DALTON

Mechanisms of alkyne trimerisation at molybdenum and tungsten centres leading to novel metallacycles: crystal and molecular structures of two isomeric forms of $[Mo\{C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)(SPr^i)\}(\eta^5\text{-}C_5H_5)]$

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The η^2-C,C vinyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **1** (M = Mo, R = Pr^i; M = W, R = Me, Et or Pr^i) reacted with dimethyl acetylenedicarboxylate $R'C\equiv CR'$ ($R' = CO_2Me$) to give products of alkyne trimerisation containing two different oligomerisation sequences depending on whether $R'C\equiv CR'$ occupies a terminal or central position in the alkyne trimer chain, *i.e.* $C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(R')C(R')$ and $C(CF_3)C(CF_3)C(R')C(R')C(CF_3)C(CF_3)$. With M = Mo, kinetic ^{19}F NMR studies established a reaction sequence proceeding above *ca.* −30 °C *via* two different butadienyl complexes $[M\{\eta^2\text{-}C(CF_3)C(CF_3)C(R')C(R')SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** and **3** to give isomeric trienyl derivatives $[Mo\{\eta^6\text{-}C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(R')C(R')SPr^i\}(\eta^5\text{-}C_5H_5)]$ **4** and $[Mo\{\eta^5\text{-}C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(R')SPr^iC(R')\}(\eta^5\text{-}C_5H_5)]$ **5** which were isolated at room temperature. X-Ray diffraction studies established that in each case the trienyl ligand is bound to the metal *via* an η^2-C,C alkenyl linkage, and two σ carbon–metal bonds. In **4** this is accompanied by co-ordination of a CO unit of a carbomethoxy carbonyl whereas in **5** the thiolate sulfur is bonded to the metal. Above room temperature **5** isomerises to give species **6** and ultimately **7** which appears to result from thiolate transfer to the metal to give a seven-membered metallacycle. With M = W, the reactions also proceed *via* a butadienyl complex **2** but this isomerises *via* two other intermediates to give trienyl products $[W\{\eta^6\text{-}C(CF_3)C(CF_3)C(R')C(R')C(CF_3)C(CF_3)SR\}(\eta^5\text{-}C_5H_5)]$ and $[WF\{\eta^5\text{-}C(=CF_2)C(CF_3)C(R')C(R')C(CF_3)C(CF_3)SR\}(\eta^5\text{-}C_5H_5)]$. X-Ray diffraction studies established that the trienyl ligand in the former is co-ordinated *via* one σ, two π alkene linkages and a thiolate sulfur. Two isomeric forms were structurally characterised which differ only in the orientation of the thiolate isopropyl substituent which can adopt *syn* or *anti* positions. In the fluoride a CF_3 fluorine has been transferred to the metal and this has generated a hexatrienyl attachment *via* a quasi π-allylic interaction and through W–C and W–S σ bonds.

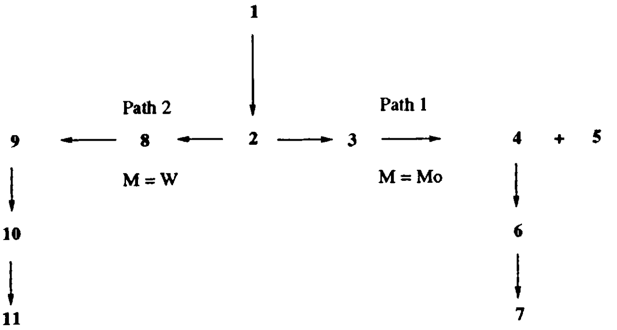
Reactions of alkynes with transition-metal complexes frequently lead to alkyne di-, tri-, tetra- and poly-merisation.[1] Their mechanisms have been widely studied over the last thirty years and in cases where cyclic oligomerisation products are observed the role of metallacyclic intermediates has been established.[1,2] However, if a reactive metal–ligand (usually metal–carbon or –hydrogen) bond is present in the metal precursor, the incoming alkyne can undergo insertion leading to linear oligomerisation products instead.[3] Previously we reported a variety of reactions in which insertion of activated alkynes into metal–sulfur bonds resulted in both linear and cyclic oligomerisation products.[4] A number of other workers have since expanded on our initial reports.[5] We have also observed that the thiolate group can reversibly migrate onto co-ordinated alkynes to give η^1- and η^2-vinyl products.[6] The substitution lability of the thiolate group is also demonstrated by the reactions of isomeric bis(alkyne) $[M(SR)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ and η^2-vinyl derivatives $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ with alkynes which lead to η^4-butadienyl products *via* several migrations between different carbon atoms and the metal.[6a,k,7] We now describe an extension of these studies involving the activated alkyne $MeO_2CC\equiv CCO_2Me$. Some of this work has been reported previously as a preliminary communication.[6a]

Results

Reactions of the η^2-C,C vinyl derivatives $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ **1** (M = Mo, R = Pr^i; M = W, R = Me, Et or Pr^i) with dimethyl acetylenedicarboxylate $MeO_2CC\equiv CCO_2Me$ (dmad) 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. 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.

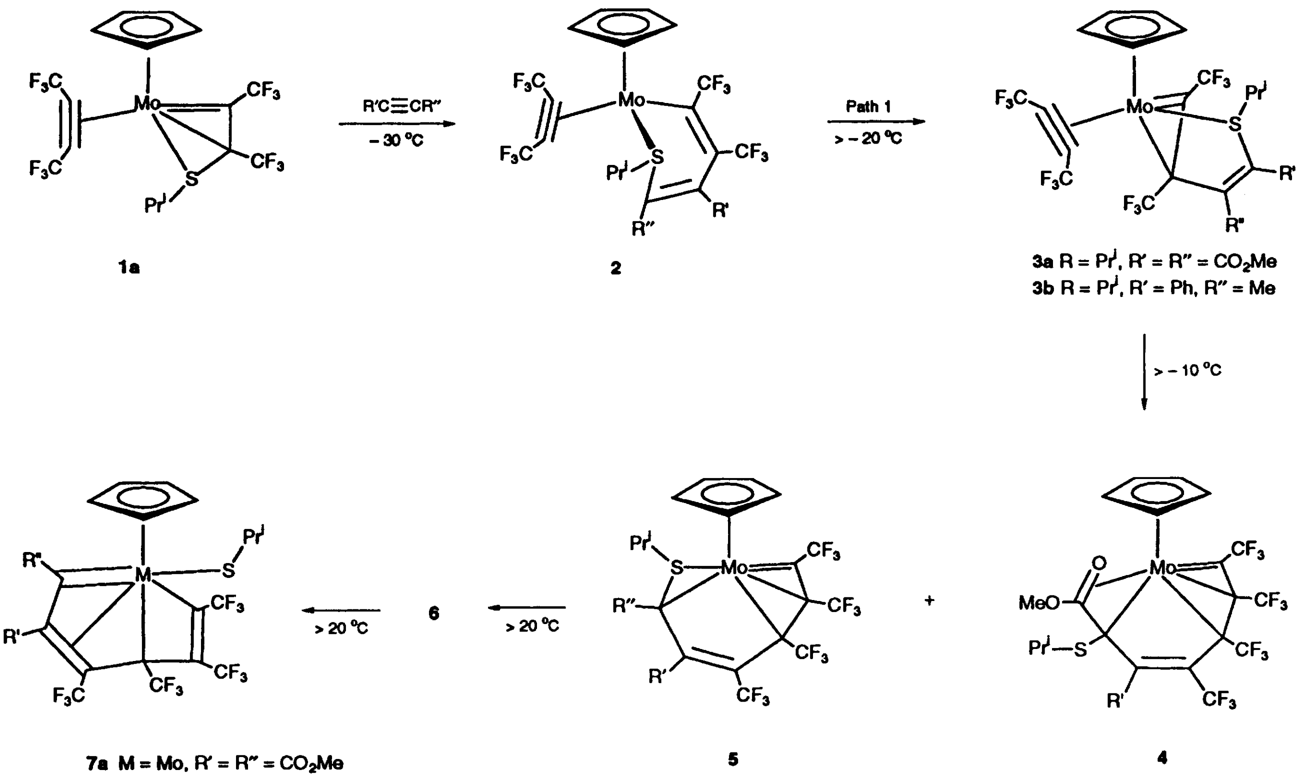
Detailed ^{19}F NMR kinetic experiments carried out in a variety of solvents (CD_2Cl_2, C_6D_6, $CD_3C_6D_5$ and $CDCl_3$) established that in all cases the same initial intermediate type **2** is formed above *ca.* −30 °C and when M = Mo (path 1, Schemes 1 and 2) this isomerises at higher temperatures to **3** followed by **4** and **5**. Compound **5** then rearranges above room temperature to give **6** and ultimately **7**. With M = W a different sequence of events was observed, with **2** isomerising into **8** which rearranges *via* **9** to give two distinct products at room temperature **10** and **11** (path 2, Schemes 1 and 3) in the case R = Pr^i. With R = Me or Et **8** and **9** were not detected, whilst only small amounts of complex **11** were detected by ^{19}F NMR spectroscopy but not isolated. Moreover, as will be described later, **10** exists in two isomeric forms when R = Pr^i and both of these were isolated and characterised by X-ray diffraction studies.

The reactions of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (R = Me or Et) with dimethyl acetylenedicarboxylate at *ca.* −30 °C were carried out on a synthetic scale and intermediates **2b** and **2c** isolated as pale yellow platelets by slow crystallisation at *ca.* −30 °C and characterised by elemental analysis, IR (Nujol) and NMR spectroscopy (at low temperatures). The spectral data do not conform to any of the structural types we have isolated previously in these studies and unfortunately attempts to obtain suitable crystals for X-ray diffraction studies were unsuccessful. However, the spectra are reasonably informative and allow a structure to be proposed with some confidence. The two sets of spectra are similar so only the data for **2c** will be described. The IR spectrum shows a ν(C≡C) band at 1775 cm^{-1}, ν(C=O) at 1705wm, 1680m and weak bands at 1618 and 1636 cm^{-1} indicating the presence of free carbon–carbon double bonds. These and the NMR data are consistent with a structure containing a co-ordinated $CF_3C{\equiv}CCF_3$ and a butadienyl ligand $C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)SR$ or $C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)SR$. Although the latter seems less likely since it apparently involves insertion of the incoming alkyne into a C–S bond of complex **1** there is well established precedent for such a reaction as the formation of **3b** testifies. Moreover, the fact that **3a** is the product of isomerisation of **2a** indicates that complexes **2** contain the $C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)SR$ moiety.

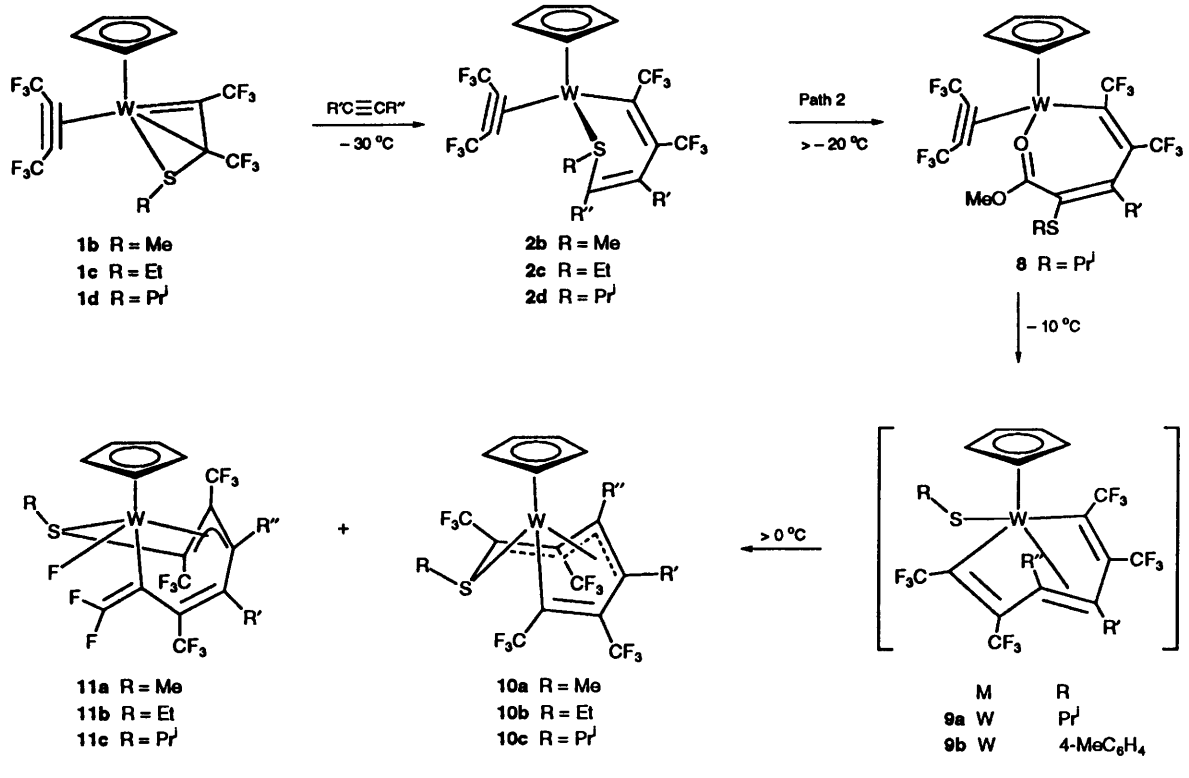


Scheme 1

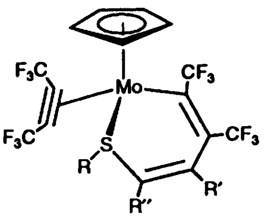
We have structurally characterised a number of complexes containing butadienyl ligands co-ordinated in a variety of ways to the metal, each of which has a distinctive ^{19}F NMR spectrum.[6b,i–k] In the case of **2c** the ^{19}F NMR (−30 °C) spectrum shows a quartet of quartets at δ −48.12 (J = 14.3, 3.7), a quartet at δ −51.52 (J = 14.2 Hz) and broad peaks at δ −53.36 and −55.87 which do not fit any of the known bonding modes. Two structures are possible, **I** and **II**, which are broadly consistent with the available data, the only difference being that in the former both C=C bonds of the butadienyl ligand are unco-ordinated whereas in **II** one is attached to the metal. The latter bonding mode has been found in the structurally characterised complex $[Mo\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i\}(PEt_3)(\eta^5\text{-}C_5H_5)]$ **12**[6j] whereas the former was suggested for the oxo complex $[Mo\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i\}O(\eta^5\text{-}C_5H_5)]$ **13**.[6i] Structure **II** is also related to that of complex **14** isolated at −25 °C from the reaction of the bis(alkyne) derivative $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with dimethyl acetylenedicarboxylate and the structure of which has been established by X-ray diffraction studies.[8] Complex **14** contains an η^4-butadienyl ligand co-ordinated *via* a σ-alkenyl linkage, an alkene function and a carbomethoxy oxygen, *cf.* **4**. However, in the case of **II** co-ordination of the thiolate sulfur rather than the terminal carbomethoxy oxygen seems more probable. This can account for the observation that on lowering the temperature the four peaks in the ^{19}F NMR spectrum broaden and separate into two sets of resonances at −60 °C. This indicates the presence of two isomeric forms which undergo rapid exchange at higher temperatures, possibly as a consequence of inversion at the bridging sulfur. The sulfur mode of bonding found in **12** and **13** also gives rise to two isomeric forms in each case although these do not undergo exchange in the ^{19}F NMR



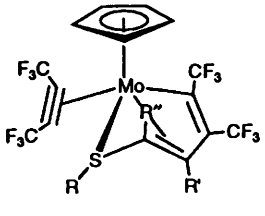
Scheme 2 R′ = R″ = CO_2Me unless stated otherwise



Scheme 3 R′ = R″ = CO_2Me

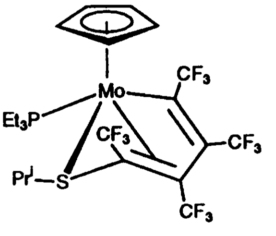


I



II

R = Pr^i



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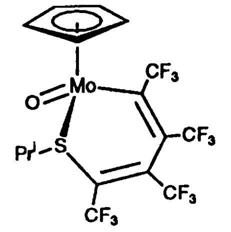

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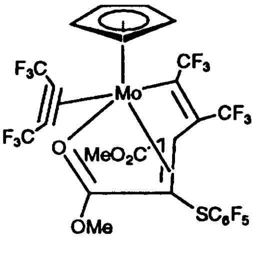

14

spectra at 20 °C. The presence of a terminal thiolate substituent in the carbomethoxy-bonded form **14** means that only one isomeric form is possible in agreement with the observed spectra.

Nonetheless, the ^{19}F NMR spectrum is perhaps more consistent with structure **I** in that the CF_3–CF_3 coupling constant *ca.* 14 Hz is somewhat larger than is normally observed for species containing a co-ordinated C=C bond, *viz.* $[Mo\{\eta^4\text{-}C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)SPr^i\}(PEt_3)(\eta^5\text{-}C_5H_5)]$ **12**, $J(F\text{–}F) = 9.4$ Hz. However, the J(F–F) value is similar to that of the aforementioned oxo complex $[Mo\{\eta^2\text{-}C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)SPr^i\}O(\eta^5\text{-}C_5H_5)]$ **13**, J(F–F) *ca.* 14–16 Hz. If the proposed structure **I** is correct, in order to achieve the preferred 18-electron configuration, the alkyne is required to donate four electrons to the metal. Such a situation is well known in this area of chemistry *i.e.* in alkyne complexes of Mo^{II} and W^{II} with d^4 configurations.[9] One of the earliest reported examples of this type of complex is $[Mo(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ which has been characterised by X-ray diffraction studies and bears some resemblance to the proposed structure **I**.[10]

Since the subsequent isomerisation of complex **2a** differs from that of the tungsten derivatives **2b**–**2d** the reactions of the molybdenum complex will be discussed first. The ^{19}F NMR studies established that **2a** isomerises above *ca.* −20 °C to an unstable intermediate **3a** which could not be isolated. However, **3a** has similar ^{19}F NMR features [a broad featureless peak, two multiplets (quartets of quartets) and a quartet] to those of a series of complexes obtained from the reactions of $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ with unactivated alkynes.[6h,k] One of these, $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(Me)=C(Ph)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$, was structurally characterised by X-ray diffraction studies[6h] and shown to have the structure illustrated, **3b**. Apart from similarities in the nature of the peaks it was also noted that the variable-temperature ^{19}F NMR spectra of **3a** are similar to those of **3b**, *i.e.* at lower temperatures the four CF_3 resonances broaden and split into two sets of peaks indicating the presence of two exchanging forms in solution. The proposed structure of **3** is not unreasonable since it merely involves rearrangement of the σ-alkenyl mode of bonding in **2** to the η^2 form in **3**. We have observed the opposite of this in a reaction reported many years ago involving isomerisation of the η^2-alkenyl derivative $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ into $[W\{\eta^2\text{-}C(CF_3){=}C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$.[11,12]

At higher temperatures complex **3** was observed by ^{19}F NMR spectroscopy to isomerise to **4** and small quantities of **5** in 6:1 ratio. In two separate, synthetic-scale experiments involving reaction of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **1a** with $MeO_2CC{\equiv}CCO_2Me$ at room temperature both of these complexes were isolated and characterised. In one experiment, recrystallisation of the product mixture gave dark red crystals of **4** as the sole product in 26% yield. The experiment was repeated and the product mixture chromatographed over Florisil. In this case **4** was not isolated; instead small quantities of **5** (15%) were obtained in addition to two other species **6** (11%) and **7a** (13%). It was subsequently found by ^{19}F NMR monitoring that heating a solution of **4** in $[^2H_8]$toluene at 30 °C resulted in isomerisation to the same two species, *i.e.* **6** and **7**. Interestingly, however, **5** was not detected indicating that **4** and **5** are not interconvertible and that they are formed as separate products from the isomerisation of **3a**.

The spectroscopic features of compounds **4** and **5** did not comply with those of known structural types and consequently single-crystal diffraction studies of both were carried out. The structural results (Figs. 1 and 2) give some insight into the stereochemistry of the reaction sequence $\mathbf{3} \longrightarrow \mathbf{4} + \mathbf{5}$. Thus **4** is formally derived from **3** by insertion of $\eta^2\text{-}CF_3C{\equiv}CCF_3$ into the Mo=C (carbene) bond. The resulting $C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(CO_2Me)SPr^iC(CO_2Me)$ trienyl chain is attached to the metal atom at one end through the three adjacent carbon atoms C(10), C(11) and C(13) and at the other end through C(20), C(21) and O(4). These ends are linked through a central C(15)–C(17) double bond which does not interact with the metal atom. The formal conversion of **4** into **5** involves replacement of C(21) and O(4) by S in the metal co-ordination sphere and requires a change of configuration at C(20). Compounds **4** and **5** are thus linkage isomers of an unusual type. Comparison of their geometries (Table 1)* reveals that replacement of C(21) and O(4) by S has remarkably little effect on the rest of the molecular structure. In both molecules the Mo–C(10) linkages are appreciably shorter than the other Mo–C bonds; their lengths are typical of M=C (carbene) distances (M = Mo or W); for example, they agree well with values of 1.914(6) and 1.924(3) Å in the two isomers of $[Mo\{\eta^2\text{-}C(CF_3)C(CF_3)PEt_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[13] and with 1.922 Å, the average of ten such distances determined by the present authors. The Mo–C(11) bonds are slightly shorter than Mo–C(13) and Mo–C(20); the lengths of the latter compare well with a typical Mo–C (alkyl) distance of 2.250 Å.[14] Likewise, the Mo–S distances in **5** agree with 2.401 Å, the mean for 66 Mo–SR bonds.[14] The structural similarity between **4** and **5** is most strikingly demonstrated by the torsion angles in the C(10)–C(11)–C(13)–C(15)–C(17)–C(20) portion of the trienyl chain: the largest difference between corresponding angles is only 8° (see Table 1). The chain conformation is such that CF_3–C–C–CF_3 torsion angles across C(10)–C(11) and C(13)–C(15) are −43(1) to −56(1)° whereas those across C(11)–C(13), formed in the transition from **3** to **4**, are 112(1)–116(1)°. Since the CF_3-substituted portions of the trienyl chains in **4** and **5** have essentially identical conformations it is perhaps to be expected that the two complexes will show similar spectroscopic features. This expectation is fulfilled: *e.g.* the ^{19}F NMR spectra of both contain four quartets of quartets under conditions of high resolution, the outer two each having two quite different coupling constants, whereas the central peaks exhibit similar values.

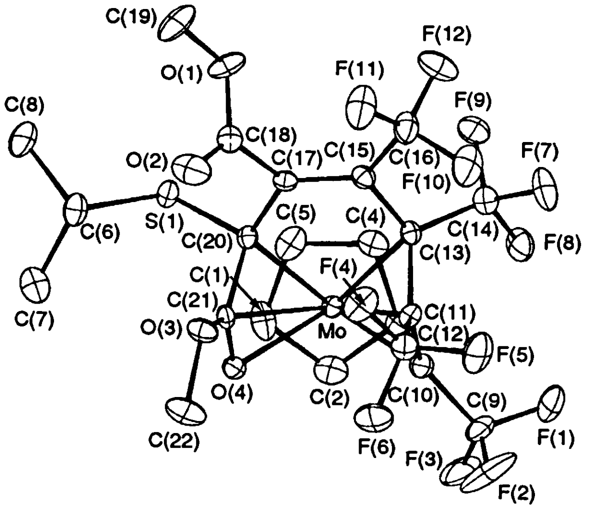

Fig. 1 View of a molecule of complex **4**. 20% Probability ellipsoids are displayed, and hydrogen atoms are omitted for clarity; C(3) is obscured by C(11)

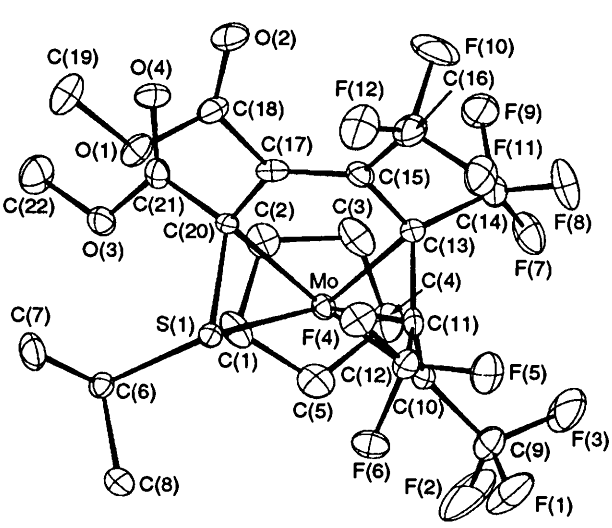

Fig. 2 View of one of the crystallographically independent molecules in crystals of complex **5**. Details as in Fig. 1

The interaction of the α-metallated CO_2Me group with Mo in complex **4** is of an unusual type. A search of the Cambridge Structural Database yielded only five related structures.[15] All contain a planar CO_2Me group with Me *cis* to C=O; the mean C–OMe and C=O bond lengths of 1.25 and 1.32 Å are similar to the C(21)–O(3) and C(21)–O(4) distances in **4**. In four of the structures (involving M = Re, Ru or Os) the C–C–O–M torsion angle is close to zero, indicating that the metal interacts almost exclusively with the oxygen lone pair (structure III).[16–19] In $[W\{CHBu^tCH_2CH(CO_2Me)\}(NC_6H_3Pr^i{}_2\text{-}2,6)\{OCMe_3(CF_3)\}_2]$[20] this torsion angle rises to −19° but the W–O and transannular W···C (carboxyl) distances of 2.372 (6) and 2.642 Å are long compared with the Mo–O(4) and Mo–C(21) distances of 2.125(5) and 2.477(6) Å in **4**; complex **14** contains a similar arrangement but with Mo–O and Mo–C distances of 2.209(3) and 2.590(4) Å.[8] Evidently the interaction between Mo and the C=O bond in **4** is unusually strong; moreover, the C(20)–C(21)–O(4)–Mo torsion angle is 32(1)°. It thus seems plausible to suggest that **4** contains an unsymmetrical η^2-C=O interaction with the metal (structure

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* The crystal structure of compound **5** contains two crystallographically independent molecules, A and B. Chemically and structurally they are identical to within experimental error.

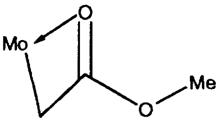
Table 1 Selected distances (Å) and angles (°) in complex **4** and in the two independent molecules (A and B) of **5**

		5	
	4	A	B
Mo–C(10)	1.918(7)	1.915(8)	1.921(6)
Mo–C(11)	2.195(7)	2.179(8)	2.176(7)
Mo–C(13)	2.266(7)	2.273(8)	2.273(8)
Mo ··· C(15)	3.187(7)	3.192(8)	3.177(8)
Mo ··· C(17)	3.203(4)	3.169(8)	3.162(8)
Mo–C(20)	2.249(7)	2.267(6)	2.282(7)
Mo–C(21)	2.477(6)	—	—
Mo–O(4)	2.125(5)	—	—
Mo–S	—	2.400(2)	2.405(2)
Mo–C(C_5H_5)	2.31(1)–2.37(1)	2.31(1)–2.36(1)	2.32(1)–2.38(1)
C(10)–C(11)	1.41(1)	1.41(1)	1.41(1)
C(11)–C(13)	1.47(1)	1.45(1)	1.43(1)
C(13)–C(15)	1.52(1)	1.53(1)	1.51(1)
C(15)–C(17)	1.32(1)	1.32(1)	1.32(1)
C(17)–C(20)	1.50(1)	1.49(1)	1.48(1)
C(20)–C(21)	1.47(1)	1.50(1)	1.50(1)
C(20)–S	1.819(7)	1.784(7)	1.789(6)
C(21)–O(3)	1.296(8)	1.312(10)	1.340(10)
C(21)–O(4)	1.248(9)	1.196(10)	1.189(9)
C(10)–Mo–C(13)	69.0(3)	69.0(3)	69.2(3)
C(10)–Mo–C(20)	125.2(3)	130.8(3)	130.5(3)
C(10)–Mo–X	101.8(3)	104.9(3)	104.4(2)
C(13)–Mo–C(20)	74.6(3)	75.7(3)	75.5(3)
C(13)–Mo–X	119.3(2)	94.8(2)	94.5(2)
C(20)–Mo–X	63.0(2)	44.8(2)	44.8(2)
Mo–C(10)–C(9)	147.7(6)	150.1(7)	148.6(7)
Mo–C(10)–C(11)	81.0(4)	80.3(5)	80.0(4)
C(9)–C(10)–C(11)	131.3(7)	129.6(8)	131.3(8)
C(10)–C(11)–C(12)	121.8(6)	121.3(7)	119.8(6)
C(10)–C(11)–C(13)	111.8(6)	113.4(7)	115.1(7)
C(12)–C(11)–C(13)	126.3(7)	125.2(7)	125.1(7)
C(11)–C(13)–C(15)	115.6(6)	115.8(6)	117.1(6)
C(13)–C(15)–C(17)	119.4(7)	118.1(7)	118.6(7)
C(15)–C(17)–C(20)	116.6(6)	120.1(7)	120.3(7)
C(17)–C(20)–S	114.1(5)	114.5(5)	115.6(5)
C(17)–C(20)–C(21)	120.1(6)	112.6(6)	112.3(6)
C(17)–C(20)–Mo	115.8(4)	113.4(5)	112.8(5)
S–C(20)–C(21)	110.3(5)	120.8(5)	121.0(5)
S–C(20)–Mo	111.6(3)	71.5(3)	71.2(3)
C(21)–C(20)–Mo	80.6(4)	118.1(5)	117.9(5)
C(20)–C(21)–Mo	63.4(4)	—	—
C(20)–C(21)–O(4)	114.7(6)	120.7(7)	120.9(7)
C(20)–C(21)–O(3)	121.0(6)	115.1(6)	115.1(6)
Mo–C(21)–O(3)	150.8(5)	—	—
Mo–C(21)–O(4)	59.1(4)	—	—
O(3)–C(21)–O(4)	124.3(6)	124.1(7)	124.0(7)
O(21)–O(4)–Mo	90.7(4)	—	—
C(20)–S–Mo	—	63.6(3)	64.0(2)
C(20)–S–C(6)	106.2(4)	118.1(3)	117.8(3)
Mo–S–C(6)	—	123.5(3)	123.1(3)
Torsion angles			
C(9)–C(10)–C(11)–C(13)	127(1)	124(1)	123(1)
C(10)–C(11)–C(13)–C(15)	153(1)	152(1)	151(1)
C(12)–C(11)–C(13)–C(15)	−31(1)	−30(1)	−31(1)
C(11)–C(13)–C(15)–C(17)	−71(1)	−79(1)	−79(1)
C(13)–C(15)–C(17)–C(20)	−4(1)	1(1)	2(1)
C(15)–C(17)–C(20)–S	−131(1)	81(1)	79(1)
C(15)–C(17)–C(20)–C(21)	95(1)	−136(1)	−136(1)
C(17)–C(20)–C(21)–O(4)	−145(1)	14(1)	12(1)
C(20)–C(21)–O(4)–Mo	32(1)	—	—
C(17)–C(20)–S–Mo	—	−108(1)	−107(1)

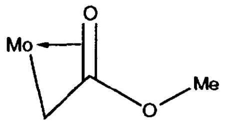
The symbol X stands for O(4) in complex **4** and for S in **5**.

IV). The evidence for a similar interaction in **14** is weaker and the difficulty of interpreting short M ··· C transannular distances has been highlighted by the work of Schrock and co-workers[21] on tungstenacyclobutane complexes where the transannular W ··· C (sp^3) distance can vary from 2.32(2) to 2.79(1) Å depending on the nature of the metal co-ordination polyhedron. The retention of an η^2-C,C (alkenyl) to metal linkage in the sequence **3** ⟶ **4** + **5** contrasts with the alternative trimerisation sequence which leads to **10**, in which a σ vinyl–metal interaction is conserved. Both sequences illustrate how easily Mo and W accommodate interchange of thiolate and carboxymethyl groups.

The final stages in the reaction involve isomerisation of complex **4** above room temperature to give **7** *via* an intermediate



III



IV

6 which was isolated and characterised by spectroscopic means. The IR spectrum shows no distinctive features whilst the ^{19}F NMR spectrum (in $CDCl_3$) contains four peaks as expected in this case at δ −51.61 [q, $J(F^1F^3)$ 10.3, 3F, CF_3], −54.19 [q, $J(F^2F^4)$ 5.2, 3 F, CF_3], −55.43 [q, $J(F^1F^3)$ 10.3, 3 F, CF_3] and −57.79 [qq, $J(F^2F^4)$ 5.4, 1.6 Hz, 3 F, CF_3]. This unfortunately does not provide unambiguous structural evidence and since all attempts to obtain suitable crystals were unsuccessful the structure of **6** remains unknown.

The final product **7a** was isolated as yellow crystals and characterised by elemental analysis and IR and NMR spectroscopy. In this case a structural assignment is possible since the spectroscopic data, in particular the IR and ^{19}F spectra, are very similar to those of a known structural type $[W\{\eta^5\text{-}C(CF_3){=}C(CF_3)C(CF_3)C(CF_3){=}C(Me)C(Ph)\}(SPr^i)(\eta^5\text{-}C_5H_5)]$ **7b**^{6h} taking into account a small additional coupling between one of the CF_3 groups and an isopropyl methyl in the latter. In both cases the IR spectrum shows a weak band near 1640 cm^{-1} assigned as a ν(C=C) band whilst the ν(C–F) region near 1100 cm^{-1} is also very similar. The ^{19}F NMR spectrum in each case shows a group of three bands (two sharp quartets and a broad singlet) between δ −52 and −55.5 and a complex multiplet (a quartet of quartets of quartets) near δ −64. The yellow crystalline complex **7b** was previously obtained from the reaction of **1b** with PhC≡CMe *via* the isolable intermediate **3b** and the structure confirmed by X-ray diffraction studies. It contains a seven-membered metallacyclic ring η^5 bonded to the metal *via* an η^4-butadienyl moiety $(CF_3)C(CF_3)C(Me)C(Ph)$ and the remaining $C(CF_3){=}C(CF_3)$ group completes the link to the metal *via* a σ bond. The thiolate ligand in the process has become detached from the C_6 chain and is now terminally bonded to the metal.

Fluorine-19 NMR monitoring of kinetic runs involving reactions between tungsten complexes $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SR)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **1b**–**1d** and dmad showed that they follow a different reaction pathway to those of the analogous molybdenum complex **1a** (R = Pr^i). As illustrated in Scheme 3 the reactions are sensitive to thiolate substituent. Although the final products **10** and **11** are the same in all cases, differences are observed in the relative amounts of the two species and in the intermediates observed. In all three cases the first intermediate, which is formed above *ca.* −35 °C, has similar spectroscopic properties to those of **2a** and consequently a similar structure is proposed. In the cases R = Me or Et this intermediate (**2b** and **2c**) rearranges at higher temperatures directly into **10** and (to a very limited extent) **11**. However, with the more bulky SPr^i group **2d** rearranges *via* two other intermediates, **8** and **9a**, which could not be isolated but which were partially characterised by ^{19}F NMR spectroscopy. Kinetic runs were carried out in a variety of solvents (CD_2Cl_2, $CDCl_3$, C_6D_6 and $C_6D_5CD_3$) in order to obtain as much data as possible, since in some solvents some intermediates were only observed in low concentration. The first intermediate following the isomerisation of the isopropyl derivative **2d** is **8** and this is formed above *ca.* −20 °C. It has similar ^{19}F NMR spectral features to that of the precursor, the only signicant difference between the two isomers being additional (and weak) spin–spin coupling between CF_3 groups in **2d**: ^{19}F NMR (CD_2Cl_2, 0 °C), **2d**, δ − 49.02 [qq, 3 F, $J(F^1F^2)$ 15.3, $J(F^1F^3)$ 4.3, 3 F, CF_3], −51.73 [q, $J(F^1F^2)$ 15.2, 3 F, CF_3], −54.60 (spt, 3 F, CF_3) and −56.84 [q, $J(F^3F^4)$ 3.8, 3 F, CF_3]; **8**, δ −45.38 [q, $J(F^1F^3)$ 14.8, 3 F, CF_3], −56.16 [q, $J(F^2F^4)$ 2.2, 3 F, CF_3], −58.95 [q, $J(F^1F^3)$ 14.8, 3 F, CF_3] and −59.19 [q, $J(F^2F^4)$ 2.0 Hz, 3 F, CF_3]. The similarity of the coupling constants suggests insignificant differences in the basic nature of the butadienyl ligand and hence that **2d** and **8** have the same basic structure. We note that unlike **2** fluxional behaviour is not observed at low temperature and therefore tentatively propose the illustrated structure in which a carbomethoxy oxygen (or C=O group) is co-ordinated to the metal rather than sulfur. The proposed structure of **8** is similar to that of **14** obtained from the reaction of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with dimethyl acetylenedicarboxylate at −25 °C^8 except that one of the C=C bonds is co-ordinated to the metal in the latter.

The structure of the other intermediate **9a** can be tentatively proposed on the basis of a comparison of ^{19}F NMR spectral parameters with those of $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)\}(SC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_5)]$ **9b** which has been structurally characterised by X-ray diffraction methods.^{6h} Both exhibit four quartets in the region δ −55 to −65 with almost identical chemical shifts and coupling constants: ^{19}F NMR, $[W\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)\}(SPr^i)(\eta^5\text{-}C_5H_5)]$ **9a**, $(CD_3)_2CO$, 0 °C, δ −55.75 [br q, $J(F^1F^3)$ 10.3, 3 F, CF_3], −56.86 [q, $J(F^2F^4)$ 7.5, 3 F, CF_3], −62.22 (br q, $J(F^1F^3)$ 10.2, 3 F, CF_3] and −64.35 [q, $J(F^2F^4)$ 7.6, 3 F, CF_3]; **9b** CD_2Cl_2, 18 °C, δ − 56.26 [br q, $J(F^1F^3)$ 10.3, 3 F, CF_3] 56.89 [q, $J(F^2F^4)$ 7.6, 3 F, CF_3] −62.87 [br q, $J(F^1F^3)$ 10.3, 3 F, CF_3] and −65.44 [q, $J(F^2F^4)$ 7.7 Hz, 3 F, CF_3]. We therefore propose structure **9a** in which the thiolate has migrated back to the metal with concomitant insertion of the remaining co-ordinated alkyne to give a seven-membered metallacyclic ring. The C_6 chain $C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)$ is bonded in an η^4 mode to the metal with the incoming $CF_3C{\equiv}CCF_3$ ligand linked to a carbon bearing a carbomethoxy rather than a CF_3 group to give a CF_3, CF_3, CO_2Me, CO_2Me, CF_3, CF_3 sequence of substituents. The presence of this sequence in the structures of **10c** and **11**, the final products of the rearrangement process which result from isomerisation of **9a** above *ca.* −10 °C, provides further support for this structural feature in **9a**.

The ^{19}F NMR monitoring illustrated that complex **9a** is converted initially above *ca.* 0 °C into a mixture of **10c** (yellow isomer) and **11c**, in a ratio of 3 : 1, but a third compound with similar spectroscopic properties to **10c** forms at slightly higher temperatures if the solution is allowed to warm slowly to room temperature. In synthetic experiments carried out at room temperature the yellow complex **10c** was isolated in a pure form along with **11c** in addition to small quantities of a second isomeric form of **10c**, as a red crystalline solid.

Reactions of the SMe and SEt adducts **1b** and **1c** in contrast gave only a single isomer **10a** and **10b** but it was not possible unambiguously to identify which, in view of the similarity of the spectra of the two forms and the fact that the complexes were orange. In both cases the NMR reactions illustrated that complex **11** was also formed but in decreasing amounts as the size of the alkyl group on the sulfur decreased. Product ratios at the end of the experiments were **10a** : **11a** = 6 : 1 and **10b** : **11b** = 3 : 1. This compares with 13 : 8 for **10c** : **11c**. In synthetic experiments only the ethyl derivative **11b** was isolated, the amount of **11a** formed being insufficient for purification to be carried out successfully. It was also observed that heating **10a** in toluene up to 60 °C, at which temperature it decomposed, did not result in isomerisation to the red form suggesting that the isomerisation is sensitive to the nature of the thiolate substituent, possibly as a result of steric effects. More significantly, no fluorine transfer to the metal to give **11a** occurred in this reaction indicating that **10** is not the precursor of **11**.

X-Ray studies of both isomers of **10c** and also of **11** have been reported.^{6a} They establish that the transition from **9** to **10** involves attachment of the SPr^i ligand to the end of the hexatrienyl chain without rupture of its linkage to the metal atom. The two isomers of **10c** differ only in the disposition of the isopropyl substituent with respect to the W(η-C_5H_5) unit: in the red form it is *syn* and in the yellow form *anti*. Otherwise the two forms of **10c** are structurally indistinguishable. The $C(CF_3)=C(CF_3)C(CO_2Me)=C(CO_2Me)C(CF_3)=C(CF_3)SPr^i$ trienyl chain is attached in an η^6 fashion to the metal: the W–S bonds [2.482(2) and 2.522(2) Å] are longer than the Mo–S distances in **5**; the four carbons adjacent to the sulfur are bonded to the metal, the W–C_δ bonds [2.284(5) and 2.303(4) Å] being longer than the rest [2.097(5)–2.144(4) Å], and the end of the chain links to the metal through a σ-W–C (alkenyl) bond [2.150(5) and 2.164(5) Å]. With the exception of the terminal double bond all the chain C–C distances are quite long [1.46(1)–1.50(1) Å] suggesting nearly complete delocalisation. There is thus a considerable difference in the trienyl–metal interactions in **5** and **10c**, though in both the metal attains a configuration of eighteen electrons through donation of seven electrons from the trienyl ligand.

The structure of $[WF\{C(=CF_2)C(CF_3)=C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)(SPr^i)\}(\eta^5\text{-}C_5H_5)]$ **11c** (see Fig. 3) arises from **10c**, at least formally, by transfer of a fluorine atom from the terminal CF_3 to the metal and the concomitant rupture of the already weak W–C_δ bond. The W–C (alkenyl) and W–S bond lengths [2.195(4) and 2.492(2) Å] are little altered from the values in **10c**. The η^5-trienyl–metal interaction is completed by an unsymmetrical quasi π-allylic linkage of the three chain carbon atoms adjacent to sulfur [W–C 2.111(4), 2.177(4) and 2.312(4) Å, respectively for C_α, C_β and C_γ].

Not surprisingly, the spectroscopic properties of complexes **11a**–**11c** are significantly different to those of other complexes described in this paper. For example the IR spectra, in addition to two ν(C=O) modes above 1700 cm^{-1} for the carbomethoxy groups and a weak ν(C=C) band near 1630 cm^{-1}, also contain a strong peak near 1650 cm^{-1}. We attribute this to the C=C stretch of the $C=CF_2$ group which is fairly polar and therefore produces a strong absorption. We have also observed such a peak in the IR spectra of $[M\{\eta^3\text{-}C(O)C(CF_3)C(CF_3)C(CF_3)C(=CF_2)\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W)[22] and $[M\{\eta^3\text{-}C(=CF_2)C(CF_3)C(CF_3)C(CF_3)SC_6F_5\}L(F)(\eta^5\text{-}C_5H_5)]$ (L = PEt_3 or PMe_2Ph).[6j] Moreover, the ^{19}F NMR spectra of complexes **11** contain a very high-field signal due to the metal co-ordinated fluorine near δ −270 in addition to five resonances in the region δ −40 to −65, ratio 3:3:1:3:1. These consist of three CF_3 resonances and two peaks due to the inequivalent $=CF_2$ fluorines. The doublet structure of the apparently isolated metal co-ordinated fluorine prompted ^{19}F homodecoupling NMR experiments on the isopropyl derivative **11c** and the resulting peak assignments are given in Fig. 4. These revealed that the metallated fluorine is coupled to one of the CF_2 fluorines δ_5, $J(F^5F^6)$ = 22.0 Hz but not to the other, δ_3. Moreover this coupling, despite the four-bond separation, is greater than that between the two adjacent CF_2 fluorines, $J(F^3F^5)$ = 18.5 Hz. We suggest that this reflects the fact that F^6 and F^5 are physically quite close, 2.78 Å, and this allows through-space coupling, a phenomenon we have encountered repeatedly in this area of chemistry. In contrast, the F^6–F^3 distance, 4.15 Å, is too great for this to occur. Such a phenomenon also accounts for the apparently long-range coupling between CF_3 (δ_2) and CF_3 (δ_4), $J(F^2F^4)$ = 3.5 Hz, the fluorines of which are separated by seven bonds. However, molecular modelling studies[23] reveal that the physical separation is relatively small, the minimum F···F distance afforded by CF_3 rotation being only 2.09 Å. This also provides an explanation for the largest coupling observed, $J(F^3F^4)$ = 28.5 Hz, where the minimum F···F separation is 2.00 Å, well within the sum of the van der Waals radii of the two nuclei. Some of these structural features are apparent in Fig. 3. We have observed close CF_3···CF_3 contacts of this type previously in molecules containing several CF_3 groups and in a number of cases low-temperature ^{19}F NMR studies have revealed slowing down and occasionally complete freezing of CF_3 rotation. Consequently low-temperature studies of the SEt derivative **11b** were carried out. As the temperature was lowered the two CF_3 peaks δ_1(−39.85) and δ_3 (−59.40) broadened and collapsed into the baseline at −60 °C and fine structure began to reappear in the δ_3 peak by −80 °C. Molecular modelling studies confirm that both CF_3 groups have relatively congested steric environments and restricted rotation at low temperatures is to be expected.

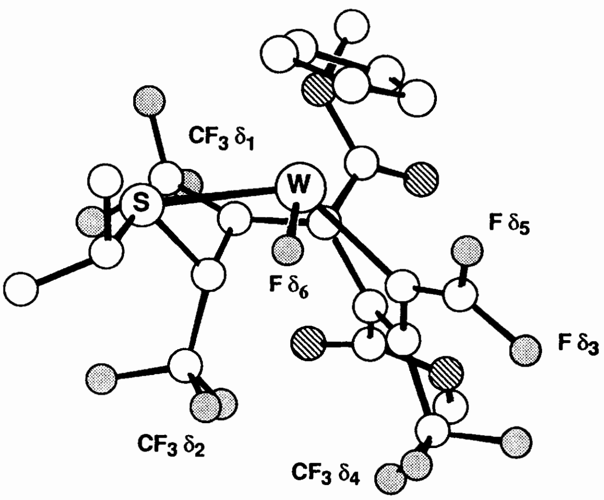


Fig. 3 Molecular structure of complex **11c**

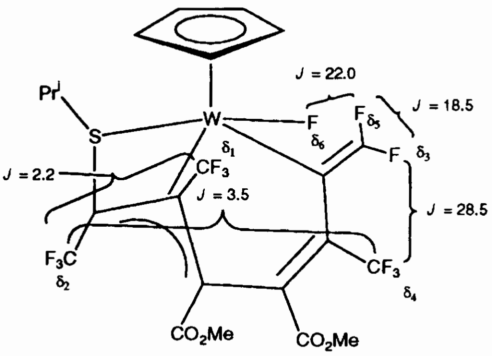


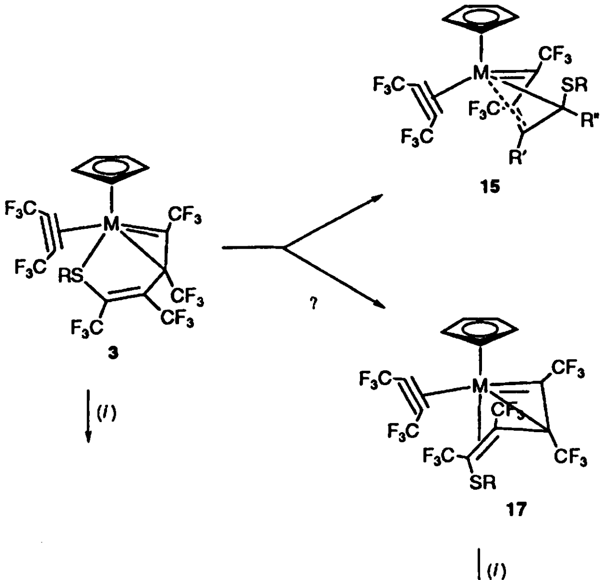
Fig. 4 The ^{19}F NMR spectral assignments (J/Hz) for $[WF\{C(=CF_2)C(CF_3)=C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)(SPr^i)\}(\eta^5\text{-}C_5H_5)]$ **11c**

Discussion

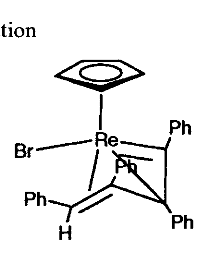
Reactions of alkynes with thiolate complexes have been studied extensively[5] following our initial investigations.[4] In many cases a key feature is the facile formation of a carbon–sulfur bond as a result of alkyne insertion into an M–S bond. Alkynes, in particular those with electronegative groups, *e.g.* CF_3 or CO_2Me, have also been found to behave similarly with other heteroatom ligands to give species containing *e.g.* carbon–phosphorus,[24] –chlorine[25] and –nitrogen[26] bonds. We have already described the existence of two isomeric forms of complexes **1** *viz.* the bis(alkyne) form $[M(SR)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ and the η^2-C,C alkenyl form $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ which provide an indication of the mechanism by which thiolate migration onto an alkyne carbon can occur.[6e] The work described herein provides a mechanistic insight into subsequent oligomerisation processes involving carbon–carbon bond formation.

These reactions, which lead to facile alkyne trimerisation, are unexpectedly complex and the products manifest a diverse range of isomeric forms. The ease with which trimerisation occurs contrasts with our previous reports in this area where we noted that addition of unactivated alkynes $R'C{\equiv}CR''$ to η^2-alkenyl derivatives $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **1** in most cases only results in coupling of the incoming alkyne and the alkenyl ligand to give η^2-C,C alkenyl derivatives $[M\{\eta^3\text{-}C(CF_3)C(CF_3)C(R''){=}C(R')SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **3** and η^4-*cis*-butadienyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3){=}C(R')C(R'')SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **15**. Complexes **3** appear to have two roles in the reactions of **1** with alkynes. With unactivated alkynes in most cases they function as precursors to the cisoid butadienyl **15**, although the tungsten complex **3b** has been observed to rearrange thermally to the metallacycle **7**. However with $MeO_2CC{\equiv}CCO_2Me$ **3a** acts as a precursor to trimerisation products. This may have mechanistic significance since we have no evidence that complexes **15** are involved in the reactions of $MeO_2CC{\equiv}CCO_2Me$ studied here whereas **3a** is formed in the early stages of the reaction of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ with $MeO_2CC{\equiv}CCO_2Me$, Scheme 2. It appears that complexes **15** may be a mechanistic dead end in reactions of this type and that the alternative is trimerisation resulting from the reaction of **3** with the remaining co-ordinated alkyne.

η^4-*cis*-Butadienyl derivatives have also been isolated by other workers, in particular Templeton in tungsten chemistry and Green whose rhodium complexes contain a ligand in which the bonding is perhaps more correctly described as alkylidene, η^3-allyl.[27] Dinuclear complexes containing a similar ligand have recently been obtained from reactions of alkynes with thiolate-bridged complexes $[Ru_2(\mu\text{-}SPr^i)_2(\eta^5\text{-}C_5Me_5)_2]$[28] but in these compounds $[Ru_2(\mu\text{-}SPr^i)\{\eta^2{:}\eta^3\text{-}\mu\text{-}C(R')CHC(CO_2Me)CHSPr^i\}(\eta^5\text{-}C_5Me_5)_2]$ ($R = CO_2Me$ or C_6H_4Me-4) the C_4 moiety functions as a bridging ligand. More recently Green and co-workers[29] reported that coupling of an alkyne and an η^2-alkenyl ligand can also result in a transoid η^4-butadienyl according to X-ray diffraction studies of the rhenium complex **16**. This structure is not unlike that of complexes **3** except that the presence of a thiolate ligand in the latter favours co-ordination of the sulfur rather than the alkene function. We note that the structure of the transoid butadienyl ligand is somewhat reminiscent of part of the trienyl ligand in complexes **4**, **5** and **7**. Thus, although it seems probable that the chemically significant trimerisation reaction occurs directly *via* coupling of the co-ordinated alkyne with the η^3-$C(CF_3)C(CF_3)C(CO_2Me){=}C(CO_2Me)SR$ moiety, it is not inconceivable that isomerisation to the transoid structure **17** is required before reaction with another molecule of alkyne can occur, see Scheme 4.



Scheme 4 (*i*) Trimerisation



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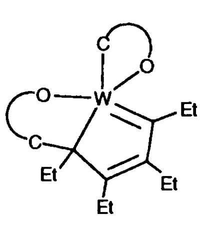
Parallels can also be drawn between our work and the work of others on reactions of tungsten complexes with alkynes. For example Rothwell and co-workers[30] reported that bis(aryl oxide) complexes $[W(OC_6H_3PhC_6H_4)_2L_2]$ ($L = PMePh_2$ or pyridine) react with an excess of $EtC{\equiv}CEt$ to give two products, the metallacycle **18** and the alkyne trimerisation product **19**. Complex **18** is very similar to the cisoid η^4-butadienyls **15** except that the C_4 ligand in the former is bonded in an η^2 mode to the metal since the internal C=C bond in the five-membered part of the metallacycle is not co-ordinated. Of more significance is the structure of **19** since it has a seven-membered metallacyclic ring with a bonding mode similar but not identical to that in complexes **7**. Again, as in **18**, the difference lies in the fact that the internal C=C bond in the five-membered part of the metallacycle is not co-ordinated. As noted by Rothwell these metallacyclic products (and hence some of those reported in our work) resemble intermediates proposed by Schrock and co-workers[31] in the trimerisation of *tert*-butylacetylene by molybdenum alkylidene complexes.

In addition to these examples, metal-promoted alkyne trimerisation reactions have been studied for a wide range of metal precursors and alkyne substituents and a variety of products obtained including free arenes. Although a number of different mechanisms has been proposed to explain metal-promoted oligomerisation and cyclisations it is apparent that no one unique mechanism applies to all systems. In relatively few cases, linking of two different alkynes has been studied and our work provides more detailed information concerning the oligomerisation process. Early work on the addition of different alkynes to dinuclear cobalt complexes $[Co_2(CO)_6(RC{\equiv}CR)]$ resulted in the formation of 'flyover' complexes $[Co_2(CO)_4(CRCRCRCRCRCR)]$ in addition to free arenes.[32] Interestingly this provided a route to arenes such as *o*-di-*tert*-butylbenzene and 1,2,4,5-tetra-*tert*-butylbenzene with substitution patterns not readily obtainable by more conventional synthetic means.[33] More recently, addition of alkynes to cyclopentadienylmolybdenum alkyne complexes $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(RC{\equiv}CR)]$ was reported to proceed *via* more complex reaction pathways resulting in the isolation of binuclear 'flyover' derivatives containing two, three and four RCCR units. Of particular relevance is the reaction of $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(HC{\equiv}CH)]$ with $RC{\equiv}CR$ ($R = CO_2Me$) which gave two oligomerisation products, the symmetric complex $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(CRCRCHCHCRCR)]$ and the less-symmetric species $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(CHCHCRCRCRCR)]$.[34] This compares with the results reported herein where different oligomerisation sequences are also observed but with different metals.



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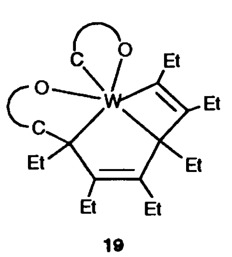

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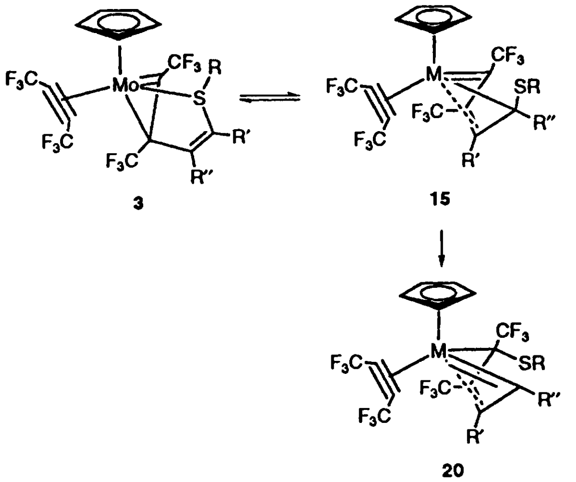
In the present case the two oligomerisation sequences $C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(R)C(R)$ and $C(CF_3)C(CF_3)C(R)C(R)C(CF_3)C(CF_3)$ can be explained in terms of the different pathways 1 and 2 (Scheme 1) available at an early stage in the reactions to the common intermediate **2**. This difference clearly depends on the metal with $CF_3C{\equiv}CCF_3$ insertion into an M=C bond of complex **3a**, path 1, being preferred with M = Mo, and metallacyclisation, path 2, with M = W. An interesting feature of these reactions is the quite different roles the isomeric metallacycles **7** and **9** play in the trimerisation pathways. Complex **9** is formed at an early stage of path 2, Scheme 1, and undergoes thiolate transfer from the metal to give trienyl products **10** and **11**. However, **7** forms the terminus of path 1 and results from the opposite reaction, *i.e.* thiolate transfer from a trienyl derivative, in this case **4**. The formation of metallacycloheptatrienes in these reactions clearly involves reversible migration of the SR group onto the growing carbon chain and in effect the thiolate ligand catalyses the alkyne trimerisation. In contrast metal-promoted alkyne trimerisation reactions normally proceed *via* simple insertion of the alkyne into a metal–carbon bond or *via* ring expansion of intermediate metallacycles.[4] The results reported herein illustrate that much more complex mechanisms may operate in some circumstances when a non-innocent ligand such as a thiolate is present. We have already demonstrated the ability of the thiolate ligand reversibly to migrate from metal to carbon and sometimes between different carbons in this area of chemistry. For example, the η^2-C,C vinyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **1** (R = Me, Et or Pr^i) show fluxional behaviour involving reversible migration of the thiolate between the two CF_3CCCF_3 moieties suggesting the intermediacy of a bis(alkyne) form which is isolable with some thiolate ligands.[6e] Even more remarkable is the reversible migration of the thiolate ligand from a bridging position in **3** to a terminal carbon bound site in **15** (Scheme 5) and subsequent 1, 4 migration across the butadienyl ligand to give complex **20**.[7b] Such transformations indicate that the thiolate group is quite unusual, if not unique, in exhibiting remarkable co-ordination abilities and mobility when co-ordinated to a metal.

The formation of the fluoro complexes $[WF\{C(=CF_2)C(CF_3){=}C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)(SR)\}(\eta^5\text{-}C_5H_5)]$ **11** is somewhat unexpected and when first reported in an earlier communication[6a] was quite novel. Subsequently, however, a number of reports of metal-promoted C–F bond fission have appeared in the literature. Most have involved fluorine bonded to aromatic nuclei and intramolecular transfer from a fluoroalkyl group is still relatively rare.[35] The large dissociation energies of C–F bonds in fluoro-alkyl and -aryl derivatives provide a thermodynamic rationalisation for the paucity of reports in this area, although conversely the high stability of metal–fluorine bonds clearly provides a strong driving force for the reaction. An obvious question in the present case concerns the nature of the precursor to the fluoro products **11**. As noted previously, heating **10a** in solution at temperatures up to 60 °C did not result in fluorine transfer indicating that **10** is not the precursor to **11**. This may indicate that the metallacycle **9a** fulfils this role although the existence of another undetected intermediate cannot be excluded. It is reasonable to assume that at some stage in the reaction the CF_3 fluorines approach to within bonding distance of the metal and co-ordinate prior to C–F bond fission. However, no close $CF_3\cdots M$ contacts are present in the metallacyclic complex $[Mo\{C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)\}(SC_6H_4Me\text{-}4)(\eta^5\text{-}C_5H_5)]$ **9b** in the solid state which may indicate that movement of the thiolate towards the carbon to which it ultimately becomes bonded in **11** is required to promote fluorine transfer.

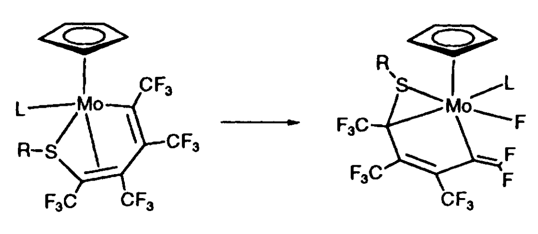
Interestingly, X-ray diffraction studies of $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$ have revealed a bonding interaction between a fluorine of one SC_6F_5 group and the metal.[36] Moreover we have also reported NMR and structural studies of SC_6F_5 derivatives $M'[M(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, M′ = Tl or Cs) in which clear evidence for contact between the sulfur-co-ordinated thalium or caesium ions and the *o*-fluorines of the C_6F_5 groups was found.[37] In these cases the metal–fluorine contacts appear to be non-bonding. Of more direct relevance is our recent report of another example of CF_3 activation in this area of chemistry in which the butadienyl complexes $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SR\}L(\eta^5\text{-}C_5H_5)]$ **21** (R = Pr^i, L = PEt$_3$ or PMe$_2$Ph; R = C$_6$F$_5$, L = PMePh$_2$) isomerise in solution at room temperature to give complexes assigned structure **22**. These are related to **11** but have one less CRCR unit in the fluorocarbon chain.[6j] Again X-ray diffraction studies of the precursor $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i\}(PEt_3)(\eta^5\text{-}C_5H_5)]$[6b] **21** failed to discern any close $CF_3\cdots M$ interaction which could account for the subsequent reaction. It seems likely that sufficient flexibility exists in the fluorocarbon chain of such species to allow movement of the CF_3 to the point where fluorine transfer occurs. It is interesting to speculate on the existence of a species containing an agostic fluorine interaction somewhat analogous to that of the well established agostic hydrogen complexes. However, current knowledge mitigates against such a possibility[38] and an intermediate with a CF_3 group co-ordinated *via* a fluorine lone pair as in the aforementioned $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$[36] would seem to be more likely.



Scheme 5 R = SC_6F_5

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 $SiMe_4$ (^{1}H, δ 0) and CCl_3F (^{19}F, δ 0). Infrared spectra were recorded as solutions on a Perkin-Elmer 580 spectrophotometer with polystyrene as reference and mass spectra on a Vacuum Generators updated A.E.I. MS 11 instrument. 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) or calcium hydride



21 **22**

(hexane, diethyl ether) and distilled just before use. The η^2-C,C vinyl complexes [M{η^3-C(CF_3)C(CF_3)SR}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] (M = Mo, R = Pr^i; M = W, R = Me, Et or Pr^i) were synthesised as described previously.[6e]

Reaction of [Mo{η^3-C(CF_3)C(CF_3)SPr^i}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] 1a with $MeO_2CC{\equiv}CCO_2Me$

^{19}F NMR (CD_2Cl_2), −40 to 0 °C, 1a ⟶ 2a ⟶ 3a. [Mo{η^2-C(CF_3)=C(CF_3)C(CO_2Me)C(CO_2Me)SPr^i}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] **2a**: ^{19}F NMR (CD_2Cl_2, −15 °C), δ −49.52 [qq, 3, F, $J(F^1F^2)$ 14.6, $J(F^1F^3)$, 3 F, CF_3], −51.16 [q, $J(F^1F^2)$ 14.7, 3 F, CF_3], −52.94 (br s, 3 F, CF_3) and −55.65 [q, $J(F^3F^4)$ 3.2 Hz, 3 F, CF_3]. [Mo{η^3-C(CF_3)=C(CF_3)C(CO_2Me)C(CO_2-Me)(SPr^i)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] **3a**: ^{19}F NMR (CD_2Cl_2, −5 °C): δ −52.97 (br s, 3 F, CF_3), −53.22 (m, 3 F, CF_3), −54.76 (br spt, 3 F, CF_3) and −57.13 (q, J 4.3 Hz, 3 F, CF_3).

Synthetic, 20 °C, 1a ⟶ 4. A solution of complex **2a** (70 mg, 0.12 mmol) in diethyl ether (10 cm^3) was treated with a slight excess of $MeO_2CC{\equiv}CCO_2Me$ in a sealed tube at 20 °C for 24 h. The resulting dark red-brown solution was filtered, concentrated *in vacuo*, hexane (4 cm^3) added and left at −15 °C for several hours to give an impure red solid. This was recrystallised twice from dichloromethane–hexane to give red crystals of [Mo{η^6-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CO_2Me)C(SPr^i)-(CO_2Me)}(η^5-C_5H_5)] **4** (23 mg, 26%) (Found: C, 37.4; H, 2.7. $C_{22}H_{18}F_{12}MoO_4S$ requires C, 37.50; H, 2.6%); m/z 702 [M^+]; IR ($CDCl_3$) ν(C=O) 1732ms, ν(C=C) 1630w cm^{-1}. NMR ($CDCl_3$): ^{1}H δ 1.05 (d, J 6.8, 3 H, Pr^i), 1.13 (d, J 7.1, 3 H, Pr^i), 2.92 (m, 1 H, Pr^i), 3.69 (s, 3 H, CO_2Me), 3.84 (s, 3 H, CO_2Me) and 5.95 (s, 5 H, C_5H_5); ^{19}F, δ −53.43 (qq, J 12.5, 2.8, 3 F, CF_3), −56.48 (br m, 3 F, CF_3), −57.46 (br m, 3 F, CF_3) and −59.83 (qq, J 13.1, 3.0 Hz, 3 F, CF_3).

Synthetic 20 °C, 1a ⟶ 5 + 6 + 7a. A solution of complex **1a** (120 mg, 0.21 mmol) in diethyl ether (20 cm^3) was treated with a slight excess of $MeO_2CC{\equiv}CCO_2Me$ in diethyl ether (20 cm^3) at 20 °C for 20 h. The resulting dark red solution was concentrated *in vacuo* and chromatographed over Florisil to give: (*a*) a yellow band eluted with diethyl ether–hexane (1:5), (*b*) a dark red band eluted with diethyl ether–hexane (2:3) and (*c*) a red band eluted with diethyl ether–hexane (3:2). The yellow band (*a*) was concentrated *in vacuo* and cooled to −15 °C to give a yellow solid. Recrystallisation from diethyl ether–hexane gave yellow crystals of [Mo{η^5-C(CF_3)=C(CF_3)-C(CF_3)C(CF_3)=C(CO_2Me)C(CO_2Me)}(SPr^i)(η^5-C_5H_5)] **7a** (20 mg, 13%) (Found: C, 37.2; H, 2.4; S, 4.6. $C_{22}H_{18}F_{12}MoO_4S$ requires C, 37.5; H, 2.6; S, 4.5%); m/z 102 [M^+]; IR ($CDCl_3$) ν(C=O) 1728m, ν(C=C) 1642w cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.26 (d, J 6.7, 3 H, Pr^i), 1.31 (d, J 6.8, 3 H, Pr^i), 3.38 (m, 1 H, Pr^i), 3.70 (s, 3 H, CO_2Me), 3.72 (s, 3 H, CO_2Me) and 5.73 (s, 5 H, C_5H_5); ^{19}F, δ −52.35 (q, J 7.2, 3 F, CF_3), −54.26 (s, 3 F, CF_3), −55.23 (q, J 8.6 Hz, 3 F, CF_3) and −65.13 (spt, 3 F, CF_3).

Concentration of the dark red solution [band (*b*)] followed by cooling to −15 °C gave a black microcrystalline solid [Mo(SPr^i){η^4-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CO_2Me)C-(CO_2Me)}(η^5-C_5H_5)] **6** (17 mg, 11%) (Found: C, 37.5; H, 2.4. $C_{22}H_{18}F_{12}MoO_4S$ requires C, 37.5; H, 2.6%); m/z 702 [M^+]; IR ($CDCl_3$) ν(C=O) 1730m, ν(C=C) 1610w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.04 (d, J 6.9, 3 H, Pr^i), 1.37 (d, J 6.7 Hz, 3 H, Pr^i), 2.95 (m, 1 H, Pr^i), 3.78 (s, 3 H, CO_2Me), 3.83 (s, 3 H, CO_2Me) and 5.64 (s, 5 H, C_5H_5).

Concentration of the red solution [band (*c*)] followed by cooling to −15 °C gave a dark red solid. This was recrystallised from diethyl ether–hexane to give dark red crystals of [Mo{η^5-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CO_2Me)C(CO_2Me)(SPr^i)}-(η^5-C_5H_5)] **5** (23 mg, 15%) (Found: C, 37.3; H, 2.4. $C_{22}H_{18}F_{12}MoO_4S$ requires C, 37.5; H, 2.6%); m/z 702 [M^+]; IR ($CDCl_3$) ν(C=O) 1745 (sh), 1727m, 1710 (sh), 1700m, ν(C=C) 1645w cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.21 (d, J 7.1, 3 H, Pr^i), 1.47 (d, J 6.5, 3 H, Pr^i), 3.78 (s, 3 H, CO_2Me), 3.79 (s, 3 H, CO_2Me), 3.85 (m, 1 H, Pr^i) and 5.68 (s, 5 H, C_5H_5); ^{19}F, δ −51.70 [qq, $J(F^1F^4)$ 11.5, $J(F^1F^3)$ 2.8, 3 F, CF_3], −54.18 [qq, ($J(F^2F^3)$ 4.4, $J(F^2F^4)$ 3.7, 3 F, CF_3], −57.16 [qq, $J(F^1F^3)$ 2.8, $J(F^2F^3)$ 4.4, 3 F, CF_3] and −59.68 [qq, $J(F^1F^4)$ 11.5, $J(F^2F^4)$ 3.7 Hz, 3 F, CF_3].

Reactions of [W{η^3-C(CF_3)C(CF_3)SMe}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] 1b

With $MeO_2CC{\equiv}CCO_2Me$, ^{19}F NMR ($C_6D_5CD_3$ or CD_2Cl_2), −30 to +20 °C, 1b (−30 °C) ⟶ 2b (> 0 °C) ⟶ 10a + 11a ratio 6:1. Compound **11a**: ^{19}F NMR ($C_6D_5CD_3$), δ −40.38 (s, 3 F, CF_3), −48.21 (br s, 3 F, CF_3), −58.8 (m, 1 F, CF_2), −59.69 (br d, J 18.6 Hz, 3 F, CF_3) and −60.83 (t, 1 F, CF_2).

With $MeO_2CC{\equiv}CCO_2Me$ at −30 °C. A solution of complex **1b** (80 mg, 0.13 mmol) in diethyl ether–hexane (1:1, 10 cm^3) was treated with a slight excess of $MeO_2CC{\equiv}CCO_2Me$ at −30 °C for *ca.* 4 h upon which a change from red to yellow was observed. The solution was held at this temperature and concentrated *in vacuo*. The temperature was reduced to −35 °C for *ca.* 2 h when crystals formed. These were collected, washed with several portions of cold hexane and dried *in vacuo* to give pale yellow crystals of [W{η^2-C(CF_3)=C(CF_3)-C(CO_2Me)=C(CO_2Me)(SMe)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] **2b** (68 mg, 69%) (Found: C, 31.0; H, 1.5. $C_{20}H_{14}F_{12}O_4SW$ requires C, 31.5; H, 1.85%); IR (KBr) ν(C≡C) 1769wm, ν(C=O) 1690s, ν(C=C) 1645w cm^{-1}. NMR (CD_2Cl_2, −20 °C): ^{1}H, δ 2.31 (s, 3 H, SMe), 3.40 (br s, 3 H, CO_2Me), 3.76 (s, 3 H, CO_2Me) and 6.14 (s, 5 H, C_5H_5); ^{19}F, δ −49.01 (qq, J 13.8, 3.8, 3 F, CF_3), −52.74 (q, J 13.9 Hz, 3 F, CF_3), −54.71 (br s, 3 F, CF_3) and −56.51 (br s, 3 F, CF_3).

With $MeO_2CC{\equiv}CCO_2Me$ at 20 °C. A solution of complex **1b** (40 mg, 0.07 mmol) in diethyl ether–hexane (1:3, 8 cm^3) was treated with a slight excess of $MeO_2CC{\equiv}CCO_2Me$ upon which an immediate change from red to yellow was observed. The solution was stirred for 15 min when small quantities of a yellow solid formed. The solution was concentrated *in vacuo* and cooled to −15 °C when more of the solid precipitated. This was collected and recrystallised from dichloromethane–hexane to give orange-red crystals of [W{η^5-C(CF_3)=C(CF_3)C(CO_2-Me)C(CO_2Me)C(CF_3)=C(CF_3) (SMe)}(η^5-C_5H_5)] **10a** (27 mg, 55%) (Found: C, 31.6; H, 1.6. $C_{20}H_{14}F_{12}O_4SW$ requires C, 31.5; H, 1.85%); m/z 762 [M^+]; IR(KBr) ν(C=O) 1716s, 1701m, ν(C=C) 1630w cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 2.14 (br s, 3 H, SMe), 3.80 (s, 3 H, CO_2Me), 3.84 (s, 3 H, CO_2Me) and 5.75 (s, 5 H, C_5H_5); ^{19}F, δ −49.98 (q, J 2.1 Hz, 3 F, CF_3), −50.78 (m, 3 F, CF_3), − 57.23 (m, 3 F, CF_3) and −65.71 (m, 3 F, CF_3).

Reactions of [W{η^3-C(CF_3)C(CF_3)SEt}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] 1c with $MeO_2CC{\equiv}CCO_2Me$, ^{19}F NMR ($C_6D_5CD_3$), −40 to +20 °C: 1c (−30 °C) ⟶ 2c (0 °C) ⟶ 10b (one isomer) + 11b, ratio 3:1

At −25 °C. A solution of complex **1c** (110 mg, 0.17 mmol) in diethyl ether–hexane (1:1, 6 cm^3) was treated with a slight excess of $MeO_2CC{\equiv}CCO_2Me$ at −40 °C. The temperature was raised to −25 °C and held for *ca.* 5 h when a small quantity of orange and yellow crystals formed. The solution was concentrated *in vacuo* and held at −30 °C for 2 h. The mother-liquor was removed, the solid washed with several portions of cold hexane and dried *in vacuo* to give orange crystals of [W{η^2-C(CF_3)=C(CF_3)C(CO_2Me)=C(CO_2Me)(SEt)}($CF_3C{\equiv}CCF_3$)-(η^5-C_5H_5)] **2c** (80 mg, 59%). (Found: C, 32.8; H, 1.9. $C_{21}H_{16}F_{12}O_4SW$ requires C, 32.45; H, 2.1%); m/z 776 [M^+]. NMR: ^{1}H (CD_2Cl_2, −20 °C), δ 1.42 (t, 3 H, SCH_2CH_3), 2.45 (m, SCH_2CH_3), 3.50 (s, 3 H, CO_2Me), 3.83 (s, 3 H, CO_2Me) and 5.94 (s, 5 H, C_5H_5); ^{19}F [$(CD_3)_2CO$, −30 °C], δ −48.12

Table 2 Fractional atomic coordinates for complex **4**

Atom	*x*	*y*	*z*
Mo	0.213 24(5)	0.116 28(4)	0.212 04(3)
S	−0.063 22(16)	0.166 72(13)	0.064 63(10)
F(1)	0.562 8(5)	0.104 9(4)	0.380 9(4)
F(2)	0.435 5(7)	0.103 5(4)	0.465 6(3)
F(3)	0.441 6(5)	0.003 1(3)	0.381 4(3)
F(4)	0.157 6(4)	0.311 6(3)	0.364 0(3)
F(5)	0.353 3(4)	0.291 5(3)	0.438 9(3)
F(6)	0.206 3(5)	0.197 9(3)	0.436 7(3)
F(7)	0.498 6(4)	0.323 7(3)	0.253 3(3)
F(8)	0.509 2(4)	0.195 2(3)	0.225 0(3)
F(9)	0.418 1(4)	0.279 8(3)	0.124 2(3)
F(10)	0.320 1(5)	0.422 5(3)	0.281 6(3)
F(11)	0.136 8(5)	0.459 1(3)	0.206 2(4)
F(12)	0.293 6(6)	0.435 0(3)	0.144 0(4)
O(1)	−0.045 8(5)	0.394 0(3)	0.069 8(3)
O(2)	−0.120 7(6)	0.363 4(4)	0.186 7(4)
O(3)	−0.063 7(5)	0.205 2(3)	0.287 4(3)
O(4)	0.040 9(4)	0.089 6(3)	0.256 6(3)
C(1)	0.155 0(7)	−0.003 7(5)	0.126 1(5)
C(2)	0.192 0(7)	0.056 6(5)	0.071 6(4)
C(3)	0.322 1(7)	0.076 9(5)	0.104 0(4)
C(4)	0.369 3(7)	0.026 2(5)	0.177 8(4)
C(5)	0.266 0(8)	−0.022 9(5)	0.193 3(5)
C(6)	−0.232 4(7)	0.178 9(5)	0.076 9(5)
C(7)	−0.280 9(8)	0.098 8(7)	0.110 6(6)
C(8)	−0.314 1(8)	0.201 1(7)	−0.012 5(7)
C(9)	0.444 1(8)	0.086 2(6)	0.388 0(5)
C(10)	0.341 5(6)	0.127 3(5)	0.319 8(4)
C(11)	0.292 8(6)	0.210 4(4)	0.312 3(4)
C(12)	0.250 8(7)	0.253 3(5)	0.386 2(5)
C(13)	0.297 6(6)	0.248 2(4)	0.227 8(4)
C(14)	0.428 4(7)	0.260 7(5)	0.208 5(5)
C(15)	0.196 8(6)	0.316 2(4)	0.195 1(4)
C(16)	0.235 0(8)	0.408 1(6)	0.205 4(6)
C(17)	0.072 8(6)	0.295 2(4)	0.168 2(4)
C(18)	−0.041 6(7)	0.354 3(5)	0.145 0(5)
C(19)	−0.151 3(9)	0.454 7(6)	0.046 6(5)
C(20)	0.041 6(6)	0.202 8(4)	0.166 6(4)
C(21)	0.002 2(6)	0.163 5(4)	0.241 1(4)
C(22)	−0.094 4(9)	0.162 9(6)	0.363 4(5)

Table 3 Fractional atomic coordinates for complex **5**

Atom	*x*	*y*	*z*
Mo(A)	0.139 82(6)	0.202 93(4)	0.495 59(4)
Mo(B)	0.329 45(6)	0.295 59(4)	0.004 11(4)
S(A)	0.232 96(17)	0.273 92(11)	0.554 08(12)
S(B)	0.545 13(16)	0.227 79(11)	−0.056 49(11)
F(A1)	−0.260 2(6)	0.320 3(5)	0.563 2(5)
F(A2)	−0.184 9(6)	0.337 7(8)	0.435 9(5)
F(A3)	−0.241 7(6)	0.215 2(5)	0.523 6(6)
F(A4)	0.034 0(5)	0.203 7(3)	0.735 0(3)
F(A5)	−0.162 8(5)	0.210 0(4)	0.731 2(3)
F(A6)	−0.070 2(5)	0.324 8(3)	0.643 0(3)
F(A7)	−0.044 2(6)	0.050 7(4)	0.559 2(4)
F(A8)	−0.076 1(6)	−0.010 3(4)	0.692 1(4)
F(A9)	0.105 4(5)	−0.056 5(4)	0.622 8(6)
F(A10)	0.174 0(7)	−0.100 2(4)	0.796 4(4)
F(A11)	0.004 3(5)	0.010 0(4)	0.805 7(3)
F(A12)	0.181 5(6)	0.009 0(5)	0.834 5(3)
F(B1)	0.110 6(6)	0.175 1(5)	−0.065 2(5)
F(B2)	0.085 4(9)	0.154 8(7)	0.063 0(5)
F(B3)	−0.011 0(5)	0.278 7(5)	−0.021 7(6)
F(B4)	0.447 8(4)	0.301 4(3)	−0.237 4(3)
F(B5)	0.255 0(5)	0.293 6(4)	−0.233 9(3)
F(B6)	0.375 2(4)	0.177 4(3)	−0.147 4(3)
F(B7)	0.056 6(5)	0.445 0(4)	−0.057 0(4)
F(B8)	0.092 0(5)	0.511 6(4)	−0.191 7(4)
F(B9)	0.161 3(5)	0.554 0(4)	−0.116 0(6)
F(B10)	0.347 7(7)	0.604 0(3)	−0.292 2(5)
F(B11)	0.298 4(5)	0.493 4(4)	−0.305 3(3)
F(B12)	0.496 3(6)	0.499 9(4)	−0.332 1(3)
O(A1)	0.453 8(5)	0.113 4(4)	0.692 9(3)
O(A2)	0.431 6(6)	−0.036 9(4)	0.751 5(4)
O(A3)	0.484 5(5)	0.197 8(3)	0.449 9(4)
O(A4)	0.513 8(5)	0.050 9(4)	0.548 6(4)
O(B1)	0.737 8(5)	0.393 2(4)	−0.193 2(3)
O(B2)	0.625 0(6)	0.542 8(4)	−0.246 6(4)
O(B3)	0.624 8(5)	0.301 7(3)	0.051 8(4)
O(B4)	0.607 3(5)	0.449 8(4)	−0.047 5(4)
C(A1)	0.251 8(8)	0.259 9(6)	0.351 9(5)
C(A2)	0.115 8(10)	0.282 4(6)	0.350 9(6)
C(A3)	0.072 0(10)	0.195 7(7)	0.385 6(5)
C(A4)	0.182 5(10)	0.122 7(6)	0.404 6(6)
C(A5)	0.293 8(8)	0.158 5(6)	0.385 9(5)
C(A6)	0.329 7(7)	0.364 3(5)	0.487 0(5)
C(A7)	0.429 6(9)	0.353 7(6)	0.536 4(6)
C(A8)	0.226 1(9)	0.457 0(5)	0.469 8(6)
C(A9)	−0.178 7(10)	0.278 5(7)	0.513 3(8)
C(A10)	−0.046 1(7)	0.235 7(5)	0.533 2(5)
C(A11)	−0.004 9(7)	0.186 4(5)	0.614 3(5)
C(A12)	−0.047 1(8)	0.229 3(5)	0.680 9(5)
C(A13)	0.075 1(7)	0.092 1(5)	0.626 1(5)
C(A14)	0.018 0(8)	0.020 6(6)	0.625 3(6)
C(A15)	0.173 9(7)	0.053 7(4)	0.687 3(5)
C(A16)	0.136 3(9)	−0.007 5(6)	0.780 4(6)
C(A17)	0.284 4(7)	0.083 4(5)	0.657 4(5)
C(A18)	0.396 9(7)	0.045 1(6)	0.708 5(5)
C(A19)	0.576 6(8)	0.086 0(8)	0.721 9(7)
C(A20)	0.309 3(6)	0.153 9(4)	0.567 2(4)
C(A21)	0.446 3(8)	0.128 6(5)	0.520 5(5)
C(A22)	0.611 6(9)	0.174 3(7)	0.397 7(7)
C(B1)	0.362 0(8)	0.237 5(6)	0.147 9(5)
C(B2)	0.245 9(9)	0.214 3(6)	0.148 0(5)
C(B3)	0.155 1(8)	0.299 2(7)	0.117 3(6)
C(B4)	0.209 0(9)	0.375 7(6)	0.096 8(6)
C(B5)	0.336 7(8)	0.338 3(6)	0.116 4(5)
C(B6)	0.666 3(6)	0.137 0(5)	0.010 4(4)
C(B7)	0.804 4(7)	0.147 6(6)	−0.041 5(6)
C(B8)	0.637 8(8)	0.044 4(5)	0.023 7(6)
C(B9)	0.101 6(9)	0.217 4(7)	−0.013 1(7)
C(B10)	0.211 6(6)	0.261 6(5)	−0.034 6(5)
C(B11)	0.279 0(6)	0.314 6(5)	−0.115 1(5)
C(B12)	0.340 7(8)	0.272 5(5)	−0.184 1(5)
C(B13)	0.280 1(7)	0.407 8(5)	−0.125 6(5)
C(B14)	0.150 6(8)	0.477 5(6)	−0.121 7(6)
C(B15)	0.396 4(8)	0.448 5(5)	−0.185 1(5)
C(B16)	0.383 3(10)	0.513 4(7)	−0.279 0(6)
C(B17)	0.507 6(7)	0.420 3(5)	−0.155 8(5)
C(B18)	0.628 2(8)	0.461 4(6)	−0.205 5(5)
C(B19)	0.860 1(9)	0.425 3(7)	−0.223 2(6)
C(B20)	0.518 8(6)	0.347 7(4)	−0.067 8(4)
C(B21)	0.586 9(7)	0.372 7(6)	−0.020 3(5)
C(B22)	0.685 4(10)	0.324 8(7)	0.100 2(7)

(qq, *J* 14.3, 3.7, 3 F, CF_3), −51.52 (q, *J* 14.2 Hz, 3 F, CF_3), −53.36 (br m, 3 F, CF_3) and −55.87 (br m, 3 F, CF_3).

At 20 °C. A solution of complex **1c** (80 mg, 0.13 mmol) in diethyl ether–hexane (1 : 1, 8 cm^3) was treated with a slight excess of $MeO_2CC{\equiv}CCO_2Me$ at room temperature for 4 h. After this time the solution was concentrated *in vacuo* and allowed to stand at −15 °C to give a yellow solid. This was recrystallised from CH_2Cl_2–hexane twice to give orange–yellow crystals of complex **10b** (34 mg, 35%). The mother-liquors from these recrystallisations were combined, centrifuged, concentrated and allowed to sit at −15 °C for 18 h to give a pale yellow powder. This was recrystallised twice from CH_2Cl_2–hexane to give off-white crystals of **11b** (14 mg, 14%).

[W{η^5-C(CF_3)=C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)=C-(CF_3)(SEt)}(η^5-C_5H_5)] **10b** (Found: C, 32.5; H, 1.8.

$C_{21}H_{16}F_{12}O_4SW$ requires C, 32.45; H, 2.1%): *m*/*z* 776 [M^+]; IR ν(C=O) 1732s, 1715s, 1710 (sh), ν(C=C) 1630w cm^{-1}; NMR: ^{1}H [$(CD_3)_2CO$], δ 1.43 (t, 3 H, Et), 2.81 (q, 2 H, Et), 3.75 (s, 3 H, CO_2Me), 3.78 (s, 3 H, CO_2Me) and 5.99 (s, 5 H, C_5H_5); ^{19}F ($CDCl_3$), δ −49.78 (m, 3 F, CF_3), −50.92 (s, 3 F, CF_3), −56.47 (qq, *J* 8.2, 4.7, 3 F, CF_3) and −65.22 (qq, *J* 8.1, 3.0 Hz, 3 F, CF_3).

[WF{C(=CF_2)C(CF_3)=C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)(SEt)}(η^5-C_5H_5)] **11b** (Found: C, 32.2; H, 2.0. $C_{21}H_{16}F_{12}O_4SW$ requires C, 32.45; H, 2.1%): *m*/*z* 776 [M^+]; IR ($CDCl_3$) ν(C=O) 1730s, 1708m (sh), ν(C=F) 1651s cm^{-1}; NMR [$(CD_3)_2CO$]: ^{1}H, δ 1.35 (t, 3 H, Et), 2.85 (q, 2 H, Et), 3.62 (s, 3 H, CO_2Me), 3.71 (s, 3 H, CO_2Me) and 6.30 (s, 5 H, C_5H_5); ^{19}F, δ −39.85 (s, 3 F, CF_3), −48.01 (br s, 3 F, CF_3), −59.40 [br d, *J*(F–CF_3) 29.9, 3 F, CF_3], −60.50 (m, 1 F, CF_2), −61.55 [dd, *J*(F–F) 21.6, 21.6, 1 F, CF_2] and −272.5 [d, *J*(F–F) 21.2, 1 F, W–F].

Reaction of [W{η^3-C(CF_3)C(CF_3)SPr^i}($CF_3C\equiv CCF_3$)(η^5-C_5H_5)] 1d with $MeO_2CC\equiv CCO_2Me$, ^{19}F NMR [CD_2Cl_2 or $(CD_3)_2CO$], −40 to +20 °C: 1d $\longrightarrow$ 2d $\longrightarrow$ 8 $\longrightarrow$ 9a $\longrightarrow$ 10c (yellow) + 10c (red) + 11c, ratio 65:39:64

A solution of complex **1d** (100 mg, 0.13 mmol) in diethyl ether (4 cm^3) at room temperature was treated with a slight excess of $MeO_2CC\equiv CCO_2Me$. The orange solution turned green over a period of *ca.* 5 min and was then allowed to react for 18 h. After this time the solution turned yellow-brown and a mixture of a white solid and yellow crystals formed. The solution was concentrated *in vacuo* and allowed to stand at room temperature to give more yellow crystals and white powder. The ^{19}F NMR spectra indicated that the solid contained a mixture of **10c** (red), **10c** (yellow) and **11c**. The mixture was separated by repeated fractional crystallisation from CH_2Cl_2–hexane at −15 °C, the less-soluble complex **11c** crystallising first. The isomeric products **10c** crystallised together and were separated by hand. Yields: **10c** (yellow) 28 mg (23%); (red), 6 mg (5%); **11c** (white), 17 mg (14%).

Yellow [W{η^3-C(CF_3)=C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)(SPr^i}(η^5-C_5H_5)] **10c** (Found: C, 33.0; H, 2.3. $C_{22}H_{18}F_{12}O_4SW$ requires C, 33.4; H, 2.3%); *m*/*z* 790 [M^+]; IR (Nujol) ν(C=O) 1743m, 1704s, ν(C=C) 1635w cm^{-1}; NMR ($CDCl_3$): ^{1}H, δ 1.41 (d, *J* 7.0, 3 H, Pr^i), 1.52 (d, *J* 6.7, 3 H, Pr^i), 2.55 (m, 1 H, Pr^i), 3.79 (s, 3 H, CO_2Me), 3.85 (s, 3 H, CO_2Me) and 5.79 (s, 5 H, C_5H_5); ^{19}F, δ −49.37 (br s, 3 F, CF_3), −54.38 (br s, 3 F, CF_3), −56.57 [qq, *J*(F^1F^3) 4.1, *J*(F^3F^4) 8.0, 3 F, CF_3] and −65.78 [qq, *J*(F^3F^4) 7.9, *J* 2.8 Hz, 3 F, CF_3].

Red **10c** (Found: C, 33.2; H, 2.2%): *m*/*z* 190 [M^+]; IR (Nujol) ν(C=O) 1742m, 1722m, ν(C=C) 1635w cm^{-1}; NMR ($CDCl_3$): ^{1}H (−20 °C), δ 1.23 (d, *J* 7.2, 3 H, Pr^i), 1.40 (d, *J* 7.0, 3 H, Pr^i), 2.99 (m, 1 H, Pr^i), 3.79 (s, 3 H, CO_2Me), 3.82 (s, 3 H, CO_2Me) and 5.70 (s, 5 H, C_5H_5); ^{19}F, δ −49.89 (br s, 3 F, CF_3) −54.06 (s, 3 F, CF_3), −57.61 [qq, *J*(F^1F^3) 3.7, *J*(F^3F^4) 7.8, 3 F, CF_3] and −66.06 [qq, *J*(F^1F^4) 2.7, *J*(F^3F^4) 8.3, 3 F, CF_3].

White [WF{C(=CF_2)C(CF_3)=C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)(SPr^i)}(η^5-C_5H_5)] **11c** (Found: C, 32.9; H, 2.4. $C_{22}H_{18}F_{12}O_4SW$ requires C, 33.4; H, 2.3%): *m*/*z* 790 [M^+]; IR (Nujol) ν(C=O) 1730s, 1707s, ν(C=C) 1655s, 1633w cm^{-1}; NMR ($CDCl_3$): ^{1}H, δ 1.43 (d, *J* 6.8, 3 H, Pr^i), 1.49 (d, *J* 6.8, 3 H, Pr^i), 3.32 (m, 1 H, Pr^i), 3.67 (s, 3 H, CO_2Me), 3.79 (s, 3 H, CO_2Me) and 6.05 (s, 5 H, C_5H_5); ^{19}F, δ_1 −39.82 [q, *J*(F^1F^2) 2.2, 3 F, CF_3], δ_2 −49.06 [qq, *J*(F^1F^2) 2.2, *J*(F^2F^4) 3.5, 3 F, CF_3], δ_3 −58.2 [dq, *J*(F^3F^5) 18.5, *J*(F^3F^4) 28.5, 1 F, CF_2], δ_4 −59.2 [dq, *J*(F^3F^4) 28.5, *J*(F^2F^4) 3.5, 3 F, CF_3], δ_5 −60.88 [dd, *J*(F^3F^5) 18.5, *J*(F^5F^6) 22.0] and δ_6 −280.5 [d, *J*(F^5F^6) 22.0 Hz, 1 F, W–F].

X-Ray analyses

Measurements were made at 24 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatised Mo-Kα radiation, λ = 0.710 73 Å. Similar experimental methods were used for both analyses. Details for complex **4** are given, followed by those for **5** in square brackets if different. The crystal specimen was a red needle with dimensions 0.56 × 0.24 × 0.20 mm [dark red plate, 0.52 × 0.44 × 0.28 mm].

Crystal data. $C_{22}H_{18}F_{12}MoO_4S$, M = 702.36, monoclinic [triclinic], space group $P2_1/c$ [$P\bar{1}$], a = 10.496(4), b = 15.881(3), c = 15.733(6) Å, β = 103.13(3)°, [a = 10.898(3), b = 16.120(4), c = 17.482(4) Å, α = 63.80(2), β = 73.11(2), γ = 71.44(2)°], U = 2554(2) [2572(1)] Å^3, Z = 4, D_c = 1.827 [1.814] g cm^{-3}, $F(000)$ = 1392, μ(Mo-Kα) = 6.9 cm^{-1}.

Measurements. Cell dimensions are based on the setting angles of 23 reflections with $12 < \theta < 15$ [14]°. The intensities of 6396 [7171] reflections with $\theta < 25.0$ [22.0], h 0–12, k −18 to 3, l − 18 to 18 [h − 11 to 11, k − 17 to 17, l − 18 to 2] were estimated from ω–2θ scans and corrected for Lorentz polarisation and absorption effects (empirical correction factors on F 0.63–1.20 [0.78–1.17]).[39] On averaging 1316 [903] duplicate measurements (R_{int} = 0.048 [0.029]) the intensities for 4470 [6268] unique reflections were obtained. Further calculations used only the 2881 [4602] unique reflections with $I > 3\sigma(I)$.

Structure analysis. The structures were solved by Patterson and Fourier methods. Refinements on F with $w = 1/\sigma^2(F)$ of 361 [721] parameters (Tables 2 and 3) converged ($\Delta/\sigma < 0.06$ [0.09]) at R = 0.046 [0.044], R' = 0.054 [0.060]. Anisotropic U_{ij} were used for all non-H atoms. The hydrogen atom positions were calculated[j] using stereochemical criteria, the orientations of methyl groups being determined from difference syntheses; H atoms rode on their parent C atoms with C–H 0.96 Å and $U(H) \approx 1.2U_{eq}(C)$. Final |Δρ| values were < 1.2 [0.63] e Å^{-3}.

The asymmetric unit of complex **5** contains two crystallographically independent molecules (A and B). The pseudo-symmetry operation $-\frac{1}{2} + x + y + z, \frac{1}{2} - y, \frac{1}{2} - z$ maps molecule B onto A and a least-squares fit of the non-hydrogen atoms of B onto the corresponding atoms of A gives a root-mean-square (r.m.s.) deviation of only 0.033 Å. The molecules are thus structurally very similar. Although crystals of **5** are metrically triclinic the molecular arrangement approximates to one based on the monoclinic space group $I2/a$; the transformation to the pseudo-monoclinic cell is $a' = -b + c$, $b' = a$, $c' = -a + b + c$. The GX package[40] was used for all calculations. Scattering factors and anomalous dispersion corrections were taken from ref. 41.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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