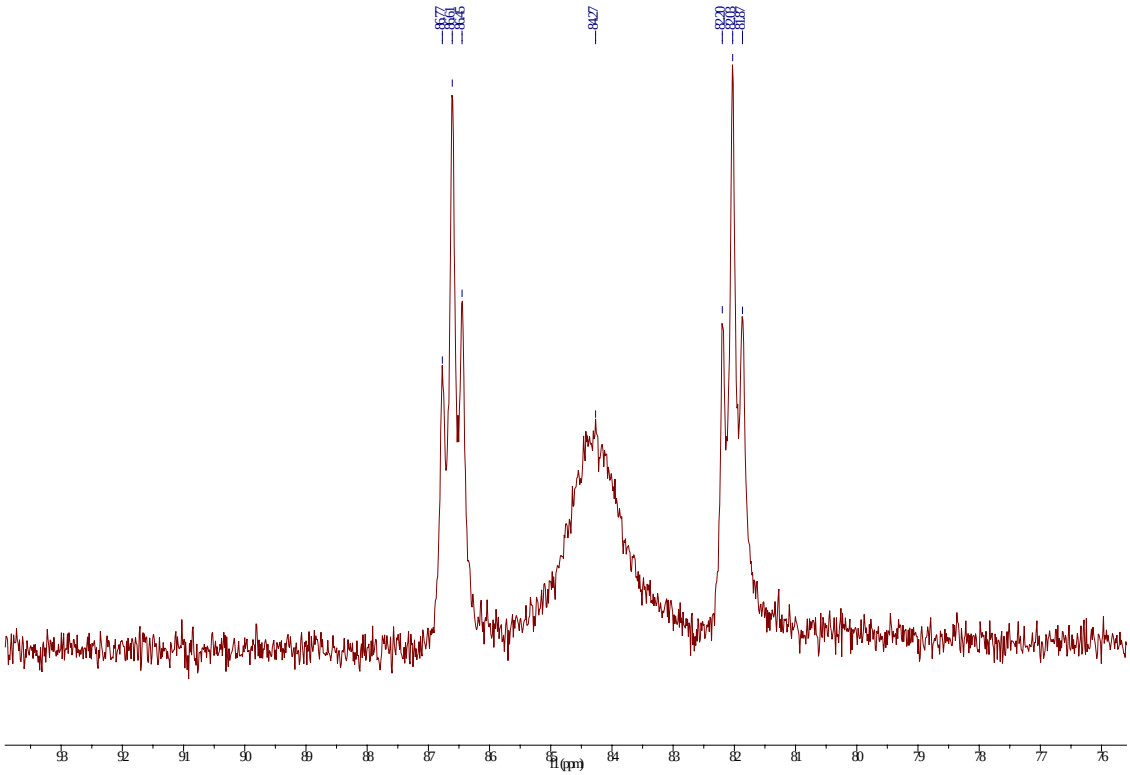


Figure S3. Detail of ^{31}P NMR spectrum of complex **2**.

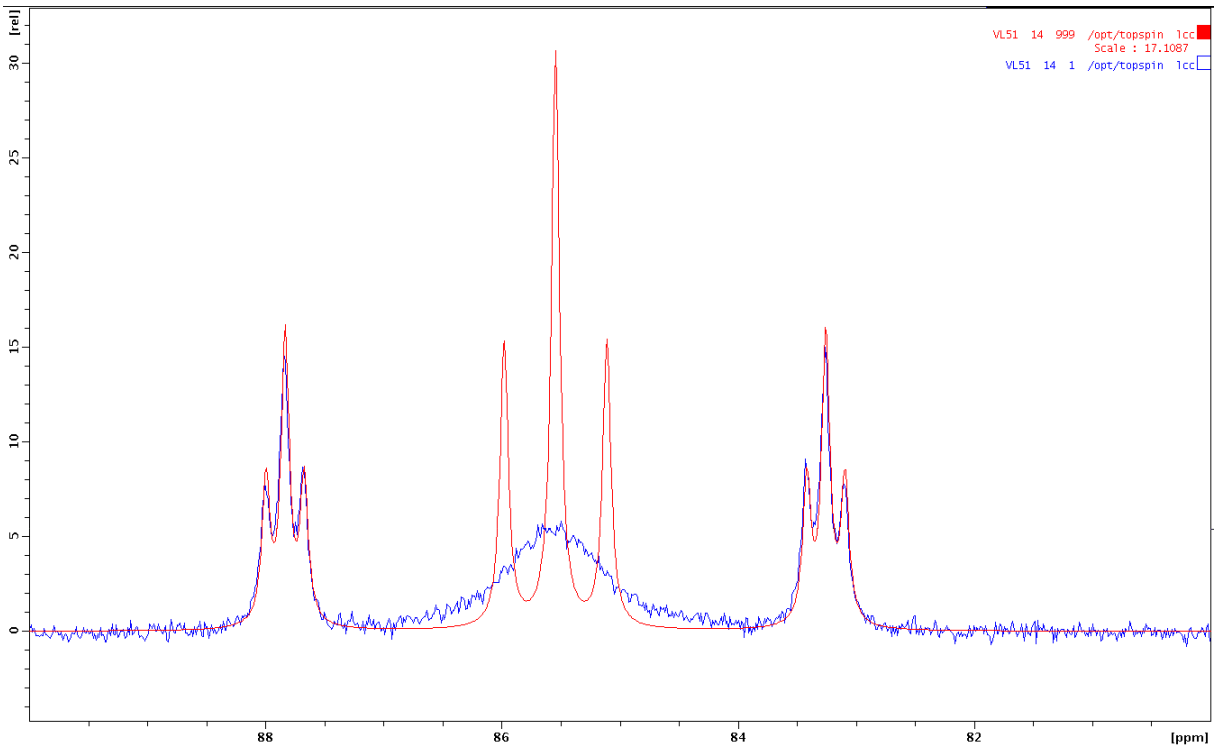


Figure S4. Simulation (red line) and ^{31}P NMR spectrum (blue line) of complex **2**.

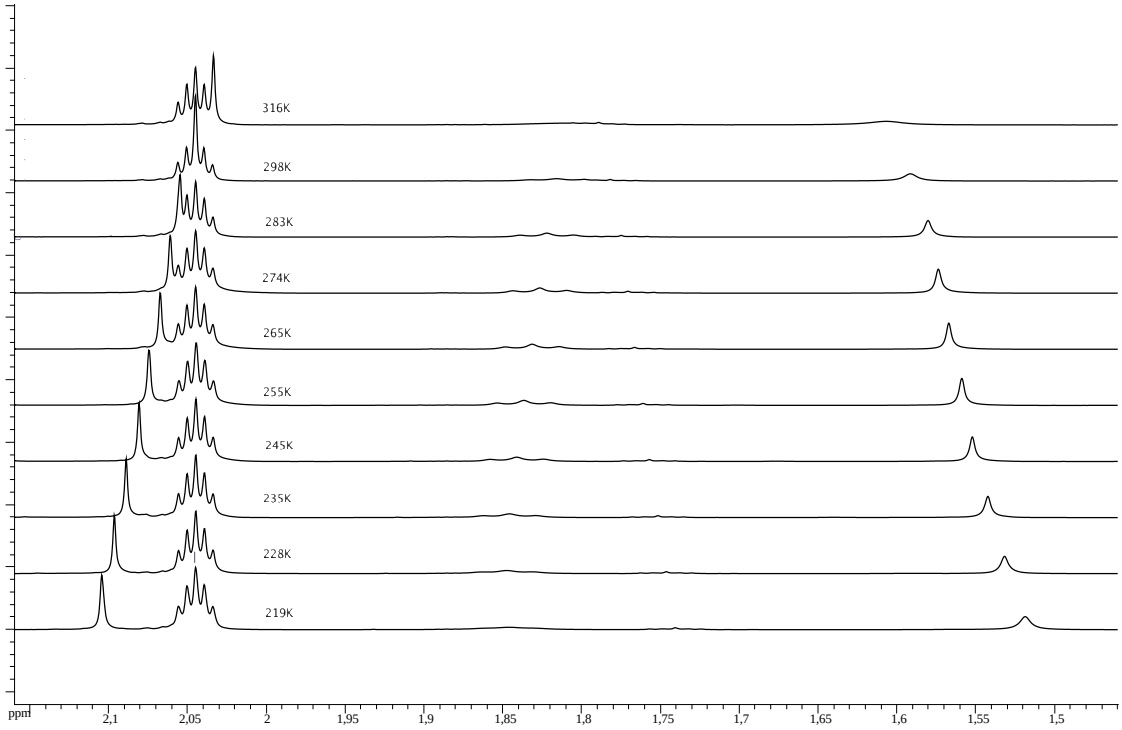


Figure S5. Variable-temperature ^{1}H NMR spectra of complex **2**.

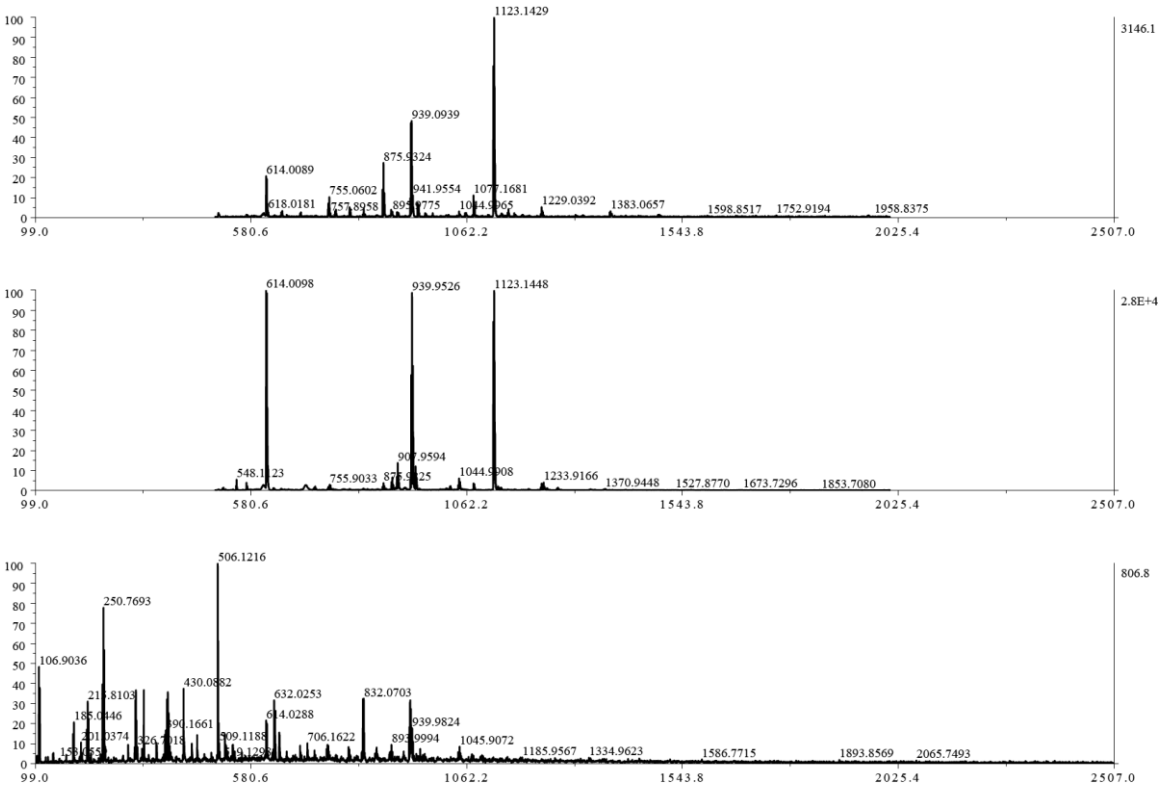


Figure S6. MALDI-TOF-MS of complex **1**·BF_4. Top spectra made with Dithranol as a matrix, middle spectra with DHB as matrix and bottom spectra without matrix.

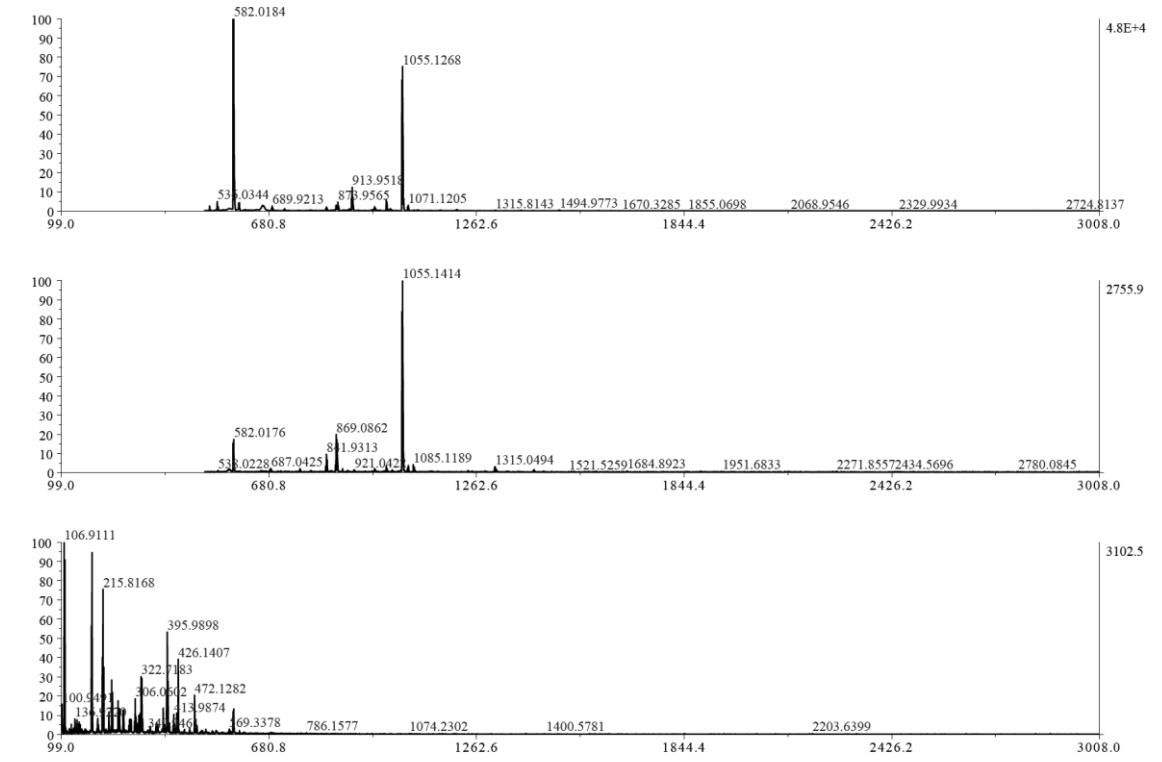


Figure S7. MALDI-TOF-MS of complex **2**. Top spectra made with Dithranol as a matrix, middle spectra with DHB as matrix and bottom spectra obtained without matrix.

Table S1. Summary of X-ray diffraction data for **1**·CH_2Cl_2[a] and **2**·THF.

Compound	**1**·CH_2Cl_2[a]	**2**·THF
Chemical formula	$C_{93}H_{81}Ag_3Cl_2N_3P_6S_3·CH_2Cl_2$ [a]	$C_{62}H_{67}Ag_2B_2F_8N_5P_4S_2·C_4H_8O$
M_r	2002.04	1531.67
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	10.4426 (2)	14.0539(4)
b (Å)	18.5138 (4)	15.7062(5)
c (Å)	25.2621 (5)	17.3266(4)
α (°)	75.624 (1)	85.636(2)
β (°)	87.474 (1)	66.492(2)
γ (°)	87.744 (1)	81.586(2)
V (Å^3)	4724.41 (17)	3468.73(17)
Z	2	2
T (K)	173(2)	173(2)
μ(Mo-Kα) (mm^{-1})	0.94	0.78
Meased. reflect.	45711	24350
Independ. reflect.	21443	16710
R_{int}	0.072	0.029
R_1 [$I > 2\sigma(I)$]	0.057	0.049
$wR(F^2)$ [$I > 2\sigma(I)$]	0.145	0.123
R_1 (all data)	0.088	0.083
$wR(F^2)$ (all data)	0.159	0.143
S on F^2	1.02	1.07
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.10, -1.24	1.57, -1.03

[a] The BF_4 anion which should balance the charge of the complex, was found severely disordered and since attempts to identify the atomic positions failed, a PLATON-SQUEEZE procedure was applied.

Table S2. Summary of X-ray diffraction data for **3**·3CH_2Cl_2 and **4**.

Compound	**3**·3(CH_2Cl_2)	**4**
Chemical formula	$C_{60}H_{50}Ag_2B_2F_8N_2P_4$·3($CH_2Cl_2$)	$C_{56}H_{58}Ag_2B_2F_8N_2P_4$
M_r	1567.04	1531.67
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a (Å)	22.4879 (6)	24.3815 (5)
b (Å)	13.4545 (4)	12.3048 (5)
c (Å)	23.2743 (6)	22.7761 (7)
α (°)	90	90
β (°)	108.176 (2)	109.652 (2)
γ (°)	90	90
V (Å^3)	6690.6 (3)	6435.0 (4)
Z	4	4
T (K)	173(2)	173(2)
μ(Mo-Kα) (mm^{-1})	0.98	0.77
Meased. reflect.	18664	19694
Independ. reflect.	7625	7348
R_{int}	0.055	0.051
R_1 [$I > 2\sigma(I)$]	0.065	0.073
$wR(F^2)$ [$I > 2\sigma(I)$]	0.164	0.199
R_1 (all data)	0.103	0.096
$wR(F^2)$ (all data)	0.198	0.212
S on F^2	1.07	1.07
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.07, -1.56	0.82, -1.34

Table S3. Selected bonds lengths (Å) and angles (º) in complexes **3**·3(CH_2Cl_2) and **4**.

Complex **3**·3(CH_2Cl_2)		Complex **4**	
Ag1—Ag1'	2.8946(7)	Ag1—Ag1'	2.8848(10)
Ag1—P1	2.4072(12)	Ag1—P1	2.4077(14)
Ag1—P2	2.4047(12)	Ag1—P2	2.4133(14)
P—N—P (aver.)	121.6(2)	P—N—P (aver.)	116.5(17)

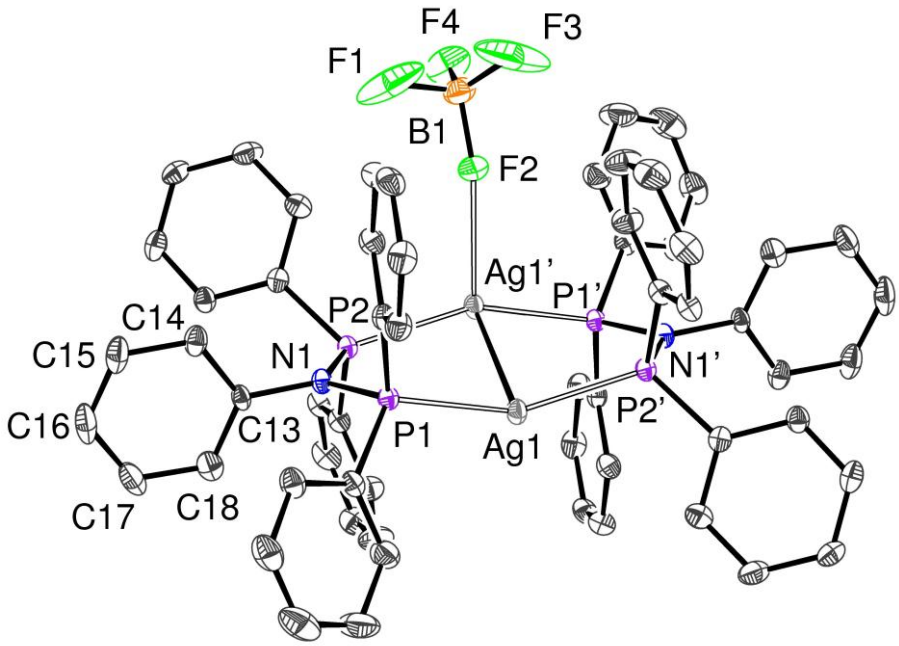


Figure S8. ORTEP view of the centrosymmetric complex **3** in **3**·3(CH_2Cl_2) showing the interaction between one of the BF_4^- anions and a silver atom. Ellipsoids represented at 30% probability levels. A BF_4^- anion and H atoms are omitted for clarity. The asymmetric unit contains half a molecule of the complex and 1.5 molecules of CH_2Cl_2 (omitted for clarity). The carbon atom of the half molecule of CH_2Cl_2 is disordered over two positions.

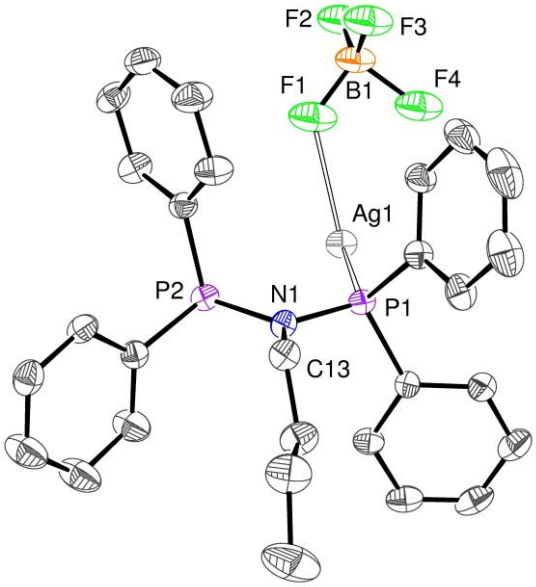
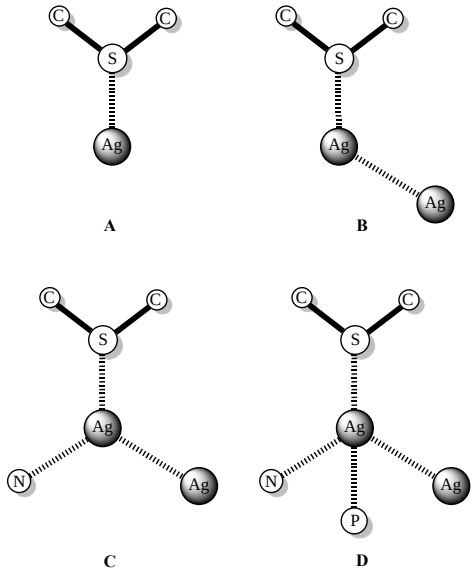


Figure S9. Partial ORTEP view of the complex **4** showing the bond between an F atom of the BF_4^- and a silver atom. Ellipsoids represented at 30% probability levels. H atoms are omitted for clarity. There is half a molecule of complex in the asymmetric unit. The F atoms of BF_4^- are disordered over 2 positions and a PLATON-SQUEEZE procedure was applied. The residual electron density was assigned to two molecules of acetone.

A search in CSD with the fragments presented in Scheme S1 gave us useful information about the Ag-S distances. The search with fragment A gave around 700 hits. Their analysis with respect to the Ag-S bond length gave a median length (non normalized) of 2.573 Å (Figure S10). For comparison, in complex **2** this distance is 2.903 Å. From the histogram shown in Figure S10 we see that this length is not of common occurrence for an Ag-S bond. For fragment B, we obtain the histogram presented in Figure S11. The number of hits was 47, and only two structures displayed almost the same Ag-S length as the one found in our complex. The median value was 2.556 Å. The search for fragment C gave 7 hits and no hit was obtained from a search with fragment D.



Scheme S1: Fragments used for the search in the CSD database.

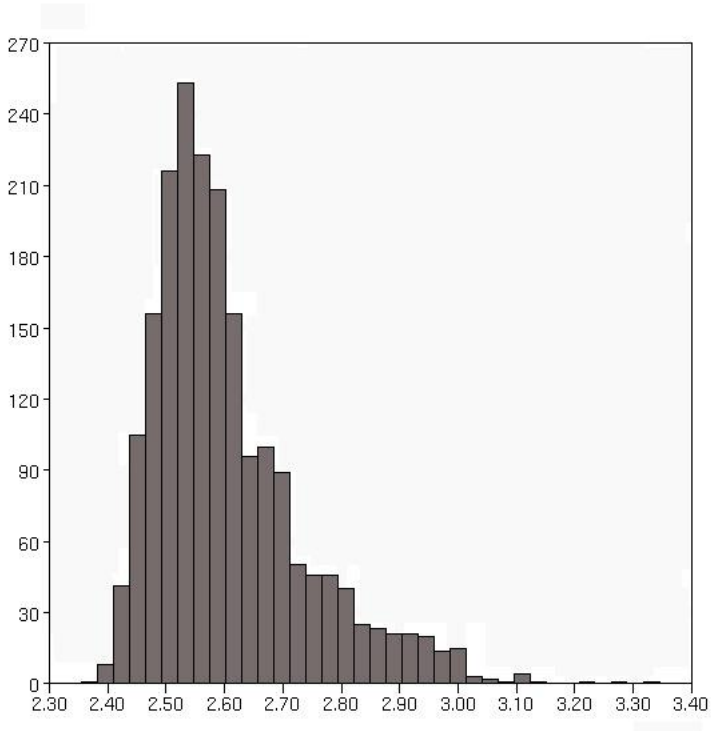


Figure S10. Histogram of the distance Ag···S results coming from fragment **A**.

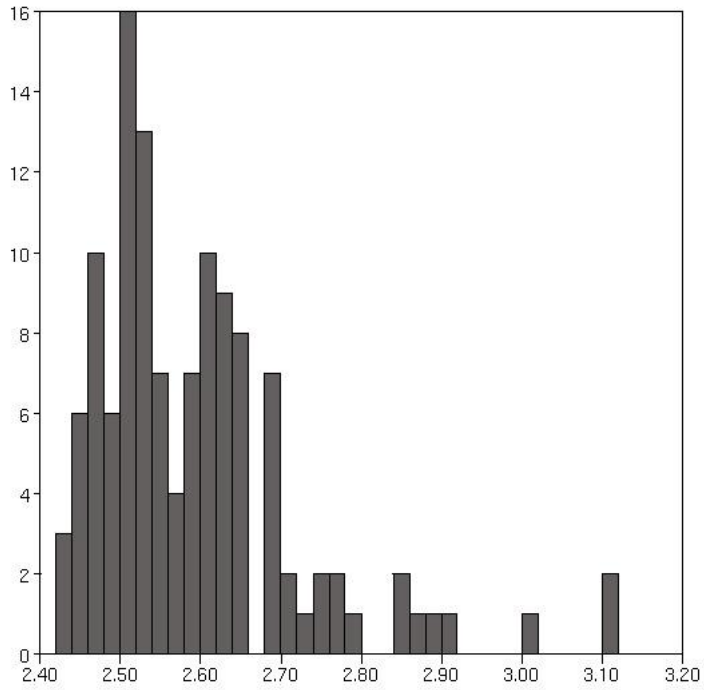


Figure S11. Histogram of distances Ag···S, results from fragment **B**.