In memory of T. A. Stephenson

Synthesis, Reactions, and Dynamic Nuclear Magnetic Resonance Studies of η^2-Vinyl Complexes of Molybdenum and Tungsten, $[M\{\eta^3\text{-}C(CF_3)C(CF_3)(L\text{–}L)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (L–L = $MeCO_2^-$, $Me_2PS_2^-$, $Et_2NCS_2^-$, or $Me_2NCS_2^-$)

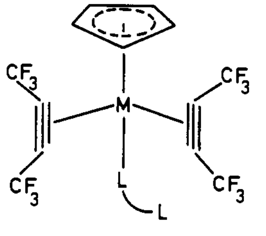
Jack L. Davidson
Heriot-Watt University, Riccarton, Currie, Edinburgh RH14 4AS

Reactions of bis(hexafluorobut-2-yne) complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with anions L–L = $MeCO_2^-$, $Me_2PS_2^-$, and $R_2NCS_2^-$ (R = Me or Et) give adducts $[M(L\text{–}L)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ which exhibit a bis(alkyne) structure containing a monodentate ligand L–L and/or an isomeric η^2-vinyl structure in which the ligand L–L forms a bridge between the metal and the η^2-vinyl ligand. In the cases M = Mo or W, L–L = R_2NCS_2 (R = Me or Et) the η^2-vinyl structure is stereochemically rigid whereas with M = Mo, L–L = $MeCO_2^-$ or $Me_2PS_2^-$; M = W, L–L = $Me_2PS_2^-$, ^{19}F n.m.r. studies reveal fluxional behaviour attributed to reversible cleavage of the (L–L)–η^2-vinyl linkage which regenerates the bis(alkyne) structure. Thermolysis of η^2-vinyl complexes $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)(L\text{–}L)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ gives tetrakis(trifluoromethyl)cyclobutadiene derivatives $[Mo(L\text{–}L)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (L–L = S_2CNR_2) in which the cyclobutadiene ring exhibits high barriers to rotation about the metal–ligand axis. Complexes of this type can also be obtained from the metathetical reactions of $[MoI(CO)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ with metal salts of $(L\text{–}L)^-$ (S_2CNMe_2 or pyridine-2-thiolate). Thermolysis of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNR_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ also gives small quantities of the η^2-vinyl complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(CF_3){=}C(CF_3)S\}(\eta^2\text{-}R_2NCS)(\eta^5\text{-}C_5H_5)]$ resulting from condensation of the two fluorocarbon units and fragmentation of the R_2NCS_2 moiety. This type of complex is the major product when the η^2-vinyl complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNR_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ is photolysed in solution.

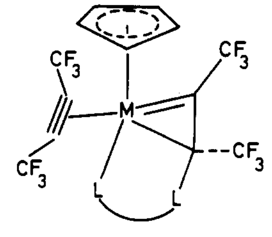
Co-ordination of unsaturated organic molecules such as alkenes and alkynes to a transition metal can, under appropriate circumstances, result in activation towards nucleophilic attack.[1] In the case of alkynes, studies have centred around cationic complexes such as $[Fe(CO)(PPh_3)(MeC{\equiv}CMe)(\eta^5\text{-}C_5H_5)]^+$,[2] $[Pt(Me)L_2(RC{\equiv}CR)]^+$ (L = tertiary phosphine or arsine, R = alkyl),[3] and $[Mo\{P(OMe)_3\}_2(RC{\equiv}CR)L]^+$ (L = η^5-C_5H_5 or η^5-C_9H_7)[4] where, in addition to simple vinyl products, a number of unusual complexes have been obtained as a result of intramolecular rearrangements.

In previous reports it has been demonstrated that neutral mono- and bis-hexafluorobut-2-yne complexes $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W)[5] and $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, X = Cl; M = W, X = SR)[6] undergo external and/or internal nucleophilic attack to give η^2-vinyl complexes. In the case of $[M(SR)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ both η^2-vinyl and bis(alkyne) isomeric forms exist depending upon the ability of the thiolate sulphur to attack an alkyne carbon atom.[6d,7] However, complexes $[M(SC_5H_4N)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (SC_5H_4N = pyridine-2-thiolate) only exist in some isomeric form containing an η^2-vinyl ligand resulting from attack of a hetero-ring nitrogen on an alkyne carbon.[6a,8] I now report the synthesis of a variety of complexes containing other potentially bidentate ligands designed to assess the effect of the ligand on the structure of such derivatives. Some of this work has been published previously as preliminary communications.[9]

Results and Discussion



(I)



(II)

Previously thallium salts have been employed to replace the chloride ligand in complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W)[10] with other anionic ligands, *e.g.* thiolates,[6d,7] but on reaction with thallium acetate pure products were not obtained easily. However, the bis(alkyne) complexes react readily with silver acetate in thf (tetrahydrofuran) at room temperature to yield off-white crystalline complexes $[M(O_2CMe)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ [M = Mo, (**1a**); M = W, (**1b**)] in good yields. The spectroscopic properties of the tungsten complex are somewhat similar to those of the parent chloride, suggesting a similar bis(alkyne) structure, (**I**),[10] and hence with a monodentate acetate ligand. Thus two ν(C≡C) bands are observed in the i.r. spectrum near 1 800 cm^{-1} while two CF_3 resonances are present in the ^{19}F n.m.r. spectrum below *ca.* −50 °C. At higher temperatures the two peaks broaden and coalesce above *ca.* 10 °C to give a singlet indicating the onset of alkyne propeller rotation.[7a]

The i.r. and n.m.r. data for the molybdenum complex (**1a**) are somewhat similar to those of (**1b**) at room temperature but at −60 °C two isomeric forms are indicated in the ^1H and ^{19}F n.m.r. spectra (see Table), ratio 5:1. The major isomer has similar spectral features to those of (**1b**), indicating structure (**I**),

Table. N.m.r. data for the complexes[a]

	^1H		^{19}F	
Complex	C_5H_5	L–L[b]	T/°C	
(1a) (I)[c]	5.77	2.03 (s, 3 H, Me)	−60	−56.87 (s, 6 F), −57.10 (s, 6 F)
(II)	6.15	2.35		−54.84 (m, 3 F), −56.54 (m, 3 F), −63.56 (br s, 3 F)
(1b)[d]	5.88	1.88 (s, 3 H, Me)	−30	−57.36 (s)
(2a)[c]	5.80	2.12 (d, 3 H), 1.32 (d, 3 H)	−40	−52.36 (qq, 3 F), −55.67 (qqq, 3 F), −56.37 (qq, 3 F), −57.20 (dq, 3 F)
(2b)[d]	5.95	2.20 (d, 6 H)	−80	−52.69 (br s, 3 F), −55.40 (m, 3 F), −56.45 (spt, 3 F), −56.62 (br m, 3 F)
(3a)[e]	5.88	3.60 (s, 3 H, Me), 3.50 (s, 3 H, Me)	20	−53.54 (spt, 3 F), −56.17 (spt, 3 F), −56.67 (q, J 3.7, 3 F), −57.14 (m, 3 F)
(3b)[e]	5.91	3.60 (s, 3 H, Me), 3.57 (s, 3 H, Me)	20	−54.95 (spt, 3 F), −56.31 (q, J 4.0, 0.3 F), −56.49 (spt, 3 F), −57.21 (m, 3 F)
(3c)[e]	5.86	3.7—4.1 (m, 4 H), 1.41 (t, 3 H), 1.30 (t, 3 H)	20	−53.38 (spt, 3 F), −56.09 (spt, 3 F), −56.49 (q, J 3.7, 3 F), −57.12 (m, 3 F)
(3d)[e]	5.84	3.8 (m, 4 H), 1.42 (t, 3 H), 1.31 (t, 3 H)	20	−54.54 (spt, 3 F), −55.70 (q, J 3.6, 3 F), −56.48 (m, 3 F), −56.69 (spt, 3 F)
(4a)[d]	5.57	3.20 (s, 6 H)	−70	−52.49 (m, 3 F), −53.0 (spt, 6 F), −55.66 (spt, 3 F)
(4b)[f]	5.03	2.90 (m, 4 H), 0.65 (t, 6 H)	−10	−52.78 (spt, 3 F), −52.99 (spt, 6 F), −55.59 (spt, 3 F)
(4c)[d]	5.68	7.60 (br d, 1 H), 7.43 (m, 1 H), 6.70 (m, 2 H)	20	−51.70 (spt, 3 F), −52.99 (spt, 3 F), −53.70 (spt, 3 F), −55.67 (spt, 3 F)
(7a)[e]	5.99	3.45 (s, 3 H), 3.28 (s, 3 H)	20	−53.44 [qq, $J(F^1F^2)$ 11.8, $J(F^1F^3)$ 2.5, 3 F], −54.29 [qqq, $J(F^2F^1)$ 11.8, $J(F^2F^3)$ 7.0, $J(F^2F^4)$ 13.3, 3 F], −56.75 [qq, $J(F^3F^1)$ 2.8, $J(F^3F^2)$ 7.0, 3 F], − 57.79 [q, $J(F^4F^2)$ 13.3, 3 F]
(7b)[e]	5.97	3.71 (q, 2 H), 3.55 (q, 2 H), 1.34 (t, 3 H), 1.23 (t, 3 H)	20	−52.96 (qq, 3 F), −54.36 (qqq, 3 F), −56.88 (qq, 3 F), −58.01 (q, 3 F)

[a] Proton n.m.r. spectra recorded at 20 °C except for **(1a)** (−60 °C). [b] L–L = $MeCO_2^-$, $Me_2PS_2^-$, $Me_2NCS_2^-$, or $Et_2NCS_2^-$ depending on the complex involved (see text). [c] In CD_2Cl_2. [d] In $(CD_3)_2CO$. [e] In $CDCl_3$. [f] In $C_6D_5CD_3$.

whereas the minor form exhibits three CF_3 peaks of equal intensity. However, it seems probable that the fourth resonance is obscured by the major isomer peaks. Thus four distinct CF_3 environments are present in the minor isomer consistent with an η^2-vinyl structure **(II)** similar to that of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SC_5H_4N\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, as revealed by X-ray diffraction studies.[6a] As the temperature is raised two effects are observed in the ^{19}F n.m.r. spectrum. The two major isomer peaks coalesce at *ca.* −20 °C while the minor isomer peaks broaden and eventually coalesce with the major isomer resonances to give a single peak above −10 °C. This indicates that the O–C bond in the η^2-vinyl structure **(II)** undergoes reversible fission to regenerate the bis(alkyne) form **(I)** and this leads to exchange between the two isomers. Similar effects have been observed with $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (R = Me, Et, Pr^i, or Pr^n) although in these cases the bis(alkyne) structure is not observed as a distinct species at low temperature.[6d,7b]

The spectra of simple η^2-vinyl thiolates such as this are in fact almost identical to those of dimethyldithiophosphinates **(2a)** or **(2b)** obtained from reactions of $Na(S_2PMe_2)$ with $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W). Complexes **(2)** and related dithiocarbamate derivatives **(3)**, see later, were originally assigned bis(alkyne) structures[9] but similar spectroscopic features to those of the pyridine-2-thiolate derivative $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SC_5H_4N\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[6a,8] suggest that structure **(II)** is more appropriate. For example the complexes exhibit only one ν(C≡C) band in the i.r. spectra while four distinct CF_3 resonances are observed in the ^{19}F n.m.r. spectra at −40 °C **(2a)** (see Figure 1) and −80 °C **(2b)** [*cf.* **(1a)**]. Moreover these broaden and coalesce at higher temperatures to give a broad singlet, again indicating reversible fission of the bond between the bidentate ligand and the fluorocarbon η^2-vinyl moiety (Scheme 1) but in this case a distinct bis(alkyne) structure **(I)** is not observed.

The variable-temperature ^1H n.m.r. spectra of complexes **(2a)** and **(2b)** are also consistent with the mechanism in Scheme 1. At −60 °C two doublets are observed in accord with structure **(II)** in which two distinct methyl group environments are present, each of which is split by coupling to phosphorus. At higher temperatures these collapse to a doublet as the two methyls exchange when the C–S bond breaks to give a monodentate S_2PMe_2 ligand.

Interestingly, at lower temperatures a second type of fluxional behaviour is observed since one of the four CF_3 resonances in the ^{19}F n.m.r. spectrum broadens and disappears into the baseline. I have observed this previously with other fluorocarbon complexes and attribute the phenomenon to restricted rotation of the CF_3 group resulting from steric interactions within the molecule.[11] This can be explained in terms of the probable structure of **(2a)** (Figure 2) which I assume is similar to that of the pyridine-2-thiolate complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SC_5H_4N\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$.[6a] This is based upon approximately octahedral co-ordination at the metal with the cyclopentadienyl ligand occupying a face and the other ligands corners of the octahedron. The alkyne C≡C axis lies approximately parallel to the Mo–S bond while the $CF_3C\text{–}CCF_3$ bond of the η^2-vinyl, constrained by attachment to the Me_2PS_2 group, is rotated by an angle θ from a similar orientation. These structural features are also exhibited by related η^2-vinyl complexes derived from bis(alkyne) derivatives $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (X = Cl or C_6H_4Me-4) where the main structural variable appears to be the η^2-vinyl orientation defined by the magnitude of θ.[6] Assuming a value of θ close to that in the pyridine-2-thiolate derivative, *ca.* 35°, molecular graphics[12] studies indicate that only the CF_3 attached to the sp^3 α-carbon of the η^2-vinyl is likely to encounter steric congestion as a result of close approach to the two CF_3 groups of the alkyne. This tentatively indicates that this CF_3 is most likely to experience restricted rotation, and in an attempt to confirm this

^{19}F homodecoupling experiments were carried out on complex (**2a**) at −40 °C which are summarised in Figure 2.

Significantly the CF_3 signal which broadens at lower temperature, δ_2, is the one which is coupled to all the remaining CF_3 groups. Since coupling in these derivatives probably has a strong contribution from a 'through-space' mechanism, particularly where intraligand CF_3–CF_3 interactions are concerned,[7b] the CF_3 on the α-carbon can be assigned to δ_2 since this group is unique in being within *ca.* 4.2 Å of the other three groups (measured in terms of the C–C distance). Moreover, the assignments in Figure 2 are consistent with those made previously[7b] and later in this paper for η^2-vinyl complexes of this type. Interestingly δ_4 also shows coupling to phosphorus (J_{P-F} = 2.0 Hz) and, in accord with the assignments, molecular graphics studies established that this CF_3 group is probably close enough to the phosphorus atom for through-space coupling to occur.

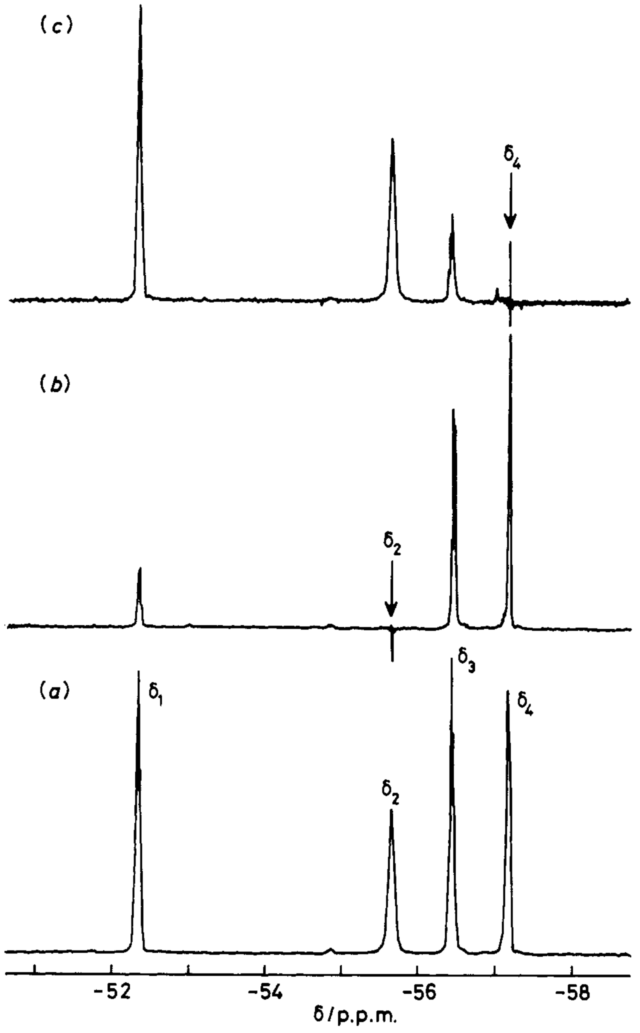
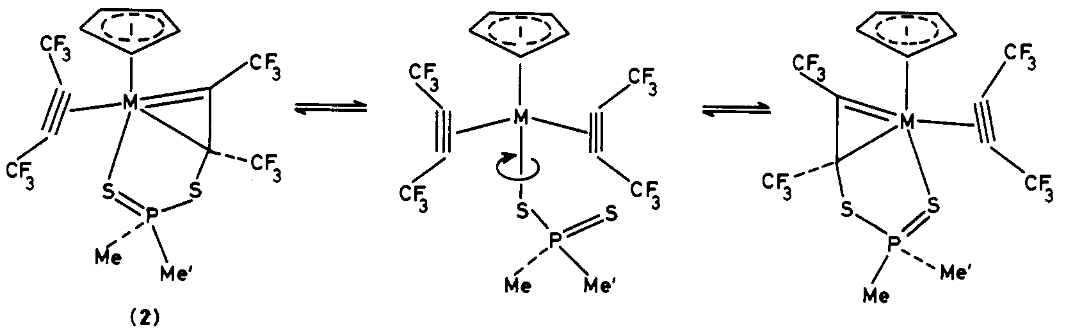


Figure 1. The ^{19}F n.m.r. spectrum of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2PMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2a**) at −40 °C: (*a*) normal spectrum; (*b*) as for (*a*) but with irradiation of δ_2; (*c*) as for (*a*) but with irradiation of δ_4

Further support for the assignments in Figure 2 was provided indirectly by the homodecoupling experiments since irradiation of $\delta_4 = -57.2$ at −40 °C resulted in δ_3 suffering a significant reduction in intensity relative to δ_1 and δ_2, while irradiating $\delta_2 = -55.67$ reduced the intensity of δ_1 markedly, Figure 1. These effects, which can be ascribed to spin-saturation transfer,[13] indicate that at −40 °C slow exchange is still occurring and that more significantly δ_1 exchanges with δ_2 while δ_3 exchanges with δ_4. This selective exchange indicates that alkyne propeller rotation as observed with (**1a**) is slow at −40 °C in (**2a**) relative to migration of the Me_2PS_2 group from one alkyne to the other. It is also apparent that fission of the C–S bond in (**II**) to generate the bis(alkyne) structure (**I**) (Scheme 1) is consistent with the n.m.r. data only if the assignments in Figure 2 are correct.

Reactions of $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with $Na(S_2CNMe_2)$ and $Na(S_2CNEt_2)$ give yellow crystalline complexes (**3a**)—(**3d**) in moderate to good yields. As with (**2a**) and (**2b**) an η^2-vinyl structure (**II**) is indicated by i.r. and n.m.r. spectra since a single ν(C≡C) mode is observed near 1 790 cm^{-1} in each case while ^{19}F n.m.r. spectra exhibit four distinct resonances at ambient temperature. The resonances consist of a quartet, two septets (qq), and a complex multiplet (qqq) thus indicating a similar coupling pattern to that of complex (**2a**) except for the absence of phosphorus coupling to the simple quartet. This was confirmed by double resonance experiments with (**3c**) which are summarised in Figure 3.

The presence of four CF_3 signals at room temperature in all four cases with well resolved multiplet structure contrasts with ^{19}F n.m.r. data for (**1**) and (**2**) and indicates that C–S bond fission leading to CF_3 scrambling does not occur with the dithiocarbamate complexes under these conditions. Comparing the behaviour of the three types of complex it is apparent that as the donor ability of the chelate ligand increases $MeCO_2^- < Me_2PS_2^- < R_2NCS_2^-$ (R = Me or Et)[14] the η^2-vinyl structure (**II**) becomes more stable relative to the bis(alkyne) form (**I**). This is also reflected in the ease with which the chelate η^2-vinyl linkage is broken as evidenced by coalescence temperatures in the ^{19}F n.m.r. spectra. This is in accord with previous studies of thiolate complexes $[W(SR)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ where the stability of the η^2-vinyl form increases as the electron-donating ability of the thiolate substituent R



(2)

Scheme 1.

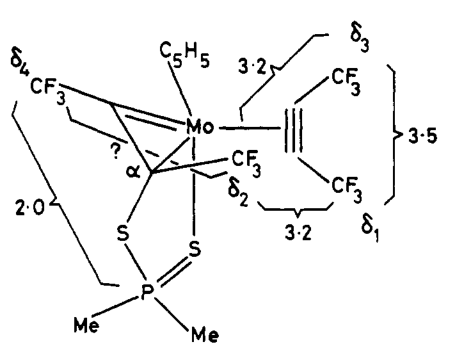


Figure 2. ^{19}F N.m.r. spectral data and assignments for [Mo{η^3-C(CF$_3$)C(CF$_3$)S$_2$PMe$_2$}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**2a**); couplings in Hz

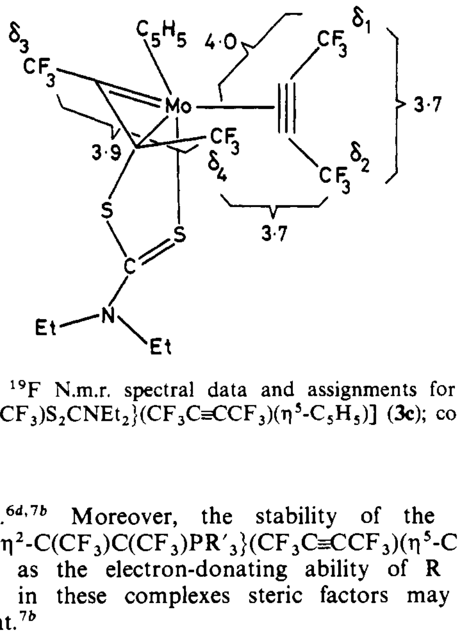
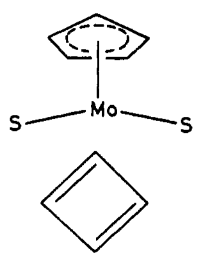


Figure 3. ^{19}F N.m.r. spectral data and assignments for [Mo{η^3-C(CF$_3$)C(CF$_3$)S$_2$CNEt$_2$}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**3c**); couplings in Hz

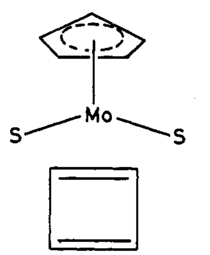
increases.[6d,7b] Moreover, the stability of the η^2-vinyls [W(SR){η^2-C(CF$_3$)C(CF$_3$)PR'$_3$}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] increases as the electron-donating ability of R increases although in these complexes steric factors may also be important.[7b]

Recently,[4,6,15,16] attention has been drawn to the role of η^2-vinyls in the chemistry of co-ordinated alkynes. It was therefore of interest to investigate their role in the cyclisation reactions of co-ordinated alkynes. Previously it was reported that bis(alkyne) complexes [MoX(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] are intermediates in the formation of cyclobutadiene [MoI(CO){η^4-C$_4$(CF$_3$)$_4$}(η^5-C$_5$H$_5$)] and cyclopentadienone complexes [MoX(CO){η^4-C$_4$(CF$_3$)$_4$CO}(η^5-C$_5$H$_5$)] (X = Cl, Br, or I)[7a,10] and this prompted me to carry out thermolysis of complexes with structure (**II**). No reaction was observed when the pyridine-2-thiolate complex [Mo{η^3-C(CF$_3$)C(CF$_3$)SC$_5$H$_4$N}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)][8] was heated in hexane at 90 °C for 20 h in a sealed tube. However (**3a**) and (**3c**) react above *ca.* 65—70 °C to give moderate yields of compounds (**4a**) and (**4b**) with the same stoicheiometry as the precursors but which exhibit quite different spectroscopic features. Complex (**4a**) was subsequently obtained by an alternative route involving reaction of the tetrakis(trifluoromethyl)cyclobutadiene derivative [MoI(CO){η^4-C$_4$(CF$_3$)$_4$}(η^5-C$_5$H$_5$)][9a] with Na(S$_2$CNMe$_2$) in thf indicating that cyclisation of the two fluorocarbon units in (**3**) had occurred on thermolysis to give the cyclobutadiene structure (**4**). Reaction of [MoI(CO){η^4-C$_4$(CF$_3$)$_4$}(η^5-C$_5$H$_5$)] with Tl(SC$_5$H$_4$N) similarly gave (**4c**) in moderate yield.

The spectroscopic features of complexes (**4a**)—(**4c**) are clearly in accord with the illustrated structure since no ν(C≡C) modes



(**4^{i}**)

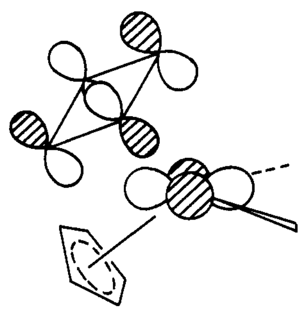


(**4^{ii}**)

are observed in the i.r. spectrum while the ^{19}F n.m.r. spectrum of (**4c**) contains four separate septets (quartet of quartets) indicating that each CF$_3$ couples to two others with very similar coupling constants of *ca.* 3—3.5 Hz. These data also indicate that the cyclobutadiene ring adopts a fixed orientation and either the staggered (**4^{i}**) or eclipsed form (**4^{ii}**) is possible. The ^{19}F n.m.r. spectra of (**4a**) and (**4b**) are somewhat broad at 20 °C but at or below −15 °C three distinct septets (qq) of ratio 1:2:1 are observed consistent with the staggered conformation (**4i**). This was subsequently confirmed by *X*-ray diffraction studies of (**4b**)[17] which revealed the presence of a plane of symmetry in the molecule which renders two CF$_3$ groups and the two alkyl groups on the dithiocarbamate ligand equivalent. Comparable structures have been determined for [Mo(CO)$_2$(η^4-C$_4$Ph$_4$)$_2$],[18] [MoCl(CO)(η^4-C$_4$Ph$_3$Me)(η^5-C$_5$H$_5$)],[19] [V(CO)$_2$(η^4-C$_4$Ph$_4$)(η^5-C$_5$H$_5$)],[20] and [Nb(CO)(PhC≡CPh)(η^4-C$_4$Ph$_4$)(η^5-C$_5$H$_5$)][21] in the solid state.

A variety of structurally related cyclobutadiene complexes has been synthesised *via* diverse synthetic routes including [MoX(CO)(η^4-C$_4$Ph$_4$)(η^5-C$_5$H$_5$)] (X = Cl, Br, I, or H)[22,23] and [V(CO)$_2$(η^4-C$_4$R$_4$)(η^5-C$_5$H$_5$)] (R = H or Ph).[20,24] Comparable tetrakis(trifluoromethyl)cyclobutadiene derivatives are more limited and comprise [MoI(CO){η^4-C$_4$(CF$_3$)$_4$}(η^5-C$_5$H$_5$)],[9a] its isocyanide substitution product [MoI(CNBu^t){η^4-C$_4$(CF$_3$)$_4$}(η^5-C$_5$H$_5$)], and the thiolate derivative [Mo(SC$_6$F$_5$)(PMe$_2$Ph){η^4-C$_4$(CF$_3$)$_4$}(η^5-C$_5$H$_5$)][11] which show similar ^{19}F n.m.r. spectral features to (**4**). Interestingly, however, the ^{1}H n.m.r. spectra of both [Mo(CO)$_2$(η^4-C$_4$Me$_4$)(η^5-C$_5$H$_5$)][BF$_4$][19] and [V(CO)$_2$(η^4-C$_4$H$_4$)(η^5-C$_5$H$_5$)][24] exhibit a single sharp cyclobutadiene proton peak at 20 °C indicating rapid rotation of the C$_4$ ring and hence the lack of an orientational preference at this temperature. In contrast this is clearly not the case with (**4**) which are stereochemically rigid at or just below ambient temperature according to ^{19}F n.m.r. data. However, as the temperature is raised the three peaks in the spectra of (**4a**) and (**4b**) broaden and coalesce to a singlet above *ca.* 75 °C. This suggests the onset of cyclobutadiene rotation about the metal–ring axis, the high coalescence temperatures indicating substantial barriers to rotation. This contrasts with the implied low barrier in [V(CO)$_2$(η^4-C$_4$H$_4$)(η^5-C$_5$H$_5$)] and in general with complexes containing η^n-C$_n$R$_n$ rings (n = 3—8) where low barriers to rotation are the norm.[25,26]

This conformational preference could reflect either electronic or steric factors, or perhaps both. Extended-Hückel calculations on a variety of cyclobutadiene complexes including [Mo(S$_2$CNMe$_2$)(η^4-C$_4$H$_4$)(η^5-C$_5$H$_5$)] suggest that the electronic contribution to a rotational barrier is dominated by the 1*a* orbital, (A), which favours the staggered form (**4^{i}**).[27] A computed barrier of 0.26 eV (*ca.* 0.416 × 10^{-19} J) for the dithiocarbamate derivative probably underestimates the value in the trifluoromethyl-substituted derivative (**4a**) although the complexity of the CF$_3$–CF$_3$ coupling prevents experimental determination of this barrier. Moreover, some contribution to the barrier might be expected from steric interactions between the cyclobutadiene



(A)

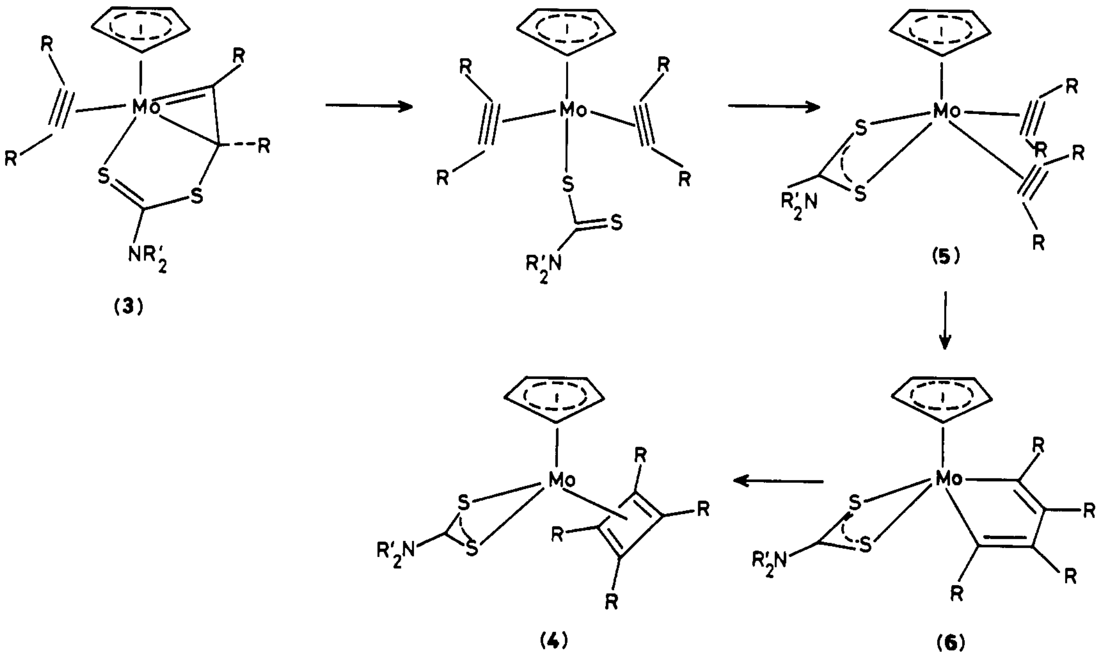
and the rest of the molecule, particularly with CF_3 substituents present. Although molecular graphics studies do not reveal any substantial interactions, van der Waals repulsions were found to be at a minimum in the staggered conformation (**4**^{i}) and a maximum in the eclipsed form (**4**^{ii}).

The metal-promoted dimerisation of two alkynes to form a cyclobutadiene ring is well documented and presents one of the most accessible synthetic routes to cyclobutadiene complexes.[25] Uncomplexed tetrakis(trifluoromethyl)cyclobutadiene has been generated previously in a low-temperature matrix at 77 K[28] whereas (**4a**) and (**4b**) represent the first fully characterised transition-metal complexes of this ligand. The isomerisation of (**3**) into (**4**), which results in alkyne dimerisation, clearly involves carbon–sulphur bond fission at some point. As illustrated earlier with (**1a**) and (**2**), Scheme 1, this could be the first stage in the reaction leading initially to a bis(alkyne) intermediate (Scheme 2) followed by nucleophilic attack at the metal by the free sulphur to generate the chelate structure (**5**). Subsequent oxidative cyclisation to give the 16-electron metallacyclic intermediate (**6**) is then followed by reductive cyclisation to give the final product (**4**).

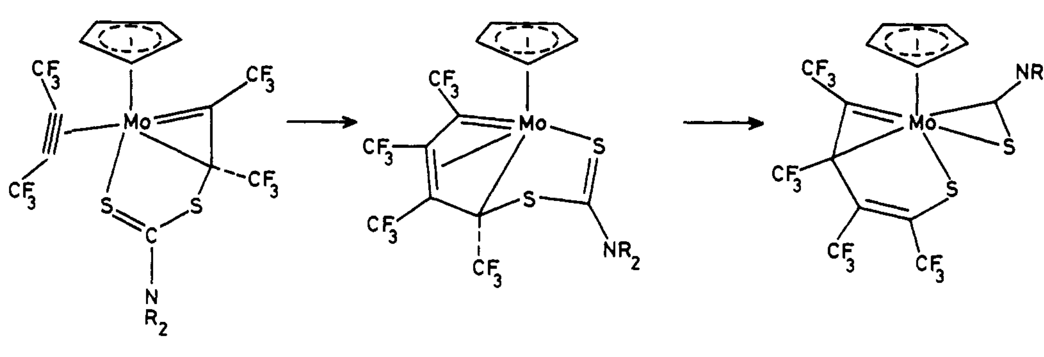
It is also possible to explain the formation of a wide variety of alkyne insertion and cyclisation products from bis(alkyne) and η^2-vinyl complexes of molybdenum and tungsten in terms of reactive bis(alkyne) intermediates similar to (**5**).[6b,9a,10,15a] Activation of the alkyne in this situation can be rationalised in terms of a switch in bonding mode from formal three-electron donation in the bis(alkyne) structure (**I**) to two-electron donation in (**5**). Subsequent metallacyclisation to give (**6**) is supported by my previous report that the bis(μ-alkyne) complexes $[(\eta^5\text{-}C_5H_5)(OC)M(\mu\text{-}CF_3C{\equiv}CCF_3)_2Co(CO)_2]$ (M = Mo or W) on reaction with CO give metallacyclopentadienes $[(\eta^5\text{-}C_5H_5)(OC)_2\overline{M\{C(CF_3){=}C(CF_3)C(CF_3){=}C}(CF_3)\}Co(CO)_2]$.[29] Moreover η^2-vinyl complexes $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (R = Pr^i or Bu^t) related to (**3**) react with 1 molar equivalent of $CNBu^t$ to give the 16-electron metallacyclic complex $[\overline{W\{C(CF_3){=}C(CF_3)C(CF_3){=}C}(CF_3)\}(SR)(CNBu^t)(\eta^5\text{-}C_5H_5)]$[11] structurally analogous to (**6**). Transformation of metallacyclopentadienes into cyclobutadienes is also a known reaction as exemplified by the thermolysis of $[\overline{Co\{C(Ph){=}C(Ph){-}C(Ph){=}C}(Ph)\}(PPh_3)(\eta^5\text{-}C_5H_5)]$ which gives $[Co(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5H_5)]$.[30]

The fact that previously it was possible to isolate and characterise the metallacycle $[\overline{W\{C(CF_3){=}C(CF_3)C(CF_3){=}C}(CF_3)\}(SBu^t)(CNBu^t)(\eta^5\text{-}C_5H_5)]$ similar to (**6**) prompted me to follow the thermolysis of (**3c**) by ^{19}F n.m.r. spectroscopy with a view to detecting intermediates. The reaction was studied in two different solvents, diethyl ether and toluene, in a sealed tube at 65 °C, but, since the same features were observed in both cases, solvent effects appear to be negligible. Moreover, no reaction intermediates were detected under these conditions but two minor products were observed in addition to the cyclobutadiene complex (**4b**). At the end of the reaction these comprised 22 and 4% of the product mixture according to integrated intensities in the ^{19}F n.m.r. spectrum, the remaining 74% being complex (**4b**). The reaction was repeated using photochemical activation when two products formed, the cyclobutadiene complex (**4b**), 10%, and the major side product of the thermal reaction (**7b**), 90%. Thus, although the thermal and photochemical reactions give essentially the same products thermolysis favours cyclisation (**3**)→(**4**) while photolysis preferentially leads to the insertion product (**7**).

The spectroscopic properties of complexes (**7a**) and (**7b**) did



Scheme 2. R = CF_3; R′ = Me or Et



(3) (8) (7)

Scheme 3. R = Me or Et

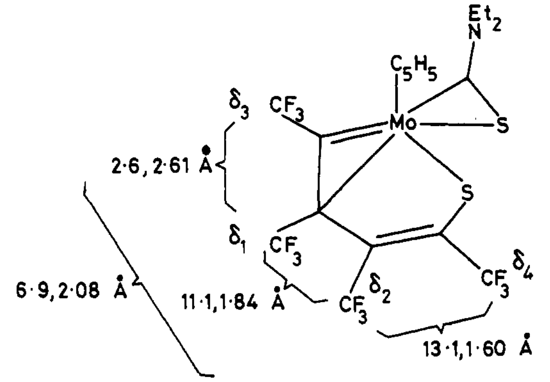
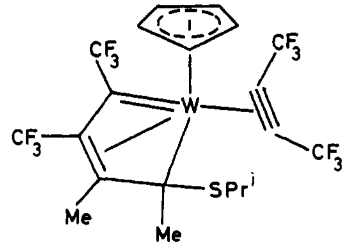


Figure 4. ^{19}F N.m.r. spectral data and assignments for [Mo{η^3-C(CF_3)C(CF_3)C(CF_3)=C(CF_3)S}(η^2-Et_2NCS)(η^5-C_5H_5)] (**7b**); couplings in Hz; including minimum F–F distances assuming free rotation of CF_3 groups

not provide unequivocal structural information but *X*-ray diffraction studies of (**7b**) established the illustrated structure which reveals that cleavage of a C–S bond within the dithiocarbamate moiety has occurred to generate an η^2-$SCNEt_2$ ligand.[11] The remaining sulphur atom is attached to an alkenyl function (presumably from the original η^2-vinyl moiety) which is further attached to a new η^2-vinyl group, formed by linking of the two fluorocarbon moieties. The overall structure is remarkably similar to that of [Mo{η^3-C(CF_3)C(CF_3)-SC_5H_4N}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)], and hence related complexes with structure (**II**), in that an η^2-vinyl is present which is co-ordinated to the metal directly *via* two carbon atoms and indirectly *via* a three-atom chain. Moreover, the η^2-thiocarboximido ligand in (**7**) adopts a co-ordination position and orientation comparable to the alkyne ligand in (**II**) in that the C–S bond lies approximately parallel to the M–S bond: the S–Mo–C–S dihedral angle of 15.6° compares with the S–Mo–C–C angle of 7.4° in the pyridine-2-thiolate complex.

The spectroscopic properties of (**7**) can be interpreted in terms of the solid-state structure, in particular the ^{19}F n.m.r. spectra where four CF_3 multiplets are observed. Homonuclear decoupling experiments were carried out on (**7b**) and these are summarised in Figure 4 along with peak assignments. The large coupling between δ_2 and δ_4, 13.1 Hz, can be assigned to the *cis*-$CF_3C{=}CCF_3S$ alkene group[31] thus identifying the quartet δ_4 as the CF_3 adjacent to sulphur. Assuming that a through-space mechanism[7b] again contributes substantially to CF_3–CF_3 coupling, remaining peak assignments are tentatively made on the basis of minimum F–F separations established by molecular graphics studies, the smaller the F–F distance the larger being the coupling constant.

The formation of (**7**) from (**3**) clearly involves C–S bond fission at some stage to generate an η^2-thiocarboximido ligand, a process for which precedents exist in molybdenum chemistry.[32,33] This can be explained in terms of the mechanism in Scheme 3 in which insertion of $CF_3C{\equiv}CCF_3$ into the M=C bond of the η^2-vinyl metal linkage to give an intermediate η^4-butadienyl complex (**8**) precedes C–S bond fission. I note that three η^4-butadienyl complexes have recently been structurally characterised[15b,34,35] one of which, (**9**), compared closely with intermediate (**8**).



(9)

Whatever the mechanistic details of the reaction, the formation of (**7**) from (**3**) illustrates that an η^2-vinyl ligand and a co-ordinated alkyne can undergo carbon–carbon bond formation at a metal centre to yield a new η^2-vinyl ligand in a process which serves as a model for metal-promoted alkyne oligomerisation reactions. Previously it has been pointed out that η^2-vinyls could function as intermediates in alkyne oligomerisations[15] and this reaction is clearly in accord with these proposals. The results of the present work and previous studies[9,15b] involving reactions of alkynes with co-ordinated η^2-vinyl ligands to give alkyne oligomerisation products can therefore be summarised as follows. The alkyne can insert directly into the M=C bond as illustrated in Scheme 3. This type of reaction finds precedent in the reactions of alkynes with a variety of metal alkylidene and alkylidyne complexes which involve insertion into the M=C[36] or M≡C bonds.[37] Alternatively this could be preceded by an $\eta^2 \longrightarrow \sigma$ vinyl transformation such that insertion occurs into a metal–carbon single bond as discussed previously.[15] Interestingly, however, reaction of the σ-vinyl alkyne complex [Mo(CO){CMe=CH-(Me)}(MeC≡CMe)(η^5-C_5H_5)] with carbon monoxide results initially in CO rather than alkyne insertion into the Mo–C vinyl bond.[38] The third possibility involves bond cleavage within the η^2-vinyl to regenerate an alkyne as in Schemes 1 and 2 and this subsequently undergoes oligomerisation with other co-ordinated alkynes. Evidence for this mechanism is provided by the diverse reactions of η^2-vinyl thiolate complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ which must proceed *via* carbon–sulphur cleavage.[15] It therefore appears that several competing mechanisms may be available for metal-promoted alkyne condensation reactions which lead to linear or cyclic oligomerisation products *via* intermediate η^2-vinyl complexes.

Experimental

N.m.r. spectra were recorded in $CDCl_3$ (unless stated otherwise) on a Bruker WP 200 SY spectrometer at 200.13 (^1H) and 188.31 MHz (^{19}F). Coupling constants are in Hz while chemical shifts are referred to $SiMe_4$ and CCl_3F, $\delta = 0$. I.r. spectra were recorded as solutions on a Perkin-Elmer 580 spectrophotometer. Reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over powdered calcium hydride (Et_2O, hexane), P_2O_5 (dichloromethane), or sodium–benzophenone (thf and toluene) and distilled just before use. Complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W)[7a] and metal salts $Tl(SC_5H_4N)$[8] and $Na(S_2PMe_2)$[39] were synthesised by known methods while $Ag(O_2CMe)$ and $Na(S_2CNR_2)$ (R = Me or Et) were obtained commercially.

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Ag(O_2CMe)$.—The complex (200 mg) and $Ag(O_2CMe)$ (120 mg) in thf (20 cm^3) were stirred at room temperature for 2 h. Volatiles were removed *in vacuo* and the liquid extracted with diethyl ether (20 cm^3) and centrifuged. The clear liquid was transferred to another vessel, hexane (10 cm^3) added, and the solution concentrated. On cooling to −15 °C pale yellow crystals formed which were recrystallised a second time from diethyl ether–hexane to give 120 mg (51%) of $[Mo(O_2CMe)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1a**) (Found: C, 32.9; H, 1.6. Calc. for $C_{15}H_8F_{12}MoO_2$: C, 36.1; H, 1.45%); i.r. (CCl_4) $\nu(C{\equiv}C)$ 1 824w (sh) and 1 810wm cm^{-1}.

Reaction of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Ag(O_2CMe)$.—The complex (250 mg) and $Ag(O_2CMe)$ (140 mg) reacted similarly to give 170 mg (65%) of off-white crystals of $[W(O_2CMe)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1b**) (Found: C, 28.7; H, 1.3. Calc. for $C_{15}H_8F_{12}O_2W$: C, 28.5; H, 1.25%); i.r. (CCl_4) $\nu(C{\equiv}C)$ 1 800w (sh) and 1 784wm cm^{-1}.

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Na(S_2PMe_2)$.—The complex (200 mg) and $Na(S_2PMe_2)$ (75 mg) in thf (20 cm^3) were stirred at room temperature for 3 h. Volatiles were removed *in vacuo* and the residue extracted with diethyl ether (25 cm^3). The extract was filtered, hexane (15 cm^3) added, and the solution concentrated. On cooling to −15 °C yellow-brown crystals were obtained which were recrystallised a second time from diethyl ether–hexane to give 120 mg (51%) of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2PMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2a**) (Found: C, 29.3; H, 1.7; S, 10.1. Calc. for $C_{15}H_{11}MoPS_2$: C, 29.5; H, 1.80; S, 10.5%); i.r. ($CHCl_3$) $\nu(C{\equiv}C)$ 1 799wm cm^{-1}.

Reaction of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Na(S_2PMe_2)$.—The complex (200 mg) and $Na(S_2PMe_2)$ similarly gave 85 mg (37%) of pale yellow-brown crystals of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)S_2PMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2b**) (Found: C, 25.9; H, 1.4. Calc. for $C_{15}H_{11}PS_2W$: C, 25.8; H, 1.60%); i.r. ($CHCl_3$) $\nu(C{\equiv}C)$ 1 764wm cm^{-1}.

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Na(S_2CNMe_2)$.—The complex (250 mg) and $Na(S_2CNMe_2)$ (130 mg) in thf (20 cm^3) were stirred at room temperature for 2 h. Volatiles were removed *in vacuo* and the residue extracted with diethyl ether (25 cm^3). The extract was filtered, hexane (15 cm^3) added, and the solution concentrated. On cooling to −15 °C yellow crystals were obtained which were recrystallised a second time from diethyl ether–hexane to give 180 mg (62%) of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3a**) (Found: C, 31.6; H, 1.6; S, 10.7. Calc. for $C_{16}H_{11}MoNS_2$: C, 31.75; H, 1.80; S, 10.6%); i.r. ($CHCl_3$) $\nu(C{\equiv}C)$ 1 811wm cm^{-1}.

Reaction of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Na(S_2CNMe_2)$.—The complex (200 mg) and $Na(S_2CNMe_2)$ (100 mg) reacted similarly to above for 16 h to give 85 mg (37%) of pale yellow crystals of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3b**) (Found: C, 27.7; H, 1.60. Calc. for $C_{16}H_{11}NS_2W$: C, 27.7; H, 1.80%); i.r. ($CHCl_3$) $\nu(C{\equiv}C)$ 1 784wm cm^{-1}.

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Na(S_2CNEt_2)$.—The complex (300 mg) and $Na(S_2CNEt_2)$ (150 mg) reacted similarly for 2 h to give 205 mg (56%) of yellow crystals of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNEt_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3c**) (Found: C, 32.7; H, 2.5; N, 2.5. Calc. for $C_{18}H_{15}MoNS_2$: C, 34.1; H, 2.35; N, 2.20%); i.r. ($CHCl_3$) $\nu(C{\equiv}C)$ 1 807wm cm^{-1}.

Reaction of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $Na(S_2CNEt_2)$.—The complex (200 mg) and $Na(S_2CNEt_2)$ (90 mg) reacted similarly for 15 h to give 80 mg (34%) of pale yellow crystals of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNEt_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3d**) (Found: C, 29.6; H, 1.9. Calc. for $C_{18}H_{15}NS_2W$: C, 29.95; H, 2.10%); i.r. ($CHCl_3$) $\nu(C{\equiv}C)$ 1 776wm cm^{-1}.

Thermolysis of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3a**).—The complex (60 mg) was dissolved in toluene (30 cm^3) and transferred to a thick glass tube fitted with a Westef stopcock. The solution was degassed using the freeze–thaw method and then heated at 65 °C for 48 h. Solvent was removed *in vacuo* and the residue extracted with diethyl ether (10 cm^3). Hexane (5 cm^3) was added and following concentration and cooling to −15 °C yellow crystals were obtained. A second crystallisation from dichloromethane–hexane gave 28 mg (47%) of $[Mo(S_2CNMe_2)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (**4a**) (Found: C, 32.1; H, 1.6; N, 2.2. Calc. for $C_{16}H_{11}MoNS_2$: C, 31.75; H, 1.80; N, 2.30%). Concentration of the mother-liquor from the first crystallisation gave an impure solid which was recrystallised twice from dichloromethane–hexane to give 5 mg (8%) of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(CF_3){=}C(CF_3)S\}(\eta^2\text{-}Me_2NCS)(\eta^5\text{-}C_5H_5)]$ (**7a**) (Found: C, 32.0; H, 1.7. Calc. for $C_{16}H_{11}MoNS_2$: C, 31.75; H, 1.80%).

Thermolysis of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNEt_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3c**).—The complex (50 mg) reacted similarly to give 16 mg (32%) of $[Mo(S_2CNEt_2)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (**4b**) (Found: C, 34.5; H, 2.3; N, 2.0. Calc. for $C_{18}H_{15}MoNS_2$: C, 34.1; H, 2.35; N, 2.20%) and 4 mg (8%) of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(CF_3){=}C(CF_3)S\}\{\eta^2\text{-}Et_2NCS\}(\eta^5\text{-}C_5H_5)]$ (**7b**) (Found: C, 33.8; H, 2.2. Calc. for $C_{18}H_{15}MoNS_2$: C, 34.1; H, 2.35%).

Photolysis of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNEt_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3c**).—The complex (150 mg) in diethyl ether (30 cm^3) was transferred to a thick glass tube under nitrogen and the solution degassed by the freeze–thaw method. The solution was irradiated with a medium-pressure mercury lamp for 10 d. Volatiles were removed and the solution extracted with dichloromethane (25 cm^3) and filtered. Addition of hexane followed by concentration and cooling to -15 °C gave yellow crystals. These were recrystallised a second time to give 105 mg (70%) of $[\mathrm{Mo}\{\eta^3\text{-}\mathrm{C(CF_3)C(CF_3)C(CF_3){=}C(CF_3)S}\}(\eta^2\text{-}\mathrm{Et_2NCS})(\eta^5\text{-}\mathrm{C_5H_5})]$ (**7b**) (Found: C, 34.3; H, 2.4; S, 10.5. Calc. for $\mathrm{C_{18}H_{15}MoNS_2}$: C, 34.1; H, 2.35; S, 10.1%); i.r. ($\mathrm{CHCl_3}$) $\nu(\mathrm{C{\equiv}C})$ 1 570w cm^{-1}.

Reaction of $[\mathrm{MoI(CO)}\{\eta^4\text{-}\mathrm{C_4(CF_3)_4}\}(\eta^5\text{-}\mathrm{C_5H_5})]$ *with* $\mathrm{Na(S_2CNMe_2)}$.—The complex (150 mg) and $\mathrm{Na(S_2CNMe_2)}$ (100 mg) were refluxed in thf (30 cm^3) under nitrogen for 5 h. Volatiles were removed and the residue extracted with diethyl ether (25 cm^3) and filtered. Hexane (10 cm^3) was added, the solution concentrated *in vacuo*, and on cooling to -15 °C yellow crystals were obtained. These were recrystallised a second time to give 32 mg (23%) of (**4a**) (Found: C, 31.2; H, 1.8; N, 2.1%).

Reaction of $[\mathrm{MoI(CO)}\{\eta^4\text{-}\mathrm{C_4(CF_3)_4}\}(\eta^5\text{-}\mathrm{C_5H_5})]$ *with* $\mathrm{Tl(SC_5H_4N)}$.—The complex (100 mg) and $\mathrm{Tl(SC_5H_4N)}$ (60 mg) in thf (10 cm^3) were stirred at reflux for 6 h. Volatiles were removed *in vacuo* and the residue extracted with diethyl ether (20 cm^3). The mixture was centrifuged, hexane (10 cm^3) added to the clear liquid, and the solution concentrated. On cooling to -15 °C orange crystals were obtained which were recrystallised from diethyl ether–hexane to give 22 mg (24%) of $[\mathrm{Mo(SC_5H_4N)}\{\eta^4\text{-}\mathrm{C_4(CF_3)_4}\}(\eta^5\text{-}\mathrm{C_5H_5})]$ (**4c**) (Found: C, 30.6; H, 1.5; N, 2.3. Calc. for $\mathrm{C_{18}H_9MoNS}$: C, 30.25; H, 1.50; N, 2.35%).

Acknowledgements

I thank the S.E.R.C. for financial support, Dr. K. W. Muir for *X*-ray diffraction data, and the Nuffield Foundation for a Science Research Fellowship.

References

1 O. Eisenstein and R. H. Hoffman, *J. Am. Chem. Soc.*, 1981, **103**, 1308 and refs. therein; 'The Chemistry of the Metal–Carbon Bond,' vol. 2, eds. F. R. Hartley and S. Patai, Wiley-Interscience, New York, 1985.

2 D. L. Reger, C. J. Coleman, and P. J. McElligott, *J. Organomet. Chem.*, 1979, **171**, 73; D. L. Reger and P. J. McElligott, *J. Am. Chem. Soc.*, 1980, **102**, 5923.

3 H. M. Chisholm and H. C. Clark, *Acc. Chem. Res.*, 1973, **6**, 202.

4 S. R. Allen, R. G. Beevor, M. Green, N. C. Norman, A. G. Orpen, and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1985, 435 and refs. therein.

5 J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 2423.

6 (*a*) J. L. Davidson, I. E. P. Murray, P. N. Preston, M. V. Russo, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1981, 1059; (*b*) J. L. Davidson, G. Vasapollo, Lj. Manojlović-Muir, and K. W. Muir, *ibid.*, 1982, 1025; (*c*) J. L. Davidson, W. F. Wilson, Lj. Manojlović-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1983, **254**, C6; (*d*) L. Carlton, J. L. Davidson, J. C. Miller, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1984, 11.

7 (*a*) J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1977, 287; (*b*) L. Carlton and J. L. Davidson, *ibid.*, 1987, 895.

8 J. L. Davidson, I. E. P. Murray, P. N. Preston, and M. V. Russo, *J. Chem. Soc., Dalton Trans.*, 1983, 1783.

9 J. L. Davidson, (*a*) *J. Chem. Soc., Chem. Commun.*, 1980, 113; (*b*) *J. Organomet. Chem.*, 1980, **186**, C19.

10 J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1976, 738.

11 J. L. Davidson, unpublished work.

12 CHEMGRAF, created by E. K. Davies, Chemical Crystallography Laboratory, Oxford University, developed and distributed by Chemical Design Ltd., Oxford.

13 B. E. Mann, *J. Chem. Soc., Perkin Trans. 2*, 1977, 84 and refs. therein; R. Benn, A. Rufinska, and G. Schroth, *J. Organomet. Chem.*, 1981, **217**, 91.

14 D. F. Steele and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1973, 2124 and refs. therein; M. G. B. Drew, W. A. Hopkins, P. C. H. Mitchell, and T. Colclough, *ibid.*, 1986, 351.

15 (*a*) J. L. Davidson, W. F. Wilson, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1985, 460; (*b*) L. Carlton, J. L. Davidson, P. Ewing, Lj. Manojlović-Muir, and K. W. Muir, *ibid.*, p. 1474.

16 J. R. Morrow, T. L. Tonker, and J. L. Templeton, *J. Am. Chem. Soc.*, 1985, **107**, 6956.

17 K. W. Muir, personal communication.

18 A. Efraty, J. A. Potenza, L. Zyontz, J. Daily, M. H. Huang, and B. Tohy, *J. Organomet. Chem.*, 1978, **145**, 315.

19 R. P. Hughes, J. W. Reisch, and A. L. Rheingold, *Organometallics*, 1984, **3**, 1761.

20 A. I. Gusev, G. G. Alexandrov, and Yu. T. Struchkov, *J. Struct. Chem.* (*U.S.S.R.*) (*Engl. Transl.*), 1969, **10**, 556.

21 A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anismov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 1969, 739.

22 J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 1975, 2531.

23 P. M. Maitlis and A. Efraty, *J. Organomet. Chem.*, 1965, **4**, 172; A. Efraty, *Can. J. Chem.*, 1969, **47**, 4695.

24 M. D. Rausch and A. V. Grossi, *J. Chem. Soc., Chem. Commun.*, 1978, 401.

25 A. Efraty, *Chem. Rev.*, 1977, **77**, 691.

26 T. A. Albright, P. Hoffman, and R. Hoffman, *J. Am. Chem. Soc.*, 1977, **99**, 7546; T. A. Albright, R. Hoffman, Y. Tse, and T. D.'Ottavio, *ibid.*, 1979, **101**, 3812.

27 S. Y. Chu and R. Hoffmann, *J. Phys. Chem.*, 1982, **86**, 1289.

28 S. Masamune, T. Machiguchi, and M. Aratani, *J. Am. Chem. Soc.*, 1977, **99**, 3524.

29 J. L. Davidson, *J. Chem. Soc., Chem. Commun.*, 1983, 1667.

30 H. Yamazaki and N. Nagihara, *J. Organomet. Chem.*, 1970, **21**, 431.

31 R. Fields, *Annu. Rep. N.M.R. Spectrosc.*, 1977, 7, 1.

32 L. Ricard, J. Estienne, and R. Weiss, *Inorg. Chem.*, 1973, **12**, 2182.

33 R. S. Herrick, S. J. Nieter-Burgmayer, and J. L. Templeton, *J. Am. Chem. Soc.*, 1983, **105**, 2599.

34 M. Crocker, M. Green, A. G. Orpen, H. P. Neumann, and C. J. Shaverien, *J. Chem. Soc., Chem. Commun.*, 1984, 1351; L. Brammer, M. Crocker, B. J. Dunne, M. Green, C. E. Morton, K. R. Nagle, and A. G. Orpen, *ibid.*, 1986, 1226.

35 J. R. Morrow, T. L. Tonker, and J. L. Templeton, *J. Am. Chem. Soc.*, 1985, **107**, 5004.

36 K. H. Dotz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587; H. Strutz, J. C. Dewar, and R. R. Schrock, *J. Am. Chem. Soc.*, 1985, **107**, 5999 and refs. therein; S. J. Landon, P. M. Schalman, and G. L. Geoffroy, *ibid.*, p. 6739 and refs. therein.

37 J. H. Frendenberger, R. R. Schrock, M. R. Churchill, A. L. Rheingold, and J. W. Zeller, *Organometallics*, 1984, **3**, 1563; T. J. Katz, T. H. Ho, N-Y. Shih, Y-C. Ying, and V. I. W. Stuart, *J. Am. Chem. Soc.*, 1984, **106**, 2659.

38 S. R. Allen, M. Green, N. C. Norman, K. E. Paddick, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1983, 1625.

39 R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.*, 1971, **10**, 2710.

Received 13*th November* 1986; *Paper* 6/2189