Dimolybdenum Complexes containing Bridging Silyl-substituted Acetylenes: Crystal and Molecular Structure of $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2]$ *

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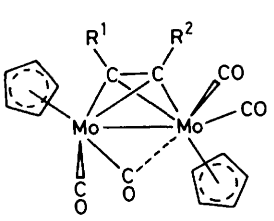
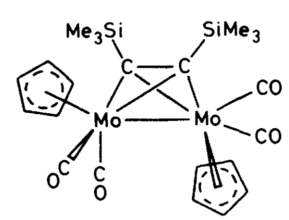
Reaction of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with the alkyne $Me_3SiC_2SiMe_3$ in toluene at reflux affords the complex $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2]$. In hexane, i.r. measurements reveal that the compound exists as an isomeric mixture, the species present having structures with or without semi-bridging CO ligands, in addition to terminally bonded CO groups. The simplicity of the n.m.r. spectra (^1H and ^{13}C) shows a rapid interconversion between isomers at room temperature, but low solubility of the complex prevented measurement of limiting spectra. The structure in the solid state was established by an *X*-ray diffraction study which shows that the molecule has C_2 symmetry in the crystal, and that the carbonyl ligands are all terminal. The alkyne ligand is bonded transversely with respect to the Mo–Mo bond [2.952(1) Å], forming a tetrahedrane type Mo_2C_2 core. The trimethylsilyl ligands bend back from the C–C bond at an angle of 137°. The $Mo(CO)_2(\eta\text{-}C_5H_5)$ moieties are in a skew (*trans*) relationship to the metal–metal bond; the actual configuration adopted in the crystal arises largely as a result of steric factors. Thus the structure in the solid is different from that established previously for compounds $[Mo_2(CO)_4(\mu\text{-alkyne})(\eta\text{-}C_5H_5)_2]$ which have been shown to have semi-bridging CO ligands. Reaction of $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ with an excess of the alkynes R_3SiC_2H (SiR_3 = $SiMePh_2$, $SiMe_3$, or $SiEt_3$) in octane at reflux affords the complexes $[Mo_2(CO)_4(\mu\text{-}R_3SiC_2H)(\eta\text{-}C_5H_5)_2]$. The spectroscopic properties of these compounds are in accord with structures containing a semi-bridging CO ligand. The compound $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2]$ reacts with $C_2(CO_2Me)_2$ to afford the complexes $[Mo_2(CO)_2\{C_6(SiMe_3)_2(CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ and $[Mo_2\{C_6(CO_2Me)_2(SiMe_3)_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$.

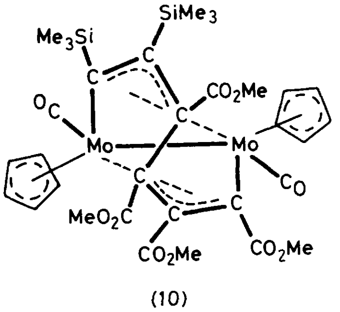
SEVERAL dimolybdenum complexes $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)(\eta\text{-}C_5H_5)_2]$ with bridging alkyne ligands are known, and *X*-ray diffraction studies[1] on those for which $R^1 = R^2 = H$ (1), Et (2), or Ph (3) have revealed the common unsymmetrical structure illustrated, containing a semi-bridging carbonyl group (s.b. CO). The i.r. spectra of all the complexes indicate that this structure is maintained in solution, with an absorption at *ca.* 1 850 cm^{-1} attributable to the s.b. CO. In the course of our studies[2] on the oligomerisation of alkynes at a dimolybdenum centre, several new complexes of this general type were synthesised. For compound (4), involving the bulky ligand bis(trimethylsilyl)acetylene, the i.r. spectrum suggested the presence of more than one structural form in solution. This paper describes an investigation of this phenomenon.



	R^1	R^2
(1)	H	H
(2)	Et	Et
(3)	Ph	Ph
(4a)	$SiMe_3$	$SiMe_3$
(5)	$SiMe_3$	Me
(6)	$SiMePh_2$	H
(7)	$SiMe_3$	H
(8)	$SiEt_3$	H
(9)	Me	H



(4b)



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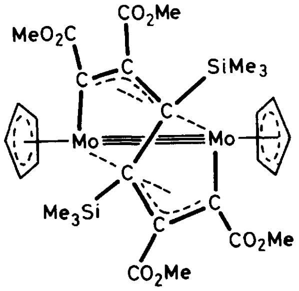

(11)

RESULTS AND DISCUSSION

Complexes $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)(\eta\text{-}C_5H_5)_2]$ are generally made by treating the formally triply metal–metal bonded species $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with the appropriate alkyne at room temperature.[1,2] This procedure affords $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2Me)(\eta\text{-}C_5H_5)_2]$ (5) in good yield. However, for the more sterically demanding alkyne $Me_3SiC_2SiMe_3$ we have found it necessary to heat the latter with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ at toluene reflux temperature in order to produce (4).

Monosilyl-substituted alkyne complexes $[Mo_2(CO)_4(\mu\text{-}R_3SiC_2H)(\eta\text{-}C_5H_5)_2]$ (6)—(8) are readily obtained by a different route. Heating (1) with an excess of R_3SiC_2H (R_3 = $MePh_2$, Me_3, or Et_3) at 100—125 °C affords

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* μ-Bis(trimethylsilyl)acetylene-tetracarbonylbis(η-cyclopentadienyl)dimolybdenum(*Mo–Mo*).

compounds (6)—(8) smoothly, in reactions which are reminiscent of the C-silylation of $[Co_3(\mu_3\text{-}CH)(CO)_9]$ when heated with silanes in toluene.[3] The greater availability of silanes R_3SiH compared with alkynes R_3SiC_2H makes this the favoured synthetic route for complexes of the type $[Mo_2(CO)_4(\mu\text{-}R_3SiC_2H)(\eta\text{-}C_5H_5)_2]$. No trace of a bis(silyl)-substituted product was observed in these reactions; neither was any product of formulation $[Mo_2(CO)_4(\mu\text{-}R_3SiC_2Me)(\eta\text{-}C_5H_5)_2]$ obtained on heating $[Mo_2(CO)_4(\mu\text{-}MeC_2H)(\eta\text{-}C_5H_5)_2]$ (9) with a silane R_3SiH. Conversely, desilylation of co-ordinated alkynes is achieved by treatment of (4) or (5) with either dilute sulphuric acid (electrophilic attack on the C–$SiMe_3$ bond) or ethanolic KOH (nucleophilic attack), generating (1) and (9) respectively, in quantitative yield.

The i.r. spectra of compounds (5)—(8) are entirely in accord with previous observations on molecules of this type; *i.e.* there are essentially three intense carbonyl absorptions, one of which occurs near 1 850 cm^{-1} and is characteristic of an s.b. CO. It thus appears that these new complexes adopt in solution the structure established previously,[1] and which is illustrated. The i.r. spectra of (1) and (5) are displayed in Figure 1. In comparison, the more complicated i.r. spectrum of (4) in solution is also shown. Although the spectrum still contains a pattern of carbonyl bands typical of the molecular structure (4a) containing an s.b. CO, there are additional, stronger bands, indicating the presence of an isomer with only terminal carbonyl ligands, *i.e.* (4b). Moreover, unlike (1)—(3) and (5)—(9), the complex (4) shows in its i.r. spectrum in the solid state no bands attributable to a bridging carbonyl. This led us to study the structure of (4) by *X*-ray diffraction.

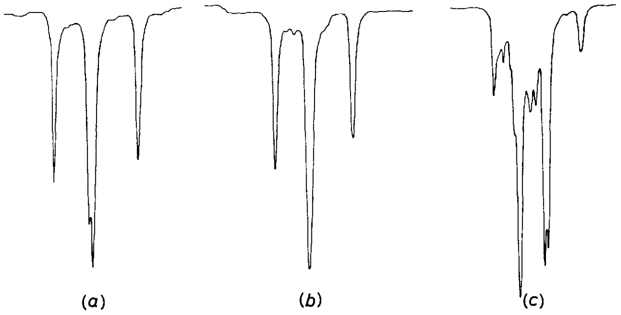


FIGURE 1 I.r. spectra (in hexane) of compounds (1) (*a*), (5) (*b*), and (4) (*c*) in the carbonyl stretching region

The molecular structure of (4) is shown in Figure 2, with the crystallographic numbering, and a stereoscopic view of the molecule is given in Figure 3. Atom co-ordinates are in Table 1, and relevant bond lengths and angles in Table 2. It is at once apparent that the molecular configuration (4b) is substantially correct and in particular that none of the carbonyl groups is semi-bridging. The whole molecule possesses (non-crystallographic) C_2 symmetry, the direction of the C_2 axis being the line joining the midpoints of C(18)–C(19) and Mo(1)–Mo(2). As expected, the trimethylsilyl groups bend away from the C≡C axis, symmetrically in relation to the metal–metal bond, at an angle of some 137°. The Si(1)–C(18)–C(19)–Si(2) chain is not quite planar, however, the torsion angle being 4.5°. The Mo_2C_2 quasi-tetrahedral core likewise shows a slight skewness in the bridge, the distances Mo(1)–C(18) and Mo(2)–C(19) being significantly longer than Mo(1)–C(19) and Mo(2)–C(18) (Table 2). The metal–metal bond itself, presumed to be of bond order 1, is of similar length [2.952(1) Å] to those found in other complexes containing a Mo_2C_2 core: *e.g.* $[Mo_2(CO)_4(\mu\text{-}C_2H_2)(\eta\text{-}C_5H_5)_2]$,[4] Mo–Mo 2.984(1) Å; $[Mo_2(CO)_4(\mu\text{-}C_2Et_2)(\eta\text{-}C_5H_5)_2]$,[5] Mo–Mo 2.977(1) Å; $[Mo_2(CO)_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]$ [for which two isomers exist,[6] a purple one with Mo–Mo 3.057(3) Å (mean of three crystallographically independent measurements) and an orange isomer with Mo–Mo 3.032(3) Å]; and $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$,[7] which has Mo–Mo 2.986 Å. These bond lengths are, however, markedly shorter than that found in $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$,[8] Mo–Mo 3.267(6) Å.

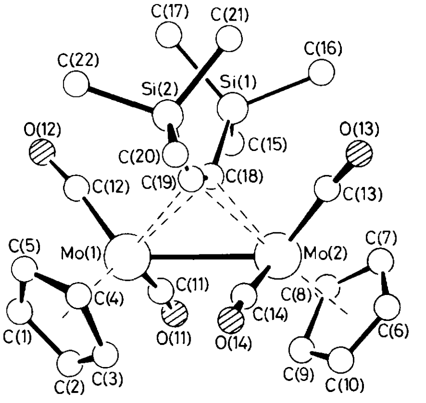
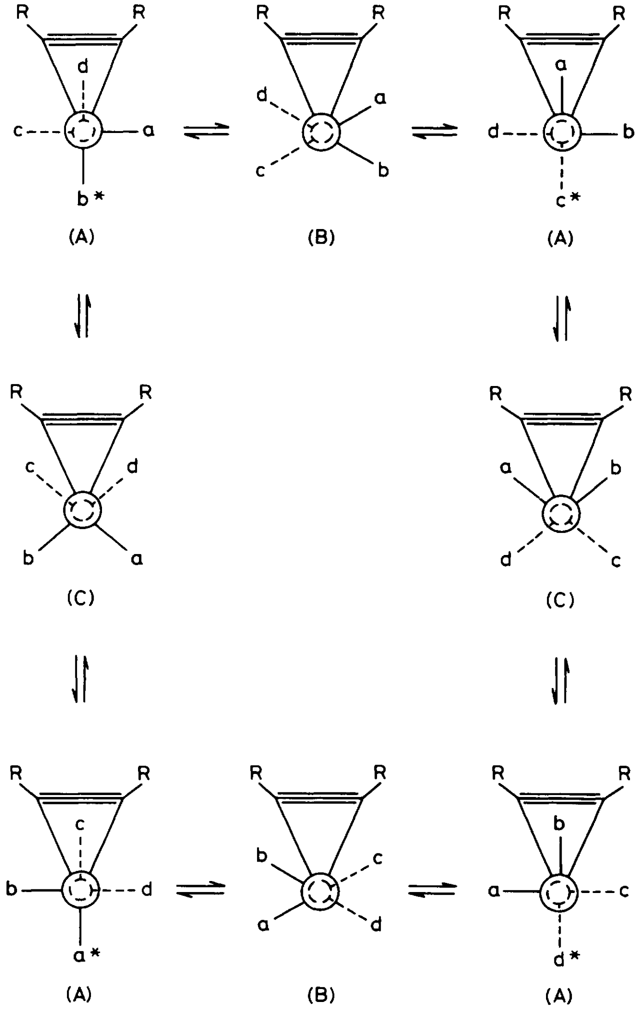


FIGURE 2 Molecular structure of $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2]$ (4) showing the crystallographic numbering

The two cyclopentadienyl rings lie *trans* to one another and are not axially related to the metal–metal bond (Figure 3). The two terminal carbonyl groups are mutually inclined at *ca.* 85°, but their orientation relative to the remainder of the molecule is undoubtedly determined by the disposition of the bulky trimethylsilyl groups on the bridging alkyne moiety. Atom C(20), for example, is approximately equidistant from atoms O(13) and O(14), while atom O(13) is in turn equidistant from both C(20) and C(21). Furthermore, the terminal carbonyl groups C(11)–O(11) and C(14)–O(14) are then positioned so that C(11) is approximately equidistant from C(1), C(2), C(8), and C(9), with C(14) similarly related to C(6), C(10), C(4), and C(3).

The i.r. spectrum of (4) in hexane establishes the existence of two, and possibly three, isomers in solution. One of these is clearly (4a), and the *X*-ray diffraction study indicates the non-carbonyl-bridged isomer in solution to be very probably of structure (4b). The simplicity of the n.m.r. spectra (^1H or ^{13}C) of (4), which have at room temperature single resonances for the CO and C_5H_5 ligands and trimethylsilyl substituents, reveals that these isomers interconvert rapidly in solution. Bailey *et al.*[1] have interpreted the variable-temperature n.m.r. spectra of the complexes $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)(\eta\text{-}C_5H_5)_2]$ in terms of a low-energy carbonyl exchange process which generates C_2 symmetry, and a higher energy process which, when operating in concert, produces C_{2v} symmetry. The effect for a symmetrically substituted alkyne is to generate one time-averaged CO environment at high temperature. Our observations lead further, and prompt us to propose that the dynamic behaviour of such complexes may be represented as in the Scheme, in which the isomer with an s.b. CO is denoted by (A) and that corresponding to structure (4b) by (B).



SCHEME a d indicate CO ligands, with an asterisk denoting an s.b. CO. The C_5H_5 ligands are omitted for clarity

The geometry about the Mo atoms in the isomers (A) and (B) can be regarded as approximately octahedral, with the alkyne and carbonyls occupying one site each and the C_5H_5 ligand, three. Thus the two idealised structures are related by 45° rotations of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ moiety about the two axes defined by the mid-point of the alkyne and each metal. We suggest that the low-energy, C_2-generating process is an (A) $\rightleftharpoons$ (B) isomerisation (top and bottom lines of Scheme); *i.e.* that a species of type (B) is an intermediate in the averaging process proposed by Bailey *et al.*[1] for the complexes which adopt isomeric form (A) preferentially. To produce overall C_{2v} symmetry the higher energy process must generate a mirror plane and it can be seen in the Scheme that this arises naturally in isomer (C) if the 45° rotations are continued. That this is a higher energy species than (A) or (B) is appreciated by inspection of molecular models, which show that in (C) a cyclopentadienyl ligand is brought into much closer contact with the substituents of the bridging alkyne than is the case within either (A) or (B). At high temperatures, when a (B) $\rightleftharpoons$ (A) $\rightleftharpoons$ (C) interconversion is occurring, a single time-averaged CO environment is therefore achieved, without any CO transfer between the metal atoms. Interaction between the cyclopentadienyl ligands and alkyne substituents is clearly lower in (B) than in an isomer of type (A), and appears the most likely cause of the stabilisation of the C_2 form for sterically demanding bis(trimethylsilyl)-acetylene.

Efforts to confirm these suggestions by recording the ^1H or ^{13}C n.m.r. spectra of (4b) at low temperatures have been frustrated by the insolubility of the complex below −40 °C. At that temperature the spectra were unchanged.

Like other μ-alkyne dimolybdenum complexes, compound (4) is capable of initiating linear oligomerisation of alkynes at octane reflux temperature. Reaction of (4) with dimethyl acetylenedicarboxylate under these conditions provides a low yield of spectroscopically identified $[Mo_2(CO)_2\{C_6(SiMe_3)_2(CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (10)

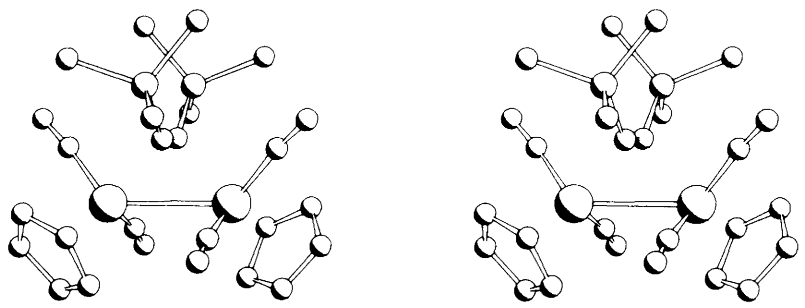


FIGURE 3 Stereoscopic view of compound (4)

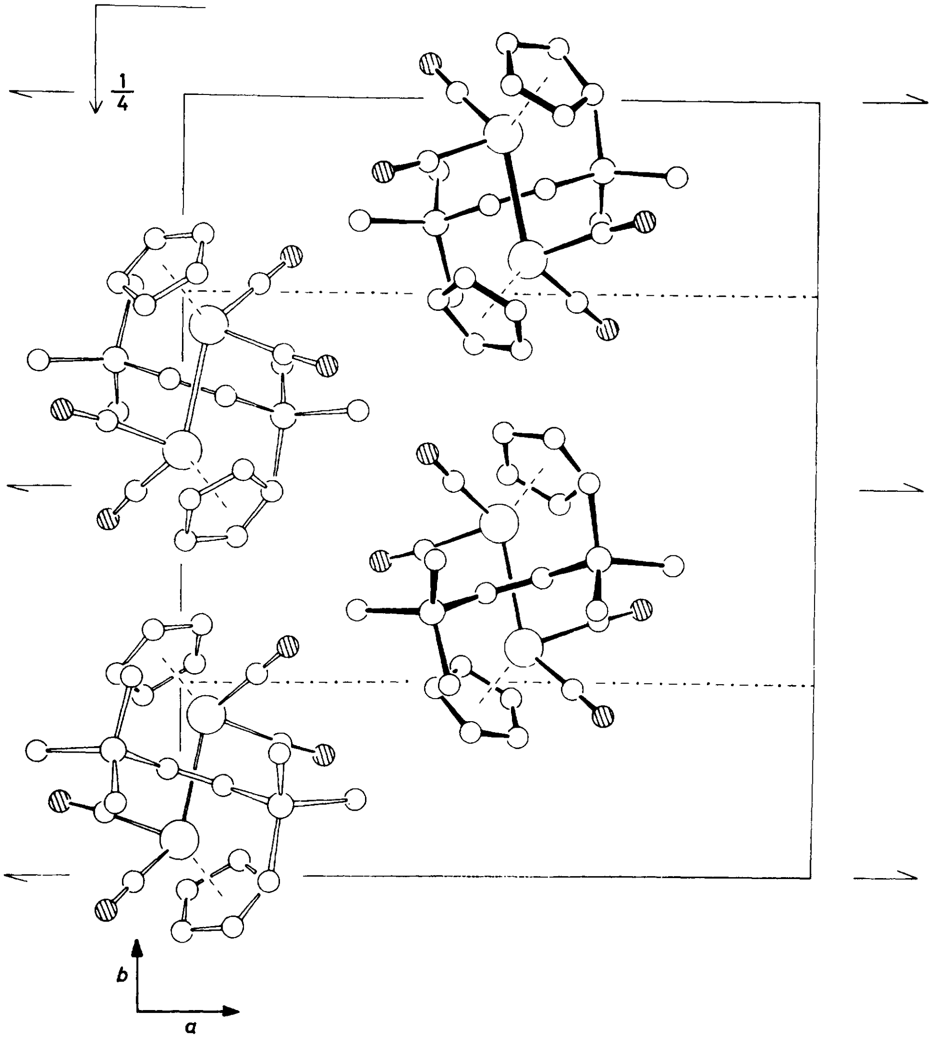


FIGURE 4 Orthorhombic unit cell of the crystal structure of (4) viewed down *c* looking towards the origin, space group symmetry $P2_1nb$ (non-standard setting of $Pna2_1$)

and a good yield of $[Mo_2\{C_6(CO_2Me)_2(SiMe_3)_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (11). Precedent for each species exists,[2] and it is particularly interesting to note that the sequence of alkyne linking reflects the presence or absence of carbonyl ligands at the dinuclear metal centre.

EXPERIMENTAL

General techniques and instrumentation were as described recently.[2,6] The complexes $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ (1) and $[Mo_2(CO)_4(\mu\text{-}MeC_2H)(\eta\text{-}C_5H_5)_2]$ (9) were prepared as previously reported.[2] All i.r. spectra were measured in hexane, and all n.m.r. spectra in $[^2H_1]$chloroform. Molecular weights were determined by mass spectrometry.

Preparation of $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2Me)(\eta\text{-}C_5H_5)_2]$ (5).—A toluene (150 cm^3) solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ was prepared by heating $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2 g, 4.08 mmol) at reflux for 16 h while purging with nitrogen. After cooling to room temperature, Me_3SiC_2Me (1.0 g, 8.9 mmol) was added, and the mixture stirred for 0.5 h. Evaporation of solvent, and chromatography of the residue on alumina, eluting with dichloromethane–hexane (3 : 7), gave a single maroon band from which maroon *crystals* of $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2Me)(\eta\text{-}C_5H_5)_2]$ (5) (1.19 g, 55%) were obtained, m.p. 70 °C (decomp.) (Found: C, 44.1; H, 4.2; *M*, 532. $C_{20}H_{22}Mo_2O_4Si$ requires C, 44.0; H, 4.0%; *M*, 532); $\nu_{max.}$ (CO) at 1 986m, 1 925s, and 1 848m cm^{-1}; n.m.r.: ^1H, τ 4.75 (s, 10 H, C_5H_5), 7.18 (s, 3 H, Me), and 9.88 (s, 9 H, SiMe); ^{13}C, δ 230.0 (CO), 117.4 (*C*Me), 91.1 (C_5H_5), 40.4 (*C*Si), 26.1 (Me), and 1.4 (SiMe) p.p.m.

Preparation of $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2]$ (4).—To a solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, prepared as above, was added $Me_3SiC_2SiMe_3$ (1.5 g, 8.8 mmol), and the mixture heated at reflux for 2 h. Chromatography, also as above, afforded a maroon band with dichloromethane–hexane (1 : 1) which contained 1.6 g (65%) of maroon *crystals* of $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2]$ (4), m.p. 170 °C (decomp.) (Found: C, 43.6; H, 4.6; *M*, 604. $C_{22}H_{28}Mo_2O_4Si_2$ requires C, 43.7; H, 4.6%; *M*, 604); $\nu_{max.}$(CO) at 1 994m, 1 984w, 1 976w, 1 958 (sh), 1 949s, 1 930m, 1 920w, 1 907s, 1 901s, and 1 840m cm^{-1}; n.m.r.: ^1H, τ 4.79 (s, 10 H, C_5H_5), and 9.71 (s, 18 H, Me); ^{13}C, δ 229.6 (CO), 88.4 (C_5H_5), and 3.2 (Me) p.p.m.

Preparation of $[Mo_2(CO)_4(\mu\text{-}R_3SiC_2H)(\eta\text{-}C_5H_5)_2]$ (R_3 =

$MePh_2$, Me_3, *or* Et_3).—(*a*) A mixture of [$Mo_2(CO)_4(\mu$-$HC_2H)(\eta$-$C_5H_5)_2$] (1) (1 g, 2.17 mmol) and $MePh_2SiH$ (2 g, 10.1 mmol) in octane (300 cm^3) was heated at reflux for 6 h. On evaporation of solvent and chromatography of the residue, elution with dichloromethane–hexane (1 : 9) gave a maroon band which afforded dark maroon *crystals* (0.67 g, 47%) of [$Mo_2(CO)_4(\mu$-$MePh_2SiC_2H)(\eta$-$C_5H_5)_2$] (6), m.p. 175—177 °C (Found: C, 52.6; H, 4.0; *M*, 656. $C_{29}H_{24}Mo_2O_4Si$ requires C, 53.0; H, 3.7%; *M*, 656); $\nu_{max.}$(CO) at 1 997m, 1 939 (sh), 1 925s, and 1 851m cm^{-1}; n.m.r.: ^1H, τ 2.41 (m, 4 H, Ph), 2.69 (m, 6 H, Ph), 3.49 (s, 1 H, CH), 4.95 (s, 10 H, C_5H_5), and 9.15 (s, 3 H, Me); ^{13}C, δ 138.5, 134.6, 129.0, 127.6 (Ph), 100.7 (CH), 90.1 (C_5H_5), 29.3 (*C*Si), and −1.8 (Me) p.p.m.

TABLE 1

Atomic positional co-ordinates (fractional cell co-ordinates) for [$Mo_2(CO)_4(\mu$-$Me_3SiC_2SiMe_3)(\eta$-$C_5H_5)_2$] (4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	0.006 9(5)	−0.070 7(2)	−0.087 2(5)
C(2)	0.013 1(4)	−0.017 5(3)	−0.200 1(5)
C(3)	0.095 3(4)	0.020 7(3)	−0.182 1(5)
C(4)	0.140 0(4)	−0.007 8(3)	−0.058 0(6)
C(5)	0.086 0(5)	−0.064 7(3)	0.000 4(6)
C(6)	0.032 2(5)	0.322 1(2)	−0.082 7(6)
C(7)	−0.042 4(6)	0.315 1(3)	0.009 6(7)
C(8)	−0.099 6(4)	0.257 4(3)	−0.044 9(7)
C(9)	−0.059 3(5)	0.229 9(3)	−0.172 0(6)
C(10)	0.021 8(4)	0.270 6(3)	−0.195 8(5)
C(11)	−0.117 3(4)	0.081 0(3)	−0.049 7(5)
C(12)	−0.071 4(4)	−0.008 2(3)	0.169 3(6)
C(13)	0.119 9(4)	0.258 7(3)	0.163 7(6)
C(14)	0.157 7(4)	0.169 7(3)	−0.058 6(6)
C(15)	−0.223 2(4)	0.159 0(4)	0.262 0(7)
C(16)	−0.077 4(4)	0.253 6(3)	0.407 8(5)
C(17)	−0.100 9(6)	0.093 1(4)	0.489 4(6)
C(18)	−0.020 1(3)	0.135 8(2)	0.191 6(5)
C(19)	0.068 4(3)	0.114 5(2)	0.187 7(4)
C(20)	0.275 4(4)	0.099 7(4)	0.236 4(8)
C(21)	0.156 3(5)	0.156 4(4)	0.481 4(6)
C(22)	0.143 1(5)	−0.006 9(3)	0.387 4(6)
Mo(1)	0.000 00 *	0.045 26(2)	0.023 47(3)
Mo(2)	0.041 45(3)	0.205 63(2)	0.023 37(3)
O(11)	−0.187 2(3)	0.094 3(2)	−0.097 1(5)
O(12)	−0.117 5(5)	−0.044 1(2)	0.246 9(5)
O(13)	0.167 2(6)	0.293 6(3)	0.234 8(7)
O(14)	0.225 0(3)	0.153 9(2)	−0.113 5(6)
Si(1)	−0.104 9(1)	0.160 0(1)	0.333 2(1)
Si(2)	0.159 0(1)	0.090 7(1)	0.320 0(1)

* The *x* co-ordinate of Mo(1) was arbitrarily fixed at zero.

(*b*) A sample of Me_3SiH (*ca.* 1 g, 13.5 mmol) was condensed at −196 °C onto a solution of [$Mo_2(CO)_4(\mu$-$HC_2H)(\eta$-$C_5H_5)_2$] (1) (0.5 g, 1.09 mmol) in octane (50 cm^3), and the mixture was then heated at 100 °C for 22 h in a sealed, evacuated glass tube. Chromatography of the resulting solution, eluting with dichloromethane–hexane (3 : 7), developed a maroon band affording dark maroon *crystals* of [$Mo_2(CO)_4(\mu$-$Me_3SiC_2H)(\mu$-$C_5H_5)_2$] (7) (0.23 g, 39%), m.p. 144—146 °C (Found: C, 41.4; H, 2.8; *M*, 532. $C_{19}H_{20}Mo_2O_4Si$ requires C, 41.0; H, 2.7%; *M*, 532); $\nu_{max.}$ (CO) at 1 995m, 1 935 (sh), 1 929s, and 1 849m cm^{-1}; ^1H n.m.r. τ 3.50 (s, 1 H, CH), 4.66 (s, 10 H, C_5H_5), and 9.16 (s, 9 H, Me).

(*c*) As in (*b*), Et_3SiH (*ca.* 1 g, 8.6 mmol) and [$Mo_2(CO)_4(\mu$-$HC_2H)(\eta$-$C_5H_5)_2$] (1) (0.4 g, 0.87 mmol) were heated in octane (50 cm^3) at 100 °C for 15 h. Chromatography, eluting with dichloromethane–hexane (1 : 9), gave maroon *crystals* of [$Mo_2(CO)_4(\mu$-$Et_3SiC_2H)(\eta$-$C_5H_5)_2$] (8) (82 mg, 21%), m.p. 121—123 °C (Found: C, 46.2; H, 4.7; *M*, 574. $C_{22}H_{26}Mo_2O_4Si$ requires C, 46.0; H, 4.5%; *M*, 574); $\nu_{max.}$(CO) at 1 992m, 1 924s, and 1 846m cm^{-1}; ^1H n.m.r.: τ 3.48 (s, 1 H, CH), 4.66 (s, 10 H, C_5H_5), and 9.25 (m, 15 H, Et).

Reaction of [$Mo_2(CO)_4(\mu$-$Me_3SiC_2SiMe_3)(\eta$-$C_5H_5)_2$] (4) *with*

TABLE 2

Bond distances (Å) and angles (°) for [$Mo_2(CO)_4(\mu$-Me_3SiC_2-$SiMe_3)(\eta$-$C_5H_5)_2$] (4), with estimated standard deviations in parentheses

(*i*) Distances

(*a*) Mo_2C_2 core			
Mo(1)–Mo(2)	2.952(1)	C(18)–C(19)	1.358(4)
Mo(1)–C(18)	2.263(4)	Mo(2)–C(18)	2.187(4)
Mo(1)–C(19)	2.199(4)	Mo(2)–C(19)	2.263(4)
(*b*) Carbonyl ligands			
Mo(1)–C(11)	1.962(5)	C(11)–O(11)	1.142(6)
Mo(1)–C(12)	1.955(5)	C(12)–O(12)	1.178(7)
Mo(2)–C(13)	1.976(5)	C(13)–O(13)	1.143(7)
Mo(2)–C(14)	1.978(5)	C(14)–O(14)	1.149(7)
(*c*) Alkyne ligand			
Si(1)–C(15)	1.862(6)	Si(2)–C(19)	1.854(4)
Si(1)–C(16)	1.863(5)	Si(2)–C(20)	1.885(6)
Si(1)–C(17)	1.873(6)	Si(2)–C(21)	1.896(5)
Si(1)–C(18)	1.854(4)	Si(2)–C(22)	1.878(5)
(*d*) Cyclopentadienyl rings			
C(1)–C(2)	1.414(7)	C(6)–C(7)	1.394(11)
C(2)–C(3)	1.401(8)	C(7)–C(8)	1.427(11)
C(3)–C(4)	1.412(8)	C(8)–C(9)	1.399(9)
C(4)–C(5)	1.403(9)	C(9)–C(10)	1.419(9)
C(5)–C(1)	1.419(9)	C(10)–C(6)	1.400(7)

(*ii*) Angles

C(5)–C(1)–C(2)	108.0(5)
C(1)–C(2)–C(3)	107.6(5)
C(2)–C(3)–C(4)	108.6(5)
C(3)–C(4)–C(5)	108.0(5)
C(4)–C(5)–C(1)	107.8(5)
Mo(1)–C(11)–O(11)	172.8(5)
Mo(1)–C(12)–O(12)	174.0(5)
Mo(2)–C(13)–O(13)	173.8(5)
Mo(2)–C(14)–O(14)	174.4(5)
C(11)–Mo(1)–C(12)	85.5(2)
C(12)–Mo(1)–C(18,19) [a]	86.1
C(18,19)–Mo(1)–C(11) [a]	99.6
C(15)–Si(1)–C(16)	109.9(3)
C(16)–Si(1)–C(17)	107.1(3)
C(17)–Si(1)–C(15)	106.9(4)
C(18)–Si(1)–C(15)	112.5(2)
C(18)–Si(1)–C(16)	108.9(2)
C(18)–Si(1)–C(17)	111.3(3)
C(10)–C(6)–C(7)	107.7(6)
C(6)–C(7)–C(8)	108.6(5)
C(7)–C(8)–C(9)	107.4(6)
C(8)–C(9)–C(10)	107.6(5)
C(9)–C(10)–C(6)	108.7(6)
Si(1)–C(18)–C(19)	137.0(4)
C(18)–C(19)–Si(2)	137.6(4)
Mo(1)–C(18,19)–Mo(2) [a]	88.0
C(13)–Mo(2)–C(14)	84.3(2)
C(14)–Mo(2)–C(18,19) [a]	99.2
C(18,19)–Mo(2)–C(13) [a]	86.2
C(20)–Si(2)–C(21)	106.4(3)
C(21)–Si(2)–C(22)	108.9(3)
C(22)–Si(2)–C(20)	109.2(3)
C(19)–Si(2)–C(20)	111.6(3)
C(19)–Si(2)–C(21)	110.6(2)
C(19)–Si(2)–C(22)	110.0(2)

TABLE 2 (*continued*)

(*iii*) Torsion angles [b]

I	J	K	L	*w*
Si(1)	C(18)	C(19)	Si(2)	4.5
C(11)	Mo(1)	Mo(2)	C(14)	−137.2
C(12)	Mo(1)	Mo(2)	C(13)	67.8

[a] C(18,19) is the midpoint of the C(18)–C(19) bond. [b] The torsion angle *w*(I J K L) is defined as the angle between the vector J I and the vector K L when viewed down J K. The sign of *w* is positive if J I is to be rotated clockwise into K L and negative if anticlockwise.

Dimethyl Acetylenedicarboxylate.—A mixture of (4) (0.5 g, 0.83 mmol) and $MeO_2CC_2CO_2Me$ (1.2 g, 8.45 mmol) was heated in octane (100 cm^3) at reflux for 3.5 h, giving a dark green solution. Chromatography on alumina, eluting with dichloromethane, gave a yellow band from which was obtained *crystals* of $[Mo_2(CO)_2\{C_6(SiMe_3)_2(CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ (10) (18 mg, 3%); $\nu_{max.}$(CO) at 1 967s and 1 930w cm^{-1}; ^1H n.m.r.: τ 4.88 (s, 5 H, C_5H_5), 5.00 (s, 5 H, C_5H_5), 6.27 (s, 3 H, CO_2Me), 6.32 (s, 3 H, CO_2Me), 6.40 (s, 6 H, CO_2Me), 9.64 (s, 9 H, MeSi), 9.76 (s, 9 H, MeSi). Further elution with dichloromethane afforded a green band which gave dark green *crystals* of $[Mo_2\{C_6(CO_2Me)_2(SiMe_3)_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (11) (0.36 g, 56%) (Found: C, 45.4; H, 5.1; *M*, 776. $C_{30}H_{40}Mo_2O_8Si_2$ requires C, 46.4; H, 5.1%; *M*, 776); n.m.r.: ^1H, τ 4.67 (s, 10 H, C_5H_5), 6.10 (s, 6 H, CO_2Me), 6.51 (s, 6 H, CO_2Me), and 9.78 (s, 18 H, MeSi); ^{13}C, δ 173.4, 166.2 (CO_2Me), 159.0, 98.6 (CCO_2Me), 93.7 (C_5H_5), 51.5, 50.4 (Me), and 1.9 (MeSi) p.p.m.

Crystal Structure Determination of $[Mo_2(CO)_4(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2]$ (4).—Crystals of (4) grow as large ruby rhombs which cleave readily to give samples of suitable size for diffraction studies. Intensities were collected on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 60°$; all of the 3 701 independent intensities measured were used in the final refinement. Two reflections (011 and 200) had intensities too strong for valid coincidence correction and these were omitted from the data set. Three check reflections were measured every 50 reflections and gave no indication of crystal decay. Scan rates varied between 0.048 8 and 0.488° s^{-1} proportionately as *I* varied between 150 and 1 500 counts in a 2-s pre-scan. Systematically absent reflections indicated either space group $Pna2_1$ (no. 33) or *Pnma* (no. 62); the former was established by the refinement. Corrections were made for Lorentz and polarisation, but not for *X*-ray absorption, effects.

Crystal data. $C_{22}H_{28}Mo_2O_4Si_2$, $M = 604.6$, Orthorhombic, $a = 14.729(6)$, $b = 18.011(4)$, $c = 9.172(2)$ Å, $U = 2\,433(1)$ Å^3, $D_m = 1.60$, $Z = 4$, $D_c = 1.65$ g cm^{-3}, $F(000) = 1\,216$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 10.4 cm^{-1}, space group $P2_1nb$ (non-standard setting of $Pna2_1$, no. 33).

The structure was solved using heavy-atom methods, and the origin of the unit cell was defined by fixing the *x* co-ordinate of Mo(1) at zero. The structure was refined with anisotropic thermal parameters for all non-hydrogen atoms. Positions of H atoms were calculated on a 'riding' model, with one isotropic thermal parameter for the cyclopentadienyl H atoms, and another for the methyl groups. Weights were optimised with $w = 0.033[\sigma^2(F) + 0.0006|F|^2]^{-1}$, and the 272-parameter model refined to convergence at *R* 0.033 (*R'* 0.032). A final electron-density difference synthesis showed no peaks >0.5 or < −1.0 e Å^{-3}. Atomic scattering factors were from ref. 9 for molybdenum, silicon, carbon, and oxygen, and from ref. 10 for hydrogen. Corrections for anomalous dispersion were applied for the molybdenum atoms only.[11] All computational work was carried out with the SHELX system of programs [12] on the ICL System 4 computers of the South Western Universities' Computer Network. Observed and calculated structure factors, hydrogen atom co-ordinates, and all thermal parameters are listed in Supplementary Publication No. SUP 23221 (24 pp.).*

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REFERENCES

[1] W. I. Bailey, M. H. Chisholm, F. A. Cotton, and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 5764, and refs. therein.

[2] S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 173; S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1978, 221.

[3] D. Seyferth and C. L. Nivert, *J. Am. Chem. Soc.*, 1977, **99**, 5209.

[4] W. I. Bailey, jun., F. A. Cotton, J. D. Jamerson, and J. R. Kolb, *J. Organomet. Chem.*, 1976, **121**, C23.

[5] W. I. Bailey, jun., D. M. Collins, and F. A. Cotton, *J. Organomet. Chem.*, 1977, **135**, C53.

[6] R. Goddard, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1976, 559; R. Goddard, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 147.

[7] S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1979, 934; M. Griffiths, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 159.

[8] M. R. Churchill and P. R. Bird, *Inorg. Chem.*, 1968, **7**, 1545.

[9] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

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

[11] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[12] G. M. Sheldrick, SHELX 76 system of programs for crystallographic computations, University of Cambridge, 1976.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.