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Synthesis and molecular structure of 
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Abstract

The metathesis reaction of \(\text{Cp}^*(\text{CO})_3\text{MoBr}\) and \(\text{NaW(\text{CO})_3Cp}\) produced \(\text{Cp}^*(\text{CO})_3\text{Mo–W(\text{CO})_3Cp}\) (1), featuring an unsupported Mo–W bond. Exposure of solutions of 1 to light leads to the quantitative formation of the corresponding homometallic dimers. In the solid state, the title complex exhibits an anti-arrangement of the \(\eta^5\)-cyclopentadienyl and the \(\eta^5\)-pentamethyl-cyclopentadienyl ligands and six terminal carbonyls. Comparison to corresponding complexes of molybdenum and tungsten reveals that the Mo–W distance is dictated by the presence of a Cp and a Cp* ligand. This is the first time that an unsupported Mo–W single bond distance is reported.

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Keywords: Molybdenum; Tungsten; Hetero bimetallic complexes; Carbonyl compounds

1. Introduction

During our studies of hetero bimetallic compounds of group 6 and group 8 metals we also synthesised the homometallic complex \(\text{Cp}^*(\text{CO})_3\text{Mo–Mo(\text{CO})_3Cp}\) [1], featuring an unsupported metal–metal bond as well as a Cp ligand on one and a Cp* ligand on the other metal centre. Structural properties of related complexes of the type \(\text{L(\text{CO})_3M–M(\text{CO})_3L}\), with \(\text{M} = \text{Mo or W}\) and \(\text{L} = \text{Cp or Cp*}\) respectively, are well-documented. Besides the common trans-arrangement of the cyclic ligands in \(\text{Cp(\text{CO})_3M–M(\text{CO})_3Cp}\) \((\text{M} = \text{Mo, W})\) [2,3], \(\text{Cp}^*(\text{CO})_3\text{Mo–Mo(\text{CO})_3Cp}\) [4,5] and \(\text{Cp}^*(\text{CO})_3\text{W–W(\text{CO})_3Cp}\) [6], there are structure reports of the gauche conformation in \(\text{Cp}^*(\text{CO})_3\text{W–W(\text{CO})_3Cp}\) [8]. However, \(\text{Cp}^*(\text{CO})_3\text{Mo–Mo(\text{CO})_3Cp}\) [1] did not yield suitable crystals for x-ray analysis and no data of corresponding homo/hetero metallic complexes bearing a Cp ligand on one and a Cp* ligand on the other metal centre are reported. To the best of our knowledge, there are only two examples of complexes with an unsupported M–M single bond and Cp and Cp* ligands coordinated to two different metal cores, both containing a ruthenium centre and a Th [9] or Mo [1] fragment, respectively, for which solid state structures are available. Here we report the preparation and molecular structure of the novel mixed-metal compound \(\text{Cp}^*(\text{CO})_3\text{Mo–W(\text{CO})_3Cp}\).

2. Results and discussion

Reaction of \(\text{NaW(\text{CO})_3Cp}\) with \(\text{Cp}^*(\text{CO})_3\text{MoBr}\) in tetrahydrofuran (THF) leads to the elimination of NaBr
and the formation of the heterobimetallic target complex Cp*(CO)3Mo–W(CO)3Cp (I) which was identified by IR, NMR, elemental analysis and X-ray crystallography. Further products of the reaction are the corresponding homometallic dimers.

\[
\text{Na}[\text{W(CO)}_3\text{Cp}] + \text{Cp}^*\text{(CO)}_3\text{MoBr} \rightarrow \\
\text{Cp}^*\text{(CO)}_3\text{Mo} \rightarrow \text{W(CO)}_3\text{Cp} (I) + [\text{Mo(CO)}_3\text{Cp}]^+_2 \\
+ [\text{W(CO)}_3\text{Cp}]_2
\]

As reported for the synthesis of Cp(CO)3Mo–W(CO)3Cp [10], after NaBr elimination, the possible formation of radicals and their statistical combination could be responsible for the formation of the homometallic dimers. They could also arise from metal–metal bond cleavage of the initially formed target complex and subsequent recombination of two moieties of the complex. When solutions of I are exposed to light under ambient conditions, the quantitative formation of the homometallic dimers is observed, which indicates an enthalpy-controlled reaction. Therefore synthesis and work-up have to be performed under rigorous light exclusion. The formation of Cp*(CO)3MoCl and Cp(CO)3WCl in solutions of I, if only in low yield.

In toluene solution, complex I looses CO upon thermal activation above 110 °C. The broad bands in the IR spectra, at 1870 and 1841 cm⁻¹/C0, indicate the formation of Cp*(CO)3Mo–Mo(CO)3Cp* and the formation of the heterobimetallic target complex. Further products of the reaction are the corresponding homo-metallic complexes. The two M(CO)3Cp fragments essentially adopt a piano-stool geometry and a mirror plane through both metal cores and the Cp or Cp* centroids is inherent in the complex. The observed Mo–W bond length of 3.2516(8) Å equals a calculated value based on the M–M bond distances in Cp(CO)3W–W(CO)3Cp, d (W–W) = 3.222(1) Å [3] and Cp*(CO)3Mo–Mo(CO)3Cp*, d (Mo–Mo) = 3.281(1) Å [4]. These data indicate that the overall bonding situation in and between the two metal fragments of the hetero bimetallic complex is comparable to that of the corresponding fragments of the two above quoted homo-metallic compounds. Taking also the M–M bond distances, the formation of homometallic dimers, which would imply a thermally induced reaction, was not detected.

\[
\text{Cp}^*\text{(CO)}_3\text{Mo} \rightarrow \text{W(CO)}_3\text{Cp} (I) \xrightarrow{\text{soln.} \rightarrow \text{hv}} \\
[\text{Mo(CO)}_3\text{Cp}]^+_2 + [\text{W(CO)}_3\text{Cp}]_2
\]

However, in contrast to Cp(CO)3Mo–W(CO)3Cp, which could not be isolated [10a,b], repeated column chromatography and recrystallisation allowed us the isolation of pure Cp*(CO)3Mo–W(CO)3Cp (I), if only in low yield.

The molecular configuration of I in the solid state is shown in Fig. 1, and details of selected bond lengths and angles are given in Table 2. Complex I consists of a Mo(CO)3Cp* and a W(CO)3Cp fragment linked by an unsupported Mo–W bond. In the solid state, the title complex features a trans-disposition of the cyclic ligands, which exhibit properties that are essentially similar to the ones reported for Cp/Cp* fragments of the corre-

![Fig. 1. ORTEP plot of Cp*(CO)3Mo–W(CO)3Cp (I) with ellipsoids drawn in 30% probability.](image-url)

Table 1

<table>
<thead>
<tr>
<th>Crystallographic data for Cp*(CO)3Mo–W(CO)3Cp (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
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<tr>
<td>Mol. wt.</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
</tr>
<tr>
<td>Cryst. syst.</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a (Å)</td>
</tr>
<tr>
<td>b (Å)</td>
</tr>
<tr>
<td>c (Å)</td>
</tr>
<tr>
<td>β (°)</td>
</tr>
<tr>
<td>V (Å³)</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>D_{oak} (g/cm³)</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
</tr>
<tr>
<td>T (K)</td>
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<tr>
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</tr>
<tr>
<td>R1</td>
</tr>
<tr>
<td>wR2</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å⁻³)</td>
</tr>
</tbody>
</table>

*a >2σ.
Table 2
Selected bond lengths (Å) and bond angles (°), Cp*(CO)3Mo–W(CO)3Cp (1)

<table>
<thead>
<tr>
<th>Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(1)–Mo(1)</td>
<td>3.2516 (8)</td>
</tr>
<tr>
<td>W(1)–C(1)</td>
<td>1.957 (10)</td>
</tr>
<tr>
<td>W(1)–C(2)</td>
<td>1.946 (15)</td>
</tr>
<tr>
<td>C(1)–O(1)</td>
<td>1.141 (12)</td>
</tr>
<tr>
<td>C(2)–O(2)</td>
<td>1.16 (2)</td>
</tr>
<tr>
<td>Mo(1)–C(6)</td>
<td>1.957 (10)</td>
</tr>
<tr>
<td>Mo(1)–C(7)</td>
<td>1.97 (2)</td>
</tr>
<tr>
<td>C(6)–O(6)</td>
<td>1.140 (13)</td>
</tr>
<tr>
<td>C(7)–O(7)</td>
<td>1.10 (2)</td>
</tr>
</tbody>
</table>

The distinctive properties of the carbonyl ligands are also reflecting the new situation imposed by the Cp/Cp* environment. The six CO are all terminal, with M–M–CO angles larger than 68.6(3) Å and M–C–O angles not smaller than 172.3(12) Å. While the W–C–O angles of the carbonyl ligands cis to the M–M bond lie approximately midway between the values observed for Cp(CO)3Mo–Mo(CO)3Cp [3] and Cp*(CO)3Mo–Mo(CO)3Cp* [4], the cis-Mo–C–O angles are by 3–5° larger than in Cp*(CO)3Mo–Mo(CO)3Cp* [4]. This could be explained with the different repulsive forces between the cis-CO of M and the cyclic ligand of Cp*. Thus, the cis-CO of the Mo(CO)3Cp* moiety in the title complex, facing the sterically less demanding W(CO)3Cp fragment, can adopt the larger Mo–C–O angles reported for Cp(CO)3Mo–Mo(CO)3Cp [3]. Accordingly, the cis–W–C–O angles of the W(CO)2Cp fragment decrease in comparison to Cp(CO)3W–W(CO)3Cp [3].

The spectroscopic properties of 1 are in accord with the solid state structure. The IR spectra compares well with the spectra of Cp*(CO)3Mo–Mo(CO)3Cp [1], featuring the basic absorption pattern invoked by the same structural family of complexes, with a red-shift of 3–4 wave numbers for the carbonyl bands, reflecting the comparatively stronger back-bonding of the CO ligands to the metal centres, due to a slightly higher electron density introduced by the W. The proton NMR spectra shows the expected two signals for the Cp*/Cp ligands in a 3:1 ratio, which excludes an intermetallic Cp/Cp* exchange. In the carbon NMR spectra, the most prominent feature for the mixed metal complex 1 is the single resonance for the carbonyl groups, which indicates a facile and rapid interchange of all the carbonyl groups of the molecule in and between the two metal moieties in solution [12,13]. The proposed structure is confirmed by the observed doublet at 89 ppm, characteristic for a Cp ligand and a singlet at 105 ppm and a quartet at 10 ppm for the Cp*.

3. Experimental

3.1. Materials and methods

All manipulations of air-sensitive materials were performed under a nitrogen atmosphere in conventional Schlenk apparatus. Solvents were distilled from Na/K or Na benzophenyl ketyl under nitrogen. Hexane for column chromatography was deoxygenated but otherwise used as received. Deuterated solvents were deoxygenated (three freeze-pump-thaw cycles) and stored under nitrogen over molecular sieves. Cyclopentadienyl sodium, pentamethyl-cyclopentadienyl sodium, M(CO)6 (M = Mo, W), (all purchased from Aldrich) were used as received. Silica gel 60 (0.063–0.200 mm, Merck) for column chromatography was kept under HV for 5 h and saturated with argon before use. Column properties: 2 × 60 cm, mobile phase at start: hexane. All steps that involve solutions of 1 were carried out under rigorous exclusion of light. NaW(CO)3Cp [14] and BrMo(CO)3Cp* [1] were prepared according to published methods.

Infrared spectra were measured on a Perkin–Elmer Spectrum One FT-IR spectrometer in THF and hexane solutions. 1H and 13C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in C6D6. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane (δ = 7.15 ppm, 127 ppm for C6D6). Elemental analysis were performed with a Perkin–Elmer Elemental Analyzer 2400 CHN.

3.2. Cp*(CO)3Mo–W(CO)3Cp (1)

At 0 °C, a solution of 1185 mg (3.0 mmol) BrMo(CO)3Cp* in 15 ml THF was added dropwise to 1068 mg (3.0 mmol) NaW(CO)3Cp in 15 ml THF. The reaction was monitored by IR spectroscopy and after 85 min under reflux it was terminated, the reaction mixture concentrated, filtered through cotton and separated into its components by repeated column chromatography. The target compound Cp*(CO)3Mo–W(CO)3Cp (1) was eluted with hexane/THF 25/1 in the first fraction(s). Re-crystallisation from hexane/THF yields 120 mg, 6 % dark red blocks. IR (hexane) [cm⁻¹]: 1949 (vs), 1910 (s), 1894 (w). 1H NMR [ppm]: 4.66 (s, 5 H, Cp), 1.77 (s, 15 H, Cp*), 13C NMR [ppm]: 235 (s, CO), 104.7 (s, Cp*), 89.1 (d, 1JCH = 178 Hz, Cp), 9.7 (q, 1JCH = 129 Hz.
Cp*), Anal. Calc. for C_{21}H_{20}O_6MoW (FW = 648.16): C, 38.91; H, 3.11. Found: C, 38.86; H, 3.06. Further fractions contained I as well as the homometallic dimers Cp*(CO)_{3}Mo–Mo(CO)_{3}Cp* and Cp(CO)_{3}W–W(CO)_{3}Cp as mixtures of up to three of the compounds.

A 10.0 mM solution of I in benzene-d6 was kept in darkness under otherwise ambient conditions. After 12 h, no significant formation of the corresponding homometallic dimers (ca. 2% conversion) could be detected by NMR. Then the sample was exposed to ambient light and after 2 h 35% (12 h, 50%; 24 h, 75%; 96 h, 88%) of I was converted. A similar experiment in the presence of 0.1 mL CDCl3 yielded the quantitative formation of Cp(CO)_{3}MoCl and Cp*(CO)_{3}WCl.

20 mg (0.03 mmol) Cp*(CO)_{3}Mo–W(CO)_{3}Cp (1) were dissolved in 5 mL toluene and the solution was gradually heated to reflux temperature. IR samples were taken at intervals of 10 °C. A reaction could be detected at 110 °C and after further 15 min under reflux the reaction was complete. The observed ν-CO bands at 1870 and 1841 cm^{-1} indicate the formation of Cp*(CO)_{2}MoW(CO)_{2}Cp. The reaction mixture was allowed to cool to RT and after the subsequent addition of carbon monoxide, the quantitative formation of starting material 1 was detected.

3.3. X-ray crystallography

The single crystal of the air sensitive compound 1 was measured in perfluoro polymer RS 3000 (Riedel-de Haen). X-ray diffraction data were collected at 150 K with a Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) and ω-scans data collection mode with a COLLECT [15] collection program. Denzo and Scalepack [16] programs were used for cell refinements and data reduction. The structure was solved by direct methods using SHELXLSHELXL 97 [17] with the WINGX [18] graphical user interface, a semi-empirical density function. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealized positions and were constrained to ride on their parent atom. Crystallographic data of 1 are summarized in Table 1 and selected bond lengths and angles are given in Table 2. The structure and the numbering scheme for complex Cp*(CO)_{3}Mo–W(CO)_{3}Cp (1) is presented in presented in Fig. 1.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with Cambridge Crystallographic Data Centre, CCDC No. 142814 for compound 1. 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 http://www.ccdc.cam.ac.uk).

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