Syntheses and Reactions of η^2-Vinyl Complexes of Molybdenum and Tungsten $[M(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)(PR_3)\}(CF_3C{\equiv}CCF_3)(cp)]$ and $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)(SPr^i)\}(CF_3C{\equiv}CCF_3)(cp)]$ (cp = η-C_5H_5)

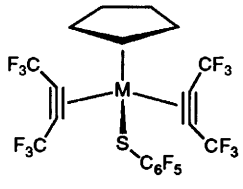
N. M. Agh-Atabay (in part), Laureano J. Canoira, Laurence Carlton and Jack L. Davidson *
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

Reactions of bis(hexafluorobut-2-yne) complexes $[M(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(cp)]$ (M = Mo, **1a**; or W, **1b** with tertiary phosphines and phosphites (L) give η^2-vinyl complexes $[M(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(cp)]$ **3** [(M = Mo or W; L = PEt_3, PMe_2Ph or $PMePh_2$; M = W, L = $P(OMe)_3$] as a result of attack at an alkyne carbon. Several isomeric forms of complexes **3** have been detected by NMR spectroscopy. Reactions of phosphines with the η^2-C,C vinyl complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(cp)]$ **2** in contrast give η^4-butadienyl derivatives $[Mo\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)(SPr^i)\}L(cp)]$ **4** (L = PEt_3, PMe_2Ph, or $MeC{\equiv}CPPH_2$) apparently as a result of insertion of the alkyne into the M=C bond of the η^2-C,C vinyl. A similar complex **4** is obtained when **3** (M = Mo, L = PMe_2Ph) is allowed to isomerise in diethyl ether at room temperature. In contrast **3** (M = Mo, L = PMe_2Ph) isomerises in refluxing hexane to the tetrakis(trifluoromethyl)cyclobutadiene complex $[Mo(SC_6F_5)(PMe_2Ph)\{\eta^4\text{-}C_4(CF_3)_4\}(cp)]$ **9**. An alternative isomerisation process is observed in diethyl ether at 18 °C where the product $[MoF\{\eta^3\text{-}C(CF_2)C(CF_3){=}C(CF_3)C(CF_3)(SC_6F_5)\}L(cp)]$ **8** (L = PEt_3 or PMe_2Ph) results from linking of two $CF_3C{\equiv}CCF_3$ ligands and a C_6F_5S group and fluorine transfer from a CF_3 to the metal. Fluxional behaviour in complexes **3**, **8** and **9** has been studied by ^{19}F NMR spectroscopy.

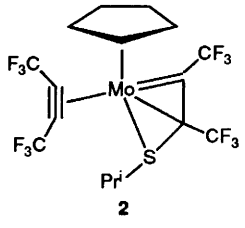
Previously we reported that addition of phosphines to bis(hexafluorobut-2-yne) complexes $[MX(CF_3C{\equiv}CCF_3)_2(cp)]$ (M = Mo or W; X = Cl; M = W; X = 4-MeC_6H_4S; cp = η-C_5H_5) gives η^2-vinyl derivatives as a result of attack at an alkyne carbon.[1] A similar reaction is observed on addition of phosphines to monoalkyne derivatives $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(cp)]$ at low temperatures except that, at room temperature, the phosphine subsequently migrates onto the metal and displaces the carbonyl ligand.[2] This interesting substitution mechanism prompted us to investigate the reactions of bis(alkyne) derivatives $[M(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(cp)]$ (M = Mo, **1a**; or W, **1b**)[3] and the related η^2-vinyl complexes $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(cp)]$ **2**[4] with phosphines as will now be described. Some of this work has been published previously as preliminary.[1,5]

Results and Discussion

Addition of tertiary phosphines L = PEt_3 or PMe_2Ph to bis(alkyne) complexes $[M(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(cp)]$ (M = Mo, **1a**; or W, **1b**) in diethyl ether at or below room temperature results in an immediate colour change from deep purple **1a** or orange **1b** to yellow and, on addition of hexane, yellow-orange crystalline complexes **3a**, **3b**, **3d** and **3e** were obtained in good yield. The reaction of **1b** with $PMePh_2$ at 0 °C similarly gave **3f** but with $P(OMe)_3$ it was necessary to cool the solution to −20 °C and use a larger excess of the ligand before the 1:1 adduct **3g** could be obtained. NMR studies (see below) revealed that this is due to the fact that **3g** dissociates in solution to give an equilibrium mixture of **1b**, **3g** and $P(OMe)_3$. The corresponding molybdenum complex was not obtained on addition of $P(Ome)_3$ to **1a**, the reaction giving intractable products, even at low temperature. The reaction of **1a** and $PMePh_2$ also gave a simple 1:1 adduct **3c** but only at lower temperatures (−20 °C) since this rearranges readily in solution at ambient temperature to give a light green solid **4a**.



1a M = Mo
1b M = W



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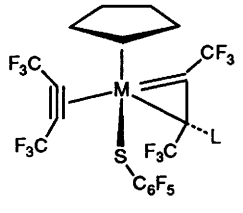
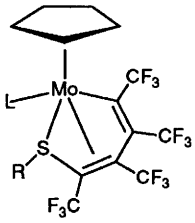


L	M = Mo	W
PEt_3	**3a**	**3d**
PMe_2Ph	**3b**	**3e**
$PMePh_2$	**3c**	**3f**
$P(OMe)_3$		**3g**



R	L
4a C_6F_5	$PMePh_2$
4b Pr^i	PEt_3
4c Pr^i	PMe_2Ph
4d Pr^i	$MeC{\equiv}CPPh_2$
4e Pr^i	$PhC{\equiv}CPPh_2$

Complexes **3** are reasonably soluble in polar solvents (CH_2Cl_2, $CHCl_3$) but less so in diethyl ether and are almost insoluble in hexane. They are only moderately air sensitive in the solid state but more so in solution. Interestingly, in a parallel study of the reactions of **1a** and related compounds with oxygen we obtained the oxo complex $[Mo\{\sigma\text{-}C(CF_3){=}C(CF_3)(SC_6F_5)\}O(CF_3C{\equiv}CCF_3)(cp)]$.[4] This, on reaction with PEt_3 and PMe_2Ph at room temperature, also gave complexes **3a** and **3b** whilst with $PMePh_2$ the green complex **4a** was obtained.

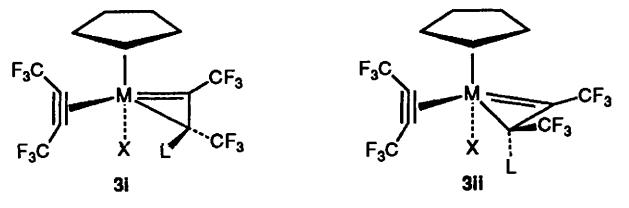


Fig. 1 Kinetic **3i** and thermodynamic **3ii** isomers of [MoCl{η^2-C(CF_3)C(CF_3)(PEt_3)}($CF_3C{\equiv}CCF_3$)(cp)]

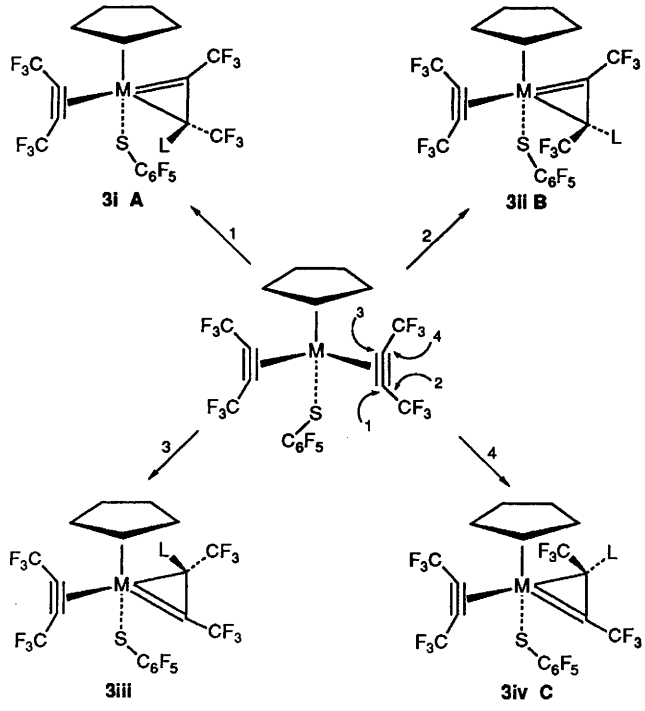


Fig. 2 Possible sites of nucleophilic attack in [M(SC_6F_5)($CF_3C{\equiv}CCF_3$)$_2$(cp)] **1** leading to isomeric forms of [M(SC_6F_5){η^2-C(CF_3)C(CF_3)(PR_3)}($CF_3C{\equiv}CCF_3$)(cp)] **3**

Complexes **3a** and **3b** were described in a recent publication,[4] but further studies concerning isomeric forms of the compounds are described herein.

Complexes **3a**–**3g** are assigned η^2-vinyl structures in view of similarities in stoichiometry and spectroscopic properties to those of [MX{η^2-C(CF_3)C(CF_3)L}($CF_3C{\equiv}CCF_3$)(cp)] obtained from reactions of phosphines and phosphites (L) with bis(alkyne) derivatives [MX($CF_3C{\equiv}CCF_3$)$_2$(cp)] (M = Mo, X = Cl; M = W, X = Cl or 4-MeC_6H_4S).[1] In some cases two isomeric forms were obtained (see Fig. 1), a kinetic isomer **3i** which can be transformed by heating in solution into a thermodynamically more stable form **3ii**. X-Ray diffraction studies of both isomers with M = Mo, L = PEt_3, X = Cl, established that the kinetic isomer results from nucleophilic attack at an alkyne carbon distal to both the cyclopentadienyl and chlorine ligands.[1a] The orientation of the resulting η^2-vinyl ligand is little different from that of the alkynes in the bis(alkyne) precursor, *i.e.* parallel to the M–Cl bond. However, isomerisation to the thermodynamic form **3ii** results in (*a*) reorientation of the η^2-vinyl ligand to lie approximatey perpendicular to the M–Cl bond and (*b*) inversion of stereochemistry at the chiral carbon bonded to phosphorus. Conformational preferences are also observed with η^2-vinyl derivatives obtained from reactions of H^- and carbon-based nucleophiles with the cationic monoalkyne complex [Mo(PhC≡CPh){$P(OMe)_3$}$_2$(cp)]$^+$ and related derivatives.[6]

The ^{19}F NMR spectra of the two forms of [MoCl{η^2-C(CF_3)C(CF_3)(PEt_3)}($CF_3C{\equiv}CCF_3$)(cp)][1a] are reasonably distinctive[1] and this enabled the structures of **3a**–**3g** to be assigned with some degree of confidence in most cases. The ^{19}F NMR spectra of **3a** and **3b** obtained from the oxo complex [Mo{σ-C(CF_3)=C(CF_3)(SC_6F_5)}O($CF_3C{\equiv}CCF_3$)(cp)] at room temperature[4] revealed the presence of small quantities of a kinetic isomer, the major peaks being due to the thermodynamic form. Previously we noted that isomerisation to the thermodynamic form occurs quite rapidly in solution at room temperature with thiolate derivatives [W(SC_6H_4Me-4){η^2-C(CF_3)C(CF_3)L}($CF_3C{\equiv}CCF_3$)(cp)][1c] and this proved to be the case with **3a** and **3b**. It was found that the proportion of the kinetic isomer of **3a** could be increased significantly by carrying out the reaction of **1a** and PEt_3 at 0 °C and crystallising the products rapidly at −15 °C following addition of hexane. However, this procedure produced little change in the isomer population of **3b** and its tungsten counterpart **3e**. In contrast the tungsten triethylphosphine derivative **3d** shows evidence for three isomeric forms in the ^{19}F NMR spectrum. This was also observed previously with [W(SC_6H_4Me-4){C(CF_3)C(CF_3)L}($CF_3C{\equiv}CCF_3$)(cp)] [L = PEt_3 or $P(OMe)_3$] where two kinetic forms rapidly isomerised to one thermodynamic form over a period of *ca.* 15 min at room temperature.[1c] However, in the case of **3d** the situation is different. Isomerisation was studied by ^{19}F NMR spectroscopy over a period of 60 h and at t = 0 three isomers were observed on addition of PEt_3 to **1b** at −25 °C. Isomer **A** exhibits a spectrum similar to the kinetic form of [MoCl{C(CF_3)C(CF_3)(PEt_3)}($CF_3C{\equiv}CCF_3$)(cp)] **3i** whereas the spectra of the other two isomers **B** and **C** are similar to those of the thermodynamic form. After 7 h at 18 °C the isomer population had changed from **A**:**B**:**C** = 33:57:10% to 2:87:11%. This indicates that the kinetic isomer **A** is converted into the thermodynamic form **B** exclusively since the concentration of the other thermodynamic form **C** remains essentially unaltered. This experiment was repeated with PEt_3 and compound **1a** but at −25 °C (t = 0) only one kinetic and one thermodynamic isomer of **3a** were observed, ratio 2:1. After 8 h at 18 °C this had changed to 1:10.

The simplest explanation for these observations is that, by analogy with [MoCl{η^2-C(CF_3)C(CF_3)(PEt_3)}($CF_3C{\equiv}CCF_3$)(cp)],[1a] the kinetic form of **3a**, **3b**, **3d** and **3e** has structure **3i** and the principal or sole thermodynamic form has structure **3ii**. The second (minor) thermodynamic form of **3d**, *i.e.* **C**, may therefore be related to **A** or **B** simply by rotation of the η^2-vinyl ligand about the metal–ligand axis, by inversion of stereochemistry at the chiral carbon, or by a combination of both. Interestingly, we note that although **A** is converted to **B** in solution, neither **A** nor **B** is transformed into **C**. Moreover, all three isomers are produced at −25 °C but the isomerisation **A** ⟶ **B** did not occur at this temperature. This possibly indicates that attack by PEt_3 on **1b** can occur in three different ways. As Fig. 2 shows, four sites of attack are available but molecular graphics[7] studies suggest that one of these **3iii** is sterically less probable.

Route 1 produces isomer **3i**, *i.e.* **A** directly, which implies that **B** and **C** may be equated with **3ii** and **3iv**. If this explanation is correct a high rotational barrier must exist sufficient to prevent facile interconversion of rotational isomers **B** and **C**. Extended-Hückel calculations of the model η^2-vinyl complex [Mo(η^2-$CHCH_2$){$P(OH)_3$}$_2$(cp)] have previously been carried out[6] and suggest that the electronic barrier to η^2-vinyl rotation should be relatively low. However, Templeton and co-workers[8] suggested that steric crowding may play an important role in determining orientational preferences in η^2-vinyl complexes. This is supported by molecular graphics[9] studies of both isomers of [MoCl{η^2-C(CF_3)C(CF_3)(PEt_3)}($CF_3C{\equiv}CCF_3$)(cp)] which, purely on the basis of van der Waals interactions, predict rotational minima for the η^2-C(CF_3)C(CF_3)(PEt_3) ligand in complete agreement with the observed orientation in the solid state. Conceivably steric interactions may be large enough to prevent interconversion of rotational isomers in complexes **3**.

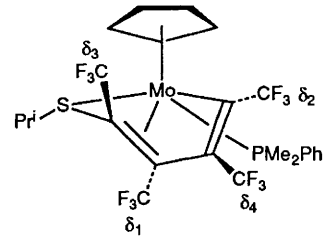
The situation with η^2-vinyl complexes derived from **1a** or **1b** and PMe_2Ph and $P(OMe)_3$ is complicated by molecular rearrangements, **3c**, fluxional behaviour, **3f**, and ligand dissoci-

ation, **3f** or **3g**. In the case of the tungsten complexes **3f** and **3g** an equilibrium exists between **1b**, the product (**3f** or **3g**) and free PMe_2Ph or $P(OMe)_3$. At −20 °C the equilibrium is almost entirely in favour of **3f** or **3g** which exist in two isomeric forms ratio 16:1 and 17:1 (thermodynamic, **3ii**:kinetic, **3i**) respectively. Moreover, in the case of **3f**, as the temperature is reduced further the major (thermodynamic) isomer peaks broaden and split into two sets of broad resonances at −50 °C. This clearly indicates that exchange between two forms of the major isomer occurs in solution. This has been noted previously with related derivatives $[MCl\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(cp)]$ (M = Mo or W; L = PMe_2Ph or $PMePh_2$)[1a] where exchange was observed between three forms of isomer **3ii** but one of the forms was only present in very small quantities. Consequently we cannot rule out the possibility that a third form is also present with **3f(ii)** but could not be observed because of the poor signal:noise ratio of the spectra.

Originally[1a] we tentatively suggested that the fluxional behaviour involved exchange between two isomers of **3ii** with different η^2-vinyl orientations, each of which has, in principle, two epimeric forms resulting from the chirality of the metal and one of the carbons of the η^2-vinyl ligand. This assumed that one of the forms was precluded by steric factors. At the present time we have not yet confirmed this proposal; indeed an alternative explanation is possible based on the fact that the phenomenon has only ever been observed with PMe_2Ph and $PMePh_2$ and never with phosphines PR_3 with a pseudo-three-fold axis of symmetry. This suggests that the isomerism and fluxional behaviour may be a consequence of restricted rotation of the phosphine about the C–P bond of the η^2-vinyl ligand which gives rise to three distinct isomers at low temperatures. Studies designed to distinguish between these two explanations are being carried out at present and will be reported in a later publication.

The reaction of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(cp)]$ with $PMePh_2$ in diethyl ether at room temperature does not give the η^2-vinyl complex **3c**; instead a green powder **4a** was obtained with the same stoichiometry. It was subsequently established that allowing solutions of **3c** to stand at room temperature resulted in isomerisation to give **4a** in moderate yield. The stoichiometry was confirmed by elemental analysis although the highest peak in the mass spectrum corresponds to $[M - PMePh_2]^+$. The IR spectrum does not contain a ν(C≡C) mode although a peak at 1620 cm^{-1} indicates the presence of a free C=C bond. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a single peak at δ 25.78 characteristic of a metal-co-ordinated $PMePh_2$ ligand and this is confirmed by the doublet splitting of the $\eta^5\text{-}C_5H_5$ resonance in the ^1H NMR spectrum, J_{PH} = 1.5 Hz. These data and the ^{19}F NMR spectrum did not uniquely define a structure for **4a** and all attempts to grow crystals for X-ray diffraction studies failed. However, it was found that similar complexes **4b** and **4c** are obtained from the reactions of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)(SPr^i)\}(CF_3C{\equiv}CCF_3)(cp)]$ **2** with PEt_3 and PMe_2Ph in Et_2O at −20 °C. In both cases dark purple crystals were isolated in 50 and 53% yield respectively. These yields are reduced significantly if the reactions are carried out at higher temperatures since the complexes proved to be unstable in solution. Suitable crystals of **4b** were obtained for X-ray diffraction studies by crystallisation from dichloromethane–hexane at −20 °C. These studies (reported elsewhere)[5] established that phosphine co-ordination to the metal had occurred resulting in formation of a butadienyl ligand, $\eta^4\text{-}C(CF_3){=}C(CF_3)\text{–}C(CF_3){=}C(CF_3)(SPr^i)$, bonded to the metal through C^1, C^3, C^4 and sulphur as illustrated.

The ^{19}F NMR data for compounds **4a**–**4c** can be interpreted in terms of the solid-state structure found for **4b**. For example **4a** and **4c** exhibit four equal-intensity CF_3 resonances whereas **4b** shows two sets of peaks ratio 5:1 indicating the presence of two isomers. Previously we synthesised and structurally characterised two isomers of $[W\{\eta^5\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)(SPr^i)\}(cp)]$ containing a η^3-$C(CF_3){=}C(CF_3)(SPr^i)$ moiety similar to that of **3b**.[10] Since the isomers differed only in the disposition of the thiolate substituent (due to inversion at sulphur) we propose a similar explanation for isomerism in **4b**. Homonuclear ^{19}F decoupling experiments were carried out on compound **4c** and, although all coupling connectivities could not be estabished, peak assignments (see Fig. 3 and Experimental section) were made on the basis that the planar *cis*-$C(CF_3){=}C(CF_3)$ unit probably gives rise to the larger J_{FF} value 10.1 Hz.[11] Interestingly, irradiation of the highest-field peak δ_4 transforms the multiplet δ_1 at −41.46 into a doublet which presumably results from coupling to phosphorus (J_{PF} = 7.5 Hz). Molecular graphics studies[7] revealed that in **4b** the CF_3 on C^1 is significantly closer to phosphorus than any of the other three trifluoromethyl groups suggesting that a through-space coupling mechanism may be operating.



δ_1 (dq), J_{PF} 7.5, $J_{1\text{–}4}$? Hz
δ_2 (q), $J_{2\text{–}4}$ 10.1 Hz
δ_3 (s)
δ_4 (qq), $J_{4\text{–}2}$ 10.1, $J_{1\text{–}4}$? Hz

Fig. 3 Fluorine-19 NMR coupling connectivities for $[Mo\{\eta^4\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i\}(PMe_2Ph)(cp)]$ **4c**

Homodecoupling experiments on compound **4a** produced similar results except that the phosphorus–fluorine coupling was not resolved whereas coupling between CF_3 (δ_3) and CF_3 (δ_4) was (J_{FF} = 2.5 Hz). Additional features were observed, in particular coupling between CF_3 (δ_3) and the C_6F_5 *ortho*-fluorines. Moreover, the spectrum is temperature dependent which affects the nature of this coupling. As Fig. 4 shows, two CF_3 resonances vary with temperature; δ_1 is a well resolved multiplet at 50 °C (doublet of quartets?) but broadens at lower temperatures and disappears into the baseline at −95 °C. We attribute this to slowing of CF_3 rotation as observed in other fluorocarbon complexes we have studied previously.[12] More significantly δ_2 exhibits triplet coupling (J_{FF} = 14.2 Hz) to two equivalent C_6F_5 *ortho*-fluorines at 50 °C. However, at lower temperatures this changes to a broad doublet (J_{FF} = 28.4 Hz) indicating that only one *ortho*-fluorine couples under these conditions. Dynamic ^{19}F NMR studies of the C_6F_5 region showed that at lower temperatures restricted rotation about the C_6F_5–S bond results in one preferred orientation being adopted such that two *ortho*-fluorine signals are observed and only one of these, the lower-field multiplet at δ −132.35, couples to CF_3 (δ_2). We have previously reported evidence for restricted rotation of this type in SC_6F_5 derivatives.[13]

In earlier studies we observed that complex **1** and its tungsten analogue react with alkynes to give alkyne trimerisation products including $[W\{\eta^5\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)(SPr^i)\}(cp)]$.[10] In view of this **1** was treated with phosphinoalkynes $RC{\equiv}CPPh_2$ (R = Me or Ph). However, both reactions gave complexes **4d** and **4e** with similar spectroscopic data to go to those of phosphine derivatives **4a**–**4c**. This suggests that the phosphinoalkynes are preferentially functioning as phosphines rather than alkynes, *i.e.* they are co-ordinating to the metal *via* phosphorus rather than undergoing oligomerisation with the alkynes. This is confirmed by the IR spectra which in each case shows a sharp peak near 2200 cm^{-1} attributable to the C≡C stretching mode of the uncoordinated alkyne function. A variety of complexes are known in which this mode of co-ordination is found

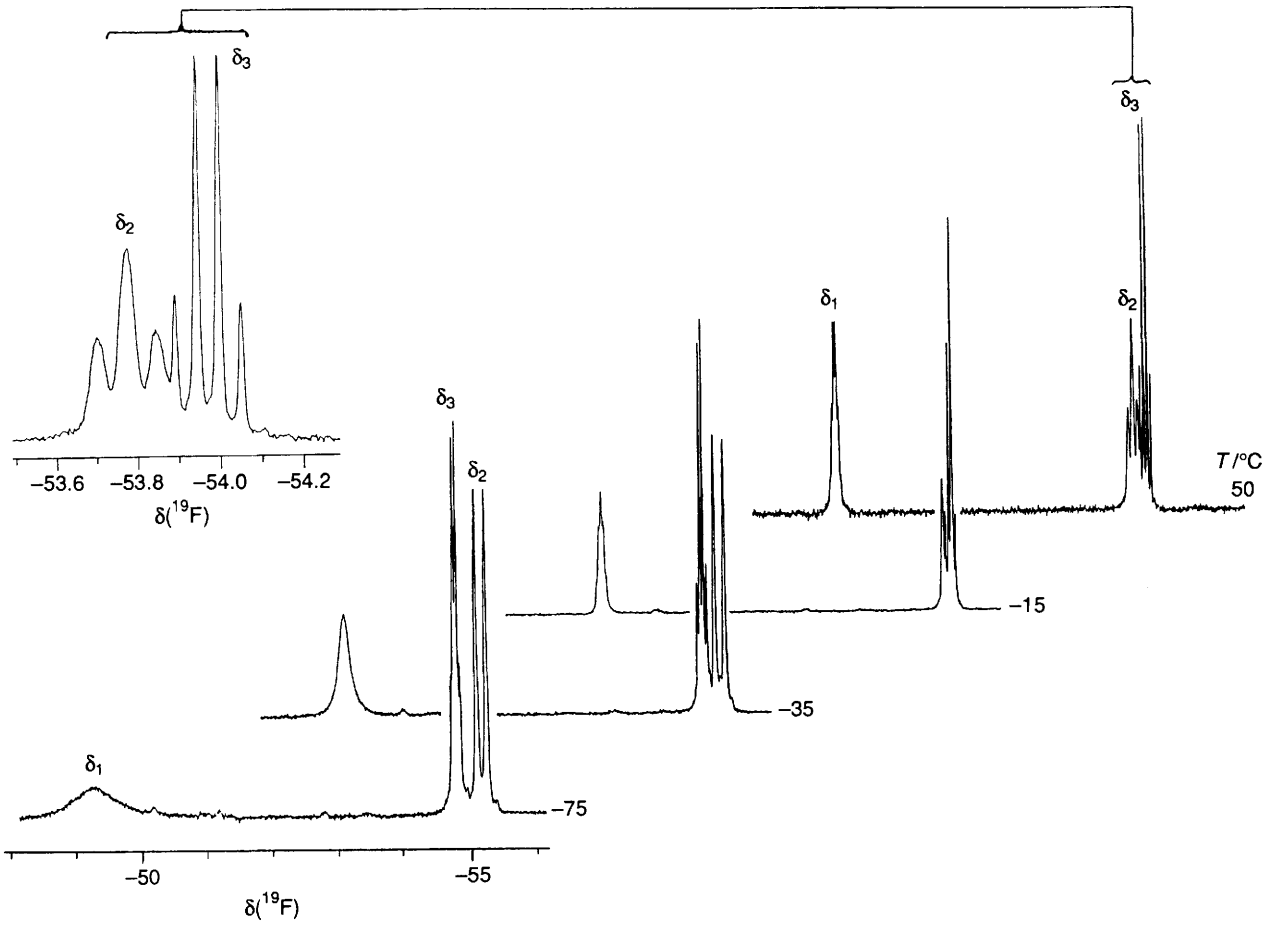
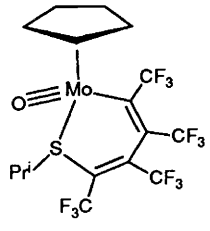


Fig. 4 Variable-temperature ^{19}F NMR spectra of $[Mo\{\eta^4\text{-}C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SC_6F_5)\}(PMePh_2)(cp)]$ **4a** in CD_2Cl_2 (−75 to 15 °C) and $CD_3C_6D_5$ (+55 °C). δ_4, which is temperature invariant, is omitted for clarity



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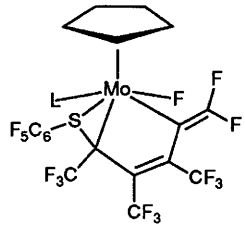
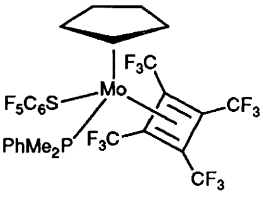
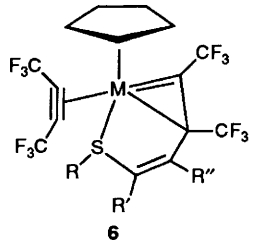


8a L = PEt_3
8b L = PMe_2Ph





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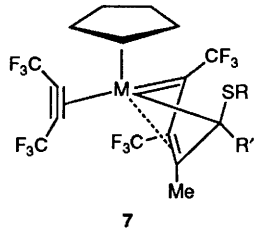
M	R	R′	R″
Mo	Pr^i	Ph	Me
W	Me	Ph	Me
W	Pr^i	Ph	Me
W	Me	Me	Me
W	Me	Et	Et
W	Pr^i	Et	Et
W	Me	Ph	Ph



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M	R	R′
Mo	Pr^i	Ph
Mo	Pr^i	Me
W	Me	Me
W	Pr^i	Me
W	Bu^t	Me

including the P-co-ordinated derivative $[W\{\sigma\text{-}SC(CF_3)=C(CF_3)H\}(\sigma\text{-}PhC{\equiv}CPPh_2)(CF_3C{\equiv}CCF_3)(cp)]$ obtained by addition of $PhC{\equiv}CPPh_2$ to the alkyne complex $[W\{\eta^3\text{-}SC(CF_3)=C(CF_3)H\}(CF_3C{\equiv}CCF_3)(cp)]$[14] which is structurally related to complex **2**. Interestingly another P-co-ordinated tungsten(II) derivative $[W(S_2CNMe_2)_2(CO)_2(\sigma\text{-}PhC{\equiv}CPPh_2)]$ has been found to rearrange to the η^2-C≡C bonded form $[W(S_2CNMe_2)_2(CO)(\eta^2\text{-}PhC{\equiv}CPPh_2)]$ on loss of carbon monoxide.[15]

It is interesting to compare the structure of **4b** with those of other butadienyl complexes we have reported previously. Of particular relevance are **5**,[5] **6**[16] and **7**[16] since these derivatives also result from addition of ligands to η^2-vinyl complexes **2**. This illustrates that butadienyl ligands are able to modify their mode of co-ordination in a variety of ways to accommodate the requirements of the metal. For example in **5** the O^{2-} is a six-electron donor and an η^2 four-electron donor butadienyl ligand is required in order that an 18-electron configuration is attained. In **4**, **6** and **7** the η^4-butadienyl is a six-electron ligand but this is achieved in three different ways. Interestingly the butadienyl ligand in compound **4** exhibits a σ-vinyl mode of bonding whereas in **6** the alternative η^2 mode of co-ordination

is found. This presumably reflects the effects of the different ancillary ligands attached to the metal. Moreover, the fact that **6** has been observed to isomerise into **7** with particular combinations of metal and substituents R and R′ indicates that in some circumstances the energy surface connecting the different isomers is quite shallow.[16]

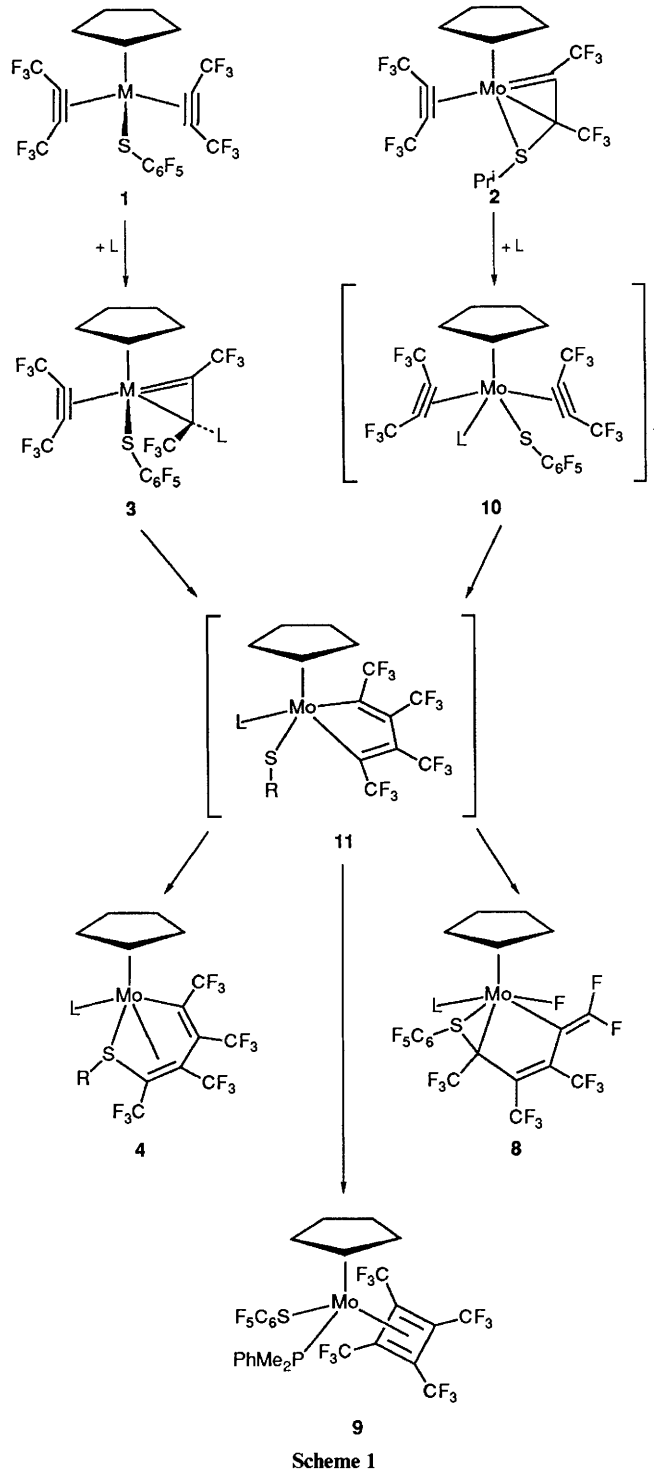
In view of the fact that the η^2-vinyl complex **3c** readily isomerises at room temperature in solution attempts were made to induce isomerisation of other complexes of type **3** with varying degrees of success. For example molybdenum derivatives **3a** and **3b** also rearrange in diethyl ether at room temperature but much more slowly than **3c** (48 h rather than 5 h) and also give different products **8a** and **8b**. Attempts to induce isomerisation of the tungsten complex **3d** were only partially successful. After 48 h in diethyl ether a small quantity of an impure solid was obtained which exhibited similar ^{19}F NMR features to those of **8a** and **8b**. Attempts to purify the product were unsuccessful and no further characterisation was carried out.

The molybdenum compounds **8a** and **8b** are red-purple solids, soluble in polar organic solvents and moderately air-sensitive in solution. They have the same stoichiometry as the precursors according to elemental analysis but appear to have quite different molecular structures. The spectroscopic data are in accord with the novel structure **8** in which a fluorine has undergone transfer from CF_3 to the metal. This accounts for the strong band in the IR spectra near 1660 cm^{-1} assigned to the ν(C=C) mode of a polar $C{=}CF_2$ group. Similar bands have been observed with other complexes containing such groupings, *e.g.* $[WF\{\eta^5\text{-}C{=}CF_2C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)(SPr^i)\}(cp)]$[10] and $[M\{\eta^3\text{-}C{=}CF_2C(CF_3)C(CF_3)C(CF_3)CO\}(CO)_2(cp)]$ (M = Mo or W).[17] The former, which has been structurally characterised by X-ray diffraction studies, also results from internal fluorine transfer from CF_3 to the metal, the latter from fluorine abstraction by another metal complex $[Co_2(CO)_8]$. The structural relationship between **8** and $[WF\{\eta^5\text{-}C{=}CF_2C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)(SPr^i)\}(cp)]$ is obvious and both give rise to similar features in the ^{19}F NMR spectra. The most distinctive of these is a broad resonance due to a single fluorine in a region of the spectrum, *ca.* δ −270, characteristic of a metal-co-ordinated fluorine. The region δ −40 to −60 contains five resonances in ratio 1:1:3:3:3 due to the two CF_2 fluorines and the three CF_3 groups. Two CF_3 peaks show distinct coupling to a unique but different fluorine nucleus $J(F\text{–}CF_3)$ = *ca.* 30 Hz in one case and *ca.* 20 Hz in the other. Apart from this none of the peaks shows well resolved couplings at 20 °C. This is in part a consequence of fluxional processes since at lower temperatures two types of change are observed in the spectra. The first of these, which is observed with both **8a** and **8b**, involves broadening of the CF_3 doublet with $J(F\text{–}CF_3)$ = *ca.* 30 Hz and eventual collapse into the baseline at below *ca.* −40 °C. We ascribe this to restricted rotation of the CF_3 about the CF_3–C bond and have observed this previously in $[WF\{\eta^5\text{-}C{=}CF_2C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)(SPr^i)\}(cp)]$[10] and several other compounds derived from **1** and **2**.[16] The other phenomenon is only found with **8b**, perhaps reflecting greater steric congestion in the PMe_2Ph derivative, and involves broadening of the signals at lower temperatures, ultimately splitting into two sets of peaks. This is consistent with the presence of two isomers which undergo fast exchange at room temperature. Tentatively this is attributed to inversion at the pyramidal sulphur and is a recurring feature of complexes containing metallacycles resulting from co-oligomerisation of the fluorocarbon ligands and the thiolate group in complexes **1** and **2**. In some cases, *e.g.* **4** and $[W\{\eta^5\text{-}C(CF_3){=}C(CF_3)C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)(SPr^i)\}(cp)]$,[10] no exchange between the isomers is observed at room temperature suggesting that the barriers to inversion may be relatively high. In other cases, *e.g.* **6**[16], exchange is rapid at 20 °C and both isomers are only detected at low temperatures.

Interestingly, the isomerisation of compound **3b** proved to be solvent dependent since on refluxing in hexane for 5 h an impure solid was obtained which, after several crystallisations, yielded small quantities of a red-brown microcrystalline solid **9**. As with **8b** no ν(C≡C) modes are present in the IR spectrum, although significantly the ν(C–F) region is much simpler in appearance. The ^1H NMR spectrum contains two PMe_2Ph doublets, aromatic signals and an $\eta^5\text{-}C_5H_5$ resonance which shows a doublet splitting with phosphorus, J_{PH} = 1.8 Hz. The ^{19}F NMR spectrum is more definitive, being temperature dependent between 60 and −80 °C. At 60 °C the CF_3 region shows one broad peak at δ −52.56 but as the temperature is reduced this broadens and splits into four equal-intensity resonances. At −20 °C one signal is still unresolved, two are septets (quartets of quartets, J_{FF} *ca.* 4 Hz), whilst the fourth is a broad triplet, J_{FF} = 17.3 Hz. Little change is observed in the C_6F_5 region over this temperature range but homodecoupling experiments revealed that, as with **4a**, the triplet structure of the peak at δ −52.42 is due to coupling with the C_6F_5 *ortho*-fluorines. The smaller coupling observed with the other CF_3 groups and the dynamic NMR behaviour is very similar to that found with $[MoI(CO)\{\eta^4\text{-}C_4(CF_3)_4\}(cp)]$[18a] and related complexes containing an η^4-tetrakis(trifluoromethyl)cyclobutadiene ring. In the case of $[Mo(S_2CNMe_2)\{\eta^4\text{-}C_4(CF_3)_4\}(cp)]$[18b] the structure has been solved by X-ray diffraction methods.[19] In the solid state the C_4 ring adopts a staggered conformation with two CF_3 groups related by a molecular plane of symmetry. This situation is maintained in solution at low temperatures giving rise to three septets (J_{FF} *ca.* 4 Hz) in the ^{19}F NMR spectrum but these collapse to a broad singlet above *ca.* −15 °C. Four septets are obtained with less-symmetric derivatives, *e.g.* $[MoI(CO)\{\eta^4\text{-}C_4(CF_3)_4\}(cp)]$ and, by analogy with the structurally characterised phenylcyclobutadiene analogues $[MoI(CO)(\eta^4\text{-}C_4Ph_4)(cp)]$[17] and $[MoCl(CO)(\eta^4\text{-}C_4Ph_3Me)(cp)]$,[20] a staggered conformation seems likely for this compound also. Accordingly we propose a cyclobutadiene structure for **9** with a staggered conformation at low temperature. Molecular graphics studies of compound **9** constructed from the atomic co-ordinates of $[MoI(CO)(\eta^4\text{-}C_4Ph_4)(cp)]$ and $[Mo(S_2CNMe_2)\{\eta^4\text{-}C_4(CF_3)_4\}(cp)]$ indicate that the C_6F_5 group will be closer to the CF_3 distal to the cyclopentadienyl ligand than any of the other CF_3 groups. Through-space coupling can therefore account for the triplet splitting of the peak at δ −52.42. As with other $\eta^4\text{-}C_4(CF_3)_4$ complexes[18] rapid rotation of the cyclobutadiene ring must occur at higher temperatures leading to total CF_3 exchange which results in a CF_3 singlet.

The results of these studies illustrate that addition of phosphines (L) to the η^2-C,C vinyl complex **2** gives oligomerisation products **4** resulting from nucleophilic attack at the metal. This contrasts with addition to the tungsten analogues $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SR)\}(CF_3C{\equiv}CCF_3)(cp)]$ (R = Pr^i or Bu^t) where η^2-vinyl complexes $[W\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(SR)(CF_3C{\equiv}CCF_3)(cp)]$ are obtained as a result of attack at carbon.[1b,c] However, addition of phosphines to bis(alkyne) complexes **1** occurs preferentially at an alkyne carbon to give η^2-vinyl derivatives **3**. Subsequent thermal rearrangement gives three different types of complex **4**, **8** or **9** which have two features in common, (*a*) the phosphine has transferred to the metal and (*b*) linking of the two $CF_3C_2CF_3$ groups has occurred. Moreover, in two cases, **4** and **8**, the thiolate group has migrated on to the resulting fluorocarbon ligand. It is possible to rationalise formation of the three products in terms of a common mechanism as illustrated in Scheme 1.

The key feature is phosphine transfer to the metal which generates a bis(alkyne) intermediate **10**. As Otsuka and Nakamura[21] pointed out many years ago bis(alkyne) complexes such as **1** are stabilised towards alkyne oligomerisation by the fact that both sets of filled C≡C π orbitals are involved in bonding with the metal, *i.e.* the alkynes formally function as three-electron donors. However, as a result of phosphine co-ordination to the metal the alkynes in **10** revert to the more conventional two-electron donor mode and, as a consequence,



Scheme 1

become activated towards oligomerisation. The most probable result in the present case is metallacyclisation to give **11** with a structure similar to that of isocyanide complexes $[W\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(SR)(CNR')(cp)]$[12,22] isolated from the reactions of η^2-C,C vinyl complexes $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SR)\}(CF_3C{\equiv}CCF_3)(cp)]$ (R = Me, Pr^i or Bu^t) with isocyanides CNR′ (R′ = Bu^t, Me, Ph or 4-MeC_6H_4).

In order to test this hypothesis the reaction of the η^2-C,C vinyl derivative **2** with PEt_3 was followed by ^{19}F NMR spectroscopy over the temperature range −50 to 20 °C. This established that an intermediate is formed at −50 °C with spectroscopic features similar to those of the isocyanide metallacycles. The intermediate exhibits four distinct CF_3 resonances, a broad multiplet at δ −47.44, a quartet of δ −50.58 (J_{FF} = 13.3 Hz) and two septets (quartets of quartets) at δ −53.04 (J_{FF} = 13.6 Hz) and −57.9 (J_{FF} = 14.7 Hz). This compares closely with ^{19}F NMR data for the metallacycle $[W\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(SPr^i)(CNC_6H_4Me\text{-}4)(cp)]$[22] *viz.* δ_1 −45.33 (q, J_{FF} = 15.2), δ_2 −53.41 (q, J_{FF} = 14.4), δ_3 −54.17 (spt, J_{FF} = 14.8) and δ_4 −57.65 (spt, J_{FF} = 15.3 Hz). Subsequent reductive ring closure leads to the cyclobutadiene complex **9**, a reaction which has known precedents in organometallic chemistry.[23] Alternatively, migration of the thiolate ligand onto an α carbon of the metallacycle **11** readily explains the formation of the butadienyl derivatives **4** and, following fluorine transfer to the metal, complex **9**. The latter process presumably occurs as a result of close approach of the appropriate CF_3 to the metal, perhaps leading *via* an agostic M–C–F interaction to fluorine transfer. This is consistent with the fact that a number of C–F interactions with metals have been reported in recent years and in some cases fluorine transfer from carbon to a transition metal has been observed.[10,24]

Experimental

NMR spectra were recorded on a Bruker WP 200SY spectrometer at 200.13 (^1H) and 188.31 MHz (^{19}F). Coupling constants are in Hz and chemical shifts are referenced to $SiMe_4$ (^1H) 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 9 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 (hexane, diethyl ether) and distilled just before use. The complexes $[M(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(cp)]$ (M = Mo or W)[3] and $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)(SPr^i)\}(CF_3C{\equiv}CCF_3)(cp)]$[4] were synthesised as described previously.

Reactions of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(cp)]$ **1a**.—*With* PEt_3. A solution of PEt_3 in diethyl ether was added dropwise to a stirred solution of complex **1a** (70 mg) in diethyl ether (20 cm^3) at 0 °C until the purple colour just turned yellow. The solution was concentrated *in vacuo* when yellow crystals began to form. Hexane (10 cm^3) was added slowly and the mixture cooled to −15 °C. The resulting product was recrystallised from CH_2Cl_2–hexane to give yellow crystals of $[Mo(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(cp)]$ **3a** (66 mg, 81%) (Found: C, 36.7; H, 2.4. $C_{25}H_{20}F_{17}MoPS$ requires C, 37.4; H, 2.5%). IR ($CHCl_3$): ν(C≡C), isomer 1, 1790wm; isomer 2, 1758wm cm^{-1}. NMR ($CDCl_3$): ^1H, isomer 1, δ 1.18 (dt, J_{PH} 17.5, J_{HH} 7.6, 9 H, Me), 2.10 (m, CH_2, 6 H) and 5.73 (s, 5 H, C_5H_5); isomer 2, δ 1.23 (dt, J_{PH} 17.6, J_{HH} 7.6, 9 H), 2.28, 2.53 (m, 6 H, CH_2) and 5.57 (s, 5 H, C_5H_5); ^{19}F, isomer 1, δ −46.50 (m, 3 F), −49.89 (m, 3 F), −54.33 (br s, 3 F) and −56.86 (m, 3 F); isomer 2, δ −45.43 (m, 3 F), −52.06 (spt, 3 F), −53.61 (br q, *J* 4.0 Hz, 3 F) and −55.39 (spt, 3 F).

With PMe_2Ph. Complex **1a** (72 mg) and PMe_2Ph at −20 °C similarly gave yellow-brown crystals of $[Mo(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMe_2Ph)\}(CF_3C{\equiv}CCF_3)(cp)]$ **3b** (60 mg, 69%) (Found: C, 38.8; H, 1.7. $C_{27}H_{16}F_{17}MoPS$ requires C, 39.4; H, 2.0%). IR ($CDCl_3$): ν(C≡C) 1795 cm^{-1}. NMR ($CDCl_3$): ^1H, isomer 2, δ 2.25 (d, J_{PH} 13.1, 3 H, Me), 2.34 (d, J_{PH} 13.2, 3 H, Me), 5.57 (s, 5 H, C_5H_5) and 7.5–7.8 (m, 5 H, Ph); ^{19}F, −45.67 (br s, 3 F), −51.62 (spt, 3 F), −53.79 (br s, 3 F) and −55.48 (m, 3 F).

With $PMePh_2$ *at* −20 °C. Complex **1a** (74 mg) and $PMePh_2$ at −20 °C similarly gave yellow microcrystalline $[Mo(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMePh_2)\}(CF_3C{\equiv}CCF_3)(cp)]$ **3c** (69 mg, 72%) (Found: C, 42.9; H, 2.2. $C_{32}H_{18}F_{17}MoPS$ requires C, 43.45; H, 2.05%). IR (KBr): ν(C≡C) 1795wm cm^{-1}. NMR ($CDCl_3$, −30 °C): ^1H, δ 2.60 (br d, *J* 12.0 Hz, 3 H, Me), 5.52

(br s, 5 H, C_5H_5) and 7.4–7.9 (m, 10 H, Ph); ^{19}F, δ −43.41 (br s, 3 F), −52.20 (br s, 6 F) and −55.69 (br s, 3 F).

With $PMePh_2$ *at* 18 °C. A solution of complex **1a** (77 mg) in diethyl ether was treated with $PMePh_2$ when the solution turned yellow before gradually becoming a light murky green. It was cooled to −15 °C to give a light blue-green solid. A second crystallisation from dichloromethane–hexane at −15 °C gave 25 mg (24%) [Mo{η⁴-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SC_6F_5)}($PMePh_2$)(cp)] **4a**.

Reactions of [W(SC_6F_5)($CF_3C{\equiv}CCF_3$)$_2$(cp)] **1b**.—*With* PEt_3. Complex **1b** (47 mg) and PEt_3 at 0 °C similarly gave pale yellow crystals of [W(SC_6F_5){η²-C(CF_3)C(CF_3)(PEt_3)}($CF_3C{\equiv}CCF_3$)(cp)] **3d** (46 mg, 85%) (Found: C, 33.4; H, 2.1. $C_{25}H_{20}F_{17}PSW$ requires C, 33.70; H, 2.25%). IR ($CDCl_3$): 1760(sh) and 1750wm cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.2 (m, 9 H, Me), 1.9–2.6 (m, 6 H, CH_2), 5.68, 5.82, 6.04 (s, 5H, C_5H_5); ^{19}F, isomer 1, δ −45.97 (m, 3F), −53.09 (q, *J* 4.3, 3F), −53.52 (m, 3 F) and −56.41 (spt, 3 F); isomer 2, −46.65 (br s, 3 F), −51.36 (m, 3F), −53.18 (br s, 3 F) and −58.14 (m, 3 F); isomer 3, −48.16 (q, *J* 3.4, 3 F), −52.21 (q, *J* 4.6 Hz, 3 F), −54.41 (br s, 3 F) and −58.15 (m, 3 F); isomer 4, −46.15 (m, 3 F), −54.85 (spt, 3 F), −55.51 (spt, 3 F), one resonance obscured by major isomer peaks.

With PMe_2Ph. Complex **1b** (43 mg) and PMe_2Ph at 0 °C similarly gave pale yellow crystals of [W(SC_6F_5){η²-C(CF_3)C(CF_3)(PMe_2Ph)}($CF_3C{\equiv}CCF_3$)(cp)] **3e** (44 mg, 87%) (Found: C, 35.3; H, 1.7. $C_{27}H_{16}F_{17}PSW$ requires C, 35.55; H, 1.75%). IR ($CDCl_3$): ν(C≡C) 1770wm cm^{-1}. NMR ($CDCl_3$): ^{1}H, isomer 2, δ 2.21 (d, J_{PH} 13.0, 3 H, Me), 2.30 (d, J_{PH} 13.1, 3 H, Me), 5.63 (s, 5 H, C_5H_5) and 7.5–7.8 (m, 5 H, Ph); ^{19}F, −46.19 (br s, 3 F), −52.91 (br q, *J* 3.7 Hz, 3 F), −53.12 (spt, 3 F) and −56.47 (spt, 3 F).

With $PMePh_2$. Complex **1b** (68 mg) and $PMePh_2$ at 0 °C similarly gave pale yellow crystals of [W(SC_6F_5){η²-C(CF_3)C(CF_3)($PMePh_2$)}($CF_3C{\equiv}CCF_3$)(cp)] **3f** (43 mg, 51%) (Found: C, 39.1; H, 1.6. $C_{32}H_{18}F_{17}PSW$ requires C, 38.90; H, 1.80%). IR (KBr): ν(C≡C) 1765wm cm^{-1}. NMR ($CDCl_3$): ^{1}H, (−20 °C) δ 2.51 (d, J_{PH} 13.1 Hz, 3 H, Me), 5.62 (s, 5 H, C_5H_5) and 7.3–7.9 (m, 5 H, Ph); ^{19}F (19 °C), δ −44.25 (br m, 3 F), −50.59 (br m, 3 F), −53.58 (br m, 3 F) and −56.89 (br m, 3 F).

With $P(OMe)_3$. Complex **1b** (44 mg) and $P(OMe)_3$ at −20 °C similarly gave pale yellow crystals of [W(SC_6F_5){η²-C(CF_3)C(CF_3)P($OMe)_3$}($CF_3C{\equiv}CCF_3$)(cp)] **3g** (33 mg, 65%) (Found: C, 29.8; H, 1.7. $C_{22}H_{14}F_{17}PSW$ requires C, 29.45; H, 1.55%). IR (KBr): ν(C≡C) 1760wm cm^{-1}. NMR ($CDCl_3$, −20 °C); ^{1}H, major isomer, δ 3.95 (d, J_{PH} 11.5, 9 H, Me) and 5.85 (s, 5 H, C_5H_5); minor isomer, δ 3.85 (d, J_{PH} 11.5, 9 H, Me) and 5.75 (s, 5 H, C_5H_5); ^{19}F, major isomer, δ −47.66 (m, 3 F), −52.21 (br s, 3 F), −55.53 (br s, 3 F) and −56.73 (q, *J* 4.5, 3 F); major isomer, δ −49.83 (br m, 3 F), −53.20 (q, *J* 4.2, 3 F), −54.69 (m, 3 F) and −57.0 (br s, *J* 4.5 Hz, 3 F).

Thermal Rearrangement of [Mo(SC_6F_5){η²-C(CF_3)C(CF_3)($PMePh_2$)}($CF_3C{\equiv}CCF_3$)(cp)] **3c**.—A solution of complex **3c** (35 mg) in diethyl ether (20 cm^3) was stirred at room temperature for 5 h. Hexane (10 cm^3) was added, the solution concentrated *in vacuo* and on cooling to −15 °C a purple solid was obtained. This was recrystallised from dichloromethane–hexane to give a light green powder. [Mo{η⁴-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SC_6F_5)}($PMePh_2$)(cp)] **4a** (19 mg, 56%) (Found: C, 43.7; H, 2.6; P, 3.5; S, 3.4. $C_{32}H_{18}F_{17}MoPS$ requires C, 43.4; H, 2.05; P, 3.50; S, 3.60%). IR ($CDCl_3$): ν(C=C) (C_6F_5) 1640w, ($CF_3C{=}CCF_3$) 1620w cm^{-1}. NMR: ^{1}H ($CDCl_3$, −20 °C), δ 2.23 (d, J_{PH} 7.8, 3 H, Me), 4.86 (d, J_{PH} 1.5, 5 H, C_5H_5) and 7.2–7.7 (m, 10 H, Ph); ^{19}F (CD_2Cl_2, 18 °C), δ_1 −49.52 (m, 3 F), δ_2 −54.47 ('filled-in' doublet, 3 F), δ_3 −54.73 (q, *J* 9.7 Hz, 3 F), δ_4 −64.46 (m, 3 F), −132.35 (m, 1 F, *o*-F of C_6F_5), −136.60 (m, 1 F, *o*-F of C_6F_5), −150.0 (m, 1 F, *p*-F of C_6F_5) and −159.39 (m, 2 F, *m*-F of C_6F_5).

Reaction of [Mo{η²-C(CF_3)C(CF_3)(SPr^i)}($CF_3C{\equiv}CCF_3$)(cp)] **2**.—*With* PEt_3. Triethylphosphine (25 mg) in diethyl ether (5 cm^3) was added slowly to a solution of complex **2** (80 mg) in diethyl ether (40 cm^3) at −20 °C. The orange-yellow solution darkened immediately and the reaction was allowed to proceed for 15 min. After this time the mixture was concentrated *in vacuo* and cold hexane (*ca.* 8 cm^3) added slowly at −20 °C. Purple-black crystals formed slowly and these were collected and washed with several portions of cold hexane to give 48 mg (50%) [Mo{η⁴-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SPr^i)}(PEt_3)(cp)] **4b** (Found: C, 41.2; H, 4.1; P, 4.5; S, 5.1. $C_{22}H_{27}F_{12}MoPS$ requires C, 40.85; H, 4.20; P, 4.80; S, 4.95%). IR ($CDCl_3$): ν(C=C) 1603w cm^{-1}. NMR ($CDCl_3$, −30 °C): ^{1}H, δ 0.85–2.0 (overlapping multiplets, 21 H, PEt_3 and SCHMe_2), 4.92 (d, J_{PH} 1.0, 5 H, C_5H_5, minor isomer) and 4.98 (d, J_{PH} 1.0, 5 H, C_5H_5, major isomer); ^{19}F, major isomer, δ −42.03 (br s, 3 F), −55.16 (q, *J* 9.4, 3 F), −56.73 (s, 3 F) and −62.06 (br m, 3 F); minor isomer, δ −38.94 (br s, 3 F), −54.52 (q, *J* 9.5 Hz, 3 F), −55.79 (s, 3 F) and −61.91 (br m, 3 F). Isomer ratio 5:1.

With PMe_2Ph. Complex **2** (36 mg) and PMe_2Ph (10 mg) similarly gave purple-black crystals of [Mo{η⁴-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SPr^i)}(PMe_2Ph)(cp)] **4c** (24 mg, 53%) (Found: C, 41.3; H, 3.2; S, 4.8. $C_{23}H_{23}F_{12}MoPS$ requires C, 41.3; H, 3.3; S, 4.6%). IR ($CDCl_3$): ν(C=C) 1607wm cm^{-1}. NMR (C_6D_6): ^{1}H, δ 0.40 (d, *J* 6.9, 3 H, Me), 1.07 (overlapping doublets, 6 H, Me), 1.67 (d, *J* 8.0, 3 H, Me), 2.56 (m, 1 H, C*H*Me_2), 4.56 (s, 5 H, C_5H_5) and 7.3–7.8 (m, 5 H, Ph); ^{19}F, δ −41.46 (m, 3 F), −54.84 (1, *J* 10.0 Hz, 3 F), −55.71 (s, 3 F) and −61.26 (m, 3 F).

With $MeC{\equiv}CPPh_2$. Complex **2** (80 mg) and $MeC{\equiv}CPPh_2$ (35 mg) similarly gave an orange powder which was recrystallised from dichloromethane–hexane to give orange crystals of [Mo{η⁴-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SPr^i)}($MeC{\equiv}CPPh_2$)(cp)] **4d** (45 mg, 40%) (Found: C, 47.4; H, 3.1. $C_{31}H_{25}F_{12}MoPS$ requires C, 47.45; H, 3.20%). IR ($CDCl_3$): ν(C≡C) 2205wm and ν(C=C) 1610wm cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 0.96 (d, *J* 6.6, 3 H, Pr^i), 1.17 (d, *J* 6.6, 3 H, CHMe_2), 2.17 (d, J_{PH} 3.0, 3 H, C≡CMe), 2.60 (m, 1 H, C*H*Me_2), 4.72 (d, J_{PH} 1.5, 5 H, C_5H_5) and 7.0–8.0 (m, 10 H, Ph); ^{19}F, major isomer, δ −40.92 (m, 3 F), −54.66 (q, *J* 10.0 Hz, 3 F), −55.27 (s, 3 F) and −60.95 (m, 3 F) (coincident with minor isomer peak); minor isomer, −37.39 (br s, 3 F), −54.0 (br m, 3 F) and −54.94 (s, 3 F). Isomer ratio 8:1.

With $PhC{\equiv}CPPh_2$. Complex **2** (50 mg) and $PhC{\equiv}CPPh_2$ (30 mg) similarly gave black crystals of [Mo{η⁴-C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SPr^i)}($PhC{\equiv}CPPh_2$)(cp)] **4e** (32 mg, 42%) (Found: C, 51.0; H, 2.9. $C_{36}H_{27}F_{12}MoPS$ requires C, 51.05; H, 3.20%). IR ($CDCl_3$): ν(C≡C) 2180wm and ν(C=C) 1609w cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.09 (d, J_{PH} 6.8, 3 H, CHMe_2), 1.29 (d, J_{PH} 6.8, 3H CHMe_2), 2.73 (m, 1 H, C*H*Me_2), 4.85 (d, J_{PH} 1.0, 5 H, C_5H_5) and 7.25–8.0 (m, 15 H, Ph); ^{19}F NMR, major isomer, δ −41.42 (m, 3 F), −55.05 (q, *J* 8.8 Hz, 3 F), −55.82 (s, 3 F) and −61.44 (br s, 3 F) (coincident with minor isomer peak); minor isomer, −38.02 (br s, 3 F), −54.49 (br m, 3 F) and −55.26 (s, 3 F). Isomer ratio 8:1.

Thermal Rearrangement of [Mo(SC_6F_5){η²-C(CF_3)C(CF_3)(PEt_3)}($CF_3C{\equiv}CCF_3$)(cp)] **3a** *in Diethyl Ether*.—A solution of complex **3a** (30 mg) in diethyl ether (20 cm^3) was stirred at room temperature under nitrogen for 48 h. The solution was filtered, hexane added and the solution concentrated to *ca.* 10 cm^3. On cooling to −15 °C red-brown crystals were obtained which were recrystallised from CH_2Cl_2–hexane to give [MoF{η³-C(CF_2)C(CF_3)C(CF_3)C(CF_3)(SC_6F_5)}(PEt_3)(cp)] **8a** (11 mg, 37%) (Found: C, 38.3; H, 2.9. $C_{25}H_{20}F_{17}MoPS$ requires C, 37.4; H, 2.5%). IR ($CDCl_3$): ν(C=CF_2) 1660m cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.20 (br, 9 H, Me), 1.9, 2.3 (br, 6 H, CH_2) and 5.89 (s, 5 H, C_5H_5); ^{19}F, δ −44.50 (br m, 1 F), −54.20 (br d, *J* 30.0, 3 F), −55.07 (br m, 1 F), −56.24 (d, *J* 20.1, 3 F), −58.21 (m, 3 F), −130.75 (m, 2 F, *o*-F of C_6F_5), −161.39 (t, *J* 21.0, 1 F, *p*-F of C_6F_5), −166.70 (m, 2 F, *m*-F of C_6F_5) and −271.3 (br s, 1 F).

Thermal Rearrangement of $[Mo(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMe_2Ph)\}(CF_3C{\equiv}CCF_3)(cp)]$ **3b**.—*In diethyl ether.* Complex **3b** (34 mg) was allowed to react similarly to give purple crystals of $[MoF(\eta^3\text{-}C(CF_2)C(CF_3)C(CF_3)C(CF_3)(SC_6F_5)\}(PMe_2Ph)(cp)]$ **8b** (15 mg, 43%) (Found: C, 39.1; H, 2.0. $C_{27}H_{16}F_{17}MoPS$ requires C, 39.4; H, 1.95%). IR ($CDCl_3$): $\nu(C{=}CF_2)$ 1665m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 1.68 (d, J_{PH} 13.0, 3 H, Me), 2.16 (br t, J 14.6, 3 H, Me), 5.89 (s, 5 H, C_5H_5) and 7.4–7.8 (m, 5 H, Ph); ^{19}F, δ −46.70 (br m, 1 F), −50.60 (m, 1 F), −54.57 (d, J 30.5, 3 F), −56.50 (br s, 3 F), −58.40 (s, 3 F), −131.72 (br m, 2 F, *o*-F of C_6F_5), −161.90 (t, J 21.0 Hz, 1 F, *p*-F of C_6F_5), −167.29 (m, 2 F, *m*-F of C_6F_5) and −269.9 (br s, 1 F).

In refluxing hexane. A solution of complex **3b** (50 mg) in hexane (20 cm^3) was heated at reflux for 5 h. Volatiles were removed *in vacuo* and the residue extracted with dichloromethane (4 cm^3) and filtered. Hexane (3 cm^3) was added, the solution concentrated *in vacuo* and cooled to −15 °C when an oily solid formed. Several more crystallisations from CH_2Cl_2–hexane gave a red-brown microcrystalline solid $[Mo(SC_6F_5)(PMe_2Ph)\{\eta^4\text{-}C_4(CF_3)_4\}(cp)]$ **9** (8 mg, 16%) (Found: C, 39.1; H, 1.8. $C_{27}H_{16}F_{17}MoPS$ requires C, 39.4; H, 1.95%). IR ($CDCl_3$): ν(C–F) 1220s(sh), 1200s, 1170s and 1162s(sh) cm^{-1}. NMR: ^1H ($CDCl_3$), δ 1.84 (d, J_{PH} 9.3, 3 H, Me), 2.02 (d, J_{PH} 9.2, 3 H, Me), 5.28 (d, J_{PH} 1.7, 5 H, C_5H_5) and 7.4–7.7 (m, 5 H, C_6H_5). ^{19}F (CD_2Cl_2, −20 °C), δ −49.89 (br s, 3 F), −52.42 (br t, J 17.3, 3 F), −53.20 (spt, J 4.3, 3 F), −57.07 (br spt, J 3.7, 3 F), −129.46 (m, 2 F, *o*-F of C_6F_5), −157.93 (t, J 21.0 Hz, 1 F, *p*-F of C_6F_5) and −163.32 (m, 2 F, *m*-F of C_6F_5).

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