Preparation and Studies of Paramagnetic Diene Complexes of Molybdenum(III); Molecular and Electronic Structures of $[MoCl_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ and $[Mo_3(\mu\text{-}Cl)(\mu_3\text{-}O)\{\mu_3\text{-}\sigma,\sigma:\eta^2:\eta^2\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_3]$†

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Reactions of complexes $[MoX\{\eta\text{-}C_2(CF_3)_2\}_2(\eta\text{-}C_5H_5)]$ with certain dienes give the paramagnetic complexes $[MoX_2(\eta\text{-diene})(\eta\text{-}C_5H_5)]$ [diene = 1,3-butadiene, X = Cl (**1a**), Br (**1b**), or I (**1c**); diene = isoprene, X = Cl (**2**); diene = *trans*-1,3-pentadiene, X = Cl (**3**)] characterised by elemental analysis, i.r. spectroscopy, and mass spectrometry. The structure of (**1a**), determined from 2 716 observed reflections measured at 185 K and refined to $R = 0.0367$ ($R' = 0.0532$), shows a molecule of near C_s symmetry. The cyclopentadienyl ligand is distorted from regular η^5 bonding by slippage of the Mo atom across the ring by 0.12 Å towards η^3 co-ordination. The 1,3-butadiene adopts a *cis-endo* configuration with internal C–C bonds shorter by 0.045 Å than terminal C–C bonds; the Mo–C bonds are shorter to terminal than to internal C atoms, and the butadiene is tilted away from a parallel geometry to assume a configuration with Mo which approaches a metallacyclopentene unit. Extended-Hückel molecular orbital (EHMO) calculations on complex (**1a**) are presented and confirm the stability of the *endo* conformation relative to the *exo* form (85 kJ mol^{-1}). A by-product in the formation of complex (**1a**) is $[Mo_3(\mu\text{-}Cl)(\mu_3\text{-}O)\{\mu_3\text{-}\sigma,\sigma:\eta^2:\eta^2\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_3]$, (**4**), which has been structurally characterised as its $0.5C_4H_6$ solvate by *X*-ray diffraction. The structure has been refined to $R = 0.0377$ ($R' = 0.0488$) using 4 215 data recorded at 185 K. A flattened isosceles triangle of metal atoms, base *ca.* 2.90 Å, base–apex *ca.* 2.58 Å, is face-capped by O and (open) edge-bridged by Cl. The $C_4(CF_3)_4$ unit is symmetrically bonded to the opposite Mo_3 face to the capping O atom, in a $2\sigma + 4\pi$ bonding mode. EHMO calculations suggest some multiple character for the base–apex Mo–Mo bonds, but little direct bonding between the basal atoms. Complex (**1a**) is interconverted with Tl(SR) into $[Mo(SR)_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ [R = C_6H_4Me-4 (**5a**) (72%) or C_6F_5 (**5b**) (15%)], characterised by analysis and spectroscopy. Cyclic voltammetric studies on complexes (**1a**), (**5a**), and (**5b**) establish a reversible reduction process in both tetrahydrofuran and dichloromethane, and also more complex oxidations. The most easily reduced complex is (**5b**), whereas (**5a**) is most readily oxidised. Complexes (**1**) and (**5**) all show e.s.r. spectra in solution with hyperfine coupling to $^{95,97}Mo$ and to ligand nuclei of $^{35,37}Cl$, $^{79,81}Br$, and diene terminal ^1H atoms. E.s.r. spectra of these complexes in frozen 2-methyltetrahydrofuran are also presented. The e.s.r. results are discussed in relation to the electronic structures of the complexes, especially the nature of the singly occupied molecular orbital, as determined by EHMO calculations on complex (**1a**).

Co-ordinatively unsaturated alkyne complexes of the type $[MoX(\eta\text{-}C_2R_2)_2(\eta\text{-}C_5H_5)]$ and corresponding tungsten(II) species have been the subjects of a number of studies. It has been established that such complexes undergo substitution reactions at ligand X,[1,2] to form binuclear complexes with alkyne-bridged metal–metal bonds[3] and are attacked at the co-ordinated alkynes to form η^2-vinyl groups[4] or a variety of other organic ligands.[1,4b] In all of these reactions the products are diamagnetic. In this paper we report the formation of paramagnetic products by reaction of some dienes with $[MoX\{\eta\text{-}C_2(CF_3)_2\}_2(\eta\text{-}C_5H_5)]$.

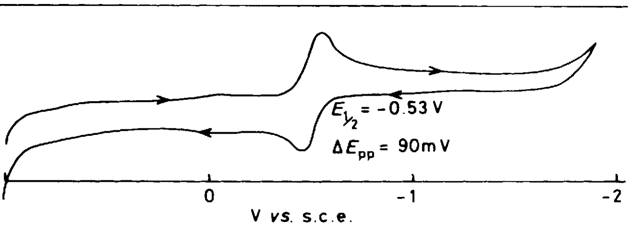

Figure 1. Cyclic voltammogram of complex (**1a**) in tetrahydrofuran, scan rate 0.05 V s^{-1}

Paramagnetic organometallics containing Mo^I (ref. 5) and Mo^V (ref. 6) have been investigated; also, molybdenum(III) complexes $[MoCl_2(PR_3)_2(\eta\text{-}C_5H_4Pr^i)]$[7] and $[Mo(\eta\text{-}C_3H_5)_2(\eta\text{-}C_5H_5)]$[8] have recently been described. The paramagnetic tungsten species $[WCl_2Me_2(\eta\text{-}C_5Me_4Bu^t)]$ and $[WCl_2(\eta\text{-}C_2Me_2)(\eta\text{-}C_5Me_4Bu^t)]$[9] are also of relevance to this work. Thus, one-electron redox chemistry may be expected in the chemistry of organometallic derivatives of molybdenum and species with unpaired electrons may play important roles in the reactivity of such derivatives.

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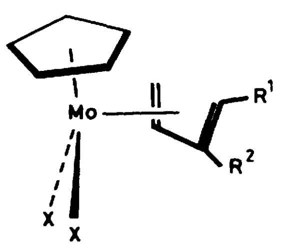
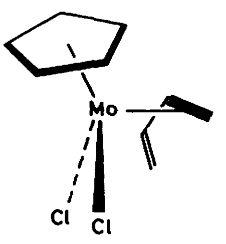
† (η-Buta-1,3-diene)dichloro(η-cyclopentadienyl)molybdenum(III) and 1,3-μ-chloro-1,2,3-tris(η-cyclopentadienyl)-μ_3-oxo-μ_3-[tetrakis(trifluoromethyl)buta-1′,3′-diene-1′,4′-diyl-$C^1(Mo^{1,2})C^2(Mo^1)C^3(Mo^3)$-$C^4(Mo^{2,3})$]-trimolybdenum (*Mo*^{1}–*Mo*^{2}, *Mo*^{2}–*Mo*^{3}).

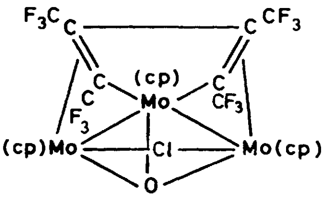
Supplementary data available (No. SUP 56530, 12 pp.): thermal parameters, H-atom co-ordinates, hydrogen-bonding contacts, least-squares planes, packing diagrams. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



(1a) X = Cl, $R^1 = R^2 = H$
(1b) X = Br, $R^1 = R^2 = H$
(1c) X = I, $R^1 = R^2 = H$
(2) X = Cl, $R^1 = H$, $R^2 = Me$
(3) X = Cl, $R^1 = Me$, $R^2 = H$
(5a) X = SC_6H_4Me-4, $R^1 = R^2 = H$
(5b) X = SC_6F_5, $R^1 = R^2 = H$



(1a′)



(4) cp = η-C_5H_5

Herein we report the characterisation and investigations of 17-electron complexes [MoX_2(η-diene)(η-C_5H_5)] (X = Cl, Br, I, SC_6H_4Me-4, or SC_6F_5; diene = 1,3-butadiene: X = Cl, diene = isoprene or *trans*-1,3-pentadiene).[10] The diamagnetic, 18-electron molybdenum(II) species [MoL(L′)(diene)(η-C_5H_5)]$^{n+}$ (*n* = 0 or 1) have been previously studied[11] and it may be noted that paramagnetic butadiene complexes of manganese, [MnL(η-C_4H_6)$_2$], are known.[12] The *X*-ray crystal structure of a by-product in the preparation of [$MoCl_2$(η-C_4H_6)(η-C_5H_5)], *i.e.* the trinuclear complex [Mo_3(μ-Cl)($μ_3$-O)\{$μ_3$-σ,σ:$η^2$:$η^2$-$C_4(CF_3)_4$\}(η-C_5H_5)$_3$], is also described in this paper.

Experimental

Reactions involving pressures above atmospheric were carried out in an evacuated glass tube fitted with a Westoff stopcock. Other reactions and operations were conducted under an atmosphere of dry, oxygen-free dinitrogen using Schlenk-type techniques. Solvents were freshly distilled under dinitrogen, after being dried by refluxing with drying agents as follows: hydrocarbons and diethyl ether with calcium hydride; tetrahydrofuran and 2-methyltetrahydrofuran with sodium diphenylketyl; dichloromethane with phosphorus pentoxide.

The complexes [$MoX(CF_3C_2CF_3)_2$(η-C_5H_5)] (X = Cl, Br, or I) were synthesised as previously described.[13] Dienes were commercial reagent-grade products (BOC, BDH, or Aldrich Chemicals) and were used as supplied. Thallium reagents, Tl(SR), were prepared by reaction between $Tl(O_2CMe)$ and RSH in methanol.

I.r. spectra were recorded using a Perkin-Elmer 580 spectrometer. Mass spectra (electron impact, e.i.) were obtained using a Vacuum Generators updated AEI MS9 instrument and field desorption (f.d.) spectra were recorded at the University of Tübingen, West Germany. Cyclic voltammetry was performed at platinum microelectrodes on solutions *ca.* 10^{-3} mol dm^{-3} in complex and 0.1 mol dm^{-3} in $NBu^n{}_4PF_6$ as supporting electrolyte, using a Princeton Applied 174A instrument at scan rates 0.02—0.1 V s^{-1} with no compensation for solution *IR* drop; in tetrahydrofuran an aqueous saturated calomel electrode (s.c.e.) connected *via* a bridge of 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ in tetrahydrofuran was employed as reference; in dichloromethane a pseudo-reference platinum wire was used. E.s.r. spectra were run on a JEOL PE1-X *X*-band spectrometer at various temperatures and were calibrated using diphenylpicrylhydrazyl and a Bruker ^{1}H n.m.r. magnetometer. Elemental analyses were performed by Butterworth Laboratories, Teddington, or by Analytische Laboratorien, Engelskirken, West Germany.

Preparation of Complexes.—[MoX_2(diene)(η-C_5H_5)] (X = Cl, Br, *or* I). (*a*) (**1a**; X = Cl, *diene* = 1,3-*butadiene*). In a manner similar to that previously reported,[1] [MoCl\{η-$C_2(CF_3)_2$\}$_2$(η-C_5H_5)] (0.2 g, 0.38 mmol) dissolved in diethyl ether (20 cm^3) in an evacuated tube was charged with an excess of 1,3-butadiene (2 cm^3, *ca.* 23 mmol). The closed tube was heated for periods between 15 and 40 h at 60 °C. Dark red-brown crystals of complex (**1a**) formed and these were washed with ether and dried *in vacuo* giving up to 40% yield (0.043 g). The product could be recrystallised from dichloromethane–hexane if desired (Found: C, 37.0; H, 3.9; Cl, 24.4. Calc.: C, 37.8; H, 3.8; Cl, 24.8%).

In one reaction complex (**1a**) was accompanied by small amounts of dark brown crystals (*ca.* 0.001 g) of complex (**4**) which could be separated from (**1a**) by hand.

(*b*) (**1b**; X = Br, *diene* = 1,3-*butadiene*). Under similar conditions to those of the above reaction, [MoBr\{η-$C_2(CF_3)_2$\}$_2$(η-C_5H_5)] (0.1 g, 0.18 mmol), butadiene (2 cm^3, *ca.* 23 mmol), and hexane (30 cm^3) were heated at 60 °C for 18 h. Dark brown crystals of complex (**1b**) formed and were collected, washed with hexane, and dried (yield *ca.* 20—25%) (Found: C, 28.1; H, 3.0. Calc.: C, 28.8; H, 2.9%).

(*c*) (**1c**; X = I, *diene* = 1,3-*butadiene*). The complex [MoI\{η-$C_2(CF_3)_2$\}$_2$(η-C_5H_5)] (0.2 g, 0.33 mmol), butadiene (2 cm^3, *ca.* 23 mmol), and hexane (20 cm^3) were heated at 60—70 °C for 18 h. Dark purple crystals of complex (**1c**) (*ca.* 10—15%) separated and were collected, washed with hexane, and dried *in vacuo*. (Found: C, 23.3; H, 2.5; I, 53.85. Calc.: C, 23.05; H, 2.4; I, 54.1%).

(*d*) (**2**; X = Cl, *diene* = *isoprene*). The complex [MoCl\{η-$C_2(CF_3)_2$\}$_2$(η-C_5H_5)] (0.1 g, 0.19 mmol), 2-methyl-1,3-butadiene (0.6 g, 8.8 mmol), and hexane (20 cm^3) were heated at 60 °C for 18 h. The brown product (**2**) was recovered as a solid and was recrystallised from dichloromethane–hexane (yield *ca.* 15%).

(*e*) (**3**; X = Cl, *diene* = trans-1,3-*pentadiene*). The complex [MoCl\{η-$C_2(CF_3)_2$\}$_2$(η-C_5H_5)] (0.14 g, 0.27 mmol), 1,3-pentadiene (1 g, 15 mmol), and hexane (20 cm^3) were heated at 60 °C for 18 h. The resulting brown solid was recrystallised from

Table 1. Fractional co-ordinates with standard deviations for complex (**1a**)

Atom	*x*	*y*	*z*
Mo	0.727 97(3)	0.264 01(2)	0.520 76(2)
Cl(1)	0.445 63(12)	0.224 49(9)	0.436 20(8)
Cl(2)	0.743 90(10)	0.407 30(8)	0.359 43(7)
C(1)	0.622 0(5)	0.251 3(4)	0.691 5(3)
C(2)	0.577 8(5)	0.370 4(4)	0.648 5(3)
C(3)	0.697 7(6)	0.448 4(4)	0.618 8(3)
C(4)	0.862 4(5)	0.407 2(4)	0.633 7(3)
C(5)	0.803 8(8)	0.063 3(5)	0.575 2(5)
C(6)	0.940 0(9)	0.140 1(7)	0.597 1(5)
C(7)	0.972 9(5)	0.183 5(5)	0.475 2(6)
C(8)	0.853 4(6)	0.126 5(4)	0.405 1(4)
C(9)	0.756 9(7)	0.056 9(4)	0.464 9(5)
H(11)	0.539(6)	0.189(5)	0.698(4)
H(12)	0.702(7)	0.236(4)	0.759(5)
H(21)	0.486(6)	0.386(5)	0.630(4)
H(31)	0.670(6)	0.526(4)	0.583(4)
H(41)	0.929(6)	0.456(5)	0.604(4)
H(42)	0.902(5)	0.363(4)	0.710(4)

dichloromethane to give brown crystals of (**3**) (0.023 g, 28%) (Found: C, 39.0; H, 4.2. Calc.: C, 40.1; H, 4.3%).

[Mo(SC_6H_4Me-4)$_2$(η-C_4H_6)(η-C_5H_5)] (**5a**). Complex (**1a**) (0.12 g, 0.42 mmol) and an excess of *p*-toluenethiolatothallium (0.5 g, 1.5 mmol) were stirred in tetrahydrofuran (20 cm^3) at room temperature for 16 h. The solution was filtered and tetrahydrofuran was evaporated from the filtrate under vacuum to leave the crude product contaminated with thallium salts. Extraction with dichloromethane, filtration, and reduction in volume of the filtrate gave deep blue-purple crystals of complex (**5a**) after addition of hexane and cooling. Yield 0.14 g (72%) (Found: C, 59.7; H, 5.3; S, 13.8. Calc.: C, 59.5; H, 5.4; S, 13.9%).

[Mo(SC_6F_5)$_2$(η-C_4H_6)(η-C_5H_5)] (**5b**). Complex (**1a**) (0.13 g, 0.45 mmol) was stirred with pentafluorobenzenethiolatothallium (0.363 g, 0.90 mmol) in tetrahydrofuran (20 cm^3) at room temperature for 16 h. The solution was filtered and evaporated to dryness *in vacuo*. The solid residue was extracted first with dichloromethane and the resulting red-purple solution filtered to remove most of the thallium by-products. This solution was again evaporated to dryness and the solid extracted with toluene to remove the more soluble red complex [MoTl(SC_6F_5)$_4$(η-C_5H_5)] (**6**). The purple solid residue was crystallised from dichloromethane to give complex (**5b**). Yield 0.041 g (15%) (Found: C, 41.6; H, 1.8. Calc.: C, 41.4; H, 2.3%).

Molecular Structure Determinations.—Single crystals of both complexes (**1a**) and (**4**) were mounted on glass fibres, and the space group and preliminary unit-cell dimensions were determined by oscillation and Weissenberg photography.

Crystal data. (**1a**), $C_9H_{11}Cl_2Mo$, M = 286.0, monoclinic, a = 8.148 0(20), b = 10.824(3), c = 11.505 9(25) Å, β = 96.304(20)°, U = 1 008.6 Å^3 (by least-squares refinement of 25 centred reflections, $11 < \theta < 12°$, $\bar{\lambda}$ =0.710 69 Å, at 185 K), space group $P2_1/n$ (alternative setting of $P2_1/c$, no. 14), Z = 4, D_c = 1.883 g cm^{-3}, $F(000)$ = 564, red-brown crystals, 0.45 × 0.35 × 0.10 mm, μ(Mo-$K_{\bar{\alpha}}$) = 17.42 cm^{-1}.

(**4**), $C_{23}H_{15}ClF_{12}Mo_3O{\cdot}0.5C_4H_6$, M = 885.5, monoclinic, a = 9.756 9(7), b = 17.440 8(20), c = 15.410 0(14) Å, β = 99.080(7)°, U = 2 589.4 Å^3 (by least-squares refinement of 25 centred reflections, $14 < \theta < 15°$, $\bar{\lambda}$ = 0.710 69 Å, at 185 K), space group $P2_1/n$, Z = 4, D_c = 2.271 g cm^{-3}, $F(000)$ = 1 708, dark brown crystals, 0.50 × 0.35 × 0.15 mm, μ(Mo-$K_{\bar{\alpha}}$) = 16.07 cm^{-1}.

Table 2. Fractional co-ordinates with standard deviations for complex (**4**)

Atom	*x*	*y*	*z*
Mo(1)	0.385 19(5)	0.156 96(3)	0.368 92(3)
Mo(2)	0.499 93(5)	0.080 62(3)	0.229 94(3)
Mo(3)	0.506 51(4)	0.226 85(3)	0.255 13(3)
Cl	0.376 02(15)	0.018 64(8)	0.338 11(9)
O	0.579 7(4)	0.141 61(22)	0.339 04(24)
C(1)	0.425 6(8)	0.243 3(5)	0.483 6(4)
C(2)	0.494 3(8)	0.176 9(5)	0.516 3(4)
C(3)	0.395 9(8)	0.118 0(5)	0.517 4(4)
C(4)	0.263 4(7)	0.150 0(4)	0.485 7(4)
C(5)	0.279 6(7)	0.226 9(4)	0.465 4(4)
C(6)	0.582 6(6)	0.031 4(4)	0.110 1(4)
C(7)	0.531 7(7)	−0.031 1(4)	0.154 1(4)
C(8)	0.620 9(7)	−0.037 8(4)	0.236 2(4)
C(9)	0.718 8(7)	0.019 0(4)	0.242 5(5)
C(10)	0.696 4(6)	0.065 6(4)	0.165 3(5)
C(11)	0.620 2(7)	0.338 4(4)	0.319 1(4)
C(12)	0.721 9(7)	0.290 3(4)	0.293 8(4)
C(13)	0.698 0(6)	0.283 6(4)	0.201 4(4)
C(14)	0.579 8(7)	0.328 2(4)	0.169 5(4)
C(15)	0.533 6(7)	0.362 8(4)	0.242 4(4)
C(16)	0.294 2(5)	0.233 9(3)	0.273 2(3)
C(17)	0.225 9(5)	0.160 5(3)	0.246 8(4)
C(18)	0.285 9(5)	0.120 3(3)	0.172 2(3)
C(19)	0.400 4(6)	0.164 5(3)	0.144 4(3)
C(20)	0.221 5(7)	0.309 9(4)	0.272 0(4)
C(21)	0.079 0(6)	0.144 8(4)	0.260 4(4)
C(22)	0.198 1(6)	0.068 4(3)	0.108 3(4)
C(23)	0.407 9(6)	0.188 7(4)	0.053 3(4)
C(24)	0.950 3(7)	0.021 5(4)	0.469 0(4)
C(25)	0.842 6(8)	0.058 0(5)	0.490 5(5)
F(1)	0.215 9(5)	0.344 67(22)	0.193 7(3)
F(2)	0.286 4(4)	0.358 90(20)	0.332 5(3)
F(3)	0.090 0(4)	0.308 8(3)	0.286 5(4)
F(4)	−0.015 7(4)	0.166 7(3)	0.191 8(3)
F(5)	0.042 2(4)	0.179 02(23)	0.331 41(25)
F(6)	0.053 5(4)	0.070 34(25)	0.273 1(3)
F(7)	0.269 3(4)	0.026 94(21)	0.057 79(22)
F(8)	0.104 3(4)	0.107 24(25)	0.051 0(3)
F(9)	0.125 5(5)	0.016 74(25)	0.145 0(3)
F(10)	0.538 9(4)	0.203 48(24)	0.040 24(23)
F(11)	0.360 4(4)	0.139 08(24)	−0.011 49(22)
F(12)	0.335 3(4)	0.253 73(23)	0.032 21(25)

Data collection and processing. For (**1a**): CAD4 diffractometer fitted with an ULT1 apparatus operating at 185 K, ω—2θ mode with ω scan width = 0.85 + 0.35 tan θ. Graphite-monochromated Mo-K_α X-radiation, 6 574 reflections measured ($1.0 \leqslant \theta \leqslant 30°$, $+h$ $+k$ $+l$ and $-h$ $-k$ $\pm l$), 2 944 unique data, merging R = 0.0381. Absorption correction (ψ scan at χ 90°) applied giving 2 716 data for which $F \geqslant 2\sigma(F)$. No detectable crystal decay or movement over 143 X-ray hours.

For (**4**): as for (**1a**) except 6 232 reflections measured ($1.0 \leqslant \theta \leqslant 22°$, $+h$ $+k$ $\pm l$), 5 650 unique data, not corrected for absorption, merging R = 0.0378, giving 4 125 amplitudes for which $F \geqslant 2\sigma(F)$. No detectable crystal decay or movement over 110 X-ray hours.

Structure solution and refinement. For (**1a**): solved by Patterson synthesis (Mo), with further non-H atoms located by subsequent Fourier difference maps. Full-matrix least-squares refinement with all non-hydrogen atoms allowed anisotropic thermal motion. Cyclopentadienyl hydrogens set in calculated positions whilst butadiene hydrogens positionally refined, U_{iso} for hydrogens fixed at 0.06 Å^2. The weighting scheme $w = 1/[\sigma^2(F) + 0.000\,424\,F^2]$ was satisfactory. R and R' = 0.0367

Table 3. Cyclic voltammetric redox data in tetrahydrofuran*

Complex	E_p^c	E_p^a	$\frac{1}{2}(E_p^a + E_p^c)$	ΔE_{pp}	i^c/i^a
(**1a**) $[MoCl_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$	−0.58	−0.49	−0.54	0.09	1.0
(**5a**) $[Mo(SC_6H_4Me\text{-}4)_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$	−0.65	−0.54	−0.60	0.11	0.95
(**5b**) $[Mo(SC_6F_5)_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$	−0.27	−0.17	−0.22	0.10	1.0

* At platinum microelectrodes: E_p^a and E_p^c are, respectively, the oxidation and reduction peak potentials in volts *vs.* s.c.e. at 22 °C; i^c and i^a, the cathodic and anodic peak currents; $[Fe(C_5H_5)_2]^+$–$[Fe(C_5H_5)_2]$ has $\frac{1}{2}(E_p^a + E_p^c) = 0.51$ V and $\Delta E_{pp} = 0.12$ V under the same conditions.

and 0.0532 respectively, $S = 1.232$;* maximum and minimum residues in final Fourier difference maps 1.21 and −0.87 e Å^{-3} respectively. Co-ordinates of refined atoms are given in Table 1.

For (**4**): solved by direct methods (Mo atoms) with further non-H atoms located in subsequent Fourier difference maps. Full-matrix least-squares refinement with all non-hydrogen atoms treated anisotropically. All hydrogen atoms set in calculated positions with $U_{iso} = 0.06$ Å^2. Weighting scheme $w = 1/[\sigma^2(F) + 0.001\,66\,F^2]$ applied. R and $R' = 0.0377$ and 0.0488 respectively, $S = 0.850$; maximum peak and minimum trough in ultimate ΔF synthesis 0.77 and −1.54 e Å^{-3} respectively. Table 2 lists co-ordinates of refined atoms.

Coefficients of analytical approximations for neutral atomic scattering factors from refs. 14 and 15. Computer programs: CADABS,[16] SHELX 76,[17] XANADU,[18] and ORTEP II.[19]

Results and Discussion

Synthesis and General Properties of Complexes.—Reaction of $[MoX\{\eta\text{-}C_2(CF_3)_2\}_2(\eta\text{-}C_5H_5)]$ (X = Cl, Br, or I) with 1,3-butadiene in diethyl ether or hexane at 60 °C leads to the formation of crystalline products $[MoX_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ [X = Cl (**1a**), Br (**1b**), or I (**1c**)] mostly in up to 40% yields. The other, easily separated, molybdenum-containing products of these reactions are amorphous solids, the nature of which has not been established. However, since the formation of the molybdenum(III) derivatives (**1**) requires redox disproportionation and halide transfer from $[MoX\{\eta\text{-}C_2(CF_3)_2\}_2(\eta\text{-}C_5H_5)]$, the maximum obtainable yield under the reaction conditions is 50%. Both co-ordinated alkyne ligands in the starting complexes are displaced in the reaction; this is unusual, since in most reported transformations of these complexes at least one alkyne or modified alkyne-containing fragment remains co-ordinated to molybdenum.[1–4] The dienes isoprene and *trans*-1,3-pentadiene react similarly to butadiene with $[MoCl\{\eta\text{-}C_2(CF_3)_2\}_2(\eta\text{-}C_5H_5)]$ to form $[MoCl_2(\eta\text{-diene})(\eta\text{-}C_5H_5)]$ [diene = isoprene (**2**) or 1,3-pentadiene (**3**)] whereas no reaction was observed between the same starting complex and the bulkier dienes *trans*-2-*trans*-4-hexadiene or 1,3-cyclohexadiene. These observations suggest that the reaction is subject to steric effects. A possible reaction pathway could involve the removal of co-ordinated alkyne by Diels–Alder cyclisation with diene; such a process would require an ordered transition state and be subject to steric restraint.

During the preparation of complex (**1a**) in diethyl ether a few crystals of a by-product, (**4**), were obtained. Since insufficient material was produced for normal characterisation procedures, the structure of this complex was determined by *X*-ray diffraction (see below). Complex (**4**), $[Mo_3(\mu\text{-}Cl)(\mu_3\text{-}O)\{\mu_3\text{-}\sigma,\sigma\text{:}\eta^2\text{:}\eta^2\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_3]$, crystallises with *trans*-1,3-butadiene in a 2:1 mol ratio but there is no interaction between the diene and the molybdenum centres. The bridging 1,3-diene-1,4-diyl ligand is derived from the originally co-ordinated alkyne ligands but the oxygen atom must be introduced from adventitious amounts of water or dioxygen, present in the reaction medium. Attempts to increase the yield of complex (**4**) by deliberately using wet ether as a solvent were unsuccessful.

The chloro-ligands of complex (**1a**) can be replaced by reaction with arylthiothallium reagents, Tl(SR), in tetrahydrofuran solution at ambient temperature. The paramagnetic product $[Mo(SR)_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ (**5a**; R = C_6H_4Me-4) is obtained in good yield but the analogous complex (**5b**; R = C_6F_5) is formed in smaller amounts and is accompanied by $[MoTl(SC_6F_5)_4(\eta\text{-}C_5H_5)]$ (**6**).[10] Complex (**6**) can be formed by reaction of (**5b**) with excess of $Tl(SC_6H_5)$ but is also produced during the preparation of (**5b**) using stoicheiometric quantities of reagents and it is possible that (**6**) is formed directly from (**1a**) under the reaction conditions.

Complexes (**1**)—(**3**) and (**5**) are paramagnetic and do not give n.m.r. spectra; e.s.r. spectra are discussed below. The i.r. spectra of (**1**) and (**5**) in the solid state show typical η^5-cyclopentadienyl vibrations. A band near 1 480 cm^{-1} [*i.e.* 1 480 (**1a**), 1 478 (**1b**), 1 477 (**1c**), and 1 483 cm^{-1} (**5a**)] may tentatively be assigned to the ν(C=C) vibration of co-ordinated butadiene, but if so, is virtually identical to that of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$.[20] For complex (**1a**), ν(Mo–Cl) vibrations occur at 301 and 270 cm^{-1}. Complexes (**1a**), (**1b**), (**1c**), (**2**), and (**3**) exhibit parent-ion peaks in their e.i. mass spectra and also fragment ions arising from loss of diene plus halogen; at higher probe temperatures, *e.g.* 150 °C for (**1c**), binuclear ions may be observed. In the presence of air, ions corresponding to $[MoX_2O(C_5H_5)]^+$ are also formed. E.i. mass spectra could not be obtained for complexes (**5**), but using the f.d. technique a mass spectrum of (**5b**) was recorded and this showed a parent ion.

Cyclic voltammetric studies of complexes $[MoX_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ [X = Cl (**1a**), SC_6H_4Me-4 (**5a**), or SC_6F_5 (**5b**)], in tetrahydrofuran show an essentially reversible reduction (see Table 3 and Figure 1); although the separations of the oxidation and reduction peaks are larger than predicted theoretically for a reversible process, no correction was made for *IR* drop in solution and the ferrocenium–ferrocene couple under these experimental conditions has similar characteristics to those of the butadiene complexes. The ease of reduction follows the order (**5b**) > (**1a**) > (**5a**), and this illustrates the significant effect of the different aryl group of ligand X = SR in (**5a**) and (**5b**). An irreversible reduction process ($E_p^c = -0.41$ V) is observed for complex (**1c**). In tetrahydrofuran, (**5a**) undergoes oxidative processes at low potentials, including a pseudo-reversible oxidation with $E_p^a = 0.38$ V, whereas, within the oxidation limit of the solvent system (*ca.* ⩽ +1 V), no well defined oxidations were observed for (**1a**) or (**5b**)

Cyclic voltammetry was carried out in dichloromethane using a platinum wire as pseudo-reference electrode and under these conditions reversible reductions are found at decreasing potentials for (**5b**) > (**5a**) > (**1a**) {*i.e.* $\frac{1}{2}(E_p^a + E_p^c) = -0.44$, −0.70, and −1.08 V, respectively; *cf.* 0.13 V for $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$}. Also, oxidation processes are observed in the order (**5a**) < (**5b**) < (**1a**) (E_p^a = 0.33, 0.67,

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* $S = [\Sigma w(F_o - F_c)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o = number of observations and N_v = number of variables.

Table 4. Interatomic distances (Å) and selected interbond angles (°) for complex (**1a**)

Mo–Cl(1)	2.435 2(10)	C(1)–H(12)	0.97(5)
Mo–Cl(2)	2.433 3(9)	C(2)–C(3)	1.364(5)
Mo–C(1)	2.236(4)	C(2)–H(21)	0.77(5)
Mo–C(2)	2.320(4)	C(3)–C(4)	1.406(6)
Mo–C(3)	2.319(4)	C(3)–H(31)	0.95(5)
Mo–C(4)	2.231(4)	C(4)–H(41)	0.86(5)
Mo–C(5)	2.326(6)	C(4)–H(42)	1.02(5)
Mo–C(6)	2.285(7)	C(5)–C(6)	1.388(9)
Mo–C(7)	2.291(6)	C(5)–C(9)	1.286(8)
Mo–C(8)	2.308(5)	C(6)–C(7)	1.530(9)
Mo–C(9)	2.351(6)	C(7)–C(8)	1.344(7)
C(1)–C(2)	1.413(5)	C(8)–C(9)	1.334(7)
C(1)–H(11)	0.96(5)		

Cl(1)–Mo–Cl(2)	86.24(3)	C(1)–C(2)–C(3)	119.4(4)
C(1)–Mo–C(2)	36.09(13)	H(21)–C(2)–C(3)	120.1(37)
C(1)–Mo–C(4)	75.11(15)	C(2)–C(3)–H(31)	120.7(28)
C(2)–Mo–C(3)	34.19(14)	C(2)–C(3)–C(4)	118.3(4)
C(3)–Mo–C(4)	35.94(15)	H(31)–C(3)–C(4)	120.8(28)
C(5)–Mo–C(6)	35.03(23)	C(3)–C(4)–H(41)	113.0(33)
C(5)–Mo–C(9)	31.92(20)	C(3)–C(4)–H(42)	117.3(26)
C(6)–Mo–C(7)	39.07(22)	H(41)–C(4)–H(42)	118.9(42)
C(7)–Mo–C(8)	33.98(18)	C(6)–C(5)–C(9)	110.8(6)
C(8)–Mo–C(9)	33.25(18)	C(5)–C(6)–C(7)	103.6(5)
H(11)–C(1)–H(12)	103.8(43)	C(6)–C(7)–C(8)	102.7(5)
H(11)–C(1)–C(2)	120.5(30)	C(7)–C(8)–C(9)	112.3(5)
H(12)–C(1)–C(2)	124.0(31)	C(5)–C(9)–C(8)	110.5(5)
C(1)–C(2)–H(21)	119.4(37)		

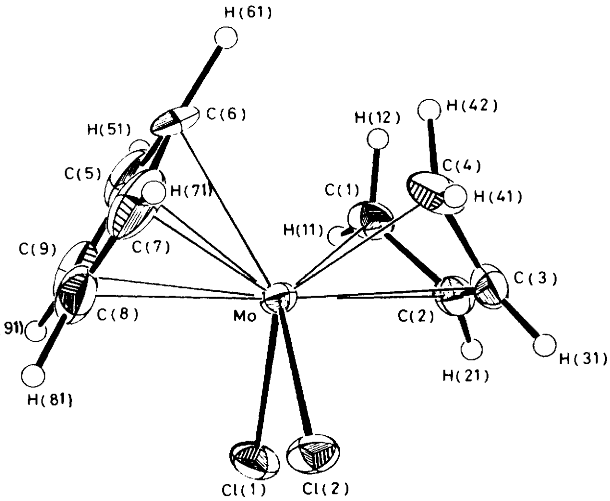

Figure 2. Perspective view of $[MoCl_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$, (**1a**), with thermal ellipsoids drawn at 50% probability level except for H atoms

and 0.75 V, respectively) with that for (**5a**) being essentially reversible (ΔE_{pp} = 0.10 V).

These 17-electron complexes appear to accept an electron reversibly but electron removal, except from complex (**5a**), appears to be an irreversible process under the conditions of these cyclic voltammetric studies (Scheme). In both tetrahydrofuran and dichloromethane, complex (**5b**; X = SC_6F_5) is the easiest to reduce and (**5a**; X = SC_6H_4Me-4) is most easily oxidised. The singly occupied molecular orbital (s.o.m.o.) in these complexes must, to some extent, involve the ligands X and the electron-withdrawing or -donating nature of aryl substituents on the sulphur ligands in complex (**5b**) or (**5a**), respectively, affects the redox processes.

$$[MoX_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)] + e \rightleftharpoons [MoX_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]^-$$

$$[MoX_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)] - e \longrightarrow [MoX_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]^+$$

$$\downarrow$$

further reaction

Scheme.

Molecular Structure of $[MoCl_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ (**1a**).—Figure 2 presents a perspective view of a single molecule of complex (**1a**) and the atomic numbering scheme. Table 4 lists interatomic distances and selected interbond angles. The complex has nearly C_s symmetry about the mirror plane that bisects the Cl–Mo–Cl angle. Only the ring deviates from this ideal to any significant degree (the magnitude of the thermal parameters of some of the cyclopentadienyl carbon atoms may additionally suggest rotational disorder).

The conformation of the co-ordinated *cis*-butadiene ligand to the $MoCl_2$ fragment is *endo*.[11] The same conformation is found in other $[MX_2(diene)(\eta\text{-}C_5H_5)]$ molecules, *e.g.* $[NbCl_2(C_4H_2Me_4)(\eta\text{-}C_5H_5)]$[21] and $[Mo(dppe)(C_6H_8)(\eta\text{-}C_5H_5)]PF_6$[22] (dppe = $Ph_2PCH_2CH_2PPh_2$), and, in addition, is that conformation of lowest potential energy as determined by semiempirical m.o. calculations (see below). Within the diene moiety the C–C (internal) bond length is shorter than the average C–C (terminal) length by 0.045(9) Å, a difference which is highly significant. This contrasts with the relative lengths in the free ligand,[23] 1.476 (internal) and 1.337 Å (terminal); in the majority of co-ordinated butadiene[24–26] fragments the C–C lengths are approximately equal. However, in contrast to the norm, the metal–carbon (terminal) bonds in complex (**1a**) are shorter than the metal–carbon (internal) due to tipping (30.7°) of the butadiene ligand out of a plane parallel to that of the $MoCl_2$ unit. This aspect of the structure is a feature of diene complexes tending towards a $2\sigma + \pi$ mode of bonding, and is reproduced by overlap populations calculated in a theoretical study [extended-Hückel molecular orbital (EHMO) calculations]; even in the parallel form [which requires distances Mo–C (terminal) > Mo–C (internal)] these show that the metal–carbon (terminal) overlap is considerably greater than metal–carbonal (internal). Upon tilting the butadiene in an idealised model to 30° we find the difference in C–C overlap populations is less than in the parallel geometry [1.0788 : 1.0291 (parallel) *vs.* 1.0908 : 1.0662 (tilted), terminal : internal]. Unfortunately, we do not find the reversal that would be consistent with the crystallographic results. However we believe that this reflects the fact that the model, using planar sp^2-type carbon atoms, is inappropriate. In the crystallographically determined structure none of the butadiene hydrogen atoms lies in the C_4 plane. Although the C–H bond distances determined by the *X*-ray method are notoriously inaccurate the trend in angular deviations from the plane is reliable. The four *syn* hydrogens [H(11), H(21), H(31), H(41)] are bent towards the metal by between 5 and 11° and those in the *anti* positions [H(12) and H(42)] bend away by 42 and 39° respectively. These compare well with the EHMO-calculated[26] values (18 for *syn* and 38° for *anti*) and with other structurally characterised butadienes.[26,27] This has been interpreted as (*a*) a twist about the terminal C–C bond and (*b*) significant sp^3 character of the peripheral carbon atoms. Both these effects would result in reduction of conjugation within the diene and lead to the relative C–C bond lengths observed.

Intramolecular steric interactions have little effect, the $H_{anti} \cdots H_{anti}$ contact being 2.24(7) Å and the three $H_{syn} \cdots H_{syn}$ contacts being 2.28(7), 2.24(7), and 2.23(6) Å (*cf.* the sum of van der Waals radii for H $\cdots$ H, 2.4 Å).

The Cl–M–Cl angle in complex (**1a**), 86.24(3)°, is significantly less than that in the 16-electron species $[NbCl_2(C_4H_2Me_4)(\eta\text{-}C_5H_5)]$.[21] This feature is readily explained by the fact that in (**1a**) the 17th electron occupies an orbital that is bonding

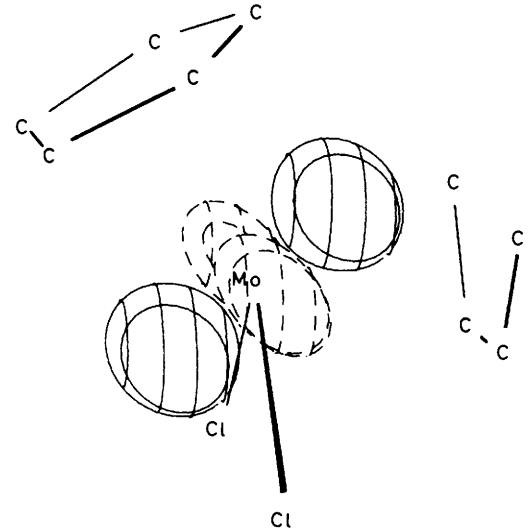

Figure 3. The s.o.m.o. of *endo*-(**1a**), calculated by the EHMO method

between the two chlorine atoms (see Figure 3). Thus in an analogous 18-electron compound such as $[ReCl_2(C_4H_6)(\eta\text{-}C_5H_5)]$ we would expect a further narrowing of Cl–M–Cl due to this orbital being fully occupied.

The cyclopentadienyl ring of (**1a**) is not symmetrically bound to the metal, C(5) and C(9) being furthest away and the C(5)–C(9) distance being the shortest of the C–C distances around the ring. Both these observations are consistent with a slippage of the ring towards a co-ordinated cyclic η^3-allyl fragment [C(6), C(7), C(8)] and a free ene [C(9)–C(5)] and is well documented for the η-C_5H_5 ligand.[28] Here the overall distortion corresponds to a slippage of the metal by *ca.* 0.12 Å across the face of the η-C_5H_5 ring. The C_5 ring is not planar [root mean square (r.m.s.) deviation = 0.0012 Å]. However the puckering does not readily correlate with either the overall C_s molecular symmetry or the slippage of the ligand, being of envelope conformation folded toward the metal about the C(9) • • • C(7) vector.

There are significant intermolecular hydrogen–chlorine contacts in the range 2.72—2.85 Å (sum of van der Waals radii = 3.0 Å) between molecules related by the inversion centre and by the *n*-glide.

Electronic Structure of $[MoCl_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ (**1a**).—In an attempt to determine whether the stereochemistry of complex (**1a**) is largely electronically controlled we have carried out EHMO calculations on an idealised model of $[MoCl_2(C_4H_6)(\eta\text{-}C_5H_5)]$ (C_s symmetry) using the parameters specified in Table 5.

The molecule may most conveniently be considered as a combination of $(\eta\text{-}C_5H_5)MoCl_2$ and C_4H_6 fragments. The frontier orbitals of this metal fragment have not been previously reported although those of the analogous moiety $(\eta\text{-}C_5H_5)Mo(CO)_2^+$ are well known.[29,30] On analysis the frontier orbitals of the two fragments are found to be similar, although in going from the dicarbonyl to the dihalide there is a marked destabilisation of the $1a'$, a'', and $2a'$ orbitals with an interchange in the order of a'' and $2a'$ as shown in Figure 4. In that the orbitals whose energies are most affected are those that are of appropriate orientation for π interaction with the ligands (CO or Cl) we interpret the qualitative features of Figure 4 as a simple consequence of the π-acceptor character of CO *vs.* the π-donor character of Cl. The π-ligand orbitals of C_4H_6 are well known, and are shown in Figure 5 labelled in only the C_s symmetry of the molecule for comparative purposes.

Table 5. Parameters used in EHMO calculations[a] (eV ≈ 1.60×10^{-19} J)

(*a*) Coefficients

Orbital		H_{ii}/eV	ζ_1	Orbital		H_{ii}/eV	ζ_1
Mo	$4d^b$	−10.50	4.54	C	2*s*	−21.40	1.625
	5*s*	−8.34	1.96		2*p*	−11.40	1.625
	5*p*	−5.24	1.92				
				O	2*s*	−32.30	2.275
Cl	3*s*	−30.00	2.033		2*p*	−14.80	2.275
	3*p*	−15.00	2.033				
	3*d*	−9.00	2.033	H	1*s*	−13.60	1.30

(*b*) Distances (Å) and angles (°)[c]

Mo–Z	2.02	Cl–Mo–Cl	90.0
Mo–Cl	2.43	Z–Mo–L	126.7
Mo–L	2.00	Cl–Mo–L	90.0
C–Z	1.21	C–C–C	120
C–C (C_4)	1.37	C_4 plane–$MoCl_2$ plane 0.0° unless otherwise stated[d]	
C–C (C_5)	1.4225		
C–H	1.09		

[a] All calculations were performed using the modified Wolfsberg–Helmholtz formula (J. H. Ammeter, H-B. Burgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686). [b] $\zeta_2 = 1.90$; $c_1 = c_2 = 0.589\,88$ (contraction coefficients used in the double-ζ expansion). [c] Z = Centroid of cyclopentadienyl ring, L = centre of gravity of C_4 fragment. [d] This is the 'parallel' form.

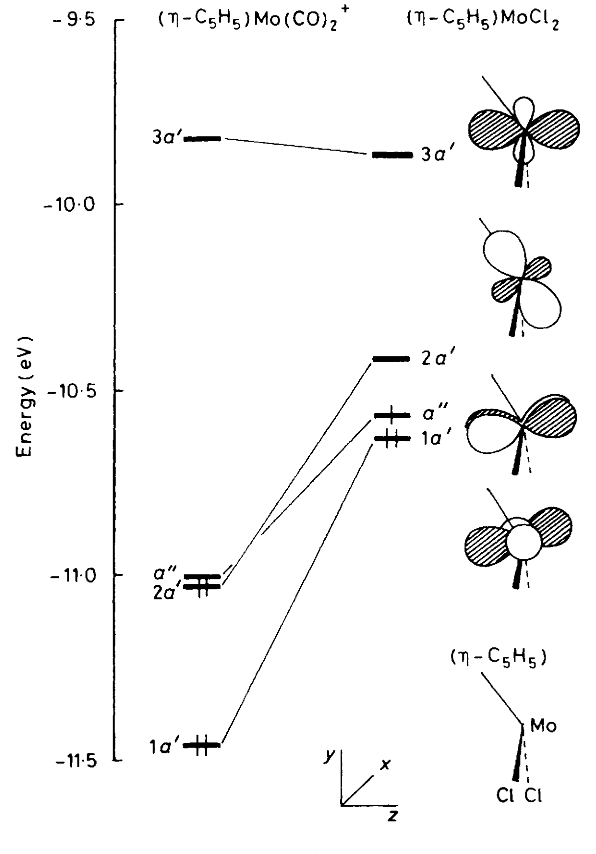

Figure 4. Relationship between the frontier orbitals of the $(\eta\text{-}C_5H_5)Mo(CO)_2^+$ fragment (left) and the $(\eta\text{-}C_5H_5)MoCl_2$ fragment (right)

An interaction diagram for both *endo* and *exo* conformations is shown in Figure 6. On the basis of this construction alone it is not possible to decide which limiting conformation would be energetically preferred and only scrutiny of the orbital overlaps, Table 6, gives an insight into the stereochemical preference.

Table 6. Orbital overlap

		Ligand			
		endo		*exo*	
	Metal	$1a''$	$2a''$	$1a''$	$2a''$
A'' Interactions	a''	0.1795	0.0470	0.1790	0.0713
		$1a'$	$2a'$	$1a'$	$2a'$
A' Interactions	$3a'$	0.1964	0.0529	0.1853	0.0348
	$2a'$	0.0113	0.1122	0.0987	0.0829
	$1a'$	0.0271	0.0120	0.0668	0.0784

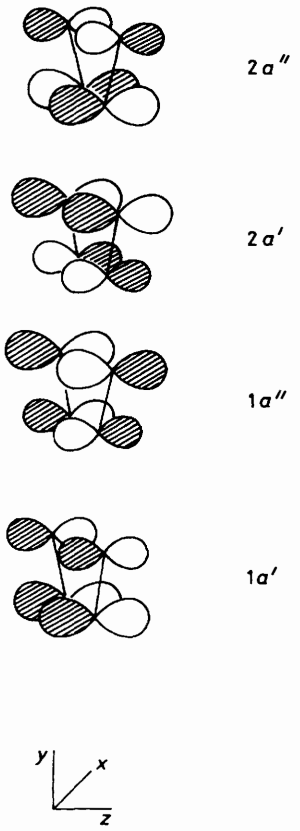

Figure 5. The π-m.o.s of *cis*-butadiene

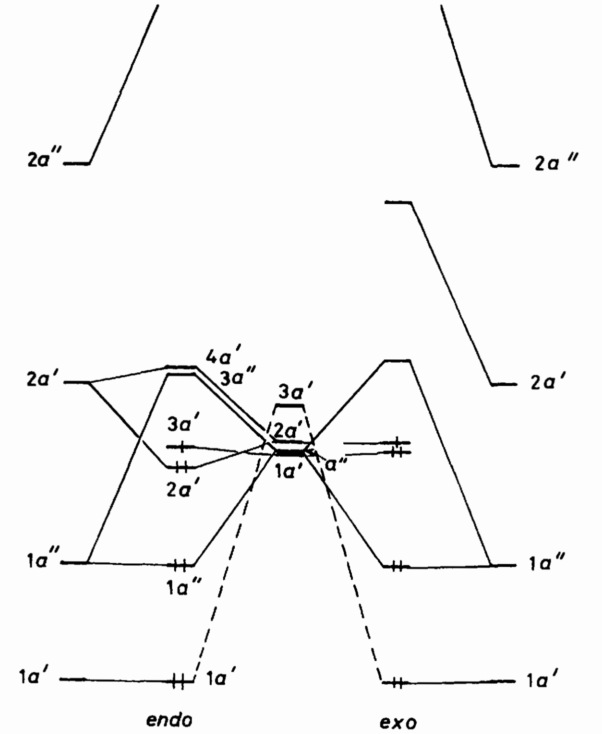

Figure 6. Interaction diagram for *endo*-(**1a**) (left) and *exo*-(**1a**) (right). The butadiene π orbitals are shown on both extremes, with the frontier m.o.s of the (η-C_5H_5)$MoCl_2$ fragment in the centre. The l.u.m.o.s. are not shown, for the sake of clarity

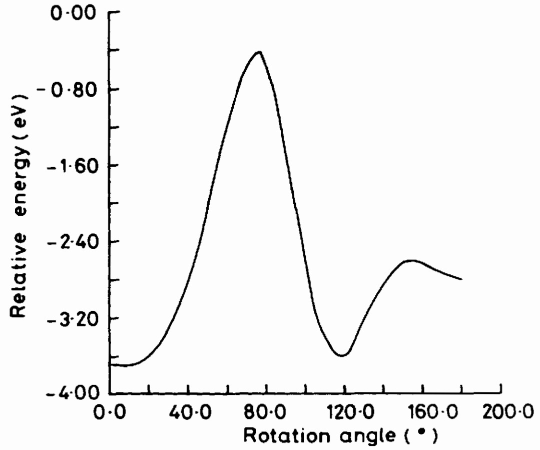

Figure 7. Energy profile for complex (**1a**) as a function of the rotation of the butadiene ligand about the z axis. The *endo* form corresponds to a rotation angle of 0° whilst the *exo* form is at 180°

From this Table it is apparent that the major interactions between the metal fragment and ligand are $3a'$–$1a'$, a''–$1a''$, and $2a'$–$2a'$. In the direction of the vacant co-ordination site the $3a'$ metal orbital is concentrated on the minus y side of the xz plane, and will therefore interact more strongly with the $1a'$ ligand orbital (the greater π components of which are on the internal carbons) when the molecule is in the *endo* conformation. Similarly the a'' metal orbital is concentrated to positive y of the xz plane and the $1a''$ ligand orbital is localised on the terminal carbon atoms, thus the interaction of these orbitals will also favour the *endo* conformation. The major lobes of the $2a'$ metal orbital are localised in the $\pm y$ directions, consistent with the relatively small metal–diene overlap in which it is involved, and we can only understand the greater magnitude of the $2a'$–$1a'$ interaction in the *exo* conformation if it is the minor lobe component of metal $2a'$ that has the greater influence in metal–ligand bonding in the z direction. This hypothesis is further consistent with the smaller difference in *exo vs. endo* overlap for $2a'$–$2a'$ given that the carbon atoms upon which the $2a'$ ligand orbital is localised [C(1) and C(4)] are relatively far apart.

A plot of relative energy *versus* θ, the clockwise angle of rigid rotation of the C_4H_6 ligand about the z axis (Figure 7*), confirms the preference for the *endo* conformation, stabilised by 85.42 kJ mol^{-1} with respect to the *exo* conformer. It also reveals an intermediate conformation, (**1a′**), almost as stable as the *endo* form (energy difference 7.46 kJ mol^{-1}) at $\theta = 120°$. This conformation corresponds to a 15-electron η^2-ethene complex,

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* The origin on the ordinate is chosen arbitrarily.

Table 7. Interatomic distances (Å) and angles (°) for complex (**4**)

Mo(1)–Mo(2)	2.893 0(7)	Mo(2)–C(9)	2.371(7)	C(4)–C(5)	1.391(10)	C(18)–C(19)	1.475(7)
Mo(1)–Mo(3)	2.572 3(7)	Mo(2)–C(10)	2.311(7)	C(6)–C(7)	1.415(9)	C(18)–C(22)	1.503(8)
Mo(1)–Cl	2.457 6(15)	Mo(2)–C(18)	2.246(5)	C(6)–C(10)	1.420(9)	C(19)–C(23)	1.479(8)
Mo(1)–O	2.040(4)	Mo(2)–C(19)	2.102(5)	C(7)–C(8)	1.422(9)	C(20)–F(1)	1.343(8)
Mo(1)–C(1)	2.308(8)	Mo(3)–O	2.025(4)	C(8)–C(9)	1.370(10)	C(20)–F(2)	1.346(8)
Mo(1)–C(2)	2.377(8)	Mo(3)–C(11)	2.375(7)	C(9)–C(10)	1.429(10)	C(20)–F(3)	1.337(8)
Mo(1)–C(3)	2.373(7)	Mo(3)–C(12)	2.366(7)	C(11)–C(12)	1.401(10)	C(21)–F(4)	1.345(8)
Mo(1)–C(4)	2.311(7)	Mo(3)–C(13)	2.376(7)	C(11)–C(15)	1.406(9)	C(21)–F(5)	1.344(7)
Mo(1)–C(5)	2.290(7)	Mo(3)–C(14)	2.382(6)	C(12)–C(13)	1.410(10)	C(21)–F(6)	1.343(7)
Mo(1)–C(16)	2.086(5)	Mo(3)–C(15)	2.398(7)	C(13)–C(14)	1.414(9)	C(22)–F(7)	1.335(7)
Mo(1)–C(17)	2.245(5)	Mo(3)–C(16)	2.137(5)	C(14)–C(15)	1.410(9)	C(22)–F(8)	1.349(7)
Mo(2)–Mo(3)	2.579 0(7)	Mo(3)–C(19)	2.147(5)	C(16)–C(17)	1.472(8)	C(22)–F(9)	1.327(7)
Mo(2)–Cl	2.458 6(15)	C(1)–C(2)	1.392(11)	C(16)–C(20)	1.502(8)	C(23)–F(10)	1.349(7)
Mo(2)–O	2.037(4)	C(1)–C(5)	1.436(10)	C(17)–C(18)	1.539(8)	C(23)–F(11)	1.347(7)
Mo(2)–C(6)	2.295(6)	C(2)–C(3)	1.407(11)	C(17)–C(21)	1.506(8)	C(23)–F(12)	1.350(7)
Mo(2)–C(7)	2.318(6)	C(3)–C(4)	1.422(10)			C(24)–C(25)	1.315(10)
Mo(2)–C(8)	2.374(7)					C(24)–C(24′)	1.458(13)

Mo(3)–Mo(1)–Cl	109.88(4)	C(11)–Mo(3)–C(12)	34.37(23)	C(11)–C(12)–C(13)	108.6(6)	C(17)–C(21)–F(5)	114.6(5)
Mo(3)–Mo(1)–O	50.49(11)	C(11)–Mo(3)–C(15)	34.25(22)	C(12)–C(13)–C(14)	107.5(6)	C(17)–C(21)–F(6)	113.4(5)
Cl–Mo(1)–O	80.47(11)	C(12)–Mo(3)–C(13)	34.60(23)	C(13)–C(14)–C(15)	107.7(6)	F(4)–C(21)–F(5)	106.0(5)
C(1)–Mo(1)–C(2)	34.5(3)	C(13)–Mo(3)–C(14)	34.57(22)	C(11)–C(15)–C(14)	108.3(6)	F(4)–C(21)–F(6)	105.6(5)
C(1)–Mo(1)–C(5)	36.4(3)	C(14)–Mo(3)–C(15)	34.30(22)	C(17)–C(16)–C(20)	124.9(5)	F(5)–C(21)–F(6)	103.4(5)
C(2)–Mo(1)–C(3)	34.5(3)	Mo(1)–Cl–Mo(2)	72.10(4)	C(16)–C(17)–C(18)	113.2(4)	C(18)–C(22)–F(7)	114.4(5)
C(3)–Mo(1)–C(4)	35.32(25)	Mo(1)–O–Mo(2)	90.39(15)	C(16)–C(17)–C(21)	121.2(5)	C(18)–C(22)–F(8)	112.6(5)
C(4)–Mo(1)–C(5)	35.19(25)	Mo(1)–O–Mo(3)	78.51(13)	C(18)–C(17)–C(21)	120.3(5)	C(18)–C(22)–F(9)	114.7(4)
C(16)–Mo(1)–C(17)	39.52(20)	Mo(2)–O–Mo(3)	78.82(13)	C(17)–C(18)–C(19)	112.0(4)	F(7)–C(22)–F(8)	104.6(5)
Mo(3)–Mo(2)–Cl	109.63(4)	C(2)–C(1)–C(5)	108.2(7)	C(17)–C(18)–C(22)	121.2(4)	F(7)–C(22)–F(9)	104.0(5)
Mo(3)–Mo(2)–O	50.38(11)	C(1)–C(2)–C(3)	108.7(7)	C(19)–C(18)–C(22)	120.3(5)	F(8)–C(22)–F(9)	105.6(5)
Cl–Mo(2)–O	80.49(11)	C(2)–C(3)–C(4)	107.2(6)	C(18)–C(19)–C(23)	125.3(5)	C(19)–C(23)–F(10)	112.7(5)
C(6)–Mo(2)–C(7)	35.71(22)	C(3)–C(4)–C(5)	109.0(6)	C(16)–C(20)–F(1)	111.2(5)	C(19)–C(23)–F(11)	117.2(5)
C(7)–Mo(2)–C(8)	35.26(23)	C(1)–C(5)–C(4)	107.0(6)	C(16)–C(20)–F(2)	112.4(5)	C(19)–C(23)–F(12)	111.4(5)
C(8)–Mo(2)–C(9)	33.56(24)	C(7)–C(6)–C(10)	109.7(6)	C(16)–C(20)–F(3)	116.6(5)	F(10)–C(23)–F(11)	103.7(5)
C(9)–Mo(2)–C(10)	35.52(25)	C(6)–C(7)–C(8)	106.1(6)	F(1)–C(20)–F(2)	106.5(5)	F(10)–C(23)–F(12)	106.1(5)
C(18)–Mo(2)–C(19)	39.48(19)	C(7)–C(8)–C(9)	109.0(6)	F(1)–C(20)–F(3)	104.6(5)	F(11)–C(23)–F(12)	104.8(5)
Mo(1)–Mo(3)–Mo(2)	68.334(19)	C(8)–C(9)–C(10)	109.8(6)	F(1)–C(20)–F(3)	104.6(5)	C(25)–C(24)–C(24′)	124.0(7)
Mo(1)–Mo(3)–O	51.01(11)	C(6)–C(10)–C(9)	105.2(6)	C(17)–C(21)–F(4)	112.9(5)		
Mo(2)–Mo(3)–O	50.80(11)	C(12)–C(11)–C(15)	107.8(6)				

structurally analogous to the [$M(CO)_2$(ethene)(η-C_5H_5)] complexes of which many examples are known.[31–33]

In (**1a′**) the co-ordinated ene function lies parallel to the *x* axis above the *xz* plane, and thus is bisected by the mirror plane of the metal fragment. The bonding in [$Mo(CO)_2$(ethene)(η-C_5H_5)]$^+$ complexes has already been discussed,[29] and, given the broad similarity between the frontier orbitals of (η-C_5H_5)$Mo(CO)_2{}^+$ and (η-C_5H_5)$MoCl_2$ fragments, it is likely that a similar description will apply here. Also apparent from the rotation–energy profile is the large barrier, *ca.* 313 kJ mol^{-1}, on both sides of the *endo* conformation which suggests that this geometry may be not only thermodynamically but also kinetically preferred. It must be remembered however that barriers calculated with a rigid-rotor model are often unrealistic (and generally over-estimated) because there is no allowance for any subtlety or complexity of the rotation process. Nevertheless, this high computed barrier to rotation of the butadiene ligand is not inconsistent with a mechanism for conformational (*endo* ⟷ *exo*) together with configurational (*syn* ⟷ *anti*) interconversion that involves not rotation but rather passage through a metallacyclopentene intermediate.[11]

In this context we would interpret the crystallographically determined structure of complex (**1a**), involving the tilted butadiene and short M–C (terminal) bonds, as representing significant passage along the reaction co-ordinate towards a $2\sigma + \pi$ bonding mode, in a manner analogous to that recently reported for a zirconium–diene complex.[34] The probability that the presence of π-donor halide ligands stabilises the high-oxidation-state intermediate involved may suggest that the potential barrier to the metallacyclopentene mechanism could be lower for (**1a**) than for [$Mo(CO)_2(C_4H_6)$(η-C_5H_5)]$^+$.

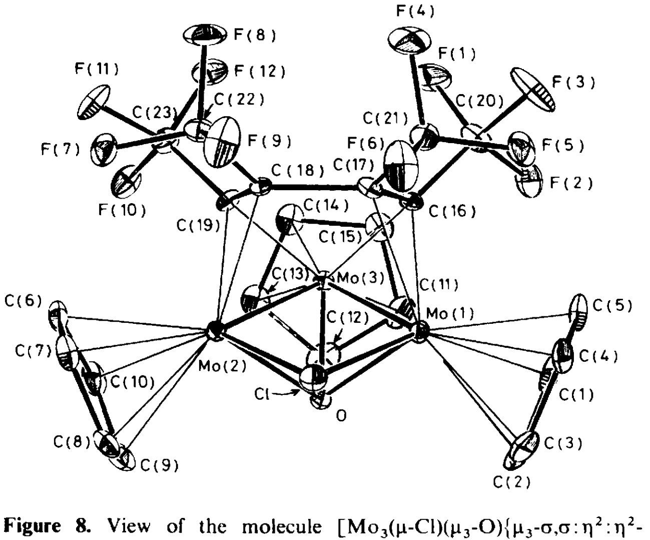

Figure 8. View of the molecule [$Mo_3(\mu\text{-}Cl)(\mu_3\text{-}O)\{\mu_3\text{-}\sigma,\sigma:\eta^2:\eta^2\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_3$], (**4**), with H atoms omitted

Molecular and Electronic Structure of [$Mo_3(\mu\text{-}Cl)(\mu_3\text{-}O)\{\mu\text{-}\sigma,\sigma:\eta^2:\eta^2\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_3$] (**4**).—Figure 8 presents a perspective view of a single molecule of complex (**4**) showing

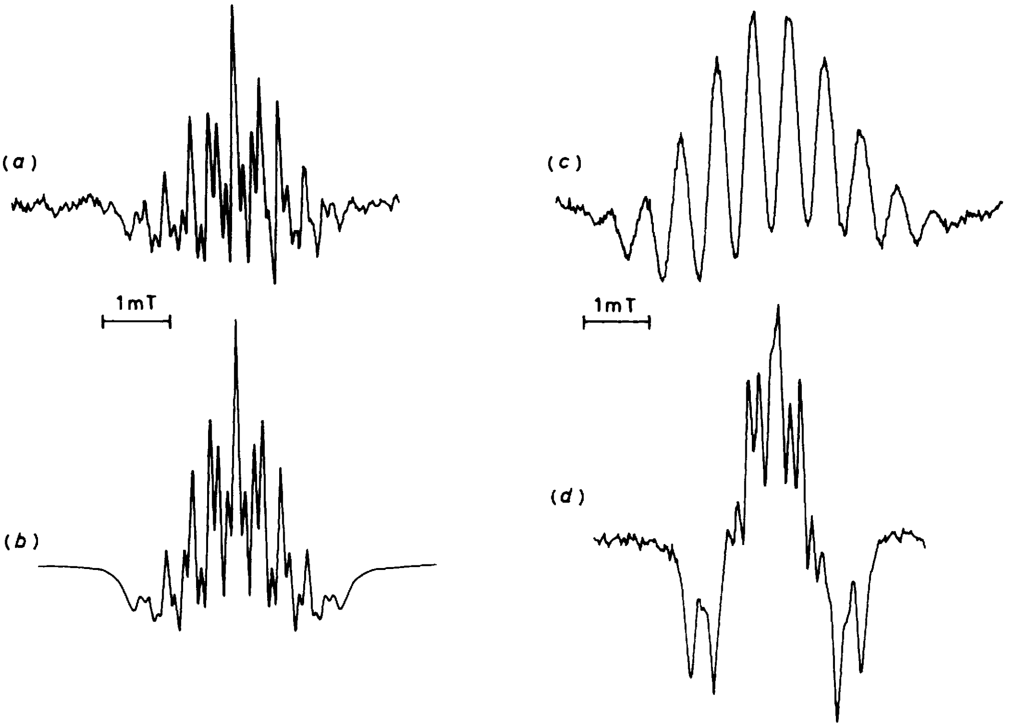

Figure 9. Central band (Mo, $I = 0$ isotopes) of second-derivative e.s.r. spectra in fluid 2-methyltetrahydrofuran with parameters and conditions as listed in Table 8: (*a*) and (*b*), respectively, experimental and simulated ($\Delta\omega = 0.2$ mT) for complex (**1a**); (*c*) (**1b**); (*d*) (**3**)

that the molecule has approximate C_s symmetry about a plane defined by Mo(3), C(12), Cl, and O. Internuclear distances and selected interbond angles are given in Table 7.

The molecule may be described as comprising a 'V' of molybdenum atoms whose open edge is bridged by Cl and one of whose faces is capped by O. On the opposite face lies a $(CF_3)_4C_4$ function, presumably formed by dimerisation of two hexafluorobut-2-yne molecules. Carbon atoms 16 and 19 of this ligand are σ-bonded to the central molybdenum forming a metallacyclopentadiene unit which π bonds to each of the outer metals. The co-ordination sphere of each molybdenum atom is completed by an η^5-cyclopentadienyl ligand.

Electron counting for this transition-metal cluster is an illuminating exercise, especially in respect of the consequent formal metal–metal bond orders. Critical to any such counting scheme is the correct identity of the face-bridging atom that we have described as oxygen. The crystal of complex (**4**) that was used in the structure determination was one of a small amount of material in a bulk sample of (**1a**). Deliberate attempts to synthesise (**4**) failed (see above). We identify the face-bridging atom as oxygen on the basis of many precedents[35,36] and the successful refinement, and assume that its origin was a trace of either moisture or O_2 in either the synthesis or work-up of (**1a**) or its precursor. We count μ_3-O as a four-electron donor to the cluster, in accord with 48-electron counts for established species such as $[\{(\eta\text{-}C_5H_5)(OC)_2Mo\}_3O]^+$[35] and $[Mo_3O_2(O_2CMe)_6(H_2O)_3]^{2+}$.[37] Chlorine is a source of three-electrons and the $(CF_3)_4C_4$ unit of six electrons ($2\sigma + 4\pi$). Counting five electrons for each $\eta\text{-}C_5H_5$ and six for Mo one arrives at a total count of 46 valence electrons, thereby requiring four metal–metal bonds if 18-electron configurations are to be achieved at each molybdenum.

In complex (**4**) there are two Mo–Mo distances [those to Mo(3)] of 2.57—2.58 Å, whilst Mo(1)–Mo(2) is much larger at 2.893 0(7) Å. Although all these lengths are well within the established range for metal–metal bonding, distance as the sole measure of the strength of an interaction is misleading in clusters of this type,[38,39] due to the stereochemical requirements of the bridging functions. In view of this we have performed an EHMO calculation on (**4**), using the crystallographic co-ordinates directly without structure idealisation, to probe the metal–metal interaction. We find overlap populations of 0.3029 and 0.3023 for Mo(1)–Mo(3) and Mo(2)–Mo(3) respectively, and only 0.0589 for Mo(1)–Mo(2). We interpret these figures in terms of *formal* Mo=Mo double bonds for the former and *no* bonding interaction for the latter.

The Mo–O distances [2.040(4) to Mo(1), 2.037(4) to Mo(2), and 2.025(4) Å to Mo(3)] are quite normal in a molecule of this type[35–38] and the Mo–O–Mo angles reflect the differing Mo–Mo distances, the widest being Mo(1)–O–Mo(2), 90.39(15)°, *cf.* 78.51(13) and 78.82(13)° for those involving Mo(3). The Mo–Cl distances [2.457 6(15) and 2.458 6(15) Å] and the Mo–Cl–Mo angle are less than those previously observed for chlorine bridging two non-bonded molybdenums[40] but probably simply represent a compromise between the demands (normal bond lengths and narrow angle or normal angle and short lengths) of a short Mo–Mo separation.

The tetrakis(trifluoromethyl)butadiene unit and Mo(3) form a 1-metallacyclopenta-2,4-diene whose alkene functions independently η^2 co-ordinate Mo(1) and Mo(2) at average distances of 2.094 Å [carbons adjacent to Mo(3)] and 2.245 Å [carbons not adjacent to Mo(3)]. As far as we are aware compound (**4**) represents the first example of a metallacyclopentadiene bridging two metal centres; there are numerous examples of η^5 co-ordination of these heterocycles to single metals.[41,42] The pattern of C–C distances within the co-ordinated metallacyclopentadiene is short–long–short, consistent with the trends observed in recently studied examples of cyclic or acyclic 1,3-dienes bridging dimetal centres[43,44] and in contrast to the sequence generally seen in 1,3-dienes co-ordinated to single metals, as already discussed. Because Mo(3) is symmetrically bound to Mo(1) and Mo(2) the metallacycle is required to

Table 8. E.s.r data for complexes in fluid 2-methyltetrahydrofuran[a]

Complex	θ_c/°C	g_{iso}[b]	$A_{iso}(^{95,97}Mo)$[c]	$A_{iso}(^1H)$[d]		A_{iso}(X)[e]
				syn	*anti*	
(**1a**) $[MoCl_2(\eta-C_4H_6)(\eta-C_5H_5)]$	−60	1.994	3.78	0.664	0.394	0.132
(**1b**) $[MoBr_2(\eta-C_4H_6)(\eta-C_5H_5)]$	−55	2.029	2.68	0.53	0.53	0.54
(**1c**) $[MoI_2(\eta-C_4H_6)(\eta-C_5H_5)]$	−55	2.085	3.3[f]		not resolved	
(**2**) $[MoCl_2(\eta-CH_2CHCMeCH_2)(\eta-C_5H_5)]$	0	1.995	3.86	0.66	0.39	0.13
(**3**) $[MoCl_2(\eta-MeCHCHCHCH_2)(\eta-C_5H_5)]$	−60	1.994	3.86	0.625	0.43/0.34	0.145
(**5a**) $[Mo(SC_6H_4Me\text{-}4)_2(\eta-C_4H_6)(\eta-C_5H_5)]$	r.t.	2.002	3.13	0.40	0.225	
(**5b**) $[Mo(SC_6F_5)_2(\eta-C_4H_6)(\eta-C_5H_5)]$	r.t.	2.004	3.35	0.66	0.66	

[a] A_{iso} values in mT. [b] Error ±0.001. [c] A_{iso}(Mo) ±0.02 mT. [d] $A_{iso}(^1H)$ for 1,4-^{1}H atoms of diene; error ±0.01 mT. [e] X = ^{35,37}Cl or ^{79,81}Br; error ± 0.01 mT. [f] Error ± 0.1 mT.

have an envelope conformation folded about the C(16) • • • C(19) vector by 38.9°. All trifluoromethyl groups pendant to the metallacycle bend away from the diene unit, those of C(20) and C(23) by *ca.* 42° and those of C(21) and C(22) by *ca.* 23°.

There are three significant intramoleculer F • • • F contacts F(3) • • • F(5) 2.433(6), F(6) • • • F(9) 2.387(6), and F(7) • • • F(11) 2.460(5) Å (*cf.* sum of van der Waals radii F • • • F, 2.7 Å), but no comparable intermolecular contacts.

Whilst the cyclopentadienyl ligand of Mo(3) is symmetrically bound (Table 7), those of Mo(1) and Mo(2) are slipped (by 0.096 and 0.104 Å respectively) such that carbon atoms 2 and 3 [Mo(1)] and 8 and 9 [Mo(2)] are furthest from the metal and more strongly bound to each other, this latter feature being particularly apparent in the latter example. All the C_5 rings are of shallow envelope conformations: C(1)—C(5) is bent towards Mo(1) about the C(2) • • • C(5) vector, C(6)—C(10) is bent away from Mo(2) about the C(7) • • • C(10) vector, whilst C(11)—C(15) bends away from Mo(3) about C(11) • • • C(14).

With regard to the *trans*-butadiene molecules of solvation, both C=C and C–C distances, 1.315(10) and 1.458(13) Å respectively, appear to be shorter (although not significantly so) than those determined by i.r., Raman, and electron-diffraction techniques,[23] although the relative difference is maintained. Furthermore, the C=C–C angle is slightly expanded to 124.0(7)°. One butadiene and several cyclopentadienyl hydrogen atoms are involved in hydrogen-bonding contacts with the fluorine atoms of the trifluoromethyl groups.

E.S.R. Spectra.—All the mononuclear diene complexes (**1**)—(**3**) and (**5**) have doublet electronic states and exhibit e.s.r. spectra both in solution at temperatures up to 100 °C and in frozen glasses of 2-methyltetrahydrofuran. The isotropic solution spectra display coupling to ^{95,97}Mo (I = 2.5, 25.18% natural abundance) and also superhyperfine coupling to ligand atoms. The latter is poorly resolved at ambient temperature for complexes (**1**)—(**3**); cooling to *ca.* −60 °C and recording in the second-derivative mode improved the resolution (Figure 9). The superhyperfine structure can be assigned with the aid of spectral simulation to coupling with ^{1}H atoms of the diene ligands and with ^{35,37}Cl or ^{79,81}Br, when present (Table 8 and Figures 9 and 10). Although the spectra do broaden at higher temperatures there is no clear evidence for fluxionality on the e.s.r. time-scale.

The isotropic g values are close to but vary from below to above 2.0023, the value for a free electron. This implies, in terms of perturbation theory, that the s.o.m.o. of the non-degenerate ground state may be mixed by spin–orbit coupling with empty and filled orbitals, respectively, in suitable excited states.[45] The relative importance of these opposing effects of spin–orbit coupling in the complexes depends on the nature of ligands X; since the larger values of g_{iso} are found in the order X = I > Br > SR > Cl, it is probable that the larger spin–orbit coupling constants of the higher-atomic-number donor atoms contribute to this variation.

Table 9. Composition of the frontier orbitals of *endo*-$[MoCl_2(\eta-C_4H_6)(\eta-C_5H_5)]$

Orbital	Percentage composition and breakdown
4*a*′	12% Mo ($d_{z^2} + d_{x^2-y^2}$); 34% Cl; 5% C(1), C(4)
3*a*″ (second l.u.m.o.)	24% Mo (d_{xz}); 25% Cl; 9% C(1), C(4)
2.*a*″ (l.u.m.o)	15% Mo ($d_{xy} + d_{xz}$); 40% Cl
3*a*′ (s.o.m.o.)	68% Mo ($-d_{x^2-y^2} + d_{z^2} + d_{yz}$); 13% Cl
2*a*′	47% Mo ($d_{x^2-y^2} + d_{yz}$); 10% Cl; 10% C(1), C(4); 5% C(2), C(3)
1*a*″	16% Mo (d_{xz}); 7% Cl; 16% C(1), C(4); 6% C(2), C(3)
1*a*′	5% Mo ($d_{z^2} + d_{yz}$); 14% Cl; 9% C(1), C(4); 19% C(2), C(3)

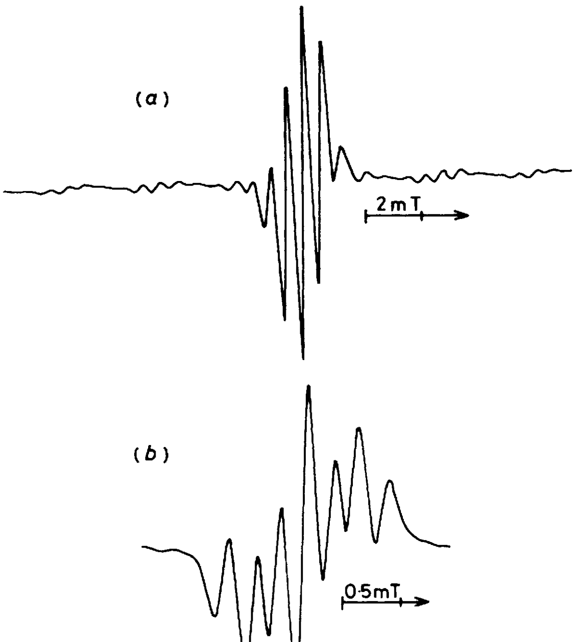

Figure 10. First-derivative e.s.r. spectra in fluid 2-methyltetrahydrofuran, with parameters and conditions as listed in Table 8: (*a*) complex (**5b**); (*b*) (**5a**) (central band only)

The compositions of the frontier orbitals of complex (**1a**) given by EHMO calculation are given in Table 9. From these

Table 10. E.s.r. data for complexes $[MoX_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ in frozen 2-methyltetrahydrofuran[a]

Complex	g_1	g_2	g_3	$\langle g \rangle$	A_1[b]	A_2[b]	A_3[b]	A_{iso}[c]
(**1a**; X = Cl)	1.977	1.999	2.006	1.994	58	29	(19)	35.2
(**1b**; X = Br)	2.05	1.995	(2.04)	(2.03)	51	25	(29)	34.9
(**1c**; X = I)	2.16	2.02	(2.08)	(2.09)	41	26	(29)	32
(**5a**; X = SC_6H_4Me-4)	2.011	2.001	1.994	2.002	47.4	(18)	24.2	29.4
(**5b**; X = SC_6F_5)	2.009	2.002	1.997	2.003	52	?	?	31.3

[a] Temperature *ca.* −140 °C; A values in units of 10^{-4} cm^{-1}; g and A values in parentheses calculated using $3g_{iso} = g_1 + g_2 + g_3$ or $3A_{iso} = A_1 + A_2 + A_3$. [b] Principal hyperfine coupling components to ^{95,97}Mo; error *ca.* $\pm 2 \times 10^{-4}$ cm^{-1}. [c] From solution, conditions as in Table 8.

calculations the orbitals with substantial metal d character which can interact with the s.o.m.o. are $3a''$ (and, to a lesser extent, the l.u.m.o. $2a''$ and $4a'$), which would reduce g below 2.0023 and $2a'$, which would increase g. In (**1a**) the former interaction appears to dominate; although the extent of mixing is inversely proportional to the energy separation of the states and the s.o.m.o. is closer in energy to $2a'$ than to the second lowest unoccupied molecular orbital (l.u.m.o.) ($3a''$), the nature of the second l.u.m.o. (largely Mo d_{xz}) favours spin–orbit coupling. For the other complexes, values of $g > 2.00$ imply that mixing with a filled orbital must become more favoured and if there is a significant ligand contribution to this orbital the higher spin–orbit coupling constants will enhance the effect of mixing. Assuming a qualitatively similar orbital scheme for all complexes, such an orbital could be $2a'$, or even $1a''$ if the relative energies of orbitals are changed (see also the discussion of e.s.r. glass spectra below).

The $A_{iso}(^{95,97}Mo)$ values are typical for doublet organometallic complexes which have substantial unpaired spin densities in a molybdenum d orbital; this is consistent with the EHMO analysis of complex (**1a**). There is a small but significant drop in A_{iso}(Mo) with change of ligand X in the order X = Cl > Br > I > SR and this may be attributed to more delocalisation of spin density onto the ligands. The difference in A_{iso}(Mo) for the thiolato complexes (**5**) (Table 8) must reflect the influence of the aryl group of the ligands SR.

The isotropic coupling to ligand atoms in the 1,3-butadiene complexes can be assigned to halogen [in (**1a**) and (**1b**)] and either four equivalent ^{1}H atoms [in (**1b**) and (**5b**)] or two equivalent pairs of ^{1}H atoms [in (**1a**) and (**5a**)]. Since the e.s.r. spectrum of the isoprene (2-methyl-1,3-butadiene) complex (**2**) is almost identical to that of (**1a**), whereas complex (**3**), containing the *trans*-1,3-pentadiene ligand, exhibits coupling to three inequivalent ^{1}H atoms, it may be concluded that only the terminal 1- and 4-^{1}H atoms of a diene ligand interact with the unpaired electron. Also, for complex (**3**) the largest A_{iso} value may be assigned to the unique *syn*-^{1}H and it is therefore likely that for (**1a**) and (**5a**) the larger $A_{iso}(^1H)$ value is similarly associated with the *syn*-^{1}H atoms, as assumed in Table 8. Coupling to ^{35,37}Cl in complexes (**1a**), (**2**), and (**3**) or to ^{79,81}Br in (**1b**) is small so that, although it may occur *via* p_π orbitals, electron delocalisation on to these ligands is slight (*cf.* ref. 6*b*).

That ligand coupling is observed only to halogen ligands and to the terminal ^{1}H atoms of the co-ordinated diene is consistent with the geometry of the s.o.m.o. determined by EHMO calculations (Figure 3); the unpaired spin density is located near these atoms, being able to interact with the nuclei by spin polarisation and/or by direct interaction with halogen p orbitals and C–H orbitals. The reason that $A_{iso}(^1H_{syn})$ is greater than $A_{iso}(^1H_{anti})$ in complexes (**1a**), (**2**), (**3**), and (**5a**) may be a consequence of the terminal C–H bonds moving out of the co-ordinated diene plane with the *syn*-^{1}H bending towards and the *anti*-^{1}H bending away from the metal, as observed in the crystal structure. This bending has previously been reported in diene complexes of cobalt.[26] In complexes (**1b**) and (**5b**) the equivalence of coupling to *anti*- and *syn*-hydrogens could be related to a different geometry of these terminal atoms or to a difference in the spatial distribution of the s.o.m.o. It is of interest that such isotropic coupling to ^{1}H atoms of co-ordinated dienes has not, to our knowledge, been previously observed (*cf.* ref. 12*b*).

The e.s.r. spectra of complexes (**1**) and (**5**) in frozen glasses of 2-methyltetrahydrofuran are not easy to analyse completely. Principal values of the g and $A(^{95,97}Mo)$ tensors are listed in Table 10; the values in parentheses are calculated by assuming the relationships to the isotropic values given in the footnotes. There is evidence for additional coupling to ^{79,81}Br ligands associated with components 2 and 3 in complex (**1b**). It is not possible to determine with certainty the orientation of components 1—3 of the g and A tensors from glass spectra but it is noted in all cases that two g values, g_2 and to a lesser extent g_3, are close to 2.002 and the other, g_1, varies significantly from below to above 2.002, in a similar manner to the g_{iso} values. The A_1 values associated with g_1 also show the greatest anisotropy in coupling to Mo. For complex (**1a**) this component is probably directed perpendicularly to the plane of the s.o.m.o. and, hence, is almost perpendicular to the cyclopentadienyl ring; this assignment gives $g_1 < 2.002$ mainly from spin–orbit coupling of the s.o.m.o. with the essentially coplanar second l.u.m.o. and gives a maximum value for anisotropic coupling to ^{95,97}Mo.

Assuming that the s.o.m.o.s of the other complexes (**1b**), (**1c**) and (**5**) are basically similar to that of (**1a**), the related g_1 components, which are >2.002, must arise from a spin–orbit coupling interaction that is predominantly with the filled $1a''$ molecular orbital. In this analysis axes of g_2 and g_3 lie in the plane of the s.o.m.o. and it may be noted that g_3 is affected more by spin–orbit coupling and shows more variation with change in ligand X than g_2. However, since $A_{aniso}(^{95,97}Mo)$ values $[A_{aniso(i)} = A_i - \langle A \rangle]$ fall with variation of X in the order X = Cl > SR > Br > I, there probably are significant differences in the compositions of the s.o.m.o.s of these complexes and such differences would be consistent with e.s.r. and electrochemical observations noted earlier and not inconsistent with the relatively small energy separations computed for (**1a**) (Figure 6). Nevertheless, such differences could also be explained in terms of variations in the contribution from the $2\sigma + \pi$ diene bonding mode, discussed earlier, resulting from changes in the ligands X*.

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* *Note added in proof.* After submission of this manuscript an important paper (H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa, and N. Kasai, *J. Am. Chem. Soc.*, 1985, **107**, 2410) has appeared in which the preparation, structural characterisation, and electronic structure of $[TaCl_2(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)]$ are reported. This 16-electron species has much in common with (**1a**), especially in that the overall molecular conformation is the same (and appears to be electronically controlled), and that there is a strong tendency towards $2\sigma + \pi$ diene-to-metal bonding.

Conclusions

The formation of paramagnetic diene complexes $[\mathrm{MoX_2(diene)(\eta\text{-}C_5H_5)}]$ by reaction of 1,3-dienes with bis(hexafluorobut-2-yne)molybdenum(II) complexes occurs for $X = Cl$, Br, and I and for several diene ligands. This synthetic reaction involves an interesting disproportionation of $\mathrm{Mo^{II}}$. With particular reference to complex (**1a**) ($X = Cl$, diene $= C_4H_6$) a structural determination has established a *cis-endo* configuration for the diene ligand, which, according to EHMO calculations, is a consequence of electronic control. Moreover, the diene bonding to the metal centre can be interpreted in terms of a substantial contribution from a $2\sigma + \pi$ mode. This interpretation is in clear accord with e.s.r. studies which reveal coupling to both chlorine atoms and, interestingly, inequivalent coupling to *anti*- and *syn*-terminal H atoms of the diene ligand.

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