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Syntheses and Characterization of Homo- and Hetero-bridged Dimolybdenum Complexes

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Current interest in molybdenum thiolate complexes arises from the known presence of Mo–S bonding in a variety of molybdo-enzymes [1–6]. Our synthetic studies of low valent chalcogen-bridged dimolybdenum complexes are directed at their electrochemical behaviour.

Recently we described the photoinduced synthesis of double-bridged $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-EPh})]_2$ (Mo=Mo) compounds by UV irradiation of $[(\eta^5\text{-MeCp})Mo(CO)_3]_2$ in the presence of Ph_2E_2 (E = Se, Te) and subsequent decarbonylation of the solids *in vacuo* [7]. We showed that two initially single-bonded molybdenum metal atoms were homolytically fissioned, then double-bridged by selenolato- or tellurolato-ligands and subsequently brought into a formally double-bonded molybdenum (Mo=Mo)–selenium or –tellurium ring. We now find that the triply bonded $[(\eta^5\text{-Cp})Mo(CO)_2]_2$ adds Ph_2E_2 to give double-bridged $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-EPh})]_2$ (E = S, Se, Te) without metal–metal bonding, as predicted by the eighteen-electron rule and in agreement with the reported flexibility of the Mo····Mo distance in dimeric organometallic compounds [8].

Various isomers are possible for these complexes, based on *cis*- or *trans*-arrangements of the cyclopentadienyl ligands (with respect to the Mo_2E_2 ring) and on mutually *syn* or *anti* orientations of the phenyl groups at sulphur, selenium or tellurium. IR and NMR spectra reveal that such isomers do exist, often interconverting rapidly on the NMR time-scale as a consequence of pyramidal sulphur, selenium or tellurium inversion. The ^{1}H NMR spectra show two signals attributable to the η^5-Cp(s, 10H, δ = 5, ppm) and Ph(m, 10H, δ = 7, ppm) protons. The infrared spectra (ν-CO) of pentane solutions of these bridged complexes are similar, revealing structural analogy and nearly same *cis*/*trans* ratio.

In the mass spectra the expected molecular ion peaks are observed for the S, Se and Te compounds ($M^+ = 652$, $M^+ = 746$, $M^+ = 844$, respectively). The fragmentation of the molecular ions occurs first by successive loss of the carbonyls and the loss of the cyclopentadienyl ligands. The isotopic distribution patterns for the three compounds are complex as expected. The degraded ions $M^+ - 4$ CO – Ph of the thiolato-, selenolato- and tellurolato-compounds show the highest intensity of the fragmentation patterns and demonstrate the stability of the Mo_2E_2 ring. In accordance with all spectroscopic data and the recently-reported molecular structure of $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-SR})]_2$ [8], we suggest for $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-EPh})]_2$ a structure containing a non-planar Mo_2E_2 ring without metal–metal bonding and with increasing Mo····Mo distance 'Mo_2Te_2' > 'Mo_2Se_2' > 'Mo_2S_2'.

Our described reaction of Ph_2S_2 with $[(\eta^5\text{-Cp})Mo(CO)_2]_2$ produces additionally the sulfur-rich by-product $[(\eta^5\text{-Cp})Mo(CO)(SPh)(\mu\text{-SPh})]_2$ isolated by column chromatography and identified by IR and mass spectra (Table I). A similar structure to the previous described $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-EPh})]_2$ is suggested for $[(\eta^5\text{-Cp})Mo(CO)(SPh)(\mu\text{-SPh})]_2$.

Using $(\eta^5\text{-Cp})Mo(CO)_3Cl$ as starting material and adding Ph_2S_2 the hetero-bridged dimolybdenum complex $[(\eta^5\text{-Cp})Mo_2(CO)_2(SPh)_2(\mu\text{-Cl})(\mu\text{-SPh})]$ was obtained. The analogous reaction of $(\eta^5\text{-Cp})Mo(CO)_3Cl$ with di-phenyldiselenide or -ditelluride in contrast leads only to the homo-bridged $[(\eta^5\text{-Cp})Mo(CO)(Cl)(\mu\text{-EPh})]_2$ (E = Se, Te) compounds. Both the homo- and hetero-bridged complexes show no molecular ion peaks in the mass spectra. Only the degraded ions $M^+ - 2$ CO are observed and exhibit the highest intensity. A similar structure to $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-SR})]_2$ [8] is proposed for the obtained homo- and hetero-bridged dimolybdenum complexes but containing a single metal–metal bond, as predicted by the eighteen electron rule.

All the described compounds were characterized by elemental analysis, ^{1}H NMR, infrared and mass spectra. The patterns of all compounds were found to correspond to that calculated from combinations of the polyisotopic elements contained. All spectroscopic data are tabulated in Table I.

Experimental

All manipulations were carried out under dry nitrogen. Solvents were dried and distilled under N_2. The C, H and O analyses were determined with a Heraeus EA 415 analyzer. Infrared spectra were recorded on a Perkin-Elmer 180 and mass spectra on a Varian MAT CH 7 (50 eV). NMR spectra were recorded on a Varian EM 360 L. Literature methods were used to prepare $[(\eta^5\text{-Cp})Mo(CO)_2]_2$ [9] and $(\eta^5\text{-Cp})Mo(CO)_3Cl$ [10].

Synthesis of $[(Cp)Mo(CO)_2(\mu\text{-SPh})]_2$

$[(Cp)Mo(CO)_2]_2$ (1.0 mmol, 434 mg) was dissolved in toluene (30 ml) and after addition of Ph_2S_2 (1.0 mmol, 218 mg) the reaction mixture was stirred

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TABLE I. Spectral Data for the Complexes

Complex	IR (ν-CO)	^{1}H NMR (ppm)	MS
$[(Cp)Mo(CO)_2(\mu\text{-}SPh)]_2$	1972sh 1953s (CH_2Cl_2) 1878sh 1859s	δ^1H(Cp) 5.2(s)(CH_3CN) δ^1H(Ph) 7.3(m)	$M^+ = 652$
$[(Cp)Mo(CO)_2(\mu\text{-}SePh)]_2$	1964s 1952s (CH_2Cl_2) 1870s 1860sh	δ^1H(Cp) 5.2(s)(CH_3CN) δ^1H(Ph) 7.3(m)	$M^+ = 746$
$[(Cp)Mo(CO)_2(\mu\text{-}TePh)]_2$	1935s 1920s (CH_2Cl_2) 1866s 1848s	δ^1H(Cp) 5.2(s)(CH_3CN) δ^1H(Ph) 7.3(m)	$M^+ = 844$
$[(Cp)Mo(CO)(SPh)(\mu\text{-}SPh)]_2$	1963sh 1958s (CH_3CN)	δ^1H(Cp) 6.1(s)(acetone) δ^1H(Ph) 7.1(m)7.3(m)	$M^+ = 804$
$[(Cp)_2Mo_2(CO)_2(SPh)_2(\mu\text{-}Cl)(\mu\text{-}SPh)]$	2021s (KBr)	δ^1H(Cp) 6.2(s)(acetone) δ^1H(Ph) 7.0–7.3(m)	$M^+ = 684^a$
$[(Cp)Mo(CO)(Cl)(\mu\text{-}SePh)]_2$	2007s 1970s (KBr) 1957s	δ^1H(Cp) 6.0(s)5.7(s) δ^1H(Ph) 7.3(m)(CH_3CN)	$M^+ = 705^a$
$[(Cp)Mo(CO)(Cl)(\mu\text{-}TePh)]_2$	1997s 1965s (KBr) 1952s	δ^1H(Cp) 5.8(s)5.4(s) δ^1H(Ph) 7.3(m)(CH_3CN)	$M^+ = 805^a$

[a] Highest ion peak observed in the mass spectra (50 eV).

for 24 h at room temperature. Column chromatography on Kieselgel (Merck < 0.063 mm, l = 40 cm) and eluation with CH_2Cl_2 gave first $[(Cp)Mo(CO)_3]_2$ and then $[(Cp)Mo(CO)_2(\mu\text{-}SPh)]_2$. After concentrating and adding n-pentane the compound was obtained (60%, deep red, m.p. 160 °C dec.). The third zone contained $[(Cp)Mo(CO)(SPh)(\mu\text{-}SPh)]_2$ (yield > 20%, deep red, m.p. 145 °C dec.).

Synthesis of $[(Cp)Mo(CO)_2(\mu\text{-}SePh)]_2$

$[(Cp)Mo(CO)_2]_2$ (1.0 mmol, 434 mg) was dissolved in toluene (30 ml) and after addition of Ph_2Se_2 (1.0 mmol, 312 mg) the reaction mixture was stirred for 3 d at room temperature. On concentration to 10 ml, the product precipitated. After filtration and recrystallization we obtained the title complex (yield 50%, red crystalline, m.p. 166–169 °C dec.).

Synthesis of $[(Cp)Mo(CO)_2(\mu\text{-}TePh)]_2$

$[(Cp)Mo(CO)_2]_2$ (1.0 mmol, 434 mg) was dissolved in toluene (30 ml) and after addition of Ph_2Te_2 (1.0 mmol, 410 mg) the reaction mixture was stirred for 4 d at room temperature. Work up was analogous to the Se-compound (yield 50%, red crystalline, m.p. 177–178 °C).

Synthesis of $[(Cp)_2Mo_2(CO)_2(SPh)_2(\mu\text{-}Cl)(\mu\text{-}SPh)]$

$(Cp)Mo(CO)_3Cl$ (2.0 mmol, 561 mg) and Ph_2S_2 (1.0 mmol, 218 mg) were dissolved in 30 ml toluene and stirred for 4 d at 50 °C. The red-brown precipitate was filtrated and washed with CH_2Cl_2/n-pentane (1:1). Extraction with CH_2Cl_2, concentration and addition of pentane affords a crystalline pure product (yield 40%, red-brown, m.p. 175 °C dec.).

Synthesis of $[(Cp)Mo(CO)(Cl)(\mu\text{-}SePh)]_2$

$(Cp)Mo(CO)_3Cl$ (2.0 mmol, 561 mg) and Ph_2Se_2 (1.0 mmol, 312 mg) were dissolved in 30 ml toluene and stirred for 6 d at 40 °C. Work up was similar to the previous described reaction of Ph_2S_2 (yield 60%, red-violet, m.p. 175–176 °C).

Synthesis of $[(Cp)Mo(CO)(Cl)(\mu\text{-}TePh)]_2$

$(Cp)Mo(CO)_3Cl$ (2.0 mmol, 561 mg) and Ph_2Te_2 (1.0 mmol, 410 mg) were dissolved in 60 ml THF and stirred for 3 d at 50 °C. The precipitate was filtrated and washed with cold THF and recrystallized from CH_2Cl_2 (yield 50%, red-violet, m.p. 181–182 °C).

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