Synthesis and molecular structure of (η5-pentamethyl-cyclopentadienyl) (η5-cyclopentadienyl) hexacarbonyl molybdenum tungsten

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Abstract

The metathesis reaction of $Cp^*(CO)_3MoBr$ and $NaW(CO)_3Cp$ produced $Cp^*(CO)_3Mo–W(CO)_3Cp$ (**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 η5-cyclopentadienyl and the η5-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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1. Introduction

During our studies of hetero bimetallic compounds of group 6 and group 8 metals we also synthesised the homometallic complex $Cp^*(CO)_3Mo–Mo(CO)_3Cp$ [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 $L(CO)_3M–M(CO)_3L$, with M = Mo or W and L = Cp or Cp* respectively, are well-documented. Besides the common *trans*-arrangement of the cyclic ligands in $Cp(CO)_3M–M(CO)_3Cp$ (M = Mo, W) [2,3], $Cp^*(CO)_3Mo–Mo(CO)_3Cp^*$ [4,5] and $Cp^*(CO)_3W–W(CO)_3Cp^*$ [6], there are structure reports of the *gauche* conformer of $Cp(CO)_3Mo–Mo(CO)_3Cp$ [7] and a *cis*

conformation in $Cp^*(CO)_3W–W(CO)_3Cp^*$ [8]. However, $Cp^*(CO)_3Mo–Mo(CO)_3Cp$ [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 $Cp^*(CO)_3Mo–W(CO)_3Cp$.

2. Results and discussion

Reaction of $NaW(CO)_3Cp$ with $Cp^*(CO)_3MoBr$ in tetrahydrofuran (THF) leads to the elimination of NaBr
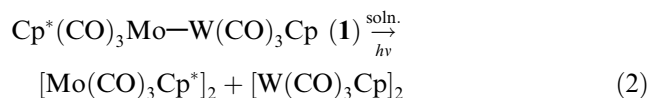
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and the formation of the heterobimetallic target complex Cp*(CO)$_3$Mo–W(CO)$_3$Cp (**1**) which was identified by IR, NMR, elemental analysis and X-ray crystallography. Further products of the reaction are the corresponding homometallic dimers.
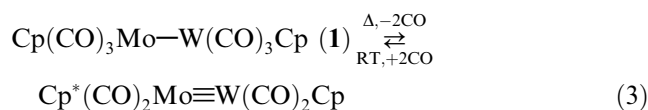
$$\text{Na[W(CO)}_3\text{Cp]} + \text{Cp*(CO)}_3\text{MoBr} \overset{\text{THF},\Delta}{\rightarrow}$$
$$\text{Cp*(CO)}_3\text{Mo}-\text{W(CO)}_3\text{Cp (1)} + [\text{Mo(CO}_3)\text{Cp*}]_2$$
$$+ [\text{W(CO)}_3\text{Cp}]_2 \qquad (1)$$
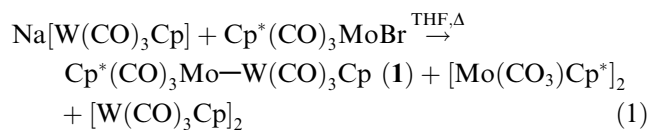
As reported for the synthesis of Cp(CO)$_3$Mo–W(CO)$_3$Cp [10], after NaBr elimination, the possible formation of radicals and their statistical combination could be responsible for the formation of the homometallic dimers. They could also arise from metal–metal bond cleavage of the initially formed target complex and subsequent recombination of two moieties of the complex. When solutions of **1** 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)$_3$MoCl and Cp(CO)$_3$WCl in presence of chloroform confirms the expected radical mechanism of the photo-induced reaction.

$$\text{Cp*(CO)}_3\text{Mo}-\text{W(CO)}_3\text{Cp (1)} \overset{\text{soln.}}{\underset{h\nu}{\rightarrow}}$$
$$[\text{Mo(CO)}_3\text{Cp*}]_2 + [\text{W(CO)}_3\text{Cp}]_2 \qquad (2)$$

However, in contrast to Cp(CO)$_3$Mo–W(CO)$_3$Cp, which could not be isolated [10a,b], repeated column chromatography and recrystallisation allowed us the isolation of pure Cp*(CO)$_3$Mo–W(CO)$_3$Cp (**1**), if only in low yield.

In toluene solution, complex **1** looses CO upon thermal activation above 110 °C. The broad bands in the IR spectra, at 1870 and 1841 cm^{-1}, are characteristic for [Cp*/Cp(CO)$_2$M]$_2$ (M = Cr, Mo, W) complexes [11] and indicate the formation of Cp*(CO)$_2$MoW(CO)$_2$Cp. Subsequent addition of carbon monoxide at RT quantitatively yielded starting material **1**. The formation of homometallic dimers, which would imply a thermally induced radical reaction, was not detected.

$$\text{Cp(CO)}_3\text{Mo}-\text{W(CO)}_3\text{Cp (1)} \overset{\Delta,-2\text{CO}}{\underset{\text{RT},+2\text{CO}}{\rightleftarrows}}$$
$$\text{Cp*(CO)}_2\text{Mo}\equiv\text{W(CO)}_2\text{Cp} \qquad (3)$$

The molecular configuration of **1** in the solid state is shown in Fig. 1, and details of selected bond lengths and angles are given in Table 2. Complex **1** consists of a Mo(CO)$_3$Cp* and a W(CO)$_3$Cp 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-
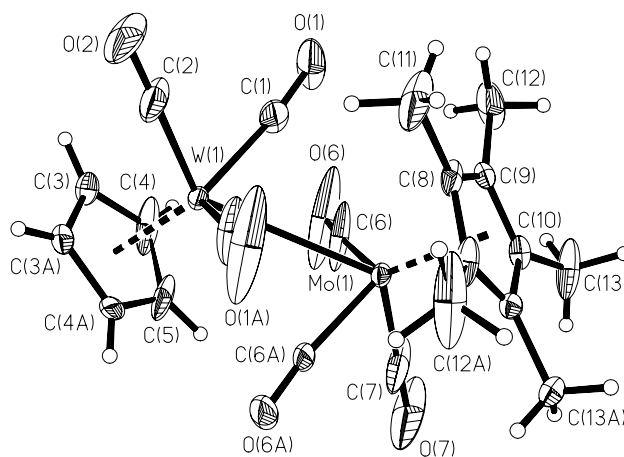

Fig. 1. ORTEP plot of Cp*(CO)$_3$Mo–W(CO)$_3$Cp (**1**) with ellipsoids drawn in 30% probability.

sponding homo-metallic complexes. The two M(CO)$_3$Cp 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)$_3$W–W(CO)$_3$Cp, d (W–W) = 3.222(1) Å [3] and Cp*(CO)$_3$Mo–Mo(CO)$_3$Cp*, 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

Table 1
Crystallographic data for Cp*(CO)$_3$Mo–W(CO)$_3$Cp (**1**)

Empirical formula	C$_{15}$H$_{10}$MoO$_6$W
Mol. wt.	648.16
Crystal size (mm)	$0.20 \times 0.10 \times 0.05$
Cryst. syst.	Orthorhombic
Space group	*Pnma*
λ (Å)	0.71073
Unit cell dimensions	
a (Å)	16.9507(3)
b (Å)	12.7667(2)
c (Å)	9.7432(2)
β (°)	90
V (Å^3)	2108.47(7)
Z	4
D_{calc} (g/cm^3)	2.042
μ (mm^{-1})	6.080
T (K)	150(2)
θ range (°)	4.00–26.00
No. of unique rflns	2160
No. of obsd. data[a]	1869
No. of params	148
R_1	0.0372
wR_2	0.0979
Largest diff. peak and hole (e Å^{-3})	1.486 and −3.683

[a] $I > 2\sigma$.

Table 2
Selected bond lengths (Å) and bond angles (°), Cp*(CO)$_3$Mo–W(CO)$_3$Cp (**1**)

W(1)–Mo(1)	3.2516 (8)
W(1)–C(1)	1.957(10)
W(1)–C(2)	1.946(15)
C(1)–O(1)	1.141(12)
C(2)–O(2)	1.16(2)
Mo(1)–C(6)	1.957(10)
Mo(1)–C(7)	1.97(2)
C(6)–O(6)	1.140(13)
C(7)–O(7)	1.10(2)
W(1)–Mo(1)–C(6)	68.6(3)
W(1)–Mo(1)–C(7)	120.7(4)
W(1)–C(1)–O(1)	172.3(12)
W(1)–C(2)–O(2)	178.9(12)
Mo(1)–W(1)–C(1)	70.9(3)
Mo(1)–W(1)–C(2)	129.8(4)
Mo(1)–C(6)–O(6)	173.1(8)
Mo(1)–C(7)–O(7)	179.3(13)

distances in Cp(CO)$_3$Mo–Mo(CO)$_3$Cp, *d* (Mo–Mo) = 3.235(1) Å [4], and Cp*(CO)$_3$W–W(CO)$_3$Cp*, *d* (W–W) = 3.288(1) Å [6] into account, it can be deduced that the observed M–M bond length in **1** is mainly dictated by the presence of one of each, a Cp and a Cp* ligand, rather than the similar atomic radii of Mo and W.

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)$_3$W–W(CO)$_3$Cp [3] and Cp*(CO)$_3$W–W(CO)$_3$Cp* [6], the *cis*-Mo–C–O angles are by 3–5° larger than in Cp*(CO)$_3$Mo–Mo(CO)$_3$Cp* [4]. This could be explained with the different repulsive forces between the *cis*-CO of M and the cyclic ligand of M′. Thus, the *cis*-CO of the Mo(CO)$_3$Cp* moiety in the title complex, facing the sterically less demanding W(CO)$_3$Cp fragment, can adopt the larger Mo–C–O angles reported for Cp(CO)$_3$Mo–Mo(CO)$_3$Cp [3]. Accordingly, the *cis*-W–C–O angles of the W(CO)$_3$Cp fragment decrease in comparison to Cp(CO)$_3$W–W(CO)$_3$Cp [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)$_3$Mo–Mo(CO)$_3$Cp [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 prom-

inent 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)$_3$Cp [14] and BrMo (CO)$_3$Cp* [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. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in C$_6$D$_6$. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane (δ = 7.15 ppm, 127 ppm for C$_6$D$_6$). Elemental analysis were performed with a Perkin–Elmer Elemental Analyzer 2400 CHN.

3.2. Cp*(CO)$_3$Mo–W(CO)$_3$Cp (**1**)

At 0 °C, a solution of 1185 mg (3.0 mmol) BrMo-(CO)$_3$Cp* in 15 ml THF was added dropwise to 1068 mg (3.0 mmol) NaW(CO)$_3$Cp 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)$_3$Mo–W(CO)$_3$Cp (**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). ^{1}H NMR [ppm]: 4.66 (s, 5 H, Cp), 1.77 (s, 15 H, Cp*). ^{13}C NMR [ppm]: 235 (s, CO), 104.7 (s, Cp*), 89.1 (d, $^1J_{CH}$ = 178 Hz, Cp), 9.7 (q, $^1J_{CH}$ = 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 **1** as well as the homometallic dimers $Cp^*(CO)_3Mo–Mo(CO)_3Cp^*$ and $Cp(CO)_3W–W(CO)_3$ Cp as mixtures of up to three of the compounds.

A 10.0 mM solution of **1** 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) can 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 **1** was converted. A similar experiment in the presence of 0.1 ml $CDCl_3$ yielded the quantitative formation of $Cp(CO)_3MoCl$ and $Cp^*(CO)_3WCl$.

20 mg (0.03 mmol) $Cp^*(CO)_3Mo–W(CO)_3Cp$ (**1**) were dissolved in 5 ml toluene and the solution was gradually heated to reach 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 $Cp^*(CO)_2MoW(CO)_2Cp$. 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 polyether RS 3000 (Riedel-de Haën). X-ray diffraction data were collected at 150 K with a Nonius Kappa CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and ϕ-scan and ω-scan 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 SHELXS97 [17] with the WINGX [18] graphical user interface, a semi-empirical multi-scan absorption correction, based on equivalent reflections (XPREP in SHELXTL version 6.12) [19] was applied ($T_{max}/T_{min} = 0.73793/0.48460$) and the refinements were carried out with the SHELXL97 program [20]. All non-hydrogen atoms were refined anisotropically. All hydrogens 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 $Cp^*(CO)_3$-$Mo–W(CO)_3Cp$ (**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).

References

[1] T. Straub, M. Haukka, T.A. Pakkanen, J. Organomet. Chem. 612 (2000) 106.
[2] F.C. Wilson, D.P. Shoemaker, J. Chem. Phys. 27 (1957) 809.
[3] R.D. Adams, D.M. Collins, F.A. Cotton, Inorg. Chem. 13 (1974) 1086.
[4] W. Clegg, N.A. Compton, J.R. Errington, N.C. Norman, Acta Crystallogr., Sect. C 44 (1988) 568.
[5] G. Lin, W.-T. Wong, J. Organomet. Chem. 522 (1996) 271.
[6] A. Rheingold, J.R. Harper, Acta Crystallogr., Sect. C 47 (1990) 184.
[7] R.O. Gould, J.B. Barker, M. Kilner, Acta Crystallogr., Sect. C 44 (1988) 467.
[8] I.R. Lyatifov, T.K. Gasanov, T.K. Kurbanov, A.N. Shnulin, V.I. Shilnikov, Koordinat. Khim. 16 (1990) 1343.
[9] R.S. Sternal, C.P. Brock, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8270.
[10] (a) T. Madach, H. Vahrenkamp, Z. Naturforsch. 34b (1979) 573;
(b) F. Calderazzo, A. Juris, R. Poli, F. Ungari, Inorg. Chem. 30 (1991) 1274;
(c) E.W. Abel, A. Singh, G. Wilkinson, J. Chem. Soc. (1960) 1321.
[11] (a) I.R. Lyatifov, T.K. Gasanov, P.V. Petrovski, A.I. Lutsenko, J. Organomet. Chem. 361 (1989) 181;
(b) D.S. Ginley, M.S. Wrighton, J. Am. Chem. Soc. 97 (1975) 3533.
[12] (a) R.D. Adams, F.A. Cotton, Inorg. Chim. Acta 7 (1973) 153;
(b) W.E. Lindsell, P.J. Tomb, J. Organomet. Chem. 378 (1989) 245.
[13] (a) X. Chen, B.E. Mann, Organometallics 15 (1996) 3703;
(b) R.D. Adams, M. Brice, F.A. Cotton, J. Am. Chem. Soc. 95 (1973) 6594;
(c) S.-G. Shyu, J.-Y. Hsu, Y.-S. Wen, J. Organomet. Chem. 453 (1993) 97;
(d) S.-G. Shyu, J.-Y. Hsu, P.-J. Lee, W.-J. Wu, S.-M. Peng, G.-H. Lee, Y.-S. Wen, Organometallics 13 (1994) 1699;
(f) A. Ricalton, M.W. Whitely, J. Organomet. Chem. 361 (1989) 101.
[14] T. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 3 (1956) 104.
[15] COLLECT Data Collection Software, Nonius, 2000.
[16] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276, Academic Press, New York, 1997, p. 307.
[17] G.M. Sheldrick, SHELXS97, Program for Crystal Structure Determination, University of Göttingen, Göttingen, 1997.
[18] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[19] G.M. Shelddrick, SHELXTL Version 6.12, Bruker Analytical X-ray Systems, Bruker AXS, Inc., Madison, Wisconsin, USA, 2001.
[20] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, 1997.