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$[Cp_2MoH_2]$–silver complexes with pseudohalide ligands

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Dedicated to Prof. M. Herberhold on the occasion of his 65th birthday

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Abstract

The reaction of $[Cp_2MoH_2]$ and $AgBF_4$ with the pseudohalide ligands SCN^-, OCN^-, CN^- and SCF_3^- afforded the complexes $[(Cp_2MoH_2)_2AgSCN]$ (**1**), $[(Cp_2MoH_2)_2AgNCO]\cdot CH_2Cl_2$ (**2**), $[(Cp_2MoH_2)_2Ag(C_3N_3H_2O_3)]\cdot 3CH_2Cl_2$ (**3**), $[(Cp_2MoH_2)_2Ag]_n$-$[(Ag_2(CN)_3)_n]$ (**4**) and $[(Cp_2MoH_2)_2AgSCF_3]\cdot CH_2Cl_2$ (**5**). **1**, **2** and **5** have a $[Cp_2MoH_2]$:Ag:ligand stoichiometry of 2:1:1. Complex **3** contains the anion of the ligand $(HNCO)_3$, formed by trimerization of HNCO. The three-dimensional structure of **4** is built up of polymeric $[Ag_2(CN)_3^-]_n$ strings and $[(Cp_2MoH_2)_2Ag]^+$ units. The compounds **1**–**5** were characterized analytically and spectroscopically. All the structures were determined by single crystal X-ray analysis. © 2001 Elsevier Science B.V. All rights reserved.

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

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1. Introduction

The complex $[Cp_2MoH_2]$ [1] has three low-lying molecular orbitals between the two bent cyclopentadienyl rings [2]. The two outer orbitals bind the σ-bonded hydride ligands, and the orbital in the middle contains a lone pair of electrons. In 1992 the reaction of $[Cp_2WH_2]$ with $AgBF_4$ was reported to give $[(Cp_2WH_2)_2Ag]BF_4$ [3].

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 [4], e.g. $[(Cp_2MoH_2AgS_2CNR_2)_2]$ [R = Et, Ph], $[(Cp_2MoH_2AgS_2CMe)_2]$, $[(Cp_2MoH_2AgS_2P(OEt)_2)_2]$, $[(Cp_2MoH_2)_2AgS_2COEt]$ and $[(Cp_2MoH_2Ag_4(S_2CO^iPr)_4)_n]$, in which the $[Cp_2MoH_2]$ ligands are coordinated to silver. Monothio ligands, such as Na(SC(O)Ph), $K(SC(O)CH_3)$ and $Na(S(NHPh)C{=}C(CN)_2)$ gave the dimeric and polymeric complexes $[(Cp_2MoH_2AgSC(O)Ph)_2]$, $[((Cp_2MoH_2)_2(AgSC(O)CH_3)_3)_n]$ and $[(Cp_2MoH_2)_2AgS(NHPh)C{=}C(CN)_2]$ [4]. With silver(I) halides different structural types were established, e.g. $[(Cp_2MoH_2)_2AgCl]$, $[(Cp_2MoH_2)_3Ag_3X_3]$ (X = Br, I) and $[(Cp_2MoH_2)_4Ag_3Br_2]PF_6$ [5]. Here we present the experimental data of the coordination chemistry of the pseudohalide ligands SCN^-, OCN^-, CN^- and SCF_3^- with $[Cp_2MoH_2]$ and $AgBF_4$ and the X-ray structure analyses of the complexes **1**–**5** [6]. In Figs. 1–6 the lines

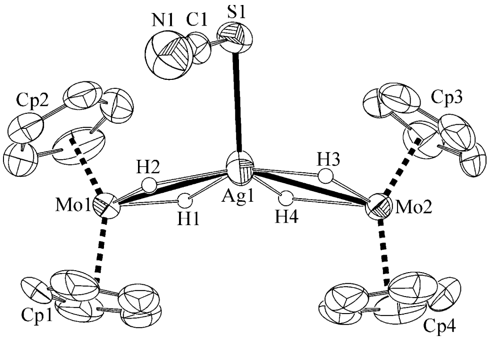

Fig. 1. Molecular structure of $[(Cp_2MoH_2)_2AgSCN]$ (**1**) (ortep plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the Cp ligands are omitted for clarity.

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[1] X-ray structure analyses.

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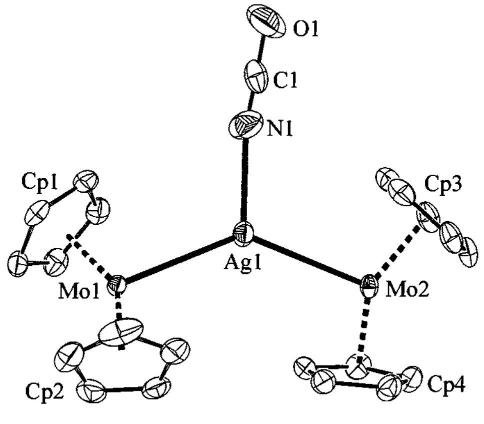

Fig. 2. Molecular structure of [$(Cp_2MoH_2)_2AgNCO$] (**2**) (ortep plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the Cp ligands are omitted for clarity.

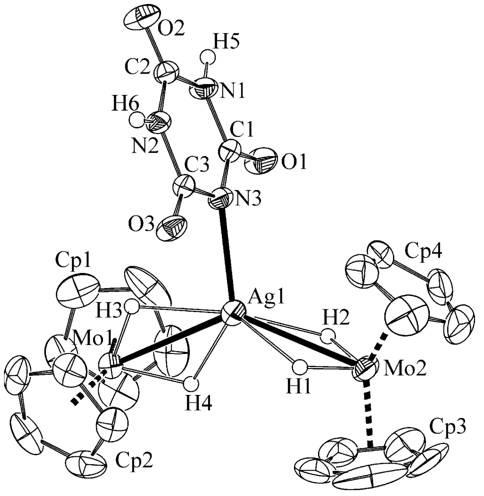

Fig. 3. Molecular structure of [$(Cp_2MoH_2)_2Ag(C_3N_3H_2O_3)$] (**3**) (ortep plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the Cp ligands are omitted for clarity.

between the molybdenum and silver atoms represent geometrical relationships. They are not intended to show real bonds.

2. Preparation of compounds 1–5

[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 [$(Cp_2MoH_2)_2Ag$]BF_4 [5].

[Cp_2MoH_2], $AgBF_4$ and NH_4SCN, dissolved in acetone, afforded the microcrystalline complex [$(Cp_2MoH_2)_2AgSCN$] (**1**). Complex **1** is insoluble in methanol, ether and toluene. In solution (CH_2Cl_2, $CHCl_3$) the complex is very air-sensitive. The solid can be handled in air for a short time. Under nitrogen **1** can be stored for months. X-ray quality single crystals were grown from methylene chloride (yellow prisms).

The compounds [$(Cp_2MoH_2)_2AgNCO$]·CH_2Cl_2 (**2**) and [$(Cp_2MoH_2)_2Ag(C_3N_3H_2O_3)$]·$3CH_2Cl_2$ (**3**) were prepared by adding solid AgNCO to a solution of [Cp_2MoH_2] in acetone (molar ratio 1:2). The crystallization of the yellow solution gave two types of crystals, rhombs of complex **2** (majority) and needles of complex **3**. Alternatively, [$(Cp_2MoH_2)_2AgNCO$]·CH_2Cl_2 (**2**) crystallized from a solution of [Cp_2MoH_2], $AgBF_4$ and KOCN in acetone–methanol (molar ratio 2:1:1).

To a solution of [Cp_2MoH_2] and $AgBF_4$ in acetone was added NaCN in methanol (molar ratio 2:1:1). After chromatography X-ray quality prisms of [$(Cp_2MoH_2)_2$-Ag]$_n$[$(Ag_2(CN)_3)_n$] (**4**) were grown from methylene chloride.

From the reaction of [Cp_2MoH_2] and $AgSCF_3$ in acetone (molar ratio 2:1) a temperature- and air-sensitive yellow complex of composition [$(Cp_2MoH_2)_2$-$AgSCF_3$]·CH_2Cl_2 (**5**) was isolated.

In the ^{1}H-NMR spectra ($CDCl_3$) of the complexes **1** and **5** two broad singlets appear for the Cp groups and the metal hydrides. Complexes **2** and **3** show a triplet for the Cp group and a multiplet for the metal hydride. The two signals in **4** are a triplet and a broad singlet.

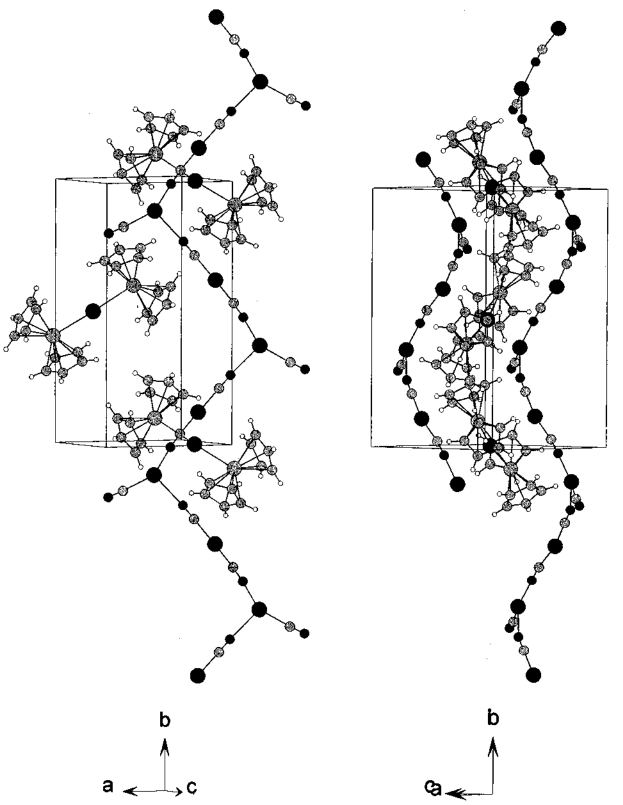

Fig. 4. Two views of the structure of [$(Cp_2MoH_2)_2Ag$]$_n$[$(Ag_2(CN)_3)_n$] (**4**).

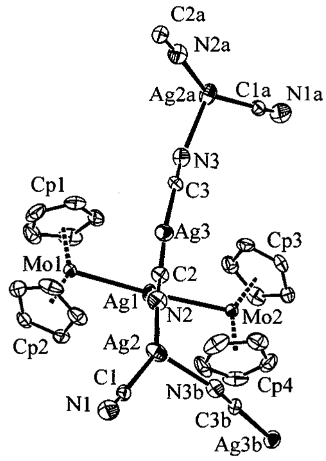

Fig. 5. Molecular structure of $[(Cp_2MoH_2)_2Ag]_n[(Ag_2(CN)_3)_n]$ (**4**) (ortep plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the Cp ligands are omitted for clarity.

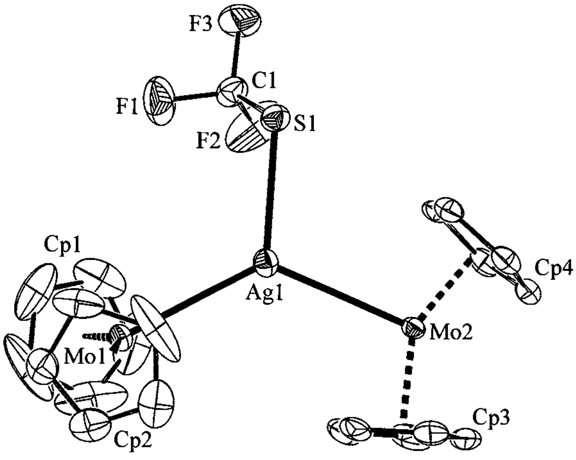

Fig. 6. Molecular structure of $[(Cp_2MoH_2)_2AgSCF_3]$ (**5**) (ortep plot; thermal ellipsoids drawn at 50% probability). The hydrogen atoms of the Cp ligands are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2)_2AgSCN]$ (**1**)

Bond lengths			
Ag1–Mo1	2.972(2)	Ag1–S1	2.827(2)
Ag1–Mo2	2.954(1)	S1–C1	1.639(5)
C1–N1	1.114(6)		
Bond angles			
Mo1–Ag1–Mo2	143.8(0)	S1–C1–N1	179.6(3)
Mo1–Ag1–S1	107.8(1)	H1–Mo1–H2	83.2(2)
Mo2–Ag1–S1	107.5(3)	H3–Mo2–H4	62.8(2)
Ag1–S1–C1	100.2(2)		

3. Description of the structures

3.1. $[(Cp_2MoH_2)_2AgSCN]$ (1)

In complex **1** (Fig. 1) the silver atom is coordinated to two $[Cp_2MoH_2]$ ligands and one thiocyanate ligand. In **1** the thiocyanate ligand binds to the sulfur atom. The Mo1–Ag1–Mo2 angle is 143.8(0)° and the two Ag–Mo distances are 2.972(2) for Ag1–Mo1 and 2.954(1) Å for Ag1–Mo2 (Table 1). In contrast to the ligands NCO^- and CN^- in **2** and **4**, and to the complex $[Pt_2Cl_2(PPr_3)_2(SCN)_2]$, in which the two thiocyanate ligands coordinate both via the sculpture atom and the nitrogen atom [7], the thiocyanate ligand in **1** does not bind with the nitrogen atom but with the sculpture atom to the silver center. The Ag1–S1 bond length is 2.827(2) Å and the angle Ag1–S1–C1 is 100.2°, whereas the S1–C1–N1 angle within the ligand is 179.6(4)°. The two Mo–Ag–S angles are 107.8(1)° for Mo1 and 107.5(3)° for Mo2. With 104° the Ag–S–C angle in AgSCN is larger than in **1** [7]. The C–S–C angle in H_3CSCN is 99.6° [8].

The positions of the hydride ligands H1–H4 were determined by the difference Fourier method. The Mo–H bonds vary between 1.611(2) and 2.030(3) Å. The smallest Ag–H bond is 1.367(1) Å and the largest 2.046(1) Å. Deviations from the two planes formed by Mo, the hydrides and Ag are small (dihedral angles 8.4° for H1–Ag1–Mo1–H2 and 7.0° for H3–Ag1–Mo2–H4). The Cp rings adopt an almost eclipsed conformation (dihedral angle = 3.8°) in **1**.

3.2. $[(Cp_2MoH_2)_2AgNCO]$ (2)

In **2** the cyanate ligand is coordinated with the nitrogen atom to the silver atom (Fig. 2). The Ag1–N1–C1 angle is 165.0(5)°, the Ag1–N1 bond 2.307(4) Å. The atoms N1, C1 and O1 are arranged linearly (177.9(6)°). In the complexes $[Cp_2M(NCO)_2]$ (M = Ti, Zr) the angles M–N–C are 171.8–177.5° and, thus, larger than in **2** [9].

The silver atom in **2** is coordinated in a trigonal planar way by N1, Mo1 and Mo2 (Table 2). The two Ag–Mo distances are 2.976(2) Å for Mo1 and 3.001(1) Å for Mo2. The positions of the hydride ligands in **2** could not be localized. The angle of the ring centroids Cg1 and Cg3 is 58.7(2)°, viewed along the Mo–Mo axis.

Table 2
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2)_2AgNCO]$ (**2**)

Bond lengths			
Ag1–Mo1	2.976(2)	Ag1–N1	2.307(4)
Ag1–Mo2	3.001(1)	N1–C1	1.069(6)
C1–O1	1.217(6)		
Bond angles			
Mo1–Ag1–Mo2	136.3(1)	Ag1–N1–C1	165.0(5)
Mo1–Ag1–N1	113.4(1)	N1–C1–O1	177.9(6)
Mo2–Ag1–N1	110.2(1)		

Table 3
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2)_2Ag(C_3N_3H_2O_3)]$ (**3**)

Bond lengths			
Ag1–Mo1	2.962(2)	Ag1–N3	2.364(3)
Ag1–Mo2	2.954(1)	N3–C1	1.358(5)
C1–O1	1.237(4)	N1–H5	0.83(6)
Bond angles			
Mo1–Ag1–Mo2	134.5(1)	Ag1–N3–C3	112.8(2)
Mo1–Ag1–N3	109.5(1)	N3–C1–O1	122.7(3)
Mo2–Ag1–N3	115.8(1)	N3–C1–N1	118.3(3)
Ag1–N3–C1	123.5(2)	C1–N1–C2	124.0(3)

Table 4
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2)_2Ag]_n$-$[(Ag_2(CN)_3)_n]$ (**4**)

Bond lengths			
Ag1–Mo1	2.848(1)	Ag2–N2	2.169(5)
Ag1–Mo2	2.855(1)	Ag2–N3b	2.499(5)
Ag2–C1	2.162(6)	Ag3–C2	2.080(6)
Ag3–C3	2.079(5)	C1–N1	1.034(9)
C2–N2	1.139(8)		
Bond angles			
Mo1–Ag1–Mo2	169.7(1)	C2–Ag3–C3	169.0(2)
Ag2–C1–N1	173.6(6)	N2–Ag2–N3b	122.7(3)
Ag2–N2–C2	175.4(5)	N2–Ag2–C1	149.1(2)
Ag3–C2–N2	123.5(2)	N3b–Ag2–C1	108.5(2)

Table 5
Selected bond lengths (Å) and angles (°) for $[(Cp_2MoH_2)_2AgSCF_3]$ (**5**)

Bond lengths			
Ag1–Mo1	3.030(2)	Ag1–S1	2.646(2)
Ag1–Mo2	3.002(1)	S1–C1	1.734(5)
C1–F1	1.350(6)		
Bond angles			
Mo1–Ag1–Mo2	129.6(1)	Ag1–S1–C1	101.7(2)
Mo1–Ag1–S1	120.5(1)	S1–C1–F1	115.8(3)
Mo2–Ag1–S1	110.0(1)	F1–C1–F2	103.9(4)

3.3. $[(Cp_2MoH_2)_2Ag(C_3N_3H_2O_3)]$ (3)

In the reaction of Cp_2MoH_2, $AgBF_4$ and KOCN in acetone, cyanuric acid is formed, which is coordinated with one of the nitrogen atoms to the silver atom as a monoanion (Fig. 3) [7]. The Ag1–N3 bond length of **3** is 2.364(3) Å. In the free cyanuric acid all the C–N distances are identical [7]. In **3**, however, C1–N1 and C3–N2 are longer than the other four C–N distances (Table 3). The two Mo–Ag–N angles are 109.5(1)° for Mo1 and 115.8(1)° for Mo2. The ligand plane is inclined by 17° with respect to the Ag1–N3 bond (Ag1–N3–C2 = 163.1°).

The hydrides H1, H2, H3 and H4 were localized by the difference Fourier method. The two planes H2–Mo1–H1–Ag1 and H3–Mo2–H4–Ag1 have dihedral angles of 4.8(4) and 8.1(3)°, respectively.

3.4. $[(Cp_2MoH_2)_2Ag]_n[(Ag_2(CN)_3)_n]$ (4)

Contrary to **1**–**3** and **5**, from a solution containing Cp_2MoH_2, Ag^+ and CN^- in a 2:1:1 ratio, a compound of the type $[(Cp_2MoH_2)_2AgCN]$ cannot be crystallized. Instead, a salt of composition $[(Cp_2MoH_2)_2Ag]_n$-$[(Ag_2(CN)_3)_n]$ (**4**) was obtained. Complex **4** is built up of $[(Cp_2MoH_2)_2Ag]$ cations and polymeric strings of $Ag_2(CN)_3$ anions (Fig. 4), which are not bonded to each other. The shortest distance is 2.859 Å (N2···H(Cp₂)). The distance between Ag1 and Ag3 is 3.258 Å (Fig. 5). The one-dimensional strings form 2_1 screw axes parallel to the crystallographic *b* axes. $[Ag_2(CN)_3]^-$ is the asymmetric unit of the polymeric string. The two silver atoms are coordinated differently. Ag2 is bonded to one carbon atom and two nitrogen atoms. The four atoms do not lie in a plane (N2–N3b–Ag2–C1 = 164.8°) (Table 4). Ag3 forms a nearly linear array with two carbon atoms (C2–Ag3–C3 = 169.0(2)°). One of the three cyanide groups is terminally coordinating via C, the other two are bridging both via C and N. The Ag–N distances are remarkably different (Ag2–N2 = 2.169(5) and Ag2–N3b = 2.499(5) Å). The torsion of the Cp rings viewed along the Mo–Mo axis (dihedral angle Cp1–Mo1–Mo2–Cp3 = 12.0°) is less than in $[(Cp_2WH_2)_2Ag]BF_4 \cdot H_2O$ (49.6°). The position of the hydride ligands in **4** could not be localized.

The Mo1–Ag1–Mo2 angle in the cation $[(Cp_2MoH_2)_2Ag]^+$ is 169.7(1)°, similar to the salts $[(Cp_2MH_2)_2Ag]X$ (M = Mo, W; X = BF_4, PF_6) [5]. With 2.848(1) and 2.855(1) Å the Mo–Ag distances in the cation of **4** are appreciably shorter than in the complexes in which another ligand is coordinated at the silver atom (range 2.91–3.06 Å) [4,5].

3.5. $[(Cp_2MoH_2)_2AgSCF_3]$ (5)

Fig. 6 shows the structure of complex **5**, which is similar to **1**–**3**. Two $[Cp_2MoH_2]$ units and the SCF_3 ligand surround the silver atom in a trigonal planar way. The angle Mo1–Ag1–Mo2 is 129.6(1)°, whereas the angles Mo1–Ag1–S1 and Mo2–Ag1–S1 are 120.5(1)° and 110.0(1)°, respectively (Table 5). The length of the Ag1–S1 bond is 2.646(2) Å and the Ag1–S1–C1 angle is 101.7(2)°. The S1–C1–F1 angle (115.8(3)°) is larger and the F1–C1–F2 angle (103.9(4)°) is smaller than the ideal tetrahedral angle. The position of the hydride ligands in **5** could not localized.

4. Experimental

Experimental techniques and analytical instruments were described before [4]. $[Cp_2MoH_2]$ [1] and $AgSCF_3$ [10] were prepared by literature methods. $AgBF_4$, NH_4SCN, KOCN, AgNCO and NaCN were purchased from Aldrich Chemicals and used without further purification.

4.1. *[(Cp_2MoH_2)$_2$AgSCN]* (**1**)

[Cp_2MoH_2] (242 mg, 1.06 mmol) was dissolved in 8 ml of acetone and cooled to −25 °C. $AgBF_4$ (98 mg, 0.50 mmol) in 2 ml of acetone was added. To the clear, yellow solution NH_4SCN (50 mg, 0.66 mmol) in 2 ml of acetone was added. The precipitate was isolated, washed with 2 × 5 ml of acetone (−25 °C) and chromatographed on silica gel. The yellow product was eluted with CH_2Cl_2–acetone 2:1 and recrystallized from CH_2Cl_2. Yield: 281 mg (90%). M.p. 85 °C (dec.). $C_{21}H_{24}AgMo_2NS$ (622.24). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.81 (bs, 20H, η^5-C_5H_5), −9.43 (bs, 4H, MoH).

4.2. *[(Cp_2MoH_2)$_2$AgNCO]* (**2**) *and [(Cp_2MoH_2)$_2$Ag($C_3N_3H_2O_3$)]* (**3**)

4.2.1. *Method (1)*

To a solution of [Cp_2MoH_2] (120 mg, 0.53 mmol) and $AgBF_4$ (55 mg, 0.28 mmol) in 10 ml of acetone was added KOCN (22 mg, 0.28 mmol) in 6 ml of methanol at −25 °C. After 30 min stirring at room temperature in darkness the solvent was removed. The residue was dissolved in CH_2Cl_2 and chromatographed on silica gel. The yellow zone was eluted with MeOH and recrystallized from CH_2Cl_2 to give complex **2**. Yield: 128 mg (63%). M.p. 86 °C (dec.). Anal. Found: C, 38.43; H, 3.76; N, 1.90. Calc. for $C_{22}H_{26}AgCl_2Mo_2NO$ (691.11): C, 38.23; H, 3.79; N, 2.03%. ^{1}H-NMR (CD_3OD, 400 MHz): δ 5.05 (t, ^3J(H,H) = 0.7 Hz, 20H, η^5-C_5H_5), −9.67 (m, ^3J(H,H) = 0.7 Hz, 4H, MoH).

4.2.2. *Method (2)*

To a solution of [Cp_2MoH_2] (112 mg, 0.49 mmol) in 8 ml of acetone solid AgNCO (35 mg, 0.23 mmol) was added at −25 °C. After 10 min the yellow precipitate was isolated and washed with Et_2O. The product was purified by extraction with CH_2Cl_2. Recrystallization from CH_2Cl_2 gave mainly rhombs of complex **2** and in addition needles of compound [(Cp_2MoH_2)$_2$Ag($C_3N_3H_2O_3$)] (**3**).

4.3. *[(Cp_2MoH_2)$_2$Ag]$_n$[($Ag_2(CN)_3$)$_n$]* (**4**)

NaCN (20 mg, 0.41 mmol) in 2 ml of MeOH was added to a solution of [Cp_2MoH_2] (147 mg, 0.64 mmol)

Table 6
Crystallographic data for **1**–**5**

	1	**2**·CH_2Cl_2	**3**·3CH_2Cl_2	**4**	**5**·CH_2Cl_2
Empirical formula	$C_{21}H_{24}AgMo_2NS$	$C_{22}H_{22}AgCl_2Mo_2NO$	$C_{26}H_{32}AgCl_6Mo_2N_3O_3$	$C_{23}H_{20}Ag_3Mo_2N_3$	$C_{22}H_{26}AgCl_2F_3Mo_2S$
Formula weight	622.24	687.06	947.00	853.91	746.12
Temperature (K)	r.t.	173(1)	173(1)	173(1)	173(1)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1$	$P\bar{1}$
Crystal color, shape	Yellow prisms	Yellow prisms	Yellow rods	Yellow prisms	Yellow prisms
Crystal size (mm^3)	0.30 × 0.35 × 0.45	0.40 × 0.40 × 0.30	0.60 × 0.10 × 0.08	0.14 × 0.12 × 0.10	0.48 × 0.39 × 0.14
a (Å)	11.200(2)	10.4372(12)	11.6716(6)	9.2106(8)	9.4273(13)
b (Å)	10.316(2)	10.7285(13)	15.8220(11)	15.4830(18)	11.1217(16)
c (Å)	19.945(4)	11.8570(12)	18.0764(10)	8.6344(8)	12.4028(18)
α (°)	90	65.108(13)	90	90	104.486(17)
β (°)	91.75(2)	74.943(14)	90	74.173(10)	90.160(17)
γ (°)	90	73.788(14)	90	90	105.754(17)
V (Å^3)	2199.4(7)	1132.2(3)	3338.1(3)	1184.7(2)	1208.3(3)
Z	4	2	4	2	2
D_{calc} (g cm^{-3})	2.01	2.015	1.884	2.394	2.051
F(000)	1300	668	1864	808	724
μ (mm^{-1})	2.23	2.20	1.83	3.48	2.16
θ Range (°)	1.50–28.75	1.92–25.81	2.08–25.77	2.30–25.77	1.97–25.76
Total data	6289	15 950	46 813	16 484	16 774
Total unique data	5712	4074	6362	4471	4291
Parameters	236	262	394	280	280
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−1.35, 1.77	−0.591, 0.780	−0.566, 0.911	−0.411, 1.117	−0.717, 1.213
R_1 [a], [$I > 2\sigma(I)$]	0.048	0.0264	0.0257	0.0241	0.0284
wR_2 [b], [$I > 2\sigma(I)$]	0.045	0.0716	0.0603	0.0542	0.0769
Goodness-of-fit S [c]	2.577	1.109	0.969	1.035	1.122

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

and $AgBF_4$ (62 mg, 0.32 mmol) in 10 ml of acetone at −20 °C. The solid was isolated and chromatographed on silica gel with CH_2Cl_2–acetone 5:1. Recrystallization from CH_2Cl_2. Yield: 85 mg (93%). M.p. 118°C (dec.). $C_{23}H_{20}Ag_3Mo_2N_3$ (853.91). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.91 (t, 20H, η^5-C_5H_5), −10.11 (bs, 4H, MoH).

4.4. [$(Cp_2MoH_2)_2AgSCF_3$] (**5**)

To the yellow suspension of [Cp_2MoH_2] (241 mg, 1.06 mmol) in 12 ml of acetone was added $AgSCF_3$ (108 mg, 0.52 mmol), dissolved in 4 ml of acetone, at −25 °C to afford a yellow precipitate. The product was washed with 2 × 10 ml of Et_2O and dried at 0 °C in vacuo. Recrystallization from CH_2Cl_2. Yield: 320 mg (93%). M.p. 64°C (dec.). Anal. Found: C, 37.70; H, 3.72; Ag, 15.89. Calc. for $C_{21}H_{24}AgF_3Mo_2S$ (665.23): C, 37.92; H, 3.64; Ag, 16.22%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.85 (s, 20H, η^5-C_5H_5), −9.67 (s, 4H, MoH).

4.5. X-ray structure determinations

Diffraction data were collected on a Syntex R3 diffractometer for **1** and STOE-IPDS diffractometer for **2**–**5** using graphite-monochromatized Mo–K_α radiation ($\lambda = 0.7107$ Å). The unit cells were determined from 25 (**1**) and 8000 (**2**–**5**) 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 6. Structure **1** was solved by Patterson–Fourier methods using the shelxtl Plus Release 4.2/800, PC version. 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** and **3**) 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. Conclusion

Cp_2MoH_2 is a good but only rarely used ligand for transition metal ions such as Ag^+. It orients two hydrogen atoms in an acute angle to the central metal atom, leading to an interesting assembly of hydrogens around the coordination center. Additional ligands, such as halides, thio ligands and pseudo halides (as shown in the present paper) result in a diversity of structure types.

6. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 160864, 160860, 160861, 160862 and 160863 for compounds **1**–**5**, 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] M.L.H. Green, J.A. McCleverty, L. Pratt, G. Wilkinson, J. Chem. Soc. (1961) 4854.

[2] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.

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

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

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

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

[7] N.N. Greenwood, A. Earnshaw, Chemie der Elemente, VCH, Weinheim, 1988, p. 374.

[8] S. Patai, Z. Rappoport, The Chemistry of Functional Groups, Wiley, New York, 1983, p. 1254 Supplement D, Part 2.

[9] S.J. Anderson, D.S. Brown, K.J. Finney, J. Chem. Soc. Dalton Trans. (1979) 152.

[10] W.A. Herrmann, G. Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 5, Georg Thieme Verlag, Stuttgart, 1999, p. 40.