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The ligand [Cp$_2$MoH$_2$] in complexes with Ag–S bonds

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Abstract

The reaction of [Cp$_2$MoH$_2$] and AgBF$_4$ with the dithio-ligands Na(S$_2$CNR$_2$) (R = Et, Ph), Na(S$_2$CMe), NH$_4$(S$_2$P(OEt)$_2$) and K(S$_2$CO^{i}Pr) gives the complexes [(Cp$_2$MoH$_2$AgS$_2$CNR$_2$)$_2$] (R = Et **1**, Ph **2**), [(Cp$_2$MoH$_2$AgS$_2$CMe)$_2$] (**3**), [(Cp$_2$MoH$_2$AgS$_2$P(OEt)$_2$)$_2$] (**4**) and [(Cp$_2$MoH$_2$AgS$_2$CO^{i}Pr)$_n$] (**6**) with probably $n = 2$, all with a [Cp$_2$MoH$_2$]:Ag:dithio-ligand stoichiometry of 1:1:1. **1**–**4** form dimers in which two dithio-ligands bridge two silver atoms. In **1** and **2** one sulphur atom is coordinated to one silver atom, whereas the other is coordinated to both silver atoms. In **3** and **4** each sulphur atom is bonded to one silver atom only. In **1**–**3** there is a silver–silver bond. However, in **4** the Ag···Ag distance is too long for an Ag–Ag bond. Crystallization of the compound **6** afforded a polymer [(Cp$_2$MoH$_2$Ag$_4$(S$_2$CO^{i}Pr)$_4$)$_n$] (**7**) with a stoichiometry [Cp$_2$MoH$_2$]:Ag:dithio-ligand = 1:4:4. The polymer forms sheets with rings surrounding a [Cp$_2$MoH$_2$] ligand bonded to one of the four silver atoms. The monomer [(Cp$_2$MoH$_2$)$_2$AgS$_2$COEt] (**5**) with a stoichiometry [Cp$_2$MoH$_2$]:Ag:dithio-ligand = 2:1:1 was prepared by addition of Na(S$_2$COEt) to [Cp$_2$MoH$_2$] and AgBF$_4$. In **5** the xanthogenate ligand is bonded with both sulphur atoms to the silver atom. The compounds **1**–**6** were characterized analytically and spectroscopically. The structures of **1**–**5** and **7** were determined by single crystal X-ray analyses. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Silver; Dithio-ligands; Clusters; Crystal structures

1. Introduction

The complex [Cp$_2$MoH$_2$] [1] has three low-lying molecular orbitals between the two bent cyclopentadienyl rings [2]. The two outer orbitals are used to bind the σ-bonded hydride ligands, the orbital in the middle contains a lone pair of electrons. The angle between the two hydrogen atoms is 75.5° and the Mo–H distance is 1.685 Å [3]. In dilute acids [Cp$_2$MoH$_2$] behaves as a base and the resulting pale yellow cation [Cp$_2$MoH$_3$]$^+$ is soluble in water [4]. Protonation and deprotonation are reversible. Addition of Lewis acids such as BF$_3$ or GaMe$_3$ [5] gives adducts like [Cp$_2$MoH$_2$·BF$_3$] [6]. By reaction with [M(CO)$_5$(thf)] (M = Cr, Mo, W) the complexes [Cp$_2$MoH$_2$–M(CO)$_5$] were obtained [7]. In 1992 the reaction of [Cp$_2$WH$_2$] with AgBF$_4$ was reported to give [(Cp$_2$WH$_2$)$_2$Ag]BF$_4$ [8]. With silver(I) halides three different structure types were isolated [(Cp$_2$MoH$_2$)$_2$AgCl], [(Cp$_2$MoH$_2$)$_3$Ag$_3$X$_3$] (X = Br, I) and [(Cp$_2$MoH$_2$)$_4$Ag$_3$Br$_2$]PF$_6$ [9]. Here we describe the coordination chemistry of dithio-ligands with [Cp$_2$MoH$_2$] and AgBF$_4$.

2. Preparation of compounds 1–7

In acetone, [Cp$_2$MoH$_2$] and AgBF$_4$ in a molar ratio of 2:1 give a yellow solution of [(Cp$_2$MoH$_2$)$_2$Ag]BF$_4$. However, [Cp$_2$MoH$_2$] and AgBF$_4$ in a molar ratio of 1:1 afford a yellow suspension, for which the composition [(Cp$_2$MH$_2$Ag)$_2$](BF$_4$)$_2$ (M = W) was proposed [8]. In the following syntheses we used both 2:1 solutions and 1:1 suspensions of [Cp$_2$MoH$_2$] and AgBF$_4$ in acetone.

Solutions of Na(S$_2$CNEt$_2$) or Na(S$_2$CNPh$_2$) in acetone reacted rapidly with [Cp$_2$MoH$_2$] and AgBF$_4$, dissolved in acetone, in a molar ratio 1:1:1 to give the microcrystalline complexes [(Cp$_2$MoH$_2$AgS$_2$CNEt$_2$)$_2$]

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[1] X-ray structure analyses.

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(**1**) and [$(Cp_2MoH_2AgS_2CNPh_2)_2$] (**2**), respectively. A twofold excess of [Cp_2MoH_2] afforded the same products. **1** and **2** are insoluble in methanol, ether and toluene. In solution (CH_2Cl_2, $CHCl_3$) the complexes **1** and **2** are very air-sensitive. The solids can be handled in air for a short time. Under nitrogen they can be stored for months. X-ray quality single crystals were grown from methylene chloride (yellow green needles of **1**) and acetone (translucent yellow plates of **2**).

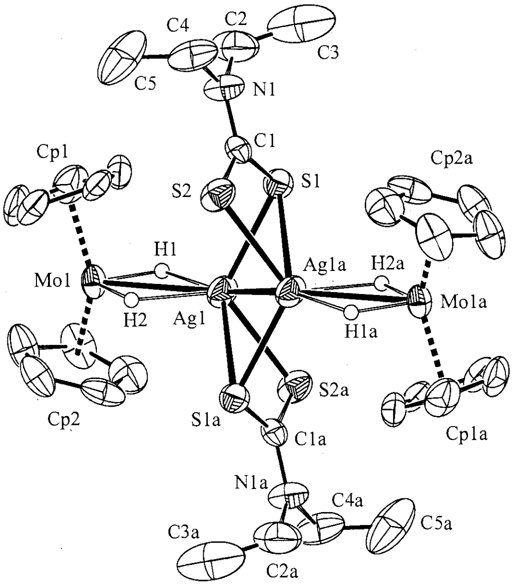


Fig. 1. Molecular structure of [$(Cp_2MoH_2AgS_2CNEt_2)_2$] (**1**) (ORTEP plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the carbamate and Cp ligands are omitted for clarity.

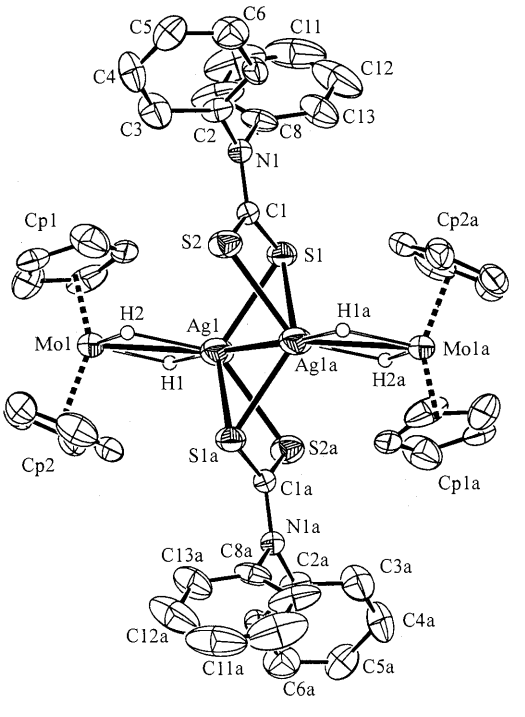


Fig. 2. Molecular structure of [$(Cp_2MoH_2AgS_2CNPh_2)_2$] (**2**) (ORTEP plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the carbamate and Cp ligands are omitted for clarity.

[$(Cp_2MoH_2AgS_2CMe)_2$] (**3**) was prepared by adding a solution of $Na(S_2CMe)$ in acetone to [Cp_2MoH_2] and $AgBF_4$ in acetone (molar ratio 1:1:1 and 1:2:1). The air-sensitive red–brown powder **3** is insoluble in ether. **3** crystallized from methylene chloride on addition of *n*-pentane as the solvate **3**·$2CH_2Cl_2$ (orange plates). $NH_4(S_2P(OEt)_2)$, dissolved in acetone, was added to [Cp_2MoH_2] and $AgBF_4$ in acetone (molar ratio 1:1:1 or 1:2:1) to give the air-sensitive complex [$(Cp_2MoH_2AgS_2P(OEt)_2)_2$] (**4**). After chromatography with methylene chloride–acetone 10:1 the product was crystallized from methylene chloride solution to get single crystals (translucent yellow prisms).

Reaction of $Na(S_2COEt)$, [Cp_2MoH_2] and $AgBF_4$ in acetone in a molar ratio 1:2:1 afforded the air-sensitive complex [$(Cp_2MoH_2)_2AgS_2COEt$] (**5**). Different from complexes **1**–**4**, product **5** has a 2:1 ratio of [Cp_2MoH_2]:dithio-ligand. **5** can be chromatograped with methylene chloride–acetone 10:1. X-ray quality single crystals (translucent yellow prisms) were grown from a saturated acetone solution.

From the reaction of $K(S_2CO^iPr)$, [Cp_2MoH_2] and $AgBF_4$ in acetone (molar ratio 1:1:1), in analogy to **1**, **2**, **3** and **4** and at variance to its xanthogenate congener **5**, an air-sensitive yellow complex of composition [$(Cp_2MoH_2AgS_2CO^iPr)_n$] (**6**) was isolated with probably $n = 2$. The 1:1 ratio of [Cp_2MoH_2]:dithio-ligand was corroborated by the ^{1}H-NMR spectrum ($CDCl_3$) and the elemental analysis. However, from a saturated solution of **6** in methylene chloride on addition of a few per cent of *n*-pentane crystals (yellow rods), suitable for X-ray structure analysis, were obtained which had the composition [$(Cp_2MoH_2Ag_4(S_2CO^iPr)_4)_n$] (**7**) with a ratio [$Cp_2MoH_2$]:Ag:dithio-ligand 1:4:4.

In the ^{1}H-NMR spectra ($CDCl_3$) of the complexes **1**–**6** a triplet appears for the Cp groups and a multiplet for the metal hydrides. Due to the fast rotation of the C–N bond in **1** and **2** the signals of the ethyl and phenyl groups coincide [10]. For complex **3** there is one methyl signal and for complex **5** one quartet and one triplet for the ethoxy group. The signals of the quartet and the triplet of complex **4** are duplicated by phosphorus coupling. The isopropyl group of **6** affords a septet and doublet.

3. Description of structures 1–5 and 7

3.1. [$(Cp_2MoH_2AgS_2CNEt_2)_2$] (1) and [$(Cp_2MoH_2AgS_2CNPh_2)_2$] (2)

Figs. 1 and 2 show the dimeric structures of **1** and **2**. The midpoint of the Ag–Ag bond (2.935(2) Å in **1** and

Table 1
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2AgS_2CNR_2)_2]$ (R = Et **1**, Ph **2**), $[(Cp_2MoH_2AgS_2CMe)_2]$ (**3**) and $[(Cp_2MoH_2AgS_2P(OEt)_2)_2]$ (**4**)

	1	**2**	**3**	**4**
Bond lengths				
Ag1–Ag1a (Ag1···Ag1a in **4**)	2.935(2)	2.926(5)	2.914(1)	3.468(2)
Ag1–Mo1	2.998(3)	2.959(0)	2.993(3)	2.971(4)
Ag1–S1	2.563(4)	2.567(2)	2.529(2)	2.539(0)
Ag1···S2	3.791(1)	3.663	3.550(4)	3.910(4)
Ag1a–S2	2.577(5)	2.663(1)	2.530(4)	2.650(1)
Ag1a–S1 (Ag1a···S1 in **3** and **4**)	2.995(4)	2.949(3)	3.483(3)	3.310(1)
C1–S1 (P1–S1 in **4**)	1.730(2)	1.718(1)	1.684(2)	1.985(3)
C1–S2 (P1–S2 in **4**)	1.698(5)	1.665(2)	1.683(2)	1.969(5)
Mo1–Cg1 [a]	1.947(4)	1.936(4)	1.959(0)	1.955(1)
Mo1–Cg2 [a]	1.958(0)	1.945(4)	1.958(2)	1.951(5)
Bond angles				
Mo1–Ag1–Ag1a	144.6(1)	145.5(1)	133.3(4)	145.6
Mo1–Ag1–S1	116.5(1)	119.9(2)	114.5(2)	128.7(0)
Mo1–Ag1–S1a	114.6(1)	112.6(3)		
Mo1–Ag1–S2a	118.0(3)	121.8(4)	116.5(0)	120.7(4)
Ag1–S1–Ag1a	63.2(0)	63.6(1)		
S1–Ag1–S1a	116.8(0)	116.4(1)		
S1–Ag1a–S2	64.1(2)	64.0(1)		
S1–C1–S2 (S1–P1–S2 in **4**)	120.5(4)	123.8(3)	125.3(3)	117.3(2)
C1–S1–Ag1 (P1–S1–Ag1 in **4**)	107.4(3)	102.6(2)	103.9(0)	103.9(1)
C1–S1–Ag1a	79.7(3)	79.6(4)		
C1–S2–Ag1a (P1–S2–Ag1a in **4**)	93.9(1)	89.8(4)	102.9(3)	93.6(2)
H1–Mo1–H2	75.6(4)	82.2(1)		81.7(3)
H1–Ag1–H2	58.9(2)	68.4(2)		62.8(2)

[a] Cp ring centroid.

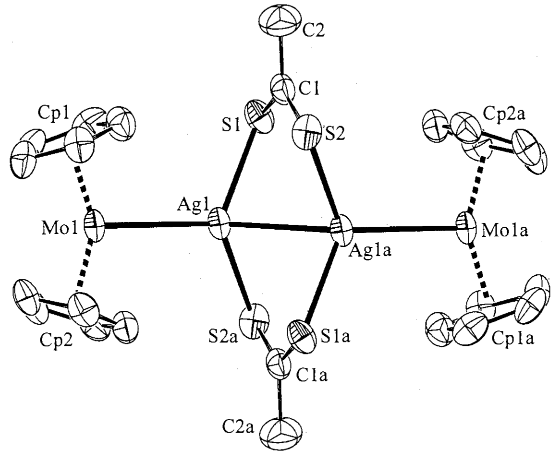


Fig. 3. Molecular structure of $[(Cp_2MoH_2AgS_2CMe)_2]$ (**3**) (ORTEP plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the dithioacetate and Cp ligands are omitted for clarity.

2.926(5) Å in **2**) is an inversion centre. $[Cp_2MoH_2]$ is bound to the silver atom via the H_2Mo moiety. In **1** the Mo1–Ag1–Ag1a angle is 144.6(1)° and in **2** 145.5(1)°. Thus, in both cases Mo1–Ag1–Ag1a–Mo1a forms a zigzag chain, all four atoms lying in one plane. The dithiocarbamate ligands coordinate to the silver atoms with both sulphur atoms. There are two types of sulphur atoms in the complexes **1** and **2**. One is bound to one silver atom, whereas the other is bound to both silver atoms. This results in shorter and longer Ag–S distances, which are listed in Table 1. The nonbonding silver–sulphur distances Ag1···S2 are 3.791(1) in **1** and 3.663 Å in **2**. The plane formed from the two silver and two of the sulphur atoms has dihedral angles (S1–Ag1–Ag1a–S1a) of almost exactly 180°.

The bond lengths C1–S1 and C1–S2 lie between a single bond and a double bond [11]. The distances to the μ_3-S are longer than to the μ_2-S. In structures where both sulphur atoms are bonded identically the values of the C–S bonds are almost equal [12,13]. The coordination of C1 by nitrogen and the two sulphur atoms is trigonal planar (sum of bond angles 360°).

The torsion of the plane S1–C1–S2 with respect to the Ag–Ag axis is 61.8(0)° in **1** and 66.8(1)° in **2**. The positions of the hydride ligands H1 and H2 were determined by the difference Fourier method. Mo1, H1, H2 and Ag1 lie in a plane (dihedral angle 2.0(1)° in **1** and 2.8(3)° in **2**). The angle H1–Mo1–H2 is 75.6(4)° for **1** and 82.2(1)° for **2** and the Mo–H distances are 1.472(3) and 1.721(2) Å for **1** and 1.524(0) and 1.912(1) Å for **2**. The dihedral angle between the normals to the Cp planes of the two $[Cp_2MoH_2]$ ligands are almost eclipsed (Cp1–Mo1–Mo1a–Cp2a 5.1(5)° for **1** and 6.0(2)° for **2**).

3.2. *$[(Cp_2MoH_2AgS_2CMe)_2]$ (3)*

The dimer **3** represents a new structure type, different from **1** and **2**, even though there is some similarity with **1** and **2**. The Ag1a–S1 distance in **3** is much larger than in **1** and **2** (Table 1). Therefore, the bonds Ag1a–S1 and Ag1–S1a, present in **1** and **2**, are missing in complex **3** (Fig. 3). The Ag–Ag bond in **3** is 2.914(1) Å and its midpoint is an inversion centre. The zigzag chain formed by Mo1–Ag1–Ag1a–Mo1a lies in a plane. Whereas the bond length Mo1–Ag1 = 2.993(3) Å in **3** is similar to **1** and **2** (Table 1), the Mo1–Ag1–Ag1a angle is 133.3(4)° and, thus, smaller than in **1** and **2**. Also, the torsion of the dithioacetate plane with respect to the Ag–Ag axis (45.9(4)°) is much less than in **1** and **2**. Therefore, each sulphur atom is bonded only to one silver atom. As a consequence, the Ag–S bonds in **3** (Ag1–S1 = 2.529(2) Å, Ag1a–S2 = 2.530(4) Å) are much shorter than in **1** and **2**. The distances between the nonbonded atoms are Ag1a···S1 = 3.483(3) Å and Ag1···S2 = 3.550(4) Å. The dithioacetate ligand is trigonal planar with a S1–C1–S2 angle of 125.3(3)°.

The position of the hydride ligands in **3** could not localized. The dihedral angle Cg1–Mo1–Mo1a–Cg2a 11.0(0)° is larger than in **1** and **2**.

3.3. *$[(Cp_2MoH_2AgS_2P(OEt)_2)_2]$ (4)*

The dimeric complex **4** (Fig. 4) has a structure similar to **1** and **2** and, in particular, to **3**. The Ag1···Ag1a distance (3.468(2) Å, Table 1) is much longer than in **1**, **2** and **3**. In effect, it is nonbonding. The midpoint is an inversion centre. The ligand diethyl dithiophosphate is coordinated in the same way as in **3**. Two ligands bridge two silver atoms; each sulphur atom bonds to one silver atom. The silver–sulphur bonds are 2.539(0) Å for Ag1–S1 and 2.6590(1) Å for Ag1a–S2, one being longer than the other, just as the nonbonding Ag···S distances (Ag1···S2 3.910(4) Å, Ag1a···S1 3.310(1) Å). In **3** and **4** the sulphur atoms S1 are coordinated only twofold, whereas in **1** and **2** they are coordinated threefold. As a consequence, the Ag1–S1 distances in **3** and **4** are shorter than in **1** and **2**. The rhomb formed by P1, Ag1, P1a and Ag1a is planar. Phosphorus is tetrahedrally coordinated by two sulphur and two oxygen atoms. The angle of the ring centroids Cg1 and Cg2a is 10.3(0)°, viewed along the Mo–Mo axis.

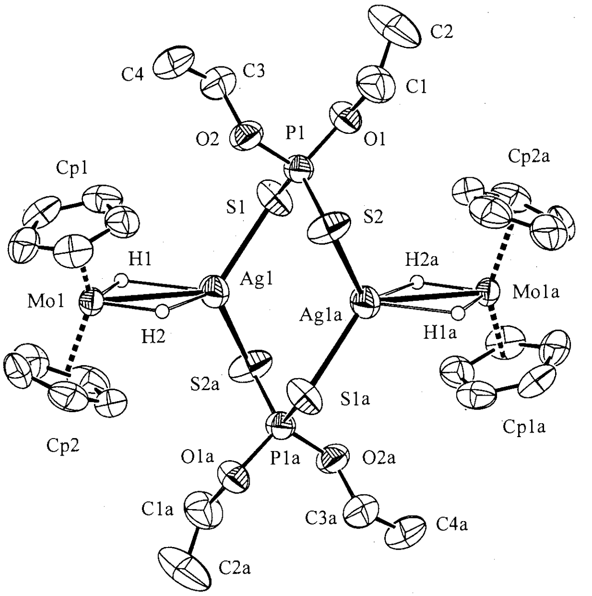


Fig. 4. Molecular structure of $[(Cp_2MoH_2AgS_2P(OEt)_2)_2]$ (**4**) (ORTEP plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the diethyl dithiophosphate and Cp ligands are omitted for clarity.

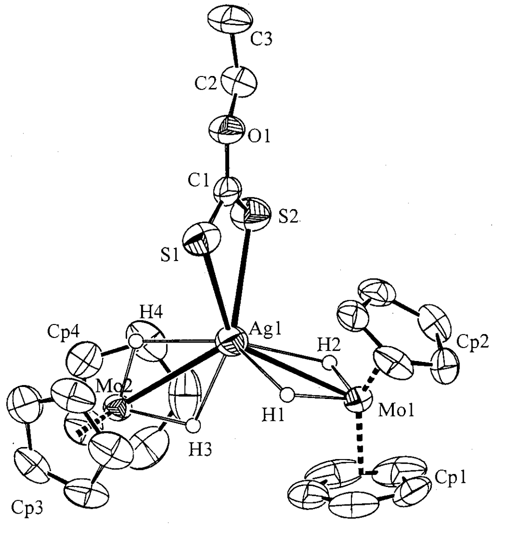


Fig. 5. Molecular structure of $[(Cp_2MoH_2)_2AgS_2COEt]$ (**5**) (ORTEP plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the ethyl xanthogenate and Cp ligands are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2)_2AgS_2COEt]$ (**5**)

Bond lengths			
Ag1–Mo1	3.062(3)	C1–S2	1.669(4)
Ag1–Mo2	3.054(2)	Mo1–Cg1	1.951(2)
Ag1–S1	2.728(3)	Mo1–Cg2	1.948(2)
Ag1–S2	2.917(3)	Mo2–Cg3	1.952(2)
C1–S1	1.685(4)	Mo2–Cg4	1.949(4)
Bond angles			
Mo1–Ag1–Mo2	127.7(1)	S1–C1–S2	125.2(2)
Mo1–Ag1–S1	111.4(2)	O1–C1–S1	112.7(2)
Mo1–Ag1–S2	111.2(1)	O1–C1–S2	122.1(3)
Mo2–Ag1–S1	114.4(2)	H1–Mo1–H2	83.0(2)
Mo2–Ag1–S2	110.8(4)	H3–Mo2–H4	83.2(2)
Ag1–S1–C1	88.5(5)	H1–Ag1–H2	59.4(4)
Ag1–S2–C1	82.6(4)	H3–Ag1–H4	60.8(0)
S1–Ag1–S2	63.6(4)		

The positions of the hydride ligands H1 and H2 were determined by the difference Fourier method. With 81.7(3)° the H1–Mo1–H2 angle in **4** is larger than in the free ligand ($[Cp_2MoH_2]$ with 74.8°). The Mo–H bonds are 1.652(1) Å for Mo1–H1 and 1.605(4) Å for Mo1–H2. The plane formed by Mo1, H1, H2, and Ag1 has a dihedral angle of 177.6(3)°.

3.4. *$[(Cp_2MoH_2)_2AgS_2COEt]$ (5)*

Complex **5** has a monomeric structure. Fig. 5 shows, that the silver atom is coordinated to two $[Cp_2MoH_2]$ ligands and one ethyl xanthogenate ligand. The Mo1–Ag1–Mo2 angle is 127.7(1)° and the two Ag–Mo bonds are 3.062(3) for Ag1–Mo1 and 3.054(2) Å for Ag1–Mo2 (Table 2).

In **5** the two $[Cp_2MoH_2]$ ligands are almost staggered (Cp2–Mo1–Mo2–Cp3 84.3(2)°). The plane S1–C1–S2 is close to perpendicular to the Mo1–Ag1–Mo2 plane (dihedral angle S2–C1–Ag1–Mo1 87.8(2)°). The two Ag–S bonds are not identical: Ag1–S2 (2.917(3) Å) is longer than Ag1–S1 (2.728(3) Å). The angle between

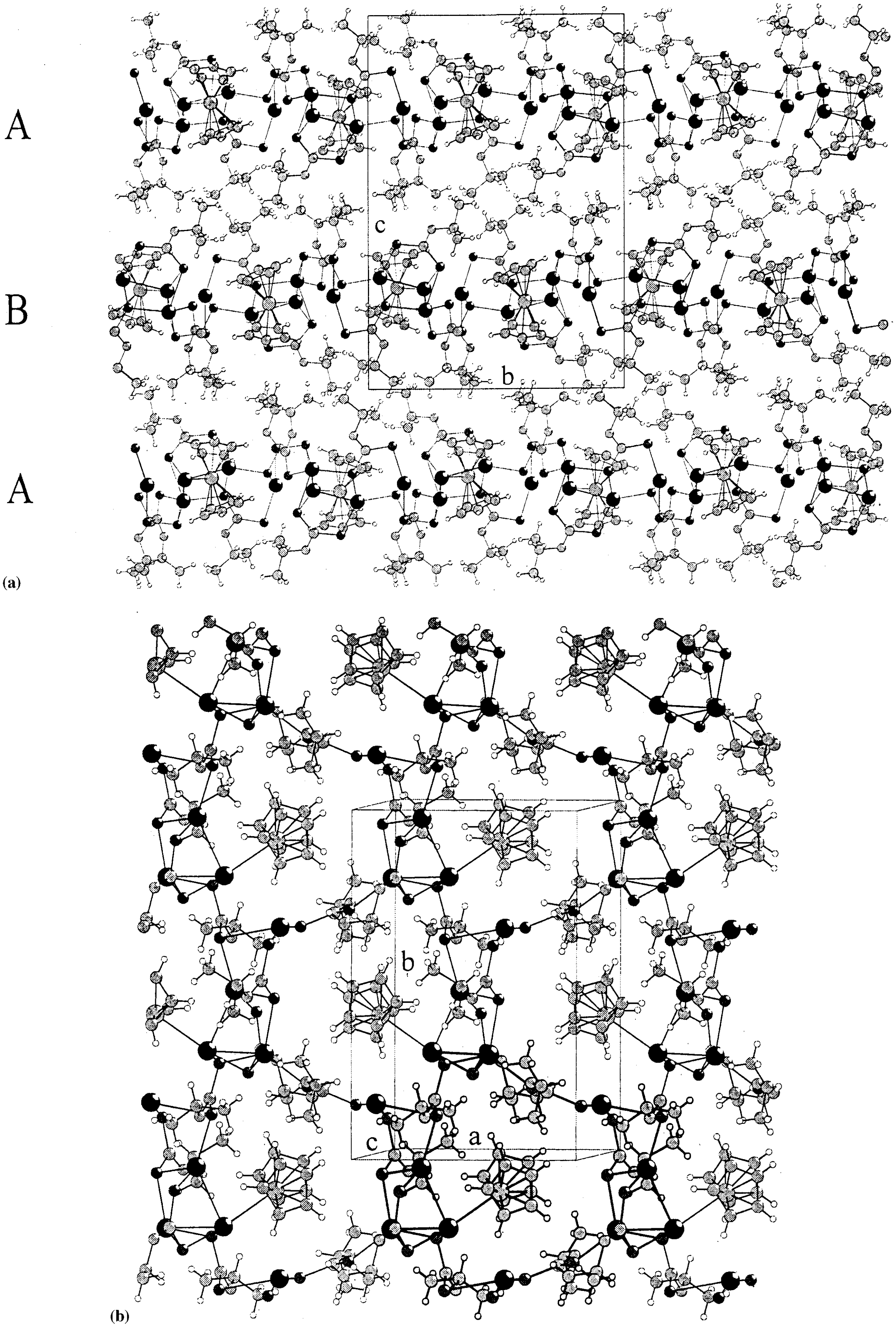


Fig. 6. Molecular structure of complex **7**: (a) side view, (b) top view.

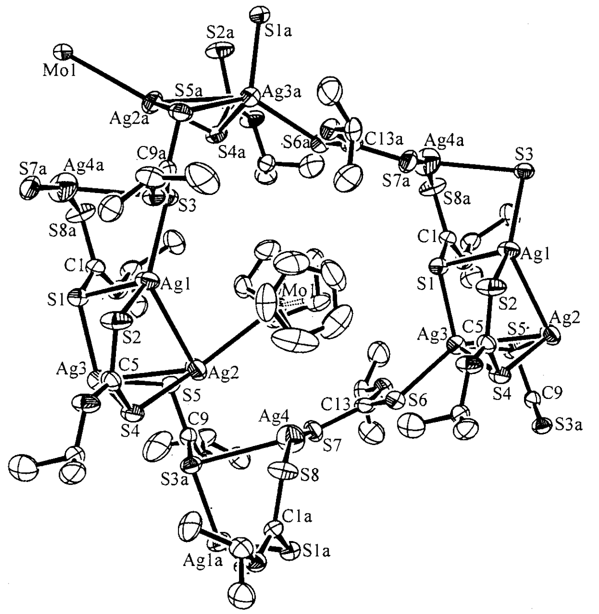
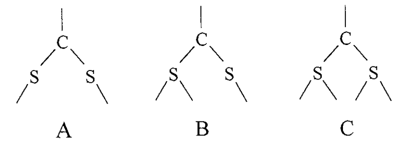


Fig. 7. Molecular structure of [(Cp$_2$MoH$_2$Ag$_4$(S$_2$CO^{i}Pr)$_4$)$_n$] (**7**) (ORTEP plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the isopropyl xanthogenate and Cp ligands are omitted for clarity. Symmetry transformations used to generate equivalent atoms $a \equiv (-x+1/2;\ y+1/2;\ -z+1/2)$.

Table 3
Selected bond lengths (Å) and angles (°) for [(Cp$_2$MoH$_2$Ag$_4$(S$_2$CO^{i}Pr)$_4$)$_n$] (**7**)

Bond lengths			
Ag1–Ag2	3.061(0)	Ag4–S7	2.426(2)
Ag2–Ag3	3.000(4)	Ag4–S8	2.447(1)
Ag2–Mo1	2.896(1)	C1–S1	1.709(4)
Ag1–S1	2.617(4)	C1–S8a	1.702(5)
Ag1–S2	2.459(1)	C5–S2	1.688(2)
Ag1–S3	2.494(5)	C5–S4	1.711(0)
Ag2–S4	2.479(2)	C9–S3a	1.709(2)
Ag2–S5	2.941(2)	C9–S5	1.680(0)
Ag3–S1	2.527(4)	C13–S6	1.676(1)
Ag3–S4	2.972(2)	C13–S7	1.695(4)
Ag3–S5	2.536(4)	Mo1–Cg1	1.961(3)
Ag3–S6	2.483(1)	Mo1–Cg2	1.972(5)
Ag4a–S3	2.959(5)		
Bond angles			
Mo1–Ag2–Ag1	79.2(0)	S3a–Ag4–S8	91.5(1)
Mo1–Ag2–Ag3	140.3(3)	Ag1–S2–C5	113.3(3)
Mo1–Ag2–S4	144.1(2)	S2–C5–S4	127.6(5)
Mo1–Ag2–S5	108.9(1)	C5–S4–Ag2	112.8(4)
S5–Ag2–S4	106.7(0)	S4–Ag2–Ag1	86.6(3)
S1–Ag1–S2	104.3(4)	Ag2–Ag1–S2	88.3(5)
Ag1–S2–C5	113.3(3)	S1–Ag3–Ag2	94.3(1)
C5–S4–Ag3	113.3(4)	Ag3–Ag2–Ag1	76.8(4)
S4–Ag3–S1	104.9(0)	Ag2–Ag1–S1	91.1(0)
Ag3–S1–Ag1	94.1(2)	Ag3–S5–Ag2	66.0(5)
Ag4–S8–C1a	100.3(3)	S5–Ag2–Ag3	50.5(3)
S8a–C1–S1	122.5(2)	Ag2–Ag3–S5	63.5(3)
C1–S1–Ag1	106.3(5)	Ag3–S4–Ag2	66.1(2)
S1–Ag1–S3	102.2(4)	S4–Ag2–Ag3	64.9(3)
Ag1–S3–Ag4a	87.0(5)	Ag2–Ag3–S4	49.1(5)



Scheme 1. Co-ordination modes of the xanthogenate ligand in complex **7**.

the two sulphur atoms at the silver atom is S1–Ag1–S2 = 63.6(4)°.

The hydrides H1, H2, H3 and H4 were localized by the difference Fourier method. The two planes H2–Ag1–H1–Mo1 and H3–Mo2–H4–Ag1 have dihedral angles of 3.7(1)° and 0.4(1)°. The hydrides form angles with molybdenum of 83.0(2)° (H1–Mo1–H2) and 83.2(2)° (H3–Mo2–H4). The Ag–H distances lie between 2.15(5) Å and 2.16(5) Å. The shortest Mo–H distance is 1.56(5) Å and the longest 1.69(5) Å. The data are listed in Table 2.

3.5. [(Cp$_2$MoH$_2$Ag$_4$(S$_2$CO^{i}Pr)$_4$)$_n$] (7)

Fig. 6a shows the sheet structure of complex **7**, consisting of two layers (A and B), one at $z \sim 1/4$ and the other at $z \sim 3/4$. The layer sequence is ABAB, with an A···A distance of 23.09 Å. Between the layers there is an inversion centre at (1/2, 1/2, 1/2). The shortest H···H contact between A and B is 2.634 Å and the shortest O···H contact is 3.143 Å, far outside the range of a hydrogen bond. The top view (Fig. 6b) shows large rings with a diameter of about 10 Å (bold part in Fig. 6b). They consist of silver and xanthogenate building blocks surrounding a [Cp$_2$MoH$_2$] ligand, which is bonded to one of the silver atoms. One of these large rings is shown in Fig. 7. It is part of the asymmetric unit. The atoms Ag1, Ag2, S1, S2, etc. are exactly one translational period in the crystallographic a direction apart of each other. The remaining atoms are generated by space group symmetry (Ag1a, Ag2a, S1a, S2a, etc.).

The asymmetric unit consists of four silver atoms, four isopropyl xanthogenates and one [Cp$_2$MoH$_2$] ligand. The positions of the hydride ligands could not be localized in this structure. Ag1 is four-coordinate. It is bonded to S1, S2, S3 and Ag2. Ag2 is connected with Ag1, Ag3, S4, S5 and [Cp$_2$MoH$_2$]. The bond length Ag2–Mo1 is 2.896(1) Å. There are two Ag–Ag–Mo angles, Ag1–Ag2–Mo1 = 79.2(0)° and Ag3–Ag2–Mo1 = 140.3(3)°. Ag3 is five-coordinate (neighbors Ag2, S1, S4, S5, S6), whereas Ag4 is only tri-coordinate (S3a, S7, S8).

The three silver atoms Ag1, Ag2 and Ag3 form a four-membered ring with S1 (dihedral angle Ag3–S1–Ag1–Ag2 15.2(4)°). The Ag–Ag distances are 3.061(0) Å for Ag1–Ag2 and 3.000(4) Å for Ag2–Ag3. The edge Ag2–Ag3 is doubly bridged by sulphur (S4 and S5). Either triangle has a short and a long Ag–S distance as obvious from Table 3.

For the xanthogenate ligands there are three different types of coordination in complex **7** (Scheme 1).

A is a bonding mode in which each sulphur atom is coordinated to one silver atom (as in complex **3**). In type **B** one sulphur is bonded to one silver atom, whereas the other is bonded to two silver atoms (examples: complexes **1** and **2**). In type **C** each sulphur atom coordinates two silver atoms. Of the four xanthogenate ligands in complex **7** there are two of type **B** and one of type **A** and **C**, respectively. The S–C distances lie between a single and a double bond, the shortest is 1.676(1) Å and the longest 1.711(0) Å.

Together with the xanthogenate ligand S2–C5–S4, Ag1 and Ag2 form a five-membered ring. The two angles at the silver atoms Ag1–Ag2–S4 (86.6(3)°) and S2–Ag1–Ag2 (88.3(5)°) are almost rectangular. However, the S2–C5–S4 angle is 127.6(5)°. The five-membered ring is not planar (dihedral angles 8.9(2)° for S4–C5–S2–Ag1 and 26.1(4)° for S2–Ag1–Ag2–S4).

There are two six-membered rings containing Ag1, S1, Ag3, S4, C5, S2 and Ag1, S3, Ag4a, S8a, C1, S1, which have boat conformation. Each consists of two silver atoms, one sulphur atom and the S–C–S part of a xanthogenate ligand. The Ag–S–Ag angles are almost rectangular (94.1(2)° for Ag3–S1–Ag1 and 87.0(5)° for Ag1–S3–Ag4a). Ag1 is included in the six-membered rings, the five- and the four-membered ring.

4. Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. The synthesis of [Cp_2MoH_2] was described in [1]. The dithio-ligands Na(S_2CNEt_2) [14], Na(S_2CNPh_2) [14], Na(S_2CMe) [15,16], Na(S_2COEt) [12] and K(S_2CO^iPr) [12] were prepared by literature methods. $AgBF_4$ and $NH_4(S_2P(OEt)_2)$ were purchased from Aldrich Chemicals and used without further purification. ^1H and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker ARX 400 instrument. ^1H-NMR chemical shifts were referenced to $CDCl_3$ or TMS and $^{31}P\{^1H\}$-NMR chemical shifts to external 85% H_3PO_4. Elemental analyses were performed by the micro-analytical laboratory of the Universität Regensburg.

4.1. *[(Cp$_2$MoH$_2$AgS$_2$CNEt$_2$)$_2$]* (**1**)

To a yellow suspension of [Cp_2MoH_2] (181 mg, 0.79 mmol) in 10 ml of acetone at −30°C was added $AgBF_4$ (153 mg, 0.79 mmol), dissolved in 2 ml of acetone, to afford a pale yellow suspension. After stirring for 10 min Na(S_2CNEt_2) (180 mg, 0.80 mmol), dissolved in 3 ml of methanol, was added. During the addition of the dithio-ligand the reaction mixture became clear and when it was complete a yellow solid had precipitated. It was filtered off, washed with methanol, dissolved in CH_2Cl_2, precipitated with methanol and recrystallized from CH_2Cl_2. Yield: 270 mg (71%). M.p. 115°C (decomp). Anal. Found: C, 36.90; H, 4.68; N, 2.97. $C_{30}H_{44}Ag_2Mo_2N_2S_4$ (968.57). Calc.: C, 37.20; H, 4.58; N, 2.89%. ^1H-NMR ($CDCl_3$, 400 MHz): δ 4.85 (t, $^3J(H,H) = 0.7$ Hz, 10H, η^5-C_5H_5), 4.00 (q, $^3J(H,H) = 7.1$ Hz, 4H, CH_2), 1.32 (t, $^3J(H,H) = 7.1$ Hz, 6H, CH_3), −9.51 (m, $^3J(H,H) = 0.7$ Hz, 2H, MoH).

4.2. *[(Cp$_2$MoH$_2$AgS$_2$CNPh$_2$)$_2$]* (**2**)

To a suspension of [Cp_2MoH_2] (183 mg, 0.80 mmol) and $AgBF_4$ (150 mg, 0.77 mmol) in 11 ml of acetone was added Na(S_2CNPh_2) (213 mg, 0.80 mmol) in 20 ml of acetone. The solvent was removed in vacuum and the yellow residue was washed with diethyl ether. **2** was purified by chromatography on silica gel with CH_2Cl_2–acetone 50:1 and recrystallized from acetone. Yield: 310 mg (69%). M.p. 117°C (decomp). Anal. Found: C, 47.09; H, 3.78; N, 2.68. $C_{46}H_{44}Ag_2Mo_2N_2S_4$ (1160.75). Calc.: C, 47.43; H, 4.15; N, 2.41%. ^1H-NMR ($CDCl_3$, 400 MHz): δ 7.19–7.52 (m, 10H, C_6H_5), 4.77 (t, $^3J(H,H) = 0.7$ Hz, 10H, η^5-C_5H_5), −9.51 (m, $^3J(H,H) = 0.7$ Hz, 2H, MoH).

4.3. *[(Cp$_2$MoH$_2$AgS$_2$CMe)$_2$]* (**3**)

Na(S_2CMe) (91 mg, 0.78 mmol) in 3 ml of acetone was added to a suspension of [Cp_2MoH_2] (169 mg, 0.74 mmol) and $AgBF_4$ (142 mg, 0.73 mmol) in 8 ml of acetone. A red–brown precipitate formed. After 60 min stirring at −30°C half of the solvent was removed and the solid was isolated. For purification it was washed first with diethyl ether (2 × 10 ml), then with cold acetone (1 × 5 ml) and recrystallized from CH_2Cl_2 (addition of *n*-pentane). Yield: 268 mg (86%). M.p. 87°C (decomp). Anal. Found: C, 34.16; H, 3.66. $C_{24}H_{26}Ag_2Mo_2S_4$ (854.38). Calc.: C, 33.74; H, 3.54%. ^1H-NMR ($CDCl_3$, 400 MHz): δ 4.82 (t, $^3J(H,H) = 0.7$ Hz, 10H, η^5-C_5H_5), 3.11 (s, 3H, CH_3), −9.51 (m, $^3J(H,H) = 0.7$ Hz, 2H, MoH).

4.4. *[(Cp$_2$MoH$_2$AgS$_2$P(OEt)$_2$)$_2$]* (**4**)

To a suspension of [Cp_2MoH_2] (166 mg, 0.73 mmol) and $AgBF_4$ (140 mg, 0.72 mmol) in 10 ml of acetone, $NH_4(S_2P(OEt)_2)$ (148 mg, 0.73 mmol) was added in 2 ml of acetone. The mixture was stirred for 10 min. The precipitate was isolated and washed with diethyl ether (2 × 10 ml). It was purified by chromatography on silica gel. Elution with CH_2Cl_2–acetone 10:1 afforded the yellow zone of **4**. Recrystallization from CH_2Cl_2. Yield: 293 mg (78%). M.p. 97°C (decomp). Anal. Found: C, 32.22; H, 4.24. $C_{28}H_{44}Ag_2Mo_2O_4P_2S_4$

Table 4
Crystallographic data for **1**–**5** and **7**

	1	**2**	**3**·2CH$_2$Cl$_2$	**4**	**5**	**7**
Elemental formula	$C_{30}H_{44}Ag_2$-$Mo_2N_2S_4$	$C_{46}H_{44}Ag_2$-$Mo_2N_2S_4$	$C_{26}H_{30}Ag_2Cl_4$-Mo_2S_4	$C_{28}H_{44}Ag_2$-$Mo_2O_4P_2S_4$	$C_{23}H_{29}Ag$-Mo_2OS_2	$C_{26}H_{38}Ag_4$-MoO_4S_8
M	968.57	1160.75	1020.20	1042.48	685.33	1198.52
Temperature (K)		297(2)	123(1)	297(2)	297(2)	173(1)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/a$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Crystal colour, shape	Yellow green needles	Yellow plates	Orange plates	Yellow prisms	Yellow prisms	Yellow rods
Crystal size (mm^3)	0.08 × 0.10 × 0.70	0.08 × 0.08 × 0.04	0.24 × 0.16 × 0.04	0.17 × 0.088 × 0.057	0.16 × 0.12 × 0.08	0.36 × 0.06 × 0.04
a (Å)	11.500(3)	12.177(4)	10.0557(3)	10.9650(7)	9.7612(11)	10.3690(10)
b (Å)	9.771(2)	21.740(4)	15.5222(15)	9.3919(5)	10.4147(6)	15.880(3)
c (Å)	15.990(3)	16.318(2)	10.9771(8)	18.3456(13)	12.5654(13)	23.090(3)
α(°)	90	90	90	90	73.94(1)	90
β	107.48(2)	90	100.15(1)	102.30(5)	77.12(4)	91.73(2)
γ	90	90	90	90	77.94(2)	90
V (Å^3)	1721.3(6)	4319.8(16)	1686.6(2)	1845.9(2)	1181.75(19)	3800.3(9)
Z	2	4	2	2	2	4
Density (g cm^{-3})	1.87	1.785	2.009	1.875	1.926	2.095
F(000)	960	2304	992	1032	676	2336
μ (mm^{-1})	2.10	1.689	2.45	2.053	2.054	2.82
2θ Range (°)	3.0–57.5	2.67–25.46	2.30–26.73	2.3–25.7	2.73–25.94	2.18–25.72
Total data	4933	4002	10269	25146	9198	12050
Total unique data	4473	4002	3437	3548	4599	6600
Parameters	187	254	172	254	274	388
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.70, 0.88	−0.967, 1.322	−0.849, 1.146	−0.372, 1.087	−0.565, 0.555	−1.010, 1.116
R_1 [a], [$I > 2\sigma(I)$]	0.055	0.0844	0.0374	0.0251	0.0249	0.0519
wR_2 [b], [$I > 2\sigma_I$]	0.046	0.0948	0.0901	0.0629	0.0494	0.1020
Goodness of fit S [c]	1.62	0.988	0.973	1.043	1.022	0.790

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$.

(1042.48). Calc.: C, 32.26; H, 4.56%. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 4.87 (t, ^3J(H,H) = 0.7 Hz, 10H, η^5-C_5H_5), 4.17 (dq, ^3J(H,H) = 7.1 Hz; ^3J(P,H) = 9.2 Hz; 4H, CH$_2$), 1.36 (dt, ^3J(H,H) = 7.1 Hz; ^4J(P,H) = 0.4 Hz, 6H, CH$_3$), −9.72 (m, ^3J(H,H) = 0.7 Hz, 2H, MoH). ^{31}P{^{1}H}-NMR (CDCl$_3$, 162 MHz): δ 109.1 (s).

4.5. *[(Cp$_2$MoH$_2$)$_2$AgS$_2$COEt] (**5**)*

To a solution of [Cp$_2$MoH$_2$] (239 mg, 1.05 mmol) and AgBF$_4$ (100 mg, 0.51 mmol) in 10 ml of acetone was added Na(S$_2$COEt) (77 mg, 0.53 mmol) in 6 ml of acetone at −30°C. The precipitate was isolated, washed with 10 ml of diethyl ether and chromatographed on silica gel. The yellow product was eluted with CH$_2$Cl$_2$–acetone 10:1. Recrystallization from acetone. Yield: 314 mg (90%). M.p. 89°C (decomp). Anal. Found: C, 40.26; H, 4.32. $C_{23}H_{29}AgMo_2OS_2$ (685.33). Calc.: C, 40.31; H, 4.26%. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 4.80 (t, ^3J(H,H) = 0.7 Hz, 20H, η^5-C_5H_5), 4.48 (q, ^3J(H,H) = 7.1 Hz, 2H, CH$_2$), 1.41 (t, ^3J(H,H) = 7.1 Hz, 3H, CH$_3$), −9.56 (m, ^3J(H,H) = 0.7 Hz, 2H, MoH).

4.6. *[(Cp$_2$MoH$_2$AgS$_2$CO^{i}Pr)$_n$] (**6**)*

K(S$_2$CO^{i}Pr) (143 mg, 0.82 mmol) was dissolved in 4 ml of acetone and added to a suspension of [Cp$_2$MoH$_2$] (186 mg, 0.82 mmol) and AgBF$_4$ (157 mg, 0.81 mmol) in 14 ml of acetone. The resulting yellow reaction mixture was stirred for 10 min. The precipitate was isolated and washed with 10 ml of diethyl ether. **6** was purified by chromatography on silica gel with CH$_2$Cl$_2$–acetone 10:1. Yield: 286 mg (75%). M.p. 95°C (decomp). Anal. Found: C, 35.79; H, 4.03. $(C_{14}H_{19}AgMoOS_2)_n$ $(471.24)_n$. Calc.: C, 35.68; H, 4.06%. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 5.39 (sept, ^3J(H,H) = 6.2 Hz, 1H, CH), 4.90 (t, ^3J(H,H) = 0.7 Hz, 10H, η^5-C_5H_5), 1.40 (d, ^3J(H,H) = 6.2 Hz, 6H, CH$_3$), −9.59 (m, ^3J(H,H) = 0.7 Hz, 2H, MoH).

4.7. *[(Cp$_2$MoH$_2$Ag$_4$(S$_2$CO^{i}Pr)$_4$)$_n$] (**7**)*

6 was dissolved in CH$_2$Cl$_2$. On addition of a few percent of n-pentane, crystals of **7** were obtained.

4.8. *X-ray structure determinations*

Diffraction data were collected on a Syntex R3 diffractometer for **1**, Enraf–Nonius CAD4 for **2** and **5** and STOE-IPDS for **3**, **4** and **7** using graphite-monochromatized Mo–K_α radiation ($\lambda = 0.7107$ Å). The unit cells were determined from 25 (**1**, **2**, **5**), 6907 (**7**) and 8000 (**3**, **4**) randomly selected reflections. Intensity data were corrected for Lorentz, polarization and absorption effects. Crystal data and details of the structure determinations are shown in Table 4. Structure **1** was solved by Patterson–Fourier methods using the SHELXTL Plus–Release 4.2/800, PC version, and **5** by using the SHELXS-97. The other structures were solved by SIR-97 (Altomare, 1993). All were refined on F^2 by the full-matrix least-squares technique (SHELXL-97). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at molybdenum (complexes **1**, **2**, **4** and **5**) were localized by the difference Fourier method and refined isotropically. All the other hydrogen atoms were calculated geometrically and a riding model was used during the refinement process.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no.s 139028, 139023, 139027, 139025, 139024 139026 for compounds **1**, **2**, **3**, **4**, **5** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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