Sulfurization and Selenization of the Halfsandwich Nitrosylmetal Complexes Cp*M(CO)2NO (M = Cr, Mo) and Cp*M(NO)I2 (M = Mo, W)

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Dedicated to Prof. Dr. h. c. mult. E. O. Fischer on the occasion of his 75th birthday

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Sulfido Metal Complexes, Selenido Metal Complexes, Halfsandwich Nitrosylmetal Compounds, X-Ray

The photo-induced decarbonylation of Cp*Cr(CO)2NO in acetonitrile solution in the presence of excess sulfur leads to the cyclo-pentasulfido complex Cp*Cr(NO)(S5)(1a), while in the case of limited sulfur supply the binuclear bis(µ-disulfido) complex Cp*Cr(NO)(µ-S2)(4a) is formed preferentially. The corresponding reaction with elemental selenium produces Cp*Cr(NO)(Se5)(4b), irrespective of the available amount of selenium. Photodecarbonylation of Cp*Mo(CO)2NO gives only the binuclear derivates Cp*Mo(NO)(µ-E2)(E = S (5a), Se (5b)) which are also obtained by treating Cp*Mo(NO)I2 with H2S or H2Se, respectively. Nitrosyl loss predominates if the tungsten complex Cp*W(NO)I2 is reacted with H2S in an argon atmosphere the products are Cp*W(S)(S2)(I)(7a) and Cp*W2(S2)(µ-S)2(8a), while in air some Cp*W(NO)(S2)(3a) and the oxo compounds Cp*W(O)(S2)(7c), Cp*W(O)(µ-S)(8c) and Cp*W2(O)(µ-S)(8d) are formed. The analogous reaction with H2Se leads to Cp*W(NO)(Se2)(3b), Cp*W2(Se2)(µ-Se)(9c) and Cp*W2(Se2)(µ-Se)(9d), respectively. The binuclear tungsten complexes 8a,c,d and 9a,c,d contain a central W(µ-E)2 framework (E = S or Se) which is unaffected by air, while terminal sulfido and selenido ligands are quantitatively converted into the corresponding terminal oxo ligands in the presence of air in CH2Cl2 or THF solution. With the preparation of Cp*W2(O)(µ-E)2 (E = S (8c) and Se (9c)), the series of dioxo complexes containing a pair of monochalcogen bridges (E = O, S, Se, Te) has become complete.

The new complexes have been characterized by their IR (v(NO)), 1H and 13C NMR (Cp*) spectra as well as by electron-impact mass spectrometry. According to the X-ray structure analyses, the binuclear compounds Cp*Cr(NO)(µ-S2)(4a) and Cp*Mo(NO)(µ-Se2)(5b) contain two 14-electron [Cp*M(NO)]2 fragments which are connected by a pair of dichalcogen (µ2-E2) bridging ligands (M = Cr or Mo, E = S or Se). The central M2E2 four-membered ring is not planar, and the binuclear molecules are chiral.

Introduction

We have recently described [1] the halfsandwich cyclo-pentasulfido and cyclo-pentaselenido complexes 1a,b, 2a and 3a,b which contain a nitrosyl ligand in addition to a voluminous pentamethylcyclopentadienyl ring:

Abbreviations: Cp = η5-cyclopentadienyl, η5-C5H5; Cp′ = η5-methylcyclopentadienyl, η5-C5H5Me; Cp∗ = η6-penta-methylcyclopentadienyl, η6-C5Me5.

The letters a and b in the numbering system refer to sulfur (a) and selenium (b) complexes, respectively.

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These compounds with a high chalcogen to metal ratio (5:1) are generally obtained [1] by treating the halfsandwich nitrosyl complexes Cp*Cr(NO)I and Cp*M(NO)I2 (M = Mo, W) with either methanolic ammonium polysulfide solutions or, in the case of selenium, with hydrogen selenide solutions, generated in situ by hydrolysis of Al2Se3. However,
side-products with a lower chalcogen to metal ratio (mostly 2:1) are always formed as well. An alternative route to sulfido and selenido compounds is the photo-induced decarbonylation of the nitrosyl complexes Cp*M(CO)2NO (M = Cr, Mo, W) in the presence of excess chalcogen. However, only 1a could be prepared by this method, whereas in the cases of molybdenum and tungsten, products with lower chalcogen content were again invariably formed.

We now describe sulfurization and selenization reactions involving the Cp* halfsandwich nitrosylmetal complexes to give products of lower chalcogen content.

Results and Discussion

1. Photodecarbonylation of Cp*M(CO)2NO (M = Cr, Mo) in the presence of sulfur or selenium

Depending on the sulfur supply, the light-induced decarbonylation of Cp*Cr(CO)2NO may lead to either Cp*Cr(NO)(S5) (1a) or Cp*2Cr2(NO)2(μ-S2)2 (4a) preferentially.

The intermediate acetonitrile complex has been characterized before [1]. Formation of the penta-sulfido complex 1a appears to be favoured; it was obtained quantitatively in the presence of excess S8 and still isolated in appreciable amounts when less sulfur was available. As expected, addition of S8 or (NH4)2Sx (x ~ 10) to an acetonitrile solution of 4a generates 1a.

The photodecarbonylation of Cp*Cr(CO)2NO in the presence of various amounts of selenium (1–10-fold excess) produced only the binuclear complex 4b. In a similar manner irradiation of Cp*Mo(CO)2NO in the presence of excess sulfur or selenium led only to the binuclear derivatives 5a and 5b; pentachalcogenide compounds such as 1b and 2a could not be isolated, although they are known [1]. The monomethyl-cyclopentadienyl complex Cp'Mo2(NO)2(S2)2 was also prepared.

The spectroscopic data obtained for 4a,b and 5a,b (Table I) are in agreement with binuclear
structures. Remarkably, in all cases two nitrosyl stretching absorptions are observed in the IR spectra, both in the solid state and in solution. This indicates that the complexes cannot be centrosymmetric, although only one type of Cp* ring ligand is seen in the $^1$H and $^{13}$C NMR solution spectra. The molecular structures of 4a and 5b were determined by X-ray crystallography (see below). The EI mass spectra contain the molecular ion in all cases; the primary fragmentation process appears to be successive loss of the two nitrosyl ligands.

Attempts to desulfurize the pentasulfides 2a and 3a using PPh$_3$ or PnBu$_3$ gave binuclear complexes of the general composition Cp*$_2$M$_2$(NO)$_2$S$_4$ (M = Mo, W). The molybdenum compound so formed is not identical with 5a. It is known that dehalogenation of Cp$_2$Ti(E$_2$) (E = S [2, 3], Se [4]) using tertiary phosphanes leads to binuclear derivatives containing a six-membered 1,4-dimetalla-cyclo-chalcogen ring.

2. Reaction of Cp*M(NO)I$_2$ (M = Mo, W) with hydrogen chalcogenide, H$_2$E (E = S, Se)

When H$_2$S gas was bubbled through the red THF solution of Cp*Mo(NO)I$_2$, the main product was Cp*$_2$Mo(NO)$_2$S$_2$ (5a) which could be isolated in about 80% yield. A similar reaction of Cp*Mo(NO)I$_1$ with H$_2$Se – obtained in situ by controlled hydrolysis of Al$_2$Se$_3$ in the THF solution itself – led to the doubly Se$_2$-bridged product 5b in about 65% yield, although loss of NO to give Cp*$_2$Mo$_2$Se$_3$ (6b) was also observed. The green side-product 6b is only sparingly soluble in organic solvents; its structure has not been determined but it is apparently different from the violet product obtained by Brunner et al. [5] by oxidative decarbonylation of Cp*$_2$Mo$_2$(CO)$_4$ using excess selenium in toluene solution.

Attempts to prepare binuclear nitrosyltungsten complexes, analogous to 4a, b and 5a, b, were not successful. The reaction of Cp*W(NO)I$_2$ with H$_2$S gas in THF solution in an argon atmosphere produced both a brown-black mononuclear compound Cp*WS$_3$(I) (7a) and a dark-red binuclear complex, Cp*$_2$W$_2$S$_4$ (8a).

If the reaction of Cp*W(NO)I$_2$ with H$_2$S gas was conducted in air, several oxo complexes such as 7c, 8c and 8d were isolated in addition to the only nitrosyl complex, Cp*W(NO)(S$_2$) (3a) which was formed in low yield (2%). The preparation of 3a from Cp*W(NO)I$_2$ and ammonium polysulfide in moderate yields (72%) and the structural characterization of the product have been described earlier [1]. The mononuclear compounds Cp*W(E)(S$_2$)I (E = S (7a) or O (7c)) correspond closely to the methyltungsten complexes Cp*W(E)(S$_2$)Me (E = S, O) studied by Faller and coworkers [6].

Binuclear complexes of the types Cp*$_2$W$_2$(E)(E')(µ-S)$_2$ (8a,c,d) are also known. In principle, several isomers are possible for complexes of the composition Cp*$_2$M$_2$S$_4$, as has been shown for the case of both M = W [7] and, in particular, M = Mo [7, 8, 9]. On the basis of the dark-red colour and the similarity of the IR data (v(W = S), one single absorption at 486 cm$^{-1}$, cf. 481 cm$^{-1}$ [7]), there are good reasons to believe that the binuclear complex obtained in the reaction of Cp*W(NO)I$_2$ with H$_2$S under argon is indeed the anti-isomer 8a first described by Brunner et al. [7]. The stepwise replacement of the two terminal sulfido by oxo ligands to give 8d and 8c, respectively, in the presence of air is also in agreement with the assumed W$_2$S$_2$ framework in the binuclear Cp*W complexes 8a,c,d.

A similar conversion of a terminal sulfido into a terminal oxo ligand was observed in the case of the mononuclear 16-electron complexes 7a,c.

The reaction of Cp*W(NO)I$_2$ with H$_2$Se in THF solution under argon gave a mixture of three products (3b, 9c and 9d), among which the mononuclear cyclo-pentaselenide 3b is preferentially
formed if the supply of H₂Se is high. The binuclear compounds 9c and 9d are typical products of limited selenium supply.

Table II. Spectroscopic data for the Cp*W complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (CsI) [cm⁻¹]</th>
<th>NMR (CDCl₃ solution) ¹H (δ values)</th>
<th>NMR (CDCl₃ solution) ¹³C (δ values)</th>
<th>EI Mass spectra (m/e [%])a</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7a Cp*W(S)(S₂)I</td>
<td>498 v(S₂) 485 v(W=0)</td>
<td>2.38 s 12.2 (Me) 120.4 (ring)</td>
<td></td>
<td>542 (12%) 510 (90%) 478 (8%)</td>
<td>M⁺⁺S⁻⁻I</td>
</tr>
<tr>
<td>7c Cp*W(O)(S₂)I</td>
<td>932 v(W=O) 543 v(S₂)</td>
<td>2.33 s 12.4 119.9</td>
<td></td>
<td>526 (100%) 494 (7%) 462 (10%)</td>
<td>M⁺⁻I</td>
</tr>
<tr>
<td>8a Cp*₂W₂(S)₂(μ-S)₂</td>
<td>486 v(W=O)</td>
<td>2.15 s 12.2 118.8</td>
<td></td>
<td>766 (80%) 734 (100%)</td>
<td>M⁺⁻Cp⁺</td>
</tr>
<tr>
<td>8c Cp*₂W₂(O)₂(μ-S)₂</td>
<td>920 v(W=O)</td>
<td>2.25 s 12.2 118.8</td>
<td></td>
<td>734 (100%) 718 (5%)</td>
<td>M⁺⁻Cp⁺</td>
</tr>
<tr>
<td>8d Cp*₂W₂(S)(O)(μ-S)₂</td>
<td>911 v(W=O) 488 v(W=0)</td>
<td>2.35 12.2/12.9 119.7/115.6</td>
<td></td>
<td>749 (98%) 733 (100%)</td>
<td>M⁺⁻H 717 (29%)</td>
</tr>
<tr>
<td>9c Cp*₂W₂(O)₂(μ-Se)₂</td>
<td>921 v(W=O)</td>
<td>2.21 12.5 112.5</td>
<td></td>
<td>828 (100%) 812 (4%)</td>
<td>693 (44%)</td>
</tr>
<tr>
<td>9d Cp*₂W₂(O)(Se)(μ-Se)₂</td>
<td>919 v(W=O)</td>
<td>2.20 12.2/12.4 111.0/112.7</td>
<td></td>
<td>892 (100%) 876 (23%)</td>
<td>757 (40%)</td>
</tr>
</tbody>
</table>

a The m/e values listed refer to the isotopes ¹⁸¹W, ³²S and ⁸⁰Se; b a W=Se stretching absorption for 9d could not be observed (due to rapid hydrolysis to 9e).

That the oxygen-free complex (9b) was not isolated might be due to the presence of water as a result of the Al₂Se₃ hydrolysis. In air, 9d is rapidly and quantitatively converted to the dioxo complex 9c.

The Cp*W compounds 8c,d and 9c,d have not been described previously. However, the CpW complexes (containing unsubstituted Cp ring ligands) Cp₂W₂(E)(E')(μ-S)₂ (E = E' = S [10, 11, 13], O [12, 13]; E = S, E' = O [13] and Cp₂W₂(E)(E')(μ-Se)₂ (E = E' = O [14]) are well-known. At the present state of knowledge, it appears that the binuclear tungsten complexes described here generally prefer the anti-configuration containing the two Cp (or Cp*) ring ligands in mutual trans-position at a planar W₂(μ-S)₂ or W₂(μ-Se)₂ center. X-ray structure determinations carried out for Cp₂W₂(N'Bu)₂(μ-S)₂ [13] and Cp₂W₂(O)₂(μ-Se)₂ [14] have confirmed this trans geometry.

The series of dioxo complexes Cp*₂W₂O₂(μ-E)₂ is now known for all chalcogens as bridging ligands.
Table IV. Selected bond distances and angles for \(\text{Cp}^*\text{Mo}_2(\text{NO})_2(\mu-\text{Se}_2)(5b)\).

<table>
<thead>
<tr>
<th>Bond distances [Å]</th>
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<tbody>
<tr>
<td>(\text{Mo}-\text{Se}(1))</td>
</tr>
<tr>
<td>(\text{Mo}-\text{Se}(2))</td>
</tr>
<tr>
<td>(\text{Mo}-\text{Se}(2a))</td>
</tr>
<tr>
<td>(\text{Mo-Cp}^*)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mo}(1)-\text{Se}(1)-\text{Se}(2a))</td>
</tr>
<tr>
<td>(\text{Mo}(1)-\text{Se}(1)-\text{Se}(2))</td>
</tr>
<tr>
<td>(\text{Mo}(1)-\text{Se}(2a)-\text{Se}(1))</td>
</tr>
<tr>
<td>(\text{Mo}(a)-\text{Se}(2)-\text{Se}(1a))</td>
</tr>
<tr>
<td>(\text{Se}(2)-\text{Mo}(a)-\text{Se}(1))</td>
</tr>
<tr>
<td>(\text{Se}(2)-\text{Mo}(a)-\text{Se}(2a))</td>
</tr>
<tr>
<td>(\text{Se}(2a)-\text{Mo}(a)-\text{Se}(1))</td>
</tr>
</tbody>
</table>

\(\text{Cp}^* = \text{centroid of the five ring carbon atoms, } \text{C}(1)-\text{C}(5).\)

The transannular distances \((\text{S}(2)\cdots\text{S}(2a))\) 2.879 Å in \(4a\), \(\text{Se}(2)\cdots\text{Se}(2a)\) 3.248 Å in \(5b\) are shorter than the sum of the van der Waals radii for sulfur (2 × 1.83 Å) and selenium (2 × 2.00 Å). As in related compounds (see below), the bond distances in the diatomic bridging ligands \((\text{S}_2\) 2.013(2) Å in \(4a\) and \(\text{Se}_2\) 2.311(2) Å in \(5a\)) are slightly shorter than the single-bond distances in \(\text{S}_8\) (2.06 Å) and \(\text{Se}_8\) (2.33 Å), although considerably longer than the double bonds in the diatomic molecules \(\text{S}=\text{S}\) (1.89 Å) and \(\text{Se}=\text{Se}\) (2.19 Å) [16].

Binuclear complexes containing a pair of bridging \(\mu-\eta^1\eta^2-E_2\) ligands are apparently formed if 8 electrons are required to reach the inert gas configurations. Thus, uncharged complexes such as \(4a\), \(5b\) and \(10a\) [17] are composed from two 14-electron fragments:

\[
\begin{align*}
\text{[Cp}^*(\text{NO})\text{Cr}(\mu-\text{S}_2)\text{[Cr(NO)Cp}^*\text{](4a)} \\
\text{S-S} \\
3.427 \text{Å} \\
2.013(2) \text{Å} \\
\text{[Cp}^*(\text{NO})\text{Mo}(\mu-\text{Se}_2)\text{[Mo(NO)Cp}^*\text{](5b)} \\
\text{Mo-Se} \\
3.565 \text{Å} \\
2.311(2) \text{Å} \\
\text{[Cp}^*\text{Co}(\mu-\text{S}_2)\text{[CoCp}^*\text{](10a)} \\
\text{S-S} \\
3.38 \text{Å} \\
2.062(6) \text{Å}
\end{align*}
\]

Decations such as \(11\) [18] and \(12\) [19] are built from two 15-electron fragments:

\[
\begin{align*}
\text{[Cp}^*(\text{PPh}_3)\text{Ru}(\mu-\text{S}_2)\text{[Ru(PPh}_3\text{)Cp}^*\text{](11b)} \\
\text{Ru-Se} \\
3.937(1) \text{Å} \\
2.279(1) \text{Å} \\
\text{[(triphos)Rh(\mu-\text{S}_2)\text{[Rh(triphos)]}^2(12a)} \\
\text{S-S} \\
2.022(3) \text{Å} \\
2.298(1) \text{Å}
\end{align*}
\]

\(\text{triphos} = \text{MeC(\text{CH}_2\text{PPh}_2)\text{_3}}\)
An unsymmetrical structure made up from a 15- and a 13-electron moiety is observed in the Cp'Fe complex 13a [20]:

$$\text{[Cp'(CO)Fe(\mu-S_2)[FeCp']}\text{]} (13a)$$

Fe...Fe

$$15\text{ el.} \quad 8\text{ el.} \quad 13\text{ el.} \quad S-S$$

In contrast to 4a and 5b, the binuclear complexes 10a, 11b and 12a,b are all centrosymmetric; the two $\mu$-$\eta^1,\eta^2$-dichalcogen bridges are arranged anti (trans) with respect to the planar central four-membered ring, at least in the solid state. However, the unsymmetrical iron complex $\text{[Cp'(CO)Fe(\mu-S_2)[FeCp']}\text{]} 13a [20]$ and its ruthenium analogue $\text{[Cp*(CO)Ru(\mu-S_2)[RuCp']}\text{]} 21$ appear to exist as an equilibrium mixture of both anti (trans) and syn (cis) form in solution, as may be deduced from two distinct v(CO) stretching absorptions in the IR spectra. The syn isomer of 13a has been structurally characterized; the four sulfur atoms are nearly coplanar [20].

As may be expected from electron book-keeping according to the inert gas rule, all these complexes are diamagnetic, and the metal--metal distances are non-bonding. Discussions concerning the structural variety of Cp(*)M(E4)MCp(*) complexes and the electron accountancy for oligochalcogenide bridging ligands may be found in recent publications by Hoffmann [9], Rauchfuss [18] and Wächter [22].

**Experimental**

All experiments were routinely carried out in an atmosphere of dry argon using Schlenk techniques. The use of dry and oxygen-free solvents is necessary.

The starting halfsandwich complexes Cp*M(CO)2 NO (M = Cr [23], Mo [1]) and Cp*M(NO)I2 (M = Mo [1], W [24]) were prepared following established procedures.

The light source for the photolyses was a high-pressure 250 W mercury lamp (Original Hanau) housed in a water-cooled glass jacket. Separation of product mixtures and purification of the components was accomplished by column chromatography over silica gel (Merck 60) which had been activated at 600 °C overnight and stored under argon.

Spectroscopic measurements: IR: Perkin-Elmer

$$3.397(4)\text{ Å}$$

$$1.980(8)\text{ Å}$$

$$2.006(8)\text{ Å}$$

983 G; 1H and 13C NMR: Jeol FX 90Q (CDCl3, 0 °C); Mass spectra: Varian MAT 8500 (70 eV).

X-ray: Nicolet R 3m with graphite monochromator.

a) Photo-induced decarbonylations in the presence of sulfur or selenium. Acetonitrile was used as a solvent in order to keep most of the chalcogen in solution

$$\text{Cp*}_2\text{Cr}_2(\text{NO})_2(\mu-S_2)_2(4a)$$

An orange suspension containing 0.56 g (2.05 mmol) Cp*Cr(CO)2 NO and 0.18 g (5.6 mmol) sulfur in 80 ml acetonitrile was irradiated 2 h at 15 °C. Carbon monoxide evolved while the colour of the reaction mixture changed gradually over red and dark-green to black. The solvent was removed from the homogeneous solution in vacuo and the residue chromatographed on silica. Elution with CH2 Cl2/pentane (1:1) gave a dark-green zone containing 0.18 g (23.3%) Cp*Cr(NO)(S5) (1a) [1], elution with CH2 Cl2/pentane (2:1) a black zone containing Cp*2Cr2(\text{NO})2(\mu-S2)2 (4a). Black prismatic crystals of 4a (0.36 g, 62.5%) were obtained by slow diffusion of hexane into a chloroform solution of 4a at −25 °C. The binuclear product 4a (m.p. 237 °C) is soluble in chloroform, dichloromethane, acetonitrile, acetone and N,N-dimethylformamide, but insoluble in saturated hydrocarbons.

$$\text{Cp*}_2\text{Cr}_2(\text{NO})_2(\mu-Se_2)_2(4b)$$

An orange suspension of 0.33 g (1.21 mmol) Cp*Cr(CO)2 NO and 0.19 g (5.6 mmol) gray selenium in 80 ml acetonitrile was photolysed for 3 h. The black reaction mixture was filtered and the concentrated solution chromatographed on silica. Elution with CH2 Cl2/pentane (1:1) gave a dark-green zone containing 0.18 g (23.3%) Cp*Cr(NO)(Se2) (1a) [1], elution with CH2 Cl2/pentane (2:1) a black zone containing Cp*2Cr2(\text{NO})2(\mu-Se2)2 (4b). Black prismatic crystals of 4b (0.36 g, 62.5%) were obtained by slow diffusion of hexane into a chloroform solution of 4b at −25 °C. The binuclear product 4b (m.p. 237 °C) is soluble in chloroform, dichloromethane, acetonitrile, acetone and N,N-dimethylformamide, but insoluble in saturated hydrocarbons.

$$\text{Cp*}_2\text{Mo}_2(\text{NO})_2(\mu-S_2)_2(5a)$$

Under irradiation the orange suspension of 0.32 g (1 mmol) Cp*Mo(CO)2 NO and 0.10 g (3.1
mmol) sulfur in 50 ml acetonitrile became dark-red, and CO gas was liberated. After 1 h photolysis the solution was concentrated and chromatographed on silica. A dark-red solution was eluted with CH$_2$Cl$_2$/pentane (1:1) from which 0.18 g (55%) dark-red prismatic crystals of 5a could be isolated. Recrystallization from CHCl$_3$/hexane at -25 °C; m.p. 163-164 °C, soluble in polar organic solvents.

**Cp*$_2$Mo$_2$(NO)$_2$(μ-S$_2$)$_2$** (5b)

The photo-induced decarbonylation (3 h) of an orange suspension containing 0.32 g (1 mmol) Cp*Mo(CO)$_2$NO and 0.32 g (4 mmol) gray selenium in 60 ml acetonitrile produced a black reaction mixture. The solvent was taken off under reduced pressure, and the residue was purified by chromatography on silica. Elution with CH$_2$Cl$_2$/pentane (1:2) C p*;w ;(0)(Se)(//-Se), (9d) black 0.10 g (22.4%)

The binuclear complexes 9c and 9d do not melt up to 250 °C.

**Reactions with Cp*W(NO)$_2$I$_2$**

1. With H$_2$S under argon: A stream of H$_2$S was bubbled for 20 min through a solution containing 0.30 g (0.5 mmol) Cp*W(NO)$_2$I$_2$ in 50 ml THF. The colour changed from green to red. The solution was stirred for 1 h under argon, then brought to dryness in vacuo, and the black residue was worked up by column chromatography on silica. Using CH$_2$Cl$_2$/pentane (3:2) two bands were eluted, a brown zone containing Cp*W(S)(S)$_2$I (7a) followed by a dark-red zone containing Cp*$_2$W$_2$(S)$_4$(μ-S)$_2$ (8a). Both products were recrystallized from chloroform/hexane at -25 °C to give 0.07 g (25.9%) 7a (black needles, m.p. 172-173 °C) and 0.09 g (47.1%) 8a (dark-red crystals, no m.p. up to 250 °C).

2. With H$_2$S in air: If the reaction of Cp*W(NO)$_2$I$_2$ (0.60 g, 1 mmol) with gaseous H$_2$S in THF solution (80 ml) was deliberately carried out under air, the chromatographic separation of the product mixture gave four complexes:

- Cp*W(NO)(S)$_2$I (3a) [1], violet, 0.01 g (2.0%)
- Cp*W(O)(S)$_2$I (7c), red, 0.19 g (36.3%)
- Cp*$_2$W$_2$(O)$_2$(μ-S)$_2$ (8c), red, 0.12 g (32.8%)
- Cp*$_2$W$_2$(S)_4 (μ-S)$_2$ (8d), red, 0.10 g (26.8%)

Both 8c and 8d were isolated as fine red crystals which did not melt up to 250 °C.

3. With H$_2$Se under argon: H$_2$Se was slowly generated by dropwise addition of H$_2$O (0.22 ml, 1.2 mmol) to a THF suspension (80 ml) containing 0.29 g (1 mmol) Al$_2$Se$_3$ and 0.60 g (1 mmol) Cp*W(NO)$_2$I$_2$. In the course of 24 h the stirred reaction mixture changed the colour from green over red and dark-red to black. Filtration and evaporation of the solvent THF under vacuum gave a black residue which was separated into three compounds by chromatography:

<table>
<thead>
<tr>
<th>Elution by</th>
<th>Product</th>
<th>Colour</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$/pentane</td>
<td>Cp*W(NO)(Se)$_2$I (3b)</td>
<td>violet</td>
<td>0.16 g (21.3%)</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$/pentane</td>
<td>Cp*$_2$W$_2$(O)$_2$(μ-Se)$_2$ (9c)</td>
<td>red</td>
<td>0.20 g (48.2%)</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$/pentane</td>
<td>Cp*$_2$W$_2$(O)(Se)(μ-Se)$_2$ (9d)</td>
<td>black</td>
<td>0.10 g (22.4%)</td>
</tr>
</tbody>
</table>

The binuclear complexes 9c and 9d do not melt up to 250 °C.
c) Preparation of Cp\textsuperscript{*} W-oxo complexes

The Cp\textsuperscript{*}W compounds containing terminal sulfido or selenido ligands are quantitatively converted into the corresponding compounds containing terminal oxo ligands if stirred in solution (CH\textsubscript{2}Cl\textsubscript{2}, THF) in the presence of air, e.g.

Cp\textsuperscript{*}W(S)(S\textsubscript{2})I (7 a) gives Cp\textsuperscript{*}W(O)(S\textsubscript{2})I (7 c) rapidly; Cp\textsubscript{*}\textsubscript{2}W\textsubscript{2}(S\textsubscript{2})(\mu-S\textsubscript{2})\textsubscript{2} (8 a) gives Cp\textsubscript{*}\textsubscript{2}W\textsubscript{2}(O)(S)(\mu-S\textsubscript{2})\textsubscript{2} (8 d) and Cp\textsubscript{*}\textsubscript{2}W\textsubscript{2}(O)(\mu-S\textsubscript{2})\textsubscript{2} (8 c) slowly; Cp\textsubscript{*}\textsubscript{2}W\textsubscript{2}(O)(Se)(\mu-Se\textsubscript{2})\textsubscript{2} (9 d) gives Cp\textsubscript{*}\textsubscript{2}W\textsubscript{2}(O)\textsubscript{2}(\mu-Se\textsubscript{2})\textsubscript{2} (9 c).

d) X-ray structure determination of Cp\textsuperscript{*}2Cr\textsubscript{2}(NO\textsubscript{2})(\mu-S\textsubscript{2})\textsubscript{2} (4a) and Cp\textsuperscript{*}2Mo\textsubscript{2}(NO\textsubscript{2})(\mu-Se\textsubscript{2})\textsubscript{2} (5b)

The crystal, data collection and refinement parameters for both 4a and 5b are given in Table V. The data collection was similar in both cases: A black crystal was mounted on a glass fiber with epoxy cement, and the unit cell parameters were deduced from the least squares fit of 25 reflections (20° < 2.9 < 25°). In both cases of 4a and 5b, the preliminary photographic data indicated either 4/m or 4/mmm Laue symmetry, and the systematic absences in the diffraction data established the space group as either P4\textsubscript{2}12 or P4\textsubscript{2}12. The Röger's test and the chemically sensible results of refinement showed that P4\textsubscript{2}12 is the correct space group for 4a and P4\textsubscript{2}12 for 5b. An empirical absorption correction was applied to the data sets (216 ψ-scan reflections, pseudoellipsoid model).

The structures were solved by direct methods which located the two metal and the four chalcogen atoms. The remaining non-hydrogen atoms were located through subsequent Fourier and least squares syntheses. All hydrogens were included as idealized isotropic contributions (d(CH) = 0.960 Å, U = 1.2 U for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. Tables VI and VII contain the atomic coordinates and equivalent isotropic thermal parameters for 4a and 5b, respectively.

Table V. Crystallographic data for Cp\textsuperscript{*}2Cr\textsubscript{2}(NO\textsubscript{2})(\mu-S\textsubscript{2})\textsubscript{2} (4a) and Cp\textsuperscript{*}2Mo\textsubscript{2}(NO\textsubscript{2})(\mu-Se\textsubscript{2})\textsubscript{2} (5b).
Table VI. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\hat{A}^2 \times 10^3$) for Cp*$^2$Cr$_2$(NO)$_2$($\mu$-S$_2$)$_2$ (4a).

<table>
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<th>Atom</th>
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<th>$z$</th>
<th>$U^*$</th>
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<tr>
<td>Cr</td>
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<td>1013.3(7)</td>
<td>5303.9(2)</td>
<td>25.7(2)</td>
</tr>
<tr>
<td>S(1)</td>
<td>8567(1)</td>
<td>1987(1)</td>
<td>5460(1)</td>
<td>37(1)</td>
</tr>
<tr>
<td>S(2)</td>
<td>8579(1)</td>
<td>214(1)</td>
<td>5489(1)</td>
<td>34(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>11538(4)</td>
<td>2229(4)</td>
<td>5529(1)</td>
<td>47(1)</td>
</tr>
<tr>
<td>N</td>
<td>10414(8)</td>
<td>1723(4)</td>
<td>5402(1)</td>
<td>30(1)</td>
</tr>
<tr>
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</tbody>
</table>

* Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table VII. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\hat{A}^2 \times 10^3$) for Cp*$^2$Mo$_2$(NO)$_2$($\mu$-Se$_2$)$_2$ (5b).

<table>
<thead>
<tr>
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</tr>
<tr>
<td>Se(2)</td>
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<tr>
<td>Mo</td>
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<td>-1559(21)</td>
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<td>61(8)</td>
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</tbody>
</table>

* Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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