Synthesis and Reactivity of Dienyl–Metal Compounds. Part 30.[1] Alkylation of Thiolato Bridges: a Route to Stable Dialkyl Sulphide Bridged Dinuclear Molybdenum Complexes. Crystal Structure Determination of $[(\eta\text{-}C_5H_5)(CO)\text{-}Mo(\mu\text{-}SMe_2)_2Mo(PMe_3)(\eta\text{-}C_5H_5)][BF_4]_2$†

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$[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SMe)\}_2]$ is alkylated in two steps by $[Me_3O]BF_4$ to give the stable cations $[\{Mo(\eta\text{-}C_5H_5)(CO)\}_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)]^+$ and $[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SMe_2)\}_2]^{2+}$. In the latter one carbonyl ligand can be replaced by PMe_3 or $P(OMe)_3$. The *X*-ray structure of $[(\eta\text{-}C_5H_5)(CO)Mo(\mu\text{-}SMe_2)_2Mo(PMe_3)(\eta\text{-}C_5H_5)][BF_4]_2$ shows a slightly lengthened Mo–Mo double bond [2.693(1) Å] combined with a short Mo–S bond (*ca.* 2.34 Å).

Dialkyl sulphides have recently found increasing attention as ligands in metal complexes.[2] In contrast to the isoelectronic fragments PR_2^- and SiR_2^{2-} only a limited number of compounds containing SR_2 in a bridging co-ordination mode has been described.[3–12] Apart from the well investigated systems $[\{PtX_2(\mu\text{-}SR_2)\}_2]$ (X = Cl or Br, R = Me or Et)[3,4] and $[M_2X_6(SR_2)_3]$ (M = Nb or Ta, X = Cl or Br, $SR_2 = SMe_2$ or SC_4H_8),[5,6] most of the compounds prepared seem to be rather atypical products of fortuitous nature isolated commonly in low yields. It has been demonstrated only recently that the reaction of reactive tetrahydrofuran metal complexes with SR_2 in a 2:1 ratio is a preparative method for the synthesis of homo- and hetero-dinuclear dialkyl sulphide bridged metal carbonyls.[7] This reaction is however limited to metal carbonyl chemistry. Although terminal co-ordination of SR_2 is commonly affected by direct reaction of the ligand with a suitable metal complex, alkylation of terminal thiolato ligands has also been shown to be a useful preparative method.[2] Similarly, alkylation of thiolato bridges should form dinuclear dialkyl sulphide bridged compounds. We have started our investigations on this area with dinuclear molybdenum compounds because of their relevance to bioinorganic chemistry.[13]

Table 1. Spectroscopic data of the compounds (**1**), (**3**), (**4**), and (**5**)

Complex	$\nu(CO)/cm^{-1}$	^1H N.m.r. (δ/p.p.m.)	^{13}C N.m.r. (δ/p.p.m.)
(**1**)	[a,b]1 875, 1 850	[b,c]C_5H_5 5.32 (s) SMe 2.28 (s)	[c]C_5H_5 91.08 SMe 32.57 CO 251.84, 246.33
(**3**)	[a]1 994, 1 969	[d]C_5H_5 6.02 (s), 5.86 (s) SMe_2 3.53 (s), 3.49 (s) SMe 2.53 (s)	[d]C_5H_5 94.03, 93.64 SMe_2 43.99, 42.87 SMe 26.97 CO 240.74, 238.54
(**4**)	[e]1 958	[e]C_5H_5 6.26 (s) SMe_2 3.66 (s)	[e]C_5H_5 96.73 SMe_2 46.92 CO 227.50
(**5a**)[f]	[e]1 927	[e]C_5H_5 6.05 (s), 5.56 (d)[g] SMe_2 3.63 (s), 3.56 (s) PMe_3 1.32 (d)[h]	[e]C_5H_5 94.58, 93.57 SMe_2 48.86, 46.08 PMe_3 25.19[i] CO 227.07[j]
(**5b**)[k]	[e]1 932	[e]C_5H_5 6.00 (s), 5.67 (d)[l] SMe_2 3.70 (s), 3.60 (s) $P(OMe)_3$ 3.53 (s)	[e]C_5H_5 95.22, 93.50 SMe_2 48.48, 46.13 $P(OMe)_3$ 55.17[m] CO 228.01[j]

[a] In CH_2Cl_2. [b] From F. Y. Petillon, J. L. Le Quere, J. E. Guerchais, and D. W. A. Sharp, *J. Organomet. Chem.*, 1980, **204**, 207. [c] In $CDCl_3$. [d] In $[^2H_6]$acetone. [e] In $[^2H_3]$nitromethane. [f] ^{31}P N.m.r.: 14.59 p.p.m. [g] ^3J(P–H) 1.9 Hz. [h] ^2J(P–H) 9.1 Hz. [i] ^1J(P–C) 35.1 Hz. [j] J(P–C) 5 Hz. [k] ^{31}P N.m.r.: 181.86 p.p.m. [l] ^2J(P–H) 1.8 Hz. [m] ^2J(P–C) 8.3 Hz.

Results and Discussion

The complexes $[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SMe)\}_2]$ (**1**) and $[\{Mo(\eta\text{-}C_5H_5)(CO)_2(\mu\text{-}SMe)\}_2]$ (**2**) were chosen as starting materials. Complex (**1**), easily prepared from $[\{Mo(\eta\text{-}C_5H_5)(CO)_2\}_2]$[14] and Me_2S_2, reacts readily with $[Me_3O]BF_4$ in dichloromethane (Scheme). From the reaction mixture the brown dimethyl sulphide complex $[\{Mo(\eta\text{-}C_5H_5)(CO)\}_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)]BF_4$ (**3**) is isolated in high yield. Although (**3**) may be stored at −20 °C for some months it decomposes in solution at room temperature over the course of 10 h.

In $[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SBu^t)\}_2]$[15] a planar Mo_2S_2 ring containing a Mo–Mo double bond has been proved by *X*-ray analysis. The butyl substituents adopt a mutual *syn* orientation while the pairs of $\eta\text{-}C_5H_5$ and CO are *trans* with respect to the Mo_2S_2 plane. According to this structure, two resonances are observed for the $\eta\text{-}C_5H_5$ ligands in the ^1H n.m.r. spectrum. The ^1H n.m.r. spectrum of (**1**) (Table 1) shows only one $\eta\text{-}C_5H_5$ signal while two resonances are obtained in the ^{13}C n.m.r. spectrum for the carbonyl groups. This is consistent with a near-linear $Mo_2(\eta\text{-}C_5H_5)_2$ arrangement, the orientation of the CO groups being *trans* with respect to the planar Mo_2S_2 ring. Apparently, alkylation at one sulphur atom results in a change in the structure towards that mentioned for $[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SBu^t)\}_2]$, two resonances for the $\eta\text{-}C_5H_5$ ligands now being present in the n.m.r. As expected,[3] alkylation of the thiolato group causes a significant downfield shift for the methyl substituents both in the ^1H and ^{13}C n.m.r. The decrease in π bonding between molybdenum and its exocyclic ligands is demonstrated by the downfield shift for the $\eta\text{-}C_5H_5$ ligands paralleled by an upfield shift for the CO groups in the ^{13}C n.m.r.

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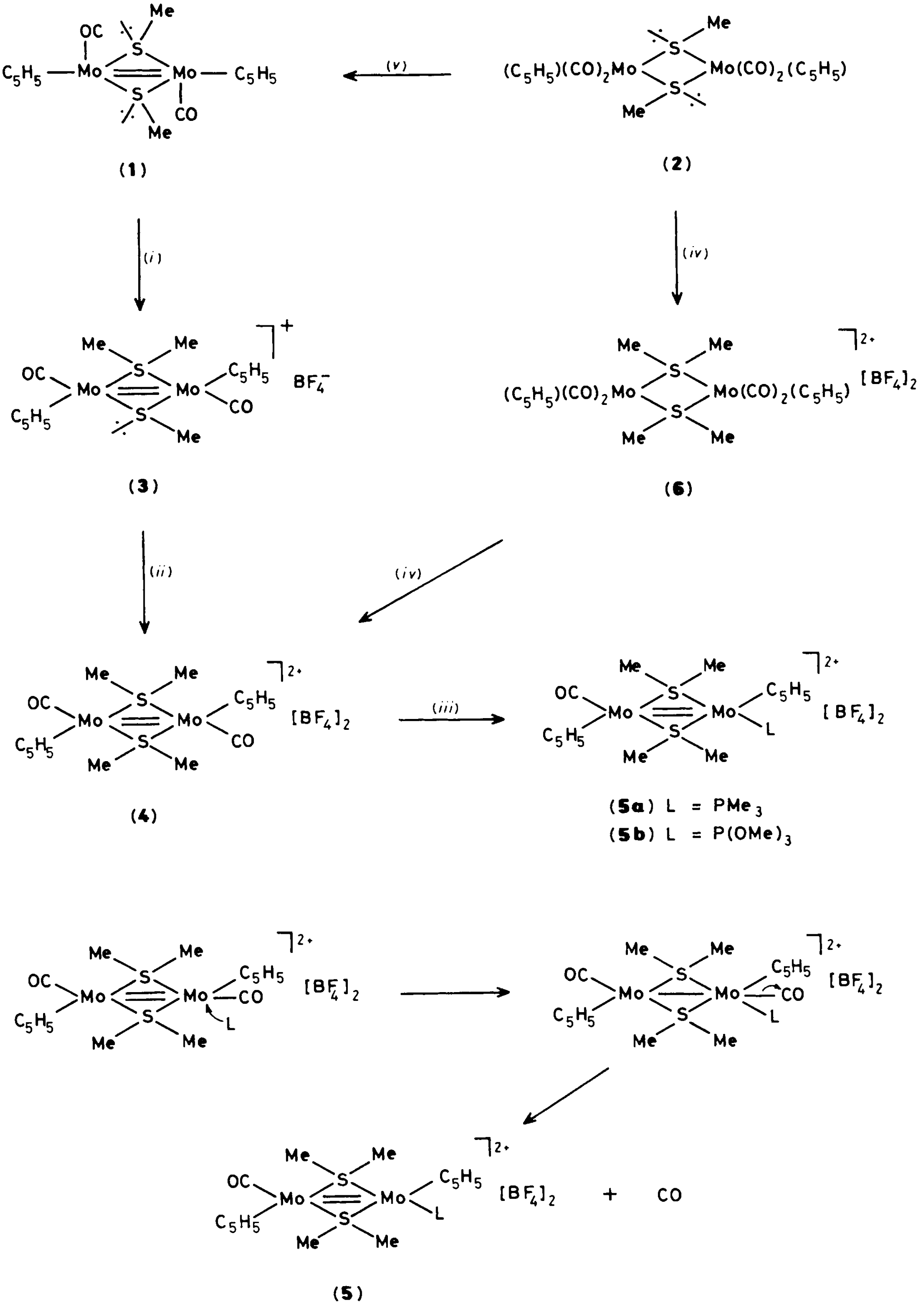
† 1-Carbonyl-1,2-bis(η-cyclopentadienyl)-di-μ-(dimethyl sulphide)-2-(trimethylphosphine)dimolybdenum(II) bis(tetrafluoroborate) (*Mo=Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



Scheme. (*i*) $[Me_3O]BF_4$ in CH_2Cl_2 at r.t. (3 h); (*ii*) $[Me_3O]BF_4$ in CH_2Cl_2 at r.t. (overnight); (*iii*) PR_3 (R = Me or OMe) in $MeNO_2$ at r.t. (5 min); (*iv*) $[Me_3O]BF_4$ in CH_2Cl_2 at −20 °C (5 min); (*v*) boiling n-heptane (5 h)

Commonly, inversion about the sulphur atoms of bridging thiolates occurs rapidly on the n.m.r. time-scale at room temperature.[16] In (3) the SMe_2 ligand shows two resonances, and no coalescence could be detected in nitromethane up to 80 °C. The high inversion barrier may be a consequence of both the rigid four-membered ring structure and the Mo–Mo double bond.

Reaction of (3) with a further equivalent of $[Me_3O]BF_4$ in dichloromethane causes the precipitation of the dicationic complex $[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SMe_2)\}_2][BF_4]_2$ (4) which may be stored indefinitely under argon and does not decompose in nitromethane in the course of one week. The equivalence of the methyl substituents in the n.m.r. spectra (Table 1) demonstrates the *anti* positions of the $\eta\text{-}C_5H_5$ and CO pairs.

Compared with the n.m.r. data of (**3**) the dicationic nature of (**4**) causes an additional downfield shift for the η-C_5H_5 ligands as well as an upfield shift for CO.

Formally, the metal–metal bond is a consequence of the unsaturated nature of the metal atoms. The triple bonded [{Mo(η-C_5H_5)$(CO)_2$}$_2$], used as a starting material for the preparation of (**1**), quickly adds carbon monoxide to give [{Mo(η-C_5H_5)$(CO)_3$}$_2$].[14,17] On the other hand [{Mo(η-C_5H_5)(CO)(μ-SBu^t)}$_2$] is said to be inert,[15] and the presence of bridging ligands in addition to the Mo–Mo double bond prevents addition of CO in (**3**) and (**4**) also.

To prepare the dicationic monocarbonyl complex [(η-C_5H_5)(CO)Mo(μ-SMe_2)$_2$MoL(η-C_5H_5)] (**5**) [L = PMe_3 or $P(OMe)_3$] we tried to alkylate [{Mo(η-C_5H_5)$(CO)_2$(μ-SMe)}$_2$] (**2**). In fact, rapid CO evolution occurs on addition of [Me_3O]BF_4 to a dichloromethane solution of (**2**) even at −20 °C, (**4**) being the only isolable product. Under these conditions, no conversion of (**2**) into the dicarbonyl complex (**1**) takes place. Therefore we suggest [{Mo(η-C_5H_5)$(CO)_2$(μ-SMe_2)$_2$}][BF_4]$_2$ (**6**) or its monoalkylated precursor to be an intermediate which stabilizes by subsequent elimination of CO and formation of the Mo–Mo double bond. In contrast to CO, phosphorus ligands PR_3 (R = Me or OMe) do react with complex (**4**) at ambient temperature, but instead of addition substitution of one carbonyl ligand occurs even in the absence of light. The resulting dications (**5a**) (PR_3 = PMe_3) and (**5b**) [PR_3 = $P(OMe)_3$] do not differ markedly from the parent compound (**4**) in stability and spectroscopic data. In particular, no change in the ^{13}C n.m.r. carbonyl shift is observed. Surprisingly, no further CO elimination proceeds on reacting (**5**) with additional phosphorus ligands under irradiation; refluxing a 1,2-dichloroethane solution of (**5**) and PR_3 leads to C_5H_5–Mo bond fission. Therefore an addition–elimination mechanism for the ligand substitution is proposed as shown in the Scheme.

Table 2. Atomic co-ordinates (× 10^4) for (**5a**)

Atom	*x*	*y*	*z*
Mo(1)	3 493(1)	0	−1 049(1)
Mo(2)	1 285(1)	1 214(1)	−2 233(1)
S(1)	2 211(1)	692(1)	184(1)
S(2)	2 356(1)	361(1)	−3 535(1)
P(1)	−1 018(1)	301(1)	−3 119(2)
O(1)	5 500(5)	1 678(3)	−764(5)
C(1)	4 711(6)	1 092(3)	−859(6)
C(2)	1 349(6)	−45(5)	1 056(6)
C(3)	3 155(7)	1 459(4)	1 670(6)
C(4)	3 426(6)	926(4)	−4 392(6)
C(5)	1 456(6)	−496(4)	−4 921(6)
C(6)	−859(7)	−022(4)	−2 696(8)
C(7)	−2 108(7)	293(4)	−5 094(6)
C(8)	−2 355(6)	667(4)	−2 427(7)
C(9)	3 653(4)	−1 527(3)	−273(5)
C(10)	4 135*	−1 464*	−1 423*
C(11)	5 417*	−908*	−934*
C(12)	5 727*	−627*	518*
C(13)	4 637*	−1 010*	927*
C(14)	1 880(3)	2 632(3)	−2 785(4)
C(15)	1 597*	2 688*	−1 508*
C(16)	83*	2 500*	−1 910*
C(17)	−570*	2 329*	−3 436*
C(18)	541*	2 411*	−3 976*
B(1)	4 791(7)	−1 770(4)	4 755(8)
B(2)	−899(8)	1 619(5)	−7 961(8)
F(1)	5 144(6)	−1 143(4)	5 873(6)
F(2)	5 982(4)	−1 892(3)	4 387(4)
F(3)	4 377(5)	−2 571(3)	5 208(6)
F(4)	3 605(6)	−1 465(5)	3 573(6)
F(5)	−891(5)	2 073(3)	−9 190(4)
F(6)	−1 662(4)	2 130(3)	−7 348(4)
F(7)	−1 513(5)	761(3)	−8 391(6)
F(8)	546(4)	1 515(3)	−6 988(4)

* Rigid group refinement.

Although bonding properties in dinuclear metal complexes containing metal–metal bonds should be discussed with care on the basis of bond lengths and angles (see *e.g.* ref. 18), we have undertaken an *X*-ray analysis of [(η-C_5H_5)(CO)Mo(μ-SMe_2)$_2$Mo(PMe_3)(η-C_5H_5)][BF_4]$_2$ (**5a**) to obtain information on the unexpected stability of the dimethyl sulphide bridged complexes described above. Atomic co-ordinates are given in Table 2 and selected bond lengths and angles in Table 3. The numbering system for the non-hydrogen atoms is shown in the Figure.

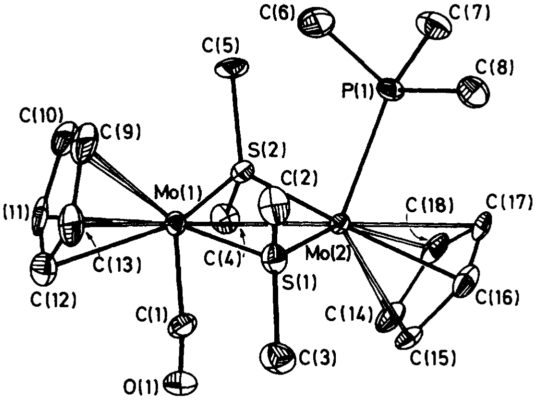


Figure. The structure of the cation of [(η-C_5H_5)(CO)Mo(μ-SMe_2)$_2$Mo(PMe_3)(η-C_5H_5)][BF_4]$_2$ (**5a**)

Table 3. Selected bond lengths (Å) and angles (°) for (**5a**); Cp(1) and Cp(2) are the geometrical midpoints of C(9)—C(13) and C(14)—C(18) respectively

Mo(1)–Mo(2)	2.693(1)	Mo(1)–S(1)–Mo(2)	70.3(1)	Mo(1)–C(1)–O(1)	174.7(5)
Mo(1)–S(1)	2.335(2)	Mo(1)–S(2)–Mo(2)	70.1(1)	C(2)–S(1)–C(3)	99.1(3)
Mo(1)–S(2)	2.341(1)	S(1)–Mo(1)–S(2)	109.5(1)	C(4)–S(2)–C(5)	98.9(3)
Mo(1)–C(1)	2.962(5)	S(1)–Mo(2)–S(2)	109.0(1)	S(1)–Mo(2)–P(1)	96.6(1)
Mo(2)–S(1)	2.342(1)	Mo(1)–Mo(2)–S(1)	54.7(1)	S(2)–Mo(2)–P(1)	94.6(1)
Mo(2)–S(2)	2.348(1)	Mo(1)–Mo(2)–S(2)	54.8(1)	S(1)–Mo(2)–Cp(2)	121.3
Mo(2)–P(1)	2.483(1)	Mo(2)–Mo(1)–S(1)	55.0(1)	S(2)–Mo(2)–Cp(2)	121.3
S(1)–C(2)	1.803(7)	Mo(2)–Mo(1)–S(2)	55.1(1)	S(1)–Mo(1)–C(1)	92.8(2)
S(1)–C(3)	1.800(6)	Mo(1)–Mo(2)–Cp(2)	147.2	S(2)–Mo(1)–C(1)	86.3(1)
S(2)–C(4)	1.811(7)	Mo(1)–Mo(2)–P(1)	106.0(1)	S(1)–Mo(1)–Cp(1)	120.6
S(2)–C(5)	1.808(5)	Cp(2)–Mo(2)–P(1)	106.8	S(2)–Mo(1)–Cp(1)	124.8
O(1)–C(1)	1.138(7)	Mo(2)–Mo(1)–C(1)	82.8(1)	Mo(1)Mo(2)S(1)–Mo(1)Mo(2)S(2)	9.1
Mo(1)–Cp(1)	1.985	Mo(2)–Mo(1)–Cp(1)	165.7	Cp(1)–Mo(1)–Mo(2)–Cp(2)	170.9
Mo(2)–Cp(2)	1.979	Cp(1)–Mo(1)–C(1)	111.6	P(1)–Mo(2)–Mo(1)–C(1)	174.7
S(1) · · · S(2)	3.819				

The four-membered Mo_2S_2 ring is slightly puckered [S(1)Mo(1)S(2)Mo(2) 7.9°] which contrasts with the planarity of $[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SBu^t)\}_2]$.[15] This may be a consequence of the unsymmetrical substitution of the molybdenum atoms as well as the Cp(1)Mo(1)Mo(2)Cp(2) dihedral angle of 170.9°. The bulky PMe_3 ligand apparently causes deviation of the Cp(2)Mo(2)Mo(1) angle (147.2°) from a near-linear $Mo_2(\eta\text{-}C_5H_5)_2$ arrangement [Cp(1)Mo(1)Mo(2) 165.7°]. The calculated Mo–S single bond length is 2.45 Å.[19] The distances observed in (**5a**) are *ca.* 0.1 Å shorter (mean 2.341 Å) but are clearly in the range observed for Mo–S single bonds (*ca.* 2.23—2.55 Å[20–26]). These bond lengths are influenced by several parameters such as molybdenum and sulphur co-ordination numbers as well as the geometry of the Mo_2S_2 core.

π Bonding can shorten the Mo–S bond down to the *ca.* 2.10 Å observed for a double bond.[27] Sulphur acceptor properties increase on bonding of the sulphur lone pair,[28] and both SR_3^+ [29] and SO_2 [30] ligands have been shown to have π-acceptor properties in dinuclear platinum complexes.[3]

The Mo–Mo distance in (**5a**) is 2.693(1) Å which is *ca.* 0.1 Å longer than commonly observed for Mo–Mo double bonds.[15,31] This may be a consequence of bonding interactions between filled Mo–Mo bonding molecular orbitals and sulphur *d* orbitals, but the Mo–Mo bond length is also significantly controlled by the Mo–S–Mo bond angle (*ca.* 70.1°) and other parts of the Mo_2S_2 geometry to obtain maximum stability.

With regard to the Mo–S bonding the structure of (**5a**) is paralleled by those of $[\{Mo(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}SC_4H_8)]$[9] [Mo–S 2.351(2) Å] and $[Mo(SH)L]^{2+}$(L = 1,5,9,13-tetrathiacyclohexadecane)[11] [Mo–S 2.320(1) and 2.380(1) Å] and the geometry observed here may be typical for stable dialkyl sulphide bridged dinuclear molybdenum complexes.

Experimental

The complexes $[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SMe)\}_2]$[32] (**1**) and $[\{Mo(\eta\text{-}C_5H_5)(CO)_2(\mu\text{-}SMe)\}_2]$[33] (**2**) were prepared according to published procedures. Reactions were routinely carried out under argon in purified solvents.

$[\{Mo(\eta\text{-}C_5H_5)(CO)\}_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)]BF_4$ (**3**).—$[Me_3O]BF_4$ (0.15 g, 2 mmol) was added to (**1**) (0.94 g, 2 mmol) in dichloromethane (40 cm^3). After stirring for 3 h the complex was precipitated on addition of diethyl ether (80 cm^3). Yield after recrystallisation from dichloromethane–diethyl ether 0.87 g (76%) as a brown solid (Found: C, 30.65; H, 3.40; Mo, 34.6. $C_{15}H_{19}BF_4Mo_2O_2S_2$ requires C, 31.15; H, 3.30; Mo, 33.20%).

$[\{Mo(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SMe_2)\}_2][BF_4]_2$ (**4**).—$[Me_3O]BF_4$ (0.15 g, 2 mmol) was added to (**3**) (1.16 g, 2 mmol) in dichloromethane (40 cm^3). After stirring overnight the solid was filtered off. Yield after recrystallisation from nitromethane–diethyl ether 0.93 g (69%). Starting from (**1**) and two equivalents of $[Me_3O]BF_4$ in dichloromethane (**4**) was prepared in 76% yield as a green solid (Found: C, 27.75; H, 3.10; Mo, 28.5. $C_{16}H_{22}B_2F_8Mo_2O_2S_2$ requires C, 28.10; H, 3.25; Mo, 28.05%).

$[(\eta\text{-}C_5H_5)(CO)Mo(\mu\text{-}SMe_2)_2Mo(PMe_3)(\eta\text{-}C_5H_5)][BF_4]_2$ (**5a**).—PMe_3 (0.046 g, 0.6 mmol) was added to (**4**) (0.34 g, 0.5 mmol) in nitromethane (5 cm^3). After stirring for 5 min the solution was filtered. The solid formed after addition of diethyl ether (20 cm^3) was collected and recrystallised from nitromethane–diethyl ether. Yield: 0.33 g (91%) as a green solid (Found: C, 29.20; H, 4.10; Mo, 26.9. $C_{18}H_{31}B_2F_8Mo_2OPS_2$ requires C, 29.55; H, 4.30; Mo, 26.20%).

$[(\eta\text{-}C_5H_5)(CO)Mo(\mu\text{-}SMe_2)_2Mo\{P(OMe)_3\}(\eta\text{-}C_5H_5)][BF_4]_2$ (**5b**).—This compound was prepared by the method described for (**5a**) using $P(OMe)_3$ (0.074 g, 0.6 mmol) instead of PMe_3. Yield: 0.34 g, (88%) as a green solid (Found: C, 27.6; H, 3.85; Mo, 25.10. $C_{18}H_{31}B_2F_8Mo_2O_4PS_2$ requires C, 27.70; H, 4.00; Mo, 24.60%).

Structure Determination of (**5a**).—*Crystal data.* $C_{18}H_{31}B_2F_8Mo_2OPS_2$, $M = 723.8$, monoclinic, $T = 115$ K, $a = 9.953(3)$, $b = 14.556(5)$, $c = 10.022(3)$ Å, $\beta = 113.94(2)°$, $U = 1\,327.1(7)$ Å^3, space group $P2_1$, $D_c = 1.743$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 11.98$ cm^{-1}, 5 432 unique intensities, 5 102 observed [$F_o \geqslant 3.5\sigma(F)$].

The structure was solved by Patterson methods and successive Fourier maps. Structure refinement was with SHELXTL[34] applying rigid groups to the C_5H_5 rings and to methyl groups. In the final model $R = 0.035$, $R' = 0.036$, $w^{-1} = \sigma^2(F) + 0.0008\,F$, and maximum residual electron density = 1.39 e Å^{-3}. The correct chirality was established by a parallel refinement which gave $R = 0.039$, $R' = 0.049$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, remaining bond lengths and angles.

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