

Seven-coordinate bromocarbonyl complexes of molybdenum(II) and tungsten(II) containing neutral sulfur donor ligands : crystal structure of [WBr₂(CO)₃{PhS(CH₂)₂SPh-S,S'}]

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Abstract—Treatment of $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo or W) with a slight excess of RS(CH₂)₂SR (R = Ph, C₆H₄F-4) in CH₂Cl₂ at room temperature gave the acetonitrile displaced products $[MBr_2(CO)_3[RS(CH_2)_2SR-S,S']]$. The complex with M = W, R = Ph was crystallographically characterised and has a distorted capped octahedral geometry with one carbonyl group in the capping position, two carbonyls and one sulfur atom in the capped face, and one sulfur and two bromines in the uncapped face. Reaction of $[WBr_2(CO)_3(NCMe)_2]$ with two equivalents of $RS(CH_2)_2SR$ in CH₂Cl₂ at room temperature gives the cationic complexes $[WBr(CO)_3\{RS(CH_2)_2SR-S,S'\}]Br$. Similarly, treatment of $[WBr_2(CO)_3(NCMe)_2]$ with one and two equivalents of Ph₂P(S)CH₂P(S)Ph₂ in CH₂Cl₂ at room temperature afforded $[WBr_2(CO)_3(NCMe)_2]$ with one and two equivalents of Ph₂P(S)CH₂P(S)Ph₂-S} {Ph₂P(S)CH₂P(S)Ph₂-S,S'] Br respectively. Reaction of $[MBr_2(CO)_3(NCMe)_2]$ with one equivalent of MeS(CH₂)_2SMe in CH₂Cl₂ at room temperature gave $[MoBr_2(CO)_3(NCMe)_2]$ with one equivalent of MeS(CH₂)_2SMe in CH₂Cl₂ at room temperature gave $[MoBr_2(CO)_3(NCMe)_2]$ with one equivalent of MeS(CH₂)_2S(CH₂)_2SMe in CH₂Cl₂ at room temperature gave $[MoBr_2(CO)_3(NCMe)_2]$ with one equivalent of MeS(CH₂)_2S(CH₂)_2SMe-S,S'] respectively. Finally, reaction of equimolar quantities of $[MoBr_2(CO)_3(MeS(CH_2)_2S(CH_2)_2SMe-S,S']$ and $[WBr_2(CO)_3(MeS(CH_2)_2S(CH_2)_2SMe-S,S']$ respectively. Finally, reaction of equimolar quantities of $[MoBr_2(CO)_2(NCMe)_2]$ and ttob (ttob = 2,5,8-trithia[9]-*o*-benzenophane) gives the S₃ bonded complex $[MoBr_2(CO)_2(ttob-S,S',S'']$. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: seven-coordinate; molybdenum(II); thioether; tungsten(II); crystal structure; sulfur donor ligands.

Molybdenum and tungsten complexes containing sulfur donor ligands are important for a number of reasons, including, for example, the fact that the active site of the nitrogenase enzyme contains molybdenum with attached sulfur donor ligands [1–3]. A number of iodocarbonyl complexes containing neutral sulfur donor ligands have been described. Over the years we have reported the reactions of $[MI_2(CO)_3(NCMe)_2]$ with thioureas [4,5], thioacetamide [5,6], SPPh₃ [7], S₂CPCy₃ [8], RS(CH₂)₂SR [9], MeS(CH₂)₂S (CH₂)₂SMe [9], Ph₂P(S)CH₂P(S)Ph₂ [10], trithiamacrocyclic ligands [11] and tetrathiamacrocyclic ligands [12]. However, apart from the 2,5-dithiahexane complexes $[MX_2(CO)_3(2,5-dithiahexane)]$ (M = Mo or W; X = Br or I) reported by Mannerskantz and Wilkinson [13] in 1962 and our crystallographically characterised complex $[MoBr(CO)_2\{Me_8[16]aneS_4-S,S',S'',S'''\}][MoBr_3$ $(CO)_4]$ [12,14] very few bromocarbonyl seven-coordinate complexes of molybdenum(II) and tungsten(II) containing neutral sulfur donor ligands have been described.

In our initial report of the synthesis of the highly versatile seven-coordinate complexes $[MX_2(CO)_3 (NCMe)_2]$ (M = Mo or W; X = Br or I) in 1986 [15] it was suggested that the dibromo complexes were considerably less stable than their diiodo counter-

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parts. However, more recently in 1994 [16] we have described an improved synthesis of the dibromotricarbonyl complexes $[MBr_2(CO)_3(NCMe)_2]$, by reacting *fac*- $[M(CO)_3(NCMe)_3]$ (prepared *in situ* [17]) with an equimolar amount of Br₂ at -78° C. In this paper, we describe the reactions of the dibromo complexes $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo or W) with the neutral sulfur donor ligands, RS(CH₂)₂SR (R = Ph or C₆H₄CF₃-4), Ph₂P(S)CH₂P(S)Ph₂, MeS (CH₂)₂S(CH₂)₂SMe and ttob (ttob = 2,5,8-trithia[9]*o*-benzenophane). The X-ray crystal structure of $[WBr_2(CO)_3{PhS(CH_2)_2SPh-S,S'}]$ is also discussed.

EXPERIMENTAL

All reactions described in this paper were carried out using standard Schlenk line techniques. The starting materials $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo or W) [15,16], RS(CH₂)₂SR (R = Ph or C₆H₄CF₃-4) [18], Ph₂P(S)CH₂P(S)Ph₂ [19], MeS(CH₂)₂S(CH₂)₂SMe [9] and ttob [20] were prepared by published methods. All chemicals used were purchased from commercial sources, and CH₂Cl₂ was dried over phosphorus pentoxide and distilled before use.

Elemental analyses (C, H and S) were obtained using a Carlo Erba Elemental Analyser MOD 1108 (using helium as a carrier gas). IR spectra were recorded on a Perkin–Elmer 1600 FT IR spectrophotometer. The 'H NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer at the University of Wales, Bangor, and referenced to SiMe₄.

$[WBr_2(CO)_3{PhS(CH_2)_2SPh-S,S'}] (2)$

To a stirred solution of $[WBr_2(CO)_3(NCMe)_2]$ (0.21 g, 0.41 mmol) in CH₂Cl₂ (15 cm³) under a stream of dry nitrogen was added PhS(CH₂)₂SPh (0.11 g, 0.45 mmol). The resulting solution was stirred for 2 h before filtering over a fine frit and the solvent was removed *in vacuo* to produce an orange brown powder. The powder was dissolved in a minimum of CH₂Cl₂ and cooled to -15° C to give orange crystals of $[WBr_2(CO)_3{PhS(CH_2)_2SPh-S,S'}]$ (2) (0.12 g, 0.19 mmol, 45%), one of which was suitable for X-ray crystallography.

A similar reaction of $[MoBr_2(CO)_3(NCMe)_2]$ (0.19 g, 0.45 mmol) with PhS(CH₂)₂SPh (0.12 g, 0.46 mmol) followed by recrystallisation from CH₂Cl₂ gave the brown complex $[MoBr_2(CO)_3{PhS(CH_2)_2SPh-S,S'}]$ (1) (0.11 g, 0.18 mmol, 40%).

$[WBr_{2}(CO)_{3} \{4 - FC_{6}H_{4}S(CH_{2})_{2}C_{6}H_{4}F - 4 - S, S'\}] (4)$

To a stirred solution of $[WBr_2(CO)_3(NCMe)_2]$ (0.25 g, 0.49 mmol) in CH₂Cl₂ (20 cm³) under a stream of dry nitrogen was added 4-FC₆H₄S(CH₂)₂SC₆H₄F-4 (0.15 g, 0.51 mmol). The resulting solution was stirred for 23 h before filtering over a fine frit and the

solvent was removed *in vacuo* to produce an orange brown powder. The powder was dissolved in a minimum of CH₂Cl₂ and cooled to -15° C to give the orange complex [WBr₂(CO)₃{4-FC₆H₄S(CH₂)₂SC₆ H₄F-4-*S*,*S*'}] (4)(0.15 g, 0.22 mmol, 44%).

A similar reaction of $[MoBr_2(CO)_3(NCMe)_2]$ (0.19 g, 0.45 mmol) with 4-FC₆H₄S(CH₂)₂SC₆H₄F-4 (0.13 g, 0.45 mmol) in CH₂Cl₂ for 4 h followed by recrystallisation from CH₂Cl₂ gave the brown complex $[MoBr_2(CO)_3[4-FC_6H_4S(CH_2)_2SC_6H_4F-4-S,S']]$ (3) (0.13 g, 0.21 mmol, 46%).

$[WBr(CO)_{3}{PhS(CH_{2})_{2}SPh-S}{PhS(CH_{2})_{2}SPh-S,S'}]Br (5)$

To a stirred solution of $[WBr_2(CO)_3(NCMe)_2]$ (0.21 g, 0.41 mmol) in CH₂Cl₂ (15 cm³) under a stream of dry nitrogen was added PhS(CH₂)₂SPh (0.21 g, 0.83 mmol). The resulting solution was stirred for 17 h before filtering over a fine frit and the solvent was removed *in vacuo* to produce an orange brown powder. The powder was dissolved in a minimum of CH₂Cl₂ and cooled to -15° C to give the brown complex [WBr(CO)₃{PhS(CH₂)₂SPh-S}{PhS(CH₂)₂SPh-S,S'}]Br (5) (0.15 g, 0.17 mmol, 41%).

A similar reaction of $[WBr_2(CO)_3(NCMe)_2]$ (0.19 g, 0.37 mmol) with 4-FC₆H₄S(CH₂)₂SC₆H₄F-4 (0.21 g, 0.75 mmol) followed by recrystallisation from CH₂Cl₂ gave the brown complex $[WBr(CO)_3$ {4-FC₆H₄S (CH₂)₂SC₆H₄F-4-S}{4-FC₆H₄S(CH₂)₂SC₆H₄F-4-*S*,*S*'}]Br (6) (0.17 g, 0.18 mmol, 47%).

$[WBr_{2}(CO)_{3}\{Ph_{2}P(S)CH_{2}P(S)Ph_{2}-S,S'\}] (7)$

To a stirred solution of $[WBr_2(CO)_3(NCMe)_2]$ (0.07 g, 0.14 mmol) in CH₂Cl₂ (15 cm³) under a stream of dry nitrogen was added Ph₂P(S)CH₂P(S)Ph₂ (0.07 g, 0.15 mmol). The resulting solution was stirred for 4 h before filtering over a fine frit and the solvent was removed *in vacuo* to produce a green sticky oil. The oil was washed with hexane and then dissolved in a minimum of CH₂Cl₂ and cooled to -15° C to give the green complex [WBr₂(CO)₃{Ph₂P(S)CH₂P(S)Ph₂-*S*,*S*'}] (7) (0.08 g, 0.09 mmol, 60%).

A similar reaction of $[WBr_2(CO)_3(NCMe)_2]$ (0.07 g, 0.14 mmol) with $Ph_2P(S)CH_2P(S)Ph_2$ (0.14 g, 0.29 mmol) in CH_2Cl_2 gave the green complex $[WBr(CO)_3\{Ph_2P(S)CH_2P(S)Ph_2-S\}\{Ph_2P(S)CH_2P(S)Ph_2-S,S'\}]Br$ (8) (0.08 g, 0.06 mmol, 45%).

$[MoBr_2(CO)_2 \{MeS(CH_2)_2S(CH_2)_2SMe-S,S',S''\}]$ (9)

To a stirred solution of $[MoBr_2(CO)_3(NCMe)_2]$ (0.30 g, 0.72 mmol) in CH₂Cl₂ (15 cm³) under a stream of dry nitrogen was added MeS(CH₂)₂S(CH₂)₂SMe (0.13 g, 0.73 mmol). The resulting solution was stirred for 5 h before filtering over cellite and the solvent was removed *in vacuo* to produce a red oily solid. The oil was washed with hexane and then dissolved in a minimum of CH_2Cl_2 and cooled to $-15^{\circ}C$ to give the red brown complex [MoBr₂(CO)₂{Me-S(CH₂)₂S(CH₂)₂SMe-S,S',S''}] (9) (0.20 g, 0.40 mmol, 55%).

A similar reaction of $[WBr_2(CO)_3(NCMe)_2]$ (0.29 g, 0.57 mmol) with MeS(CH₂)₂S(CH₂)₂SMe (0.11 g, 0.575 mmol) in CH₂Cl₂ (15 cm³) for 12 h followed by washing with hexane and recrystallisation from CH₂Cl₂ gave the green complex $[WBr_2(CO)_3 {MeS(CH_2)_2S(CH_2)_2SMe-S,S'}]$ (10) (0.19 g, 0.31 mmol, 54%).

 $[MoBr_2(CO)_2\{ttob-S,S',S''\}]$ (11)

To a stirred solution of $[MoBr_2(CO)_3(NCMe)_2]$ (0.41 g, 0.99 mmol) in CH₂Cl₂ (15 cm³) under a stream of dry nitrogen was added ttob (0.26 g, 1.00 mmol). The resulting solution was stirred for 4 h before filtering over cellite and the solvent was removed *in* vacuo to produce a brown solid. The solid was washed with hexane and then dissolved in a minimum of CH₂Cl₂ and cooled to -15° C to give the brown complex [MoBr₂(CO)₂{ttob-S,S',S''}] (11) (0.34 g, 0.59 mmol, 60%).

Crystallography. Crystal data for 2 are given in Table 1, together with refinement details. Data were collected with Mo- K_{α} radiation using the MAR Research Image Plate System. The crystal was posi-

tioned at 80 mm from the Image Plate. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [21]. The structure was solved using direct methods with the Shelx86 program [22]. Apart from the carbon atoms in the carbonyl groups, the nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An absorption correction was applied using DIFABS [23]. The structure was then refined using Shelx1 [24]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Bond lengths and angles in the metal coordination sphere are given in Table 2.

RESULTS AND DISCUSSION

The reaction of $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo or W) with a slight excess of $RS(CH_2)_2SR$ (R = Ph or C_6H_4F -4) in CH₂Cl₂ at room temperature gave the seven-coordinate complexes $[MBr_2(CO)_3{R-S(CH_2)_2SR-S,S'}]$ (1–4) in reasonable yields. Complexes 1–4 were characterised by elemental analysis C, H and S (Table 3), IR spectroscopy (Table 4) and ¹H NMR spectroscopy (Table 5). All four complexes are soluble in dichloromethane and DMSO, but are totally insoluble in diethyl ether, the molybdenum com-

Empirical formula	$C_{17}H_{14}Br_{2}O_{3}S_{7}W$
Formula weight	674.07
Temperature (K)	293(2)
Wavelength Å	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	12.438(12)
$b(\mathbf{A})$	13.162(12)
$c(\mathbf{A})$	12.728(12)
β(°)	106.11(1)
$V(\hat{A}^3)$	2002(3)
Z	4
$D_{\rm calc}$ (g cm ⁻³)	2.237
Absorption coefficient mm ⁻¹	9.984
F(000)	1264
Crystal size (mm)	$0.25 \times 0.25 \times 0.30$
θ range for data collection (°)	2.30 to 23.61
Index ranges	$0 \le h \le 13, -14 \le k \le 14, -14 \le l \le 13$
Reflections collected	3661
Independent reflections	$2503 [R_{int} = 0.0831]$
Weighting Scheme (a,b)"	0.059, 52.08
Data/restraints/parameters	2503/0/212
Goodness-of-fit on F^2	1.079
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0819, wR_2 = 0.1941$
R indices (all data)	$R_1 = 0.1124, wR_2 = 0.2063$
Largest diff. peak and hole (e $Å^{-3}$)	0.792 and -1.071

^{*a*} Weighting scheme $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$, where $P = (F_o^2 + 2F_c^2)/3$

Table 2. Bond lengths (Å) and angles ([°]) in the metal coordination sphere for 2

W(1)—C(300)	1.81(2)
W(1) - C(100)	1.96(4)
W(1) - C(200)	2.01(3)
W(1) - S(2)	2.557(7)
W(1) - S(1)	2.573(7)
W(1)— $Br(2)$	2.626(3)
W(1)— $Br(1)$	2.659(4)
C(300) - W(1) - C(100)	71.9(12)
C(300) - W(1) - C(200)	106.0(10)
C(100) - W(1) - C(200)	75.4(13)
C(300) - W(1) - S(2)	113.0(7)
C(100) - W(1) - S(2)	74.2(11)
C(200) - W(1) - S(2)	118.7(7)
C(300) - W(1) - S(1)	87.0(7)
C(100) - W(1) - S(1)	134.8(11)
C(200) - W(1) - S(1)	149.7(7)
S(2) - W(1) - S(1)	78.4(2)
C(300) - W(1) - Br(2)	80.1(6)
C(100) - W(1) - Br(2)	129.2(11)
C(200) - W(1) - Br(2)	72.7(7)
S(2) - W(1) - Br(2)	156.5(2)
S(1) - W(1) - Br(2)	83.1(2)
C(300) - W(1) - Br(1)	164.4(6)
C(100) - W(1) - Br(1)	123.6(10)
C(200) - W(1) - Br(1)	79.0(7)
S(2) - W(1) - Br(1)	75.6(2)
S(1) - W(1) - Br(1)	82.0(2)
Br(2) - W(1) - Br(1)	87.58(11)

plexes being more soluble than their tungsten analogues. Complexes 1–4 are all very air-sensitive in solution and only slightly less so in the solid state, and much less stable than their diiodo analogues. Hence, the complexes were handled in air only for very short periods of time and decomposed very rapidly in solution. Conductivity measurements in acetone showed complexes 1–4 to be non-electrolytes as was expected.

The IR spectra of complexes 1–4 were recorded as KBr disks. No solution infrared spectra were obtained due to the extremely air-sensitive nature of the complexes. Three carbonyl stretching bands were observed for all of the four complexes (Table 4). This is consistent with the complexes being seven-coordinate tricarbonyl complexes and having one conformation in the solid-state. The ¹H NMR spectra (Table 5) showed the coordinated thioether resonances to be shifted slightly downfield compared to the free thioether ligands.

The solid-state structure of the tungsten complex 2 has been solved by X-ray crystallography and is shown in Fig. 1, together with atomic numbering scheme. It is likely that the three other complexes 1, 3 and 4 will have similar geometries in the solid state. The structure can best be considered as a distorted capped octahedron with one carbonyl C(100) in the capping position, two carbonyls C(200), C(300) and

one sulfur S(2) in the capped face and the two bromides and the other sulfur S(1) in the uncapped face. The structure is very similar to that previously found for $[WI_2(CO)_3 \{4-MeC_6H_4S(CH_2)_2SC_6H_4Me-4-S,S'\}]$ [9] both in the details of their metal coordination spheres and in the conformation of the Ph-S--CH2-CH2-S-Ph moiety. In the present structure one bromine atom Br(1) is *trans* to the carbonyl group C(300) at 2.659(4) Å while the other Br(2) is trans to S(2) at 2.626(3) Å. The two W—S(1) distances are equivalent within experimental error despite their different positions in the coordination sphere $\{2.557(7), 2.573(7) \text{ Å}\}$. More variation is $[WI_2(CO)_3]$ 4-MeC₆H₄S(CH₂)₂SC₆ obtained for $H_4Me-4-S,S'$ [9] where the mutually trans W---S and W-I are shorter at 2.54(3), 2.836(1) Å than those *trans* to carbonyl 2.59(3), 2.875(1) Å.

The reactions of $[WBr_2(CO)_3(NCMe)_2]$ with two equivalents of RS(CH₂)₂SR (R = Ph or C₆H₄F-4) gave the cationic complexes $[WBr(CO)_3] RS(CH_2)_2 SR$ - $S_{\rm S}^{\rm RS}(CH_2)_2SR-S,S'$]Br (R = Ph or 4-FC₆H₄) (5 and 6) respectively in good yield. Complexes 5 and 6 were characterised by elemental analysis C, H and S (Table 3), IR spectroscopy (Table 4) and ¹H NMR spectroscopy (Table 5). The found sulfur analysis for complex 5 is low, and is most likely to be due to the instability of this complex when exposed to air. Both complexes were soluble in dichloromethane and DMSO, but are totally insoluble in diethyl ether. They are very air-sensitive in solution, and only slightly less so in the solid state. Conductivity measurements in acetone showed both complexes to be typical 1:1 electrolytes ($\Lambda_m = 123$ and 126 S cm² mol⁻¹). These data suggest that one of the sulfur atoms from the second thioether ligand has displaced one of the bromide groups from the starting material.

The IR spectra of both complexes are recorded as KBr disks. Three carbonyl stretching bands were observed for both complexes (Table 4). This is consistent with the complexes being seven-coordinate and having one conformation in the solid-state. The ¹H NMR spectra (Table 5) again showed the coordinated thioether resonances to be shifted downfield compared to those of the free thioethers. In these cases, however, resonances are also observed for the uncoordinated end of the monodentately bound thioether ligand. It may be likely that given the similarities in spectroscopic data between complexes 5 and 6 and the crystallographically characterised product 2, they will have similar solid-state structures, i.e. capped octahedral (Fig. 2). Several unsuccessful attempts were made to obtain ³¹P NMR spectra for complexes 5 and 6. These very weak spectra showed a number of resonances due to rapid decomposition of the complexes in solution.

Treatment of $[WBr_2(CO)_3(NCMe)_2]$ with one or two equivalents of $Ph_2P(S)CH_2P(S)Ph_2$ gave the green seven-coordinate complexes $[WBr_2(CO)_3\{Ph_2P(S)$ $CH_2P(S)Ph_2-S,S'\}]$ (7) and $[WBr(CO)_3\{Ph_2P(S)$ $CH_2P(S)Ph_2-S\}\{Ph_2P(S)CH_2P(S)Ph_2-S,S'\}]Br$ (8)

Complex	Yield (%)	Colour	C(%)	H(%)	S(%)
$1 [MoBr_2(CO)_3 {PhS(CH_2)_2 SPh-S,S'}]$	40	brown	34.6	2.9	10.5
			(34.8)	(2.4)	(10.9)
$2 \left[WBr_2(CO)_3 \left\{ PhS(CH_2)_2 SPh-S, S' \right\} \right]$	45	orange	30.1	2.7	10.3
		-	(30.3)	(2.1)	(9.5)
$3 [MoBr_2(CO)_3 \{4-FC_6H_4S(CH_2)_2SC_6H_4F-4-S,S'\}]$	46	brown	32.7	1.8	10.0
			(32.8)	(1.9)	(10.3)
$4 [WBr_{2}(CO)_{3} \{4-F-C_{6}H_{4}S(CH_{2})_{2}SC_{6}H_{4}F-4-S,S'\}]$	44	orange	28.0	1.9	9.2
		-	(28.8)	(1.7)	(9.0)
$5 [WBr(CO)_{3} {PhS(CH_{2})_{2}SPh-S} {PhS(CH_{2})_{2}SPh-S,S'}]Br$	41	brown	40.1	3.6	12.4
			(40.5)	(3.1)	(13.9)
6 [WBr(CO) ₃ {4-FC ₆ H ₄ S(CH ₂) ₂ SC ₆ H ₄ F-4-S}{4-FC ₆ H ₄ S	47	brown	37.5	2.0	12.4
$(CH_2)_2SC_6H_4F-4-S,S'$]Br			(37.5)	(2.4)	(12.9)
7 $[WBr_2(CO)_3{Ph_2P(S)CH_2P(S)Ph_2-S,S'}]$	60	green	38.3	2.6	7.8
		C	(38.4)	(2.5)	(7.3)
8 [WBr(CO) ₃ {Ph ₂ P(S)CH ₂ P(S)Ph ₂ -S}{Ph ₂ P(S)CH ₂ P(S)	45	green	48.2	3.5	8.0
Ph ₂ - <i>S</i> , <i>S</i> '}]Br		e	(48.8)	(3.6)	(9.5)
9 $[MoBr_2(CO)_2 \{MeS(CH_2)_2S(CH_2)_2SMe-S,S',S''\}]$	55	red	18.9	2.4	19.1
		brown	(19.5)	(2.9)	(19.5)
10 $[WBr_2(CO)_3 MeS(CH_2)_2S(CH_2)_2SMe-S,S']$	54	green	16.8	1.9	16.2
		e	(16.5)	(2.4)	(16.5)
11 $[MoBr_2(CO)_2 \{ttob-S, S', S''\}]$	60	brown	30.1	2.7	16.0
			(29.6)	(2.8)	(16.9)

Table 3. Physical and analytical data" for thioether and diphosphine disulfide dibromocarbonyl seven-coordinate complexes of molybdenum(II) and tungsten(II)

"Calculated values in parentheses.

Table 4. IR data" for thioether and diphosphine disulfide bromocarbonyl seven-coordinate complexes of molybdenum(II) and tungsten(II)

Complex	$v(C \equiv O) (cm^{-1})$
1	2042 (s), 1959 (s), 1901 (s)
2	2035 (s), 1965 (s), 1908 (s)
3	2022 (s), 1968 (s), 1915 (sh)
4	2025 (s), 1965 (s), 1908 (sh)
5	2043 (s), 1960 (s), 1896 (s)
6	2047 (s), 1965 (s), 1905 (s)
7	2034 (s), 1960 (s), 1892 (s)
8	2037 (s), 1961 (s), 1893 (s)
9	1962 (s), 1862 (s)
10	2036 (s), 1950 (s), 1905 (s)
11	1951 (s), 1871 (s)

"Spectra recorded as KBr disks.

respectively in good yield. Both complexes were characterised by elemental analysis C, H and S (Table 3), IR spectroscopy (Table 4) and ¹H NMR spectroscopy (Table 5). Both complexes are soluble in dichloromethane and DMSO, but are totally insoluble in diethyl ether. The complexes are very air-sensitive in solution and only slightly less so in the solid state.

Table 5. ¹H NMR data^{*a*} for thioether and diphosphine disulfide bromocarbonyl seven-coordinate complexes of molybdenum(II) and tungsten(II)

Complex	1 H (δ) (ppm)
1	7.4 (m, 10H, Ph), 3.55 (s, 4H, CH ₂)
2	7.5 (m, 10H, Ph), 3.55 (s, 4H, CH ₂)
3	7.4 (m, 4H, C_6H_4), 7.2 (m, 4H, C_6H_4), 3.1
4	(s, 4H, CH ₂) 7.35 (m, 4H, C ₆ H ₄), 7.1 (m, 4H, C ₆ H ₄), 3.1 (s, 4H, CH.)
5	(3, 411, C112) 7.3 (m, 15H, Ph, coord), 7.1 (m, 5H, Ph, uncoord), 3.2 (s, 8H, CH ₃)
6	7.4 (m, 8H, C_6H_4), 7.2 (m, 8H, C_6H_4), 3.1 (s, 8H, CH ₂)
7	8.0 (m, 8H, Ph-ortho), 7.5 (m, 12H, Ph- meta + para), 4.6 (t, $J_{PH} = 15$ Hz, 2H, CH ₂)
8	7.9 (m, 16H, Ph-ortho), 7.4 (m, 24H, Ph-m and p), 4.6 (brdd, 4H, CH ₂)
9	3.1 (m, 8H, CH ₂), 2.3 (s, 6H, CH ₃)
10	3.76 (m, 4H, CH ₂ SCH ₂ , coord), 3.66 (m, 2H, CH ₂ SCH ₃ , coord), 2.9 (s, 3H, SCH ₃ , coord), 2.5 (m, 2H, CH ₂ SCH ₃ , uncoord), 2.2 (s, 3H, SCH ₂ , uncoord)
11	7.51 (m, 4H, Ph-H), 4.2 (m, 4H, PhCH ₂ S), 2.75 (m, 8H, SCH ₂ CH ₂ S)

"Spectra recorded in dimethylsulfoxide at $25^{\circ}C$ and referenced to $SiMe_4$.

Hence, the complexes were handled in air only for very short periods and were used very quickly in order to avoid decomposition. Conductivity measurements of complex 7 showed the complex to be a non-electrolyte in acetone, however, complex 8 was shown to be a typical 1:1 electrolyte ($A_m = 128 \text{ S cm}^2 \text{ mol}^{-1}$) in acetone. The conductivity data suggests that in complex 8 one of the sulfur atoms from the second diphosphine disulfide ligand has displaced one of the bromide ligands from the starting material.

The IR spectra of both complexes were recorded as KBr disks. Three carbonyl stretching bands were observed for both complexes (Table 4). This is consistent with the complexes being seven-coordinate and having one conformation in the solid-state. The ¹H NMR spectra (Table 5) again showed the coordinated diphosphine disulfide resonances to be shifted slightly downfield compared to those of the free ligand. Similar reactions were attempted with the molybdenum complex [MoBr₂(CO)₃(NCMe)₂], however no pure products could be isolated, which is probably due to their greater instability.

The reaction of $[MBr_2(CO)_3(NCMe)_2]$ with an equimolar amount of MeS(CH₂)₂S(CH₂)₂SMe in CH2Cl2 at room temperature gave the seven-coordinate dicarbonyl complex $[MoBr_2(CO)_2]$ {MeS(CH₂)₂S(CH₂)₂SMe-S,S',S''}] (9) and the tricarbonyl complex [WBr₂(CO)₃{MeS(CH₂)₂S $(CH_2)_2SMe-S,S'$ (10), respectively in high yield. Complexes 9 and 10 were characterised by elemental analysis C, H and S (Table 3), IR spectroscopy (Table 4) and ¹H NMR spectroscopy (Table 5). Both com-



Fig. 2. Proposed structure of $[WBr(CO)_3 \{RS(CH_2)_2SR-S\}$ $\{RS(CH_2)_2SR-S,S'\}$]Br (5 and 6) (R = Ph or C₆H₄CF₃-4).

plexes are soluble in dichloromethane and DMSO but are totally insoluble in diethyl ether; the molybdenum complex is less soluble than its tungsten analogue. Both complexes are very air-sensitive in solution and only slightly less sensitive in the solid state. Conductivity measurements in acetone showed both complexes to be non-electrolytes. The IR spectra of both complexes were recorded as KBr disks (Table 4). Complex 9 showed two carbonyl stretching bands suggesting a dicarbonyl complex while three carbonyl stretching bands were observed for complex 10.

The ¹H NMR spectra (Table 5) of both complexes showed the coordinated thioether resonances to be shifted downfield compared to those of the free thioethers. However, in the case of complex **10** a resonance



Fig. 1. The structure of **2**, together with the atom numbering scheme. Ellipsoids are shown at 30% probability. Hydrogen atoms are drawn with small arbitrary radii.

can be assigned to the methyl group of the uncoordinated sulfur atom. The geometry for complex 9 may be a capped octahedron (Fig. 3) for the dicarbonyl molybdenum complex $[MoBr_2(CO)_2]$ {MeS(CH₂)₂S(CH₂)₂SMe-S,S',S''}] (9) since the previously confirmed crystallographically determined structure of the diiodo-complex [WI₂(CO)₂{MeS $(CH_2)_2S(CH_2)_2SMe-S,S',S''$ [9], is capped octahedral, and their spectral properties are also very similar. Several unsuccessful attempts to prepare the analogous tungsten complex [WBr₂(CO)₂{MeS $(CH_2)_2S(CH_2)_2SMe-S,S',S''$ were made by using longer reaction times. The greater lability of molybdenum carbonyl complexes compared to tungsten carbonyl complexes is well known [25].

Treatment of [MoBr₂(CO)₃(NCMe)₂] with an equimolar amount of 2,5,8-trithia[9]-o-benzeneophane (ttob) gave the seven-coordinate dicarbonyl complex $[MoBr_2(CO)_2\{ttob-S, S', S''\}]$ (11) in high yield. Complex (11) was light brown in colour and was characterised by elemental analysis C, H and S (Table 3), IR spectroscopy (Table 4) and ¹H NMR spectroscopy (Table 5). The complex was soluble in dichloromethane and DMSO but was totally insoluble in diethyl ether. As expected the complex was very airsensitive in both solution and in the solid state and hence was handled accordingly. Conductivity measurements in acetone showed the complex to be a non-electrolyte. The IR spectrum was recorded as a KBr disk (Table 4). The complex showed two carbonyl stretching bands suggesting a dicarbonyl complex similar to that of previously described complex (9). Similar reactions of [WBr₂(CO)₃(NCMe)₂] with an equimolar amount of 2,5,8-trithia[9]-o-benzeneophane (ttob) were attempted, but resulted in a mixture of unstable products. Attempts to separate the products were unsuccessful due to decomposition occurring while recrystallisation was attempted.

In conclusion, the results described in this paper closely mimic those previously observed for the related reactions of the diiodo complexes,



Fig. 3. Proposed structure of $[MoBr_2(CO)_2\{MeS(CH_2)_2 S(CH_2)_2SMe-S,S',S''\}]$ (9).

 $[MI_2(CO)_3(NCMe)_2]$ with neutral sulfur donor ligands previously described.

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