Reactions of Co-ordinated Ligands. Part 32.[1] The Reaction of Sulphur Nucleophiles with Cationic Molybdenum Alkyne Complexes: Alkyne Rotation and the Molecular Structures of the Complexes [Mo(SC6H4NO2-p){P(OMe)3}(η2-MeC2Me)(η-C5H5)] and [Mo(SC6H4SPh-o)(CO)(η2-MeC2Me)(η-C5H5)] †

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Treatment of [Mo{P(OMe)3}2(η2-MeC2Me)(η-C5H5)][BF4] with NaSR (R = Me, p-NH2C6H4, p-MeOC6H4, p-MeC6H4, C6H5, or p-NO2C6H4) leads to displacement of P(OMe)3 and formation of [Mo(SR){P(OMe)3}(η2-MeC2Me)(η-C5H5)]. Similar reactions afforded [Mo(SePh){P(OMe)3}-(η2-MeC2Me)(η-C5H5)] and [Mo(SMe){P(OMe)3}(η2-ButC2H)(η-C5H5)]. Barriers to rotation of the but-2-yne ligand present in these complexes are related to electronic effects of the substituents on the thiolate ligand. The molecular structure of [Mo(SC6H4NO2-p){P(OMe)3}(η2-MeC2Me)-(η-C5H5)] has been established by single-crystal X-ray crystallography. Crystals are monoclinic, space group $P2_1/n$ with a = 8.968(3), b = 20.104(9), c = 11.452(5) Å, β = 95.77(3), and Z = 4. Using 3 601 reflections measured on a four-circle diffractometer at 200 K, the structure has been refined to R 0.028, R' 0.032. The molecule adopts the familiar three-legged piano stool geometry, in which the but-2-yne ligand is orientated such that the central C−C bond lies approximately parallel to the Mo−P vector. In contrast, [Mo(CO)(η2-MeC2Me)2(η-C5H5)][BF4] reacts with NaSMe to give the complexes [Mo(SMe)(CO)(η2-MeC2Me)(η-C5H5)] and [Mo2(CO)4(μ-MeC2Me)(η-C5H5)2], whereas the corresponding reaction with [Mo(NCMe)(η2-MeC2Me)2(η-C5H5)][BF4] affords [Mo(SMe)-(η2-MeC2Me)(η-C5H5)]. Reaction of sodium dimethyldithiocarbamate with [Mo(NCMe)(R1C2R2)2-(η-C5H5)][BF4] (R1 = R2 = Me or R1 = But, R2 = H) gives the monoalkyne complexes [Mo(S2C-NMe2)(η2-R1C2R2)(η-C5H5)]. In contrast the anion [SC6H4SPh-o]⁻ affords a separable mixture of [Mo(SC6H4SPh-o)(η2-R1C2R2)2(η-C5H5)] and [Mo(SC6H4SPh-o)(η2-R1C2R2)(η-C5H5)]. Reaction of the S,S'-bidentate species with carbon monoxide gives [Mo(SC6H4SPh-o)(CO)(η2-MeC2Me)-(η-C5H5)], which was structurally identified by X-ray crystallography. Crystals are orthorhombic, space group $P2_12_12_1$ (no. 19) with Z = 4 in a unit cell of dimensions a = 9.852(3), b = 11.486(4), and c = 18.476(6) Å. From 1 714 independent intensities measured at 292 K the structure has been refined to R 0.059, R' 0.041. The molecule adopts a piano stool geometry with the but-2-yne lying parallel to the Mo−CO vector. The dithioaryl ligand is monodentate.

We have previously described a study of the reaction of tetra-hydroborate anions with the cationic alkyne complexes [Mo{P-(OMe)3}2(η2-RC2R')(η-C5H5)][BF4] [2,3] (R = R' = Me or Ph; R = But, R' = H) and [Mo(CO)(η2-MeC2Me)2(η-C5H5)]-[BF4],[4] and have discussed how nucleophilic attack can, in principle, occur either at carbon or at the metal centre. With a view to understanding more fully the factors controlling these competing reaction pathways we have examined related reactions with 'soft' sulphur nucleophiles.

Results and Discussion

A suspension of NaSMe and [Mo{P(OMe)3}2(η2-MeC2Me)-(η-C5H5)][BF4][5] in tetrahydrofuran (thf) reacted instantane-ously at room temperature to give a deep blue solution that afforded, on work-up, blue-black crystals of (1) (Table 1). Elemental analysis and ¹H n.m.r. spectroscopy indicated that the reaction had resulted in the replacement of one trimethyl phosphite ligand by SMe⁻. Thus, the ¹H n.m.r. spectrum

showed a doublet [³J(HP) 11.5 Hz] due to the P(OMe)3 ligand, which integrated 9 : 5 to the η-C5H5 signal. The methyl protons of the co-ordinated but-2-yne resonated as a 6 H singlet at 2.77 p.p.m. and those of the SMe group as a doublet [⁴J(HP) 1 Hz]. Although the ¹H n.m.r. signal due to the but-2-yne remained sharp at −90 °C in toluene, the ¹³C-{¹H} spectrum revealed the alkyne contact carbons as broad re-sonances and cooling to −50 °C transformed the broad signal into two equal resonances either side of the original at 195.6 [²J(CP) 4.4 Hz] and 185.0 p.p.m. [²J(CP) 38.1 Hz]. This sug-gested the illustrated structure for (1), in which the alkyne functions as a four-electron donor, and rotates at room temperature about an axis through the metal and the mid-point of the C−C bond.

Similar reactions between NaSMe and the cations [Mo{P-(OMe)3}2(η2-ButC2H)(η-C5H5)][BF4] [5] and [Mo{P(OMe)3}2-(η2-PhC2Ph)(η-C5H5)][BF4] [5] afforded respectively the crystal-line complexes (2) and (3), which showed the expected spectro-scopic features (Tables 1 and 2). As in the case of (1) the ³¹P coupling to the contact alkyne carbons is greatest for the high-field ¹³C resonance suggesting that this carbon lies closer to the ³¹P nucleus of the phosphite ligand.

In order to explore whether molecules of this type dimerise in solution to form species such as [Mo2(μ-SMe)2{P(OMe)3}2-(η2-MeC2Me)2(η-C5H5)2], the selenate analogue [Mo(SePh)-{P(OMe)3}(η2-MeC2Me)(η-C5H5)] (4) was also synthesised, and the variable-temperature ⁷⁷Se n.m.r. spectrum recorded.

Table 1. Analytical [a] and mass-spectroscopic data for monoalkyne complexes

Complex	Colour	Yield (%)	C (%)	H (%)	M [a,b]
(1) [Mo(SMe){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)]	Blue	70	40.5 (40.4)	6.4 (6.0)	386 (386)
(2) [Mo(SMe){P(OMe)₃}(η²-BuᵗC₂H)(η-C₅H₅)]	Blue	85	43.9 (43.5)	7.1 (6.6)	414 (414)
(3) [Mo(SMe){P(OMe)₃}(η²-PhC₂Ph)(η-C₅H₅)]	Green	80	53.7 (54.1)	5.2 (5.3)	510 (510)
(4) [Mo(SePh){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)]	Green	44	43.6 (43.7)	5.1 (5.1)	495 (495)
(5) [Mo(SC₆H₄NH₂-p){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)]	Green	80			463 (463)
(6) [Mo(SC₆H₄OMe-p){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)]	Green	80	48.2 (47.7)	6.0 (5.7)	478 (478)
(7) [Mo(SC₆H₄Me-p){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)]	Green	83	49.7 (49.4)	6.1 (5.8)	462 (462)
(8) [Mo(SPh){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)]	Blue	86	48.2 (48.2)	5.6 (5.6)	448 (448)
(9) [Mo(SC₆H₄NO₂-p){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)] [c]	Green	78	44.2 (43.8)	5.0 (4.9)	
(11) [Mo(SMe)(CO)(η²-MeC₂Me)(η-C₅H₅)] [d]	Purple	17	45.8 (45.5)	5.0 (5.0)	290 (290)
(13) [Mo(S₂CNMe₂)(η²-MeC₂Me)(η-C₅H₅)]	Green	47	42.7 (43.0)	5.7 (5.1)	
(14) [Mo(S₂CNMe₂)(η²-BuᵗC₂H)(η-C₅H₅)]	Green	50	46.1 (46.3)	5.9 (5.8)	
(17) [Mo(SC₆H₄SPh-o)(η²-MeC₂Me)(η-C₅H₅)]	Green	23	58.2 (58.3)	4.8 (4.6)	
(18) [Mo(SC₆H₄SPh-o)(η²-BuᵗC₂H)(η-C₅H₅)]	Green	26	61.5 (61.7)	5.6 (5.4)	
(19) [Mo(SC₆H₄SPh-o)(CO)(η²-MeC₂Me)(η-C₅H₅)] [e]	Red	76	58.0 (57.4)	4.9 (4.4)	

[a] Calculated values are given in parentheses. [b] Parent ion ⁹⁶Mo. [c] N 2.7 (2.8)%. [d] v_{CO}(hexane) 1 936s and 1 920 cm⁻¹. [e] v_{CO}(hexane) 1 925s cm⁻¹.
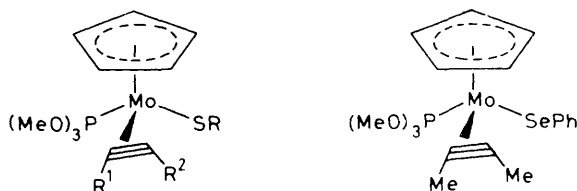
(1; R = R¹ = R² = Me)
(2; R = Me, R¹ = H, R² = Buᵗ)
(3; R = Me, R¹ = R² = Ph)
(5; R = p-NH₂C₆H₄, R¹ = R² = Me)
(6; R = p-MeOC₆H₄, R¹ = R² = Me)
(7; R = p-MeC₆H₄, R¹ = R² = Me)
(8; R = C₆H₅, R¹ = R² = Me)
(9; R = p-NO₂C₆H₄, R¹ = R² = Me)

(4)

Figure 1. The molecular structure of [Mo(SC₆H₄NO₂-p){P(OMe)₃}-(η²-MeC₂Me)(η-C₅H₅)] (9) showing the crystallographic numbering scheme

This showed a single resonance [²J(SeP) 36.6 Hz] centred at 215.7 p.p.m., a chemical shift typical of that observed [6] with mononuclear M(SeR) systems. The spectrum was temperature invariant suggesting that dimerisation does not occur in solution.

In view of recent interest [5,7–9] in the conformational preferences and barriers to rotation of co-ordinated alkynes a series of para-substituted phenyl thiolates were also reacted with [Mo{P(OMe)₃}₂(η²-MeC₂Me)(η-C₅H₅)][BF₄], affording the neutral complexes (5)—(9) which were characterised by elemental analysis and ¹H, ¹³C, and ³¹P n.m.r. spectroscopy (Tables 1 and 2). A single-crystal X-ray diffraction study with the p-nitro-substituted system [Mo(SC₆H₄NO₂-p){P(OMe)₃}-(η²-MeC₂Me)(η-C₅H₅)] (9) established the molecular structure illustrated in Figure 1, which also shows the atom-numbering scheme. Fractional atomic co-ordinates and bond lengths and angles are listed in Tables 3 and 4 respectively.

The geometry about molybdenum is of the familiar three-legged piano stool type,[10] with an η⁵-cyclopentadienyl ligand forming the 'seat' of the stool, and a S-bonded thiolate ligand, a trimethyl phosphite, and a π-bound but-2-yne ligand forming the 'legs'. The four-electron donor but-2-yne shows 'bend back' angles of the alkyne substituents [C(1)–C(2)–C(3), 137.2(3) and C(2)–C(3)–C(4), 140.4(3)°],* which compare with those observed for [Mo(CO)(PEt₃)(η²-MeC₂Me)(η⁵-

C₉H₇)][BF₄] [139.8(4) and 141.7(5)°],[5] [Mo(PMe₃)₂(η²-MeC₂Me)(η⁵-C₉H₇)][BF₄] [133.8(9) and 138.7(9)°],[5] and [Mo(η²-o-Ph₂PC₆H₄CH=CH₂)(η²-MeC₂Me)(η-C₅H₅)][BF₄] [136.7(7) and 142.0(8)°].[11] The orientation of the but-2-yne ligand is such that the central C–C bond lies approximately parallel to the Mo–P vector [torsion angle C(2)–C(3)–Mo–P −12.4(2)°]. The C(2)–C(3) but-2-yne bond shows the expected lengthening [1.305(4) Å]. As with the four-electron but-2-yne complexes mentioned above some asymmetry in the Mo–C distances [Mo–C(2), 2.057(3) and Mo–C(3), 2.020(3) Å] is observed with (9), the contact carbon cis to the phosphorus atom of the phosphite ligand being further from the molybdenum.

The thiolate sulphur atom shows a Mo–S–C(13) angle of 110.2(1)°. The aryl ring is planar and lies at an angle of 31.8° to the Mo–S–C(13) plane; the NO₂ moiety is planar and virtually coplanar with the aryl ring (interplanar angle 3.2°). Other molecular dimensions, bond lengths and angles are as expected and fall within the ranges observed for related structures.

The complexes (5)—(9) showed temperature-dependent ¹H n.m.r. spectra, which were used to determine [12] the barriers to but-2-yne rotation, $\Delta G_{Tc}^{\ddagger}$, listed in Table 2. In complexes of this type the alkyne functions as a four-electron donor, as

* Estimated standard deviations in the last significant digit are given in parentheses here and throughout this paper.

Table 2. N.m.r. data [a] and rotational barriers for monoalkyne complexes

| Complex	¹H N.m.r. (δ/p.p.m.)	¹³C-{¹H} N.m.r. (δ/p.p.m.)	$\Delta G_{Tc}^{\ddagger}/$ kJ mol⁻¹
(1) [b]	5.00 (5 H, s, C₅H₅), 3.59 [d, 9 H, POMe, J(HP) 11.5], 2.77 (6 H, s, MeC≡C), 2.38 [3 H, d, SMe, J(HP) 1.0] ([²H₈]toluene, +30 °C)	195.6 [d, MeC≡C, J(CP) 4.4], 185.0 [d, MeC≡C, J(CP) 38.1], 93.4 (s, C₅H₅), 52.6 (s, POMe), 31.9 [d, SMe, J(CP) 10.3], 21.1 (s, MeC≡C), 19.3 [d, MeC≡C, J(CP) 10.3] ([²H₈]toluene, −50 °C)	
(2) [c]	10.22 [1 H, d, HC≡C, J(HP) 30.9], 5.26 (5 H, s, C₅H₅), 3.75 [9 H, d, POMe, J(HP) 10.8], 2.69 [3 H, d, SMe, J(HP) 1.0], 1.61 (9 H, s, BuᵗC≡C) ([²H₆]benzene, +30 °C)	210.7 [d, BuᵗC≡C, J(CP), 2.9], 175.4 [d, HC≡C, J(CP) 42.5], 92.1 (s, C₅H₅), 52.2 [d, POMe, J(CP) 2.9], 40.9 [d, CMe₃, J(CP) 2.9], 32.1 (s, CMe₃), 31.4 [d, SMe, J(CP) 8.8] (CD₂Cl₂, −50 °C)	
(3) [d]	7.7—6.9 (10 H, m, PhC≡C), 5.18 (5 H, s, C₅H₅), 3.57 [9 H, d, POMe, J(HP) 7.4], 2.79 (3 H, s, SMe) ([²H₆]benzene, +30 °C)	196.4 [d, PhC≡C, J(CP) 2.9], 193.7 [d, PhC≡C, J(CP) 35.2], 145.1 [d, PhC≡C, ipso-C, J(CP) 10.3], 138.0 [d, PhC≡C, ipso-C, J(CP) 2.9], 130.0, 128.9, 127.6, 125.7, 125.6 (PhC≡C), 92.9 (s, C₅H₅), 52.3 [d, POMe, J(CP) 4.4], 31.7 [d, SMe, J(CP) 10.3] (CD₂Cl₂, −60 °C)	
(4) [e]	7.8—7.0 (5 H, m, PhSe), 4.78 (5 H, s, C₅H₅), 3.50 [9 H, d, POMe, J(HP) 11.5], 2.76 (6 H, s, MeC≡C) ([²H₈]toluene, +30 °C)	202.2 [d, MeC≡C, J(CP) 5.9], 193.3 [d, MeC≡C, J(CP) 38.1], 143.4 [d, PhSe, ipso-C, J(CP), 1.7], 133.4 (s, PhSe, ortho-C), 127.5 (s, PhSe, meta-C) 124.4 (s, PhSe, para-C), 93.8 (s, C₅H₅), 52.3 [d, POMe, J(CP) 4.4], 21.8 [d, MeC≡C, J(CP) 2.9], 19.3 [d, MeC≡C, J(CP) 10.3] (CD₂Cl₂, −60 °C)	55.3 ± 2
(5) [f]	7.26 (2 H, m, p-NH₂C₆H₄, ortho-H), 6.34 (2 H, m, p-NH₂C₆H₄, meta-H), 4.87 (5 H, s, C₅H₅), 3.65 [9 H, d, POMe, J(HP) 11.3], 3.09 (2 H, br s, NH₂), 2.92 (6 H, br s, MeC≡C) ([²H₈]toluene, +30 °C) [g]	197.2 [d, MeC≡C, J(CP) 5.9], 187.8 [d, MeC≡C, J(CP), 38.1], 143.7 (s, p-NH₂C₆H₄, para-C), 141.8 [d, p-NH₂C₆H₄, ipso-C, J(CP), 11.7], 132.2 (s, p-NH₂C₆H₄, ortho-C), 114.3 (s, p-NH₂C₆H₄, meta-C), 94.3 (s, C₅H₅), 52.1 (s, POMe), 21.3 (s, MeC≡C), 18.9 [d, MeC≡C, J(CP) 10.3] (CD₂Cl₂, −60 °C)	65.0 ± 2
(6) [h]	7.40 (2 H, m, p-MeOC₆H₄, ortho-H), 6.76 (2 H, m, p-MeOC₆H₄, meta-H), 4.88 (5 H, s, C₅H₅), 3.64 [9 H, d, POMe, J(HP) 11.0], 3.48 (3 H, s, OMe), 2.88 (6 H, br s, MeC≡C) ([²H₈]toluene, +30 °C) [i]	198.3 [d, MeC≡C, J(CP) 5.9], 189.0 [d, MeC≡C, J(CP) 10.0], 156.5 (s, p-MeOC₆H₄, para-C), 144.9 [d, p-MeO₆H₄, ipso-C, J(CP) 11.7], 132.4 (s, p-MeOC₆H₄, ortho-C), 112.7 (s, p-MeOC₆H₄, meta-C), 94.4 (s, C₅H₅), 55.4 (s, OMe), 52.2 [d, POMe, J(CP) 4.4], 21.4 [d, MeC≡C, J(CP), 2.9], 18.9 [d, MeC≡C, J(CP) 10.3] (CD₂Cl₂, −60 °C)	60.5 ± 2
(7) [j]	7.47 (2 H, m, p-MeC₆H₄, ortho-H), 6.99 (2 H, m, p-MeC₆H₄, meta-H), 4.87 (5 H, s, C₅H₅), 3.58 [9 H, d, POMe, J(HP) 11.5], 2.87 (6 H, br s, MeC≡C), 2.20 (3 H, s, Me) ([²H₈]toluene, +30 °C) [k]	199.0 [d, MeC≡C, J(CP) 4.4], 189.5 [d, MeC≡C, J(CP) 38.1], 149.8 [d, p-MeC₆H₄, ipso-C, J(CP) 10.3], 133.2 (s, p-MeC₆H₄, para-C), 131.3 (s, p-MeC₆H₄, ortho-C), 128.2 (s, p-MeC₆H₄, meta-C), 94.3 (s, C₅H₅), 52.2 [d, POMe, J(CP), 4.4], 21.4 [d, MeC≡C, J(CP) 4.4], 21.1 (s, Me), 18.9 [d, MeC≡C, J(CP) 10.3] (CD₂Cl₂, −60 °C)	59.9 ± 2
(8) [l]	7.8—7.1 (5 H, m, PhS), 4.94 (5 H, s, C₅H₅), 3.66 [9 H, d, POMe, J(HP) 11.5], 2.90 (6 H, br s, MeC≡C) ([²H₈]toluene, +30 °C) [m]	199.9 [d, MeC≡C, J(CP) 5.9], 190.3 [d, MeC≡C, J(CP) 38.1], 153.1 [d, PhS, ipso-C, J(CP) 11.7], 131.5 (s, PhS, ortho-C), 127.4 (s, PhS, meta-C), 123.7 (s, PhS, para-C), 94.4 (s, C₅H₅), 52.2 [d, POMe, J(CP) 4.4], 21.5 [d, MeC≡C, J(CP) 2.9], 19.1 [d, MeC≡C, J(CP) 10.3] (CD₂Cl₂, −60 °C)	58.5 ± 2
(9) [n]	7.81 (2 H, m, p-NO₂C₆H₄, meta-H), 7.28 (2 H, m, p-NO₂C₆H₄, ortho-H), 4.72 (5 H, s, C₅H₅), 3.45 [9 H, d, POMe, J(HP) 11.5], 2.76 (6 H, s, MeC≡C) ([²H₈]toluene, +30 °C) [o]	204.6 [d, MeC≡C, J(CP) 5.9], 195.7 [d, MeC≡C, J(CP), 38.1], 163.2 [d, p-NO₂C₆H₄, ipso-C, J(CP) 11.7], 143.6 (s, p-NO₂C₆H₄, para-C), 131.5 (s, p-NO₂C₆H₄, ortho-C), 122.6 (s, p-NO₂C₆H₄, meta-C), 94.7 (s, C₅H₅), 52.5 [d, POMe, J(CP) 4.4], 21.9 [d, MeC≡C, J(CP) 4.4], 19.5 [d, MeC≡C, J(CP) 10.3]	52.4 ± 2
(11)	4.92 (5 H, s, C₅H₅), 2.66 (3 H, br s, MeC≡C), 2.52 (3 H, s, SMe), 2.48 (3 H, br s, MeC≡C) ([²H₆]benzene, +30 °C)		
(13)	5.10 (5 H, s, C₅H₅), 3.12 (6 H, s, MeC≡C), 2.58 (6 H, s, NMe₂) ([²H₆]benzene, +30 °C)	218.8 (s, MeC≡C), 92.8 (s, C₅H₅), 38.2, 20.9 (s, Me)	
(14)	13.90 (1 H, s, HC≡C), 5.18 (5 H, s, C₅H₅), 2.55 (6 H, s, NMe₂), 1.46 (9 H, s, BuᵗC≡C) ([²H₆]benzene, +30 °C)		
(17)	8.0—6.7 (9 H, br m, Ph), 4.60 (5 H, s, C₅H₅), 2.76 (6 H, s, MeC≡C) ([²H₈]toluene, −90 °C)	208.7 (s, MeC≡C), 154.5, 143.3, 132.0, 131.4, 129.9, 129.6, 129.4, 128.5, 124.2 (Ph), 95.2 (s, C₅H₅), 18.9 (s, MeC≡C) (CDCl₃, +30 °C)	
(18)	10.23 (1 H, s, HC≡C), 7.9—6.6 (9 H, br m, Ph), 4.92 (5 H, s, C₅H₅), 1.32 (9 H, s, BuᵗC≡C) ([²H₆]benzene, +30 °C)		

Table 2 (*continued*)

Complex	¹H N.m.r. (δ/p.p.m.)	¹³C-{¹H} N.m.r. (δ/p.p.m.)	$\Delta G_{Tc}^{\ddagger}$/ kJ mol⁻¹
(19)	7.5—6.6 (9 H, br m, Ph), 4.97 (5 H, s, C₅H₅), 2.74 (3 H, s, MeC≡C), 2.67 (3 H, s, MeC≡C) ([²H₆]benzene, +30 °C)	234.5 (s, CO), 181.0 (s, MeC≡C), 178.9 (s, MeC≡C), 151.9, 139.7, 135.5, 135.0, 134.3, 129.0, 126.8, 126.0, 125.0 (Ph), 96.4 (s, C₅H₅), 20.5 (s, MeC≡C), 17.2 (s, MeC≡C)	

ᵃ Downfield from SiMe₄; J values in Hz. ᵇ ³¹P-{¹H} ([²H₈]toluene, +30 °C), 198.3 p.p.m. ᶜ ³¹P-{¹H} (CD₂Cl₂, −50 °C), 195.1 (s) p.p.m. ᵈ ³¹P-{¹H} (CD₂Cl₂, +30 °C), 188.3 (s) p.p.m. ᵉ ⁷⁷Se-{¹H} ([²H₈]toluene, +30 °C), 215.7 p.p.m. [d, SePh, J(SeP) 36.6]; ³¹P-{¹H} (CD₂Cl₂ +30 °C), 197.6 (s) p.p.m. ᶠ ³¹P-{¹H} (CD₂Cl₂, +30 °C), 195.7 (s) p.p.m. ᵍ At −20 °C the singlet at 2.92 is replaced by resonances at 3.02 and 2.83. Coalescence temperature +12 °C. ʰ ³¹P-{¹H} (CD₂Cl₂, +30 °C), 194.5 (s) p.p.m. ⁱ At −40 °C two signals, 3.05 and 2.90 replace the resonance at 2.88. Coalescence temperature +8 °C. ʲ ³¹P-{¹H} (CD₂Cl₂, +30 °C), 194.9 (s) p.p.m. ᵏ At −40 °C two signals, 2.92 (3 H, s) and 2.76 [3 H, d, J(HP) 1.5] replace the resonance at 2.87. Coalescence temperature +6 °C. ˡ ³¹P-{¹H} (CD₂Cl₂, +30 °C), 194.6 (s) p.p.m. ᵐ At −50 °C the signal at 2.90 becomes two resonances at 2.80 (3 H, s) and 2.68 [3 H, d, J(HP) 1.5]. Coalescence temperature −3 °C. ⁿ ³¹P-{¹H} resonance (CD₂Cl₂, 0 °C), 190.6 (s) p.p.m. ° At −80 °C the signal at 2.76 is replaced by resonances at 2.78 (3 H, s) and 2.67 [3 H, d, J(HP) 1.5]. Coalescence temperature −31 °C.

Table 3. Atomic co-ordinates (× 10⁴) for (9)

Atom	x	y	z
Mo	2 390(1)	2 154(1)	3 381(1)
P	1 617(1)	1 055(1)	3 565(1)
S	1 248(1)	2 502(1)	5 093(1)
O(1)	1 764(3)	616(1)	4 751(2)
O(2)	2 496(2)	579(1)	2 746(2)
O(3)	−63(2)	862(1)	3 018(2)
O(4)	3 440(4)	5 665(1)	5 756(3)
O(5)	1 354(3)	5 711(1)	6 556(2)
N	2 299(4)	5 402(1)	6 063(3)
C(1)	5 155(4)	1 078(2)	4 551(3)
C(2)	4 317(3)	1 667(1)	4 024(2)
C(3)	4 637(3)	2 263(2)	3 673(3)
C(4)	5 948(3)	2 674(2)	3 439(3)
C(5)	1 749(6)	881(2)	5 897(3)
C(6)	2 252(4)	−131(2)	2 706(3)
C(7)	−1 298(3)	1 057(2)	3 647(3)
C(8)	1 507(4)	2 105(2)	1 449(3)
C(9)	2 650(3)	2 588(2)	1 554(2)
C(10)	2 153(4)	3 135(2)	2 200(3)
C(11)	697(4)	2 996(2)	2 462(3)
C(12)	280(4)	2 361(2)	2 012(3)
C(13)	1 585(3)	3 359(1)	5 362(2)
C(14)	2 900(3)	3 670(1)	5 104(2)
C(15)	3 153(3)	4 337(2)	5 340(3)
C(16)	2 056(4)	4 695(1)	5 834(3)
C(17)	744(4)	4 396(2)	6 127(3)
C(18)	519(4)	3 732(2)	5 892(3)
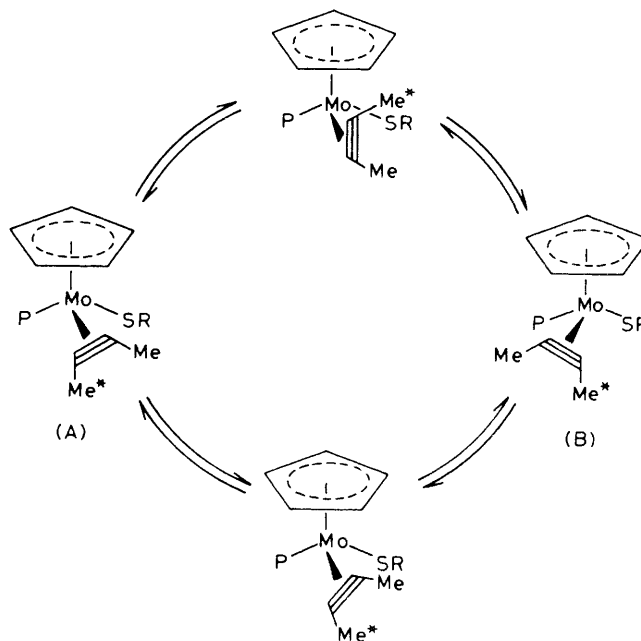
Scheme 1. P = P(OMe)₃; R = p-XC₆H₄ [X = NH₂ (5), OMe (6), Me (7), H (8), or NO₂ (9)]

reflected in the low-field ¹³C chemical shifts observed for the contact carbons. Molecular orbital calculations on related alkyne complexes ⁷⁻⁹ show that their conformational behaviour is dominated by the interaction of the empty alkyne π* orbital with filled metal d_π orbitals. In particular for the unsymmetrical d^4 complexes [Mo(η²-alkyne)LL'(η-C₅H₅)], the barrier to rotation of the alkyne has been traced to the difference in the π-acceptor functions of the ligands L and L' (L = CO and L' = CH₃ in ref. 8). Thus, in the ground-state conformation of these complexes the C–C bond of the alkyne lies approximately parallel to the Mo–L vector (where L is a stronger π-acceptor than L'); in this orientation the π-acceptor function of L and the alkyne (π*) combine to stabilise the metal d_π orbital most efficiently. The transition-state conformation has the C–C vector parallel to the Mo–L' bond, where the poorer π-acceptor function of L' cannot so efficiently assist the alkyne π* in stabilising the metal d_π orbital. Thus, in the case of complexes (5)—(9) the greater the disparity in π-acceptor ability of the trimethyl phosphite and thiolate ligands, the greater the barrier to rotation of the but-2-yne ligand. This dis-

parity in the case of thioaryl ligands might be expected to be a function of the charge at sulphur and therefore of the *para* substituent. That this is indeed the case is illustrated by the linearity of $\Delta G_{Tc}^{\ddagger}$ vs. σ Hammett substituent constants for complexes (5)—(9). It is, therefore, suggested that the barriers noted in Table 2 for these complexes may be most satisfactorily interpreted in terms of electronic effects in a rotational process traversing the rotamers [ground state (A), transition state (B)] shown in Scheme 1.

The reactivity of [Mo(CO)(η²-MeC₂Me)₂(η-C₅H₅)][BF₄] towards neutral phosphorus nucleophiles is well established,⁵ the nucleophile attacks the metal centre with displacement of one alkyne ligand. In contrast lithium dimethylcuprate affords [Mo(CO)(η²-MeC₂Me)(σ-CMe=CMe₂)(η-C₅H₅)], whereas reaction with K[BHBuˢ₃] followed by treatment with CO gives a vinyl ketone complex.⁴ It was, therefore, important to examine the corresponding reaction with a thiolate anion.

Reaction of NaSMe with [Mo(CO)(η²-MeC₂Me)₂(η-C₅H₅)]-[BF₄] in thf at room temperature followed by a chromatographic work-up afforded two products: a red crystalline complex which was identified as the known ¹³ dimolybdenum

Table 4. Bond lengths (Å) and angles (°) for complex (9)

Mo–P	2.332(1)	Mo–S	2.406(1)
Mo–C(2)	2.057(3)	Mo–C(3)	2.020(3)
Mo–C(8)	2.276(3)	Mo–C(9)	2.300(3)
Mo–C(10)	2.388(3)	Mo–C(11)	2.440(3)
Mo–C(12)	2.370(3)	P–O(1)	1.615(2)
P–O(2)	1.601(2)	P–O(3)	1.620(2)
S–C(13)	1.770(3)	O(1)–C(5)	1.419(4)
O(2)–C(6)	1.444(4)	O(3)–C(7)	1.435(4)
O(4)–N	1.234(5)	O(5)–N	1.233(4)
N–C(16)	1.457(4)	C(2)–C(1)	1.497(4)
C(2)–C(3)	1.305(4)	C(3)–C(4)	1.484(4)
C(8)–C(9)	1.408(4)	C(8)–C(12)	1.427(5)
C(9)–C(10)·	1.421(5)	C(10)–C(11)	1.398(5)
C(11)–C(12)	1.412(5)	C(13)–C(14)	1.392(4)
C(13)–C(18)	1.400(4)	C(14)–C(15)	1.382(4)
C(15)–C(16)	1.385(4)	C(16)–C(17)	1.393(5)
C(17)–C(18)	1.372(4)		

P–Mo–S	92.7(1)	P–Mo–C(2)	76.3(1)
S–Mo–C(2)	104.9(1)	P–Mo–C(3)	112.8(1)
S–Mo–C(3)	109.5(1)	C(2)–Mo–C(3)	37.3(1)
P–Mo–C(8)	88.2(1)	S–Mo–C(8)	132.0(1)
C(2)–Mo–C(8)	121.7(1)	C(3)–Mo–C(8)	114.2(1)
P–Mo–C(9)	120.0(1)	S–Mo–C(9)	136.2(1)
C(2)–Mo–C(9)	110.4(1)	C(3)–Mo–C(9)	85.3(1)
C(8)–Mo–C(9)	35.8(1)	P–Mo–C(10)	145.4(1)
S–Mo–C(10)	101.6(1)	C(2)–Mo–C(10)	128.3(1)
C(3)–Mo–C(10)	92.0(1)	C(8)–Mo–C(10)	58.8(1)
C(9)–Mo–C(10)	35.2(1)	P–Mo–C(11)	121.2(1)
S–Mo–C(11)	81.5(1)	C(2)–Mo–C(11)	161.6(1)
C(3)–Mo–C(11)	124.3(1)	C(8)–Mo–C(11)	58.0(1)
C(9)–Mo–C(11)	57.4(1)	C(10)–Mo–C(11)	33.6(1)
P–Mo–C(12)	90.1(1)	S–Mo–C(12)	96.3(1)
C(2)–Mo–C(12)	155.1(1)	C(3)–Mo–C(12)	143.8(1)
C(8)–Mo–C(12)	35.7(1)	C(9)–Mo–C(12)	58.6(1)
C(10)–Mo–C(12)	57.4(1)	C(11)–Mo–C(12)	34.1(1)
Mo–P–O(1)	126.5(1)	Mo–P–O(2)	110.2(1)
O(1)–P–O(2)	99.3(1)	Mo–P–O(3)	117.8(1)
O(1)–P–O(3)	100.8(1)	O(2)–P–O(3)	97.1(1)
Mo–S–C(13)	110.2(1)	P–O(1)–C(5)	124.4(2)
P–O(2)–C(6)	121.8(2)	P–O(3)–C(7)	118.3(2)
O(4)–N–O(5)	122.8(3)	O(4)–N–C(16)	118.7(3)
O(5)–N–C(16)	118.5(3)	Mo–C(2)–C(1)	153.0(2)
Mo–C(2)–C(3)	69.8(2)	C(1)–C(2)–C(3)	137.2(3)
Mo–C(3)–C(2)	72.9(2)	Mo–C(3)–C(4)	145.6(2)
C(2)–C(3)–C(4)	140.4(3)	Mo–C(8)–C(9)	73.0(2)
Mo–C(8)–C(12)	75.7(2)	C(9)–C(8)–C(12)	107.5(3)
Mo–C(9)–C(8)	71.2(2)	Mo–C(9)–C(10)	75.8(2)
C(8)–C(9)–C(10)	108.3(3)	Mo–C(10)–C(9)	69.0(2)
Mo–C(10)–C(11)	75.3(2)	C(9)–C(10)–C(11)	107.9(3)
Mo–C(11)–C(10)	71.1(2)	Mo–C(11)–C(12)	70.2(2)
C(10)–C(11)–C(12)	108.7(3)	Mo–C(12)–C(8)	68.6(2)
Mo–C(12)–C(11)	75.7(2)	C(8)–C(12)–C(11)	107.6(3)
S–C(13)–C(14)	122.2(2)	S–C(13)–C(18)	118.9(2)
C(14)–C(13)–C(18)	118.8(3)	C(13)–C(14)–C(15)	121.3(3)
C(14)–C(15)–C(16)	118.4(3)	N–C(16)–C(15)	118.8(3)
N–C(16)–C(17)	119.5(3)	C(15)–C(16)–C(17)	121.7(3)
C(16)–C(17)–C(18)	119.0(3)	C(13)–C(18)–C(17)	120.8(3)

species (10) (Scheme 2), and a purple crystalline material which was characterised (analysis, m.s., and n.m.r.) as the complex [Mo(SMe)(CO)(η²-MeC₂Me)(η-C₅H₅)] (11). The ¹H n.m.r. spectrum of this species consisted of a 5 H singlet at 4.92 p.p.m. (η-C₅H₅), a 3 H singlet at 2.52 p.p.m. (SMe), and two 3 H singlets (broader than that assigned to the SMe group) at 2.66 and 2.48 p.p.m. which are assigned to the methyl groups on a static but-2-yne ligand lying approximately parallel to the Mo–CO bond. Thus, the barrier to alkyne rotation is significantly higher in (11) than its trimethyl phosphite
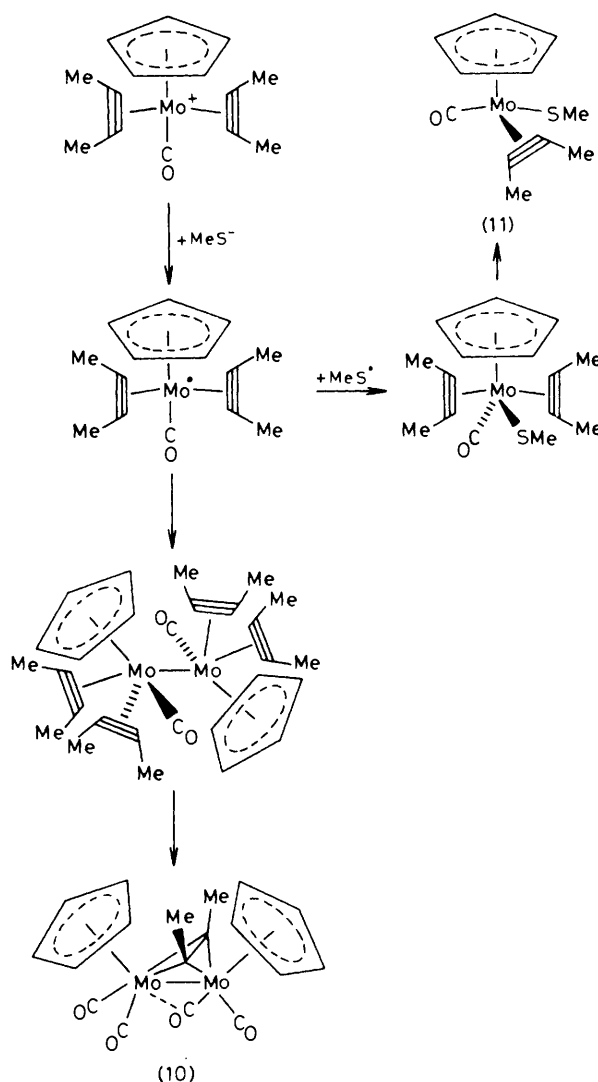
Scheme 2.

analogue (1). The solution i.r. spectrum of (11) showed two terminal carbonyl ligands at 1 936 and 1 920 cm⁻¹. This may be explained by the existence of two orientations of the methyl group attached to the sulphur atom, which interconvert slowly on the i.r. time-scale. In the solid-state structures of (9) and (19) (see later) the L–Mo–S–C [L = P(OMe)₃ in (9) and CO in (19)] angles are 178.6(2) and 179.3(2) respectively. This conformation may be electronically preferred, and presumably the orientation with this dihedral angle ∼0° would be equally acceptable on electronic grounds but sterically untenable when the substituent at sulphur is large, as in (9) and (19). In the case of (11) it is therefore likely that a second conformer with the (OC)–Mo–S–Me angle different from 180° is both electronically and sterically feasible.

The yields of (10) (20%) and (11) (17%) are low, and it is suggested that the MeS⁻ anion undergoes a one-electron transfer reaction with the molybdenum cation producing (Scheme 2) a neutral bis(but-2-yne)carbonyl species, which may dimerise or combine with the radical MeS·. The dimer, however, must be unstable, decomposing to liberate carbon monoxide, which is scavenged by any as yet not decomposed dimer forming the stable complex (10).

These observations serve to underline the possibility that in the formation of complexes (1)—(9), one-electron transfer
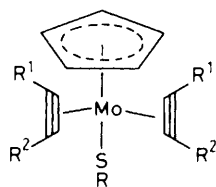
(12; R = R^1= R^2= Me)
(15; R = C$_6$H$_4$SPh−o, R^1 = R^2 = Me)
(16; R = C$_6$H$_4$SPh−o, R^1 = H, R^2 = Bu^t)

(13; R^1 = R^2 = Me)
(14; R^1 = H, R^2 = Bu^t)

(17; R^1 = R^2 = Me)
(18; R^1 = H, R^2 = Bu^t)

reactions may also be involved, in which the odd-electron species [Mo{P(OMe)$_3$}$_2$(η^2-MeC$_2$Me)(η-C$_5$H$_5$)]* is an intermediate. Support for this suggestion is provided by the preliminary observation [14] that [Mo{P(OMe)$_3$}$_2$(η^2-MeC$_2$Me)(η-C$_5$H$_5$)][BF$_4$] readily undergoes a reversible one-electron reduction (−1.04 V in CH$_2$Cl$_2$, 0.1 mol dm^3 [NBu$^n_4$][BF$_4$], saturated calomel electrode), and that on the same scale NaSPh is reported to have an oxidation potential of approximately −1 V.

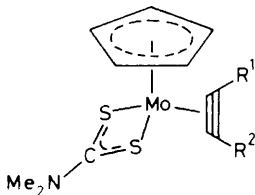The formation of (1)—(9) by sulphur attack on molybdenum is also in interesting contrast to the report by Reger and McElligott,[15] who reported that the iron-alkyne complex [Fe(CO)(PPh$_3$)(η^2-MeC$_2$Me)(η-C$_5$H$_5$)][BF$_4$] reacts with MeS$^-$ to form the σ-vinyl complex [Fe{σ-(E)-C(Me)=C(Me)SMe}-(CO)(PPh$_3$)(η-C$_5$H$_5$)]. This difference in chemoselectivity presumably arises because of the inclusion of π donation in the molybdenum-alkyne bonding, which is of little significance in the bonding of the iron-alkyne complex.

Attention was next directed to the acetonitrile-substituted complex [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$],[5] which reacted with NaSMe to give the orange crystalline complex (12) characterised by analysis and n.m.r. as a bis(but-2-yne) complex. As mentioned when discussing the monoalkyne complexes (1)—(9), it has been suggested that a correlation exists between the ^{13}C chemical shift of the alkyne contact carbon, and the number of electrons donated by the alkyne to the metal.[5,8,16] Merrick and Templeton [16] have recorded the ^{13}C spectra of a number of bis(alkyne) complexes of the type [Mo(S$_2$CNR$_2$)$_2$(η^2-R^{1}C$_2$R^2)$_2$], which are thought to contain two net three-electron donor alkynes, where the contact carbon chemical shifts fall in the range 167—190 p.p.m. Complex (12) shows (−90 °C) shifts at 161.3 and 180.5 p.p.m., which are similar to those observed [5] for the cations [Mo(L)-(η^2-R^{1}C$_2$R^2)(η-C$_5$H$_5$)][BF$_4$] (L = CO or NCMe) suggesting that in (12) the alkynes are each formally donating three electrons to the molybdenum. At room temperature the ^{13}C spectrum shows only a single resonance for the but-2-yne and methyl carbons at 171.6 and 16.6 p.p.m. respectively, and in addition the ^{1}H spectrum shows only one methyl signal. This is consistent with a dynamic process occurring in solution involving a possible cogwheel propeller rotation [17] of the two alkyne ligands. It has been observed [16] that the complexes [Mo(S$_2$CNMe$_2$)$_2$(η^2-R^{1}C$_2$R^2)$_2$] (R^1 = R^2 = Et or R^1 = H,

R^2 = Ph) also show temperature-dependent spectra, and the barrier to rotation for the hex-3-yne complex has been calculated as 64.3 ± 0.8 kJ mol^{-1}. Variable-temperature [13]C n.m.r. studies on complex (12) afforded a value for but-2-yne rotation of 45.0 ± 0.5 kJ mol^{-1}.

Davidson [18,19] has characterised a range of bis(hexafluorobut-2-yne) complexes [W(SR)(η^2-CF$_3$C$_2$CF$_3$)$_2$(η-C$_5$H$_5$)] (R = CF$_3$, C$_6$F$_5$, Ph, p-MeC$_6$H$_4$, Bu^t, Pr^i, or Et), and in agreement with the present study alkyne rotation is fast on the n.m.r. time-scale down to −90 °C. However, for R = Pr^i and Bu^t, the molecules are stereochemically rigid, and it is suggested [19] that this is because the complexes are dimeric with bridging SR ligands.

Treatment of the cations of [Mo(NCMe)(η^2-R^{1}C$_2$R^2)$_2$(η-C$_5$H$_5$)][BF$_4$] (R^1 = R^2 = Me or R^1 = H, R^2 = Bu^t) with the dithiocarbamate anion [S$_2$CNMe$_2$]$^-$ affords the air-sensitive green crystalline compounds (13) and (14) (Tables 1 and 2). [1]H and [13]C n.m.r. spectra were in agreement [5,20] with the illustrated structures showing that the dithiocarbamate anion had displaced both the acetonitrile and one alkyne ligand. It is interesting to compare this observation with the report [21] that the NN-diethyldithiocarbamate anion reacts with [MoCl(η^2-CF$_3$C$_2$CF$_3$)$_2$(η-C$_5$H$_5$)] affording the bis(hexafluorobut-2-yne) complex [Mo(η^2-CF$_3$C$_2$CF$_3$)$_2$(S$_2$CNEt$_2$)(η-C$_5$H$_5$)] where the alkynes function as two-electron donors. In the reaction which produces (13) and (14) there was no evidence for the presence of a bis(alkyne) complex, and attempts to react (13) with an excess of but-2-yne led only to decomposition products.

In contrast, the dithioaryl anion [22,23] [SC$_6$H$_4$SPh-o]$^-$ reacts with [Mo(NCMe)(η^2-R^{1}C$_2$R^2)$_2$(η-C$_5$H$_5$)][BF$_4$] (R^1 = R^2 = Me or R^1 = H, R^2 = Bu^t) to afford (15) and (17), and (16) and (18) respectively. In (17) and (18) the dithioaryl ligand is acting as an S,S'-bidentate three-electron ligand. The n.m.r. spectra of the other two products (15) and (16) showed that in the reaction leading to their formation only acetonitrile had been displaced, and that the sulphur ligand is σ-bonded as illustrated, the alkyne ligands acting as three-electron donors as in complex (12).

Whereas the hexafluorobut-2-yne complex [Mo(η^2-CF$_3$C$_2$CF$_3$)$_2$(S$_2$CNEt$_2$)(η-C$_5$H$_5$)] has been reported [21] to rearrange to an η^4-bonded cyclobutadiene species [Mo{η^4-C$_4$(CF$_3$)$_4$}(S$_2$CNEt$_2$)(η-C$_5$H$_5$)], (15) and (16) did not undergo a similar rearrangement. This is surprising, and the reasons for this difference in reactivity are not clear.

Reaction (50 °C, 24 h) of (17) with an excess of but-2-yne resulted in the formation of the bis(but-2-yne) complex (15), the sulphur ligand undergoing a S,S'-bidentate to σ transformation. This suggests that in the reaction at low temperature leading to the formation of (15) and (17), initial attack by the dithioaryl anion affords an intermediate (A) (Scheme 3), which collapses either by acetonitrile loss to form (15), or via but-2-yne loss followed by acetonitrile to give (17).

In an attempt to force the but-2-yne ligand present in (17) to change its bonding mode from (4e) η^2 to (2e) η^2 the reaction with the small ligand carbon monoxide was next examined. A
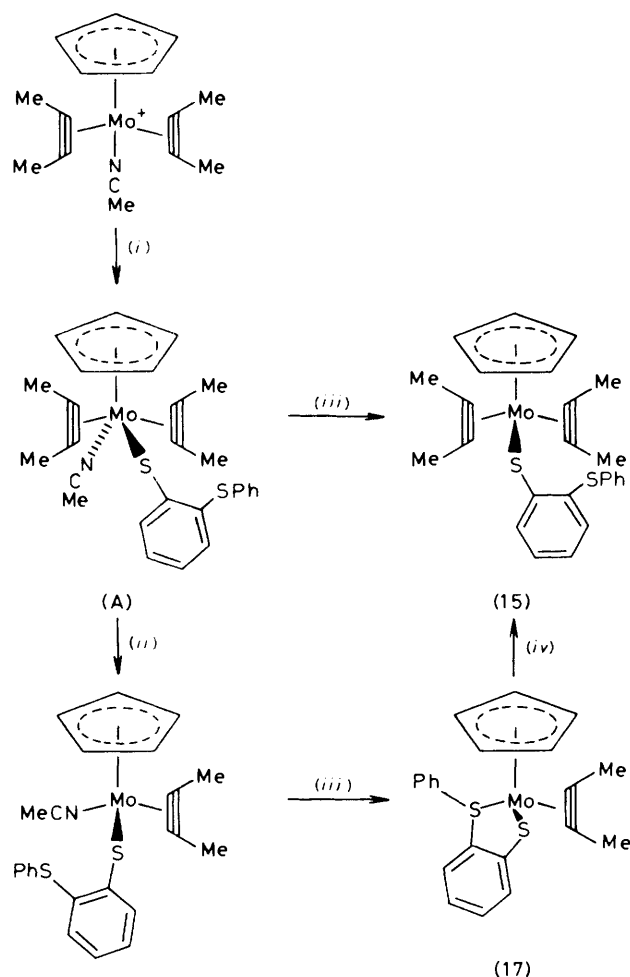
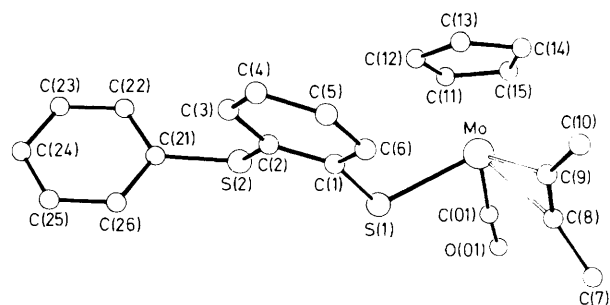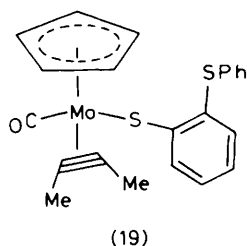**Scheme 3.** (i) + [SC₆H₄SPh-o]⁻; (ii) − MeC₂Me; (iii) − MeCN; (iv) + MeC₂Me

(19)

Figure 2. The molecular structure of the complex [Mo(SC₆H₄-SPh-o)(CO)(η²-MeC₂Me)(η-C₅H₅)] (19) showing the crystallographic numbering scheme

Table 5. Atomic co-ordinates (× 10⁴) for (19)

Atom	x	y	z
Mo	1 166(1)	324(1)	2 359(1)
S(1)	2 543(2)	2 005(2)	2 412(1)
S(2)	2 863(3)	4 143(2)	1 410(2)
C(1)	3 734(9)	1 951(7)	1 690(4)
C(2)	3 898(10)	2 912(7)	1 244(4)
C(3)	4 856(10)	2 866(7)	677(5)
C(4)	5 618(10)	1 874(8)	565(5)
C(5)	5 463(10)	941(8)	1 012(5)
C(6)	4 510(9)	967(8)	1 563(4)
C(7)	1 624(11)	− 946(10)	4 026(4)
C(8)	1 726(8)	− 709(7)	3 240(4)
C(9)	2 285(7)	− 1 080(6)	2 665(5)
C(10)	3 140(9)	− 2 051(7)	2 342(5)
C(11)	− 511(11)	940(9)	1 547(5)
C(12)	660(11)	936(11)	1 142(5)
C(13)	1 145(12)	− 146(12)	1 105(5)
C(14)	219(13)	− 883(8)	1 467(5)
C(15)	− 774(9)	− 190(9)	1 753(5)
C(01)	263(8)	918(7)	3 209(4)
O(01)	− 315(8)	1 202(5)	3 723(3)
C(21)	3 703(9)	5 287(7)	958(4)
C(22)	3 100(10)	5 829(9)	361(5)
C(23)	3 658(12)	6 797(9)	51(5)
C(24)	4 822(12)	7 248(8)	323(5)
C(25)	5 449(12)	6 706(8)	896(5)
C(26)	4 898(10)	5 755(8)	1 218(5)

rapid reaction (15 min) occurred on bubbling CO through a solution of (17) at room temperature to afford a dark red crystalline complex (19), which showed a single strong terminal carbonyl band in the i.r. spectrum at 1 925 cm⁻¹. However, the ¹³C-{¹H} n.m.r. spectrum showed resonances due to the but-2-yne contact carbons at 181.0 and 178.9 p.p.m. suggesting that the alkyne was still functioning as a four-electron donor and was not rotating. In order to confirm the structural identity of (19), and to establish the orientation of the but-2-yne a single-crystal X-ray diffraction study was carried out.

The molecular geometry and atomic numbering scheme are shown in Figure 2, and the results of the X-ray analysis are listed in Tables 5 and 6.

The molecule has a similar structure to that found for (9) and that proposed for (11). The but-2-yne ligand lies approxi-

mately parallel [5,24] to the carbonyl ligand. This orientation can be seen clearly from Figure 3, which shows a stereoscopic view of the molecule, and is also evident from the C(8)−C(9)−Mo−C(01) torsion angle [179.1(2)°]. The Mo−C(8) and Mo−C(9) separations of 2.088(8) and 2.033(7) Å appear to be significantly different from each other. Thus, it is the carbon atom *cis* to the carbonyl ligand which lies furthest from the molybdenum atom, *cf.* similar behaviour in (9). The molybdenum-alkyne separations in (19) are larger than in (9) and in those reported [24] in the related complex [Mo(SC₆F₅)(CO)-(CF₃C₂CF₃)(η-C₅H₅)] [2.051(5) and 2.017(5) Å], implying a weaker binding of the but-2-yne fragment in (19) than in (9) and in the hexafluorobut-2-yne ligand. This is also indicated by the shorter alkyne carbon–carbon separation in (19) [1.271(12), *cf.* 1.305(4) and 1.298(6) Å in (9) and CF₃C₂CF₃ complex], and the smaller degree of 'bend back' of the methyl groups in (19) [mean internal alkyne C−C−C angle of 143.2(8)° compared with 138.8(3)° in (9) and 137.2(5)° in the hexafluorobut-2-yne complex]. This effect can be related to the π-acceptor abilities of the ligands in these complexes.

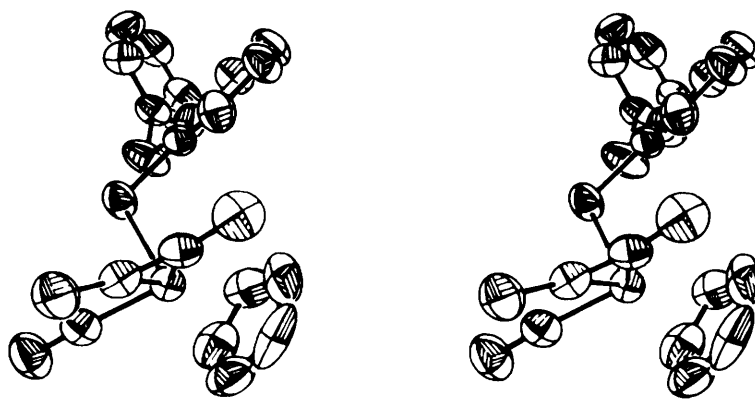The carbonyl group is slightly distorted from linearity

Figure 3. A stereoscopic view of the structure of complex (19)

[Mo–C(01)–O(01), 175.5(7)°], and the molybdenum–carbon separation of 1.929(8) Å is significantly shorter than that of 1.995(5) Å found [24] in [Mo(SC₆F₅)(CO)(CF₃C₂CF₃)(η-C₅H₅)]. This is probably a further manifestation of the difference in π-acceptor ability of the two alkynes. However, any difference between the two carbon–oxygen bond lengths does not appear to be significant.

There are, to our knowledge, no other structures with which the stereochemistry of the dithioaryl ligand can be directly compared; the phenyl groups are presumably orientated in such a way as to minimise steric interactions. The molybdenum–sulphur separation of 2.362(2) Å is very close to that found [24] in [Mo(SC₆F₅)(CO)(CF₃C₂CF₃)(η-C₅H₅)] [2.366(1) Å] and rather shorter than in (9) [2.406(1) Å]. Both phenyl rings are essentially planar with a dihedral angle of 103° between their mean planes. The angles at the sulphur atoms Mo–S(1)–C(1) and C(2)–S(2)–C(21) are 108.7(3) and 104.1(4)° respectively. The cyclopentadienyl ligand shows no substantial deviations from the expected geometry.

Experimental

The ¹H, ¹³C-{¹H}, ³¹P-{¹H}, and ⁷⁷Se-{¹H} n.m.r. spectra were recorded on JEOL FX 90 Q and FX 200 spectrometers, as appropriate. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer. Mass spectra were obtained on an A.G.I. MS 902 instrument operating at 70 eV. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen free, nitrogen. All solvents were dried and distilled immediately prior to use.

Synthesis of [Mo(SMe){P(OMe)₃}(η²-MeC₂Me)(η-C₅H₅)] (1).—A suspension of NaSMe (*ca.* 4 mmol) in thf was prepared by adding MeS₂Me (0.2 cm³, 2 mmol) to Na/Hg (0.1 g of Na in 8 cm³ Hg) in thf (20 cm³). After 2 h of rapid stirring the resultant solution was added to a stirred suspension of [Mo{P(OMe)₃}₂(η²-MeC₂Me)(η-C₅H₅)][BF₄] (1 g, 1.8 mmol) in thf (10 cm³). After 1 h at room temperature the volatile material was removed *in vacuo* and the residue extracted with diethyl ether and filtered through Keiselguhr. The solvent was removed and the blue material chromatographed on alumina. Elution with 25% diethyl ether–hexane gave a blue band, which was collected and recrystallised (−78 °C) from hexane to give blue *crystals* of (1).

A similar procedure was followed in the preparation of complexes (2)—(4). Except for the preparation of the thiolate anion, which was obtained by deprotonation of the respective thiol with NaH, the compounds (5)—(9) were similarly synthesised.

Reaction of [Mo(CO)(η²-MeC₂Me)₂(η-C₅H₅)][BF₄] *with* NaSMe.—A suspension of NaSMe (0.1 g, 1.4 mmol) and [Mo(CO)(η²-MeC₂Me)₂(η-C₅H₅)][BF₄] (0.4 g, 1 mmol) in thf (20 cm³) was stirred at room temperature. After 1 h the resultant brown solution was reduced to a solid by removal of the solvents *in vacuo*. The residue was extracted into toluene and filtered through a pad (2 × 2 cm) of alumina. The volume of the filtrate was reduced (1 cm³) and the residue dissolved in hexane and chromatographed on alumina. Elution with 10% diethyl ether–hexane gave first a red band, which was collected and recrystallised (−78 °C) from hexane to give red *crystals* of [Mo₂(CO)₄(μ-MeC₂Me)(η-C₅H₅)₂] (10) (0.05 g, 20%) (Found: C, 44.7; H, 3.3%; *M*, 488. C₁₈H₁₆Mo₂O₄ requires C, 44.3; H, 3.3%; *M*, 488), νᴄᴏ(hexane) 1 985s, 1 955m, 1 923 (sh), 1 917s, 1 905m (sh), and 1 845s cm⁻¹. ¹H N.m.r. ([²H₆]benzene): δ 4.78 (10 H, s, C₅H₅) and 2.36 p.p.m. (6 H, s, MeC₂Me). Further elution gave a purple band, which on crystallisation (−78 °C) from hexane gave purple *crystals* of (11) (0.05, g, 17%) (see Tables 1 and 2).

Reaction of [Mo(NCMe)(η²-MeC₂Me)₂(η-C₅H₅)][BF₄] *with* (a) NaSMe.—Dimethyl disulphide (0.20 g, 2.13 mmol) in thf (20 cm³) was added with stirring to Na/Hg (0.15 g Na in 10 cm³ Hg). After 2 h the resultant solution was added dropwise with stirring (room temperature) to a suspension of [Mo(NCMe)(η²-MeC₂Me)₂(η-C₅H₅)][BF₄] (1.0 g, 2.52 mmol) in thf (20 cm³). A colour change from yellow to red was observed in 5 min and the reaction mixture was allowed to stir for a further 2 h at room temperature. The solvent was removed *in vacuo* and the residue dissolved in hexane and chromatographed on alumina. Elution with diethyl ether gave an orange band, which was collected and recrystallised from hexane–diethyl ether (1 : 1, −78 °C) to give orange *crystals* of (12) (0.20 g, 25%) (Found: C, 53.5; H, 6.7%; *M*, 316. C₁₄H₂₀MoS requires C, 53.2; H, 6.3%; *M*, 316). N.m.r.: ¹H (CD₂Cl₂, +30 °C): δ 5.18 (5 H, s, C₅H₅), 2.65 (3 H, s, SMe), 2.58 (12 H, s, MeC≡C); ¹³C-{¹H} (CD₂Cl₂, −90 °C): δ 180.5 (s, MeC≡C), 161.3 (MeC≡C), 98.3 (s, C₅H₅), 31.2 (s, SMe), 20.8 (s, MeC≡C), 12.8 (s, MeC≡C); ¹³C-{¹H} (CD₂Cl₂, +30 °C): δ 171.6 (s, MeC≡C) and 16.6 p.p.m. (s, MeC≡C); coalescence temperature −40 °C.

(b) Na(S₂CNMe₂). Sodium *NN*-dimethyldithiocarbamate was prepared by sodium amalgam reduction (2 h) of the dimer [Me₂NC(S)S]₂ (0.15 g, 0.7 mmol) in thf (10 cm³). The resultant solution was added to a stirred suspension of [Mo(NCMe)-(η²-MeC₂Me)₂(η-C₅H₅)][BF₄] (0.5 g, 1.26 mmol) in thf (10 cm³). An immediate colour change to green was observed. After 4 h at room temperature the solvent was removed *in vacuo*, and the toluene soluble material chromatographed on

Table 6. Bond lengths (Å) and angles (°) for (19)

Mo–S(1)	2.362(2)	Mo–C(8)	2.088(8)
Mo–C(9)	2.033(7)	Mo–C(11)	2.341(10)
Mo–C(12)	2.408(11)	Mo–C(13)	2.380(10)
Mo–C(14)	2.347(10)	Mo–C(15)	2.294(9)
Mo–C(01)	1.929(8)	S(1)–C(1)	1.777(9)
S(2)–C(2)	1.770(9)	S(2)–C(21)	1.763(8)
C(1)–C(2)	1.387(11)	C(1)–C(6)	1.384(12)
C(2)–C(3)	1.410(13)	C(3)–C(4)	1.380(13)
C(4)–C(5)	1.361(13)	C(5)–C(6)	1.386(13)
C(8)–C(7)	1.481(12)	C(8)–C(9)	1.271(12)
C(9)–C(10)	1.519(12)	C(11)–C(12)	1.375(15)
C(11)–C(15)	1.377(14)	C(12)–C(13)	1.333(19)
C(13)–C(14)	1.413(17)	C(14)–C(15)	1.367(15)
C(01)–O(01)	1.154(11)	C(21)–C(22)	1.400(12)
C(21)–C(26)	1.380(13)	C(22)–C(23)	1.366(14)
C(23)–C(24)	1.355(16)	C(24)–C(25)	1.374(14)
C(25)–C(26)	1.357(14)		

S(1)–Mo–C(8)	106.3(2)	S(1)–Mo–C(9)	109.0(2)
C(8)–Mo–C(9)	35.9(3)	S(1)–Mo–C(11)	100.6(3)
C(8)–Mo–C(11)	149.0(3)	C(9)–Mo–C(11)	143.1(3)
S(1)–Mo–C(12)	85.3(3)	C(8)–Mo–C(12)	161.5(4)
C(9)–Mo–C(12)	127.1(4)	C(11)–Mo–C(12)	33.6(4)
S(1)–Mo–C(13)	103.3(3)	C(8)–Mo–C(13)	129.2(4)
C(9)–Mo–C(13)	95.4(4)	C(11)–Mo–C(13)	55.8(4)
C(12)–Mo–C(13)	32.3(4)	S(1)–Mo–C(14)	137.7(3)
C(8)–Mo–C(14)	108.4(3)	C(9)–Mo–C(14)	86.7(3)
C(11)–Mo–C(14)	56.5(4)	C(12)–Mo–C(14)	55.6(4)
C(13)–Mo–C(14)	34.8(4)	S(1)–Mo–C(15)	135.2(3)
C(8)–Mo–C(15)	117.0(3)	C(9)–Mo–C(15)	112.5(3)
C(11)–Mo–C(15)	34.5(4)	C(12)–Mo–C(15)	56.4(4)
C(13)–Mo–C(15)	57.2(4)	C(14)–Mo–C(15)	34.2(4)
S(1)–Mo–C(01)	86.7(2)	C(8)–Mo–C(01)	71.9(3)
C(9)–Mo–C(01)	107.8(3)	C(11)–Mo–C(01)	95.1(3)
C(12)–Mo–C(01)	124.1(4)	C(13)–Mo–C(01)	150.3(4)
C(14)–Mo–C(01)	126.7(4)	C(15)–Mo–C(01)	96.0(3)
Mo–S(1)–C(1)	108.7(3)	C(2)–S(2)–C(21)	104.1(4)
S(1)–C(1)–C(2)	119.6(6)	S(1)–C(1)–C(6)	121.4(6)
C(2)–C(1)–C(6)	119.0(8)	S(2)–C(2)–C(1)	117.8(7)
S(2)–C(2)–C(3)	123.0(6)	C(1)–C(2)–C(3)	119.3(8)
C(2)–C(3)–C(4)	120.4(8)	C(3)–C(4)–C(5)	119.9(9)
C(4)–C(5)–C(6)	120.3(9)	C(1)–C(6)–C(5)	121.1(8)
Mo–C(8)–C(7)	148.3(6)	Mo–C(8)–C(9)	69.7(5)
C(7)–C(8)–C(9)	142.0(8)	Mo–C(9)–C(8)	74.4(5)
Mo–C(9)–C(10)	140.7(6)	C(8)–C(9)–C(10)	144.5(8)
Mo–C(11)–C(12)	75.9(6)	Mo–C(11)–C(15)	70.9(5)
C(12)–C(11)–C(15)	107.8(10)	Mo–C(12)–C(11)	70.5(6)
Mo–C(12)–C(13)	72.6(6)	C(11)–C(12)–C(13)	109.3(11)
Mo–C(13)–C(12)	75.0(6)	Mo–C(13)–C(14)	71.4(6)
C(12)–C(13)–C(14)	107.7(10)	Mo–C(14)–C(13)	73.9(6)
Mo–C(14)–C(15)	70.7(5)	C(13)–C(14)–C(15)	107.2(9)
Mo–C(15)–C(11)	74.6(6)	Mo–C(15)–C(14)	75.0(6)
C(11)–C(15)–C(14)	107.9(9)	Mo–C(01)–O(01)	175.5(7)
S(2)–C(21)–C(22)	120.4(7)	S(2)–C(21)–C(26)	121.8(6)
C(22)–C(21)–C(26)	117.5(8)	C(21)–C(22)–C(23)	121.5(9)
C(22)–C(23)–C(24)	119.7(9)	C(23)–C(24)–C(25)	119.6(9)
C(24)–C(25)–C(26)	121.4(10)	C(21)–C(26)–C(25)	120.2(9)

alumina. Elution with toluene afforded a air-sensitive green band, which on crystallisation (-78 °C) from toluene–hexane gave dark green *crystals* of (13) (0.20 g, 47%) (see Tables 1 and 2 for analytical and n.m.r. data).

(c) Na(SC$_6$H$_4$SPh-*o*). The dimer [SC$_6$H$_4$SPh-*o*]$_2$ (0.43 g, 1 mmol) was reduced (2 h) with Na/Hg (0.1 g Na in 8 cm^3 Hg) in thf (10 cm^3). The resultant solution of the anion [SC$_6$H$_4$-SPh-*o*]$^-$ was added dropwise with stirring to a suspension of [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] (0.77 g, 2 mmol) in thf (10 cm^3) at room temperature resulting in a rapid colour change to dark red. After 2 h the solvent was removed *in vacuo*

and the residue dissolved in toluene and chromatographed on alumina. Elution with toluene afforded a dark green, air-sensitive band, which was collected and crystallised from toluene–hexane to give dark green *crystals* of (17) (0.2 g, 23%) (see Tables 1 and 2 for data). Further elution with toluene gave a red band, which on crystallisation (-30 °C) from hexane gave red *crystals* of (15) (0.25 g, 26%) (Found: C, 61.5; H, 5.6. C$_{21}$H$_{26}$MoS$_2$ requires C, 61.7; H, 5.4%). N.m.r.: ^{1}H ([^{2}H$_6$]benzene, $+30$ °C): δ 7.6—6.7 (9 H, br m, Ph), 4.95 (5 H, s, C$_5$H$_5$), 2.44 (12 H, s, MeC≡C); ^{13}C-{^{1}H} ([^{2}H$_6$]benzene, $+30$ °C): δ 171.7 (s, MeC≡C), 149.5, 140.8, 137.0, 134.0, 131.5, 129.3, 127.3, 125.0, 122.2 (Ph), 99.9 (s, C$_5$H$_5$), and 16.9 p.p.m. (s, *Me*C≡C).

Similar reactions between [Mo(NCMe)(η^2-Bu^{t}C$_2$H)(η-C$_5$H$_5$)][BF$_4$] and Na(S$_2$CNMe$_2$) or Na(SC$_6$H$_4$SPh-*o*) afforded respectively (14) (data in Tables 1 and 2), (16) (27%) (Found: C, 64.1; H, 6.0. C$_{29}$H$_{34}$MoS$_2$ requires C, 64.2; H, 6.3%). N.m.r.: ^{1}H ([^{2}H$_6$]benzene, $+30$ °C): δ 9.32 (2 H, s, HC≡C), 7.70, 7.59, 7.56—6.88 (9 H, m, Ph), 5.05 (H, s, C$_5$H$_5$), 1.37 (18 H, s, Bu^{t}C≡C); ^{13}C-{^{1}H} (CD$_2$Cl$_2$, $+30$ °C): δ 161.7 (s, HC≡C), 148.0, 144.3, 136.2, 134.7, 133.6, 129.5, 127.7, 125.0, 124.3 (Ph), 99.2 (s, C$_5$H$_5$), 39.5 (s, Me$_3$CC≡C), and 31.1 p.p.m. (s, *Me*$_3$CC≡C); and (18) (Tables 1 and 2).

Synthesis of [Mo(SC$_6$H$_4$SPh-*o*)(CO)(η^2-MeC$_2$Me)(η-C$_5$H$_5$)] (19).—Carbon monoxide was bubbled (15 min) through a solution of (17) (0.5 g, 1.2 mmol) in toluene (20 cm^3). The colour changed from dark green to red-purple. The volume was reduced (2 cm^3) *in vacuo*, and the reaction mixture chromatographed on alumina. Elution with toluene gave a single purple band, which was collected. Recrystallisation (-30 °C) from hexane–diethyl ether (1 : 1) gave red purple *crystals* of (19) (analytical, i.r., and n.m.r. data listed in Tables 1 and 2).

Crystal Structure Determinations of (9) *and* (19).—A green crystal of (9) (dimensions 0.5 × 0.4 × 0.3 mm) obtained from a hexane recrystallisation was used for the *X*-ray structure analysis.

Crystal data for (9). C$_{16}$H$_{24}$MoNO$_5$PS, *M* = 470, monoclinic, *a* = 8.968(3), *b* = 20.104(9), *c* = 11.452(5) Å, β = 95.77(3)°, *U* = 2 054(2) Å^3 (by least-squares refinement on diffractometer angles for 15 centred reflections with 38 < 2θ < 44°), space group *P*2$_1$/*n* (alternative *P*2$_1$/*c*, no. 14), *Z* = 4, *D$_c$* = 1.41 g cm^{-3}, *F*(000) = 960, graphite-monochromated Mo-*K$_x$* *X*-radiation, λ = 0.710 69 Å, μ(Mo-*K$_x$*) 8.2 cm^{-1}, *T* = 200 K.

Intensity data were collected on a Nicolet P3m diffractometer at 200 K by θ/2θ scans of width (2.4 · Δx$_1$x$_2$)° for a unique quadrant of reciprocal space in the range 4 < 2θ < 60°. 4 605 Intensities were measured yielding 3 763 unique data of which 3 601 with *I* > 2σ(*I*) were used. The structure was solved by Patterson and difference-Fourier methods, all atoms being located directly. Blocked-cascade full-matrix least-squares refinement with all non-hydrogen atoms assigned anisotropic vibrational parameters and hydrogen atoms isotropic (in idealised geometries with C–H = 0.96 Å) converged to final residuals *R* 0.028, *R'* 0.032.* The chosen weighting scheme, *w* = [σ^2(*F$_o$*) + 0.0001*F$_o$*^{2}]$^{-1}$, gave a satisfactory analysis of variance with respect to |*F$_o$*|, sin θ, and |*h*|, |*k*|, |*l*|. The final-difference electron-density map showed no features > 0.7 or < -0.5 e Å^{-3}. Scattering factors, corrected for anomalous dispersion were taken from ref. 25, and programs of the SHELXTL package [26] on a Nicolet R3m/E structure determination facility were used throughout.

Crystal data for (19). C$_{22}$H$_{20}$MoOS$_2$, *M* = 460.4, orthor-

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* $R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

hombic, space group $P2_12_12_1$ (no. 19), $a = 9.852(3)$, $b = 11.486(4)$, $c = 18.476(6)$ Å, $U = 2091(1)$ Å³, $Z = 4$, $D_c = 1.46$ g cm⁻³, $F(000) = 936$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 8.1$ cm⁻¹.

The structure analysis of (19) proceeded as for (9) with the following exceptions. Intensity data were collected at 292 K on a purple-red crystal of dimensions 0.05 × 0.25 × 0.27 mm in the range $2.9 < 2\theta < 60°$, yielding 3 448 independent data of which 1 714 with $I > 2\sigma(I)$ were used. An absorption correction based on the indexed crystal faces was applied to all the data. Refinement as for (9) converged to final residuals R 0.059, R' 0.041 with weights $w = [\sigma^2(F_o) + 0.00005\ F_o^2]^{-1}$. A final-difference electron-density synthesis showed no features > 1.3 or < -0.7 e Å⁻³. The chirality of (19) in the particular crystal chosen was established by an η-refinement,[27] the value of the imaginary anomalous scattering component multiplier (η) refined to 1.4(3) establishing the choice of enantiomer depicted.

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