DALTON
FULL PAPER

Reactions of alkynes with molybdenum and tungsten bis(alkyne) complexes $[M(SR)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, R = C_6F_5; M = W, R = $C_6H_4Me\text{-}4$): crystal and molecular structure of $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CO_2Me)C(CO_2Me)(SC_6F_5)\}(CF_3C{\equiv}CCF_3)\text{-}(\eta^5\text{-}C_5H_5)]$ †

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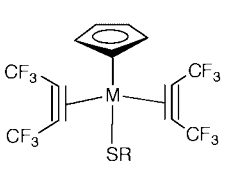
The reaction of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1a** with $MeO_2CC{\equiv}CCO_2Me$ at −30 °C gave a butadienyl complex $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CO_2Me)C(CO_2Me)(SC_6F_5)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ which has been shown by X-ray analysis to contain an $(\eta^5\text{-}C_5H_5)Mo(\eta^2\text{-}CF_3C{\equiv}CCF_3)$ unit attached to the $C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)SC_6F_5$ butadienyl ligand through a CO_2Me carbonyl oxygen atom and C_α, C_γ, and C_δ of the butadiene chain. The structure and bonding in this complex and in related butadienyl and co-ordinated ester complexes are compared. It rearranges above *ca.* −20 °C to give isomeric complexes $[Mo\{\eta^5\text{-}C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(CO_2Me){=}C(CO_2Me)SC_6F_5\}(\eta^5\text{-}C_5H_5)]$ in which linkage of the butadienyl and co-ordinated alkynes has occurred to give η^5 or η^6 tris(alkyne) ligands. The complex $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1b** and $MeO_2CC{\equiv}CCO_2Me$ reacted at −20 to −15 °C to give a butadienyl complex $[W\{\eta^5\text{-}C(CF_3){=}C(CF_3)C(CO_2Me)C(CO_2Me)(SC_6H_4Me\text{-}4)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ similar to the molybdenum complex but containing a co-ordinated thiolate sulfur instead of a carbomethoxy oxygen bonded to the metal. It isomerises above *ca.* −10 °C to give the sixteen electron complex $[W(SC_6H_4Me\text{-}4)\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)\}(\eta^5\text{-}C_5H_5)]$ containing a novel seven-membered metallacyclic ring. In contrast **1b** and non-activated alkynes $RC{\equiv}CR'$ (R = R′ = Me; R = Me or Ph, R′ = Ph) reacted to give the η^3- and η^4- butadienyl complexes $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(R){=}C(R')SC_6H_4Me\text{-}4\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ and $[W\{\eta^4\text{-}C(CF_3)C(CF_3){=}C(Me)C(Me)SC_6H_4Me\text{-}4\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ with no evidence for alkyne trimerisation. The pathways which lead to different alkyne oligomerisation patterns are discussed.

Introduction

Reactions of alkynes with thiolate complexes continue to be studied extensively[1] though our initial investigations of this chemistry[2] were made more than twenty years ago. In many cases, particularly when the alkyne has electronegative groups such as CF_3 or CO_2Me, its insertion into the metal–thiolate bond is observed. Alkynes have been found to behave similarly with other sulfur-containing species[3] and other heteroatom ligands can give rise to complexes containing, amongst others C–P,[4] C–Cl[5] and C–N[6] bonds formed *via* alkyne insertion. We previously reported that complexes $[M(SR)(CF_3C_2CF_3)_2\text{-}(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) exist in two isomeric forms: a bis(alkyne) form **1** and the η^2-C,C alkenyl form $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **2**,[7] resulting from partial migration of the thiolate onto one of the alkynes. In some cases the two forms were found to exist in equilibrium in solution. This provides a model for the well known insertion (ligand migration) process and in the present context provides an insight into the mechanism by which thiolate migration onto an alkyne carbon can occur.



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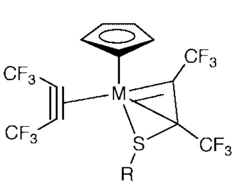

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In subsequent studies into the chemistry of these two isomeric compounds we observed multiple alkyne insertions leading to both linear and cyclic oligomerisation products.[8] Of particular note are reactions with alkynes $R'C{\equiv}CR''$ which lead to the η^3- and η^4-butadienyl products $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(R'){=}C(R'')SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ and $[Mo\{\eta^4\text{-}C(CF_3)C(CF_3){=}C(R')C(R'')SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *via* a sequence of thiolate migrations between different carbon atoms and the metal.[9,10] More complex reactions were observed between η^2-C,C alkenyl derivatives $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}\text{-}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) and dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$ (DMAD), in which linking of all three alkynes occurred to give two different oligomerisation sequences ABA and AAB (A = $F_3CC_2CF_3$, B = $MeO_2CC_2CO_2Me$).[9,11,12]

Since changing the metal or the thiolate ligand appears to have a significant effect on the mechanistic course of these reactions, we decided to extend our studies to reactions in which a third alkyne is added to the bis(alkyne) complexes $[M(SR)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$. Unfortunately, a logical approach in which the metal and the thiolate substituent are changed systematically and independently was not possible. Very few stable molybdenum derivatives are isolable whilst alkanethiolates of tungsten exist in the isomeric η^2-C,C alkenyl

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† *Supplementary Data Available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3883/

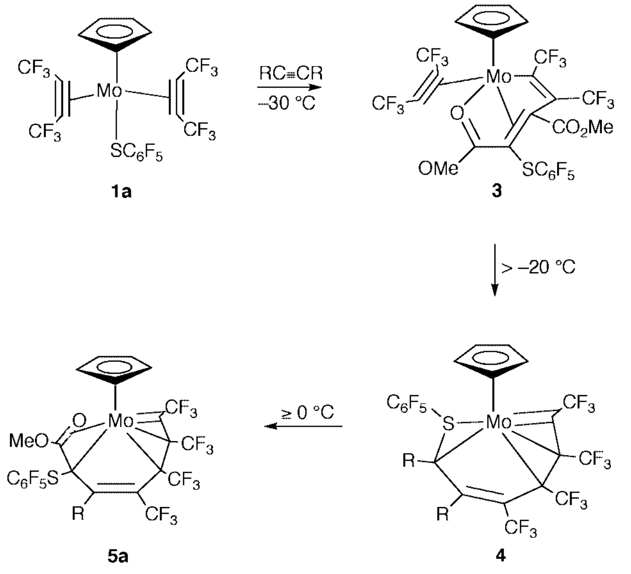
form $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **2**. Consequently our studies were restricted to arenethiolate derivatives (M = Mo, R = C_6F_5 **1a**; M = W, R = $C_6H_4Me\text{-}4$ **1b** or C_6F_5 **1c**) the results of which are reported herein. Some of this work has been communicated previously in preliminary form.[11]

Results and discussion

Our previous studies revealed that reactions between alkynes and η^2-C,C alkenyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, R = Pr^i; M = W, R = Me, Et or Pr^i) proceeded at temperatures as low as −40 °C and that at higher temperatures quite complex rearrangements occurred.[12] In consequence, reactions of the bis(alkyne) complexes $[Mo(SC_6F_5)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1a** and $[W(SC_6H_4Me\text{-}4)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$ **1b** or C_6F_5 **1c**) with dimethyl acetylenedicarboxylate were initially studied over the temperature range −40 to +20 °C by ^{19}F NMR spectroscopy to establish the sequence of events following mixing of the reagents. These established that the tungsten derivative **1c** was unreactive towards the alkyne substrate under these conditions, whereas reactions of **1a** and **1b** proceeded readily above *ca.* −30 °C *via* one or more intermediates. Once the reaction conditions leading to the various species involved had been identified, synthetic scale reactions were carried out with a view to isolating and characterising these derivatives. Studies involving $[Mo(SC_6F_5)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1a** will be described first.

Reaction of $[Mo(SC_6F_5)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ 1a

This reaction (Scheme 1) proceeds above *ca.* −30 °C in diethyl ether–hexane to give an intermediate 1 : 1 adduct **3** which was isolated as yellow crystals by maintaining the reaction at *ca.* −25 °C. Above *ca.* −20 °C isomerisation occurs, giving **4** initially followed by a complex reaction to give, according to ^{19}F NMR studies, several minor products which were not identified and one major product **5a** which was isolated from the reaction at 20 °C and characterised.



Scheme 1 R = CO_2Me.

The composition of complex **3** was established by elemental analysis but the spectroscopic features did not permit structure identification. The IR spectrum contains, in addition to carbomethoxy $\nu(C{=}O)$ bands above 1700 cm^{-1}, a weak-medium band at 1852 cm^{-1} which could be assigned as the $\nu(C\equiv C)$ mode of a co-ordinated alkyne. However, ^{19}F NMR data, apart from indicating the presence of four distinct CF_3 environments, were uninformative. Consequently, crystals of **3** suitable for X-ray diffraction studies were obtained from a reaction solution (diethyl ether) by layering with hexane at *ca.* −25 °C.

Table 1 Selected distances [Å] for complex **3**

Mo–O2	2.209(2)	Mo–C2	2.168(4)
Mo–C3	2.141(4)	Mo–C6	2.217(3)
Mo···C5	2.593(3)	Mo–C7	2.212(3)
Mo–C11	2.223(3)	Mo–C (Cp)	2.326(4)–2.354(4)
O1–C5	1.291(4)	O3–C8	1.195(4)
O2–C5	1.253(4)	C5–C6	1.460(4)
O4–C8	1.333(4)	C7–C10	1.476(4)
C2–C3	1.255(5)	C10–C11	1.317(5)
C6–C7	1.465(4)	C7–C8	1.491(5)

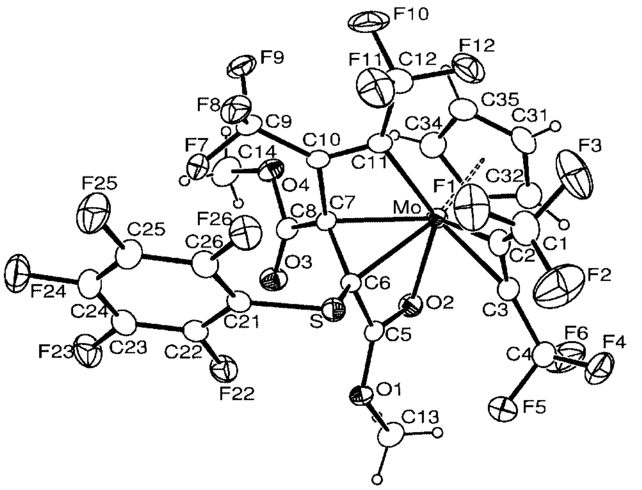


Fig. 1 A view of a molecule of complex **3** showing the atom numbering and 20% probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary size.

X-Ray diffraction studies established that complex **3** (Fig. 1, Table 1) contains a butadienyl ligand $C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)(SC_6F_5)$ bonded to molybdenum *via* C11, C7, C6 and O2, the carbonyl oxygen of an ester group (but see below for a discussion of the Mo···C5 distance). This ligand is formally derived from the three constituents by first inserting the incoming alkyne DMAD into the Mo–S bond and then linking it to one of the co-ordinated $CF_3C\equiv CCF_3$ ligands. This follows the general pattern of behaviour we have previously observed with the reactions between alkynes and η^2-C,C alkenyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** in that the thiolate ligand bonds preferentially to the incoming alkyne, rather than to the co-ordinated $CF_3C\equiv CCF_3$, even when the SR group is initially attached to a $C(CF_3)$ moiety.

Complex **3** belongs to a small group of $(\eta^5\text{-}C_5H_5)ML$ complexes (M = Mo or W, L = $\eta^2\text{-}CF_3C\equiv CCF_3$ or PEt_3) in which the metal completes an 18-electron configuration by accepting five electrons from a butadienyl ligand $(CR)_4SR$ derived by condensing two alkynes with a thiolate. Six such complexes (Table 2) ‡,[13,14] have now been structurally characterised and they display three distinct modes of butadienyl bonding.

In mode **(i)** the metal bonds only to the four butadienyl carbon atoms, the carbene-like M–C_α bond being especially short, and the butadienyl chain is nearly planar. Mode **(i)** has been observed in complexes where the butadienyl carries substituents which are themselves capable of co-ordinating to the metal so that the alternative bonding modes **(ii)** and **(iii)** are

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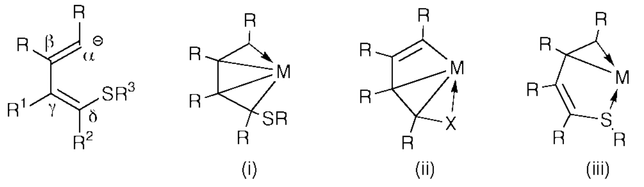
‡ The Cambridge Structural Database (November, 1998 version) was surveyed with the programs QUEST and VISTA mounted at the Daresbury National Laboratory, Warrington, England. Numerical values in Tables 2 & 3 not available in the original papers were calculated using these programs.

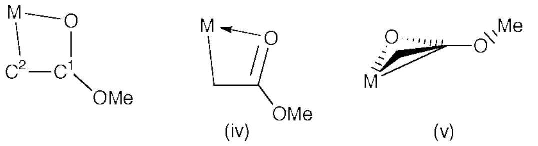
Table 2 Dimensions (Å and °) in $[M\{C(R)=C(R)C(R^1)=C(R^2)SR^3\}L(\eta^5\text{-}C_5H_5)]$ butadienyl complexes



Ref.	M	R	R^1	R^2	R^3	Mode	M–C_α	M–C_β	M–C_γ	M–C_δ	M–S	τ[a]
13	W	CF_3	Me	Mo	Pr^i	**(i)**	1.940(5)	2.347(5)	2.423(5)	2.238(5)	—	7
14	Mo	CF_3	Me	CO_2Me	C_6F_5	**(i)**	1.949(6)	2.313(6)	2.412(6)	2.291(6)	—	9
14	Mo	Ph	CF_3	CF_3	C_6F_5	**(i)**	1.965(6)	2.381(5)	2.381(7)	2.254(7)	—	15
8[b]	Mo	CF_3	CF_3	CF_3	Pr^i	**(ii)**	2.170(4)	2.738	2.243(3)	2.154(3)	2.514(1)	70
[c]	Mo	CF_3	CO_2Me	CO_2Me	C_6F_5	**(ii)**	2.223(3)	2.728(3)	2.212(3)	2.217(3)	—	63
11	Mo	CF_3	Me	Ph	Pr^i	**(iii)**	1.915(5)	2.239(5)	3.216	3.343	2.468(2)	62

[a] $\tau = |C_\alpha–C_\beta–C_\gamma–C_\delta|$. [b] L = PEt_3 only for this compound. Otherwise L = $\eta^2\text{-}F_3CC_2CF_3$. [c] This work.

Table 3 Dimensions (Å and °) in C_α-metallated alkyl ester chelate complexes



Ref.	M	φ[a]	M···C^1	M–C^2	M–O	C^1=O	C^1–OMe	C^1–C^2
16	Re	10.4	2.591	2.115	2.243	1.239	1.312	1.482
[b]	Mo	20.5(3)	2.593(3)	2.217(3)	2.209(2)	1.253(4)	1.291(4)	1.460(4)
17	W	31.6	2.507	2.231	2.256	1.244	1.314	1.464
12	Mo	32.3	2.478	2.249	2.126	1.248	1.295	1.468
18	Mo	37.8	2.427	2.283	2.172	1.276	1.336	1.413
17	W	42.2	2.435	2.303	2.234	1.249	1.322	1.435
19	Ru	47.5	2.333	2.195	2.294	1.252	1.344	1.412
19	Ru	47.8	2.353	2.257	2.260	1.268	1.309	1.539
Mean		33.8	2.464	2.230	2.224	1.254	1.316	1.459

[a] $\varphi = |M–O=C^1–C^2|$. Species with $\varphi < 5°$ are excluded. [b] This work.

possible. Detachment of C_β from the metal and substantial weakening of the M-C_α linkage, compensated by donation of an electron pair from a substituent, gives mode **(ii)**. This is found with the thiolate S atom bonded to the metal atom, in $[Mo\{\eta^4\text{-}C(CF_3)=C(CF_3)C(CF_3)C(CF_3)SPr^i\}(PEt_3)(\eta^5\text{-}C_5H_5)]$, obtained from reaction of PEt_3 with the η^2-C,C alkenyl complex $[Mo\{\eta^3\text{-}C(CF_3)=C(CF_3)SPr^i\}(\eta^2\text{-}CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$.[8] Mode **(ii)** also occurs in **3** but with the carbomethoxy group, rather than the thiolate sulfur atom, completing the metal co-ordination. Alternatively {mode **(iii)**} the M-C_α carbene linkage is retained but both C_γ and C_δ detach, as found in $[Mo\{\eta^4\text{-}C(CF_3)C(CF_3)C(Me)=C(Ph)SPr^i\}(\eta^2\text{-}CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$.[11] Both **(ii)** and **(iii)** involve loss of conjugation in the butadienyl chain (τ > 60°) and contain fixed double bonds (C=C 1.32–1.34 Å). Other chain C–C distances in these complexes are 1.40–1.47 Å except for slight lengthening (to 1.48–1.51 Å) adjacent to a double bond. The ability of the butadienyl chain to provide 5 electrons **(i)** or 3, with another pair coming from a substituent, as in **(ii)** and **(iii)** greatly complicates the interpretation of the chemistry of these species.

The interaction of the metal with the carbomethoxy ester function in complex **3** is sufficiently unusual to merit comment. The Mo–O2 and Mo–C6 distances [2.209(2) and 2.217(3) Å] are typical of normal single bonds.[15] The Mo–O2–C5–C6 ring [torsion angle 20.5(3)°] is non-planar, so that the transannular Mo···C5 distance is 2.593(3) Å, only 0.24 Å longer than the longest Mo–C (Cp) distance. Examples of MOC_2 chelate rings formed by co-ordination of an ester oxygen atom are now known for Mn and for all second and third row metals of Groups 6–9 except Tc, but in most cases the rings are close to planar.‡ However, in a few recently characterised complexes, mainly of Mo and W, the absolute value of the M–O=C–C torsion angle, φ, is greater than 5° (Table 3).[16–19] Indeed, φ can range up to nearly 50°, with the transannular M···C distance decreasing as φ increases, indicating a switch from co-ordination by the O lone pair in the planar case **(iv)** to an asymmetric interaction between M and the C=O π orbitals **(v)**. The data in Table 3 represent structures lying at various stages along the path from **(iv)** to **(v)**, with **3** lying fairly close to **(iv)**. Schrock and co-workers[20] have discussed a similar structural feature in tungstenacyclobutane complexes where the transannular W···C sp^3 distance varies from 2.32(2) to 2.71(1) Å depending on the nature of the tungsten co-ordination.

Whatever the value of φ in Table 3 the C=O distance in these complexes is typically lengthened to *ca.* 1.25 Å from its unperturbed value of 1.196 Å[15] and the C–OR bond is slightly shortened, this effect being particularly noticeable in **3**. Compared with the ester chelate ring the C7–C10–C11–Mo ring is flatter [torsion angle 8.6(3)°] and the Mo···C10 distance correspondingly longer [2.728(3) Å].

The $(\eta^5\text{-}C_5H_5)Mo(\eta^2\text{-}CF_3C\equiv CCF_3)$ moiety in complex **3** is characterised by relatively long Mo–C2 and Mo-C3 distances [2.168(4) and 2.141(4) Å; *cf.* values of 2.02–2.19 Å in 18 $(\eta^5\text{-}C_5H_5)M(\eta^2\text{-}CF_3C\equiv CCF_3)$ complexes of Mo and W].‡ The C2–C3 vector makes an angle of 86° with the CpMoX plane (Cp centroid of C31–C35, X midpoint of C2–C3), close to its

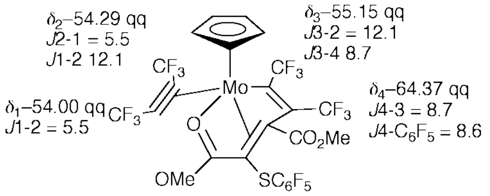


Fig. 2 The ^{19}F NMR assignments for $[Mo\{\eta^4\text{-}C(CF_3)=C(CF_3)\text{-}C(CO_2Me)=C(CO_2Me)(SC_6F_5)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **3**.

maximum value of 90°. In other $(\eta^5\text{-}C_5H_5)M(\eta^2\text{-}CF_3C\equiv CCF_3)$ complexes of Mo and W this angle varies from 38 to 86°.

Finally, anticipating the discussion of the ^{19}F NMR spectrum, we note that the shortest intramolecular F · · · F contact in complex **3** occurs in the C_6F_5 ring [F22 · · · F23 2.677(4) Å]; the shortest contacts of this kind between adjacent CF_3 groups are F1 · · · F11 and F8 · · · F11 [both 2.793(4) Å] and F2 · · · F4 [2.856(6) Å].

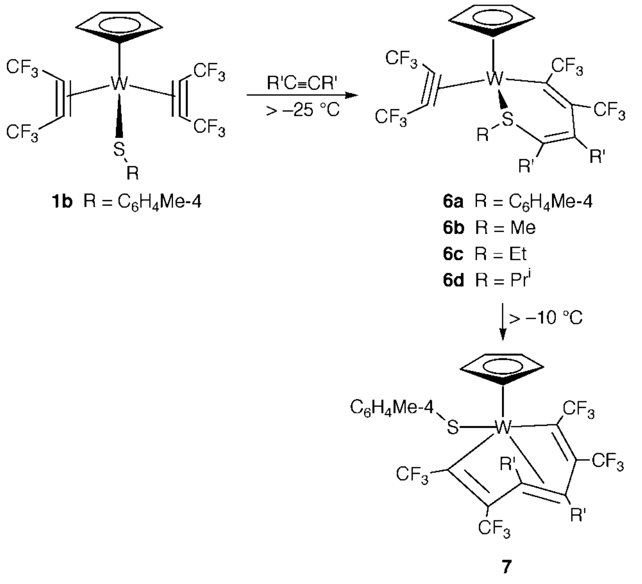
Each of the butadienyl structures listed in Table 2 has a distinctive set of spectroscopic features, in particular the ^{19}F NMR spectrum. This is also true for $[Mo\{\eta^4\text{-}C(CF_3)=C(CF_3)C\text{-}(CO_2Me)=C(CO_2Me)(SC_6F_5)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **3** where the data can be interpreted in terms of the solid state structure. The ^{19}F NMR spectrum shows four peaks in the CF_3 region in addition to the expected three C_6F_5 resonances and homodecoupling of the CF_3 peaks established the coupling connectivities shown in Fig. 2. On the basis that the C4 alkyne CF_3 group is distal to the $C10(CF_3)=C11(CF_3)$ portion of the butadienyl ligand and is therefore only capable of coupling with the C1 alkyne CF_3, we assign this to the quartet δ_1. The other assignments follow from this. Interestingly, this reveals a large $J_{2\text{–}3}$ coupling of 12.1 Hz between the alkyne and butadienyl CF_3 groups which compares with a $J_{3\text{–}4}$ value of 8.7 Hz for the $C(CF_3)=C(CF_3)$ moiety of the butadienyl ligand. This apparent anomaly is explicable if we assume that the primary F–F coupling mechanism involves a 'through space' interaction, a phenomenon we have encountered repeatedly in this area of chemistry.[12] If free rotation about the C–CF_3 bonds is assumed, molecular graphics studies[21] of complex **3** reveal that the minimum F · · · F distances for CF_3 δ_2 · · · CF_3 δ_3 and CF_3 δ_3 · · · CF_3 δ_4 are 1.66 and 1.87 Å respectively; *i.e.* the greater the distance the smaller is the coupling constant. We also note that CF_3 δ_4 couples with the two *ortho* fluorines of the C_6F_5 group, a phenomenon we have noted previously in butadienyl ligands where CF_3 and SC_6F_5 substituents are in close proximity.[10,22]

It is of interest to compare the structure of complex **3** with that proposed for the first intermediates **6**, generated from the reaction of DMAD with the η^2-C,C alkenyl complexes $[W\{\eta^3\text{-}C\text{-}(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** (R = Me, Et or Pr^i) and, as discussed later, the bis(alkyne) complex **1b**, Scheme 2.[12] Both **3** and **6** contain the sequence $CF_3C_2CF_3$–DMAD–SR but in **6** neither the carbomethoxy CO nor the alkenyl R′C=CR′ bond is co-ordinated to the metal which instead bonds to the thiolate sulfur atom. Moreover, **6** formally has a 16 electron configuration unless, as seems probable, the alkyne functions as a 4 electron donor. In **6** isomerism is possible due to inversion at the pyramidal sulfur and was detected by dynamic NMR studies. This is clearly not possible with **3** and, unsurprisingly, only one form of this compound was observed in the ^{19}F NMR spectrum. Significantly, in the aforementioned phosphine derivative $[Mo\{\eta^4\text{-}C(CF_3)=C(CF_3)C(CF_3=C(CF_3)SR\}(PEt_3)\text{-}(\eta^5\text{-}C_5H_5)]$ the thiolate ligand is bound to the metal, playing a similar role to the carbomethoxy oxygen in **3**. The phosphine complex[8,22] also exists in two isomeric forms in solution, probably due to inversion at the thiolate sulfur.

The isomerisation of complex **3** (see Scheme 1), which was followed by ^{19}F NMR spectroscopy in the CF_3 region, proceeds slowly above *ca.* −20 °C, more rapidly above *ca.* −10 °C. The first intermediate **4** has a distinctive spectrum with four CF_3 peaks, a quartet of quartets J 11.5, 3.5 Hz, two septets (quartets of quartets with similar coupling constants) and a quartet of quartets J 11.4, 2.9 Hz. This species was not isolated and on warming further a complex reaction ensued to produce a mixture of species at 20 °C, the major product being **5a**. The reaction between **1a** and $MeO_2CC\equiv CCO_2Me$ was then carried out on a synthetic scale at room temperature and after several crystallisations of the product mixture a pure sample of **5a** was isolated. This exhibits a ^{19}F NMR spectrum quite similar to that of **4** but with slightly different coupling constants, δ_1 qq, J 13.8, 2.2; δ_2 septet; δ_3 septet; δ_4 qq, J 13.7, 3.3 Hz, indicating that **4** and **5a** have similar but not identical structures. Significantly the spectra are almost identical to those of the two isomers isolated from the reactions of the η^2-C,C vinyl complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** with DMAD, namely **5b** (see Scheme 3) in which a carbomethoxy methyl is bound to the metal and the thiolate is free and an isomer where the reverse is true.[12] Complex **5b** and its isomer have been structurally characterised by X-ray diffraction studies and we therefore propose similar structures for **4** and **5a** (Scheme 1), with the $C(CF_3)C(CF_3)C(CF_3)C(CF_3)=C(CO_2Me)C(CO_2Me)SC_6F_5$ ligand bonded to the metal *via* an η^2-C,C alkenyl linkage and two Mo–C σ bonds. They differ only in the co-ordination of the terminal portion of the ligand, with sulfur co-ordination in **4** and an unsymmetrical η^2-C–O linkage to the metal in **5a** which is similar to that in **3**. The similarity of the ^{19}F NMR spectra of the two isomers is therefore not surprising.

Reactions of $[W(SC_6H_4Me\text{-}4)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ 1b

^{19}F NMR studies established that the reaction of $[W(SC_6H_4\text{-}Me\text{-}4)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1b** with $MeO_2CC\equiv CCO_2Me$ proceeds above −25 °C to give an intermediate **6a** (Scheme 2) which isomerises at higher temperatures (*ca.* −10 °C) to the trimerisation product **7**. Complex **6a** was characterised exclusively from its ^{19}F NMR spectrum which is virtually identical to those of similar intermediates **6b**, **6c**, **6d** observed in the reactions of the η^2-C,C alkenyls $[W\{\eta^3\text{-}C(CF_3)C\text{-}(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** (R = Me, Et or Pr^i) with DMAD at −20 °C; **6b** has been fully characterised by elemental analysis, IR and NMR spectroscopy.[12] The ^{19}F NMR spectrum of **6a** consists of a quartet of quartets, $J_{1\text{–}2}$ 14.2, $J_{1\text{–}3}$ 4.0 Hz, a quartet, $J_{1\text{–}2}$ 14.2 Hz, another quartet of quartets $J_{3\text{–}1}$ 4.0, $J_{3\text{–}4}$ 3.9 Hz and a second quartet, $J_{4\text{–}3}$ 3.9 Hz.



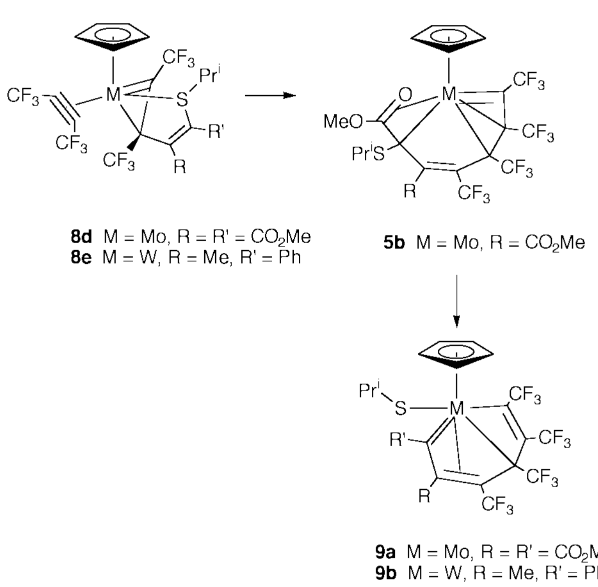
Scheme 2 R′ = CO_2Me.

Above *ca.* −10 °C complex **6a** undergoes a relatively clean transformation into **7** according to NMR studies, although small amounts of a second species were observed. The amount of the latter was insufficient for it to be isolated even when the reaction between [W(SC$_6$H$_4$Me-4)(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] **1b** and DMAD was carried out on a synthetic scale at 20 °C. This reaction gave black crystals of **7** in 18% yield from diethyl ether–hexane. The possibility of isomerisation of **7** at higher temperatures was investigated by ^{19}F NMR spectroscopy. However, thermolysis in deuteriated toluene at temperatures up to 70 °C only led to decomposition to give a complex mixture of products, none of which was identified.

The spectroscopic features of complex **7** are unusually simple: in particular, the ^{19}F NMR spectrum consists of four distinct quartets exhibiting two coupling constants *J* 10.3 and 7.6 Hz. This was insufficient to identify the structure and a single crystal diffraction study was therefore carried out.[11] This analysis established that the three alkynes had linked together to produce a seven-membered metallacyclic ring. Interestingly, the incoming alkyne occupies a central rather than terminal position in the C$_6$ chain which bonds to the metal through both terminal carbon atoms [σ-W–C 2.24(2) and 2.12(2) Å] and by an η^2-alkene interaction involving the central C=C bond [π-W–C 2.21(2) and 2.29(2) Å] leaving only the carbon atoms at positions 2 and 5 in the chain unco-ordinated [W · · · C 2.79(2) and 2.67(2) Å]. There are fixed double bonds [C=C 1.34(3)–1.35(3) Å] at the ends of the C=CC=CC=C chain and the C–C–C torsion angle sequence [66(2), −166(2), 51(2)°] indicates that the chain has a symmetrical conformation with a *trans* configuration at the central double bond which cannot conjugate effectively with the terminal C=C bonds. A similar mode of bonding has been found previously in [Ni{η^4-C(CF$_3$)=C(CF$_3$)-C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)}(AsMe$_2$Ph)$_2$] which results from the reaction of CF$_3$C≡CCF$_3$ with the hexafluorobut-2-yne derivative [Ni(CF$_3$C≡CCF$_3$)(AsMe$_2$Ph)$_2$].[23]

We note that both complex **7** and the nickel complex can formally be regarded as 16 electron derivatives. This configuration is common in nickel(II) chemistry but significantly less so in organometallic compounds of tungsten. Unsaturated cyclopentadienyl tungsten(II) complexes are known, *e.g.* [WX(CO)$_2$(η^5-C$_5$H$_5$)] (X = AsBu$^t_2$), [WX(PMe$_3$)L(η^5-C$_5$Me$_5$)] (X = PCy$_2$, L = PMe$_3$; X = PPh$_2$, L = PMe$_3$ or PHPh$_2$), which are probably stabilised by π donation from the ligand X (which can formally be regarded as a 3 electron donor) or alternatively by steric protection by the bulky substituents on the ligands.[24,25] Poli and co-workers[26] have isolated stable 16 electron molybdenum(II) complexes [MoClL$_2$(η^5-C$_5$H$_5$)] (L = PMe$_3$ or PMe$_2$Ph) which prove to be paramagnetic in the ground state. However, since **7** is formally a tungsten(IV) complex it is perhaps more comparable with the 16 electron thiolate derivatives we have reported previously such as [W(SR)$_3$(CO)(η^5-C$_5$H$_5$)] (R = C$_6$H$_5$, C$_6$H$_4$Me-4, C$_6$F$_5$ or C$_6$F$_4$-H-4) and [W(SC$_6$F$_5$)$_4$(η^5-C$_5$H$_5$)]$^-$ some of which have been characterised by X-ray diffraction studies.[27]

It is apparent that subtle factors control the stability of the 16-electron configuration in complexes such as **7**. This is emphasised by the existence of a metallacycle structure closely analogous to **7**, namely that found[11] in complexes **9a**, **9b** (Scheme 3). These were obtained on thermolysis of the η^3-butadienyl complexes **8d**, **8e** in which the η^3 bonding mode **(iii)** (Table 2) of the butadienyl ligand is displayed. Structural studies of [W(SPr^i){η^5-C(CF$_3$)C(CF$_3$)C(CF$_3$)C(CF$_3$)C(Me)-C(Ph)}(η^5-C$_5$H$_5$)] **9b** revealed that the metallacycle contains a C$_6$ chain which is attached to the metal *via* an η^5 mode of bonding which allows the metal access to a full 18-electron configuration: the W–C distances [2.242(2), 2.766(4), 2.195(4), 2.351(4), 2.489(3) and 2.017(3) Å] indicate that the terminal C(Me)=C(Ph) unit donates three electrons to the metal (rather than one as in **7**) and the C–C–C–C torsion angle sequence [−64.3(4), 149.0(5) and −22.4(5)°] indicates that the C(CF$_3$)=C(CF$_3$)C(Me)=C(Ph) end of the chain is nearly planar. Interestingly, the W–S distance [2.374(1) Å] is somewhat longer than in **7** [2.318(7) Å], perhaps reflecting the 18-electron configuration in the former and the 16-electron configuration in the latter. It is therefore possible that sulfur–metal π donation provides a stabilising influence on the electronic unsaturation found in **7**.



8d M = Mo, R = R' = CO$_2$Me
8e M = W, R = Me, R' = Ph

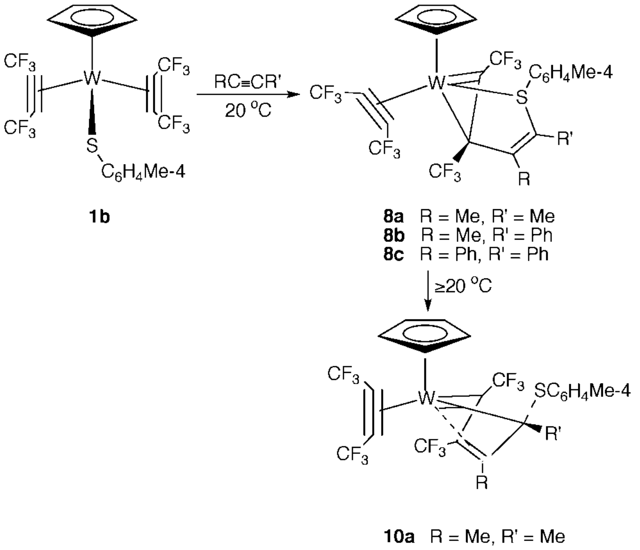
5b M = Mo, R = CO$_2$Me

9a M = Mo, R = R' = CO$_2$Me
9b M = W, R = Me, R' = Ph

Scheme 3

Reactions of non-activated alkynes

Previously we studied the reactions of non-activated alkynes with the bis(hexaflurobut-2-yne) derivative [Mo(SC$_6$F$_5$)(CF$_3$-C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] **1a**[10] and the isomeric η^2-C,C alkenyl derivatives [M{η^3-C(CF$_3$)C(CF$_3$)SR}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] **2** (M = Mo, R = Pr^i; M = W, R = Me, Pr^i or Bu^t).[9] A notable feature of these reactions was the formation of aforementioned η^4-butadienyl derivatives [M{η^4-C(CF$_3$)C(CF$_3$)=C(R′)C(R″)-SR}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (R, R′ and R″ = alkyl or aryl) of type **10**, *via* η^3-butadienyl intermediates [M{η^3-C(CF$_3$)C-(CF$_3$)SR}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] of type **8** (see Scheme 4).



1b

8a R = Me, R' = Me
8b R = Me, R' = Ph
8c R = Ph, R' = Ph

10a R = Me, R' = Me

Scheme 4

Since the latter also functions as a precursor to the alkyne trimerisation products **5b** and **9a**, **9b** (Scheme 3) it was of interest to investigate the reactions of [W(SC$_6$H$_4$Me-4)(CF$_3$C≡CCF$_3$)$_2$-(η^5-C$_5$H$_5$)] **1b** with non-activated alkynes, MeC≡CMe, PhC≡CMe and PhC≡CPh. The results of these studies are summarised in Scheme 4.

In each of the three reactions studied the initial product is the η^3-butadienyl isomer $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(R){=}C(R')\text{-}SC_6H_4Me\text{-}4\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**8a** R = R′ = Me; **8b** R = Me, R′ = Ph; **8c** R = R′ = Ph) and this also proved to be the terminal product with PhC≡CMe and PhC≡CPh (Scheme 4). However, the MeC≡CMe adduct **8a** isomerises slowly in solution at 20 °C, more readily at 50 °C, to the thermodynamically more stable η^4-butadienyl form $[W\{\eta^4\text{-}C(CF_3)C(CF_3){=}C(Me)C(Me)SC_6H_4Me\text{-}4\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **10a** which was isolated as orange crystals. These two structural types were identified by comparison of spectroscopic data, in particular IR and ^{19}F NMR spectra, with those of complexes $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[11] and $[W\{\eta^4\text{-}C(CF_3)C(CF_3){=}C(Me)C(Me)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[13] whose structures have been confirmed by X-ray diffraction studies. Although the unsymmetrical alkyne PhC≡CMe could react to give two isomers depending on the relative positions of the Ph and Me on the butadienyl ligand, only one was found with $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ and this proved to have the Me adjacent to one of the the $C(CF_3)$ moieties with the Ph adjacent to the thiolate. This also appears to be the case with **8b** since, as with the latter complex, a small quartet coupling, $J_{H\text{–}F}$ *ca.* 2.1 Hz is observed in one of methyl signals.

Attempts to induce isomerisation of complex **8b** by heating in deuteriated toluene were followed by ^{19}F NMR spectroscopy. However, thermolysis at temperatures up to 85 °C merely resulted in decomposition of the complex and no identifiable products were obtained. A photochemically induced reaction in diethyl ether–light petroleum (bp 60–80 °C) was also unsuccessful, with no change in the ^{19}F NMR spectrum after 22 h or following photolysis for 90 h in the presence of an excess of $CF_3C{\equiv}CCF_3$. These results are similar to those reported previously for 1:1 adducts derived from the reactions of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1a** and the η^2-C,C alkenyl derivatives $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** with alkynes, where we observed that bulky alkyne substituents tended to stabilise the η^3-butadienyl form **8** with respect to the η^4 bonded isomer **10**.[10] However, isomerisation of η^3-alkenyls $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)SC_6F_5\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ and $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, type **8**, to the η^4 butadienyl form, type **10**, proceeds readily above 0 °C from which it may be inferred that the thiolate substituent also has a significant effect on this process.

We note that Green and co-workers[28] have previously observed the opposite process, *i.e.* conversion of an η^4- into η^3-butadienyl on addition of a two electron donor to $[Ru\{\eta^4\text{-}CPhCPhCPhC(H)Ph\}(\eta^5\text{-}C_5H_5)]$, although in this case the lack of a thiolate donor results in a $\sigma + \eta^2$-alkene mode of co-ordination of the butadienyl ligand. In some respects this ruthenium derivative is more akin to butadienyls $[Mo\{\eta^3\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i\}(L)(\eta^5\text{-}C_5H_5)]$ (L = PEt_3 or $PMePh_2$) we have reported previously[22] which also display a σ-η^2 rather than η^2 alkenyl co-ordination of the butadienyl ligand.

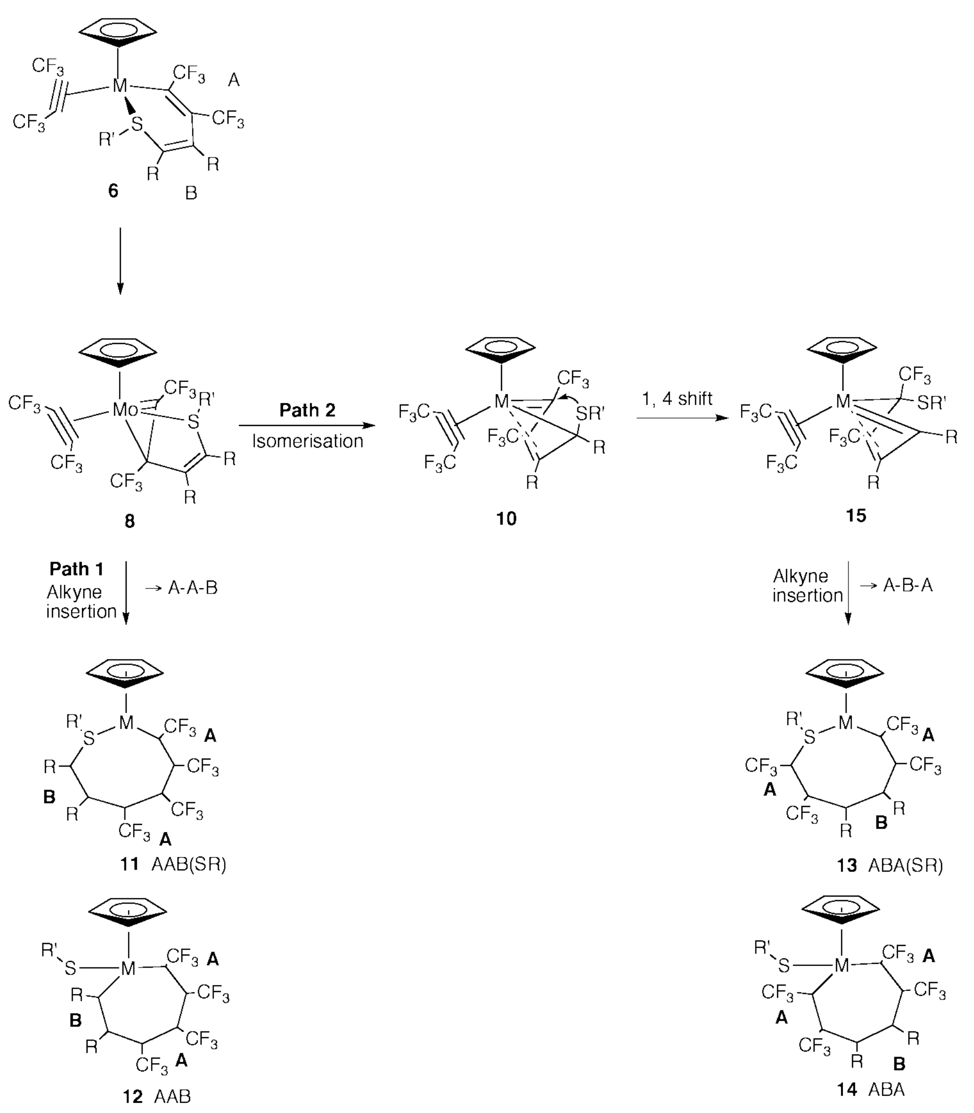
η^4-Butadienyl complexes have now been isolated from a variety of reactions in addition to those involving linking of two alkynes and a thiolate group as reported here and earlier in this series of publications. These include hydride-promoted ring opening of the cyclobutadiene ligand in $[Ru(NCMe)(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5H_5)][BF_4]$,[28,29] protonation of bis alkyne complexes $[W(PhC_2Ph)_2(\eta^2\text{-}S_2CNEt_2)_2]$,[30] $[MoBr(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_9H_7)]$,[31] and $[MoX(RC_2R)_2(\eta^5\text{-}C_5H_5)]$ (X = Cl, Br or I, R = Me or Et),[32] hydride addition to the bis alkyne complex $[ReBr(PhC{\equiv}CPh)_2(\eta^5\text{-}C_5H_5)][PF_6]$,[33] hydrolysis of bis alkyne derivatives $[W(NCMe)(PhC_2Ph)_2(\eta^4\text{-}C_4Ph_4)]$,[34] and linking of an alkyne and an allyl with concomitant hydrogen transfer in the reaction of $[NbCl_2(PhC_2Ph)\{HB(dmpz)_3\}]$ ($HB(dmpz)_3$ = tris(3,5-dimethylpyrazoyl)hydroborate) with $CH_2{=}CHCH_2MgCl$.[35] Although Green has drawn attention to the concept of latent or stored co-ordinative unsaturation in such species, *i.e.* the η^4 five electron donor butadienyls can act as precursors to η^3 three electron donor derivatives the examples of type **10** we have studied to date show little tendency to undergo ring opening to the η^3-bonded form.

Previously we observed fluxional behaviour in complexes of type **8**, primarily due to fast exchange between two isomeric forms which could be observed at low temperature.[9] This was attributed to inversion at the pyramidal sulfur atom. We therefore carried out dynamic ^{19}F NMR studies of all three complexes **8a**, **8b**, **8c** but in none of these isomerism was detected down to −90 °C in CD_2Cl_2. However, in all three cases the broad, high frequency peak near δ −50 broadened further at low temperatures, collapsed into the baseline and reappeared as three distinct resonances, each due to one individual fluorine. This was demonstrated most clearly in the case of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Ph)SC_6H_4Me\text{-}4\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **8b** where at −92 °C three distinct triplets were obtained: δ −45.95, J 120.6; −51.36, 121.7; −56.50, 117.7 Hz. This suggests complete freezing of CF_3 rotation such that each fluorine is in a distinct environment and coupled to the other two to give a doublet of doublets with similar coupling constants, *ca.* 120 Hz. This type of dynamic behaviour was also observed in our previous work where molecular graphics studies illustrated that the CF_3 group on the chiral β carbon of the η^2-C,C alkenyl moiety is in a particularly congested steric environment.[9] Effectively it is completely surrounded by the other three CF_3 groups and the substituent on the adjacent carbon of the alkene portion of the C_4 chain.

We also carried out variable temperature ^1H NMR studies of complexes **8a**, **8b**, **8c** since in all three cases the tolyl signals exhibited significant broadening at room temperature. The absence of additional phenyl resonances in the tolyl region of the spectrum enabled the clearest data to be obtained with **8a**. Two very broad signals (2 × 1 H) and one sharp peak (2 H) at δ 6–8 are observed at room temperature and these gradually transformed into three sharp resonances, ratio 1:2:1, below *ca.* −20 °C, indicating freezing out of tolyl group rotation. This has been observed previously in complexes of this type and molecular graphics studies of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me){=}C(Me)SC_6F_5\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ suggest that steric interactions between the thiolate C_6F_5 substituent and one of the CF_3 groups may be responsible.[10] An electronic origin for the preferred tolyl group orientation seems unlikely although this is possible when aryl groups are attached directly to a transition metal[36] or to Fischer carbene ligands.[37] What is apparent is that the two types of fluxional behaviour identified in tolyl complexes **8a**, **8b**, **8c** are not directly related: tolyl rotation is not affected by the CF_3 group on the β-carbon and *vice versa* since they are too far apart on the C_4S chain.

Conclusion

Reactions between $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1a** or $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1b** and non-activated alkynes both lead initially to η^3-butadienyl derivatives **8**. The only real difference appears to be the ease with which isomerisation occurs to give η^4-butadienyls **10**, since this occurs more readily with the molybdenum derivatives. However, reactions with the activated alkyne DMAD show significant differences and, as Schemes 1 and 2 show, the reactions initially proceed in a similar, but not identical manner. The incoming DMAD in each case combines with the thiolate ligand and one co-ordinated hexafluorobut-2-yne to give a butadienyl ligand in **3** or **6a** with the same linkage sequence AB(SR) (A = hexafluorobut-2-yne; B = DMAD) but with different modes of co-ordination. Thereafter **3** undergoes facile ring expansion



Scheme 5

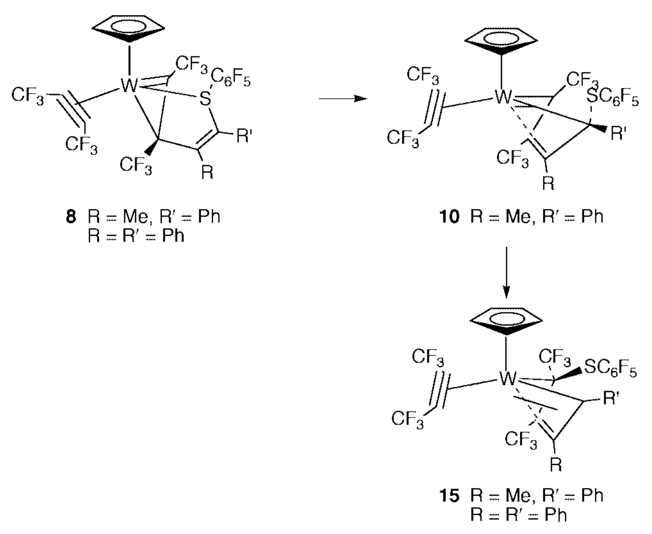
to give alkyne trimerisation products, *i.e.* **3** ⟶ **4** ⟶ **5a**, Scheme 1, whilst **6a** gives the metallacycle **7**, Scheme 2.

The most significant feature of these reactions is the different trimerisation sequence AAB found in complexes **4** and **5a** compared to ABA in **7**. A metal effect was also observed previously in reactions of η^2-C,C alkenyl derivatives $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** with DMAD.[12] With M = Mo, R = Pr^i the AAB linkage sequence was observed whereas ABA occurred in reactions of the tungsten derivatives M = W, R = Me, Et or Pr^i. We previously discussed possible reasons for this difference[12] but further deliberation, taking into account this and earlier work, provides a new and more satisfying explanation.

This is summarised in terms of the two mechanistic pathways 1 and 2 illustrated in Scheme 5. Path 1 involves AAB formation whilst the alternative ABA is depicted in Path 2. In both cases hexatriene AAB, ABA and hexatrienethiolato derivatives AAB(SR) and ABA(SR) (illustrated schematically by **11**–**14**) have been observed in this and previous work.[9,12] It should be noted that both **3** and **6** are precursors to complexes with the sequence AAB whereas **6** can also react to give products with the ABA moiety. This is explained by the fact that, as established previously,[12] complex **6** initially isomerises into the η^3-butadienyl derivative **8** which also contains the AB(SR) linkage. Complex **8**, as we will now demonstrate, appears to be the key intermediate in processes which differentiate mechanistically between the two linkage sequences. The formation of sequence AAB (Path 1) is straightforward since it presumably involves insertion of the co-ordinated $CF_3C\equiv CCF_3$ (A) into an M=C bond of the η^3-butadienyl ligand AB(SR) in **8** . This generates a range of isomeric complexes containing a hexatrienyl ligand AAB(SR) **11** which, in the case of **5** (Scheme 3), extrudes the thiolate group above *ca.* 25 °C to give a metallaheptatriene of type **12**, *i.e.* **9**.[9,12]

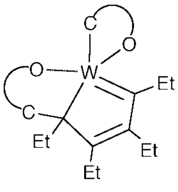
However, in order to explain the formation of sequence ABA we have to account for the fact that the thiolate has transferred, either to a carbon bearing a CF_3 group to give complexes **13** containing hexatrienyl thiolate ligands ABA(SR), *e.g.* $[W\{\eta^6\text{-}C(CF_3){=}C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)SR\}(\eta^5\text{-}C_5H_5)]$,[12] or alternatively to the metal to give metallaheptatrienes **14**, *e.g.* **7**. This can be explained by the transformations depicted in Scheme 5, Path 2, *i.e.* **8** ⟶ **10** ⟶ **15** ⟶ **13** or **14**. As observed in this work (Scheme 4) and previously[9,10] the first step involves isomerisation of the η^3-butadienyl **8** into the η^4-butadienyl form **10**. Crucially, in two previous cases (Scheme 6) this was followed by a 1,4-thiolate shift to give an isomeric η^4-butadienyl structure **15**.[10] This thiolate transfer provides the key to understanding the formation of ABA systems since in the final stage of Path 2, **15**, or some variant of it, can undergo ring expansion with the remaining co-ordinated alkyne (*cf.* **8** ⟶ **9**, Scheme 3) to give product(s) **13** and **14**. We therefore propose that Scheme 5, based on established molecular transformations, provides a satisfactory explanation for the different alkyne oligomerisation sequences AAB and ABA described in this and previous work.[9,12]

Finally we draw attention to parallels between our work and

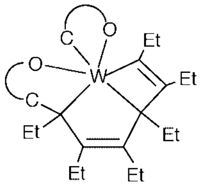


Scheme 6

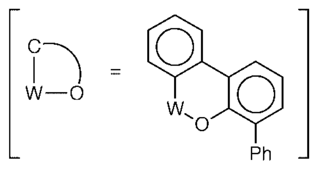
that of Rothwell and co-workers[38] who reported that bis (aryl oxide) complexes $[W(C\text{-}O)_2(L)_2]$ (C-O = $OC_6H_3Ph\text{-}C_6H_4$, L = $PMePh_2$ or pyridine) react with an excess of EtC≡CEt to give alkyne dimerisation and trimerisation products **16** and **17**.



16



17



These compounds, although showing structural features strikingly similar to those of complexes reported in our present and previous work, exhibit detailed differences in the mode of bonding of the C_4 and C_6 ligands. However, in conjunction with our observations they serve to illustrate the wide range of closely related structural types which are involved in alkyne di- and tri-merisation reactions at molybdenum and tungsten centres. Consequently an important conclusion is to be drawn from this work, *viz.* attempts to rationalise metal promoted alkyne oligomerisation reactions in terms of simple mechanisms involving one or two intermediates must be treated with caution particularly when a non-innocent ligand such as a thiolate is present.

Experimental

The NMR spectra were recorded on a Bruker WP 200SY spectrometer at 200.13 (^{1}H) and 188.13 MHz (^{19}F); chemical shifts are referenced to Me_4Si (^{1}H, δ 0) and CCl_3F (^{19}F, δ 0). The IR spectra were recorded 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_2O_5 (CH_2Cl_2), calcium hydride (hexane, diethyl ether) and distilled just before use. The complexes $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$[39] and $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$[7] were prepared as described previously. The alkynes were obtained commercially and used without further purification.

Reactions of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ 1a

With $MeO_2CC{\equiv}CCO_2Me$ at −30 °C. A solution of complex **1a** (45 mg, 0.066 mmol) in diethyl ether–hexane (8 cm^3, 1 : 1) was treated with a slight excess (1 : 1.1 molar ratio) of $MeO_2CC{\equiv}CCO_2Me$ at *ca* −25 °C for *ca.* 3 h changing from deep purple to yellow and small quantities of yellow crystals formed. The solution was held at −25 °C and concentrated to *ca.* 3 cm^3 *in vacuo*. After 2 h at −25 °C the mother liquor was removed and the solid washed with several portions of cold hexane and dried *in vacuo*. This gave yellow crystals of $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)(SC_6F_5)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **3** (32 mg, 59%) (Found: C, 36.2; H, 1.2. $C_{25}H_{11}F_{17}MoO_4S$ requires C, 36.34; H, 1.34%); *m/z* 826 [M^+]; IR (KBr) ν(C≡C) 1852wm, 1820w, ν(C=O) 1714s, ν(C=C) 1639wm cm^{-1}. NMR [$(CD_3)_2CO$, −30 °C]: ^{1}H, δ 3.81 (s, 3 H, CO_2Me), 3.97 (s, 3 H, CO_2Me) and 6.21 (s, 5 H, C_5H_5); ^{19}F [$(CD_3)_2CO$, −30 °C], δ −54.00 (q, J_{1-2} 5.5, 3F, CF_3), −54.29 (qq, J_{2-1} 5.5, J_{2-3} 12.1, 3F, CF_3), −55.15 (qq, J_{3-2} 12.1, J_{3-4} 8.7, 3F, CF_3) and −64.37 (tq, $J_{4-C_6F_5}$ 8.6, J_{4-3} 8.7 Hz, 3F, CF_3).

With $MeO_2CC{\equiv}CCO_2Me$ at 20 °C. A solution of complex **1a** (200 mg, 0.29 mmol) in diethyl ether–hexane (25 cm^3, 1 : 1) was treated with a slight excess (1 : 1.1 molar ratio) of $MeO_2CC{\equiv}CCO_2Me$ at 20 °C for *ca.* 3 h changing from deep purple to dark red brown. The reaction mixture was filtered, reduced *in vacuo* and cooled to −15 °C to give a sticky brown solid. This was recrystallised from diethyl ether–hexane another two times at −15 °C to give dark red-brown crystals of $[Mo\{\eta^6\text{-}C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)(SC_6F_5)\}(\eta^5\text{-}C_5H_5)]$ **5a** (30 mg, 12%) (Found: C, 35.8; H, 1.0. $C_{25}H_{11}F_{17}MoO_4S$ requires C, 36.34; H, 1.34%); *m/z* 826 [M^+]; IR (KBr) ν(C=O) 1725(br) m, ν(C=C) 1640w cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 3.63 (s, 3 H, CO_2Me), 3.70 (s, 3 H, CO_2Me) and 6.10 (s, 5 H, C_5H_5); ^{19}F [$(CD_3)_2CO$], δ −53.37 (qq, J 13.8, 2.2, 3F, CF_3), −57.11 (m, 3F, CF_3), −58.35 (m, 3F, CF_3) and −60.12 (qq, J 13.7, 3.3 Hz, 3F, CF_3).

Reactions of $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ 1b

With $MeO_2CC{\equiv}CCO_2Me$ at −15 °C (NMR reaction). Complex **6a**, NMR ($C_6D_5CD_3$): ^{19}F, δ −48.61 (qq, J_{1-2} 14.2, J_{1-3} 4.0, 3F), −52.38 (q, J_{1-2} 14.2, 3F), −54.83 (qq, J_{3-1} 4.0, J_{3-4} 3.9, 3F) and −56.27 (q, J_{4-3} 3.9 Hz, 3F).

With $MeO_2CC{\equiv}CCO_2Me$ at 20 °C. A solution of complex **1b** (50 mg, 0.07 mmol) in diethyl ether–hexane (10 cm^3, 1 : 1) was treated with a slight excess (0.02 g, 0.14 mmol) of $MeO_2CC{\equiv}CCO_2Me$ at 20 °C for 18 h changing from deep purple to red. The solution was evaporated to dryness, the residue dissolved in a small quantity of CH_2Cl_2 and chromatographed over Florisil with diethyl ether–hexane (1 : 1) as eluent. A yellow band was collected and on concentration *in vacuo* and cooling to −15 °C black crystals of $[W(SC_6H_4Me\text{-}4)\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)\}(\eta^5\text{-}C_5H_5)]$ **7** (11 mg, 18%) were obtained (Found: C, 36.8; H, 2.0. $C_{26}H_{18}F_{12}O_4SW$ requires C, 37.25; H, 2.16%); *m/z* 838 [M^+]; IR (KBr) ν(C=O) 1710s, ν(C=C) 1660wm, 1639wm, 1619wm cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 7.14 (m, 4 H, C_6H_4Me-4), 5.78 (s, 5 H, C_5H_5), 3.95 (s, 3 H, CO_2Me), 3.67 (s, 3 H, CO_2Me) and 2.53 (s, 3 H, C_6H_4Me-4); ^{19}F (CD_2Cl_2, 20 °C), δ −56.26 (q, J_{1-3} 10.3, 3F, CF_3), −56.89 (q, J_{2-4} 7.6, 3F, CF_3), −62.87 (q, J_{3-1} 10.3, 3F, CF_3) and −65.44 (q, J_{4-2} 7.6 Hz, 3F, CF_3).

With MeC≡CMe at 5 °C. A solution of complex **1b** (35 mg, 0.05 mmol) in diethyl ether–light petroleum (bp 60–80 °C) (1 : 2, 10 cm^3) was transferred to a thick glass tube fitted with a Teflon stopcock and then degassed with N_2. A 2 molar excess of MeC≡CMe was condensed in at −196 °C, the tube sealed and allowed to warm to 5 °C. The mixture was allowed to react for 48 h at 5 °C when the purple solution turned dark yellow.

Concentration *in vacuo* followed by cooling to −15 °C gave a small quantity of a yellow solid. This was recrystallised from CH_2Cl_2–light petroleum to give yellow crystals of [W{η^3-C(CF_3)C(CF_3)C(Me)=C(Me)SC_6H_4Me-4}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] **8a** (8 mg, 21%) (Found: C, 38.2; H, 2.6. $C_{24}H_{18}F_{12}SW$ requires C, 38.42; H, 2.42%); IR (KBr) ν(C≡C) 1795wm cm^{-1}. NMR (CD_2Cl_2, −30 °C): ^1H, δ 1.80 (s, 3 H), 2.07 (br s, 3 H, Me and C_6H_4*Me*-4), 2.35 (s, 3 H, Me), 5.53 (s, 5 H, C_5H_5), 6.36 (m, 1H, C_6*H_4*Me-4), 7.25 (m, 2 H, C_6*H_4*Me-4) and 7.54 (m, 1 H, C_6*H_4*Me-4); ^{19}F (CD_2Cl_2, 19 °C), δ −51.7 (m, 3F, CF_3), −54.93 (m, 3F, CF_3), −55.50 (app. sept, 3F, CF_3) and −57.08 (q, *J* 4.2 Hz, 3F, CF_3).

The mother liquor was allowed to stand overnight at 20 °C and on further concentration and cooling to −20 °C small quantities of orange brown crystals of [W{η^4-C(CF_3)C(CF_3)=C(Me)C(Me)SC_6H_4Me-4}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] **10a** were obtained (5 mg, 13%).

With MeC≡CMe at 50 °C. A solution of complex **1b** (150 mg, 0.22 mmol) in diethyl ether–light petroleum (2 : 1, 30 cm^3) was transferred to a thick glass tube fitted with a Teflon stopcock and then degassed with N_2. A 2 molar excess of MeC≡CMe was condensed in at −196 °C, the tube sealed and warmed to room temperature. The mixture was allowed to react for 96 h at 20 °C when the purple solution turned dark yellow; ^{19}F NMR indicated the presence of two species, **8a** and **10a**. Volatiles were removed *in vacuo* and light petroleum (40 cm^3) was added to the brown residue. The flask was resealed and heated to 50 °C for 6 h. Concentration of the resulting solution *in vacuo* and cooling to −15 °C gave a brown solid which was recrystallised several times from diethyl ether–light petroleum to give orange crystals of **10a** (26 mg, 16%); (Found: C, 38.5; H, 2.2. $C_{24}H_{18}F_{12}SW$ requires C, 38.42; H, 2.42%); *m/z* 748 [M^+] IR ($CDCl_3$) ν(C≡C) 1749wm, cm^{-1}. NMR {$(CD_3)_2CO$, 19 °C}: ^1H, δ 2.32 (s, 3 H, C_6H_4*Me*-4), 2.39 (br s, 3 H, Me), 2.42 (s, 3 H, Me), 6.16 (s, 5 H, C_5H_5) and 7.05–7.31 (m, 4 H, C_6*H_4*Me-4); ^{19}F {$(CD_3)_2CO$, 19 °C}, δ −49.79 (q, *J* 6.9, 3F, CF_3), −52.29 (q, *J* 5.2 Hz, 3F, CF_3), −57.41 (m, 3F, CF_3) and −58.84 (m, 3F, CF_3).

With PhC≡CMe. A solution of complex **1b** (150 mg, 0.22 mmol) in diethyl ether–light petroleum (bp 60–80 °C) (2 : 1, 30 cm^3) was treated with a 2 molar excess of PhC≡CMe at 20 °C for 4 h. Addition of light petroleum followed by concentration and cooling to −15 °C gave yellow crystals of [W{η^3-C(CF_3)C(CF_3)C(Me)=C(Ph)SC_6H_4Me-4}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] **8b** (134 mg, 77%) (Found: C, 42.7; H, 2.3. $C_{29}H_{20}F_{12}SW$ requires C, 42.88; H, 2.48%); *m/z* 810 [M^+]; IR (KBr) ν(C≡C) 1796wm cm^{-1}. NMR {CD_2Cl_2, 19 °C}: ^1H, δ 2.08 (q, $J_{H\text{–}F}$ 2.1 Hz, Me), 2.30 (s, 3 H, C_6H_4*Me*-4), 5.79 (s, 5 H, C_5H_5), 7.03–7.31 (m, 9 H, Ph + C_6*H_4*Me-4); ^{19}F {$(CD_3)_2CO$, 20 °C}, δ −50.12 (br s, 3F, CF_3), −53.72 (br m, 3F), −54.26 (app. sept, 3F, CF_3) and −56.33 (q, $J_{4\text{–}1}$ 4.2 Hz, 3F, CF_3).

With PhC≡CPh. A solution of complex **1b** (145 mg, 0.21 mmol) and PhC≡CPh (42 mg, 0.236 mmol) in diethyl ether–light petroleum (2 : 1, 30 cm^3) was degassed with N_2 and then allowed to react at 20 °C for 18 h changing from purple to red. The solution was heated to 50 °C under reflux for 14 h and the resulting brown solution evaporated to dryness, the residue dissolved in diethyl ether and the solution filtered. Addition of light petroleum followed by concentration *in vacuo* and cooling to −15 °C gave yellow crystals of [W{η^3-C(CF_3)C(CF_3)C(Ph)=C(Ph)SC_6H_4Me-4}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] **8c** (64 mg, 35%) (Found: C, 47.0; H, 2.3. $C_{34}H_{22}F_{12}SW$ requires C, 46.70, H, 2.54%); *m/z* 872 [M^+]; IR ($CDCl_3$) ν(C≡C) 1784wm cm^{-1}. NMR {$(CD_3)_2CO$, 20 °C}: ^1H, δ 2.27 (s, 3 H, C_6H_4*Me*-4), 5.87 (s, 5 H, C_5H_5), 6.7–7.6 (m, 9 H, Ph + C_6*H_4*Me-4); ^{19}F {$(CD_3)_2CO$, 20 °C}, δ −48.60 (br, 3F, CF_3), −53.54 (br m, 3F, CF_3), −54.27 (app. sept, 3F, CF_3) and −55.22 (q, *J* 4.1 Hz 3F).

X-Ray analysis of [Mo{η^4-C(CF_3)=C(CF_3)C(CO_2Me)C(CO_2Me)(SC_6F_5)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] 3

Crystal data. $C_{25}H_{11}F_{17}MoO_4S$, $M = 826.34$, monoclinic, space group $P2_1/n$, $a = 10.875(2)$, $b = 15.302(4)$, $c = 17.119(2)$ Å, $\beta = 103.89(2)°$, $V = 2765.5(9)$ Å^3, $T = 23$ °C, $Z = 4$, $D_c = 1.985$ g cm^{-3}, μ(Mo-Kα) = 0.699 mm^{-1}, 11 329 intensities measured, 6012 unique ($R_{int} = 0.032$), with 3609 $I > 2\sigma(I)$. Refining 435 parameters from all 6012 F^2 values gave $R[F, I > 2\sigma(I)] = 0.037$, $wR(F^2$, all data) = 0.098 and final $|\Delta\rho|$ values < 0.53 e Å^{-3}.[40]

CCDC reference number 186/1660.

See http://www.rsc.org/suppdata/dt/1999/3883/ for crystallographic files in .cif format.

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