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NMR analysis of trinuclear silver(I) complexes with μ_2-H bridged group VI metallocene hydrides as ligands and X-ray structure analysis of $\{[(\eta^5\text{-MeC}_5H_4)_2Mo(\mu_2\text{-H})_2]_2Ag\}PF_6$

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Abstract

A mixture of the complexes $\{[Cp_2Mo(\mu_2\text{-H})_2]_2Ag\}PF_6$ (**1**), $\{[Cp_2W(\mu_2\text{-H})_2]_2Ag\}PF_6$ (**2**) and $[Cp_2Mo(\mu_2\text{-H})_2Ag(\mu_2\text{-H})_2WCp_2]PF_6$ (**3**) was synthesized. ^{1}H- and ^{1}H{^{109}Ag}-NMR experiments gave detailed information about structure, bonding and exchange behaviour. Further, the methyl substituted complex $\{[(\eta^5\text{-C}_5H_4Me)_2Mo(\mu_2\text{-H})_2]_2Ag\}PF_6$ (**4**) was synthesized and characterized by X-ray analysis. ^{1}H-, ^{1}H{^{109}Ag}- and ^{95}Mo-NMR data are reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Bridged trinuclear Ag–Mo- and Ag–W-hydride complexes; ^{1}H-NMR; ^{109}Ag-NMR; ^{95}Mo-NMR; Single-crystal X-ray structure analysis

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1. Introduction

The coinage metals Cu, Ag and Au show an extraordinary tendency to form tri- or multinuclear μ_2-hydride bridged complexes with metallocene hydrides of the transition metal groups V and VI [1–3]. In a previous study [4] we have presented new Ag(I) and Cu(I) complexes with Cp_2MH_2 (M = Mo, W) ligands differing in structure and bonding. In the present paper we analyze the ^{1}H-NMR spectra of these compounds, mainly with respect to the ^{107}Ag,^{1}H and ^{109}Ag,^{1}H coupling. We synthesized a mixture of the complexes $\{[Cp_2Mo(\mu_2\text{-H})_2]_2Ag\}PF_6$ (**1**), $\{[Cp_2W(\mu_2\text{-H})_2]_2Ag\}PF_6$ (**2**) and $[Cp_2Mo(\mu_2\text{-H})_2Ag(\mu_2\text{-H})_2WCp_2]PF_6$ (**3**) and the complex $\{[(\eta^5\text{-C}_5H_4Me)_2Mo(\mu_2\text{-H})_2]_2Ag\}PF_6$ (**4**). The structure of the methyl substituted complex **4** was determined by X-ray analysis. Detailed ^{109}Ag decoupling experiments gave information about the bonding and the exchange behavior of the complexes **1**, **2**, **3** and **4**. The ^{95}Mo-NMR spectrum of **4** is presented.

2. The system Cp_2MoH_2, Cp_2WH_2 and $AgPF_6$

The reaction of Cp_2MH_2 (M = Mo, W) with $AgPF_6$ in a molar ratio 2:1 in acetone at low temperatures yields the complexes $\{[Cp_2M(\mu_2\text{-H})_2]_2Ag\}PF_6$ (M = Mo **1**, W **2**) [2,4]. Similarly, the reaction of equimolar amounts of Cp_2MoH_2, Cp_2WH_2 and $AgPF_6$ at −35°C in acetone gives an olive yellow raw product (Scheme 1) from which yellow crystals can be grown from a mixture of CH_2Cl_2, tetrahydrofuran and toluene 5:1:1 at −20°C.

The IR spectrum (KBr) of the isolated yellow mixture of **1**, **2** and **3** shows aromatic ν(C–H) bands and a very broad band of the bridging hydride stretch at 1710 cm^{-1}.

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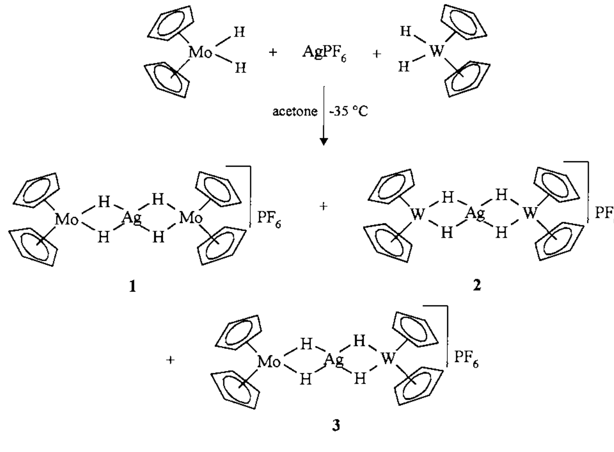
The room temperature ^{1}H-NMR spectrum of a solution of the yellow crystals in acetone-d_6 exhibits in the Cp region two triplets at δ ^{1}H = 5.10 [^3J(H,H) 0.8 Hz, Cp^{Mo}] and 5.03 [^3J(H,H) 0.8 Hz, Cp^W] identical with the shifts for the pure complexes **1** and **2** (Fig. 1). The molybdenum hydride signal (H^{Mo}) appears as a broad singlet at −9.48. It is shifted downfield in comparison to pure **1**. The tungsten hydride resonance is a broad singlet with tungsten satellites which are found at higher field (δ ^{1}H = −12.33) compared to pure **2**. The ^{1}H-NMR data of the room temperature spectrum of the isolated product of the equimolar reaction of Cp_2MoH_2, Cp_2WH_2 and $AgPF_6$ as well as of the pure compounds **1** and **2** are summarized in Table 1.

At −90°C the Cp signals split into four broad singlets with equal intensity. For the molybdenum hydrides as well as for the tungsten hydrides two doublets due to coupling to each of the isotopes ^{107}Ag and ^{109}Ag (natural abundance 51.8 and 48.2%, respectively) can be detected. All four hydride signals have the same intensity (Fig. 2/I). In the literature only a few examples of couplings to ^{107}Ag and ^{109}Ag have been reported [5,6]. In Table 2 the resonances and the $^1J(^{107/109}$Ag,^{1}H) values are compared with the values of the pure complexes **1** and **2**. It is interesting to note that for the pure complexes no silver splitting could be obtained even at low temperatures. Caulton [2] reported a splitting for **2** without $^{107/109}$Ag fine structure but gave no data for the coupling constants. The coupling constants (Table 2) are in the range of one-bond Ag–H coupling [6]. Thus, the formation of M–H–Ag (M = Mo, W) bridges is evident. Geminal coupling would support a donor-acceptor bond M → Ag (M = Mo, W) with the hydrides terminally bonded to Mo and W.

The formation of the three different complexes **1**, **2** and **3** in Scheme 1 is supported by heteronuclear double resonance ^{1}H{^{109}Ag} experiments. In Fig. 2 the hydride part of the ^{1}H-NMR spectrum (I) and the ^{1}H{^{109}Ag}-NMR spectra with different decoupling frequencies (II–IV) at −90°C are displayed. Obviously, three different decoupling frequencies (δ ^{109}Ag = 1230 ± 5 for H^{Mo2}, 1270 ± 5 for H^{Mo1} and H^{W2} and 1310 ± 5 for H^{W1}) are necessary to affect all four ^{109}Ag/^{1}H doublets. Thus, three species of ^{109}Ag nuclei with different chemical environment are present in solution, the complexes **1**, **2** and **3** in a combinatorically plausible ratio of 1:1:2. The decoupling experiments demonstrate that the hydride signals at δ^{1}H = −9.51 (H^{Mo1}) and −12.66 (H^{W2}) must be assigned to H^{Mo} and H^W of the mixed ligand species **3** (Table 2). The ^{109}Ag nuclear shielding of **1**–**3** is rather low when compared with other compounds containing silver in the oxidation state +1 [7].

Upon warming the solution from −90 to −80°C the four Cp singlets coalesce to two. At −30°C two triplets are present in the Cp region. The hydride signals begin to coalesce at −70°C. They appear as broad resonances at −60°C which sharpen upon warming up to room temperature. These phenomena are consistent with an equilibrium between the complexes **1**, **2** and **3** and their free ligands Cp_2MH_2 (M = Mo, W), which cannot be detected by ^{1}H-NMR spectroscopy. Exchange of the metallocene ligands at room temperature is so fast on the NMR time-scale that averaged resonances without silver coupling in the Mo–H and W–H region are observed. Upon cooling the exchange processes are slowed down and below −80°C silver coupling with the μ_2-H ligands can be detected. The Cp resonances behave similarly. The Cp^{Mo} and Cp^W triplets at room temperature are averaged signals. They broaden upon cooling. At −60°C two broad singlets are observed and at −80°C the Cp signals split into four singlets (Table 2). The singlet at 5.15 ppm is the Cp^{Mo} signal of complex **1** the resonances at δ^{1}H = 5.13 and 5.09 must be assigned to compound **3** and the singlet at 5.06 belongs to compound **2**.



Scheme 1. Reaction of equimolar amounts of Cp_2MoH_2, Cp_2WH_2 and $AgPF_6$.

3. [(η^5-$C_5H_4Me)_2Mo(\mu_2$-H$)_2Ag(\mu_2$-H$)_2Mo(\eta^5$-C_5H_4-$Me)_2]PF_6$ (4)

The reaction of (η^5-$C_5H_4Me)_2MoH_2$ with $AgPF_6$ in a molar ratio of 2:1 in acetone at −40°C gave the lemon coloured complex **4** (Scheme 2). Crystals suitable for X-ray analysis were grown in CH_2Cl_2/diethyl ether 50:1.

The IR spectrum (KBr) of compound **4** shows aromatic and aliphatic ν(C–H) vibrations. Compared to the terminal Mo–H stretch of free (η^5-$C_5H_4Me)_2MoH_2$ at 1850 cm^{-1} the μ_2-H bridge (Mo–H–Ag) stretch is lowered to 1690 cm^{-1} and broadened ($\Delta\nu_{1/2}$ ~ 110 cm^{-1}).

The ^{1}H-NMR spectrum of **4** in CD_2Cl_2 at room temperature exhibits pseudo-triplets (δ ^{1}H = 4.88, 4.74)

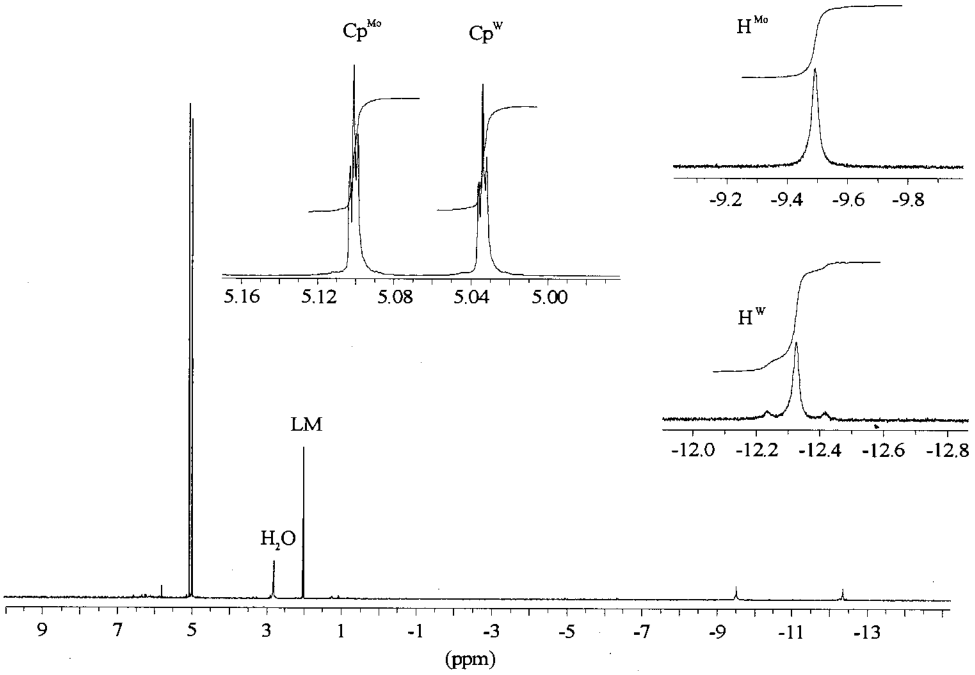


Fig. 1. 400 MHz ^{1}H-NMR spectrum of the products of the reaction between Cp_2MoH_2, Cp_2WH_2 and $AgPF_6$ 1:1:1 in acetone-d_6 at room temperature.

Table 1
Comparison of the chemical shifts of the mixture of **1**, **2** and **3** (molar ratio 1:1:2) and the pure complexes **1** and **2**[a]

Resonances	**1**, **2** and **3** (ratio 1:1:2)		**1**		**2**	
	δ/ppm	J/Hz, mult.	δ/ppm	J/Hz, mult.	δ/ppm	J/Hz, mult.
Cp^{Mo}	5.10	0.8, *t*	5.10	0.9, *t*	–	–
Cp^{W}	5.03	0.8, *t*	–	–	5.04	0.7, t
H^{Mo}	−9.48	br s	−9.64	br s	–	–
H^{W}	−12.33	73.8, W satellites	–	–	−12.20	73.8, W satellites

[a] All data from 400 MHz ^{1}H-NMR spectra in acetone-d_6 at room temperature.

for the AA'BB' spin system of the η^5-C_5H_4Me rings. The methyl singlet appears at $\delta\,^1$H 2.07. Different from the 1:1:2 mixture of the complexes **1**, **2** and **3**, coupling to $^{107/109}$Ag for the hydrides of complex **4** is already observed at ambient temperature: there is a broad doublet at $\delta\ ^1H = -9.32$ [$^1J(^{107/109}Ag,^1H)$ 68 Hz].

At −80°C the splitting due to the coupling is resolved. The coupling constants are 67.5 Hz for ^{107}Ag–^{1}H and 71.5 Hz for ^{109}Ag–^{1}H. A ^{1}H{^{109}Ag}-NMR spectrum verifies the one-bond Ag–H coupling and consequently the μ_2-H bridges between the silver ion and the molybdenum atom.

An interesting phenomenon is detected when a solution of **4** in CD_2Cl_2 (nitrogen atmosphere) is left for 10–15 h. In contrast to a freshly prepared sample, the hydride resonance forms a broad singlet instead of a broad doublet in the ^{1}H-NMR spectrum at room temperature. On cooling to −80°C the highly resolved $^{107/109}$Ag pattern is found again. On warming to ambient temperature the broad singlet reappears. The coalescence point in this experiment was found at −3°C. An explanation could be that **4** is decomposed partly after several hours liberating the ligand $(\eta^5$-$C_5H_4Me)_2MoH_2$ in spite of the nitrogen protection. Increasing concentrations of free ligand increase the rate of ligand exchange. Thus, the Ag–H bonds are cleaved more rapidly and the Ag–H coupling disappears. Freshly prepared samples of **4**, to which small amounts (~1%) of $(\eta^5$-$C_5H_4Me)_2MoH_2$ had been added, showed no Ag–H coupling in the ^{1}H-NMR spectrum at room temperature, but also no resolution of the coupling at −80°C. Interestingly, compared to the unsubstituted complexes **1**, **2** and **3** the methyl substituted complex **4** in solution is more stable towards the exchange of the metallocene ligand.

The ^{95}Mo-NMR spectrum of **4** in CD_2Cl_2 at room temperature consists of a very broad resonance at $\delta\ ^{95}Mo = 3953 \pm 10$ ($\Delta\nu_{1/2} = 8400 \pm 200$ Hz). For molybdenum in the oxidation state IV no comparable downfield shift has been reported yet [8]. Even more impressive is the extreme chemical shift of more than 6000 ppm with respect to the ligand $(\eta^5\text{-}C_5H_4Me)_2MoH_2$. Unsubstituted $(\eta^5\text{-}C_5H_5)_2MoH_2$ is detected at $\delta\ ^{95}Mo = -2507$ [8] and $(\eta^5\text{-}C_5H_4Me)_2MoH_2$ should experience a slight high field shift of its ^{95}Mo resonance caused by the methyl donor groups. Thus, the silver(I) ion has a strong deshielding effect on the molybdenum nuclei.

A single-crystal X-ray structure analysis was carried out for complex **4**. Relevant crystallographic data are given in Table 3 and selected bond distances and angles are listed in Table 4. A SCHAKAL view of the structure with the atomic numbering is shown in Fig. 3 [9].

The Mo–Ag–Mo axis in **4** is exactly linear. The M–Ag–M angles of the similar complexes $\{[Cp_2M(\mu_2\text{-}H)_2]_2Ag\}PF_6$ (M = Mo **1**, W **2**) are 175.2 and 170.8° [4]. The $(\eta^5\text{-}C_5H_4Me)_2MoH_2$ ligands adopt a nearly eclipsed conformation. The dihedral angle ring centroid–Mo1–Mo2–ring centroid is 5.4°. The position of the hydrides could not be localized. These are supposed to lie in planes perpendicular to the molybdenum-$(\eta^5\text{-}C_5H_4Me)$ centroid planes surrounding the silver ion as a square slightly distorted to a rhombic disphenoid. The methyl substituents orient towards the silver ion. Taking the silver ion as the origin of a coordinate system the methyl substituents occupy octants diagonally opposing each other. This orientation avoids steric hindrance. Interestingly, the distances from the molybdenum atoms to each of the cyclopentadienyl carbons vary from 2.23 Å for C1–Mo1 up to 2.37 Å for C3–Mo1. The methyl substituents are distorted slightly out of the ring planes. The angle centroid of ring 1 (CT1)–C3–C6 is 174.9°. Thus, the methyl substituents enforce a slight tipping of the cyclopentadienyl rings out of the molecular center rather than interact agostically with the silver atom (C6–Ag = 3.79 Å).

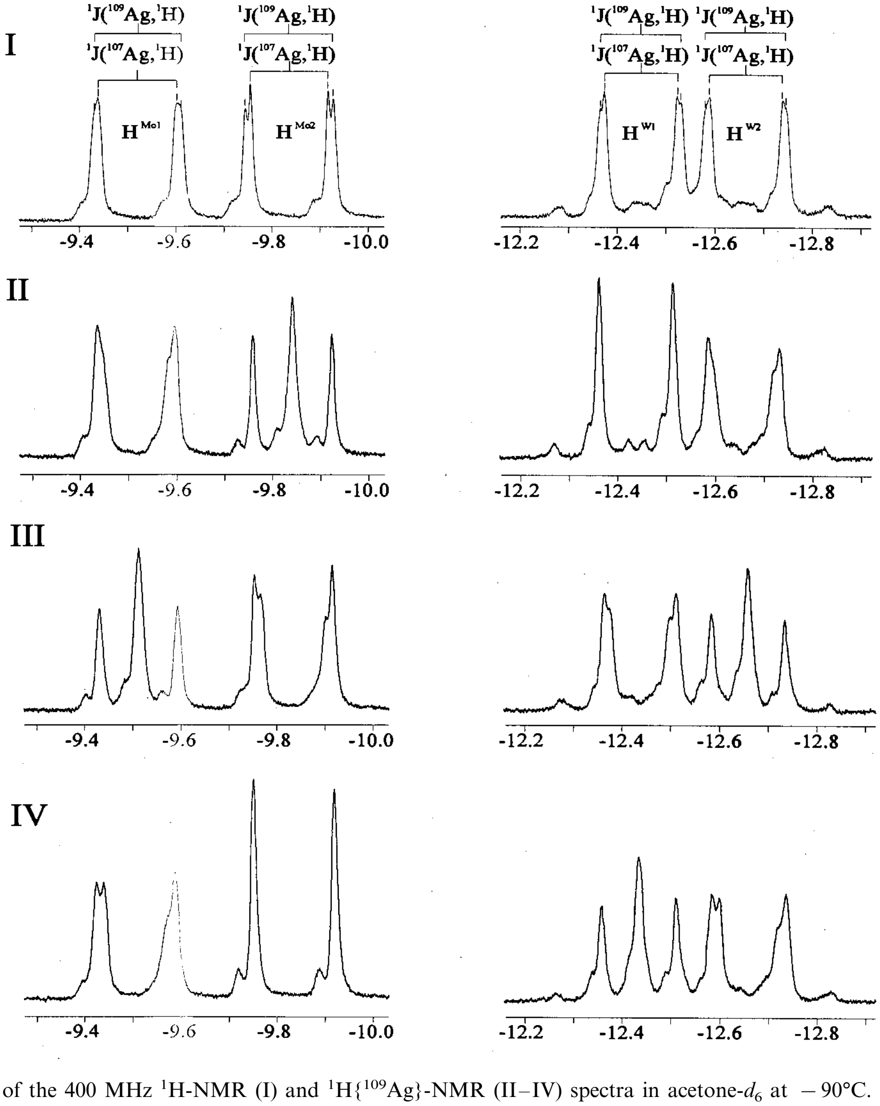


Fig. 2. Hydridge region of the 400 MHz ^1H-NMR (I) and $^1H\{^{109}Ag\}$-NMR (II–IV) spectra in acetone-d_6 at −90°C. Decoupling frequencies $\delta\ ^{109}Ag = 1230 \pm 5$ (II), 1270 ± 5 (III), 1310 ± 5 (IV).

Table 2
Comparison of the chemical shifts and $^1J(^{107/109}Ag,^1H)$ coupling constants of the mixture of **1**, **2** and **3** (molar ratio 1:1:2) and the pure complexes **1** and **2**[d]

Resonances	**1**, **2** and **3** (ratio 1:1:2)		**1**		**2**	
	δ/ppm	J/Hz, mult.	δ/ppm	J/Hz, mult.	δ/ppm	J/Hz, mult.
Cp^{Mo1}	5.15	[a]	5.15	[a]	–	–
Cp^{Mo2}	5.13	[a]	[b]	[a]	–	–
Cp^{W1}	5.09	[a]	–	–	[b]	[a]
Cp^{W2}	5.06	[a]	–	–	5.05	[a]
H^{Mo1}	−9.51	65.2/71.8	[b]	[c]	–	
H^{Mo2}	−9.83	64.1/73.5	−09.83	[c]	–	–
H^{W1}	−12.44	59.2/65.9	–	–	−12.42	[c]
H^{W2}	−12.66	59.8/65.7	–	–	[b]	[c]

[a] A splitting caused by Ag coupling was never detected in the Cp signals.
[b] The pure complexes **1** and **2** do not exhibit Ag splitting.
[c] Due to the missing splitting the Ag–H coupling constants could not be measured.
[d] All data from 400 MHz ^1H NMR spectra in acetone-d_6 at −90°C.

Compared to free $(\eta^5\text{-}C_5H_4Me)_2MoH_2$ no widening of the ring centroid–Mo–ring centroid angle is observed.

4. Experimental

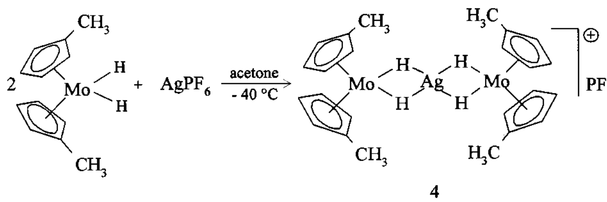
All complexes were prepared under an atmosphere of dried nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use according to standard procedures. Infrared spectra were recorded on a Beckman IR 4240 spectrometer. ^1H- and $^1H\{^{109}Ag\}$-NMR spectra were obtained on Bruker ARX 250 and ARX 400 spectrometers (250.13, 400.13 MHz). The ^{95}Mo-NMR spectrum was measured on a Bruker ARX 250 spectrometer (16.30 MHz). Chemical shifts δ ^1H are in ppm downfield from TMS, δ $^{109}Ag = 0$ for $Ag^+_{\infty aq}$ with $\Xi(^{109}Ag) = 4.653623$ MHz and δ $^{95}Mo = 0$ for 2 M Na_2MoO_4 in D_2O with $\Xi(^{95}Mo) = 6.516919$ MHz, respectively [10]. FD mass spectra were determined on a Finnigan MAT 95 instrument. Literature methods were used to prepare the metallocene hydrides $(\eta^5\text{-}C_5H_4)_2MH_2$ (M = Mo, W) [11] and $(\eta^5\text{-}MeC_5H_4)_2MoH_2$ [12].

4.1. *Reaction of Cp_2MoH_2,Cp_2WH_2 and $AgPF_6$*

Cp_2MoH_2 (114 mg, 0.50 mmol) and Cp_2WH_2 (158 mg, 0.50 mmol) were dissolved in 10 ml of acetone at −35°C and a solution of $AgPF_6$ (126 mg, 0.50 mmol) in 5 ml of acetone was added slowly. After 20 min the olive suspension was brought to dryness while cold. The solid was washed three times with 3 ml of diethyl ether and once with 3 ml of tetrahydrofuran. The product was dissolved in CH_2Cl_2 and filtered. The yellow filtrate was evaporated and the product crystallized from a mixture of CH_2Cl_2, toluene and tetrahydrofuran 5:1:1. Yield 301 mg (76%, based on the mixture of **1**, **2** and **3** in the ratio 1:1:2), m.p. 105°C (decomp.). Anal. Found: C, 30.05; H, 3.21; Ag, 13.44. Calc. (for the mixture of **1**, **2** and **3** in the ratio 1:1:2): C, 30.14; H, 3.04; Ag, 13.53. IR (KBr, cm^{-1}): 3120m (arom. C–H), 1710m (br) (Ag–H–M) (M = Mo, W), 1420s (arom. C=C), 835vs (P–F), 560s (deform. P–F).

4.2. *$[(\eta^5\text{-}C_5H_4Me)_2Mo(\mu_2\text{-}H)_2Ag(\mu_2\text{-}H)_2Mo(\eta^5\text{-}C_5H_4Me)_2]PF_6$ (4)*

A solution of $(\eta^5\text{-}C_5H_4Me)_2MoH_2$ (256 mg, 1.00 mmol) in 10 ml of acetone was cooled down to −40°C. Slowly, a solution of $AgPF_6$ (126 mg, 0.50 mmol) in 5 ml of acetone was added. After 2 min the solution turned opaque. The volatiles were removed at −40°C and the residue was washed three times with 3 ml of diethyl ether. The product was dissolved in a mixture of CH_2Cl_2 and acetone 2:1 and chromatographed on silica affording a lemon coloured band. Single crystals suitable for X-ray analysis were obtained from a solution in CH_2Cl_2 with small amounts of diethylether. Yield 365 mg (95%), m.p. 110°C (decomp.). Anal. Found: C, 37.71; H, 4.30. $C_{24}H_{32}AgF_6Mo_2P$ (765.23). Calc.: C, 37.67; H, 4.21. IR (KBr, cm^{-1}): 3120m (arom. C–H), 2980, 2940m (aliph. C–H), 1690s (br) (Ag–H–Mo), 1455s (arom. C=C), 840vs (P–F), 570s (deform. P–F). ^1H-NMR (CD_2Cl_2): δ 4.88 (m, 2H, Cp–H), 4.74 (m, 2H, Cp–H), 2.07 (s, 3H, CH_3), −9.32 (d (br),



4

Scheme 2.

Table 3
Summary of crystal data, data collection and structure refinement for complex **4**

Crystal parameters	
Elemental formula	$C_{24}H_{32}AgF_6Mo_2P$
M	765.23
Crystal system	Rhombic
Space group (no.)	D_{2h}^{24}, *Fddd* (70)
a (Å)	12.714(3)
b (Å)	18.435(4)
c (Å)	21.859(7)
V (Å^3); Z; D_c (g cm^{-3})	5123(2); 8; 1.98
F(000)	3008
μ (mm^{-1})	1.84
Crystal colour, shape	Yellow–brown, prismatic
Crystal size (mm^3)	0.15 × 0.25 × 0.30
Data collection	
hkl ranges	0–18; 0–25; 0–30
2θ range (°)	3.0–57.5
Total no. of unique reflections	1674
No. of observed reflections ($I > 2.5\ \sigma_I$)	1086
Min., max. transmission factors	0.85; 1.00
Data refinement	
No. of reflections, 2θ range (°) for empirical absorption correction	7; 4.0–41.0
No. of LS-parameters	90
Largest shift/esd in final cycle	0.1
$\Delta\rho_{min}$, $\Delta\rho_{max}$: (e Å^{-3})	−0.64; 0.82
R; R_w	0.047; 0.042

Table 4
Selected bond lengths [Å] and angles [°] of **4**[c]

Mo1–Ag	2.829(1)	Mo1–Ag–Mo2	180(1)
Mo1–H1[a]	1.730	Mo1–H1[a]–Ag	107.4
Ag–H1[a]	1.780	H1[a]–Mo1–H2[a]	73.8
Ag–C6	3.786	H1[a]–Ag–H2[a]	71.4
Mo1–CT1[b]	1.961	CT1[b]–Mo1–CT2[b]	144.8
Mo1–C1	2.259(8)	CT1[b]–C3–C6	174.9
Mo1–C2	2.321(7)	CT1[b]–Mo1–Mo2–CT3[b]	5.4
Mo1–C3	2.373(7)	CT1[b]–Mo1–H1[a]–Ag	99.5
Mo1–C4	2.297(7)		
Mo1–C5	2.228(7)		

[a] The hydrogen atoms were calculated by the option HF1X of the SHELXTL program package [13].

[b] CT = ring centroid.

[c] Estimated standard deviations are shown in parentheses.

$^1J(^{107/109}Ag,^1H)$ 67.7 Hz, 1H, Mo–H–Ag). ^{95}Mo-NMR (CD_2Cl_2): δ 3953 ± 10 (s (br), $\Delta\nu_{1/2} = 8400 \pm 200$ Hz, Mo).

4.3. X-ray structure analysis of 4

X-ray diffraction data were collected at 20°C with a Syntex–Nicolet R3 diffractometer using Mo–K_α radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator. The structure was solved using the Patterson–Fourier method with SHELXTL Plus (release 4.2/800), PC version [13]. The hydrogen atoms were calculated by the option HFIX of the SHELXTL program package. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (e-mail: crysdata@FIZ-karlsruhe.de) on quoting the depository CSD number CSD-410319.

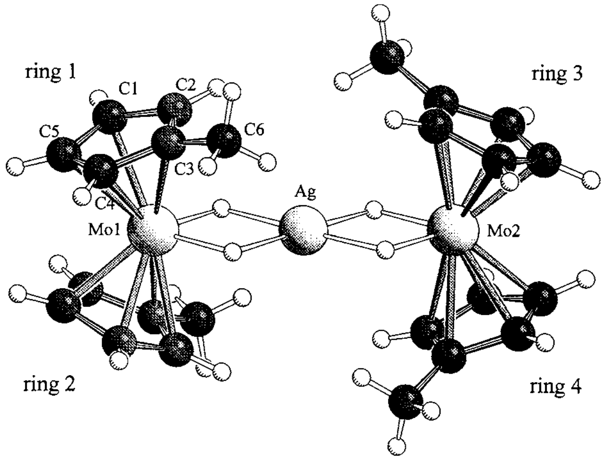


Fig. 3. SCHAKAL view of the molecular structure of the complex cation of $\{[\eta^5\text{-}C_5H_4Me)_2Mo(\mu_2\text{-}H)_2]_2Ag\}PF_6$ (**4**). The positions of the bridging hydrides are calculated.

References

[1] G.L. Soloveichik, B.M. Bulychev, Russ. Chem. Rev. 52 (1983) 43.

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

[3] A. Antiñolo, F. Carrillo-Hermosilla, B. Chaudret, M. Fajardo, J. Fernández-Baeza, M. Lanfranchi, H.-H. Limbach, M. Maurer, A. Otero, M.A. Pellinghelli, Inorg. Chem. 35 (1996) 7873.

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

[5] A. Albinati, H. Lehner, L.M. Venanzi, M. Wolfer, Inorg. Chem. 26 (1987) 3933.

[6] S.S.D. Brown, P.J. McCarthy, I.D. Salter, P.A. Bates, M.B. Hursthouse, I.J. Colquhoun, W. McFarlane, M. Murray, J. Chem. Soc. Dalton Trans. (1988) 2787.

[7] P. Granger, in: P.S. Pregosin (Ed.), Transition Metal Nuclear Magnetic Resonance, Elsevier, Amsterdam, 1991, p. 264.

[8] G.A. Webb, Annual Reports on NMR-Spectroscopy, vol. 33, Academic Press, NY, 1997, p. 151.

[9] E. Keller, SCHAKAL92, A Program for Graphical Representations of Crystal Structures, University of Freiburg, 1992.

[10] C.G. Young, M. Minelli, J.H. Enemark, W. Hussain, C.J. Jones, J.A. McCleverty, J. Chem. Soc. Dalton Trans. (1987) 619.

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

[12] N.D. Silavwe, M.P. Castellani, D.R. Tyler, Inorg. Synth. 29 (1992) 204.

[13] G.M. Sheldrick, SHELXTL Plus, A program for crystal structure determination, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.