Preparation and Characterisation of Seven-co-ordinate Trifluoroacetate and Oxalate Complexes of Molybdenum(II) and Tungsten(II)†

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The 1:1 reaction of sodium trifluoroacetate with either $[MBr_2(NCMe)(CO)_2(PR_3)_2]$ (M = Mo or W, PR_3 = PMe_2Ph or $PMePh_2$) or $[MBr_2(CO)_2(PPh_3)_2]$ (M = Mo or W) formed the mononuclear complexes $[MBr(O_2CCF_3)(CO)_2(PR_3)_2]$ containing a bidentate carboxylate ligand. Addition of a second equivalent of the carboxylate salt generated $[M(O_2CCF_3)_2(CO)_2(PR_3)_2]$ in which the oxygen-donor ligands adopt one bidentate and one monodentate bonding mode. Single-crystal X-ray diffraction studies of $[MoBr(O_2CCF_3)(CO)_2(PPh_3)_2]$ confirm a 4:3 polytopal form. The treatment of $[MBr_2(NCMe)(CO)_2(PR_3)_2]$ (M = Mo, PR_3 = $PMePh_2$; M = W, PR_3 = PMe_2Ph or $PMePh_2$) or $[MBr_2(CO)_2(PPh_3)_2]$ (M = Mo or W) with a suspension of sodium oxalate in acetone yielded the complexes $[\{MBr(CO)_2(PR_3)_2\}_2(\mu\text{-}C_2O_4)]$. The tungsten species $[\{WBr(CO)_2(PMe_2Ph)_2\}_2(\mu\text{-}C_2O_4)]$ crystallises in two forms both of which contain a planar oxalate bridge linking two seven-co-ordinate metal centres, but have different 4:3 geometries. The triangular face of the polygon in each of the three structures is occupied by a bromine atom and two oxygens of a carboxylate group, and the quadrilateral face by pairs of carbonyl and phosphine ligands.

The structural and bonding properties of early transition-metal carboxylates, and their corresponding sulfur-containing analogues are of considerable interest because of their role in biological modelling,[1] materials chemistry,[2] catalysis[3] and C_1 activation processes.[4] Mononuclear carboxylates and thiocarboxylates are formed in CO_2 and CS_2 insertion reactions,[5] and dinuclear derivatives containing the tetrathiolate and oxalate dianions result from metal-promoted head-to-head reductive dimerisation of these molecules.[6] Reductive disproportionation of CO_2 can also be induced by a molybdenum–phosphine derivative,[7] and although much attention has been devoted to the synthesis and characterisation of low, positive oxidation state model complexes of molybdenum and tungsten containing bidentate sulfur ligands, as typified by seven-co-ordinate molybdenum(II) and tungsten(II) derivatives of the type $[M(CO)_{3-n}(PR_3)_n(L\text{–}L)_2]$ (n = 1 or 2; L–L = $R_2NCS_2^-$, $R_2PS_2^-$, or $ROCS_2^-$),[8] analogous mononuclear compounds containing phosphines and anionic oxygen-donor ligands have by contrast received much less attention,[9–11] and dinuclear analogues are rare.[7] This imbalance can in part be traced to the limited number of known, stable, six-co-ordinate complexes $[MX_2(CO)_2(PR_3)_2]$ (X = halogen), which can be used conveniently as synthons for the introduction of 'hard' donors. In an earlier study[12] we showed that the yellow, monomeric seven-co-ordinate complexes $[MX_2(NCMe)(CO)_2(PR_3)_2]$ (M = Mo or W), formed by decarbonylation of $[MX_2(CO)_3(PR_3)_2]$ in acetonitrile, readily lost MeCN in chlorinated solvents to form highly coloured six-co-ordinate d^4 $[MX_2(CO)_2(PR_3)_2]$ derivatives, presumably stabilised by a 'token ligand' consisting of a very weakly bonded solvent molecule.[13] Many of these pseudo six-co-ordinate species are not available by thermolysis of the tricarbonyl compound, and as part of our investigations concerning the reactivity of these complexes[14] we now describe their use for the synthesis of mono- and dinuclear carbonyl derivatives containing carboxylate and oxalate ligands respectively.

Experimental

Starting Materials.—The complexes $[MBr_2(NCMe)(CO)_2(PR_3)_2]$ (M = Mo or W, PR_3 = $PMePh_2$ or PMe_2Ph) and $[MBr_2(CO)_2(PPh_3)_2]$ (M = Mo or W) were prepared by literature methods.[12,15,16] All solvents were dried, distilled and deoxygenated prior to use, and reactions were carried out under an atmosphere of dry dinitrogen gas, using finely ground, anhydrous sodium salts of the two anions. Product yields, microanalyses and selected spectroscopic data are given in Table 1.

Syntheses of Complexes.—$[MBr(O_2CCF_3)(CO)_2(PR_3)_2]$ **1**–**4**. Freshly prepared solid $[MBr_2(CO)_2(PPh_3)_2]$ or $[MBr_2(NCMe)(CO)_2(PMePh_2)_2]$ (1.0 mmol) suspended or dissolved in acetone (30 cm^3) was stirred with sodium trifluoroacetate (136 mg, 1.0 mmol) at room temperature for 1 h (PR_3 = $PMePh_2$) or under reflux (PR_3 = PPh_3) for 12 h. With the exception of $[WBr(O_2CCF_3)(CO)_2(PPh_3)_2]$ **3**, the orange reaction mixtures were filtered, reduced to dryness *in vacuo* and the product dissolved in dichloromethane (5 cm^3). Addition of light petroleum (b.p. 40–60 °C), where necessary, to the filtered dichloromethane solution and cooling (−5 °C) yielded the dark orange crystalline products, which were finally recrystallised from CH_2Cl_2–hexane. Complex **3** precipitated from the reaction mixture as an orange-yellow microcrystalline powder contaminated with NaBr. The solid was separated by filtration, washed with acetone and then light petroleum (b.p. 40–60 °C) and dried *in vacuo* before recrystallising from CH_2Cl_2–hexane.

$[M(O_2CCF_3)_2(CO)_2(PR_3)_2]$ **5**–**10**. These complexes (M = Mo or W; PR_3 = PPh_3, $PMePh_2$ or PMe_2Ph) were prepared by the same general method. A solution of sodium trifluoroacetate (272 mg, 2.0 mmol) in acetone (30 cm^3) was stirred at ambient temperature for 1 h with freshly prepared solid $[MBr_2(CO)_2(PPh_3)_2]$ or $[MBr_2(NCMe)(CO)_2(PR_3)_2]$ (PR_3 = $PMePh_2$ or PMe_2Ph) (1.0 mmol). The reaction mixture was filtered to remove NaBr and the filtrate evaporated to low volume under vacuum. Addition of light petroleum (b.p. 40–60 °C) (10 cm^3) and storage at −5 °C yielded yellow crystals which were recrystallised from CH_2Cl_2–hexane.

$[\{MBr(CO)_2(PR_3)_2\}_2(\mu\text{-}C_2O_4)]$ **11**–**15**. The reaction for 15 h

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Characterization data for trifluoroacetate and oxalate complexes of molybdenum and tungsten

Complex	Yield (%)	Analysis (%)[a]		$\nu(CO)$[b]/ cm^{-1}	$\nu_{asym}(CO_2)$[b]/ cm^{-1}	^{31}P NMR[c] (δ)
		C	H			
1 $[MoBr(O_2CCF_3)(CO)_2(PPh_3)_2]$[d]	63	55.2 (55.2)	3.30 (3.45)	1963 1878	1604	61.93
2 $[MoBr(O_2CCF_3)(CO)_2(PMePh_2)_2]$[d]	50	48.0 (48.3)	3.50 (3.50)	1954 1866	1608	47.98
3 $[WBr(O_2CCF_3)(CO)_2(PPh_3)_2]$	49	49.8 (50.2)	3.05 (3.15)	1942 1857	1603	34.11 (164)
4 $[WBr(O_2CCF_3)(CO)_2(PMePh_2)_2]$[d]	54	42.8 (43.2)	3.15 (3.10)	1931 1845	1607	19.88 (168)
5 $[Mo(O_2CCF_3)_2(CO)_2(PPh_3)_2]$	47	55.3 (55.9)	3.40 (3.35)	1962 1865	1691 1605	65.21
6 $[Mo(O_2CCF_3)_2(CO)_2(PMePh_2)_2]$	51	48.9 (49.3)	3.20 (3.35)	1955 1860	1693 1611	50.50
7 $[Mo(O_2CCF_3)_2(CO)_2(PMe_2Ph)_2]$	39	39.9 (40.4)	3.10 (3.35)	1961 1837	1714 1610	
8 $[W(O_2CCF_3)_2(CO)_2(PPh_3)_2]$	48	50.2 (50.9)	3.05 (3.10)	1940 1846	1695 1596	37.44 (172)
9 $[W(O_2CCF_3)_2(CO)_2(PMePh_2)_2]$	46	43.8 (44.3)	3.05 (3.00)	1935 1842	1700 1602	22.42 (178)
10 $[W(O_2CCF_3)_2(CO)_2(PMe_2Ph)_2]$	35	34.8 (35.6)	2.70 (2.95)	1940 1847	1712 1608	8.00 (176)
11 $[\{MoBr(CO)_2(PPh_3)_2\}_2(\mu-C_2O_4)]$	69	56.6 (56.3)	3.75 (3.70)	1941 1850	1622	*e*
12 $[\{MoBr(CO)_2(PMePh_2)_2\}_2(\mu-C_2O_4)]$	66	48.1 (49.2)	3.60 (3.70)	1946 1856	1631	58.62
13 $[\{WBr(CO)_2(PPh_3)_2\}_2(\mu-C_2O_4)]$	73	53.0 (52.7)	3.25 (3.40)	1923 1832	1624	*e*
14 $[\{WBr(CO)_2(PMePh_2)_2\}_2(\mu-C_2O_4)]$	67	45.2 (45.5)	3.40 (3.40)	1931 1840	1640	*e*
15 $[\{WBr(CO)_2(PMe_2Ph)_2\}_2(\mu-C_2O_4)]$	51	34.3 (35.6)	3.40 (3.45)	1920 1825	1640	8.08 (175)

[a] Calculated values in parentheses. $[\{MoBr(CO)_2(PR_3)_2\}_2(\mu-C_2O_4)]$ complexes calculated as the CH_2Cl_2 adduct. Br: complex **2** 10.70 (10.75); complex **9**, Br found <0.75%. [b] As Nujol mulls. [c] In CD_2Cl_2, values relative to H_3PO_4, $J(^{183}W-^{31}P)$ coupling constants (in Hz) in parentheses. [d] Molar conductivity/S cm^2 mol^{-1} in acetone (*ca.* 10^{-3} mol dm^{-3}): complex **1** 11.09; **2** 6.11; **4** 9.87; **5** 6.86. [e] Complex too insoluble for NMR spectrum.

at ambient temperature of excess of sodium oxalate (500 mg, 3.75 mmol) suspended in acetone (50 cm^3) with either $[MBr_2(CO)_2(PPh_3)_2]$ (M = Mo or W) (1.0 mmol) or $[MBr_2(NCMe)(CO)_2(PR_3)_2]$ (M = Mo, $PR_3 = PMePh_2$; M = W, $PR_3 = PMePh_2$ or PMe_2Ph) (1.0 mmol) yielded an orange reaction mixture which was taken to dryness *in vacuo*, and the residue extracted five times with dichloromethane (20 cm^3). The combined extracts were reduced in volume to *ca.* 50 cm^3 and stored at −5 °C after addition of hexane (5 cm^3). Complex $[\{WBr(CO)_2(PMe_2Ph)_2\}_2(\mu-C_2O_4)]$ **15** deposited as mainly orange rectangular crystals **15a**, admixed with a few yellow blocks **15b**.

X-Ray Crystallography.—Samples of $[\{WBr(CO)_2(PMe_2Ph)_2\}_2(\mu-C_2O_4)]$ **15a** and **15b** and of $[MoBr(O_2CCF_3)(CO)_2(PPh_3)_2]$ **1** were recrystallised twice from CH_2Cl_2–hexane at −5 °C to produce crystals suitable for an X-ray single-crystal structure determination. Crystallographic data are listed in Table 2. The structures were solved by conventional Patterson methods and refined using the SHELX[18] suite of programs. Scattering factors and anomalous dispersion corrections were obtained from ref. 19. In the final least-squares cycles for complexes **1** and **15b** the metal, Br and P atoms were refined anisotropically, all other atoms isotropically. For **15a**, W, Br, P and O atoms were refined anisotropically. Hydrogen atoms were included at calculated positions in complex **1** only. Atomic coordinates are listed in Tables 3 and 4. Important intramolecular bond distances and angles are given in Tables 5–7, and the asymmetric units of **1**, **15a** and **15b** are shown in Figs. 1–3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Physical Measurements.—Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 599B spectrometer, and molar conductivity data in acetone were obtained using a Jenway 4010 conductivity meter. Proton and ^{31}P NMR spectra were obtained for CD_2Cl_2 solutions of the complexes on JEOL GX-270 and -400 MHz spectrometers, using trimethylsilane or external 85% H_3PO_3 as references respectively. Elemental analyses were carried out by Analytical Services at Bath University (C, H) and by Butterworth Laboratories Ltd., Teddington, Middlesex (Br).

Results and Discussion

A limited number of molybdenum(II) carboxylate complexes of general formulae $[Mo(O_2CR')_2(CO)_2(PR_3)_2]$ and $[MoX(O_2CR')(CO)_2(PR_3)_2]$ (R′ = H, Me, Et or Ph; X = halide) have been prepared previously[9,10] by direct treatment of $[MoX_2(CO)_n(PR_3)_2]$ (n = 2 or 3) with the appropriate sodium carboxylate salt. However, to date this method has been successfully employed only where a relatively stable, six-coordinate 16-electron dicarbonyl complex $[MoX_2(CO)_2(PR_3)_2]$ can be isolated (R = Ph or Et), and since few such monomers are known the method is not generally applicable. In addition, attempts to prepare analogous tungsten complexes from the bi- or tricarbonyl complexes $[MX_2(CO)_n(PR_3)_2]$ using this method have proved unsuccessful, the products isolated containing no carbonyl groups.[9] An alternative route to a single bis(carboxylate) complex of molybdenum has been reported,[11]

Table 2 Crystal data and data collection parameters for $[MoBr(O_2CCF_3)(CO)_2(PPh_3)_2]$ **1** and $[\{WBr(CO)_2(PMe_2Ph)_2\}_2(\mu\text{-}C_2O_4)]$ **15a** and **15b**[a]

	1	**15a**	**15b**
Formula	$C_{40}H_{30}BrF_3MoO_4P_2$	$C_{38}H_{44}Br_2O_8P_4W_2$	$C_{38}H_{44}Br_2O_8P_4W_2$
M	869.24	1280.2	1280.2
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	18.490(5)	9.964(2)	10.810(2)
b/Å	11.810(3)	19.103(15)	15.213(4)
c/Å	18.752(4)	11.968(4)	13.488(3)
β/°	116.86(2)	104.51(2)	103.08(1)
U/Å^3	3653.0	2205.4	2160.4
Z	4	2	2
D_c/g cm^{-3}	1.59	1.93	1.96
Crystal dimensions/mm	0.15 × 0.15 × 0.15	0.25 × 0.3 × 0.25	0.3 × 0.3 × 0.35
μ(Mo-Kα)/cm^{-1}	15.09	76.33	77.82
hkl	0–19, 0–12, −18 to 18	0–10, 0–19, −12 to 12	0–11, 0–15, −14 to 14
2θ range/°	4–44	4–44	4–44
F(000)	1744	1228	1228
Data collected	4897	3006	2949
Unique data [$I \geqslant 3\sigma(I)$]	2882	1992	1822
No. of variables	237	159	129
Maximum shift/e.s.d. in final cycle	0.05	0.004	0.005
Maximum, minimum residual density/e Å^{-3}	0.42, −0.34	0.97, −0.94	0.87, −1.16
Maximum, minimum transmission factors		1.06–0.97	1.13–0.97
R	0.0774	0.0512[b]	0.0531[b]
R'	0.0707[c]		

[a] Details in common: data collection at room temperature on a Hilger and Watts Y290 automatic four-circle diffractometer; a standard reflection measured every 4500 s of beam time during data collection showed no systematic variation in intensity; data corrected for Lorentz and polarisation effects, and, in the case of **15a** and **15b**, for absorption (ref. 17). [b] Unit weights employed. [c] Weighting scheme $w = 3.0065/[\sigma^2(F_o) + 0.0010(F_o)^2]$.

Table 3 Fractional atomic coordinates for $[MoBr(O_2CCF_3)(CO)_2(PPh_3)_2]$ **1**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Mo	0.237 30(7)	0.102 48(10)	0.000 05(6)	C(20)	0.415 6(9)	0.284 4(12)	0.065 5(8)
Br	0.168 14(10)	0.250 89(12)	−0.113 15(9)	C(21)	0.189 0(8)	−0.045 4(11)	−0.195 4(7)
P(1)	0.371 02(2)	0.090 63(3)	0.121 03(2)	C(22)	0.220 1(8)	0.047 8(12)	−0.218 6(8)
P(2)	0.168 72(2)	−0.041 49(3)	−0.108 09(2)	C(23)	0.235 6(9)	0.037 8(13)	−0.283 9(8)
O(1)	0.218 4(5)	−0.103 0(8)	0.092 3(5)	C(24)	0.220 2(10)	−0.060 3(13)	−0.328 0(9)
O(2)	0.367 4(6)	0.054 1(8)	−0.058 9(6)	C(25)	0.188 5(9)	−0.151 4(13)	−0.305 5(8)
O(3)	0.135 3(6)	0.164 5(8)	0.030 3(5)	C(26)	0.173 2(8)	−0.144 2(11)	−0.239 1(8)
O(4)	0.245 9(6)	0.265 9(7)	0.070 6(5)	C(27)	0.060 5(8)	−0.014 8(10)	−0.149 9(7)
C(1)	0.228 9(8)	−0.029 1(11)	0.059 8(7)	C(28)	0.021 2(9)	−0.031 3(11)	−0.102 7(8)
C(2)	0.318 6(8)	0.070 0(11)	−0.036 1(8)	C(29)	−0.060 6(10)	−0.008 0(12)	−0.132 4(9)
C(3)	0.371 8(8)	0.127 1(10)	0.216 0(7)	C(30)	−0.104 0(11)	0.030 7(13)	−0.207 2(9)
C(4)	0.304 0(9)	0.124 9(11)	0.227 7(8)	C(31)	−0.065 8(9)	0.049 8(12)	−0.254 1(9)
C(5)	0.306 6(10)	0.150 3(13)	0.301 2(9)	C(32)	0.016 5(9)	0.027 1(11)	−0.227 6(8)
C(6)	0.378 6(9)	0.180 5(12)	0.364 3(9)	C(33)	0.183 4(8)	−0.190 6(11)	−0.078 1(7)
C(7)	0.448 7(11)	0.185 1(14)	0.354 5(10)	C(34)	0.259 3(10)	−0.232 2(14)	−0.036 0(8)
C(8)	0.445 4(9)	0.157 7(11)	0.280 1(8)	C(35)	0.274 7(11)	−0.345 3(14)	−0.013 5(9)
C(9)	0.418 5(8)	−0.046 9(11)	0.140 7(7)	C(36)	0.210 4(10)	−0.417 8(14)	−0.033 9(9)
C(10)	0.406 4(8)	−0.122 9(11)	0.191 0(8)	C(37)	0.132 8(12)	−0.379 4(16)	−0.077 7(10)
C(11)	0.434 0(9)	−0.234 6(13)	0.198 2(8)	C(38)	0.116 3(10)	−0.264 9(12)	−0.099 5(9)
C(12)	0.473 3(10)	−0.268 7(14)	0.156 2(9)	C(39)	0.179 5(8)	0.250 4(11)	0.062 9(7)
C(13)	0.488 6(10)	−0.195 7(14)	0.106 8(9)	C(40)	0.140 0(12)	0.339 7(15)	0.096 4(11)
C(14)	0.461 3(9)	−0.086 5(12)	0.100 3(8)	F(1)	0.118 4(13)	0.432 7(16)	0.048 1(11)
C(15)	0.443 5(9)	0.188 6(12)	0.110 9(8)	F(2)	0.186 5(13)	0.363 9(18)	0.171 3(12)
C(16)	0.526 8(10)	0.167 6(13)	0.150 2(9)	F(3)	0.065 6(13)	0.308 3(17)	0.086 6(12)
C(17)	0.578 8(11)	0.243 9(13)	0.139 6(9)	F(4)	0.193 9(16)	0.426 2(22)	0.129 1(15)
C(18)	0.551 0(10)	0.338 0(14)	0.093 1(9)	F(5)	0.125 4(15)	0.300 4(19)	0.151 0(14)
C(19)	0.467 9(10)	0.360 2(13)	0.055 2(9)	F(6)	0.076 2(17)	0.384 1(23)	0.042 1(15)

involving the treatment of $[Mo(CO)_3(PEt_3)_3]$ with trifluoroacetic acid. However in contrast to the halide substitution route in which yields of 60–80% were attainable, this alternative approach results in only a 12% yield of the product $[Mo(O_2CCF_3)_2(CO)_2(PEt_3)_2]$. Although there are many bi-, tri- and poly-nuclear oxalate complexes of molybdenum and tungsten in high oxidation states,[21] we are unaware of any oxalate complexes of these metals containing a d^4 carbonyl centre, with the exception of a brief reference to a single organometallic molybdenum compound.[22]

There are many examples in molybdenum(II) and tungsten(II) chemistry of facile displacement of weakly bonded nitrile ligands, and we have used the intermediacy of $[MBr_2(NCMe)(CO)_2(PR_3)_2]$ to provide a general route to the mononuclear trifluoroacetate complexes $[MBr(O_2CCF_3)(CO)_2(PR_3)_2]$ and $[M(O_2CCF_3)_2(CO)_2(PR_3)_2]$, and to the dinuclear oxalate complexes $[\{MBr(CO)_2(PR_3)_2\}_2(\mu\text{-}C_2O_4)]$, in yields of 40–65% (Table 1) on reaction of the nitrile complex with the sodium salt of the appropriate oxoanion. Contamination of the mono(bromotrifluoroacetate) complexes **1**–**4** with the bis(carboxylate) derivatives was minimal provided the correct stoichiometry was used initially and yields of the recrystallised products were

Table 4 Fractional atomic coordinates for $[\{WBr(CO)_2(PMe_2Ph)_2\}_2(\mu\text{-}C_2O_4)]$ **15a** and **15b** with e.s.d.s in parentheses

15a

Atom	*x*	*y*	*z*
W(1)	0.124 98(7)	0.061 83(3)	0.219 78(6)
Br(1)	0.177 5(2)	0.147 4(1)	0.061 8(2)
P(1)	0.262 1(5)	−0.037 0(2)	0.319 0(4)
P(2)	0.032 7(5)	0.164 6(2)	0.302 3(4)
O(1)	−0.053 6(12)	−0.005 2(7)	0.370 2(12)
O(2)	0.379 2(14)	0.131 4(7)	0.388 8(13)
O(3)	0.161 3(11)	−0.013 1(6)	0.093 2(10)
O(4)	−0.072 7(11)	0.049 9(6)	0.088 2(13)
C(18)	0.286 8(20)	0.103 1(9)	0.324 9(19)
C(19)	0.066 6(19)	−0.017 0(8)	0.001 3(16)
C(1)	0.172 7(19)	−0.120 3(10)	0.289 0(17)
C(2)	0.310 9(19)	−0.035 0(10)	0.475 6(17)
C(3)	0.424 1(17)	−0.052 1(10)	0.275 4(16)
C(4)	0.497 2(21)	−0.116 5(11)	0.316 5(19)
C(5)	0.616 4(27)	−0.129 6(14)	0.273 9(25)
C(6)	0.663 8(24)	−0.084 9(12)	0.215 4(23)
C(7)	0.594 5(24)	−0.018 9(13)	0.172 4(22)
C(8)	0.471 7(19)	−0.005 9(10)	0.211 4(18)
C(9)	0.111 2(18)	0.249 7(9)	0.285 9(16)
C(10)	0.044 1(22)	0.162 3(12)	0.458 0(21)
C(11)	−0.150 9(17)	0.179 1(9)	0.225 9(16)
C(12)	−0.253 6(26)	0.177 7(13)	0.289 8(24)
C(13)	−0.396 7(27)	0.185 5(14)	0.221 6(27)
C(14)	−0.421 8(25)	0.195 7(13)	0.109 2(24)
C(15)	−0.322 9(24)	0.202 6(12)	0.042 7(22)
C(16)	−0.182 8(20)	0.193 8(10)	0.111 3(18)
C(17)	0.018 2(18)	0.018 0(9)	0.317 7(16)

15b

Atom	*x*	*y*	*z*
W(1)	0.046 62(8)	0.105 18(6)	0.333 30(6)
Br(1)	−0.184 8(2)	0.147 5(2)	0.351 0(2)
P(1)	−0.048 4(6)	0.162 5(4)	0.160 9(4)
P(2)	0.275 6(5)	0.073 5(4)	0.392 8(4)
C(1)	−0.174 6(18)	0.097 0(14)	0.084 2(15)
C(2)	−0.203 3(20)	0.014 2(15)	0.117 3(16)
C(3)	−0.300 1(22)	−0.037 9(16)	0.054 2(18)
C(4)	−0.365 8(22)	−0.005 8(16)	−0.040 4(18)
C(5)	−0.335 7(23)	0.079 5(16)	−0.072 1(19)
C(6)	−0.241 1(20)	0.127 3(15)	−0.010 4(16)
C(7)	0.061 3(22)	0.183 8(17)	0.078 4(18)
C(8)	−0.118 7(22)	0.275 4(16)	0.156 7(18)
C(9)	0.358 2(19)	0.132 9(14)	0.505 5(15)
C(10)	0.348 9(22)	0.101 6(18)	0.601 9(18)
C(11)	0.418 7(25)	0.144 5(19)	0.692 6(21)
C(12)	0.487 6(26)	0.221 2(19)	0.680 5(22)
C(13)	0.500 9(25)	0.250 8(19)	0.589 1(21)
C(14)	0.431 0(22)	0.212 8(16)	0.495 6(18)
C(15)	0.309 8(22)	−0.042 7(16)	0.426 5(18)
C(16)	0.373 7(21)	0.095 3(16)	0.300 7(17)
C(17)	0.130 1(18)	0.214 0(13)	0.324 8(14)
C(18)	0.094 7(19)	0.028 3(14)	0.231 8(15)
C(19)	0.028 2(18)	0.034 8(13)	0.538 0(14)
O(1)	0.116 4(16)	−0.023 8(12)	0.175 1(13)
O(2)	0.176 1(16)	0.283 5(12)	0.315 8(13)
O(3)	0.071 7(11)	0.103 6(9)	0.499 4(9)
O(4)	−0.025 6(12)	−0.025 7(9)	0.372 3(9)

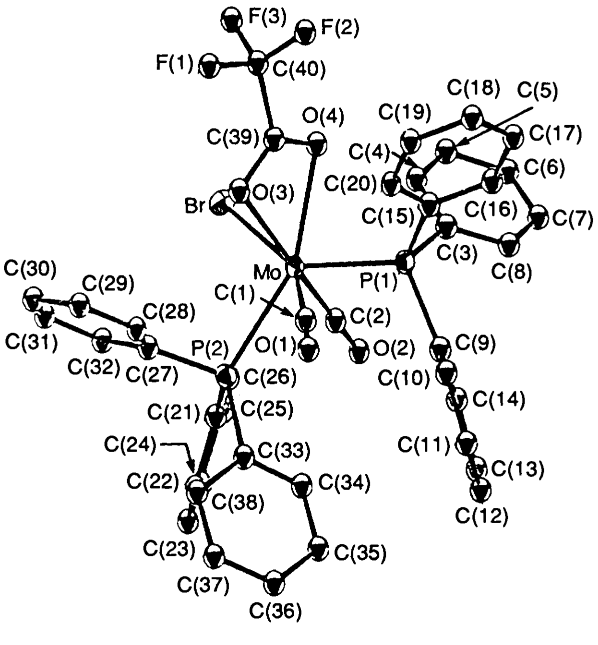

Fig. 1 An ORTEP[20] representation of $[MoBr(O_2CCF_3)(CO)_2(PPh_3)_2]$ **1** showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 33% probability level

kept below 70%. The complexes were characterised analytically and by their IR spectra as detailed in Table 1. The spectra of $[MBr(O_2CCF_3)(CO)_2(PR_3)_2]$ **1**–**4** exhibit only one asymmetric CO_2 stretching mode at *ca.* 1605 cm^{-1}, in keeping with a bidentate bonding mode for the trifluoroacetate ligand, and absorptions at *ca.* 1700 cm^{-1} for the monodentate co-ordination of a trifluoroacetate group as found in **5**–**10** were absent. In solution these complexes exhibited single ^{31}P NMR signals (Table 1), typical of those noted for other dynamic seven-co-ordinate complexes of similar stoichiometries.[9] Rapid exchange between the mono- and bi-dentate co-ordination modes of the carboxylate ligand has been noted[9] in solutions of $[Mo(O_2CH)_2(CO)_2(PEt_3)_2]$, even at −90 °C, and an analogous exchange process has been described for carboxylate ligands in the related compounds $[Ru(O_2CR')_2(CO)(PPh_3)_2]$ (R′ = Me, CF_3, C_2F_5 or C_6F_5).[23]

Structure of $[MoBr(O_2CCF_3)(CO)_2(PPh_3)_2]$ **1**.—Fig. 1 shows an ORTEP view of the molecule and the atomic numbering scheme used. Key structural parameters are given in Table 5. The central molybdenum atom can be described as seven-co-ordinate, being bonded to a pair of *cis* carbonyl carbon atoms [Mo–C(1) 1.96(1), Mo–C(2) 1.95(1) Å], two phosphine groups [Mo–P(1) 2.492(4), Mo–P(2) 2.507(4) Å], one bromine atom [Mo–Br 2.600(2) Å] and the two oxygen atoms of the trifluoroacetate group [Mo–O(3) 2.320(9), Mo–O(4) 2.304(9) Å]. The geometry can be best described as 4:3, with the bromine and acetate groups occupying the triangular face, and the two phosphine ligands and two carbonyl groups the quadrilateral face. This can be compared with the structures of the two related complexes $[Mo(O_2CH)_2(CO)_2(PEt_3)_2]$ and $[Mo(O_2CCF_3)_2(CO)_2(PEt_3)_2]$.[9,11] The former adopts a 4:3 geometry with the three oxygen atoms of the mono- and bi-dentate carboxylate groups occupying the triangular cap, and the carbonyl and phosphine ligands forming the rectangular base of the molecule as in **1**. The capped trigonal prismatic form of $[Mo(O_2CCF_3)_2(CO)_2(PEt_3)_2]$ contains the oxygen of the monodentate trifluoroacetate ligand in the capping position, one carbonyl, one phosphine and the bidentate trifluoroacetate ligand in the quadrilateral plane and the remaining carbonyl and phosphine groups on the unique edge. Despite these differences and the differing cone angles[24] of triphenylphosphine (θ = 145°) and triethylphosphine (θ = 132°), the average bond lengths and angles within the P–Mo–P unit in **1** and in the bis(formate) and bis(trifluoroacetate) analogues are very similar [2.50(1), 2.49(2) and 2.47(1) Å, and 129.0(1), 129.5(0) and 131.4(1)° respectively]. For complex **1** these data compare well with the corresponding values of

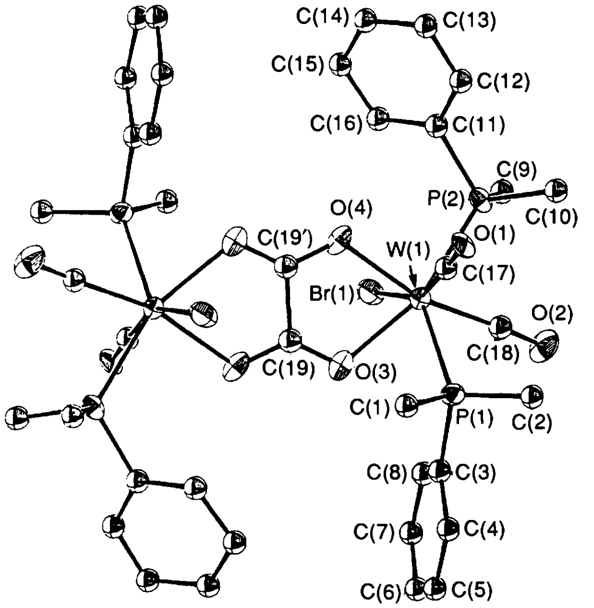

Fig. 2 An ORTEP representation of the structure of [{WBr(CO)$_2$-(PMe$_2$Ph)$_2$}$_2$(μ-C$_2$O$_4$)] **15a**

Table 5 Important bond distances (Å) and angles (°) for [MoBr-(O$_2$CCF$_3$)(CO)$_2$(PPh$_3$)$_2$] **1**, with e.s.d.s in parentheses

Mo–Br	2.600(2)	Mo–O(4)	2.304(9)
Mo–P(1)	2.492(4)	O(3)–C(39)	1.27(1)
Mo–P(2)	2.507(4)	O(4)–C(39)	1.18(1)
Mo–C(1)	1.96(1)	C(39)–C(40)	1.57(2)
Mo–C(2)	1.95(1)	C(1)–O(1)	1.13(1)
Mo–O(3)	2.320(9)	C(2)–O(2)	1.18(2)
Br–Mo–P(1)	134.5(1)	C(1)–Mo–C(2)	108.4(5)
Br–Mo–P(2)	85.1(1)	C(1)–Mo–O(3)	80.1(4)
Br–Mo–C(1)	149.7(4)	C(1)–Mo–O(4)	109.8(4)
Br–Mo–C(2)	91.2(4)	C(2)–Mo–O(3)	171.3(4)
Br–Mo–O(3)	80.3(2)	C(2)–Mo–O(4)	120.1(4)
Br–Mo–O(4)	77.6(2)	O(3)–Mo–O(4)	56.5(3)
P(1)–Mo–P(2)	129.0(1)	Mo–O(3)–C(39)	87.3(8)
P(1)–Mo–C(1)	74.8(4)	Mo–O(4)–C(39)	90.1(8)
P(1)–Mo–C(2)	72.6(4)	O(3)–C(39)–O(4)	126.0(1)
P(1)–Mo–O(3)	112.2(2)	O(3)–C(39)–C(40)	114.0(1)
P(1)–Mo–O(4)	75.0(2)	O(4)–C(39)–C(40)	120.0(1)
P(2)–Mo–C(1)	77.5(4)	Mo–C(1)–O(1)	175.0(1)
P(2)–Mo–C(2)	76.8(4)	Mo–C(2)–O(2)	178.0(1)
P(2)–Mo–O(3)	104.0(2)		
P(2)–Mo–O(4)	155.6(2)		

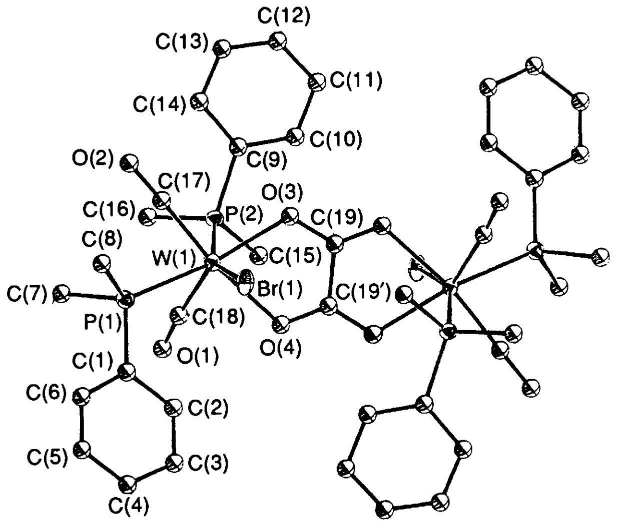

Fig. 3 An ORTEP representation of the structure of [{WBr(CO)$_2$-(PMe$_2$Ph)$_2$}$_2$(μ-C$_2$O$_4$)] **15b**

Table 6 Important bond distances (Å) and angles (°) for [{WBr(CO)$_2$-(PMe$_2$Ph)$_2$}$_2$(μ-C$_2$O$_4$)] **15a**, with e.s.d.s in parentheses

W(1)–Br(1)	2.649(2)	W(1)–O(3)	2.18(1)
W(1)–P(1)	2.455(4)	W(1)–O(4)	2.20(1)
W(1)–P(2)	2.476(4)	O(3)–C(19)	1.26(2)
W(1)–C(17)	1.96(2)	C(19)–C(19′)	1.47(3)
W(1)–C(18)	1.95(2)	C(17)–O(1)	1.15(2)
		C(18)–O(2)	1.17(2)
Br(1)–W(1)–P(1)	129.4(1)	P(2)–W(1)–C(18)	75.6(6)
Br(1)–W(1)–P(2)	87.4(1)	P(2)–W(1)–O(3)	160.2(3)
Br(1)–W(1)–C(17)	157.8(5)	P(2)–W(1)–O(4)	90.7(4)
Br(1)–W(1)–C(18)	86.1(6)	C(17)–W(1)–C(18)	105.8(9)
Br(1)–W(1)–O(3)	79.2(3)	C(17)–W(1)–O(3)	110.2(6)
Br(1)–W(1)–O(4)	81.7(4)	C(17)–W(1)–O(4)	82.0(6)
P(1)–W(1)–P(2)	129.4(2)	C(18)–W(1)–O(3)	117.4(7)
P(1)–W(1)–C(17)	72.6(5)	C(18)–W(1)–O(4)	162.0(6)
P(1)–W(1)–C(18)	74.2(5)	O(3)–W(1)–O(4)	73.1(5)
P(1)–W(1)–O(3)	70.2(3)	W(1)–O(3)–C(19)	115.0(1)
P(1)–W(1)–O(4)	123.7(3)	W(1)–C(17)–O(1)	175.0(1)
P(2)–W(1)–C(17)	77.8(5)	W(1)–C(18)–O(2)	176.0(2)
		W(1)–O(4)–C(19′)	118.7(9)

Table 7 Important bond distances (Å) and angles (°) for [{WBr(CO)$_2$-(PMe$_2$Ph)$_2$}$_2$(μ-C$_2$O$_4$)] **15b**, with e.s.d.s in parentheses

W(1)–Br(1)	2.646(2)	W(1)–O(3)	2.20(1)
W(1)–P(1)	2.478(6)	W(1)–O(4)	2.24(1)
W(1)–P(2)	2.470(6)	O(3)–C(19)	1.30(2)
W(1)–C(17)	1.90(2)	C(19)–C(19′)	1.50(4)
W(1)–C(18)	1.96(2)	C(17)–O(2)	1.19(2)
		C(18)–O(1)	1.16(2)
Br(1)–W(1)–P(1)	78.4(2)	P(2)–W(1)–C(17)	74.6(6)
Br(1)–W(1)–P(2)	156.4(1)	P(2)–W(1)–C(18)	72.9(6)
Br(1)–W(1)–C(17)	105.4(6)	P(2)–W(1)–O(3)	77.5(3)
Br(1)–W(1)–C(18)	127.9(6)	P(2)–W(1)–O(4)	97.3(3)
Br(1)–W(1)–O(3)	79.1(3)	C(17)–W(1)–C(18)	105.8(8)
Br(1)–W(1)–O(4)	79.0(3)	C(17)–W(1)–O(3)	96.9(7)
P(1)–W(1)–P(2)	123.0(2)	C(17)–W(1)–O(4)	169.0(7)
P(1)–W(1)–C(17)	74.8(6)	C(18)–W(1)–O(3)	135.7(7)
P(1)–W(1)–C(18)	70.9(6)	C(18)–W(1)–O(4)	78.2(7)
P(1)–W(1)–O(3)	153.0(4)	O(3)–W(1)–O(4)	73.7(5)
P(1)–W(1)–O(4)	116.1(3)	W(1)–O(3)–C(19)	116.0(1)
		W(1)–C(17)–O(2)	176.0(2)
		W(1)–C(18)–O(1)	173.0(2)

2.51(4) Å and 127.8(4)° found in [MoBr$_2$(CO)$_2$(PPh$_3$)$_2$],[16] which may be regarded as its precursor. Although the OC–Mo–CO angles [108.4(5), 105.6(1) and 102.2(7)°] are comparable in the three seven-co-ordinate complexes, they are significantly less than that of 119(2)° observed in the six-co-ordinate complex [MoBr$_2$(CO)$_2$(PPh$_3$)$_2$].[16] Thus the addition of a seventh, electronegative donor atom to the highly distorted octahedral structure of the six-co-ordinate d^4 complex [MoBr$_2$(CO)$_2$(PPh$_3$)$_2$] results in a large perturbation of the M(CO)$_2$ unit, but has little effect on the dimensions of the M(PR$_3$)$_2$ moiety.

Bond lengths and angles in monodentate carboxylate ligands have been noted elsewhere.[9,11] The lower electronegativity and greater size of the bromine atom results in a long Mo–Br bond [2.600(2) Å] replacing the much shorter Mo–O separations found in analogues containing monodentate formate [2.148(2) Å] or trifluoroacetate [2.215(15) Å] groups. However, the most notable differences between the three structures are the relative positions of the O-donor atoms of the bidentate carboxylate groups and the carbonyl carbon atoms. In complex **1** the C(2) atom of the carbonyl group is approximately *trans* to O(3) with a C–M–O angle of 171.3(4)°, which is similar to the corres-

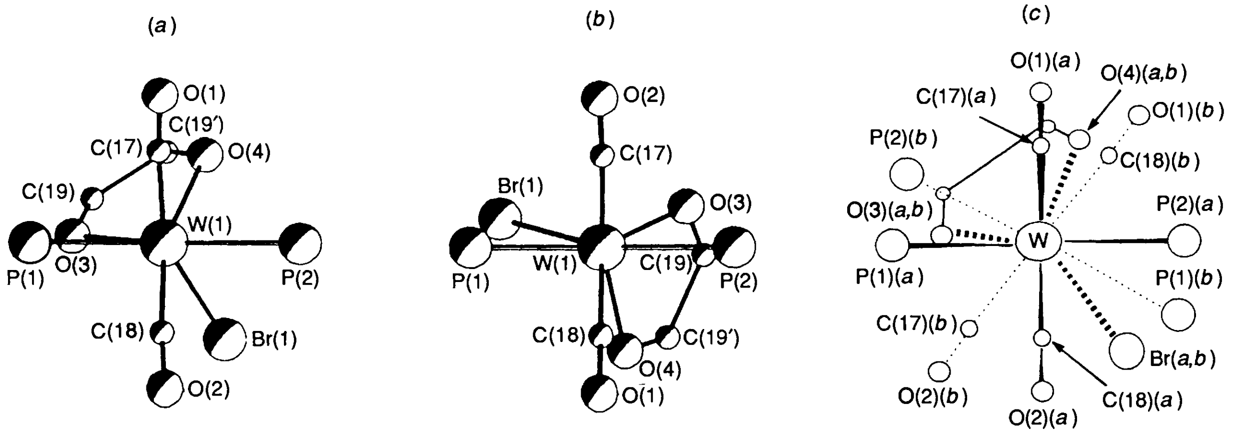

Fig. 4 Projections of the tungsten co-ordination spheres in **15a** (*a*) and **15b** (*b*) through the bisector of the P(1)–W–P(2) angle and (*c*) superimposition of the views in (*a*) and (*b*) with Br(1), O(3) and O(4) in common

ponding angle observed in [Mo$(O_2CH)_2(CO)_2(PEt_3)_2$] (168.7°), but contrasts with the much smaller angle of 117.8° in [Mo$(O_2CCF_3)_2(CO)_2(PEt_3)_2$]. The angle C(1)–Mo–O(4) in **1** [109.8(4)°] is close (within 5°) to those found in both of the above complexes. Corresponding Mo–O bond lengths involving the bidentate carboxylates are similar for all three complexes, with the exception of one significantly shorter distance [2.139(12) Å] in [Mo$(O_2CCF_3)_2(CO)_2(PEt_3)_2$].

Structures of [{WBr$(CO)_2(PMe_2Ph)_2$}$_2$(μ-C_2O_4)] **15a** *and* **15b**.—Replacement of sodium trifluoroacetate by sodium oxalate in the reaction described above yields only one isolable binuclear product irrespective of the stoichiometry of the reaction. Complexes **11–15** were less soluble in common organic solvents than the mononuclear trifluoroacetate complexes, and only **15** readily formed crystals suitable for a structure determination. The molecular structures of the two forms of **15** are illustrated in Figs. 2 and 3, and significant internuclear parameters are given in Tables 6 and 7. In each form the molecules contain a centre of inversion at the midpoint of the C–C bond of the planar, bridging oxalate ligand, and seven-co-ordination around each tungsten centre is completed by a bromine atom, and pairs of phosphine and carbonyl ligands [P–W–P 129.4(2) and 123.0(2)°, OC–W–CO 105.8(9) and 105.8(8)° for **15a** and **15b** respectively]. These angles are not dissimilar from those noted above for [Mo$(O_2CR)_2(CO)_2(PR_3)_2$].[9,11] Bond lengths within the chelate rings defined by the W atoms and the bridging oxalate ligand are not significantly different in **15a** and **15b**, with W–O separations averaging 2.21(3) Å. This compares with the very dissimilar W–O(oxalate) distances of 2.41(1) and 2.09(2) Å found in the [{WO$(O_2)_2$}$_2$(μ-C_2O_4)]$^{2-}$ ion,[25] presumably reflecting the influence of the terminal oxygen atom bonded *trans* to the long W–O(oxalate) linkage in this species.

Although the corresponding tungsten–ligand bond *lengths* do not vary significantly between the two forms, several bond *angles* are noticeably different. Fig. 4(*a*) and 4(*b*) present views of the tungsten co-ordination spheres in both forms of **15**, taken through the bisector of the angle between the P–W–P bond. In **15a** the ligand disposition conforms quite closely to that expected for a 4:3 polytopal form, with the quadrilateral plane defined by P(1)–C(17)–C(18)–P(2) (dihedral angle, 173°), almost parallel to the triangular face defined by the 'hard donors' O(3), O(4) and Br(1) (angle of intersection of quadrilateral and triangular faces, 6°). Rotation of the O(3),O(4),Br(1) triangle by approximately 150°, followed by a tip of O(3) away from the quadrilateral face, plus an increase in the coplanarity of the tungsten atoms with respect to the oxalate plane (in **15a** this unit adopts a shallow chair conformation with an interplanar angle of 9.5°), generates the essential features of **15b** [Fig. 4(*b*)].

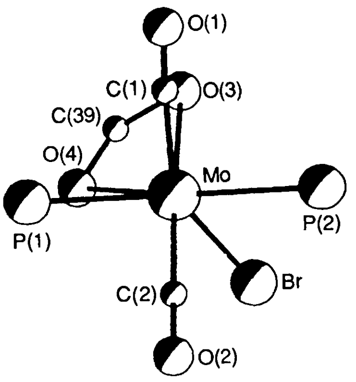

Fig. 5 Projection of the metal co-ordination sphere of complex **1** through the bisector of the P(1)–Mo–P(2) angle

The metal co-ordination sphere of **15b** can also be viewed as a distorted 4:3 structure [dihedral angle P(1)–C(17)–C(18)–P(2) 179°; angle of intersection of quadrilateral and triangular faces 6°], or alternatively as a highly distorted capped trigonal prismatic arrangement* with O(3) capping the quadrilateral face generated by C(17), P(2), O(4) and Br(1) [dihedral angles P(2)–O(4)–C(17)–Br(1) 163, O(3)–Br(1)–C(17)–P(1) 49 and O(3)–O(4)–P(2)–C(18) 43°]. On superimposing the triangular faces defined by atoms Br(1), O(3), O(4) in Fig. 4(*a*) and 4(*b*) the relationship between the two tetragonal bases defined by the carbonyl and phosphine ligands in **15a** and **15b** becomes apparent [Fig. 4(*c*)]. In both arrangements the closest non-bonding interactions between atoms on the triangular face and the tetragonal base are comparable [C(18)···Br(1) 3.21, C(17)···O(4) 2.74, P(1)···O(3) 2.68 Å in **15a**; P(1)···Br(1) 3.24, P(2)···O(3) 2.93, C(18)···O(4) 2.66 Å in **15b**], but involve different atom pairs. In particular, the halogen atom in **15a** has a carbonyl ligand as its nearest non-bonded neighbour within the metal co-ordination sphere, whereas in **15b** the corresponding ligand is a phosphine.

On dissolution in CD_2Cl_2 both **15a** and **15b** exhibit identical ^{1}H NMR spectra, and both have a single singlet resonance centred at δ 8.08 at 293 K in their ^{31}P spectra, showing satellites with coupling constants to ^{183}W of 175 Hz. Thus only one dynamic form of **15** exists in solution at ambient temperature

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* These structures can also be defined in terms of the alternative stereochemistry predicted by Dewan *et al.*[26] for M(L)$_5$(L–L) complexes (L = monodentate ligand, L–L = bidentate ligand), which takes into account ligand bite size but not ligand type. As this consideration is likely to be a significant factor in these complexes we have not adopted their method.

but two polymorphs are formed when the solid slowly crystallises from this solvent. These forms represent the two distinct conformers of the basic 4:3 geometric arrangement predicted by Muetterties and Wright.[27]

Although complex **1** contains molybdenum and **15a** and **15b** contain tungsten, it is instructive to view the structure of **1** through the bisector of the P–Mo–P angle in order to compare the metal co-ordination sphere of all three complexes (Fig. 5). The projections of **1** are very similar to that of **15a** with respect to six of the seven metal-bonded atoms. The larger bite of the oxalate ligand (*ca.* 1.20) compared to the trifluoroacetate ligand (*ca.* 0.90) accounts for the change in the relative position of the final oxygen atom.

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