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Reactions of molybdenum and tungsten η^2-*C*,*C*-vinyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ with alkynes leading to novel metallacycles *

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Abstract

The reactions of $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$($M = Mo$, $R = {}^iPr$; $M = W$, $R = Me$, ${}^iPr$, ${}^tBu$) with alkynes $R'C\equiv CR''$, ($R' = R'' = Me$, Et, Ph; $R' = Ph$, $R'' = Me$) gives isomeric η^2-vinyl $[M\{\eta^3\text{-}C(CF_3)C(CF_3)C(R'')=C(R')(SR)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ and/or η^4-butadienyl complexes $[M\{\eta^4\text{-}C(CF_3)C(CF_3)=C(R'')C(R')(SR)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (not all cases) apparently as a result of insertion of the incoming alkyne into the C–S bond of the $\eta^3\text{-}C(CF_3)C(CF_3)SR$ ligand. Thermolysis of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me)=C(Ph)S^iPr\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ in hexane at 55 °C gives $[WS^iPr\{\eta^5\text{-}C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(Me)C(Ph)\}(\eta^5\text{-}C_5H_5)]$. In contrast thermolysis of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)\text{-}C(Me)=C(Me)S^iPr\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ in hexane at 70 °C gives $[Mo\{\eta^4\text{-}C(Me)C(Me)=C(CF_3)\text{-}C(CF_3)(H)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ via the intermediate $[Mo\{\eta^4\text{-}C(CF_3)C(CF_3)=C(Me)C(Me)S^iPr\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$. Fluxional behaviour in complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)C(R'')=C(R')(SR)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ has been studied by variable temperature ^{19}F NMR spectroscopy and two processes detected. The first involves rapid exchange between two isomeric forms and is ascribed to inversion at either the sulphur or the β-carbon of the $C(CF_3)C(CF_3)C(R'')=C(R')SR$ ligand. The second appears to involve restricted rotation of the CF_3 attached to the β-carbon.

Introduction

Early studies of reactions between alkynes and metal alkyl and metal hydride complexes illustrated that insertion into the metal–carbon or metal–hydrogen bond is a favoured process particularly with activated alkynes such as $CF_3C\equiv CCF_3$ and $MeO_2CC\equiv CCO_2Me$. In many cases the resulting product contains a η^1-alkenyl group but in some instances a second alkyne insertion occurs to give η^1 or η^3 butadienyl derivatives [1]. Recently we and others have drawn attention to the possible role of η^2-vinyl complexes in alkyne insertion reactions [2]. We previously reported the synthesis of η^2-vinyl complexes **1** and showed that the complexes exhibited fluxional behaviour involving reversible thiolate migration via a bis alkyne

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* Dedicated to Professor P.L. Pauson on the occasion of his retirement.

** In part.

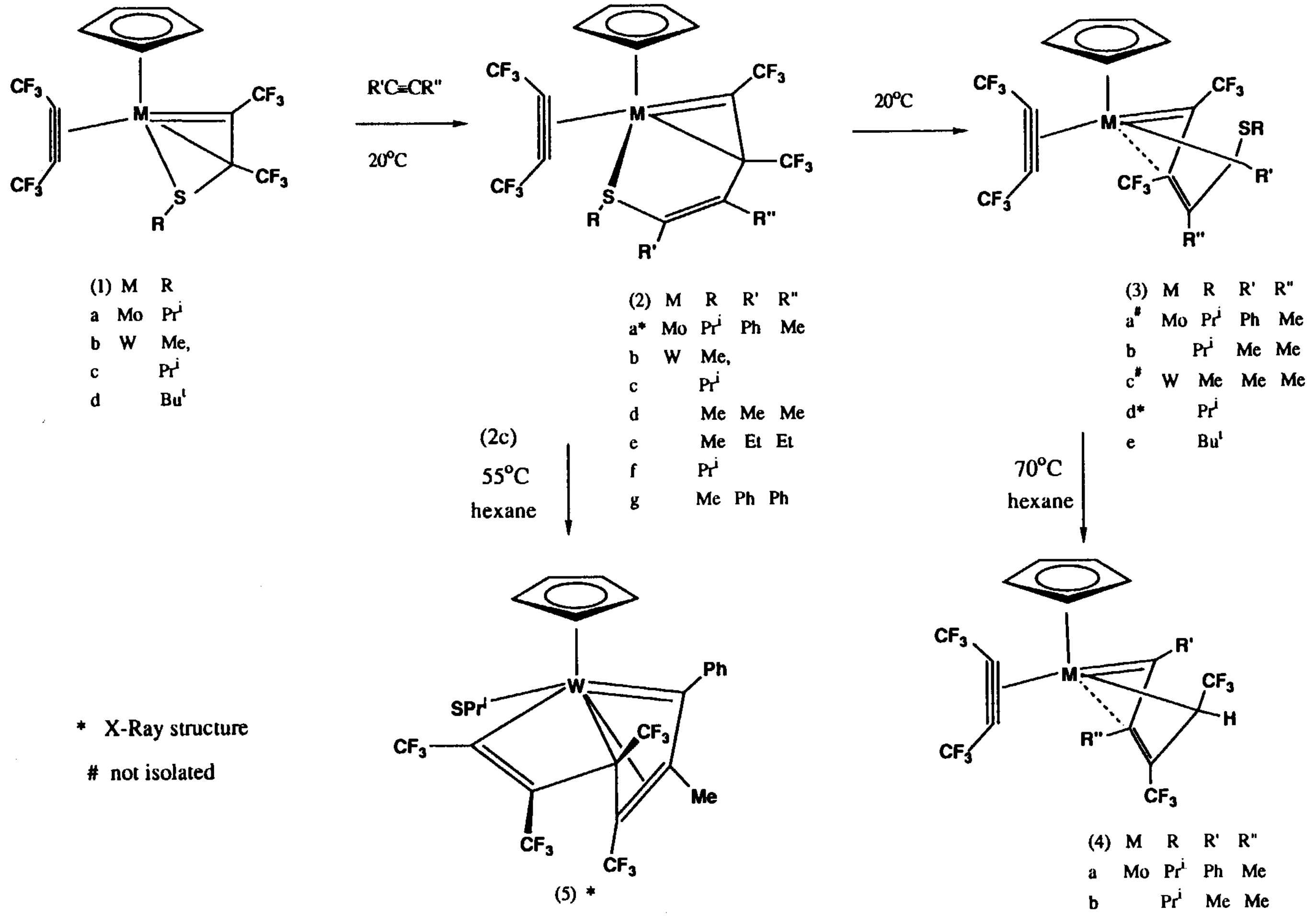
intermediate [3]. More recently we observed that addition of tertiary phosphines promoted insertion of the coordinated alkyne into the M=C bond of the η^2-vinyl derivatives to produce a variety of oligomerisation products [4]. It was therefore of interest to carry out reactions of complexes of type **1** with alkynes with a view to obtaining more information about alkyne insertion reactions. We now report the results of our initial studies, some of which have been published previously as preliminary communications [5].

Results and discussion

The reactions of **1a–d** with alkynes MeC≡CMe, EtC≡CEt, PhC≡CMe and PhC≡CPh, (not all combinations) when carried out in diethyl ether, hexane or diethyl ether/hexane mixtures at room temperature give, in most cases, a single product **2** or **3** as shown in Scheme 1.

In some instances NMR studies of the crude product revealed a mixture of both with one complex predominating. Analytical data of both **2** and **3** are in accord with simple 1 : 1 adducts $[MSR\{C_4(CF_3)_4\}(R'C_2R'')(C_5H_5)]$ and this is confirmed by the mass spectra which show molecular ions. The IR spectra also show some similarities, in particular a medium intensity band near 1800 cm^{-1} consistent with the presence of a co-ordinated $CF_3C{\equiv}CCF_3$. However, the spectra of **2** also exhibit one, or in some cases, two bands near 1650 cm^{-1} indicating the presence of a free C=C bond whereas these peaks are absent from the spectra of **3**. The ^1H and ^{19}F NMR spectra, although showing distinctive features, did not allow unambiguous structural assignments to be made and consequently single crystal X-ray diffraction studies of **2a** and **3d** were carried out by Dr. K.W. Muir, University of Glasgow [5]. These revealed that in the case of **2a** the incoming alkyne had apparently inserted into the carbon–sulphur bond of the η^2-vinyl ligand of the precursor **1a** to give the structure illustrated in Scheme 1. The result is an η^3-butadienyl ligand bonded to the metal through the sulphur and two carbons via an η^2-vinyl mode of attachment. Consequently there is no change in the metal co-ordination and, not surprisingly, the corresponding bond lengths in **1c** and **2a** are quite similar. The structure of **2a** is more closely related to that of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(CF_3){=}C(CF_3)\text{-}S\}(SCNMe_2)(\eta^5\text{-}C_5H_5)]$ which was previously obtained from photolysis of the η^2-*C*,*C*-vinyl complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ [6]. The $\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)S^iPr$ ligand can be regarded as a 5-electron donor and therefore the co-ordinated hexafluorobut-2-yne is only required to donate two electrons to the metal to achieve the favoured 18-electron configuration. Interestingly the structure can be compared with that of $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)\text{-}C(CF_3){=}C(CF_3)S^iPr\}(PEt_3)(\eta^5\text{-}C_5H_5)]$ where the butadienyl ligand preferentially adopts an η^4 mode of co-ordination containing an η^1 vinyl moiety [4]. In the molybdenum(IV) derivative $[Mo\{\eta^2\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)S^iPr\}(O)(\eta^5\text{-}C_5H_5)]$ the ability of the oxo ligand O^{2-} to formally act as a four-electron donor results in the butadienyl ligand donating three electrons via an η^1-vinyl moiety and a sulphur lone pair [2d,4].

The ^{19}F NMR spectra of complexes **2** can be interpreted in terms of the solid state structure with the additional feature that two types of fluxional behaviour are observed. In each case the spectra were recorded over the temperature range −80 °C to 20 °C and basically similar features were observed in each case. For this



(1)	M	R
a	Mo	Pr^i
b	W	Me,
c		Pr^i
d		Bu^t

(2)	M	R	R'	R"
a*	Mo	Pr^i	Ph	Me
b	W	Me,		
c		Pr^i		
d		Me	Me	Me
e		Me	Et	Et
f		Pr^i		
g		Me	Ph	Ph

(3)	M	R	R'	R"
a#	Mo	Pr^i	Ph	Me
b		Pr^i	Me	Me
c#	W	Me	Me	Me
d*		Pr^i		
e		Bu^t		

(4)	M	R	R'	R"
a	Mo	Pr^i	Ph	Me
b		Pr^i	Me	Me

* X-Ray structure

\# not isolated

Scheme 1

reason only the spectra of **2c** will be described in detail. At 20 ° C the spectrum consists of a broad signal δ_1, two quartets of quartets, δ_2 and δ_3, and a quartet δ_4. As Fig. 1 shows, the peaks broaden at lower temperatures and separate out below ca. -25 ° C into two distinct sets of peaks indicating the existence of two isomeric forms.

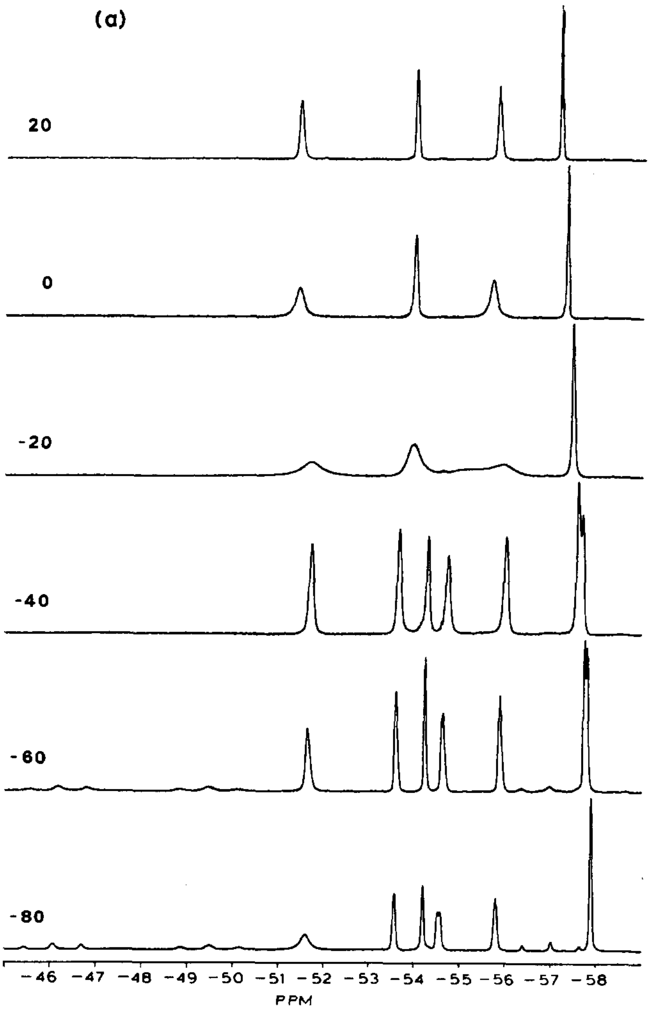
The two most likely sources of isomerism in this type of complex are inversion at sulphur and inversion at the chiral β carbon of the η^2-vinyl moiety, Scheme 2. The latter process has precedent in our previous report that η^2-vinyl complexes $[MCl\{\eta^2\text{-}C(CF_3)C(CF_3)(PR_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) exist in two isomeric forms, a kinetic and a thermodynamic form [7]. In the case of $[Mo(Cl)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ X-ray diffraction studies revealed that isomerisation of the kinetic isomer into the thermodynamic form involves changes in the reorientation and inversion of stereochemistry at the chiral C_β carbon atom of the η^2-vinyl ligand [7]. In the case of complexes **2**, inversion at carbon would result in isomerisation of the structure found in the solid state **2i** to the alternative form **2ii**. This could proceed via a planar transition state **2iii** (Scheme 2, path a) in which the metal has a 16-electron configuration, or via path b involving intermediate **2iv** with an 18-electron configuration. The latter process is suggested by our recent characterisation of $[Mo(PEt_3)\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\text{-}S^iPr\}(\eta^5\text{-}C_5H_5)]$ with a similar η^4 mode of attachment for the $C(CF_3){=}C(CF_3)\text{-}C(CF_3){=}C(CF_3)S^iPr$ ligand [4]. Inversion at sulphur is a simpler and more common phenomenon and would result in exchange of isomers **2i** and **2v**. Unfortunately the data available do not distinguish unambiguously between the two inversion processes.

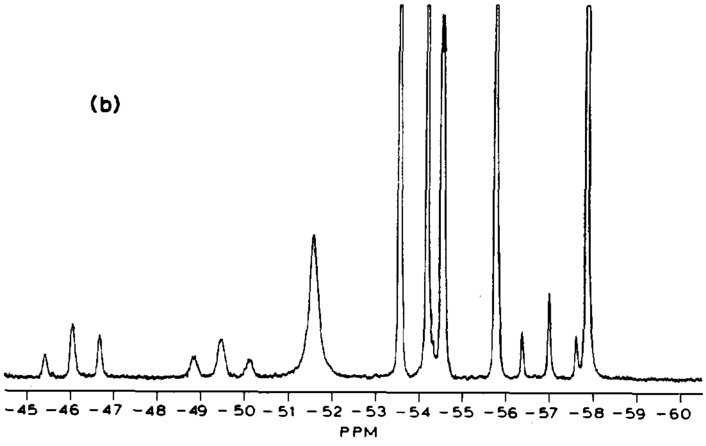
The second type of fluxional behaviour only affects δ_1 which broadens at low temperatures, collapses into the base line and eventually reappears as three distinct triplets (doublets of doublets) below -70 ° C (Fig. 1b). This clearly indicates that this particular CF_3 has stopped rotating with the result that each fluorine has a discrete chemical environment. Presumably this is due to severe steric crowding which imposes a kinetic barrier sufficient to prevent CF_3 rotation at low temperature. We have observed this previously in a variety of compounds with η^2-vinyl structures including $[M\{\eta^3\text{-}C(CF_3){=}C(CF_3)S_2PMe_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) [6a]. This is not entirely surprising in view of the structural similarity between these two types of η^2-vinyl complex. Interestingly, in cases where the two types of fluxional behaviour are well separated in temperature (**2b**, **c**, **e**, **f**, **g**), it was observed that broadening of the δ_1 CF_3 resonance of one isomer invariably occurred at a significantly different temperature to that of the other e.g. **2b** at -50° and -75 ° C. This may imply that steric crowding of CF_3 δ_1 also differs in the two isomers.

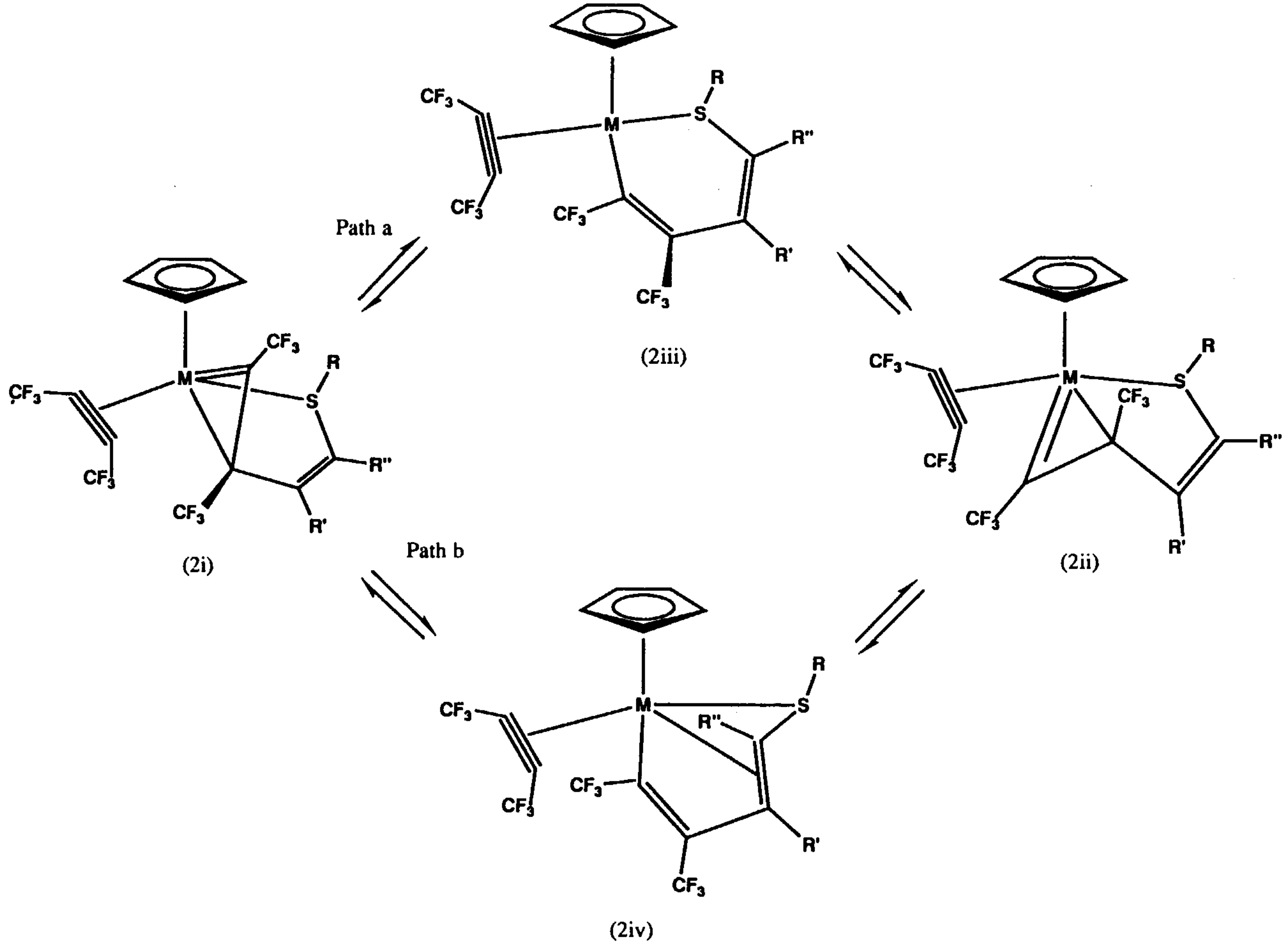
Molecular graphics studies of **2a** were carried out which indicate that the CF_3 on the chiral β carbon of the η^2-vinyl moiety is significantly more sterically crowded than the other three. Restricted rotation of the β-$C(CF_3)$ is also thought to be

Fig. 1a. Variable temperature ^{19}F NMR spectra of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)(S^iPr)\}\text{-}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2c**) in CD_2Cl_2. Temperature in ° C.

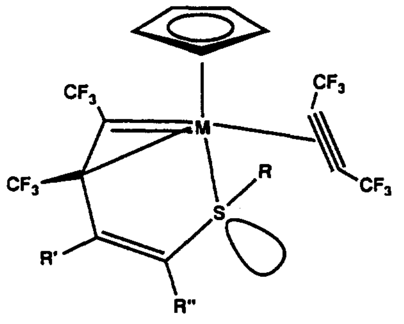
Fig. 1b. ^{19}F NMR spectrum of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)(S^iPr)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2c**) in CD_2Cl_2 at -80 ° C (expanded vertical scale).


(a)
20
0
-20
-40
-60
-80
-46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58
PPM

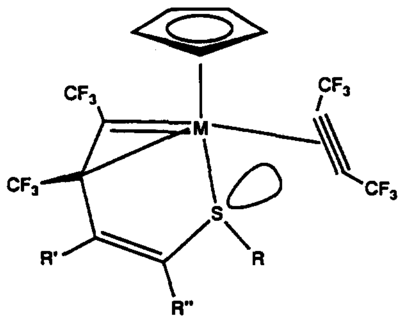

(b)
-45 -46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60
PPM



Scheme 2



2(i)



2(v)

involved with the aforementioned complexes $[\mathrm{M}\{\eta^3\text{-C(CF}_3\text{)=C(CF}_3\text{)S}_2\text{PMe}_2\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ (M = Mo, W). For reasons discussed previously [6a] CF_3–CF_3 coupling in these types of complex is likely to occur via a through-space mechanism. Thus the quartet δ_4 in **2** can be assigned to the butadienyl CF_3 distal to the alkyne group in view of the large separation between this and the alkyne CF_3 groups. This will only allow coupling to the other butadienyl CF_3. Assignment of the other CF_3 peaks (see Fig. 2) follows from the results of double irradiation experiments.

The mechanism of formation of **2** poses an interesting question since formally the incoming alkyne has inserted into the carbon sulphur bond of the η^3-$\text{C(CF}_3\text{)=C(CF}_3\text{)SR}$ ligand in **1**. This is probably a mechanistic simplification of the overall process in view of our recent observation that the isomeric bis alkyne complex $[\text{Mo(SC}_6\text{F}_5\text{)(CF}_3\text{C}\equiv\text{CCF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ reacts with alkynes $\text{MeC}\equiv\text{CH}$, $\text{MeC}\equiv\text{CMe}$, $\text{MeC}\equiv\text{CCO}_2\text{Me}$ and $\text{PhC}\equiv\text{CH}$ at low temperatures (ca. − 40 °C) to give the prone η^4-butadienyl complex **6** (Scheme 3) which isomerises into complexes of type **2** above ca. −20 °C [8]. Despite this observation it is still necessary to account for the fact that the thiolate ligand migrates from a $\text{C(CF}_3\text{)=C(CF}_3\text{)SR}$ moiety onto

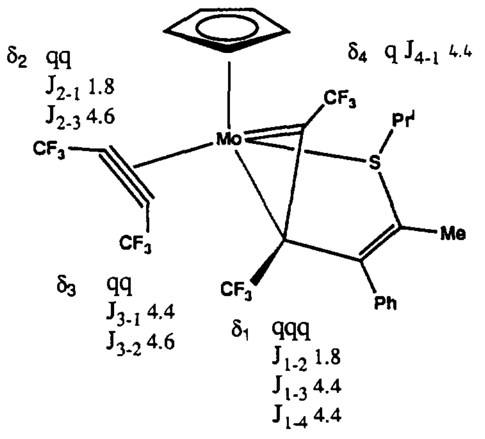


Fig. 2. ^{19}F NMR coupling connectivities for $[\text{Mo}\{\eta^3\text{-C(CF}_3\text{)C(CF}_3\text{)C(Me)=C(Ph)(S}^i\text{Pr)}\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ (**2a**).

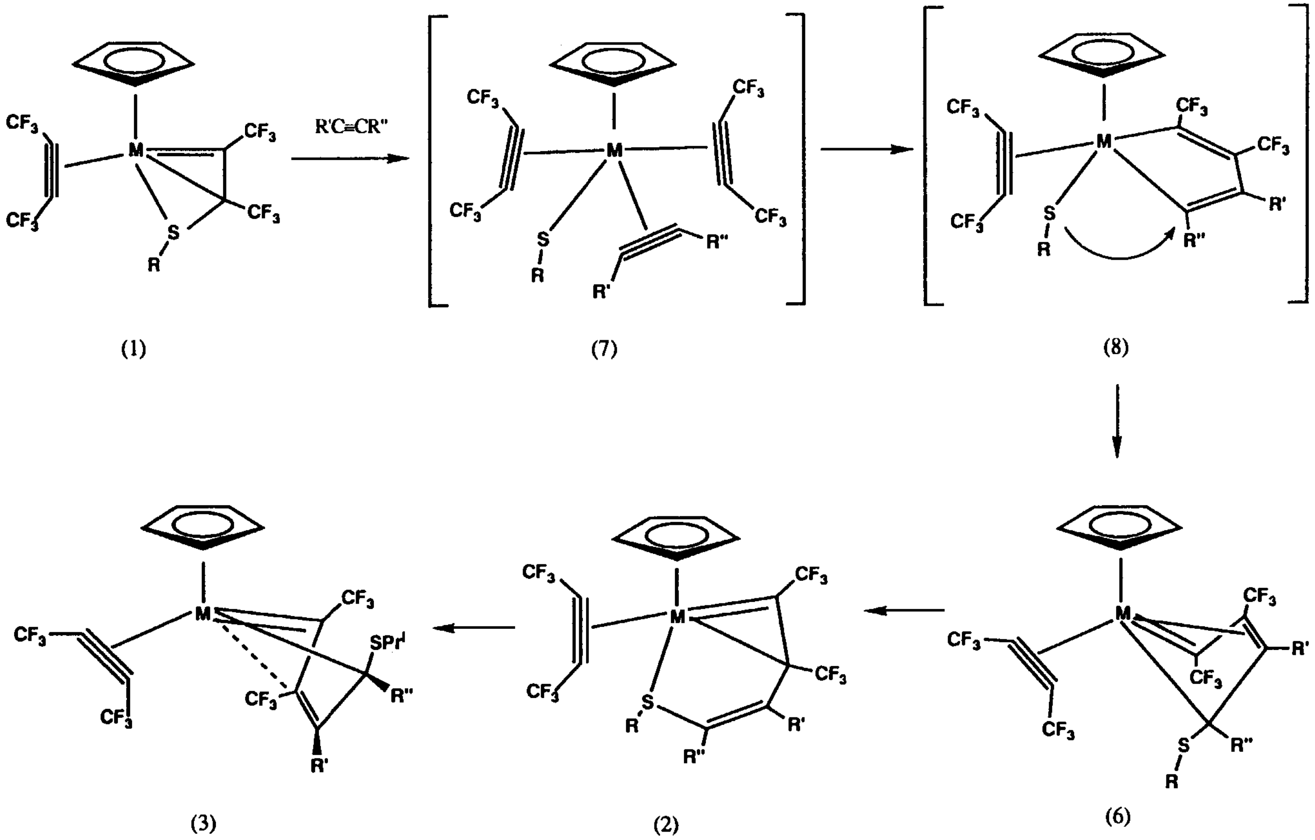
the incoming alkyne. The simplest explanation is that the alkyne inserts directly into the C–S bond. However, as far as we are aware this has no mechanistic precedent, and is in any case, less likely with non activated alkynes. Instead we propose a more plausible explanation involving the intermediacy of bis alkyne and metallacyclic complexes **7** and **8** as shown in Scheme 3.

We have previously postulated the existence of similar intermediates in the reactions of complexes **1** which lead to linkage of two alkynes or an alkyne and an η^2-vinyl. In some instances it has proved possible to detect or even isolate such species thus leading credence to our proposals [2,4,8]. The crucial part of the reaction leading to complexes **2** is therefore migration of the terminally bound thiolate ligand onto the metallacycle followed by rearrangement of the bonding in the resulting butadienyl derivative. We note that in the case of the unsymmetrical alkyne PhC≡CMe formation of the metallacycle **8** can occur in two different ways with the C(Ph) or the C(Me) attached to the metal. Since only one isomer of **2** is obtained with the SR group on the C(Ph) carbon we assume that metallacycle formation is regiospecific. Moreover, migration of the thiolate could also proceed in two different ways, i.e. onto either of the two metallated carbons of the metallacycle. This step also proceeds regiospecifically giving the isomer resulting from migration onto the CR′ carbon.

The structure of **3d** is similar to that of **2a** in that the metal is co-ordinated by an η^5-C_5H_5, an η^2-$CF_3C{\equiv}CCF_3$ and a butadienyl ligand $C(CF_3){=}C(CF_3)C(Me){=}C(Me)$-$S^iPr$. However, the last is co-ordinated in a novel η^4 manner to the metal as illustrated in Scheme 1. The short W–Cα(CF_3) distance suggests a formal double bond as found in **1c** and **2a**. Moreover, the coplanarity of the $WC(CF_3)C(CF_3)$-$C(Me){=}C(Me)S$ unit and the extreme length of the two W–C(internal) bonds are indicative of an η^2-alkene–W interaction, whereas the valency angles round the butadienyl C(4) carbon and the shorter W–C distance are consistent with W–C σ bonding [5b]. A closely related η^4-butadienyl ligand bonded to ruthenium has recently been described [9] but the three non-carbenoid Ru–C distances are nearly equal consistent with a symmetrical π-allylic system rather than the irregular $\sigma + \pi$ attachment of the ligand in **3d**. However, protonation of the bis alkyne complexes $[M(S_2CNR_2)_2(PhC{\equiv}CPh)_2]$ (M = Mo, W; R = Me, Et) gives $[M(S_2CNR_2)_2\{\mu$-$C(Ph)C(Ph)C(Ph){=}C(Ph)(H)\}]^+$ in which the metal–η^4-butadienyl bonding is closely related to that of **3** [10]. More recently it has been observed [11] that addition of tertiary phosphines to η^2-vinyl-alkyne complexes $[MoX\{\eta^2$-$C(Me)C(Me)H\}$-$(MeC{\equiv}CMe)(C_5H_5)]^+$ (X = Cl, Br) gives η^4-butadienyl complexes $[MoX\{\eta^4$-$C(Me)$-$C(Me)C(Me)C(Me)H\}(PR_3)(C_5H_5)]^+$. This clearly parallels the formation of **3** from **1** in that coupling of η^2-vinyl and alkyne ligands is promoted by coordination of another ligand. However, in the present case the incoming ligand, an alkyne, becomes incorporated into the resulting η^4-butadienyl ligand.

Variable temperature studies of complexes **3** showed that, unlike **2**, the structure is stereochemically rigid over the temperature range ca. −80 °C – +20 °C. ^{19}F homodecoupling experiments on **3d** were carried out and these, in conjunction with molecular graphics studies, established the connectivities shown in Fig. 3.

In an effort to establish the kinetic and thermodynamic relationship between **2** and **3** the reaction between $[Mo\{\eta^3$-$C(CF_3)C(CF_3)S^iPr\}(CF_3C{\equiv}CCF_3)(\eta^5$-$C_5H_5)]$ and PhC≡CMe at 20 °C was followed by ^{19}F NMR spectroscopy. This revealed that over a 48 h period the only product formed is **2a**. However, when a pure sample of


CF3
CF3
M
CF3
CF3
S
R
(1)
R'C≡CR"
CF3
CF3
M
CF3
CF3
S
R
R"
R'
(7)
CF3
CF3
M
CF3
CF3
R'
S
R
R"
(8)
CF3
M
CF3
CF3
R'
S
R
R"
CF3
(6)
CF3
CF3
M
CF3
CF3
S
R
R"
R'
(2)
CF3
M
CF3
SPr^i
R"
CF3
R'
CF3
(3)

Scheme 3

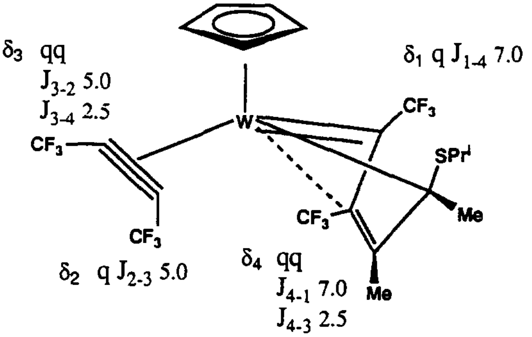
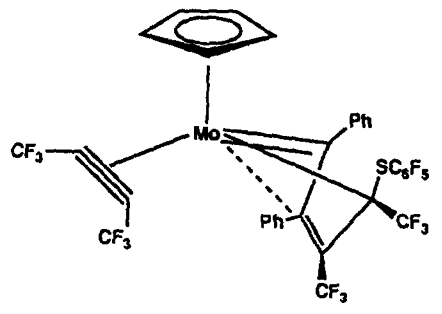


Fig. 3. ^{19}F NMR coupling connectivities for [W{η^4-C(CF_3)C(CF_3)C(Me)=C(Me)(S^{i}Pr)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] (3c).

2a was heated in $CD_3C_6D_5$ above 60 °C the growth of distinctive signals due to a complex of structure **3** was observed (**3a** δ −51.53, q, J 6.5 Hz; −52.45, q, J 4.5 Hz; −56.41, m; −59.02, m), illustrating that **2** is the kinetic isomer. On prolonged heating new signals appeared, indicating the formation of a second species **4a** which grew as the peaks due to **3a** declined in intensity. When the reaction was complete, apart from minor peaks, the sole product appeared to be complex **4a**. The reaction was repeated on a synthetic scale but it did not prove possible to isolate **4a** in a pure form. However, thermolysis of **3b** at 70 °C for 48 h in diethylether/hexane gave yellow crystals of **4b** in 65% yield with a similar ^{19}F NMR spectrum to that of **4a**. The analytical and mass spectral data suggest a molecular formula [Mo{$C_4(CF_3)_4$-C(Me)C(Ph)(H)}(C_5H_5)] in which a S^{i}Pr group has been replaced by a hydrogen. Previously we have observed a related reaction on thermolysis of η^2-C,C-vinyl precursors **1** (M = Mo, W; R = ^{t}Bu) which gives η^3-ethenethiolate complexes [12]. However, in these two instances the sulphur is retained and only the butyl group is replaced by hydrogen.

The structure of **4b** cannot be assigned unambiguously from the spectroscopic data available and crystals suitable for X-ray diffraction studies could not be obtained. However, the data obtained suggest the structure illustrated in Scheme 1. The IR spectrum of **4b** shows a single ν(C≡C) band at 1765 cm^{-1} but no ν(C=C) modes between 1500 and 1700 cm^{-1}. The ^{1}H NMR spectrum shows a C_5H_5 singlet, two Me resonances and a quartet J(H–F) 9.6, corresponding to one hydrogen at δ 1.57. The chemical shift of the last is clearly indicative of a proton attached to an sp^3 hybridized carbon whilst the coupling is similar to that observed in C(H)(CF_3) groups, e.g. [Ru{η^3-C(R)=C(R)C(CF_3)=C(CF_3)(H)}(PPh_3)(η^5-C_5H_5)], R = CO_2Me, J(H–F) = 10.0 Hz; R = CF_3, J(H–F) = 8.8 Hz [1a]. The ^{19}F NMR spectrum of **4b** contains three complex multiplets and a quartet and is very similar to that of [Mo{η^4-C(Ph)C(Ph)=C(CF_3)C(CF_3)SC_6F_5}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] (**9**).

This complex has been structurally characterised by X-ray diffraction studies and shown to have a structure similar to that proposed for **4** but with the unique hydrogen replaced by a SC_6F_5 group [8]. Although the complexity of the spectra did not permit full analysis of the coupling connectivities from double irradiation experiments, the coupling patterns observed for both complexes are sufficiently similar to enable us to propose structure **5** with some confidence. The ^{19}F NMR



(9)

coupling connectivities for $[\mathrm{Mo}\{\eta^4\text{-C(Me)C(Me)=C(CF}_3\text{)C(CF}_3\text{)H}\}(\mathrm{CF_3C{\equiv}CCF_3})(\eta^5\text{-C}_5\mathrm{H}_5)]$ (**4b**) are provided in Fig. 4.

In order to compare the reactivity of corresponding molybdenum and tungsten derivatives the reaction between $[\mathrm{W}\{\eta^3\text{-C(CF}_3\text{)C(CF}_3\text{)S}^i\text{Pr}\}(\mathrm{CF_3C{\equiv}CCF_3})(\eta^5\text{-C}_5\mathrm{H}_5)]$ and PhC≡CMe was also studied by ^{19}F NMR spectroscopy. This revealed that at room temperature the reaction is similar to that of the molybdenum complex **1a** except that the reaction was essentially complete within ca. 4 h, the only product again being of type **2**. However, when **2c** was heated in $\mathrm{CD_3C_6D_5}$ at 55 °C signals due to a new type of complex gradually replaced those of **2c**. Repeating the reaction on a synthetic scale in diethylether/hexane gave pale yellow crystals of complex **5** (50% yield) which, on the basis of elemental analysis and mass spectrometry, has the same composition as the precursor **2c**, i.e. unlike the corresponding molybdenum reaction the thiolate group has not been replaced by hydrogen. The IR spectrum of **5** shows a ν(C=C) mode at 1634 cm^{-1} but no ν(C≡C) peak suggesting that alkyne oligomerisation had occurred. This was subsequently confirmed by X-ray diffraction studies [5b] which revealed the structure illustrated in Scheme 1.

This reveals that the η^2-CF$_3$C≡CCF$_3$ ligand of **2c** has been incorporated into a W(CR)$_6$ metallacycle with extrusion of the thiolate group which remains bonded to

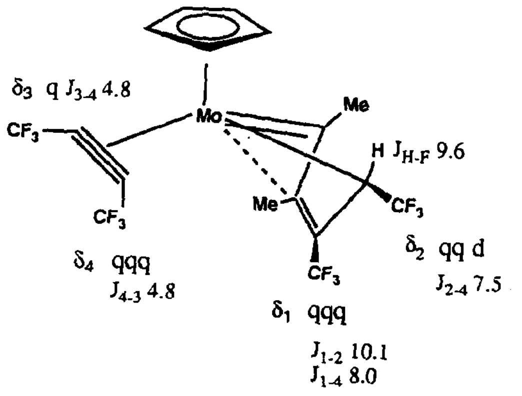
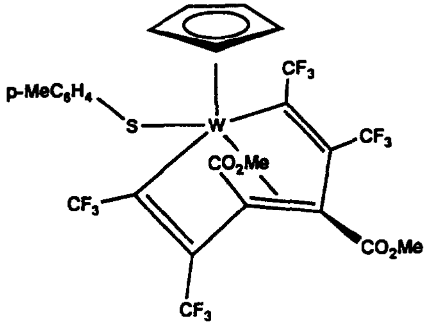


Fig. 4. ^{19}F NMR coupling connectivities for $[\mathrm{Mo}\{\eta^4\text{-C(Me)C(Me)=C(CF}_3\text{)C(CF}_3\text{)H}\}(\mathrm{CF_3C{\equiv}CCF_3})(\eta^5\text{-C}_5\mathrm{H}_5)]$ (**4b**).

the metal. Five of the six carbon atoms of the carbon chain are bonded to the metal with four of these bonding in η^4-butadienyl fashion reminiscent of the η^4-butadienyl group in **3**. The rest of the carbon chain comprises a bridging alkene $-C(CF_3)=C(CF_3)-$ which links the butadienyl group with the metal. The latter as a consequence attains an 18-electron configuration. Formally the bridging alkene replaces the thiolate group on the *sp*^{3} carbon of the butadienyl ligand in **3**. This novel mode of bonding provides a contrast with that previously reported for the related nickel complex [Ni{η^4-$C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)$}-$(PMe_2Ph)$] [13] where a *cis rans cis* $C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)$ chain is bonded to the metal through four of the six carbons. More recently we reported that a similar mode of attachment is found in [W{η^4-$C(CF_3)=C(CF_3)$-$C(CO_2Me)=C(CO_2Me)C(CF_3)=C(CF_3)$}S4-$MeC_6H_4$($\eta^5$-$C_5H_5$)] (**10**) isolated from the reaction of [WS4-$MeC_6H_4(CF_3C{\equiv}CCF_3)_2$($\eta^5$-$C_5H_5$)] with $MeO_2CC{\equiv}CCO_2Me$ [5b].



(10)

The latter is clearly related to **5** except for the different mode of coordination of the C_6 ring and the sequence of alkyne oligomerisation i.e. $C(CF_3)=C(CF_3)C(CR)=C(R)C(CF_3)=C(CF_3)$ versus $C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CR)=C(R)$. The mechanistic significance of the latter observation will be discussed in a future publication.

The NMR data for **5** are consistent with the solid state structure and ^{19}F double irradiation experiments established the coupling connectivities summarised in Fig. 5. The lack of coupling between two adjacent CF_3 groups δ_1 and δ_2 can be explained by the large torsion angle, ca. 106°, due to twisting of both substituents in opposite directions away from planarity. Interestingly CF_3 δ_1 shows weak coupling to both the adjacent methyl group and CF_3 δ_4, the latter being explained by the close proximity of the two groups due to the aforementioned twisting.

The formation of **5** from **2c** presumably proceeds via insertion of the remaining co-ordinated $CF_3C{\equiv}CCF_3$ into a metal–carbon bond of the MC_4 chain. This may simply involve insertion into the M=C bond of the η^2-vinyl moiety in **2c** followed by extrusion of the thiolate group. Interestingly there was no evidence for the intermediacy of an η^4-butadienyl derivative of type **3** in this reaction, a fact which may explain the differences observed between the two thermolysis reactions carried out. Thus on thermolysis two routes may be available to **2**, the first involving isomerisa-

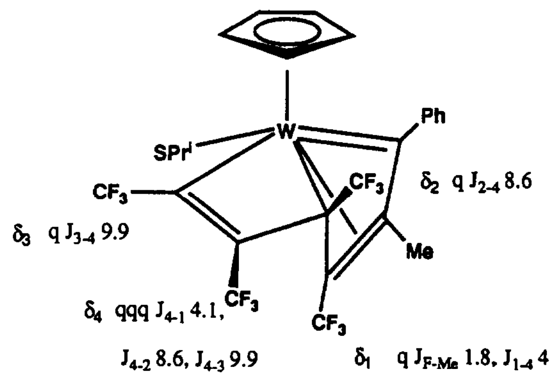


Fig. 5. ^{19}F NMR coupling connectivities for [W(S^{i}Pr){η^5-C(CF$_3$)C(CF$_3$)C(CF$_3$)C(CF$_3$)C(Me)C(Ph)}(η^5-C$_5$H$_5$)] (**5**).

tion to the η^4-butadienyl form **3** which subsequently reacts to give **4**. The second route involves preferential insertion of the CF$_3$C≡CCF$_3$ into the M=C bond to give the oligomerisation product **5**. This implies that isomerisation to **3** prevents alkyne insertion and in this respect the reactions differ from that of the ruthenium η^4-butadienyl complex [Ru{η^4-C(Ph)C(Ph)=C(Ph)C(Ph)(H)}(η^5-C$_5$H$_5$)]. On reaction of the latter with PhC≡CPh alkyne insertion is clearly preferred to isomerisation since the oligomerisation product [Ru{η^5-C(Ph)C(Ph)C(Ph)C(Ph)C(Ph)C(Ph)-(H)}(η^5-C$_5$H$_5$)] is obtained [9].

Experimental

NMR spectra were recorded on a Bruker WP 200SY spectrometer at 200.13 MHz (^{1}H) and 188.31 MHz (^{19}F). Coupling constants are in herz and chemical shifts are referenced to Me$_4$Si (^{1}H $\delta = 0$ ppm) and CCl$_3$F (^{19}F $\delta = 0$ ppm). IR spectra were recorded as solutions on a Perkin–Elmer 580 spectrophotometer with polystyrene as reference and mass spectra on an Vacuum Generators updated A.E.I. MS 11. Reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over P$_2$O$_5$ (CH$_2$Cl$_2$), calcium hydride (hexane, diethyl ether) and distilled just before use.

Reaction of [Mo{η^3-C(CF$_3$)C(CF$_3$)S^{i}Pr(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (1a) with PhC≡CMe

A solution of complex **1a** (40 mg, 0.07 mmol) and PhC≡CMe (22 mg, 18 mmol) in diethylether/hexane 3 : 2 (15 cm^3) was allowed to react at 20 °C for 72 h. The resulting orange-red solution was evaporated to dryness, the residue dissolved in dichloromethane (ca. 1.5 cm^3) and chromatographed over florisil. Elution with diethyl/ether hexane (1 : 1) gave a yellow band which on crystallisation produced yellow crystals of [Mo{η^3-C(CF$_3$)C(CF$_3$)C(Me)=C(Ph)S^{i}Pr}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**2a**), 21 mg, 43%. M^+: m/z 676. (Found: C 44.5, H 2.8. C$_{25}$H$_{20}$F$_{12}$MoS calc.: C 44.38, H 2.96%); IR (KBr) ν(C≡C) 1802 (wm), ν(C=C) 1609 (br.w), cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 0.82 (d, J 6.9, 3H, ^{i}Pr), 1.05 (d, J 6.9, 3H, ^{i}Pr), 2.03 (q, J(H–F) 2.1, 3H, *Me*C=), 3.05 (m, 1H, ^{i}Pr), 5.90 (s, 5H, C$_5$H$_5$), 7.25–7.6 (m, 5H, Ph); ^{19}F NMR (CD$_2$Cl$_2$, 19 °C) δ −50.81 (qqq, J(1–2) 1.8, J(1–3) 4.4, J(1–4) 4.4, 3F), −52.73

(qq, J(2–1) 1.8, J(2–3) 4.6, 3F), −54.49 (qq, J(3–1) 4.4, J(3–2) 4.6, 3F), −57.11 (q, J(4–1) 4.4, 3F).

Reaction of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S^iPr(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *(1a) with* $MeC{\equiv}CMe$

A solution of complex **1a** (50 mg, 0.09 mmol) in diethyl ether/hexane 1 : 3 (20 cm^3) was treated with excess $MeC{\equiv}CMe$ at 40 °C for 48 h. Volatiles were removed *in vacuo*, the residue dissolved in the minimum amount of dichloromethane and chromatographed over Florisil eluting with diethyl ether/hexane (1 : 1). A yellow band was collected and, following concentration and cooling to −15 °C, yellow crystals of $[Mo\{\eta^4\text{-}C(CF_3)C(CF_3){=}C(Me)C(Me)S^iPr\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3b**) were obtained (25 mg, 45%). M^+ m/z 614. (Found: 38.9, H 3.0. $C_{20}H_{18}F_{12}MoS$ calc.: C 39.10, H 2.93%); IR ($CDCl_3$) $\nu(C{\equiv}C)$ 1775 (wm), cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.98 (d, J 6.9, 3H, ^iPr), 1.13 (d, J 6.9, 3H, ^iPr), 2.29 (bs, 3H, Me), 2.53 (s, 3H, Me), 5.75 (s, 5H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −50.37 (q, J 7.1, 3F), −51.08 (q, J 4.5, 3F), −56.35 (m, 3F), −59.02 (m, 3F).

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SMe\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *(1b) with* $MeC{\equiv}CMe$

A solution of complex **1b** (35 mg, 0.06 mmol) was transferred to a thick glass tube fitted with a teflon stopcock and then degassed by four freeze–thaw cycles. Excess $MeC{\equiv}CMe$ (ca. 10%) was condensed in at −196 °C, the tube sealed and warmed to room temperature. The mixture was allowed to react for 18 h when the red solution turned yellow. Volatiles were removed *in vacuo* and the residue recrystallised from dichloromethane/hexane to give yellow crystal of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Me)SMe\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2b**) *, 17 mg, 45%. M^+: m/z 672. (Found: C 31.6, H 2.0. $C_{18}H_{14}F_{12}SW$ calc.: C 32.05, H 2.08%); IR (KBr) $\nu(C{\equiv}C)$ 1768 (wm), $\nu(C{=}C)$ 1638 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, −22 °C), δ 1.98, 2.0, 2.13, 2.35, 3.03, (s, Me), 5.93 (s, C_5H_5); ^{19}F NMR (CD_2Cl_2, −22 °C), isomer A δ −51.74 (m, 3F), −54.25 (qq, J 2.3, J 5.2, 3F), −55.99 (app. sept, 3F), −57.97 (q, J 4.2, 3F); isomer B δ −52.07 (m, 3F), −54.76 (qq, J 1.1, J 4.2, 3F), −55.29 (app. sept, 3F), −57.97 (q, J 3.9, 3F).

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)S^iPr\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *(1c) with* $MeC{\equiv}CMe$

A solution of complex **1c**, (62 mg, 0.1 mmol) in diethyl ether (10 cm^3) was treated with excess $MeC{\equiv}CMe$ at 20 °C for 24 h. Volatiles were removed *in vacuo* and the residue extracted with diethyl ether (10 cm^3) and filtered. Addition of hexane (5 cm^3) followed by concentration *in vacuo* and cooling to −15 °C gave orange yellow crystals of $[W\{\eta^4\text{-}C(CF_3)C(CF_3){=}C(Me)C(Me)S^iPr\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3d**) 28 mg, 42%. M^+ m/z 700. (Found: C 35.0, H 2.6, S 4.7. $C_{20}H_{18}F_{12}SW$ calc.: C 34.2, H 2.6, S 4.6%); IR ($CDCl_3$) $\nu(C{\equiv}C)$ 1750 (wm), cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.0 (d, J 7.0, 3H, ^iPr), 1.15 (d, J 6.5, 3H, ^iPr), 2.44 (q, J(H–F) 0.8, 3H, *Me*C≡), 2.66 (s, 3H,

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* ^{19}F NMR studies of the crude product mixture showed traces of the isomeric form **3c**, δ −50.99 (q, J 6.9, 3F), −53.20 (q, J 5.1, 3F), −58.30 (m, 3F), −59.66 (m, 3F); but these were removed by crystallisation.

*Me*C≡), 3.15 (m, 1H, ^{i}Pr), 5.83 (s, 5H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −50.75 (q, *J* 7.0, 3F), −52.79 (q, *J* 5.0, 3F), −57.94 (qq, *J* 5.0, *J* 2.5, 3F), −60.03 (qq, *J* 7.0, *J* 2.5, 3F).

Reaction of [W{η^3-C(CF$_3$)C(CF$_3$)S^{t}Bu(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (1d) with MeC≡CMe

A solution of complex **1d** (25 mg, 0.04 mmol) in diethylether (10 cm^3) was treated with excess MeC≡CMe at 20 °C for 80 h. The resulting mixture was centrifuged, hexane (ca. 4 cm^3) added and then concentrated *in vacuo*. On cooling to −15 °C a yellow brown solid was obtained which was recrystallised several times from dichloromethane/hexane to give orange crystals of [W{η^4-C(CF$_3$)C(CF$_3$)=C(Me)-C(Me)S^{t}Bu}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**3e**), 5 mg, 18.5%. M^+: *m/z* 712. (Found: C 35.7, H 2.6. $C_{21}H_{20}F_{12}S$ calc.: C 35.29, H 2.81%); IR ($CDCl_3$) ν(C≡C) 1750 (wm), cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 9H, ^{t}Bu), 2.49 (bs, 3H, Me), 2.78 (s, 3H, Me), 5.84 (s, 5H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −51.07 (q, *J* 7.0, 3F), −52.59 (q, *J* 5.0, 3F), −57.93 (m, 3F), −60.05 (m, 3F).

Reaction of [W{η^3-C(CF$_3$)C(CF$_3$)SMe}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (1b) with EtC≡CEt

A solution of complex **1b** (35 mg, 0.06 mmol) in hexane (8 cm) was treated with excess EtC≡CEt in a sealed tube at 20 °C for 20 h. The resulting yellow solution was concentrated *in vacuo* and cooled to −15 °C to give a yellow solid. Recrystallisation from dichloromethane/hexane gave yellow crystals of [W{η^3-C(CF$_3$)C(CF$_3$)C(Et)=C(Et)SMe}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**2e**), 30 mg, 75%. M^+: *m/z* 700. (Found: C 33.9, H 2.6. $C_{20}H_{18}F_{12}SW$ calc.: C 34.19, H 2.56%); IR (KBr) ν(C≡C) 1774 (wm), ν(C=C) 1620 (w), cm^{-1}. ^{1}H NMR (CD_2Cl_2, −22 °C) δ 0.91 (overlapping t, CH_2CH_3), 2.05, 2.44, 2.62 (m, CH_2, CH_3), 2.29, 2.97 (s, SMe), 5.94 (s, C_5H_5); ^{19}F NMR (CD_2Cl_2, −22 °C) isomer A, δ −51.48 (br.m, 3F), −54.18 (qq, *J* 2.5, *J* 5.1, 3F), −55.79 (app. sept, 3F), −57.62 (q, *J* 4.0, 3F); isomer B, δ −51.73 (br.m, 3F), −54.41 (q, *J* 4.3, 3F), −54.79 (app. sept, 3F), −57.02 (q, *J* 3.8, 3F).

Reaction of [W{η^3-C(CF$_3$)C(CF$_3$)S^{i}Pr}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (1c) with EtC≡CEt

A solution of complex **1c** (35 mg, 0.05 mmol) in hexane (10 cm^3) was treated with excess EtC≡CEt in a sealed tube at 75 °C for 48 h. The resulting yellow solution was centrifuged, concentrated *in vacuo* and cooled to −15 °C to give a brown powder. Repeated recrystallisation from dichloromethane/hexane gave yellow crystals of [W{η^3-C(CF$_3$)C(CF$_3$)C(Et)=C(Et)S^{i}Pr}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**2f**), 5 mg, 12%. M^+: *m/z* 728. (Found: C 36.4, H 3.2. $C_{22}F_{12}SW$ calc.: C 36.16, H 3.01%); IR (KBr) ν(C≡C) 1678 (wm), ν(C=C) 1648 (w), cm^{-1}. ^{1}H NMR (CD_2Cl_2), δ 1.04 (2 overlapping t, *J* 11.6, 6H, CH_2*CH_3*), 1.17 (d, *J* 6.8, 3H, ^{i}Pr), 1.54 (d, *J* 6.8, 3H, ^{i}Pr), 2.45 (m, 4H, *CH_2*, CH_3), 3.42 (m, 1H, ^{i}Pr), 5.90 (s, 5H, C_5H_5); ^{19}F NMR (CD_2Cl_2).

Reaction of [W{η^3-C(CF$_3$)C(CF$_3$)SMe}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (1b) with PhC≡CMe

Complex **1b** (45 mg, 0.07 mmol), PhC≡CMe (17 mg, 0.14 mmol) and hexane (10 cm^3) were transferred to a thick glass tube fitted with a teflon stopcock. The solution was degassed using four freeze–thaw cycles and the mixture allowed to react at 20 °C for 20 h, when the colour changed from red to yellow and a yellow solid deposited. Concentration of the mixture *in vacuo* and colling to −15 °C gave more of the yellow solid which was recrystallised from dichloromethane/hexane to give yellow crystals of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)SMe\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2b**), 40 mg, 75%. M^+: m/z 734. (Found: C 37.3, H 2.3. $C_{23}H_{16}F_{12}SW$ calc.: C 37.50, H 2.17%); IR (KBr) $\nu(C{\equiv}C)$ 1765 (wm), $\nu(C{\equiv}C)$ 1621 (w), cm^{-1}. ^1H NMR (CD_2Cl_2, −10 °C) δ 1.93 (br.m, 3H, *Me*C=), 2.13, 2.71 (s, 3H, SMe), 5.98, 6.01 (s, 5H, C_5H_5), 7.2–7.6 (m, 5H, C_6H_5); ^{19}F NMR (CD_2Cl_2, −30 °C) isomer A, δ −51.87 (br, 3F), −54.32 (m, 3F), −55.67 (app. sept, 3F), −58.16 (q, *J* 4.1, 3F); isomer B, δ −51.43 (br, 3F), −54.52 (q, *J* 4.8, 3F), −54.85 (app. sept, 3F), −58.06 (q, *J* 3.8, 3F).

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)S^iPr\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (1c) with $PhC{\equiv}CMe$ at 20 °C

A solution of complex **1c** (50 mg, 0.68 mmol) and $PhC{\equiv}CMe$ (20 mg, 0.07 mmol) in 1 : 1 diethyl ether/hexane (15 cm^3) was reacted at 20 °C for 72 h. The resulting pale yellow solution was concentrated *in vacuo* and cooled to −15 °C to give a yellow solid in two batches. These were recrystallised from diethyl ether/hexane to give pale yellow crystals of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)S^iPr\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2c**), 30 mg, 55%. M^+: m/z 762. (Found: C 39.2, H 2.5, S 4.2. $C_{25}H_{20}F_{12}SW$ calc.: C 39.27, H 2.62, S 4.19%); IR (nujol) 1744 (wm), cm^{-1}. ^1H NMR ($C_6D_5CD_3$, 19 °C) δ 0.43 (d, *J* 6.8, 3H, ^iPr), 0.57 (d, *J* 6.8, 3H, Pr), 2.02 (bs, 3H, *Me*C=), 2.82 (br, 1H, ^iPr), 5.22 (s, 5H, C_5H_5), 6.93 (bs, 5H, Ph); ^{19}F NMR ($CD_3C_6D_5$) δ −50.89 (br.s, 3F), −53.22 (br.s, 3F), −54.88 (br.s, 3F), −56.66 (q, *J* 5.3, 3F).

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)S^iPr\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (1c) with $PhC{\equiv}CMe$ at 55 °C

A solution of complex **1c** (50 mg, 0.08 mmol) and $PhC{\equiv}CMe$ (20 mg, 0.17 mmol) in diethyl ether/hexane 1 : 1 (15 cm^3) was heated at 55–60 °C in a sealed tube for 48 h. The orange solution was concentrated *in vacuo* and cooled to −15 °C to give an orange solid. This was recrystallised from dichloromethane/hexane to give orange-yellow crystals of $[WS^iPr\{\eta^5\text{-}C_4(CF_3)_4C(Me)C(Ph)\}(\eta^5\text{-}C_5H_5)]$ (**5**), 35 mg, 50%. M^+: m/z 762. (Found: C 39.6, H 2.3. $C_{25}H_{20}F_{12}SW$ calc.: C 39.26, H 2.62%); IR (nujol) $\nu(C{\equiv}C)$ 1644 (w), cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.0 (d, *J* 6.8, 3H, ^iPr), 1.33 (d, *J* 6.8, 3H, ^iPr), 1.99 (q, *J*(H–F) 1.8, 3H, *Me*C≡), 3.13 (m, 1H, ^iPr), 5.84 (s, 5H, C_5H_5), 7.0–7.6 (m, 5H, *Ph*C≡); ^{19}F NMR ($CDCl_3$) δ 51.86 (dq, *J*(F–Me) 1.8, *J*(F–F) 4.1, 3F), −53.59 (q, *J*(2–4) 8.6, 3F), −54.23 (q, *J*(3–4) 9.8, 3F), −63.84 (qqq, *J*(4–1) 4.1, *J*(4–2) 8.6, *J*(4–3) 9.8, 3F).

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SMe\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (1b) with $PhC{\equiv}CPh$

A solution of complex **1b** (35 mg, 0.06 mmol) and $PhC{\equiv}CPh$ (17 mg, 0.1 mmol) in diethyl ether/hexane 1 : 1 (8 cm^3) was reacted at 30 °C in a sealed tube for 20 h. The resulting yellow solution was concentrated *in vacuo* and cooled to −15 °C to give yellow crystals. These were recrystallised from dichloromethane/hexane to give 27 mg, 60% of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Ph){=}C(Ph)SMe\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2g**). M^+: m/z 796. (Found: C 41.4, H 2.6. $C_{28}H_{18}F_{12}SW$ calc.: C 42.10, H 2.26%); IR (KBr) $\nu(C{\equiv}C)$ 1781 (wm), $\nu(C{=}C)$ 1640 (w), 1620 (w), cm^{-1}. ^1H NMR (CD_2Cl_2) δ 1.54 (s, 3H, SMe), 6.06 (s, 5H, C_5H_5), 6.9–7.3 (m, 10H, Ph); ^{19}F NMR (CD_2Cl_2), 40 °C), δ −50.05 (m, 3F), −54.35 (qq, J 1.4, J 4.4, 3F), −55.26 (br.m, 3F), −56.37 (br.s, 3F).

Thermolysis of [Mo{η^3-C(CF$_3$)C(CF$_3$)=C(Me)C(Me)S^{i}Pr}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (3b)

A suspension of complex **3b** (22 mg, 0.036 mmol) in hexane (10 cm^3) was allowed to react at 70 °C in a sealed tube for 48 h when the colour changed from yellow to pale yellow. The solution was filtered, concentrated *in vacuo* to ca. 4 cm^3 and cooled to −15 °C to give a pale yellow solid. Further concentration and cooling of the mother liquor gave a second crop. Recrystallisation of the combined batches from hot hexane gave a pale yellow microcrystalline solid [Mo{η^4-C(Me)C(Me)=C(CF$_3$)-C(CF$_3$)(H)}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**4b**) (15 mg, 65%). M^+: m/z 540. (Found: C 37.4, H 2.0. $C_{17}H_{12}F_{12}Mo$ calc.: C 37.78, H 2.22%); IR (CDCl$_3$) ν(C≡C) 1765 (m), cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 5.63 (s, 5H, C$_5$H$_5$), 2.73 (s, 3H, Me), 1.92 (dq, J(H–H) 0.8, J(H–F) 2.0, 3H, Me), 1.57 (br.q, J(H–F) 9.6, 1H); ^{19}F NMR (CDCl$_3$) δ −51.13 (m, 3F, CF$_3$), −54.65 (m, 3F, CF$_3$), −55.40 (dist. q, J ca. 5.0, 3F), −55.48 (m, 3F).

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