Crystal Structures of Two Closely Related Compounds of Molybdenum-(II) and -(IV): Carbonylcyclopentadienylhexafluorobut-2-yne(pentafluorophenylthio)molybdenum and Cyclopentadienyl(hexafluorobut-2-yne)oxo(pentafluorophenylthio)molybdenum

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The co-ordinatively unsaturated species [Mo(CO)(η^5-C_5H_5)($CF_3C_2CF_3$)(SC_6F_5)] (I) undergoes slow oxidation in diethyl ether to give [Mo(O)(η^5-C_5H_5)($CF_3C_2CF_3$)(SC_6F_5)], (II). *X*-Ray diffraction studies show that the co-ordinated hexafluorobut-2-yne moiety has its bond axis approximately parallel to the Mo–C–O bonds in the Mo^{II} carbonyl compound but that this has turned through 90° to become parallel to the Mo–S bond in the Mo^{IV} oxo-compound. Crystals of (I) are triclinic, space group $P\bar{1}$, with Z = 2 in a unit cell of dimensions: a = 8.267(4), b = 13.548(5), c = 8.337(3) Å, α = 99.16(3), β = 97.08(4), γ = 86.61(4)°; the structure was solved by heavy-atom methods from 2 722 independent diffracted intensities measured on a diffractometer, and refined to R 0.038. Crystals of (II) are orthorhombic, space group *Pbca*, with Z = 8 in a unit cell of dimensions: a = 25.130(6), b = 10.933(4), c = 13.210(4) Å, and the structure has been similarly elucidated from 2 251 independent reflections (R 0.050).

In both compounds the co-ordinated acetylene is non-linear, with CF_3–C–C angles of 136 and 138° (I), 138 and 142° (II), and C–C 1.29 (I), 1.27 (II), but all four carbon atoms are approximately coplanar with the molybdenum atom. The Mo–O distance in (II) is 1.678 Å, and Mo–S distances are 2.366 (I) and 2.403 (II). The co-ordination around the Mo atom is approximately octahedral with the cyclopentadienyl ligand occupying three facial sites.

REACTION of tricarbonylcyclopentadienyl(pentafluorophenylthio)molybdenum, [Mo(CO)$_3$(η^5-C_5H_5)(SC_6F_5)], with hexafluorobut-2-yne at 333 K yields a monoacetylene complex (I), [Mo(CO)(η^5-C_5H_5)($CF_3C_2CF_3$)(SC_6F_5)].[1] This product is formally a co-ordinatively unsaturated (sixteen-electron) species which is structurally interesting in itself, but it undergoes slow oxidation under controlled conditions[1] to give (II), [Mo(O)(η^5-C_5H_5)($CF_3C_2CF_3$)(SC_6F_5)], and for this latter compound there is spectroscopic evidence to suggest that the mode of bonding of the acetylene fragment may be different from that operating in (I). We report here the results of structural studies by *X*-ray diffraction on (I) and (II) which establish the reality and the nature of this difference.

EXPERIMENTAL

Compound (I).—[Mo(CO)(η^5-C_5H_5)($CF_3C_2CF_3$)(SC_6F_5)] crystallises as dark blue prisms elongated along c. The crystal chosen for intensity-data collection was of dimensions 0.35 × 0.35 × 0.25 mm; it was sealed into a Lindemann glass tube. Intensities were collected on a Syntex $P2_1$ four-circle diffractometer in the range $2.9° < 2\theta < 50°$ with Mo-K_α *X*-radiation and a graphite monochromator, according to methods described earlier.[2] Of 3 464 independent measured intensities, 3 000 satisfied the criterion $I > 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure. Data were corrected for Lorentz and polarisation effects but not for *X*-ray absorption.

Crystal Data for (I).—$C_{16}H_5F_{11}OSMo$, (I), M = 550. Triclinic, a = 8.267(4), b = 13.548(5), c = 8.337(3) Å, α = 99.16(3), β = 97.08(4), γ = 86.61(4)°, U = 979 Å^3, D_m(flotation) = 1.82, Z = 2, D_c = 1.87 g cm^{-3}, $F(000)$ = 532. Mo-K_α *X*-radiation, λ = 0.710 69 Å; μ(Mo-K_α) = 8.78 cm^{-1}. Space group $P\bar{1}$ (No. 2).

Structure Solution and Refinement for (I).—The molybdenum atom was located from a Patterson synthesis and remaining non-hydrogen atoms by successive electron-density difference syntheses. Hydrogen atoms were incorporated at calculated positions (C–H 0.950 Å) but were kept invariant during refinement (U_{iso} 5.0 × 10^{-2} Å^2). In allowing all non-hydrogen atoms to have anisotropic thermal motion it became necessary to define two block matrices for the final refinement, and a weighting scheme of the type $1/w = (\sigma_F)^2 + 0.045|F_o|^2$ (in which σ_F is the standard deviation derived from counting statistics) was introduced. This gave a satisfactory weight analysis. Refinement converged at R 0.038 (R' 0.043), with a mean shift-to-error ratio in the last two cycles of 0.03. A final electron-density difference synthesis showed no peaks >0.2 or <0.3 eÅ^{-3}. The scattering factors used were those of ref. 3 for molybdenum, fluorine, carbon, oxygen, and sulphur, and of ref. 4 for hydrogen. Corrections for anomalous dispersion[5] ($\Delta F'$, $\Delta F''$) were applied for the molybdenum and sulphur atoms.† Computational work was carried out using the '*X*-Ray' system of programmes.[6] Final atomic positional and thermal parameters are listed in Table 1.

Compound (II).—[Mo(O)(η^5-C_5H_5)($CF_3C_2CF_3$)(SC_6F_5)], crystallises as yellow prisms elongated along c. Diffracted intensities were collected as for (I) from a crystal of dimensions 0.65 × 0.45 × 0.30 mm. Of 3 649 independent reflections in the range $2.9° < 2\theta < 50°$, 2 251 were considered observed, and only these were used in the structure solution and refinement. Corrections were applied for Lorentz and polarisation effects but not for *X*-ray absorption.

Crystal Data for (II).—$C_{15}H_5F_{11}OSMo$, (II), M = 538. Orthorhombic, a = 25.130(6), b = 10.933(4), c = 13.210(4) Å, U = 3 628 Å^3, D_m(flotation) = 1.93, Z = 8, D_c = 1.97 g cm^{-3}, $F(000)$ = 2 080. μ(Mo-K_α) = 9.45 cm^{-1}. Space group *Pbca* (No. 61).

Structure Solution and Refinement for (II).—The same

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† Observed and calculated structure factors for both compounds are listed in Supplementary Publication No. SUP 21543 (24 pp., 1 microfiche). See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[1] J. A. Davidson and D. W. A. Sharp, preceding paper.

[2] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June 1972.

TABLE 1

Atomic positional (fractional co-ordinates) and thermal parameters ($\times 10^2$) for (I), with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.069 18(5)	0.245 03(3)	0.135 21(4)	4.86(2)	4.10(2)	3.09(2)	−0.80(2)	−0.08(2)	0.49(1)
S	0.2519(2)	0.1059(1)	0.1615(1)	7.2(1)	5.0(1)	4.2(1)	0.7(1)	0.4(1)	0.4(1)
Carbonyl group									
C(6)	0.0359(7)	0.1920(4)	−0.1030(6)	7.1(4)	5.9(3)	4.3(3)	−0.7(3)	0.1(3)	0.5(2)
O(6)	0.0091(6)	0.1681(3)	−0.2407(4)	10.8(4)	10.1(3)	3.9(2)	−1.4(3)	−1.1(2)	−0.9(2)
Cyclopentadienyl ring									
C(1)	−0.1298(7)	0.3314(4)	0.2777(6)	6.7(4)	6.1(3)	6.1(3)	0.1(3)	2.0(3)	1.0(3)
H(1)	−0.132	0.401	0.298	*					
C(2)	−0.0541(7)	0.2643(4)	0.3820(6)	6.0(4)	8.6(4)	4.6(3)	−1.3(3)	0.7(3)	1.1(3)
H(2)	0.011	0.283	0.484	*					
C(3)	−0.0849(7)	0.1682(4)	0.3060(7)	5.5(3)	7.6(3)	6.6(3)	−0.7(3)	0.7(3)	3.1(3)
H(3)	−0.044	0.110	0.351	*					
C(4)	−0.1758(6)	0.1733(4)	0.1536(6)	5.5(4)	6.6(3)	6.5(3)	−1.7(2)	−0.4(2)	1.7(2)
H(4)	−0.216	0.116	0.080	*					
C(5)	−0.2048(6)	0.2747(4)	0.1367(6)	5.0(3)	7.3(3)	6.1(3)	−0.5(3)	−0.1(2)	2.6(3)
H(5)	−0.262	0.301	0.045	*					
Hexafluorobutyne ligand									
C(71)	−0.2534(9)	0.4539(5)	0.3331(8)	9.1(5)	5.9(3)	8.1(4)	−2.5(3)	0.4(3)	−0.6(3)
F(711)	0.2696(8)	0.4313(3)	0.4779(4)	28.2(7)	13.8(4)	5.5(2)	−10.1(4)	0.6(3)	−1.5(2)
F(712)	0.1542(7)	0.5302(3)	0.3286(7)	17.0(5)	9.1(3)	21.7(6)	2.1(3)	−4.8(4)	−7.3(3)
F(713)	0.3950(7)	0.4861(4)	0.3132(6)	14.5(5)	14.2(4)	12.9(4)	−9.3(4)	0.7(3)	−2.2(3)
C(7)	0.1992(6)	0.3692(3)	0.2033(6)	5.3(3)	4.6(2)	4.9(2)	−1.0(2)	0.2(2)	0.6(2)
C(8)	0.1962(6)	0.3458(3)	0.0460(5)	5.3(3)	4.6(2)	4.8(3)	−0.2(2)	0.8(2)	1.3(2)
C(81)	0.2579(8)	0.3874(5)	−0.0862(7)	7.7(4)	7.3(4)	6.6(4)	−0.9(4)	1.6(3)	3.0(3)
F(811)	0.2321(10)	0.4808(3)	−0.0799(7)	31.6(8)	9.6(3)	16.8(4)	4.0(4)	11.6(5)	8.5(3)
F(812)	0.2083(8)	0.3453(4)	−0.2300(5)	24.5(7)	22.3(5)	5.9(2)	−12.2(5)	1.1(3)	3.9(3)
F(813)	0.4156(7)	0.3745(4)	−0.0845(7)	11.1(4)	22.4(6)	17.7(5)	−0.5(4)	6.0(4)	10.4(5)
Pentafluorophenyl ligand									
C(9)	0.3373(6)	0.1225(3)	0.3687(5)	4.8(3)	4.4(2)	4.7(2)	0.6(2)	0.3(2)	0.9(2)
C(10)	0.4572(6)	0.1910(3)	0.4278(6)	4.2(3)	5.1(3)	7.1(3)	−0.1(2)	0.7(3)	1.9(2)
F(10)	0.5043(4)	0.2497(2)	0.3298(4)	6.2(2)	9.4(2)	10.2(2)	−1.6(2)	1.2(2)	4.3(2)
C(11)	0.5287(7)	0.2015(4)	0.5876(7)	4.3(3)	5.5(3)	8.4(4)	−0.6(3)	−1.0(3)	0.6(3)
F(11)	0.6461(5)	0.2681(3)	0.6394(5)	7.8(3)	9.2(3)	13.0(3)	−3.5(2)	−2.7(2)	2.0(2)
C(12)	0.4843(7)	0.1432(4)	0.6922(6)	6.7(4)	5.7(3)	5.4(3)	0.2(3)	−0.8(3)	0.6(2)
F(12)	0.5544(5)	0.1532(3)	0.8475(4)	11.5(3)	10.0(2)	7.2(2)	−1.0(2)	−4.1(2)	1.2(2)
C(13)	0.3660(7)	0.0749(3)	0.6392(6)	6.1(4)	5.2(3)	5.2(3)	0.4(3)	0.1(3)	1.6(2)
F(13)	0.3225(4)	0.0178(2)	0.7425(3)	10.2(3)	8.4(2)	6.4(2)	−1.1(2)	0.1(2)	3.5(2)
C(14)	0.2957(6)	0.0647(3)	0.4801(6)	5.2(3)	4.1(2)	5.6(3)	−0.2(2)	−0.2(2)	1.0(2)
F(14)	0.1832(4)	−0.0048(2)	0.4338(4)	8.0(2)	5.8(2)	8.0(2)	−2.3(2)	−1.4(2)	2.2(2)

* U_{iso} fixed at 6.33×10^{-2}. Anisotropic thermal parameters are in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

methods and constraints were used as for (I), and a weighting scheme: $1/w = x.y$, where $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta > b$, and $y = F/a$ if $F > a$, $y = 1$ if $F < a$ ($a = 70.0$, $b = 0.22$), gave convergence at R 0.050 (R' 0.057). The final electron-density difference synthesis showed no peaks >0.5 or <0.4 eÅ^{-3}. Final positional and thermal parameters are listed in Table 2.

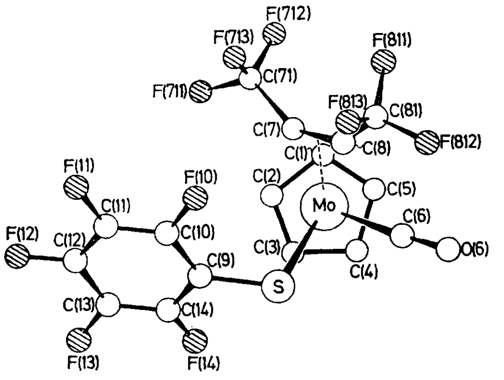


FIGURE 1 Molecular structure of (I) seen normal to the plane of the cyclopentadienyl ring

DISCUSSION

The molecular structures of (I) and (II) are illustrated in Figures 1 and 2 (which also show the crystallographic atom numbering system), and unit-cell contents in Figures 3 and 4. Bond distances and angles are in Table 3. Both molecules contain a molybdenum atom in approximately octahedral co-ordination, with three facial sites occupied by a (η^5-C_5H_5) ligand, one site by a (SC_6F_5) ligand, one by a π-bonded ($CF_3C{:}CCF_3$) ligand, and the sixth site by carbonyl in (I) or oxygen in (II). It is apparent, however, that whereas the axis of the acetylenic ligand C(7)–C(8) lies approximately parallel to the Mo–C–O direction in (I), this ligand has turned through 90° around the π-bond direction (dotted in the Figures) to become approximately parallel to the Mo–S bond in (II): a most interesting case of steric non-equivalence.

TABLE 2

Atomic positional (fractional co-ordinates) and thermal parameters ($\times 10^2$) for (II), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.387 35(2)	0.464 85(5)	0.420 92(4)	4.59(2)	5.72(3)	4.64(2)	0.46(3)	−0.24(3)	0.49(3)
O	0.4417(2)	0.5456(5)	0.3896(4)	5.5(3)	7.3(3)	8.0(3)	−1.0(3)	0.3(2)	1.1(3)
S	0.3827(1)	0.3015(2)	0.2996(1)	7.9(1)	8.1(1)	5.1(1)	0.4(1)	−1.1(1)	−0.7(1)
Cyclopentadienyl ring									
C(1)	0.3724(5)	0.4932(9)	0.5948(6)	14.1(9)	8.2(6)	4.7(4)	3.9(6)	−0.0(5)	−0.7(4)
H(1)	0.362	0.578	0.610	*					
C(2)	0.4250(3)	0.4508(10)	0.5861(6)	7.8(5)	10.0(6)	5.9(4)	−1.2(5)	−1.5(4)	0.2(5)
H(2)	0.456	0.499	0.603	*					
C(3)	0.4224(4)	0.3372(9)	0.5486(6)	9.6(7)	8.8(6)	5.4(4)	3.1(6)	0.2(4)	1.5(4)
H(3)	0.452	0.284	0.539	*					
C(4)	0.3704(5)	0.3022(9)	0.5392(6)	13.7(9)	7.0(5)	5.2(4)	−2.1(6)	0.7(5)	0.8(4)
H(4)	0.357	0.223	0.515	*					
C(5)	0.3390(3)	0.3949(11)	0.5672(6)	6.4(5)	13.2(8)	5.3(4)	−0.5(6)	1.7(4)	0.7(5)
H(5)	0.302	0.394	0.575	*					
Hexafluorobutyne ligand									
C(6)	0.2988(7)	0.6954(13)	0.4478(13)	13.7(11)	9.8(9)	15.3(12)	6.7(9)	−0.8(10)	1.0(9)
F(61)	0.2665(5)	0.6651(11)	0.5176(11)	26.4(13)	21.7(11)	29.7(14)	13.2(10)	18.1(12)	5.4(10)
F(62)	0.2718(6)	0.7581(11)	0.3906(8)	38.0(17)	24.6(11)	20.5(9)	25.0(13)	−6.1(10)	−0.7(8)
F(63)	0.3304(5)	0.7680(10)	0.4944(11)	21.2(10)	15.9(9)	32.7(16)	6.3(8)	−0.4(10)	−11.5(10)
C(7)	0.3259(3)	0.5903(8)	0.4016(7)	6.3(4)	8.0(5)	8.0(6)	2.7(4)	0.1(4)	1.7(5)
C(8)	0.3262(3)	0.5238(8)	0.3230(6)	5.9(4)	9.3(6)	6.0(4)	0.7(4)	−0.8(4)	2.0(5)
C(9)	0.2951(4)	0.5111(12)	0.2292(9)	7.0(6)	14.9(10)	9.4(8)	−0.2(7)	−3.1(6)	3.3(7)
F(91)	0.2695(5)	0.6086(11)	0.2047(8)	27.2(12)	24.7(11)	18.9(8)	12.4(10)	−14.2(8)	−0.2(8)
F(92)	0.3245(3)	0.4956(9)	0.1489(5)	15.2(6)	22.7(9)	8.7(4)	−1.1(6)	−4.0(4)	2.4(5)
F(93)	0.2641(4)	0.4222(11)	0.2287(7)	21.1(9)	35.2(15)	16.2(7)	−19.0(11)	−11.6(7)	10.7(8)
Pentafluorophenyl ligand									
C(10)	0.4325(4)	0.1930(7)	0.3313(5)	9.9(6)	5.5(4)	4.7(4)	0.4(4)	0.7(4)	−0.9(3)
C(11)	0.4870(4)	0.2216(7)	0.3266(6)	8.7(6)	6.1(5)	6.4(5)	1.2(4)	0.5(4)	−0.5(4)
F(11)	0.5026(2)	0.3328(4)	0.3010(4)	9.2(3)	7.7(3)	11.3(4)	0.3(3)	0.6(3)	−0.2(3)
C(12)	0.5258(5)	0.1331(11)	0.3445(7)	11.5(9)	10.1(8)	6.9(5)	3.8(7)	−0.5(6)	−2.5(6)
F(12)	0.5772(3)	0.1664(7)	0.3398(5)	10.9(5)	16.1(6)	13.2(5)	5.2(4)	−0.1(4)	−2.4(5)
C(13)	0.5113(7)	0.0205(12)	0.3711(8)	19.9(14)	7.7(8)	6.5(6)	6.8(9)	1.4(8)	0.0(5)
F(13)	0.5484(4)	−0.0635(7)	0.3941(5)	24.9(9)	13.3(5)	11.0(5)	12.2(6)	2.7(5)	0.6(4)
C(14)	0.4593(8)	−0.0126(10)	0.3761(8)	21.1(15)	5.7(6)	7.7(6)	1.6(9)	3.3(9)	0.1(5)
F(14)	0.4455(4)	−0.1256(6)	0.4032(6)	31.6(12)	6.3(4)	15.9(6)	1.4(5)	7.4(7)	0.9(4)
C(15)	0.4197(5)	0.0745(9)	0.3577(7)	13.7(9)	6.7(6)	7.4(6)	−1.5(6)	2.6(6)	−1.3(4)
F(15)	0.3687(3)	0.0420(6)	0.3637(5)	17.1(6)	8.5(4)	14.1(5)	−4.7(4)	3.6(5)	−1.5(4)

* See footnotes in Table 1

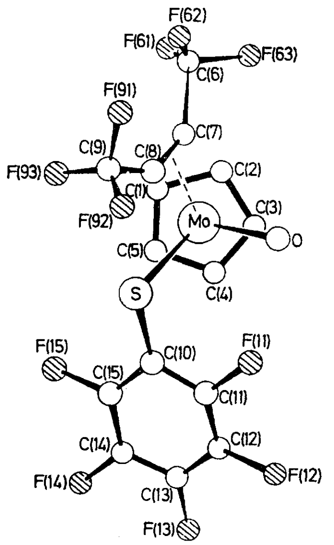


FIGURE 2 Molecular structure of (II) seen normal to the plane of the cyclopentadienyl ring

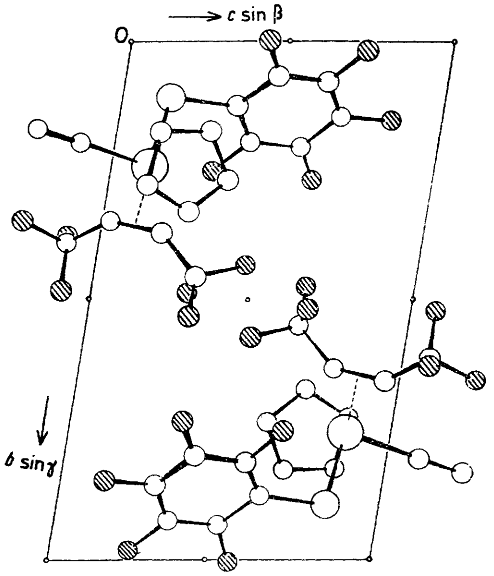


FIGURE 3 The contents of the triclinic unit cell of (I), looking towards the origin along *a*

In both structures the $CF_3{\cdot}C{:}C{\cdot}CF_3$ sequence is non-linear and, as expected, the CF_3 groups bend away from the metal but the C_4 skeleton remains approximately coplanar with the metal.

TABLE 3

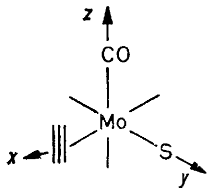
Bond lengths (Å) and angles (°)

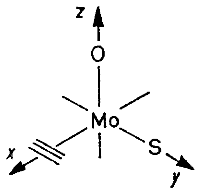
(*a*) Distances [comparable values for (I) and (II) are printed on the same line]

	(I)		(II)
Mo–S	2.366(1)	Mo–S	2.403(2)
Mo–C(6)	1.995(5)		
C(6)–O(6)	1.141(6)		
		Mo–O	1.678(5)
Mo–C(7)	2.017(5)	Mo–C(7)	2.082(8)
Mo–C(8)	2.051(5)	Mo–C(8)	2.109(8)
C(7)–C(8)	1.298(6)	C(7)–C(8)	1.267(12)
C(7)–C(71)	1.495(7)	C(7)–C(6)	1.468(18)
C(71)–F(711)	1.282(8)	C(6)–F(61)	1.270(22)
C(71)–F(712)	1.284(8)	C(6)–F(62)	1.226(21)
C(71)–F(713)	1.313(9)	C(6)–F(63)	1.281(21)
C(8)–C(81)	1.472(9)	C(8)–C(9)	1.473(14)
C(81)–F(811)	1.263(8)	C(9)–F(91)	1.286(17)
C(81)–F(812)	1.274(7)	C(9)–F(92)	1.305(14)
C(81)–F(813)	1.306(8)	C(9)–F(93)	1.246(17)
Mo–C(7,8)	1.922(4)	Mo–C(7,8)	1.980(8)
S–C(9)	1.770(4)	S–C(10)	1.776(9)
C(9)–C(10)	1.390(6)	C(10)–C(11)	1.406(13)
C(10)–C(11)	1.380(7)	C(11)–C(12)	1.393(15)
C(11)–C(12)	1.360(8)	C(12)–C(13)	1.331(18)
C(12)–C(13)	1.371(7)	C(13)–C(14)	1.357(27)
C(13)–C(14)	1.372(6)	C(14)–C(15)	1.399(20)
C(14)–C(9)	1.392(6)	C(15)–C(10)	1.380(12)
C(10)–F(10)	1.332(7)	C(11)–F(11)	1.321(9)
C(11)–F(11)	1.349(6)	C(12)–F(12)	1.345(14)
C(12)–F(12)	1.343(6)	C(13)–F(13)	1.345(18)
C(13)–F(13)	1.338(6)	C(14)–F(14)	1.332(13)
C(14)–F(14)	1.342(6)	C(15)–F(15)	1.332(15)
Mo–C(1)	2.305(6)	Mo–C(1)	2.349(8)
Mo–C(2)	2.381(5)	Mo–C(2)	2.384(8)
Mo–C(3)	2.412(6)	Mo–C(3)	2.360(9)
Mo–C(4)	2.332(6)	Mo–C(4)	2.406(9)
Mo–C(5)	2.281(5)	Mo–C(5)	2.408(8)

(*b*) Angles

S–Mo–C(6)	86.7(1)	S–Mo–O	105.5(2)
Mo–C(6)–O(6)	174.7(5)		
S–Mo–C(7)	107.1(1)	S–Mo–C(7)	111.8(2)
S–Mo–C(8)	105.5(1)	S–Mo–C(8)	77.4(2)
C(8)–Mo–C(6)	79.8(2)	C(8)–Mo–O	106.3(3)
C(7)–Mo–C(6)	116.9(2)	C(7)–Mo–O	103.1(3)
C(81)–C(8)–C(7)	136.6(5)	C(9)–C(8)–C(7)	137.7(9)
C(8)–C(7)–C(71)	137.8(5)	C(8)–C(7)–C(6)	142.5(10)
C(7)–C(71)–F(711)	113.6(5)	C(7)–C(6)–F(61)	113.3(12)
C(7)–C(71)–F(712)	111.0(5)	C(7)–C(6)–F(62)	115.9(14)
C(7)–C(71)–F(713)	112.3(5)	C(7)–C(6)–F(63)	113.3(13)
C(8)–C(81)–F(811)	114.1(5)	C(8)–C(9)–F(91)	113.5(11)
C(8)–C(81)–F(812)	115.0(6)	C(8)–C(9)–F(92)	113.3(9)
C(8)–C(81)–F(813)	112.5(5)	C(8)–C(9)–F(93)	114.3(10)
Mo–S–C(9)	105.7(1)	Mo–S–C(10)	107.7(2)
S–C(9)–C(10)	121.6(4)	S–C(10)–C(11)	121.9(6)
S–C(9)–C(14)	122.5(4)	S–C(10)–C(15)	121.4(8)





As has been discussed in the preceding paper, a simplistic view of the bonding readily explains this difference in orientation. In the oxo-compound (II) the Mo–O distance (1.68 Å) suggests [7] that this bond is best regarded as a triple bond, making the molecule an eighteen-electron species. If the oxygen, (SC_6F_5), and $(CF_3C_2CF_3)$ ligands are considered to occupy respectively the positive z, y, and x axes of the octahedral bonding system, the oxo-ligand can donate 2ε into the z oriented d^2sp^3 hybrid orbital on the Mo atom to form a σ-bond but will then require each of d_{xz} and d_{yz} to be singly occupied in order to form the two π-components of the triple bond. The two electrons left on the molybdenum will thus be forced into the d_{xy} orbital and would be able to give excellent back-donation to the acetylene ligand provided that this were oriented parallel to y. The π-MO's of the acetylene could then donate not only into one of the octahedral hybrids but also into d_{xz} (reinforcing the oxygen bonding).

In the carbonyl compound (I) the CO group on the z axis will be most strongly bound if the four electrons on the metal occupy d_{xz} and d_{yz} so as to give maximum back-donation. As this will leave d_{xy} empty, the acetylene will tend to orient itself parallel to z in order to donate into both an octahedral hybrid and into d_{xy}. Back-donation can occur through d_{xz} but will tend to weaken the M–CO bond.

Several other features of the bonding are important, although they are more difficult to account for quantitatively. In (I) the stretching frequency of the acetylenic bond (1 738 cm^{-1}) is lower than in (II) (1 836 cm^{-1}); consistently, the bond length in (I) is longer [1.298(6) *vs.* 1.267(12) Å]. The remaining geometry of the acetylene–metal moiety is, however, less clearly distinguished, because in the carbonyl compound the angles at the two acetylenic carbon atoms are equal (137°) but the two metal–carbon bond lengths appear to be different [2.017 and 2.051(5) Å], whereas in the oxo-compound the angles are different (138 and 142°) but the bond lengths the same [2.095(8) Å]. For both, the molybdenum is not exactly in the plane of the C_4 unit: in (I) the plane is $\|^1$ M–CO and tilts slightly away from M–S, whereas in (II) it is $\|^1$ M–S and tilts slightly towards M–O. The fluorine atoms of the trifluoromethyl groups, as frequently happens, show high thermal activity, and the mean C–C–F angle is larger than the ideal tetrahedral value [113.4° (I), 113.9° (II)].

In both compounds the SC_6F_5 ligand is planar and of the expected geometry, but the Mo–S bond length in (I) is shorter [2.366(1) Å] than in (II) [2.403(2) Å]. Finally, the cyclopentadienyl ring bears a different relationship to the unique ligand (CO or O), as seen in Figures 1 and 2: in (I) the site *trans* to acetylene is occupied by one side of the C_5 ring [atoms C(3) and C(4)] whereas in (II) a single atom [C(4)] is most nearly *trans* to the acetylene. Furthermore the C_5 ring is significantly nearer to the metal in (I) (mean Mo–C 2.34 Å) than in (II) (2.38 Å).

A possible interpretation of these results (which show that in the carbonyl compound the other ligands are all

[7] 'Molecular Structures and Dimensions,' vol. A1, International Union of Crystallography, Utrecht, 1972.

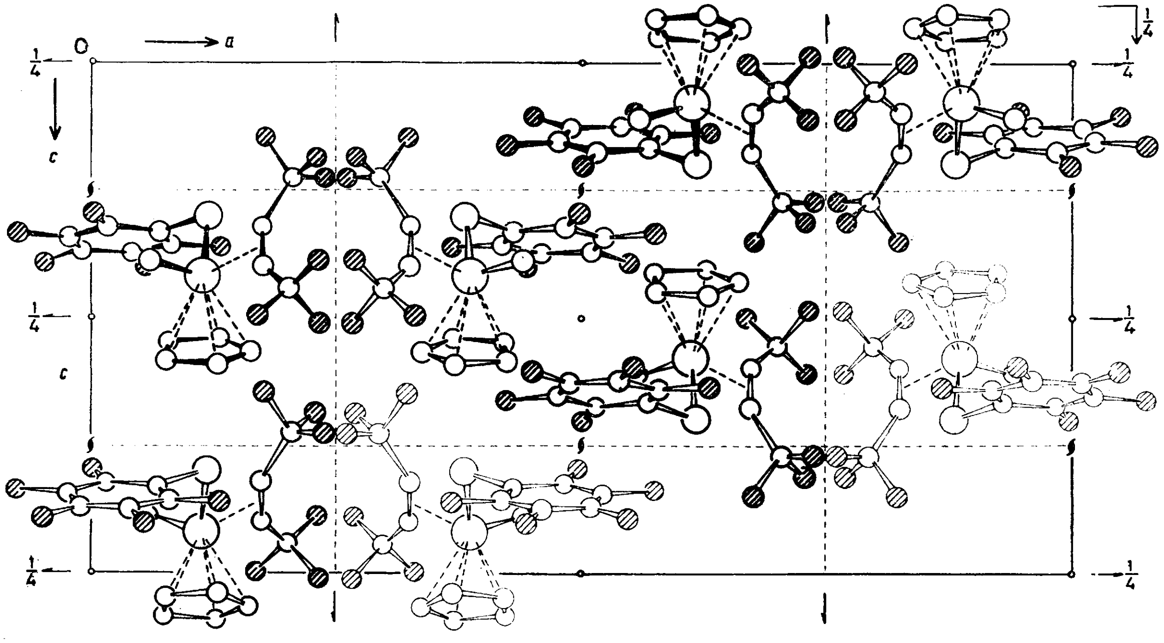


FIGURE 4 The contents of the orthorhombic unit cell of (*B*), looking towards the origin along *b*

more strongly bonded to the metal than they are in the oxo-compound) would be to regard the acetylene as a four-electron donor, thereby converting the carbonyl compound also into an eighteen-electron species. Little can be deduced from the metal–carbonyl or –oxygen bond lengths, as these are so variable in other molybdenum compounds which have been investigated.[8-15] The most nearly similar molecule of known structure is $[W(\eta^5\text{-}C_5H_5)(O)(PhC_2Ph)(Ph)]$.[16]

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