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Monomeric, dimeric and polymeric [Cp_2MoH_2] complexes with Ag–S bonds

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Abstract

The reaction of [Cp_2MoH_2] and $AgBF_4$ with the dithio ligands Na(S_2CPh) and K(S_2CO^iPr) afforded the complexes [($Cp_2MoH_2AgS_2CPh$)$_2$] (**1**) and [($Cp_2MoH_2AgS_2CO^iPr$)$_2$] (**2**). Using the monothio ligands Na(SC(O)Ph), K(SC(O)CH_3) and Na(S(NHPh)C=C(CN)$_2$) the complexes [(Cp_2MoH_2AgSC(O)Ph)$_2$] (**3**), [((Cp_2MoH_2)$_2$(AgSC(O)CH_3)$_3$)$_n$] (**4**) and [(Cp_2MoH_2)$_2$AgS(NHPh)C=C(CN)$_2$] (**6**) were formed. The reaction of thiobenzamide and [(Cp_2MoH_2)$_2$AgCl] gave the complex [(Cp_2MoH_2Ag(Cl)S(NH_2)CPh)$_2$] (**5**). Complexes **1** and **2** have a dimeric structure with the two dithio ligands bridging the two silver atoms. Complex **3** is also a dimer, however, the monothio ligands are coordinated with their single sulphur atoms to the silver atoms. In the polymer **4** the thioacetate ligand has the same bonding mode as in **3**. The three-dimensional structure of **4** is built-up of parallel strings. In the dimer **5** the thiobenzamide ligands bind with the sulphur atom to a silver atom each. Complex **6** has a monomeric structure in which the silver atom is coordinated to two [Cp_2MoH_2] ligands and to the sulphur atom of the S(NHPh)C=C(CN)$_2$ ligand. Compounds **1**–**6** were characterised analytically and spectroscopically and the structures were determined by single crystal X-ray analyses. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Silver; Thio ligands; Clusters; Crystal structures

1. Introduction

The reaction of [Cp_2MoH_2] and $AgBF_4$ with dithio ligands, such as dithiocarbamates, dithioacetates, dithiophosphates and xanthogenates gave monomeric, dimeric and polymeric complexes [1]. The following air-sensitive compounds have been isolated and characterised: [($Cp_2MoH_2AgS_2CNR_2$)$_2$] [R = Et (**A**), Ph (**B**)], [($Cp_2MoH_2AgS_2CMe$)$_2$] (**C**), [($Cp_2MoH_2AgS_2P(OEt)_2$)$_2$] (**D**), [(Cp_2MoH_2)$_2AgS_2COEt$] (**E**) and [($Cp_2MoH_2Ag_4$(S_2CO^iPr)$_4$)$_n$] (**F**). The X-ray structures show that the [Cp_2MoH_2] ligands are coordinated to silver. The dithio ligands are bonded with their sulphur atoms to two silver atoms in the dimeric complexes and to one silver atom in the monomeric complexes. The bonding mode of the sulphur atoms varies from μ_2 to μ_3 in the monomeric, dimeric and polymeric compounds. The composition and structure of the monomeric complex [(Cp_2MoH_2)$_2AgS_2COEt$] is similar to the halide complex [(Cp_2MoH_2)$_2$AgCl] [2]. Here, we present the X-ray structures and experimental data of the coordination chemistry of other dithio and monothio ligands with [Cp_2MoH_2] and $AgBF_4$ [3].

2. Preparation of compounds 1–6

[Cp_2MoH_2] reacts rapidly with $AgBF_4$ in acetone at low temperature. A 2:1 molar ratio gives a yellow air-sensitive solution of [(Cp_2MoH_2)$_2$Ag]BF_4 [2] and a 1:1 molar ratio affords a yellow very air-sensitive suspension, for which the composition [(Cp_2MH_2Ag)$_2$](BF_4)$_2$ (M = W) has been proposed [4].

For the synthesis of [($Cp_2MoH_2AgS_2CPh$)$_2$] (**1**), [Cp_2MoH_2] and $AgBF_4$ were mixed in a molar ratio 1:1, and Na(S_2CPh), dissolved in acetone, was added to give a dark red precipitate. From methylene chloride X-ray quality single crystals of **1**·2CH_2Cl_2 were grown. The

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[1] X-ray structure analyses.

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solid can be handled in air for a short time. In solution (CH_2Cl_2, $CHCl_3$) **1** is air-sensitive.

The reaction of $K(S_2CO^iPr)$, $[Cp_2MoH_2]$ and $AgBF_4$ in a molar ratio 1:1:1 afforded the air-sensitive complex $[(Cp_2MoH_2AgS_2CO^iPr)_2]$ (**2**). After chromatography the yellow product crystallised from methylene chloride on addition of a few percent of *n*-pentane to give **2**. In addition, polymeric crystals of the composition $[Cp_2MoH_2]$–$AgBF_4$–dithio-ligand 1:4:4 were obtained. The X-ray structure of this complex $[(Cp_2MoH_2Ag_4(S_2CO^iPr)_4)_n]$ (**F**) was described in the literature [1].

The reaction of $[Cp_2MoH_2]$, $AgBF_4$ and Na(SC(O)Ph) in acetone (molar ratio 1:1:1) gave an air-sensitive yellow complex **3** of composition $[(Cp_2MoH_2AgSC(O)Ph)_2]$. Complex **3** can be chromatographed with methylene chloride–acetone (10:1). X-ray quality single crystals were grown from a saturated methylene chloride solution.

$[Cp_2MoH_2]$, $AgBF_4$ and $K(SC(O)CH_3)$ in acetone (molar ratio 1:1:1) afforded a yellow precipitate. After chromatography with methylene chloride–acetone (5:1) and crystallisation from methylene chloride (addition of a few percent of *n*-pentane) the complex $[((Cp_2MoH_2)_2(AgSC(O)CH_3)_3)_n]$ (**4**) was isolated.

$[(Cp_2MoH_2Ag(Cl)S(NH_2)CPh)_2]$ (**5**) was prepared in methylene chloride by adding a solution of thiobenzamide to $[(Cp_2MoH_2)_2AgCl]$. The starting material $[(Cp_2MoH_2)_2AgCl]$ was obtained from $[(Cp_2MoH_2)_2Ag]BF_4$ and NBu_4Cl [2].

The complex $[(Cp_2MoH_2)_2AgS(NHPh)C{=}C(CN)_2]$ (**6**) was formed by reacting $[Cp_2MoH_2]$, $AgBF_4$ and $Na(S(NHPh)C{=}C(CN)_2)$ in a molar ratio of 2:1:1. After chromatography and crystallisation from methylene chloride (addition of a few percent of *n*-pentane) the yellow air-sensitive product **6** could be isolated.

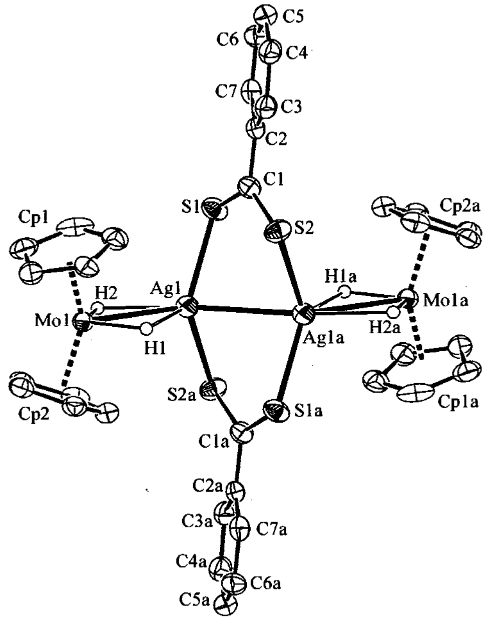

Fig. 1.

In the ^1H-NMR spectra ($CDCl_3$) of the complexes **2**–**6** a triplet appears for the Cp ligands and a multiplet for the metal hydrides. In **1** there are two broad singlets for these ligands and a multiplet for the phenyl group. The isopropyl group of **2** affords a septet and doublet. The thiobenzoate and thioacetate ligands in **3** and **4** exhibit the expected multiplets for the phenyl rings and singlets for the methyl groups. Crystals of **4** have a polymeric structure. However, they are soluble in $CDCl_3$. The ^1H-NMR spectrum of **4** shows the proton ratio $2[Cp_2MoH_2]$ (20H–4H):3($SC(O)CH_3$) (9H). The two protons at nitrogen in **5** give two signals. One of them is obscured by the phenyl multiplet as confirmed by an exchange experiment with methanol-d_4 [3]. The phenyl group and the hydrogen at the nitrogen in **6** afford a broad singlet and a multiplet.

3. Description of the structures

The lines between the molybdenum and silver atoms in Figs. 1–6 represent geometrical relationships. They are not intended to show real bonds.

3.1. $[(Cp_2MoH_2AgS_2CPh)_2]$ (**1**)

Fig. 1 shows the dimeric structure of **1**. It belongs to the same type as the methyl complex $[(Cp_2MoH_2AgS_2CMe)_2]$ (**C**) [1]. The midpoint of the Ag–Ag bond (2.885(2) Å) is an inversion centre. The two molybdenum and the two silver atoms form a zigzag chain, all four atoms lying in one plane (dihedral angle 180.0(1)°). The Mo–Ag–Ag angle is 137.1(2)°. Each sulphur atom of the dithio ligand is coordinated to a silver atom. The two Ag–S distances are almost equal (Ag1–S1 = 2.538(3), Ag1a–S2 = 2.558(2) Å). The double bond in the dithiobenzoate is delocalised over both C–S groups, resulting in a bond distance between a single and a double bond (Table 1). The coordination of C1 by S1, S2 and C2 is trigonal planar. The torsion of the plane S1–C1–S2 with respect to the Ag–Ag axis is 50.2(3)°. 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 4.80(1)°). The dihedral angle Cp1–Mo1–Mo1a–Cp2a between the normals to the Cp planes of the two $[Cp_2MoH_2]$ ligands is 13.9(0)° showing that they are almost eclipsed.

3.2. $[(Cp_2MoH_2AgS_2CO^iPr)_2]$ (**2**)

The dimer **2** has a structure similar to **1** (Fig. 2). The Ag–Ag bond (2.942(4) Å) in **2** is longer than in **1** and

Table 1
Selected bond lengths (Å) and angles (°) for [(Cp$_2$MoH$_2$AgS$_2$CPh)$_2$] (**1**) and [(Cp$_2$MoH$_2$AgS$_2$CO^{i}Pr)$_2$] (**2**)

	1	**2**		**1**	**2**
Bond lengths					
Ag1–Ag1a	2.885(2)	2.942(4)	C1–S2	1.702(9)	1.694(5)
Ag1–Mo1	2.966(2)	2.968(4)	Mo1–Cg1 [a]	1.955(1)	1.952(2)
Ag1–S1	2.538(3)	2.515(4)	Mo1–Cg2 [a]	1.951(5)	1.955(2)
Ag1···S2	3.474	3.506	Ag1–H1	2.16(9)	2.11(7)
Ag1a–S2	2.558(2)	2.572(3)	Ag1–H2	2.17(8)	2.03(6)
Ag1a···S1	3.522	3.422	Mo1–H1	1.57(8)	1.56(8)
C1–S1	1.693(8)	1.694(5)	Mo1–H2	1.61(9)	1.72(6)
Bond angles					
Mo1–Ag1–Ag1a	137.1(2)	137.0(2)	C1–S1–Ag1	104.7(3)	102.9(3)
Mo1–Ag1–S1	116.8(1)	118.7(4)	C1–S2–Ag1a	103.4(3)	98.7(3)
Mo1–Ag1–S2a	113.3(1)	117.1(0)	H1–Mo1–H2	81.7(3)	84(3)
S1–C1–S2	122.5(5)	125.6(3)	H1–Ag1–H2	62.9	64(3)

[a] Cp ring centroid.

its midpoint is an inversion centre. The Mo–Ag–Ag angle is 137.0(2)° and the Mo–Ag distance is 2.968(4) Å. The zigzag chain formed by Mo1–Ag1–Ag1a–Mo1a lies in a plane. Each sulphur atom of the xanthogenate ligand is bonded to one silver atom. The values of the bonding and nonbonding Ag–S distances are nearly the same as in **1** (Table 1). Both C–S bonds are identical (1.694(5) Å). The torsion of the S1–C1–S2 plane with respect to the Ag–Ag axis is 52.6(2)°. The isopropyl groups in Fig. 2 orient to the front and to the back, respectively; the C1–O1–C2 angle is 122.6(5)°. The hydrides H1 and H2 were localised by the difference Fourier method. With 2.11(7) Å (Ag1–H1) and 2.03(6) Å (Ag1–H2) the Ag–H bonds are longer than the Mo–H bonds (Mo1–H1 = 1.56(8), Mo1–H2 = 1.72(6) Å). The angle of the ring centroids Cg1 and Cg2a is 14.2(0)° viewed along the Mo–Mo axis.

*3.3. [(Cp$_2$MoH$_2$AgSC(O)Ph)$_2$] (**3**)*

Together with Ag$^+$ and [Cp$_2$MoH$_2$] the thiobenzoate ligand gives a dimer which has a structure different from the dimers **1** and **2** (Fig. 3). Both sulphur atoms are bonded to both silver atoms. The Ag1–S1 distance is shorter than its Ag1a–S1 counterpart (Table 2). With 3.098 Å for O1···Ag1a and 3.729 Å for O1···Ag1 the O···Ag distances are outside bonding distance. The midpoint of the Ag–Ag bond (2.828(4) Å) is an inversion centre. The two silver atoms and the two sulphur atoms form a planar four-membered ring with a dihedral angle of 180.0(1)°. In this structure type the Mo–Ag–Ag angle (168.33(1)°) is much larger than in the dimers **1** and **2**. With 2.906(2) Å the Ag–Mo distance in **3** is similar to **1** and **2**. The C1–S1 distance in the ligand (1.751(2) Å) is a single bond, whereas C1–O1 (1.221(3) Å) is a double bond. The S1–C1–O1 angle (123.7°) is larger than the other two angles

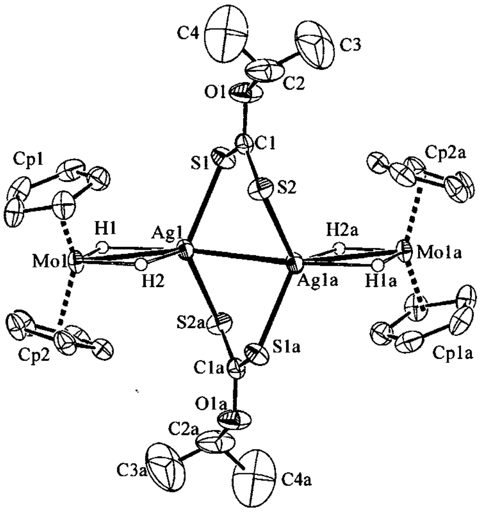

Fig. 2.

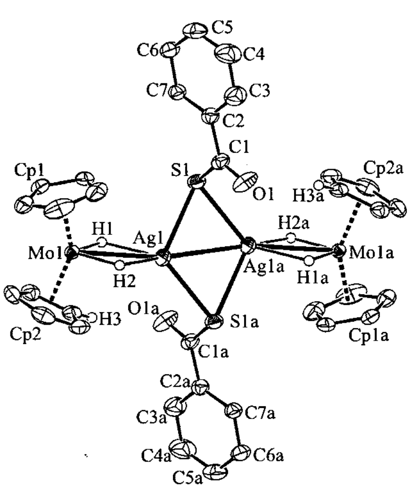

Fig. 3.

Table 2
Selected bond lengths (Å) and angles (°) for [$(Cp_2MoH_2AgSC(O)Ph)_2$] (**3**)

Bond lengths			
Ag1–Ag1a	2.828(4)	C1–O1	1.221(3)
Ag1–Mo1	2.906(2)	Mo1–Cg1	1.957(1)
Ag1a–S1	2.693(1)	Mo1–Cg2	1.957(1)
Ag1–S1	2.559(2)	Ag1–H1	2.05(3)
Ag1···O1	3.729	Ag1–H2	2.03(3)
Ag1a···O1	3.098	Mo1–H1	1.69(3)
C1–S1	1.751(2)	Mo2–H2	1.68(3)
Bond angles			
Mo1–Ag1–Ag1a	168.3(3)	C1–S1–Ag1a	95.2(5)
Mo1–Ag1–S1a	131.3(1)	S1–C1–O1	123.7
Ag1–S1–Ag1a	65.2(2)	H1–Ag1–H2	68.9(12)
S1–Ag1–S1a	114.8(2)	H1–Mo1–H2	86.6(14)
C1–S1–Ag1	104.0(2)		

S1–C1–C2 (117.1°) and O1–C1–C2 (119.0°). The phenyl group does not lie in the ligand plane; the dihedral angle is 12.73°. The torsion of the thiobenzoate plane S1–C1–O1 with respect to the Ag–Ag axis is 70.7°. The positions of the hydrides H1 and H2 were determined by the difference Fourier method. The angle H1–Mo1–H2 is 86.6(14)° and H1–Ag1–H2 68.9(12)°. The normals to the Cp planes of the two [Cp_2MoH_2] ligands are almost eclipsed (dihedral angle Cp1–Mo1–Mo1a–Cp2a = 4.20°).

3.4. [$((Cp_2MoH_2)_2(AgSC(O)CH_3)_3)_n$] (4)

Fig. 4 shows the polymeric structure of **4**. It is built-up from one-dimensional strings extending along the ‘a’ direction and having three 2_1 screw axes parallel to the crystallographic axes. The distance between two strings (Ag1···Ag1) is 14.67 Å. The symmetry operations along the *b* and *c* axes multiply the strings.

The asymmetric unit consists of three silver atoms, three thioacetate ligands and two [Cp_2MoH_2] ligands. The hydrides could be localised at Mo2, but not at Mo1 (Fig. 5). Ag1 is bonded to Mo1, S1 and S3b (Table 3). Ag2 and Ag3 are four-coordinate. Between these two atoms the distance is 3.179(3) Å. Ag2 is also connected with S1, S2b and Mo2. Ag3 has three sulphur atoms as neighbours (S1, S2, S3). In **4** there are short Ag–Mo distances (2.869(2) Å for Ag1–Mo1, 2.856(2) Å for Ag2–Mo2). With S1 and S3b the three silver atoms form a five-membered ring. The angles Ag3b–Ag2–S1, Ag2a–Ag3–S3 and S1–Ag1–S3b are almost rectangular. S2 bridges the two silver atoms Ag2a and Ag3 to form a triangle (Ag2a–S2–Ag3 = 79.2(3)°).

The sulphur atoms of the thioacetate ligands are coordinated to two silver atoms, respectively (S1, Ag1, Ag3; S2, Ag2a, Ag3; S3, Ag1a, Ag3). S1 is additionally connected to Ag2. This Ag2–S1 bond (2.812(4) Å) is longer than the others. The shortest nonbonding Ag···O distance is 3.008 Å (Ag1···O3) and the longest 4.629 Å (Ag1···O2).

The zigzag chain extends along the crystallographic ‘*a*’ direction including three different Ag centres. The sulphur atoms S1 and S3 bridge Ag1 and Ag3 as well as Ag3 and Ag1a with angles of 116.0(3) and 120.7(3)°.

3.5. [$(Cp_2MoH_2Ag(Cl)S(NH_2)CPh)_2$] (5)

Fig. 6 shows the dimeric structure of **5**. In this new type the chloride and the thiobenzamide ligands are coordinated to the silver atoms. The middle of the Ag–Ag distance (3.142(1) Å) is an inversion centre, although the phenyl rings are disordered. The Mo–Ag–Ag angle (73.2(3)°) is much shorter than in the dimers **1** and **2**. Therefore, with 2.125 Å the distance between Ag1 and H2a is within bonding range (triply bridging hydrogen). The values of Ag1–H1 (2.106 Å) and Ag1–H2 (2.071 Å) are shorter (Table 4). The two silver atoms, H2 and H2a lie in a plane. The dihedral angle H2–Ag1–H1–Mo1 is 6.3(5)°.

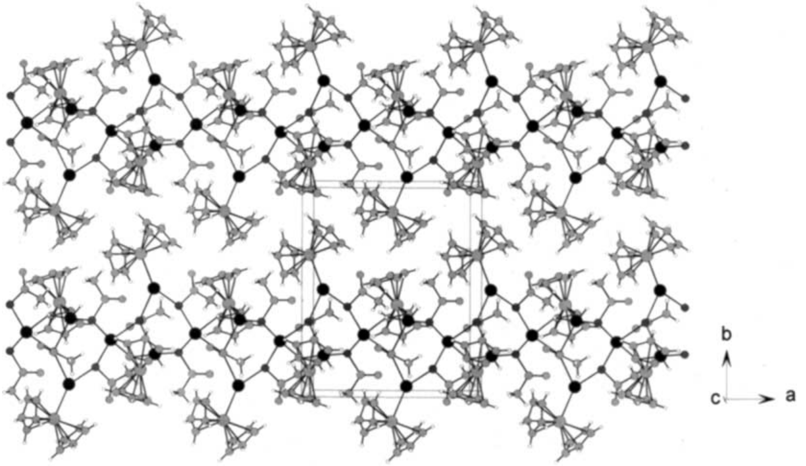

Fig. 4.

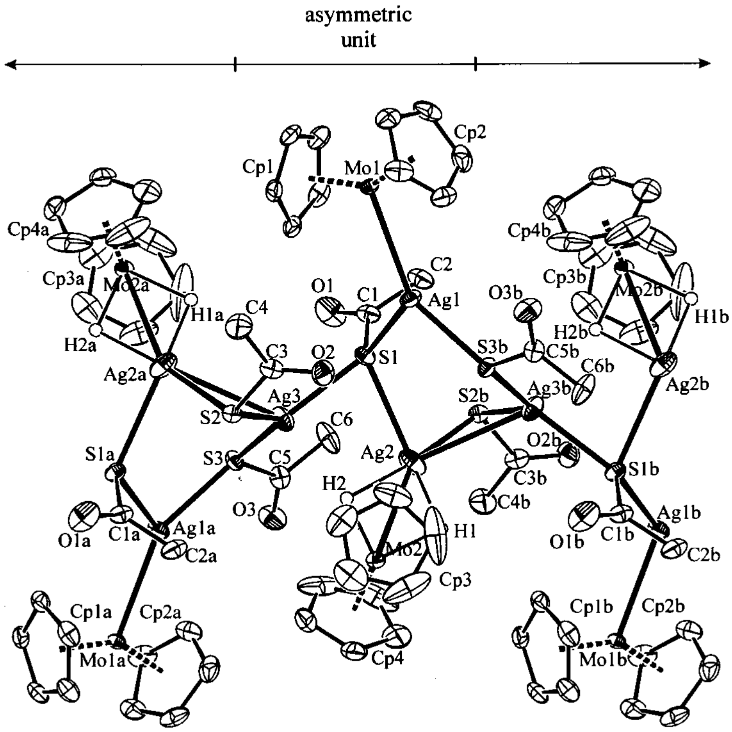

Fig. 5.

With 2.645(4) Å the Ag–Cl bond in **5** is longer than in [$(Cp_2MoH_2)_2AgCl$] (2.583(3) Å) [2]. The intermolecular distance Cl1···H4 = 2.390 Å is shorter than the intramolecular distance Cl1···H3 = 2.440 Å. The thiobenzamide ligand is coordinated to silver with the sulphur atom (Ag1–S1 = 2.557(5) Å). The Ag1···N1 distance (3.527 Å) is large, whereas Ag1···H4 is only 2.932 Å. The angle of the ring centroids Cg1 and Cg2a is 13.5(1)° viewed along the Mo–Mo axis.

3.6. [$(Cp_2MoH_2)_2AgS(NHPh)C{=}C(CN)_2$] (6)

The monomer **6** contains two [Cp_2MoH_2] ligands, one *N*-phenyl-dicyanothioacetamide ligand and one silver atom (Fig. 7). The thio ligand is coordinated to the silver atom with its sulphur atom only. The Ag···N distance of 3.041 Å in this molecule is shorter than in complex **5** (Table 5). In complex **6** the two [Cp_2MoH_2] ligands are almost staggered (dihedral angle Cp1–Mo1–Mo2–Cp3 = 86.2°). The Ag–Mo distances are 3.017(3) Å for Ag1–Mo1 and 3.039(4) Å for Ag1–Mo2. The Mo1–Ag1–Mo2 angle is 129.3(1)°. This value corresponds to that of the complex [$(Cp_2MoH_2)_2AgS_2CCH_3$] (**C**) [1]. The Ag1–S1 bond is 2.598(1) Å and the Ag1–S1–C1 angle 117.4(2)°. The dihedral angle C2–C1–Ag1–Mo1 (92.1°) describes the position of the thio ligand with respect to the Mo–Ag–Mo axis. The coordination of N1 is trigonal planar (C1, C5 and H5). The angles including hydrogen C1–N1–H5 and C5–N1–H5 are 117.2(2)°. The third angle C1–N1–C5 is 125.6(3)°. The two planes formed by Mo, two hydrides and Ag have dihedral angles of 2.45(1)° (H2–Ag1–H1–Mo1) and 0.57(1)° (H4–Ag1–H3–Mo2). The H1–Mo1–H2 angle is 78.8(8)° and the H3–Mo2–H4 angle 86.6(5)°. The shortest Mo–H bond in **6** is 1.423 Å and the longest 1.634 Å. The Ag–H distances lie between 2.028 and 2.227 Å.

Table 3
Selected bond lengths (Å) and angles (°) for [$((Cp_2MoH_2)_2(AgSC(O)CH_3)_3)_n$] (**4**)

Bond lengths			
Ag2–Ag3b	3.179(3)	C1–S1	1.755(4)
Ag1–Mo1	2.869(2)	C1–O1	1.202(5)
Ag2–Mo2	2.856(2)	C3–S2	1.763(5)
Ag1–S1	2.621(4)	C3–O2	1.215(6)
Ag1–S3b	2.443(3)	C5–S3	1.746(4)
Ag2–S1	2.812(4)	C5–O3	1.210(5)
Ag2–S2b	2.447(4)	Mo1–Cg1	1.946(1)
Ag3–S1	2.463(5)	Mo1–Cg2	1.939(1)
Ag3–S2	2.539(1)	Mo2–Cg3	1.949(1)
Ag3–S3	2.461(5)	Mo2–Cg4	1.947(1)
Bond angles			
Mo2–Ag2–Ag3b	118.7(1)	Ag1–S1–Ag2	116.0(3)
Mo1–Ag1–S1	117.7(1)	Ag1–S1–Ag3	116.0(3)
Mo1–Ag1–S3b	148.9(2)	Ag1a–S3–Ag3	120.7(3)
Mo2–Ag2–S1	121.5(5)	Ag2–S1–Ag3	75.3(4)
Mo2–Ag2–S2b	151.8(3)	Ag2a–S2–Ag3	79.2(3)
Ag2a–Ag3–S1	115.6(5)	S1–Ag1–S3b	91.3(3)
Ag2a–Ag3–S2	49.1(3)	S1–Ag2–S2b	86.2(2)
Ag2a–Ag3–S3	87.3(5)	S1–Ag3–S2	105.8(4)
Ag3b–Ag2–S1	87.3(5)	S1–Ag3–S3	132.1(2)
Ag3–Ag2a–S2	51.7(3)	S2–Ag3–S3	120.0(3)

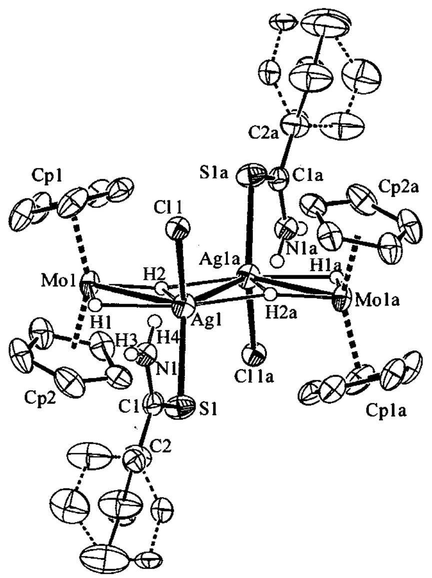

Fig. 6.

Table 4
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2Ag(Cl)S(NH_2)CPh)_2]$ (**5**)

Bond lengths			
Ag1–Ag1a	3.142(1)	Mo1–Cg1	1.955(2)
Ag1–Mo1	3.017(1)	Mo1–Cg2	1.956(6)
Ag1–S1	2.557(5)	Ag1–H1	2.106
Ag1–*Cl*1	2.645(4)	Ag1–H2	2.071
Ag1···N1	3.527	Ag1–H2a	2.125
C1–S1	1.685(5)	Ag1···H4	2.932
C1–N1	1.309(6)	Mo1–H1	1.558
*Cl*1···H4	2.390	Mo1–H2	1.642
Bond angles			
Mo1–Ag1–Ag1a	73.2(3)	S1–Ag1–*Cl*1	108.7(2)
Mo1–Ag1–S1	114.1(1)	S1–C1–N1	122.4(4)
Mo1–Ag1–*Cl*1	110.5(0)	H2–Ag1–H2a	83.0(4)
Ag1a–Ag1–S1	124.2(4)	Ag1–H2–Ag1a	96.9(6)
Ag1a–Ag1–*Cl*1	120.3(1)	H1–Mo1–H2	81.3(1)
Ag1–S1–C1	110.2(1)	H1–Ag1–H2	59.9(0)

4. Experimental

Experimental techniques and analytical instruments were described before [1]. $[Cp_2MoH_2]$ [5], the ligands $Na(S_2CPh)$ [6,7], $K(S_2CO^iPr)$ [8] and $Na(S(NHPh)C{=}C(CN)_2$ [9] and the complex $[(Cp_2MoH_2)_2Ag]BF_4$ [4] were prepared by literature methods. $AgBF_4$, $K(SC(O)CH_3)$ and $SC(NH_2)Ph$ were purchased from the Aldrich Chemicals and used without further purification.

4.1. *[(Cp₂MoH₂AgS₂CPh)₂]* (**1**)

To a yellow solution of $[Cp_2MoH_2]$ (153 mg, 0.67 mmol) and $AgBF_4$ (63 mg, 0.32 mmol) in 10 ml of Me_2CO was added $Na(S_2CPh)$ (60 mg, 0.22 mmol) in 4 ml of Me_2CO at −30°C. The resulting dark red reaction mixture was stirred for 20 min. The precipitate was isolated, washed first with 10 ml of cold Me_2CO and then with 10 ml of Et_2O. Recrystallisation from CH_2Cl_2 afforded the yellow product **1**. Yield: 112 mg (99%), m.p. (dec.) 105°C — Anal. Found: C, 41.05; H, 3.53. Calc. for $C_{34}H_{34}Ag_2Mo_2S_4$ (978.52): C, 41.73; H, 3.50% — ^1H-NMR ($CDCl_3$, 400 MHz, δ ppm): 8.36–7.29 (m, 5H, C_6H_5); 4.87 (bs, 10H, η^5-C_5H_5); −9.65 (bs, 2H, MoH).

4.2. *[(Cp₂MoH₂AgS₂COⁱPr)₂]* (**2**)

$K(S_2CO^iPr)$ (143 mg, 0.82 mmol) in 4 ml Me_2CO was added to a suspension of $[Cp_2MoH_2]$ (186 mg, 0.82 mmol) and $AgBF_4$ (157 mg, 0.81 mmol) in 14 ml of

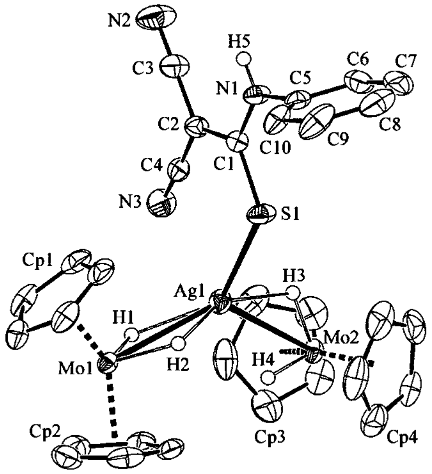

Fig. 7.

Table 5
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2)_2AgS(NHPh)C{=}C(CN)_2]$ (**6**)

Bond lengths			
Ag1–Mo1	3.017(3)	Ag1–H1	2.064
Ag1–Mo2	3.039(4)	Ag1–H2	2.028
Ag1–S1	2.598(1)	Ag2–H3	2.227
Ag1···N3	3.041	Ag2–H4	2.214
S1–C1	1.707(3)	Mo1–H1	1.599
N1–C1	1.346(4)	Mo1–H2	1.634
N1–C5	1.430(4)	Mo2–H3	1.477
N2–C3	1.146(6)	Mo2–H4	1.423
N3···H	2.697		
Bond angles			
Mo1–Ag1–Mo2	129.3(1)	C1–N1–H5	117.2(2)
Mo1–Ag1–S1	112.4(1)	C5–N1–H5	117.2(2)
Mo2–Ag1–S1	114.5(2)	H1–Mo1–H2	78.8(8)
Ag1–S1–C1	117.4(2)	H3–Mo2–H4	86.6(5)
S1–C1–N1	119.2(3)	H1–Ag1–H2	60.5(19)
C1–N1–C5	125.6(3)		

Me_2CO. The mixture was stirred for 10 min. The precipitate was isolated, washed with cold Me_2CO (2 × 5 ml) and 10 ml of Et_2O. Complex **2** was purified by chromatography on silica gel with CH_2Cl_2–Me_2CO (10:1) and recrystallised from CH_2Cl_2 (addition of *n*-pentane). Complex $[(Cp_2MoH_2Ag_4(S_2CO^iPr)_4)_n]$ (**F**) crystallised from the same reaction mixture [1]. Yield: 286 mg (75%), m.p. (dec.) 95°C — Anal. Found: C, 35.79; H, 4.03. Calc. for $C_{28}H_{38}Ag_2Mo_2O_2S_4$ (942.48): C, 35.68; H, 4.06% — ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 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).

4.3. $[(Cp_2MoH_2AgSC(O)Ph)_2]$ (**3**)

To a suspension of $[Cp_2MoH_2]$ (140 mg, 0.61 mmol) and $AgBF_4$ (114 mg, 0.59 mmol) in 10 ml of Me_2CO was added Na(SC(O)Ph) (95 mg, 0.59 mmol) in 4 ml of Me_2CO. During the addition of the monothio ligand the reaction mixture became clear. After 5 min a yellow solid precipitated. After isolation the product was washed with 10 ml of Et_2O. It was purified by chromatography on silica gel. With CH_2Cl_2–Me_2CO (10:1) the yellow zone of **3** was eluted. Recrystallisation from CH_2Cl_2. Yield: 259 mg (93%), m.p. (dec.) 73°C — Anal. Found: C, 42.97; H, 3.71. Calc. for $C_{34}H_{34}Ag_2Mo_2O_2S_2$ (946.39): C, 43.15; H, 3.62% — ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 8.21–8.18 (m, 2H, C_6H_5); 7.43–7.30 (m, 3H, C_6H_5); 4.92 (t, [$^3J(H,H) = 0.7$ Hz], 10H, η^5-C_5H_5); -9.74 (m, [$^3J(H,H) = 0.7$ Hz], 2H, MoH).

4.4. $[((Cp_2MoH_2)_2(AgSC(O)CH_3)_3)_n]$ (**4**)

To a yellow suspension of $[Cp_2MoH_2]$ (167 mg, 0.73 mmol) and $AgBF_4$ (150 mg, 0.77 mmol) in 6 ml of Me_2CO was added $K(SC(O)CH_3)$ (87 mg, 0.76 mmol) in 3 ml of Me_2CO. After 5 min stirring at −30°C a yellow solid had precipitated. The isolated product was washed with Et_2O. Complex **4** was purified by chromatography on silica gel with CH_2Cl_2–Me_2CO (5:1) and recrystallised from CH_2Cl_2 (addition of *n*-pentane). Yield: 223 mg (88%), m.p. (dec.) 84°C — Anal. Found: C, 31.13; H, 3.11. Calc. for $C_{26}H_{33}Ag_3Mo_2O_3S_3$ (1003.21): C, 31.07; H, 3.31% — ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 4.95 (t, [$^3J(H,H) = 0.7$ Hz], 20H, η^5-C_5H_5); 2.55 (s, 9H, CH_3); -9.78 (m, [$^3J(H,H) = 0.7$ Hz], 4H, MoH).

4.5. $[(Cp_2MoH_2Ag(Cl)SC(NH_2)Ph)_2]$ (**5**)

An excess of NBu_4Cl (84 mg, 0.27 mmol) in 4 ml Me_2CO was added to $[(Cp_2MoH_2)_2Ag]BF_4$ (172 mg, 0.26 mmol), dissolved in 16 ml of Me_2CO at −20°C, to give the complex $[(Cp_2MoH_2)_2AgCl]$ [2]. The yellow solid was washed with 10 ml of cold Me_2CO and 10 ml of Et_2O.

The ligand $SC(NH_2)Ph$ (43 mg, 0.31 mmol) in 3 ml CH_2Cl_2 was added to $[(Cp_2MoH_2)_2AgCl]$ (154 mg, 0.26 mmol) dissolved in 8 ml of CH_2Cl_2 to afford an orange precipitate. For purification the product **5** was washed with 10 ml of CH_2Cl_2 at 0°C and 3 × 10 ml of Et_2O at 22°C. Recrystallisation from CH_2Cl_2. Yield: 120 mg (93%), m.p. (dec.) 94°C — Anal. Found: C, 39.97; H, 3.78; N, 2.68. Calc. for $C_{34}H_{38}Ag_2Cl_2Mo_2N_2S_2$ (1017.34): C, 40.22; H, 3.57; N, 2.76% — ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 10.45 (s, 1H, NH_2); 7.85–7.82 (m, 2H, C_6H_5); 7.57–7.41 (m, 4H, C_6H_5, NH_2); 4.89 (t, [$^3J(H,H) = 0.7$ Hz], 10H, η^5-C_5H_5); -9.69 (m, [$^3J(H,H) = 0.7$ Hz], 2H, MoH).

4.6. $[(Cp_2MoH_2)_2AgS(NHPh)C{=}C(CN)_2]$ (**6**)

To a suspension of $[Cp_2MoH_2]$ (168 mg, 0.74 mmol) in 8 ml of Me_2CO at −25°C was added $AgBF_4$ (62 mg, 0.32 mmol) and $Na(S(NHPh)C{=}C(CN)_2)$ (80 mg, 0.36 mmol) in 3 ml of Me_2CO, respectively. The yellow solid was isolated, washed first with 10 ml of cold Me_2CO and then with 10 ml of Et_2O. For purification it was dissolved in CH_2Cl_2 and chromatographed on silica gel. Elution with CH_2Cl_2–Me_2CO (10:1) gave the yellow zone of **6**. Recrystallisation from CH_2Cl_2 (addition of *n*-pentane). Yield: 200 mg (82%), m.p. (dec.) 78°C — Anal. Found: C, 45.86; H, 4.16; N, 5.38. Calc. for $C_{30}H_{30}AgMo_2N_3S\frac{1}{2}CH_2Cl_2$ (806.87): C, 45.40; H, 3.87; N, 5.21% — ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 7.89 (bs, 1H, NH); 7.43–7.20 (m, 5H, C_6H_5); 4.82 (t, [$^3J(H,H) = 0.6$ Hz], 20H, η^5-C_5H_5); -9.60 (m, [$^3J(H,H) = 0.6$ Hz], 4H, MoH).

4.7. X-ray structure determinations

Diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromatised Mo–K_α radiation ($\lambda = 0.7107$ Å). The unit cells were determined from 8000 randomly selected reflections. Intensity data were corrected for Lorentz, polarisation and absorption effects. Crystal data and details of the structure determinations are shown in Table 6. The structures were solved by SIR-97 (Altomare, 1993) and refined on F^2 by the full-matrix least-squares technique (SHELXL-97). All nonhydrogen atoms were refined anisotropically. The hydrogen atoms at molybdenum were localised by the difference Fourier method and refined isotropically. All the other hydro-

Table 6
Crystallographic data for **1**–**6**

	1·$2CH_2Cl_2$	**2**·$2CH_2Cl_2$	**3**	**4**	**5**·$2CH_2Cl_2$	**6**
Empirical formula	$C_{36}H_{38}Ag_2Cl_4Mo_2S_4$	$C_{30}H_{42}Ag_2Cl_4Mo_2O_2S_4$	$C_{34}H_{34}Ag_2Mo_2O_2S_2$	$C_{26}H_{31}Ag_3Mo_2O_3S_3$	$C_{36}H_{42}Ag_2Cl_6Mo_2N_2S_2$	$C_{30}H_{30}AgMo_2N_3S$
Formula weight	1148.36	1112.34	946.39	1003.21	1187.18	764.40
Temperature (K)	173(1)	173(1)	173(1)	293(1)	173(1)	173(1)
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
Crystal colour, shape	Brown prisms	Yellow prisms	Yellow plates	Yellow prisms	Yellow prisms	Orange prisms
Crystal size (mm^3)	0.18 × 0.08 × 0.06	0.42 × 0.40 × 0.16	1.00 × 0.60 × 0.08	0.80 × 0.30 × 0.20	0.18 × 0.08 × 0.06	0.05 × 0.10 × 0.15
Unit cell dimensions						
a (Å)	8.2963(9)	10.0413(8)	12.5183(13)	11.742(4)	9.5032(7)	10.5288(10)
b (Å)	9.0120(10)	15.7305(12)	10.1686(8)	14.673(5)	23.7595(12)	12.6476(13)
c (Å)	13.2027(17)	12.2210(11)	13.2744(15)	16.717(5)	9.6791(7)	13.2472(13)
α (°)	92.702(15)	90	90	90	90	103.116(12)
β (°)	107.070(14)	90.269(10)	108.588(12)	90	107.298(9)	94.508(12)
γ (°)	92.175(13)	90	90	90	90	107.271(11)
V (Å^3)	952.5(2)	1930.3(3)	1601.6(3)	2880.2(16)	2086.6(3)	1620.2(3)
Z	1	2	2	4	2	2
Density (g cm^{-3})	2.002	1.914	1.962	2.314	1.890	1.828
F(000)	564	1096	928	1936	1168	882
μ (mm^{-1})	2.18	2.15	2.13	3.10	2.03	1.699
Theta range for data collection (°)	2.27–25.72	2.11–25.79	2.64–27.88	2.1–26.0	2.73–25.94	2.0–25.8
Total data	13 202	21 847	26 631	41 121	18 556	25 215
Total unique data	3368	3675	3757	5592	3869	6413
Parameters	223	207	258	342	271	350
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.687, 1.961	−1.983, 2.274	−0.718, 0.894	−1.81, 0.78	−1.199, 1.193	−0.35, 0.82
R_1 [a], [$I>2\sigma(I)$]	0.0512	0.0372	0.0238	0.0221	0.0363	0.0263
WR_2 [b], [$I>2\sigma(I)$]	0.1247	0.0950	0.0634	0.0533	0.0870	0.0550
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] $S = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{param})\}^{1/2}$.

gen atoms were calculated geometrically and a riding model was used during the refinement process.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 154507, 154509, 154504, 154506, 154508 and 154505 for compounds **1**–**6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] H. Brunner, A. Hollman, M. Zabel, B. Nuber, J. Organomet. Chem. 609 (2000) 44.

[2] H. Brunner, M. Muschiol, T. Neuhierl, B. Nuber, Chem. Eur. J. 4 (1998) 168.

[3] A. Hollman, Ph.D. Thesis, Universität Regensburg, 2000.

[4] L.F. Rhodes, J.C. Huffman, K.G. Caulton, Inorg. Chim. Acta 198 (1992) 639.

[5] M.L.H. Green, J.A. McCleverty, L. Pratt, G. Wilkinson, J. Chem. Soc. (1961) 4854.

[6] J. Houben, Ber. Dtsch. Chem. Ges. 39 (1906) 3219.

[7] C. Furlani, M.L. Luciani, Inorg. Chem. 7 (1968) 1586.

[8] E. Carmona, L. Contreras, L.J. Sánchez, E. Gútierrez-Puebla, A. Monge, J. Chem. Soc. Dalton Trans. (1989) 2003.

[9] D. Wobig, Liebigs Ann. Chem. (1990) 115.