Synthesis, Structures, and Reactions of Ethenethiolato Complexes of Molybdenum and Tungsten $[M\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W). Their Relevance to the Mechanism of Metal-promoted Isomerisation of Carbon–Carbon Double Bonds

Naz M. Agh-Atabay and Jack L. Davidson *
Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS

Thermolysis of the η^2-*C,C*-vinyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SBu^t\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1**) (M = Mo or W) gives η^3-ethenethiolato complexes *Z*-*endo*-$[M\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2**). With M = W an intermediate *E*-*exo*-$[W\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3**) was isolated and structurally characterised, illustrating that *exo* ⟶ *endo* and *E* ⟶ *Z* isomerisations are concomitant processes. The relevance of this observation for mechanism(s) of metal-promoted alkyne isomerisations is discussed. Reactions of (**2**) and (**3**) with tertiary phosphines and dioxygen give σ-ethenethiolato complexes $[M\{SC(CF_3)=C(CF_3)H\}L(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, L = O or PPh_3; M = W, L = O, PPh_3, PMe_2Ph, or $PPh_2C\equiv CPh$) with retention of stereochemistry about the C=C bond. Dynamic ^{19}F n.m.r. studies reveal fluxional behaviour in some complexes due to alkyne propeller rotation.

Metal-promoted alkyne oligomerisation reactions are frequently thought to proceed *via* repeated insertion of an alkyne into the M–C single bond of intermediate metal–vinyl (alkenyl) complexes.[1] In recent years we[2] and others[3] have established that vinyl ligands are capable of stabilising co-ordinative unsaturation in metal complexes by co-ordinating in a dihapto manner and therefore functioning as formal three-electron donors to the metal. In extreme valence bond terms the metal–η^2-vinyl unit can be represented by a metallacyclopropene structure as shown in complexes (**1**). Since alkynes are known to undergo a variety of reactions with M=C bonds[4] an alternative pathway for metal-promoted alkyne oligomerisation may involve alkyne insertion into the M=C bond of η^2-vinyl intermediates.[5] We are currently investigating this possibility by exploring the chemistry of η^2-*C,C*-vinyl complexes, (**1**), which also contain a co-ordinated alkyne.[2,5]

We now report some of our initial studies which have previously appeared as a preliminary publication.[6]

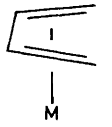
Results and Discussion

With a view to establishing whether or not the co-ordinated alkyne in (**1**) was capable of reacting with the η^2-*C,C*-vinyl ligand these complexes were heated in hexane at elevated temperatures in a sealed tube. No reaction was observed with the isopropyl derivative (**1c**) at 75 °C and the complex was recovered virtually unchanged. However, under similar conditions the butyl derivatives (**1a**) and (**1b**) afforded dark green (M = Mo) and dark red (M = W) crystalline complexes $[M\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ [M = Mo (**2a**) or W (**2b**)] in good yield (60—80%). ^{19}F N.m.r. studies established that the reactions proceeded *via* an intermediate complex (**3**) with an isomeric structure and this was isolated in the case of M = W by use of milder conditions (60 °C) and shorter reaction times (8 h instead of 20 h). However, the instability of the analogous molybdenum derivative prevented its isolation.

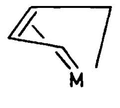
The analytical and mass spectral data for (**2a**), (**2b**), and (**3**) indicated that in each case thermolysis had resulted in loss of a butyl group and incorporation of a hydrogen into the molecule. The i.r. spectra exhibit a single, moderately intense peak near 1 760 cm^{-1}, close to that in the precursors (**1**), in accord with the presence of a co-ordinated $CF_3C\equiv CCF_3$ moiety. The ^1H n.m.r. spectra contain a cyclopentadienyl group singlet in addition to a quartet due to a single hydrogen near δ 5 [(**2a**) and (**2b**)]. In the case of (**3**) a similar quartet is observed but at significantly higher field, δ 1.49. The ^{19}F n.m.r. data for (**2a**) and (**2b**) are similar except that two of the peaks in the former partially overlap and consequently the latter will be described. Four distinct CF_3 multiplets are present, a doublet δ_1 −55.29, two quartets δ_2 −58.43 and δ_4 −61.83, and a quartet of quartets δ_3 −58.80. The doublet δ_1 clearly arises from coupling to the unique proton and hence indicates the presence of a $C(CF_3)=C(CF_3)H$ group. Moreover, the absence of coupling to the other CF_3 on this moiety is indicative of a *trans* arrangement of the CF_3 substituents.[7] In contrast the intermediate (**3**) appears to have a *cis* arrangement since the corresponding groups in the ^{19}F n.m.r. spectrum show a coupling of 10.2 Hz.[7]

In an attempt to confirm this, single-crystal *X*-ray diffraction studies of both (**2b**) and (**3**) were carried out by Dr. K. W. Muir (University of Glasgow) the results of which have been published previously as a communication.[6] These revealed that in each case the molecule consists of an ethenethiolate ligand $SC(CF_3)=C(CF_3)H$ bonded in an η^3 manner *via* the sulphur and two alkene carbons to the metal of a $[W(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ moiety. The η^3 mode of co-ordination is reminiscent of the $SC(CF_3)=C(CF_3)$ co-ordination found in $[Mo\{\eta^4\text{-}C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)SPr^i\}(PEt_3)(\eta^5\text{-}C_5H_5)]$[8] and $[W\{\eta^6\text{-}Pr^iSC(CF_3)=C(CF_3)C(CO_2Me)=C(CO_2Me)C(CF_3)=C(CF_3)\}(\eta^5\text{-}C_5H_5)]$.[5] In agreement with n.m.r. data, the ethenethiolate ligand in (**3**) was found to have a *cis* arrangement of CF_3 groups, whereas in the thermodynamically favoured form, (**2b**), isomerisation to a *trans* structure has occurred. The second, but unexpected, structural feature of interest concerns the orientation of the $SC(CF_3)=C(CF_3)$ ligand. As illustrated this is different in the two isomers, with an *exo* configuration in (**3**) and an *endo* configuration in (**2b**). These configurations can be compared with *exo* and *endo* rotamers observed in η^3-allyl complexes such as $[M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$[9] (M = Mo or W) and it is relevant to consider the W–$\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}$ bonding as quasi-π-allylic in character. However, this formalism should not be taken too far since differences are apparent. For example the W–S distances in (**2b**) and (**3**) are on average 0.17 Å shorter than in the otherwise comparable complex (**1c**).[10] This suggests a contribution to the W–S bond from S→W π donation. In a formal sense the η^3-SC(CF$_3$)=C(CF$_3$)H$^-$ ligand can be considered as a six-electron donor, whereas the η^3-C$_3$H$_5$$^-$ group can only donate a maximum of four electrons to a metal. Secondly, there is no evidence for a σ-η^3-σ rearrangement which is commonly found in allyl complexes.[11] In the present case this would provide a mechanism for *exo–endo* isomerism but, significantly, would not result in a *cis–trans* rearrangement.

In this respect the complexes bear closer comparison with η^4-diene derivatives such as $[\mathrm{Mo(CO)_2(diene)(\eta^5\text{-}C_5H_5)}]^+$ [12] and $[\mathrm{MCl_2(diene)(\eta^5\text{-}C_5H_5)}]$ (M = Ta or Nb),[13] which can also exist in both *exo* and *endo* isomeric forms. In complexes of this type the metal-diene bonding ranges from conventional η^4-co-ordination, (**6**), through to the bent σ^2-π structure, (**7**). In many cases, particularly when the latter mode of bonding is adopted, fluxional behaviour is observed which can be attributed to rapid ring inversion *via* a planar metallacyclopentene species.[12,13] This provides a mechanism for *exo–endo* isomerisation which is similar to that we proposed for the rearrangement of (**3**). The fact that (**3**) $\longrightarrow$ (**2**) involves concomitant *exo→endo* and *cis→trans* isomerisations strongly suggests a common pathway for the two processes. As Scheme 1 illustrates an $\eta^3 \longrightarrow \eta^2 \longrightarrow \eta^3$ rearrangement proceeding *via* an intermediate or transition state, (**8**), containing a planar metallacyclic ring system readily accomplishes both isomerisation reactions.



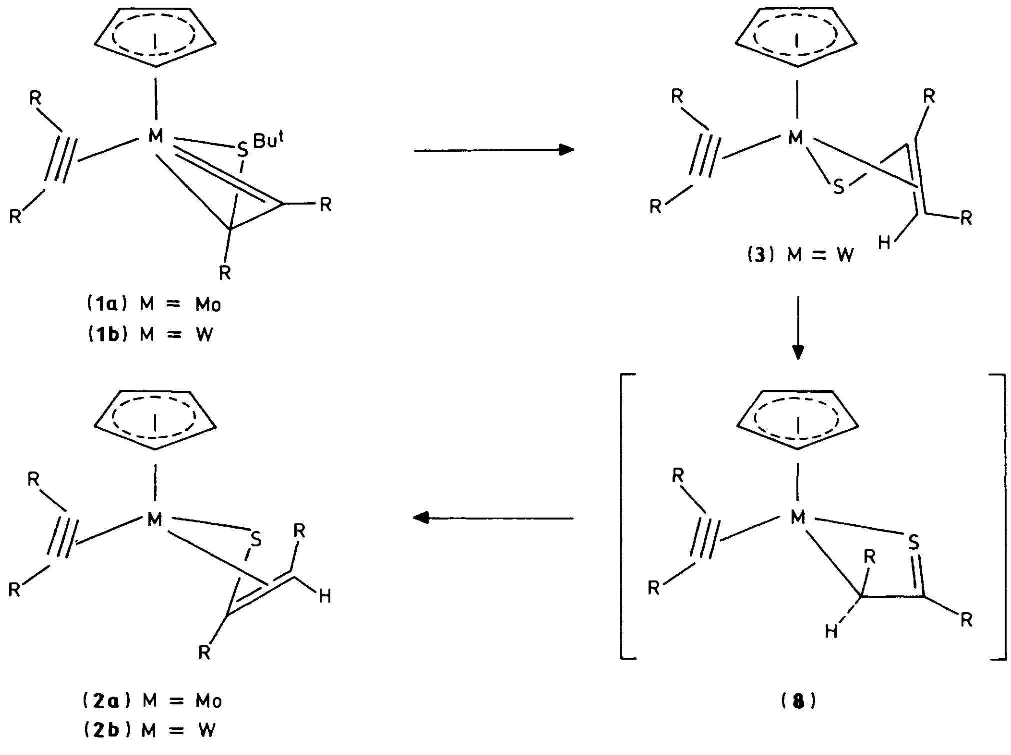
(**6**)



(**7**)

This mechanism may have important implications for the stereochemistry of metal-promoted alkyne oligomerisation reactions. Previously, it has been thought that if σ vinyl intermediates are involved in such reactions the stereochemistry of the polyalkene product, *cis* or *trans*, reflected the stereochemistry of the insertion step, *i.e. cis* insertion leads to *cis* products.[1] However Bergman's elegant work[14] demonstrated that this does not necessarily follow, such that *cis* insertion could lead to *trans* products. Moreover, we have recently suggested that if η^2-vinyl intermediates are involved, the mode of ring opening $\eta^2 \longrightarrow \sigma$ could determine the stereochemistry of the product.[2,15] A further alternative becomes feasible if the growing polymer chain remains attached to the metal at carbons C$_a$ and C$_b$ as in (**9**) (Scheme 2) since isomerisation *via* a ring-flip mechanism related to that in Scheme 1 could equally well change the stereochemistry of the C=C bond. We note that η^4-butadienyls, structurally related to (**9**), have recently been isolated,[5,16,17] one of which, $[\mathrm{W\{\eta^4\text{-}C_2(CF_3)_2C_2Me_2SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$,[5] we obtained from the reaction of 2-butyne with the η^2-*C,C*-vinyl complex (**1c**). Further credence is lent to our mechanistic proposals by the recent isolation of $[\mathrm{Nb\{\eta^2\text{-}C(Me)C(Me){=}C(Me)C(H)Me\}(\eta^5\text{-}C_5H_5)_2}]$[18] which contains a planar η^2-butadienyl ligand of the type required for the intermediate (**10**) in a ring-flip mechanism. Moreover, the reaction of P(OMe)$_3$ with the η^4-butadienyl $[\mathrm{Ru\{\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(H)Ph\}(\eta^5\text{-}C_5H_5)}]$ to give an η^3-butadienyl complex $[\mathrm{Ru\{\eta^3\text{-}C(Ph){=}C(Ph)C(Ph){=}C(Ph)H\}\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)}]$ results in a change of stereochemistry of the C(H)Ph moiety.[17] We note that this is readily explained in terms of the ring-flip mechanism in Scheme 2.

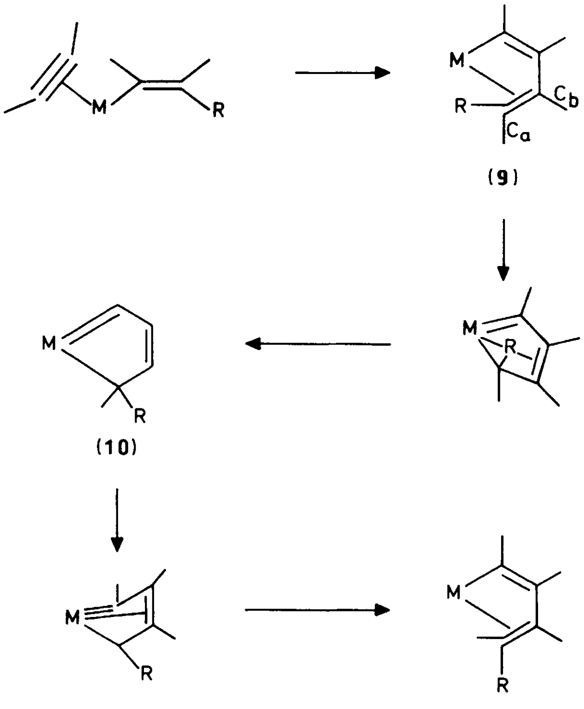
It is instructive to compare the structures of (**2**) and (**3**) with that of the η^2-*C,C*-vinyl precursor (**1**), which also contains an η^3-S–C–C ligand bonded to a $[\mathrm{M(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$ fragment. *X*-Ray diffraction studies of (**1c**) have been carried out previously[10] and, significantly, a close structural relationship between (**1c**) and the *trans* isomer (**2**) is readily apparent. In



Scheme 1. R = CF$_3$

particular, the S–C–C skeleton adopts an *endo* configuration in both species whilst the alkyne ligands exhibit similar orientations. Moreover, related derivatives $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (R = Me, Et, or Pr^n) have been found to exist in two isomeric forms at low temperature, one of which appears to be similar to (**1c**). The structure of the other form is less well defined but we have previously proposed an alternative *exo* form which has structural similarities to complex (**3**).

Comparisons with heteroallyl derivatives are also pertinent in particular with η^3-1-oxo- and 1-aza-allyl complexes, $[W\{\eta^3\text{-}OC(NEt_2)CH_2\}(CO)_2(\eta^5\text{-}C_5H_5)]$[19] and $[Mo\{\eta^3\text{-}N(H)C(C_6H_4Me\text{-}4)CH_2\}(CO)_2(\eta^5\text{-}C_5H_5)]$[20] whose structures have also been elucidated by *X*-ray diffraction studies. η^3-Acryloyl complexes, $[W\{C(O)C(CF_3){=}C(CF_3)H\}(CO)L(\eta^5\text{-}C_5H_5)]$ (L = CO or PEt_3)[21] have similarly been studied although the $C(CF_3)H$ moiety was observed to adopt a *trans* arrangement in every case. Moreover, in all of these complexes the η^3 ligand adopts an *endo* configuration with respect to the cyclopentadienyl ligand and consequently the structures most closely resemble (**2**). No evidence for the *exo* form [*cf.* (**3**)] was obtained in any of these studies.

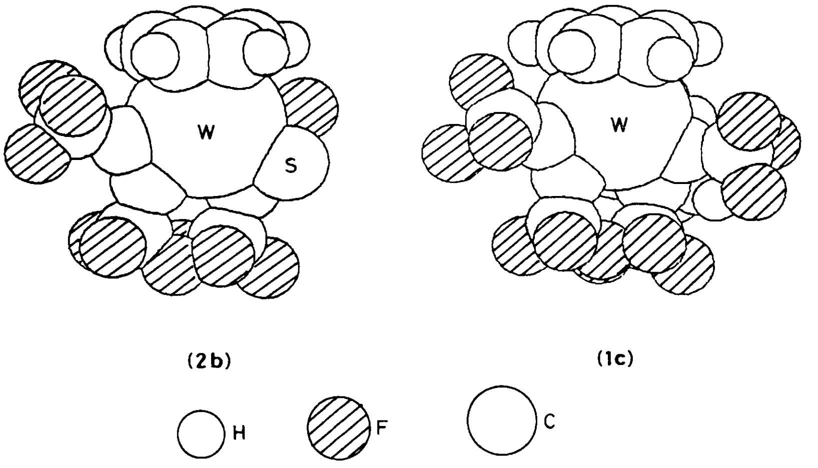


Scheme 2.

An interesting consequence of the structural relationship between (**1**), and (**2**), and (**3**) concerns the dynamic properties of the complexes, in particular the presence or absence of alkyne propeller rotation. Complexes (**1a**), (**1b**), and (**1c**) exhibit four well resolved signals in the ^{19}F n.m.r. spectra at 20 °C consistent with a rigid structure, as do their structural analogues (**2a**) and (**2b**). However, the *exo* complex (**3**) exhibits two overlapping alkyne CF_3 multiplets at -20 °C in CD_2Cl_2, whereas at higher temperatures (20 °C) the coupling is lost and a singlet is obtained. Although this may simply reflect a temperature effect leading to accidental degeneracy of the two peaks it is also consistent with the onset of alkyne rotation, a well known phenomenon in cyclopentadienyl molybdenum and tungsten alkyne complexes.[22] If the latter interpretation is correct a possible explanation for differences in dynamic behaviour between *exo* (**3**) and *endo* complexes (**1**) and (**2**) is provided by molecular graphics studies.[23] These reveal that free rotation of the alkyne in (**3**) is possible but in (**1**) and (**2**) this is inhibited by significant steric interaction between the alkyne CF_3 substituents and the apical CF_3 on the η^3 ligand (see Figure). The contribution to the barrier to rotation from electronic effects is of course not known.

A second point of comparison between η^2-vinyls (**1**) and the ethenethiolato derivatives concerns the metal–alkyne bonding. As noted earlier, *X*-ray diffraction studies reveal an unusually short tungsten–sulphur distance consistent with some sulphur–metal π donation. If, as a consequence, the $\eta^3\text{-}SC(CF_3){=}C(CF_3)H^-$ ligand should be formally regarded as a six-electron donor, it is only necessary for the co-ordinated hexafluorobut-2-yne to donate two electrons to the metal in order that the tungsten achieves an 18-electron configuration. Templeton and Ward[24] pointed out that the ^{13}C n.m.r. shifts of co-ordinated alkyne carbon atoms are sensitive to metal–alkyne bonding, with four-electron donors exhibiting significant shifts to high frequency. It was therefore of interest to compare ^{13}C n.m.r. shifts of the alkyne ligands in complexes (**2**) with those in (**1**) and related η^2-*C*,*C*-vinyl and alkyne complexes.[25]

As the Table shows, the C≡C resonances of the ethenethiolato complex (**2b**) are observed at δ 167.28 and 162.24, close to that of the bis(alkyne) complexes $[MoX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (X = Cl or I), in particular the iodo complex. Formally, the



(**2b**) (**1c**)

Figure. Space filling diagrams of (**1c**) and (**2b**) illustrating CF_3–CF_3 non-bonding interactions

Table. ^{13}C-$\{^{19}F\}$ N.m.r. data for ethenethiolato, η^2-vinyl, and alkyne complexes*

Complex	δ_1	δ_2	δ_3	δ_4
$[W\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$			167.28	162.24
$[W\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$	207.62	52.21	157.48	148.19
$[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SBu^t\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$	223.12	56.07	151.28	145.88
$[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2PMe_2\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$	219.39	53.18d	144.72	137.99
$[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNMe_2\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$	217.05	53.75	141.55	138.35
$[MoCl(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$			170.84	169.55
$[MoI(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$			167.15	162.82

* δ_1, M=*C*(CF$_3$); δ_2, M–*C*(CF$_3$); δ_3 and δ_4, $CF_3C\equiv CCF_3$.

alkynes in the latter are acting as three-electron donors and, if the chemical shift of the alkyne carbons provides a reasonable assessment of metal–alkyne bonding, the alkyne in the ethenethiolato derivative, (**2b**), must also be considered a three-electron donor. It may therefore be realistic to conclude that, as suggested by *X*-ray diffraction studies some sulphur→metal π donation occurs such that the metal–sulphur bond in (**3**) has partial double-bond character. In the absence of sulphur π donation the alkyne would be required to function as a four-electron donor, but in practice the participation of the alkyne π $\perp$ set of orbitals with the metal must be somewhat reduced as a consequence. With regard to the η^2-*C*,*C*-vinyl complexes, the fact that the chemical shift of the alkyne carbons exhibits a shift to lower δ values implies that, relative to (**2b**), the alkyne is donating less electron density to the metal. In each case some participation of the π $\perp$ orbitals in bonding is indicated by the extreme δ value of *ca.* 120 p.p.m. found in complexes where only two-electron donation is possible.[24] Although extra π donation from sulphur does not appear to be significant in complexes (**1**) the η^2-*C*,*C*-vinyl carbons more than compensate for this and, as the chemical shifts δ_1 and δ_2 indicate, the bonding approaches the extreme metallacyclopropene valence-bond structure illustrated.

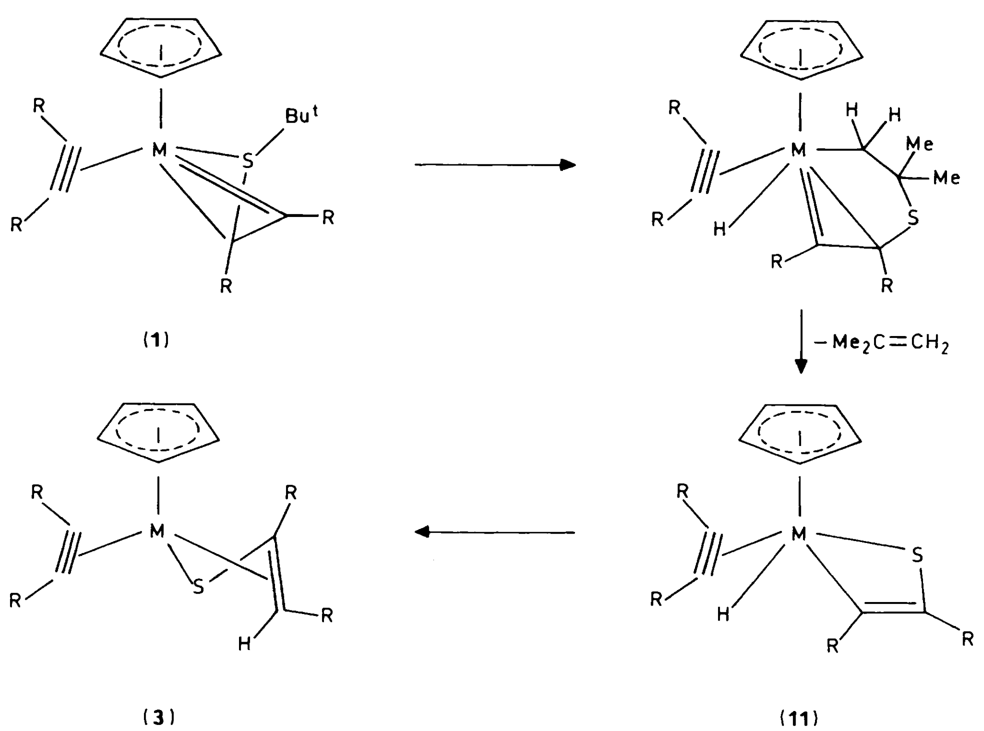
Finally, in this section we note that thermolysis of complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$, (**1a**)—(**1c**), does not result in alkyne insertion into the M=C bond of the metallacyclopropene moiety. This negative result is of interest since addition of tertiary phosphines, oxygen,[8] or alkynes[10] to complexes (**1**) results in insertion under very mild conditions ($\leqslant 20$ °C). This points to a requirement for co-ordination of another ligand before insertion can occur. It may be that co-ordination of another ligand leads to an $\eta^2\rightarrow\sigma$ transformation and insertion then occurs into the M–C single bond of the vinyl ligand, although other explanations are possible.[8] Further studies currently in progress may help to resolve this question.

However, other questions still remain, such as the mechanism of the reaction, which results in loss of a butyl group from complexes (**1a**) and (**1b**) and, ultimately, formation of the ethenethiolato complexes (**2**) and (**3**). A related question concerns the fact that the butyl complexes (**1a**) and (**1b**) undergo this reaction whereas the isopropyl derivative is unreactive. A possible explanation for the latter observation lies in the fact that (**1a**) and (**1b**) retain their η^2-*C*,*C*-vinyl structure at temperatures required to effect the transformation into (**2**) and (**3**). However, ^{19}F n.m.r. studies of (**1c**) have established that the complex is fluxional above 20 °C as a consequence of carbon–sulphur bond fission which regenerates the bis (alkyne) structure $[W(SPr^i)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$.[2a] It is conceivable that the ethenethiolato ligand can only be generated from an η^2-*C*,*C*-vinyl ligand and not from discrete alkyne and thiolate groups.

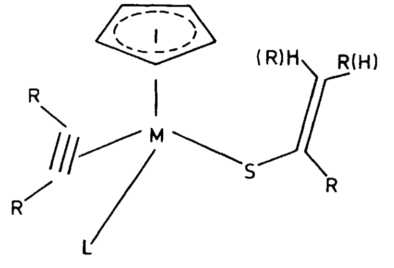
With regard to the mechanism of reaction several possibilities are readily apparent. The first involves homolysis of the carbon–sulphur bond to generate a butyl radical and an organometallic 17-electron species containing an ethenesulphido group M–SC(CF$_3$)=C(CF$_3$) which can extract a hydrogen from the solvent. However this seems unlikely since thermolysis of (**1**) in deuteriated toluene did not result in deuterium incorporation into the product (**2**). Alternatively, we note that tertiary butyl derivatives readily undergo elimination (E_1) reactions to generate isobutene and a proton *via* a carbonium ion intermediate Me_3C^+.[26] In the present case stereospecific protonation of the resulting anion $[M\{SC(CF_3)=C(CF_3)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]^-$ could provide a route to the *E exo* product (**3**).

Despite these observations we favour an intermolecular process which is suggested by the well known ability of transition metals to activate C–H bonds.[27] Of particular relevance are reactions involving oxidative cleavage of C–H bonds in trimethylphosphine complexes which lead to η^2-CH_2PMe_2 metal hydride derivatives.[28] It is therefore conceivable that the transformation of (**1**) into (**3**) proceeds *via* the related process in Scheme 3 in which hydrogen transfer to the metal leads to elimination of isobutene and formation of an intermediate hydrido derivative (**11**). Stereospecific delivery of the hydrogen to the β-carbon of the metallacyclic ring system will then generate the *E-exo* ethenethiolato complex (**3**). A related hydrogen-transfer process from a methyl to the CH$_2$ of a co-ordinated η^3-2,3-dimethylbutadienyl ligand has been reported, although in this case no elimination reaction is involved.[29] A key feature of the latter reaction is the presence of an agostic hydrogen on the methyl group. Although no evidence is available for agostic hydrogen interactions involving the butyl group in (**1a**) and (**1b**), molecular graphics studies of the isopropyl derivative (**1c**) reveal that an isopropyl methyl hydrogen can approach to within 2.4 Å of the metal, which is within the sum of the van der Waals radii of tungsten and hydrogen.

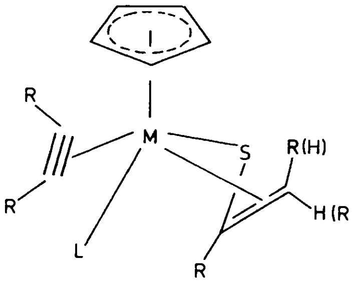
Previously we have reported the synthesis of alkyne thiolate complexes $[M(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$[22b] which are clearly related to the ethenethiolato derivatives (**2**) and (**3**). The former have been observed to undergo carbonyl substitution reactions with tertiary phosphines and dioxygen under very mild conditions. Consequently it was of interest to investigate the reactivity of the ethenethiolate complexes towards the same reagents. Reactions of (**2a**) with PPh$_3$, and (**2b**) with PPh$_3$, PMePh$_2$ and the phosphinoalkyne $PPh_2C\equiv CPh$ proceed readily at 70 °C in hexane to give 1:1 adducts $[M\{SC(CF_3)=C(CF_3)H\}L(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ [M = Mo, L = PPh$_3$ (**4a**); M = W, L = PPh$_3$ (**4b**), L = PMePh$_2$ (**4c**), L = $PPh_2C\equiv CPh$ (**4d**)] in moderate (40—60%) yield. Reactions with dioxygen were carried out at 40 °C to give oxo derivatives $[M\{SC(CF_3)=C(CF_3)H\}O(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ [M = Mo (**5a**) or W (**5b**)]. Although of similar stoicheiometry the phosphine and oxo derivatives have quite different spectroscopic properties as a consequence of the different oxidation states of the metal which affects the detailed structure of the molecules.



Scheme 3. R = CF_3



(4)

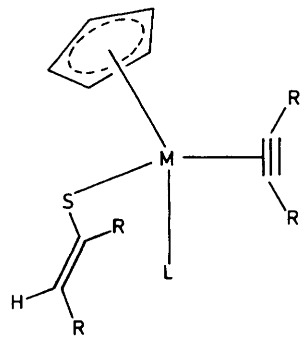


(12)

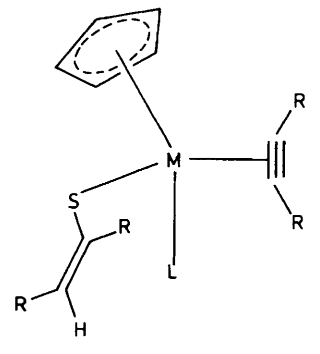
The phosphine derivatives all exhibit a single $\nu_{C\equiv C}$ mode in the i.r. spectrum at 1 672 cm^{-1} (**4a**) and near 1 635 (**4b**)—(**4d**) close to those of $[M(SC_6F_5)L(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, L = tertiary phosphine or phosphite).[22b] A weak band at 2 184 cm^{-1} in the spectrum of (**4d**) suggests the presence of a free, rather than a co-ordinated, C≡C triple bond in the $PPh_2C{\equiv}CPh$ ligand, thus indicating co-ordination *via* the phosphorus lone pair rather than *via* the alkyne C≡C bond. Co-ordination of phosphinoalkynes *via* either mode has been observed previously and in one particular case [equation (1)] the P-donor mode can be converted into the alkyne-donor mode under mild conditions.[30] However, despite the more vigorous conditions employed in the synthesis of (**4d**) no trace of the η^2-bonded form was detected. This is not entirely surprising since previous attempts to convert the related carbonyl complex $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ into the known bis(alkyne) derivative $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ by heating at 70 °C with $CF_3C{\equiv}CCF_3$ were unsuccessful.[25]

$$[W(CO)_2(\sigma\text{-}PPh_2C{\equiv}CPPh_2)(S_2CNEt_2)_2] \xrightarrow[-CO]{r.t.} [W(CO)(\eta^2\text{-}PPh_2C{\equiv}CPPh_2)(S_2CNEt_2)_2] \quad (1)$$

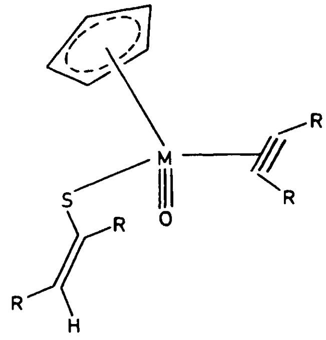
A weak band is also observed in the i.r. spectrum of the molybdenum complex (**4a**) at 1 625 cm^{-1} which can be attributed to a ν(C=C) mode. Since the ν(C≡C) band occurs in this region a similar well resolved band is not observed with the tungsten complexes although a shoulder on the ν(C≡C) mode was observed with (**4c**). This observation is consistent with the presence of an unco-ordinated alkene and hence indicates that phosphine co-ordination leads to cleavage of the metal–alkene linkage. Of the two basic structures available for these complexes (**4**) and (**12**) it is clear that the co-ordinatively unsaturated form (**4**) is preferred. As with $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ the alkyne ligand must be acting as a formal four-electron donor as a consequence of both sets of filled C≡C π orbitals being involved in bonding with the metal.[31] The very low ν(C≡C) frequencies observed with these derivatives are probably a consequence of this mode of bonding. It is interesting that, thermodynamically, this appears to be preferable to two-electron donation by both the alkene and the alkyne as would be required by structure (**12**). Interestingly, reaction of the η^3-oxoallyl complex $[W\{\eta^3\text{-}OC(OEtOCH_2)\}(CO)_2(\eta^5\text{-}C_5H_5)]$ with phenylacetylene gives complex (**13**), also containing a four-electron donor alkyne.[19] However, in this case, fission of one carbon, and one oxygen, to metal bond occurs such that the σ-oxoallyl ligand is co-ordinated to tungsten *via* a



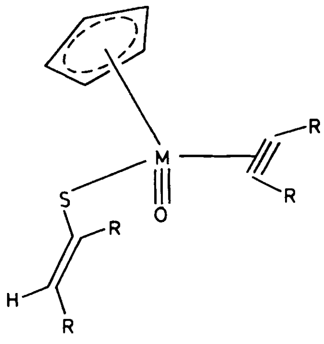
(4^{i})



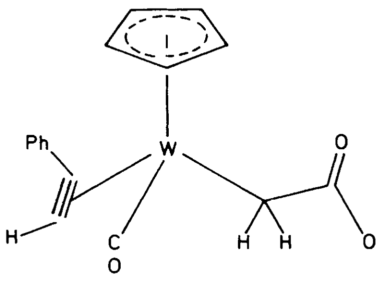
(4^{ii})



(5^{i})



(5^{ii})



(**13**)

carbon atom, *i.e.* as σ-enolate. Simultaneous co-ordination of an alkene and an alkyne to Mo^{II} and W^{II} has been observed previously in complexes $[M(alkene)(RC{\equiv}CR')(S_2CNEt_2)_2]$ (M = Mo or W; alkene = maleic anhydride, tetracyanoethylene, or *trans*-dicyanoethylene; R,R' = H, Me, or Ph)[32] and $[Mo(\eta^2\text{-dpps})(RC{\equiv}CR')(\eta^5\text{-}C_5H_5)]^+$ (dpps = *o*-diphenylphosphinostyrene; R = H, R' = Bu^t; R = R' = Me)[33] but, significantly, in these derivatives the electronic requirements of the metal are such that the alkyne functions as a four-, rather than a two-electron donor. This again emphasises the importance of the second set of alkyne π orbitals in bonding in alkyne complexes of metals with a d^4 electron configuration.

As a consequence of the d^4 electron configuration of the metal the alkyne ligand in (**4**) should exhibit an orientational preference in which the C≡C bond axis lies perpendicular to the M–S axis so as to maximise orbital overlap.[31,34] This preference has been demonstrated previously in a structural study of $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[34] and other complexes with d^4 configurations.[35] The n.m.r. spectra of (**4**) provide evidence for a preferred alkyne orientation at low temperatures in addition to providing unequivocal identification of the stereochemistry about the C=C bond in the ethenethiolato ligand. For example, the ^{19}F n.m.r. spectra of (**4b**) and (**4d**) show clear evidence for a *cis* ethene structure (**4**^{i}) since the ethenethiolate CF_3 resonances exhibit *J*(F–F) = 10.5 Hz in each case, whereas with (**4c**) *J*(F–F) = 0 in accord with a *trans* arrangement of CF_3 groups (**4**^{ii}). The ^{19}F n.m.r. spectrum of (**4a**), in contrast, exhibits two sets of resonances consistent with the presence of both isomeric forms, ratio *cis*:*trans* = 1:12.

All of these derivatives exhibit temperature-dependent spectra involving the alkyne signal which appears as a single broad resonance at ambient temperature but which splits into two distinct peaks at lower temperatures (*ca.* −40 °C). This parallels the behaviour of comparable thiolate derivatives $[M(SC_6F_5)(L)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ [M = Mo or W; L = CO, $P(OMe)_3$, PMe_2Ph, or PEt_3] which also exhibit alkyne propeller rotation with relatively low coalescence temperature in the ^{19}F n.m.r. spectra.[22b]

The spectroscopic data for the oxo complexes (**5a**) and (**5b**) are comparable, where appropriate, with those of SC_6F_5 derivatives $[M(SC_6F_5)O(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[22b] and, as with phosphine derivatives (**4**), suggest a structure with a σ-

$SC(CF_3)=C(CF_3)H$ ligand. The i.r. spectra exhibit a $\nu(C\equiv C)$ band which lies some 170 cm^{-1} to high frequency of that of the phosphine complexes which results in clear observation of a $\nu(C=C)$ mode of the σ-ethenethiolato ligand near 1 630 cm^{-1}. N.m.r. data for the two complexes are also consistent with σ-ethenethiolato ligand and, in the case of (**5a**), a *trans* stereochemistry (5^{i}) is indicated. The ^{19}F n.m.r. spectrum, unlike those of the phosphine derivatives (**4**), is temperature invariant and shows four well resolved signals at room temperature which parallels the behaviour of the oxo derivatives $[M(SC_6F_5)O(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ (M = Mo or W)[22b] and $[Mo\{C(CF_3)=C(CF_3)SC_6F_5\}O(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$[8] which are also stereochemically rigid. By analogy with the oxo–alkyne derivatives mentioned above we assume that the alkyne adopts a preferred orientation in which the C≡C axis lies parallel to the M–S axis, *i.e.* at 90° to that in complexes (**4**). The ^{19}F n.m.r. spectrum contains two quartets δ −51.38 and −54.85 which can be assigned to the alkyne CF_3 groups in view of the typical *J*(F–F) value 3.6 Hz for co-ordinated hexafluorobut-2-yne.[22b] The other two peaks each show coupling to the ethenethiolato proton and to each other with a *J*(F–F) value 1.7 Hz typical of a *trans*-$CF_3C=CCF_3$ group. The tungsten analogue (**5b**) shows similar spectroscopic features to (**5a**) except that two sets of n.m.r. resonances are observed, one due to the *trans* isomer (5^{i}), the other due to the *cis* isomer (5^{ii}).

Finally, we note the variable stereochemistry of the σ-ethenethiolate in both phosphine and oxo complexes (**4**) and (**5**). Superficially the stereochemistry appears to be influenced by both the metal and the incoming ligand. Alternatively the different stereochemistries observed in (**4**) and (**5**) could merely reflect the stereochemistry of the η^3 ligand in the starting material employed in each individual reaction. In order to resolve this situation the oxidation of $[W\{\eta^3-SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ in air was studied by ^{19}F n.m.r. spectroscopy. It was observed that a mixture of both *E exo* and *Z endo* isomers produced a mixture of *cis*- and *trans*-$[W\{\sigma-SC(CF_3)=C(CF_3)H\}O(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ (**5b**) with no change in isomer ratio, within experimental error. We therefore conclude that the substitution reactions proceed with retention of stereochemistry about the C=C bond.

Experimental

N.m.r. spectra were recorded on a Bruker WP 200 SY spectrometer at 200.13 (^{1}H), 188.31 (^{19}F), and 50.31 (^{13}C) MHz; chemical shifts are referred to $SiMe_4$ and CCl_3F (δ = 0). I.r. spectra were recorded as solutions on a Perkin-Elmer 580 spectrometer and mass spectra on a Vacuum Generators updated AEI MS9 instrument at 70 eV. Reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried over powdered calcium hydride (Et_2O, hexane) or P_2O_5 (dichloromethane) and distilled under nitrogen just before use. Complexes $[M\{\eta^3-C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ (**1a**)—(**1c**) were obtained according to literature methods.[2a]

Thermolysis of $[Mo\{\eta^3-C(CF_3)C(CF_3)SBu^t\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$, (**1a**).—A solution of complex (**1a**) (90 mg, 0.16 mmol) in hexane–diethyl ether (2:1, 20 cm^3) was heated at 60 °C in a sealed tube fitted with a Westef stopcock for 20 h whereupon the colour changed from orange to dark green. The resulting solution was filtered, concentrated *in vacuo* to *ca.* 5 cm^3, and, on cooling, to −15 °C dark green crystals of $[Mo\{\eta^3-SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ (**2a**) (53 mg, 65%) were obtained (Found: C, 30.0; H, 1.1. $C_{13}H_6F_{12}MoS$ requires C, 30.1; H, 1.2%); *m/z* 518 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 788wm cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$, 20 °C), δ 6.0 (s, 5 H, C_5H_5) and 4.92 [q, *J*(H–F) 8.3, 1 H, $=C(CF_3)H$]; ^{19}F ($CDCl_3$), δ −53.93 [d, *J*(F–H) 8.3, 3 F], −57.36 (2 overlapping signals, 6 F), and −62.13 p.p.m. [q, *J*(F–F) 4.2 Hz, 3 F].

Thermolysis of $[W\{\eta^3-C(CF_3)C(CF_3)SBu^t\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$, (**1b**), *at* 75 °C.—A suspension of complex (**1b**) (120 mg, 0.18 mmol) in hexane (20 cm^3) was heated at 75 °C for 20 h in a sealed tube whereupon a colour change from pale yellow to purple was observed. Solvent was removed *in vacuo* and the residue chromatographed over Florisil with hexane–diethyl ether (1:5) as eluant. The resulting red-purple band was collected, concentrated and cooled to −20 °C whereupon red-purple crystals of $[W\{\eta^3-SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$, (**2b**) (90 mg, 80%) were obtained (Found: C, 26.0; H, 1.1. $C_{13}H_6F_{12}SW$ requires C, 25.8; H, 1.0%); *m/z* 604 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 763wm cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$), δ 6.08 (s, 5 H, C_5H_5) and 4.83 [q, *J*(H–F) 8.4, 1 H, $=C(CF_3)H$]; ^{19}F ($CDCl_3$), δ −55.29 [d, *J*(F–H) 8.4, 3 F], −58.43 [q, *J*(F–F) 2.8, 3 F], −58.80 [qq, *J*(F–F) 2.7, 4.3, 3 F] and −61.83 p.p.m. [q, *J*(F–F) 4.3, 3 F]; $^{13}C-\{^{1}H\}$ [$(CD_3)_2CO$, −10 °C], δ 167.28 [br q, *J*(C–F) 45.0, $CF_3\mathit{C}\equiv$], 162.24 [br q, *J*(C–F) 47.2, $CF_3\mathit{C}\equiv$], 129.41 [q, *J*(C–F) 275.1, CF_3], 125.93 [q, *J*(C–F) 270.0, CF_3], 125.70 [q, *J*(C–F) 271.3, CF_3], 123.53 [q, *J*(C–F) 272.0, CF_3], 58.68 [qq, *J*(C–F) 42.2, 4.4, $S-\mathit{C}(CF_3)=$], and 30.67* p.p.m. [q, *J*(C–F) 35.8 Hz, $\equiv\mathit{C}(CF_3)H$].

Thermolysis of $[W\{\eta^3-C(CF_3)C(CF_3)SBu^t\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$, (**1b**) *at* 60 °C.—A suspension of complex (**1b**) (80 mg, 0.12 mmol) in hexane–diethyl ether (1:1, 15 cm^3) was heated at 60 °C in a sealed tube for 8 h when a colour change from pale yellow to dark red was observed. The solution was centrifuged, concentrated to *ca.* 4 cm^3, and cooled to −15 °C to give a red powder consisting of two isomers of $[W\{\eta^3-SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$, (**2b**) + (**3**), according to ^{19}F n.m.r. spectroscopy. Following sublimation (0.1 mmHg, 45 °C) and repeated crystallisation from CH_2Cl_2–hexane pure red crystals of $[W\{\eta^3-SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ (**3**) were obtained (34 mg, 47%) (Found: C, 26.0; H, 1.0. $C_{13}H_6F_{12}SW$ requires C, 25.8; H, 1.0%); *m/z* 604 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 755wm cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$), δ 5.59 (s, 5 H, C_5H_5) and 1.49 [q, *J*(H–F) 10.0, 1 H, $=C(CF_3)\mathit{H}$]; ^{19}F ($CDCl_3$, 18 °C) δ −52.69 [dq, *J*(F–H) 9.8, *J*(F–F) 10.3, 3 F], −54.95 [q, *J*(F–F) 10.2 Hz], and −59.57 p.p.m. (s, 6 F).

Reaction of $[Mo\{\eta^3-SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ *with* PPh_3.—A solution of the complex (55 mg, 0.11 mmol) and PPh_3 (33 mg, 0.13 mmol) in hexane (20 cm^3) was heated at 70 °C in a sealed tube for 24 h when a colour change from dark to light green was observed. The solution was centrifuged, concentrated *in vacuo*, and cooled to −15 °C to give a light green solid. Recrystallisation from CH_2Cl_2–hexane gave light green crystals of $[Mo\{SC(CF_3)=C(CF_3)H\}(PPh_3)(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ (**4a**) (44 mg, 53%) (Found: C, 47.9; H, 2.6. $C_{31}H_{21}F_{12}MoPS$ requires C, 47.7; H, 2.7%); *m/z* 780 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 672wm, $\nu(C=C)$ 1 625w cm^{-1}. N.m.r. ^{1}H ($CDCl_3$, 20 °C), δ 7.1—7.8 (br m, 15 H, PPh_3), 6.29 [q, *J*(H–F) 7.6, 1 H, $=C(CF_3)H$], and 4.96 [d, *J*(H–P) 0.75, 5 H, C_5H_5]; ^{19}F ($CDCl_3$, −50 °C), *cis* isomer, δ −52.03 (m, 3 F), −53.92 (br s, 3 F, CF_3), −55.62 (m, 3 F), and −60.4 [q, *J*(F–F) 10.7, 3 F]; *trans* isomer, −51.97 (br s, 3 F), −55.38 (br s, 3 F), −58.78 [dq, *J*(F–H) 7.5, *J*(F–F) 1.3 Hz, 3 F], and −62.25 p.p.m. (br m, 3 F), ratio *cis*:*trans* 1:12.

Reaction of $[W\{\eta^3-SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ *with* PPh_3.—A solution of the complex (45 mg, 0.07 mmol) and PPh_3 (21 mg, 0.08 mmol) in hexane (10 cm^3) in a

---

* CD_2Cl_2, 28 °C [obscured by solvent peak in $(CD_3)_2CO$].

sealed tube was heated at 70 °C for 24 h. A colour change from red-purple to green was observed. The solution was centrifuged and then concentrated *in vacuo* and cooled to −15 °C to give green crystals of $[W\{SC(CF_3)=C(CF_3)H\}(PPh_3)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**4b**) (26 mg, 40%) (Found: C, 42.8; H, 2.4. $C_{31}H_{21}F_{12}PSW$ requires C, 42.9; H, 2.4%) *m/z* 866 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 636m cm^{-1}. N.m.r.: ^1H ($CDCl_3$, 20 °C), δ 7.2—7.7 (br m, 15 H, PPh_3), 6.09 [q, J(H-F) 9.3, 1 H, $=C(CF_3)H$], and 4.98 [d, J(H-P) 1.0 Hz, 5 H, C_5H_5]; ^{19}F ($CDCl_3$, −50 °C), δ −53.0 (br s, 3 F), −54.89 (br s, 3 F), −56.25 [qd, J(F-F) 10.5, J(F-H) 9.3, 3 F], and −61.28 p.p.m. [q, J(F-F) 10.5 Hz, 3 F].

Reaction of $[W\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* $PMePh_2$.—A solution of the complex (40 mg, 0.07 mmol) and $PMePh_2$ (0.17 mg, 0.08 mmol) in hexane (10 cm^3) was heated at 70 °C in a sealed tube for 24 h when a colour change from red-purple to green was observed. The solution was centrifuged, concentrated *in vacuo* to *ca.* 5 cm^3, and cooled to −15 °C to give green crystals of $[W\{SC(CF_3)=C(CF_3)H\}(PMePh_2)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**4c**) (30 mg, 56%) (Found: C, 36.7; H, 2.4. $C_{26}H_{19}F_{12}PSW$ requires C, 38.6; H, 2.4%); *m/z* 804 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 642wm, $\nu(C=C)$, 1 633 (sh) cm^{-1}. N.m.r.: ^1H ($CDCl_3$), δ 7.4 (m, 10 H, $PMe\mathit{Ph}_2$), 6.33 [br q, J(H-F) 6.6, 1 H, $=C(CF_3)H$], 4.96 [d, J(H-P) 1.2, 5 H, C_5H_5], and 2.65 [d, J(H-P) 8.9. 3 H, $P\mathit{Me}Ph_2$]; ^{19}F ($CDCl_3$, −50 °C), δ −53.69 (s, 3 F, CF_3), −56.60 (s, 3 F, CF_3), −58.81 [d, J(F-H) 7.5, 3 F, CF_3], and −61.07 p.p.m. (s, 3 F, CF_3).

Reaction of $[W\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* $Ph_2PC\equiv CPh$.—A solution of the complex (50 mg, 0.08 mmol) and $Ph_2PC\equiv CPh$ (26 mg, 0.09 mmol) in hexane (10 cm^3) was heated in a sealed tube at 70 °C for 24 h when the colour changed from red-purple to green. The solution was centrifuged, concentrated *in vacuo*, and on cooling to −15 °C green crystals of $[W\{SC(CF_3)=C(CF_3)H\}(Ph_2PC\equiv CPh)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**4d**) (44 mg, 60%) were obtained (Found: C, 44.0; H, 2.3; P, 3.5. $C_{33}H_{21}F_{12}PSW$ requires C, 44.4; H, 2.4; P, 3.5%); *m/z* 890 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 2 184wm, $\nu(C\equiv C)$ 1 632wm cm^{-1}. N.m.r.: ^1H ($CDCl_3$), δ 7.9—7.3 (m, 15 H, Ph), 6.07 [q, J(H-F) 9.2, 1 H, $=C(CF_3)H$], and 5.05 [d, J(H-P) 1.4, 5 H, C_5H_5]; ^{19}F ($CDCl_3$, −50 °C), δ −53.18 (br s, 3 F), −54.93 (br s, 3 F), −56.18 [dq, J(H-F) 9.0, J(F-F) 10.5, 3 F], and −61.27 p.p.m. [q, J(F-F) 10.5 Hz, 3 F].

Reaction of $[Mo\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2a**) *with Oxygen.*—A solution of complex (**2a**) (25 mg, 0.048 mmol) in hexane (5 cm^3) was held at 40 °C in a sealed tube under an oxygen atmosphere for 48 h. The resulting pale green solution was centrifuged, concentrated to *ca.* 3 cm^3, and cooled to −15 °C to give pale green crystals. These were recrystallised from CH_2Cl_2–hexane to give $[Mo\{SC(CF_3)=C(CF_3)H\}O(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**5a**) (18 mg, 70%) (Found: C, 29.3; H, 1.0. $C_{13}H_6F_{12}MoOS$ requires C, 29.2; H, 1.1%); *m/z* 534 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 830wm, $\nu(C=C)$ 1 630w cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 6.98 [qq, J(H-F) 7.3, 1.0, 1 H, $=C(CF_3)H$], and 6.25 (s, 5 H, C_5H_5); ^{19}F, δ −51.38 [q, J(F-F) 3.6, 3 F], −54.85 (q, J 3.6, 3 F), −58.43 [dq, J(F-F) 1.7, J(F-H) 7.3, 3 F], and −63.90 p.p.m. [dq, J(F-F) 1.7, J(H-F) 1.0 Hz, 3 F].

Reaction of $[W\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with Oxygen.*—A solution of the complex (25 mg, 0.04 mmol) in hexane (5 cm^3) was saturated with oxygen and then heated in a sealed tube at 40 °C for 72 h. The resulting colourless solution was centrifuged and concentrated *in vacuo* to give a white powder. This was recrystallised from CH_2Cl_2–hexane to give white crystals of $[W\{SC(CF_3)=C(CF_3)H\}O(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**5b**) (18 mg, 72%) (Found: C, 25.1; H, 0.8. $C_{13}H_6F_{12}OSW$ requires C, 25.1; H, 1.0%); *m/z* 620 [M^+]; i.r. ($CDCl_3$) $\nu(C\equiv C)$ 1 803wm, $\nu(C=C)$ 1 633w cm^{-1}. N.m.r. ($CDCl_3$): ^1H, *cis* isomer, δ 6.58 [q, J(H-F) 8.7, 1 H, $=C(CF_3)H$] and 6.35 (s, 5 H, C_5H_5); *trans* isomer, δ 6.91 [qq, J(F-H) 7.3, 1.0, 1 H, $=C(CF_3)H$] and 6.33 (s, 5 H, C_5H_5); ^{19}F, *cis* isomer, δ −52.70 [q, J(F-F) 4.1, 3 F], −56.66* [q, J(F-F) 4.1, 3 F], −57.50 [dq, J(F-F) 11.3, J(F-H) 8.7, 3 F], and −61.60 [q, J(F-F) 11.3, 3 F]; *trans* isomer, δ −53.22 [q, J(F-F) 4.1, 3 F], −56.66* [q, J(F-F) 4.1, 3 F], −58.91 [qd, J(F-F) 1.4, J(F-H) 7.3, 3 F], and −64.39 p.p.m. [qd, J(F-F) 1.4, J(F−H) 1.0 Hz, 3 F].

Acknowledgements

We thank the S.E.R.C. for support.

References

1 L. P. Yur'eva, *Russian Chem. Rev.*, 1974, **43**, 1; S. Shirakawa and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 929; G. Wegner, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 361.

2 (*a*) L. Carlton and J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1987, 895; (*b*) J. L. Davidson, *ibid.*, p. 2175; J. L. Davidson and W. F. Wilson, *ibid.*, 1988, 28 and refs. therein.

3 M. Green, *J. Organomet. Chem.*, 1986, **300**, 93; D. C. Bower, K. R. Birdwhistell, and J. L. Templeton, *Organometallics*, 1986, **5**, 95.

4 R. Schrock, *J. Organomet. Chem.*, 1986, **300**, 249, K. H. Dötz, 'Reactions of Co-ordinated Ligands,' ed. P. S. Braterman, vol. 1, ch. 4, Plenum, New York, 1986; K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587.

5 L. Carlton, J. L. Davidson, P. Ewing, Lj. Manojlovic-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1985, 1474.

6 N. M. Agh-Atabay, J. L. Davidson, G. Douglas, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1987, 1526.

7 W. R. Cullen, D. S. Dawson, and G. E. Styan, *Can. J. Chem.*, 1965, **43**, 3393.

8 W. A. W. Abu Bakar, L. Carlton, J. L. Davidson, Lj. Manojlovic-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1988, **352**, C54.

9 A. Davison and W. C. Rode, *Inorg. Chem.*, 1967, **6**, 2124; R. G. Hayter, *J. Organomet. Chem.*, 1968, **13**, P1.

10 L. Carlton, J. L. Davidson, J. C. Miller, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1984, 12.

11 K. Vrieze, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, ch. 11, Academic Press, New York, 1975.

12 J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, 1977, **99**, 4859.

13 H. Yasuda and A. Nakamura, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 723.

14 J. M. Huggins and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 3002.

15 J. L. Davidson, W. F. Wilson, Lj. Manojlovic-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1983, **254**, C6.

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

17 M. Crocker, M. Green, A. G. Orpen, H. P. Neumann, and C. J. Schaverien, *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.

18 G. E. Herbereich, B. Hessner, and H. Mayer, *J. Organomet. Chem.*, 1986, **314**, 123.

19 E. R. Burkhardt, J. J. Doney, R. G. Bergman, and C. H. Heathcock, *J. Am. Chem. Soc.*, 1987, **109**, 2022.

20 M. Green, R. C. Mercer, C. E. Morton, and A. G. Orpen, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 422.

21 F. Y. Pétillon, J-L. Le Quéré, F. Le Floch-Pérennou, J-E. Guerchais, M. B. Gomes de Lima, Lj. Manojlovic-Muir, K. W. Muir, and D. W. A. Sharp, *J. Organomet. Chem.*, 1984, **255**, 231.

22 (*a*) B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am.*

---

* Two coincident peaks.

Chem. Soc., 1979, **101**, 585; (*b*) J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 2423; (*c*) S. R. Allen, P. K. Baker, S. G. Barnes, M. Green, L. Trollope, Lj. Manojlovic-Muir, and K. W. Muir, *ibid.*, 1981, 873.

23 CHEMGRAF, created by E. K. Davies and distributed by Chemical Design Ltd., Oxford.

24 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 3288.

25 J. L. Davidson, unpublished work.

26 P. Sykes, 'A Guidebook to Mechanism in Organic Chemistry,' Longman, London, 1986.

27 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395; H. Raboa, J-Y. Saillard, and R. Hoffman, *J. Am. Chem. Soc.*, 1986, **108**, 4327 and refs. therein.

28 T. P. Kee, V. C. Gibson, and W. Clegg, *J. Organomet. Chem.*, 1987, **325**, C14 and refs. therein.

29 O. W. Howarth, C. H. McAteer, P. Moore, and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 1981, 506.

30 B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, 1980, **102**, 1532.

31 J. L. Templeton, P. B. Winston, and B. C. Ward, *J. Am. Chem. Soc.*, 1981, **103**, 7713.

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

33 S. R. Allen, M. Green, G. Moran, A. G. Orpen, and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1984, 441.

34 J. A. K. Howard, R. D. F. Stansfield, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1976, 247.

35 J. L. Davidson, G. Vasapollo, J. C. Millar, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1987, 2165; L. Carlton and J. L. Davidson, *ibid.*, in the press and refs. therein.

Received 16*th June* 1988; *Paper* 8/02416B