Reactions of the Molybdenum Bis(alkyne) Complex $[Mo(SC_6F_5)(F_3CC{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with Alkynes leading to Isomeric and Fluxional η^4-Butadienyl Complexes

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Reactions of the bis(hexafluorobut-2-yne) complex $[Mo(SC_6F_5)(F_3CC{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1** with alkynes $RC{\equiv}CR'$ give the novel η^4-butadienyl complex prone-$[Mo\{\eta^4\text{-}C(CF_3)C(CF_3){=}CRCR(SC_6F_5)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** (R = R' = Me; R = H, R' = Me or Ph; R = Me, R' = CO_2Me) which undergoes isomerisation *via* an η^2-C,C vinyl intermediate $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)CR{=}CR'(SC_6F_5)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **3** (R = R' = Me, Et or Ph; R = Me, R' = CO_2Me or Ph; R = H, R' = Ph) to the supine isomer **4** (R = R' = Me or Et; R = Me, R' = CO_2Me or Ph; R = H, R' = Me or Ph) followed by a novel 1,4 thiolate migration to give supine-$[Mo\{\eta^4\text{-}CR'CR{=}C(CF_3)C(CF_3)(SC_6F_5)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **5** (R = R' = Ph; R = Me, R' = Ph). Fluorine-19 NMR studies established that with $PhC{\equiv}CPh$ **3** and **5** exist in solution as an equilibrium mixture. With $PhC{\equiv}CMe$ exchange between **3**, **4** and **5** is faster which allowed study by dynamic ^{19}F NMR and spin-saturation-transfer experiments.

Early studies of reactions between alkynes and metal alkyl and metal hydride complexes illustrated that insertion into the metal–carbon or –hydrogen bond is a favoured process particularly with activated alkynes such as $F_3CC{\equiv}CCF_3$ and $MeO_2CC{\equiv}CCO_2Me$.[1] In many cases the resulting product contains a σ-alkenyl group but in some instances a second alkyne insertion occurs to give σ- or η^3-butadienyl derivatives.[2] The stereochemistry of the double bond(s) found in these derivatives has been a focus of interest in view of the possible link between the mechanism of the insertion reaction and the resulting *cis* or *trans* products. For example it was originally thought that *cis* products resulted from a concerted *cis* insertion reaction and *trans* insertion could similarly result in *trans* products.[3] However, it was eventually realised that it is important to distinguish between the primary, kinetic insertion products and the thermodynamic products produced as a result of subsequent isomerisation. This was highlighted recently when some early reactions were reinvestigated in more detail and in several instances a reappraisal of the mechanism has been found to be necessary.[4] Interestingly, in this connection Huggins and Bergman[5] have shown that *cis* insertion of alkynes into the Ni–Me bond in $[NiMe(acac)(PPh_3)]$ (acac = acetylacetonate) can lead to *trans* kinetic products as a result of isomerisation at the σ-alkenyl double bond. The mechanism of isomerisation, which was catalysed by phosphine, was thought to involve attack by PR_3 at a *cis* vinyl carbon of a σ-vinyl intermediate to give the *trans* product.[5] The subsequent isolation of related species containing an η^2-$CHCH_2CMe_2Ph{=}CPhCPh(PMe_3)$ ligand lends support to such a suggestion.[6]

Recently we and others have shown that alkenyl ligands can adopt the alternative η^2 mode of co-ordination[7–9] and similarly butadienyl groups have been found to co-ordinate *via* all four carbons in an η^4 manner.[10–12] These observations must now be taken into account when considering the stereochemistry of alkyne-insertion reactions since η^2-alkenyl and η^4-butadienyl modes of bonding could also provide pathways by which the stereochemistry of the double bond(s) in σ-alkenyl and η^3-butadienyl derivatives can change after the crucial insertion reaction has occurred.[10a] This possibility prompted us to carry out a detailed study of the formation of η^4-butadienyl complexes. Initially we studied the reactions of η^2-C,C alkenyls $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, R = Pr^i, M = W, R = Me, Pr^i or Bu^t) with alkynes $R'C{\equiv}CR''$ which led to η^3-butadienyl, $[M\{\eta^3\text{-}C(CF_3)C(CF_3)CR{=}CR'(SR)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, and η^4-butadienyl, $[M\{\eta^4\text{-}C(CF_3)C(CF_3){=}CRCR'(SR)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, derivatives[13] and we now report similar studies of the interaction of a wider range of alkynes with $[Mo(SC_6F_5)(F_3CC{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ which has the isomeric bis(alkyne) structure **1**. Some of this work has been published previously as a preliminary communication.[14]

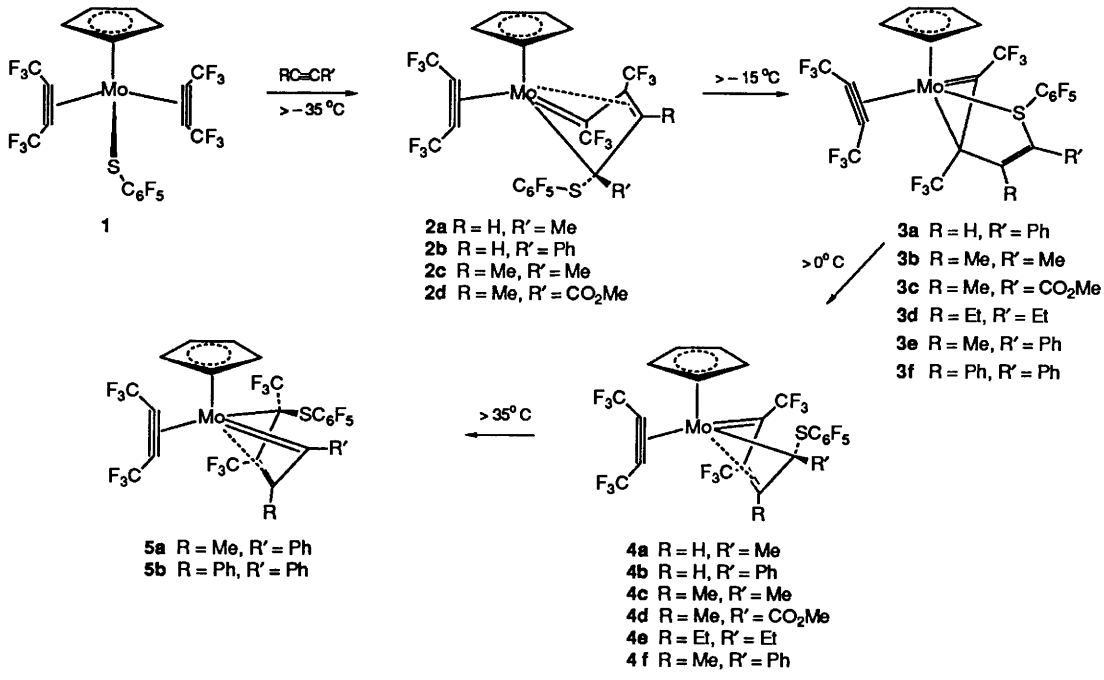
$$\begin{array}{c}
MeC{\equiv}CH \longrightarrow \mathbf{2a}^a \longrightarrow \mathbf{3'}^b \longrightarrow \mathbf{4a}^a \\
PhC{\equiv}CH \longrightarrow \mathbf{2b}^c \longrightarrow \mathbf{3a}^a \longrightarrow \mathbf{4b}^a \\
MeC{\equiv}CMe \longrightarrow \mathbf{2c}^a \longrightarrow \mathbf{3b}^c \longrightarrow \mathbf{4c}^a \\
MeC{\equiv}CCO_2Me \longrightarrow \mathbf{2d}^d \longrightarrow \mathbf{3c}^c \longrightarrow \mathbf{4'}^b \longrightarrow \mathbf{4d}^a \\
EtC{\equiv}CEt \longrightarrow \mathbf{3d}^c \longrightarrow \mathbf{4e}^a \\
PhC{\equiv}CMe \longrightarrow \mathbf{3e}^c \rightleftharpoons \mathbf{4f}^a \rightleftharpoons \mathbf{5a}^a \\
PhC{\equiv}CPh \longrightarrow \mathbf{3f}^a \rightleftharpoons \mathbf{5b}^d
\end{array}$$

Scheme 1 [a] Isolated and characterised by comparison with known structural type; [b] structure unknown; [c] characterised by ^{19}F NMR spectroscopy; [d] characterised by X-ray diffraction studies

Results

Reactions of the bis(alkyne) complex $[Mo(SC_6F_5)(F_3CC{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ **1** with alkynes $RC{\equiv}CR'$ (R = R' = Me, Et or Ph; R = H, R' = Me or Ph; R = Me, R' = CO_2Me or Ph) were initially studied over the temperature range −50 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 subsequently carried with a view to isolating and characterising these derivatives. The results of these studies are summarised in Schemes 1 and 2.

Detailed ^{19}F NMR kinetic experiments established that the first detectable intermediate prone-$[Mo\{\eta^4\text{-}C(CF_3)C(CF_3){=}CRCR'(SC_6F_5)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **2** is formed in most cases above *ca.* −35 °C. This isomerises at higher temperatures to $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)CR{=}CR'(SC_6F_5)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **3** followed by supine-$[Mo\{\eta^4\text{-}C(CF_3)C(CF_3){=}CRCR'(SC_6F_5)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **4** and ultimately supine-$[Mo\{\eta^4\text{-}CR'CR{=}C(CF_3)C(CF_3)(SC_6F_5)\}(F_3CC{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ **5**. In two instances, with $MeC{\equiv}CH$ and $MeC{\equiv}CCO_2Me$, intermediates **3'** and **4'** were detected (but not isolated); their spectra did not comply with those



Scheme 2

of compounds of known structure and therefore structural assignments could not be carried out with any certainty. In general the reactions appear to be sterically controlled in that **2** is only observed with alkynes bearing at least one small substituent H or Me, *i.e.* MeC≡CH, PhC≡CH, MeC≡CMe and MeC≡CCO$_2$Me, whereas thiolate migration to give **5** is only observed when more bulky substituents are present as with PhC≡CMe and PhC≡CPh. Moreover, the rate of reaction is also sensitive to steric effects since with MeC≡CH and PhC≡CH the reaction proceeds at temperatures as low as −45 °C whereas with PhC≡CPh it is slow even at 20 °C.

Previously we established that complexes of type **3**[10b] and **4**[10a] are obtained from reactions of alkynes with η^2-C,C vinyl complexes [M{η^3-C(CF$_3$)C(CF$_3$)SR}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)] (M = Mo, R = Pr^i, M = W, R = Me, Pr^i or Bu^t) and the SPr^i derivatives have been structurally characterised by X-ray methods. Consequently these species were identified by their distinctive ^{19}F NMR features, in particular the characteristic coupling connectivities of the four CF$_3$ groups. Isolation of these and other intermediates also proved possible in some cases and X-ray diffraction studies of [Mo{η^4-C(CF$_3$)C(CF$_3$)=CMeC(CO$_2$Me)(SC$_6$F$_5$)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)] **2d** and [Mo{η^4-CPhCPh=C(CF$_3$)C(CF$_3$)(SC$_6$F$_5$)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)] **5b** established the illustrated structures.[14] In view of the similarity of the various reactions and compounds only some will be discussed in detail. Specific details of each are provided in the Experimental section.

Fluorine-19 NMR monitoring of the reaction between [Mo(SC$_6$F$_5$)(F$_3$CC≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] and MeC≡CCO$_2$Me in (CD$_3$)$_2$CO established that the first intermediate **2d** is formed above 40 °C and this isomerises above *ca.* 0 °C into **3c**, **4'** and **4d**. The only product observed after allowing the reaction to proceed to completion at room temperature is isomer **4d**. A synthetic-scale reaction between [Mo(SC$_6$F$_5$)(F$_3$CC≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] and MeC≡CCO$_2$Me in diethyl ether–hexane was then carried out at −25 °C when the purple solution slowly turned yellow over a period of 3 h. Work-up at −25 to −30 °C gave yellow crystals of the 1:1 adduct **2d** in 50% yield. Spectroscopic data suggested a new structural form and consequently a single-crystal X-ray diffraction study was carried out, details of which have been published previously.[14]

The structure of [Mo{η^4-C(CF$_3$)C(CF$_3$)=CMeC(CO$_2$Me)(SC$_6$F$_5$)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)] **2d** is related to that previously established for [W{η^4-C(CF$_3$)C(CF$_3$)=CMeCMe(SPr^i)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)], *i.e.* of type **4**, in that the metal is co-ordinated by η^5-C$_5$H$_5$, η^2-F$_3$CC≡CCF$_3$ and a butadienyl ligand, in this case C(CF$_3$)C(CF$_3$)=CMeC(CO$_2$Me)(SC$_6$F$_5$). The last is co-ordinated in a novel η^4 manner as shown in Scheme 2. The short Mo–C$_\alpha$(CF$_3$) distance suggests a formal double bond as found in [W{η^4-C(CF$_3$)C(CF$_3$)=CMeCMe(SPr^i)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)].[10a] Moreover the coplanarity of the six carbons of the *C*(CF$_3$)*C*(*C*F$_3$)*C*(*C*H$_3$)=*C*(CO$_2$Me) unit and the extreme length of the two Mo–C(internal) bonds are indicative of an η^2-alkene–molybdenum interaction whereas the valency angles round the butadienyl sp^3-hybridised carbon and the shorter Mo–C distance are consistent with σ Mo–C bonding. An alternative mode of metal η^4-butadienyl bonding has been proposed for related ruthenium derivatives in which the M=C (carbene) bond is accompanied by a metal–η^3-allyl interaction.[11] In both [W{η^4-C(CF$_3$)C(CF$_3$)=CMeCMe(SPr^i)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)] and [Mo{η^4-C(CF$_3$)C(CF$_3$)=CMeC(CO$_2$Me)(SC$_6$F$_5$)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)] **2d** the SR substituent adopts an *exo* position on the metallacycle. However, the structure of **2d** differs from that of [W{η^4-C(CF$_3$)C(CF$_3$)=CMeCMe(SPr^i)}(F$_3$CC≡CCF$_3$)(η^5-C$_5$H$_5$)] in that the butadienyl ligand adopts a prone disposition with respect to the η^5-C$_5$H$_5$Mo moiety whereas in the latter a supine position is observed.

The spectroscopic data for complex **2d** can be interpreted in terms of the structure found in the solid state. The IR spectrum (KBr) shows a ν(C≡C) band and shoulder at 1803 and 1783 cm^{-1} accompanied by carbonyl ν(CO) modes near 1700 cm^{-1}. The ^{19}F NMR spectrum (−30 °C) in the CF$_3$ region consists of a quartet δ_1, a septet (quartet of quartets) δ_2, a quartet of quartets δ_3 and a quartet of quartets δ_4. Fluorine-19 spin–spin coupling in species of this type frequently involves a through-space mechanism[15] and is therefore sensitive to the separation of the CF$_3$ groups. It is therefore possible to assign the unique quartet δ_1 to the alkyne CF$_3$ distal to the CF$_3$ groups on the butadienyl ligand since they are too far away to couple. The other assignments then follow naturally as shown in Fig. 1. These are confirmed by the presence of ^{1}H (CH$_3$) coupling on δ_4 which is assigned to the CF$_3$ adjacent to the methyl group on the butadienyl ligand. The same coupling is observed in the

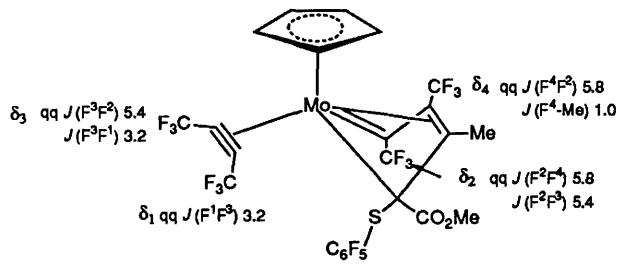


Fig. 1 Fluorine-19 NMR peak assignments and coupling connectivities (J/Hz) for prone-[Mo{η^4-C(CF_3)C(CF_3)=CMeC(CO_2Me)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **2d**

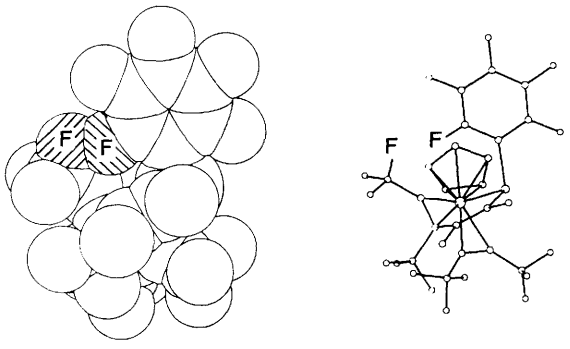
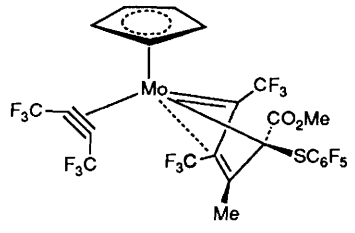
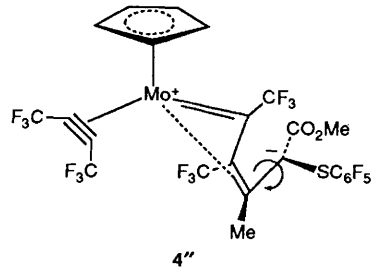


Fig. 2 Space-filling and ball-and-stick representations of [Mo{η^3-C(CF_3)C(CF_3)CMe=CMe(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3b** showing non-bonding F ··· F contact (CF_3 ··· C_6F_5)



4′



4″

methyl signal in the proton NMR spectrum which appears as a quartet.

The other intermediates observed in this reaction at higher temperatures, [Mo{η^3-C(CF_3)C(CF_3)CMe=C(CO_2Me)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3c** and **4′**, were characterised by ^{19}F NMR spectroscopy. The spectrum of the former is characteristic of a structure previously established for [Mo{η^3-C(CF_3)=C(CF_3)CMe=CPh(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)]. This is related to that of complexes **2** except that the mode of bonding between the C(CF_3)C(CF_3)CRCR′(SPr^i) ligand has changed from butadienyl η^4-*C*–*C*=*C*–*C* to η^3-*C*–*C*–C=C–*S*, *i.e.* η^2-C,C vinyl with a co-ordinated thiolate substituent. This clearly involves twisting of the metallaring so as to enable the sulfur to approach within bonding distance of the metal. In most reactions studied here complexes of type **3** were not isolated due to their instability but were identified by comparison of their characteristic ^{19}F NMR spectrum with that of [Mo{η^3-C(CF_3)C(CF_3)CMe=CPh(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)].[13] In cases where isolation and full characterisation was carried out, [Mo{η^3-C(CF_3)C(CF_3)CH=CPh(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3a** and [Mo{η^3-C(CF_3)C(CF_3)CPh=CPh(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3f**, IR spectra confirmed the presence of a free C=C bond with a band near 1610 cm^{-1} (in addition to that due to the C_6F_5 group at *ca.* 1640 cm^{-1}) which is absent from the spectra of the other isomeric forms **2**, **4** and **5**. The ^{19}F NMR spectra consist of a poorly resolved multiplet δ_1 (quartet of quartets of quartets), a quartet of quartets δ_2, a septet (quartet of quartets) δ_3 and a multiplet δ_4. In the case of the previously reported SPr^i complexes[13] the last peak is a quartet but ^{19}F double-resonance experiments with **3a**, **3b** and **3f** established that in the SC_6F_5 derivatives additional coupling between this CF_3 and one of the *ortho*-fluorines of the C_6F_5 group occurs. Molecular graphics studies[16] of [Mo{η^3-C(CF_3)C(CF_3)CMe=CMe(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] (see Fig. 2) constructed from the atomic coordinates of the structurally characterised SPr^i derivative [Mo{η^3-C(CF_3)C(CF_3)CMe=CPh(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] revealed close contact between this CF_3 and the C_6F_5 *ortho*-fluorines with a minimum F ··· F separation in the region of 190 pm, close enough for significant through-space coupling to occur. The fact that only one fluorine couples probably arises because the C_6F_5 group in **3a** and **3f** (and presumably in the other derivatives) appears to be locked into a particular conformation since it gives rise to five distinct fluorine signals in the NMR spectrum. In one case, **3a**, the low-field peak δ_1 is a broad quartet which may indicate slight differences in the structure or alternatively a completely different isomeric form. However, all the other features are similar including the presence of five distinct C_6F_5 resonances which suggests the latter explanation is unlikely.

Interestingly, only one isomeric form of complexes **3** was observed whereas two interconverting forms of the isopropyl derivatives [M{η^3-C(CF_3)C(CF_3)CR=CR′(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] were found.[13] However, we attach no real significance to this observation since the absence of a second isomer and the restricted rotation of the C_6F_5 group presumably result from increased steric congestion in **3**. This possibly results from the bulkiness of the C_6F_5 group since we note that only one isomer of the tolyl derivatives [W{η^3-C(CF_3)=C(CF_3)CMe=CR(SC_6H_4Me-4)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] (R = Me or Ph) is found in addition to which the tolyl group also exhibits restricted rotation according to dynamic ^{1}H NMR studies.[17]

The third intermediate, **4′**, in the reaction of complex **1** with $MeC{\equiv}CCO_2Me$ was not observed in reactions of other alkynes carried out in this study. Interestingly it has a ^{19}F NMR spectrum in the CF_3 region, δ −50.99 (q, J 8.7, 3 F), −53.48 (q, J 4.2, 3 F), −55.86 (m, 3 F, CF_3) and −57.76 (br m, 3 F) almost identical to that of the final product **4d**, *i.e.* δ −49.95 (q, J 7.5, 3 F, CF_3), −52.42 (q, J 3.9, 3 F, CF_3), −56.29 (m, 3 F, CF_3) and −58.83 (br m, 3 F, CF_3). Unambiguous assignment of a structure to **4′** is not possible with the limited data available but we note that, in addition to structures observed for **2**–**5**, other isomeric bonding modes are available to the C(CF_3)C(CF_3)CRCR′(SC_6F_5) ligand. In view of the close similarity of the spectra of supine-[Mo{η^4-C(CF_3)C(CF_3)=CRCR′(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4** and **4′** we tentatively propose the structure illustrated in which the only difference involves the stereochemistry at the chiral α-carbon bearing CO_2Me and SC_6F_5 substituents. To isomerise to complex **4** would require inversion of stereochemistry possibly *via* a dipolar species of type **4″** as postulated on numerous occasions in metal alkene and vinyl isomerisations.[18]

The final product in most reactions is the aforementioned η^4-butadienyl derivative supine-[Mo{η^4-C(CF_3)C(CF_3)=CRCR′-(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4** which was isolated and characterised in all cases except the reaction with PhC≡CPh. As noted earlier this type of complex has been structurally

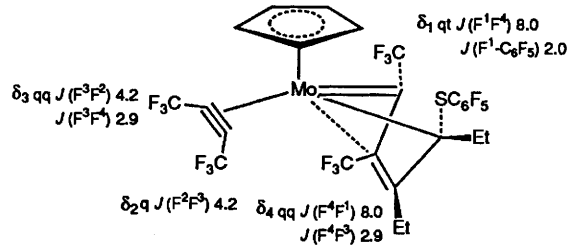


Fig. 3 Fluorine-19 NMR peak assignments and coupling connectivities for prone-[Mo{η^4-C(CF_3)C(CF_3)=CEtCEt(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4e**

characterised in the case of [W{η^4-C(CF_3)C(CF_3)=CMeCMe(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] where the supine conformation for the butadienyl ligand was established.[10] As with **3** the ^{19}F NMR spectrum of each complex is quite distinctive showing two quartets and two quartets of quartets thus enabling unambiguous structural assignment. We have previously assigned the spectrum of supine-[W{η^4-C(CF_3)C(CF_3)=CMeCMe(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)][13] and following ^{19}F double-resonance experiments this was also carried out for the hex-3-yne product **4e** as shown in Fig. 3. The coupling constants and connectivities are very similar to those of the SPr^i derivative except for the presence of coupling between δ_1 and the C_6F_5 *ortho*-fluorines. This is of interest since it is not observed in the spectra of other complexes of this structure *i.e.* **4a–4d** and **4f**. Molecular graphics studies were carried out on supine-[Mo{η^4-C(CF_3)C(CF_3)=CEtCEt(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4e** constructed using the atomic coordinates of supine-[W{η^4-C(CF_3)C(CF_3)=CMeCMe(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] as a basis. Assuming that the coupling is again *via* a through-space mechanism it is clear that the $C_6F_5 \cdots CF_3(\delta_1)$ distance is short enough to enable coupling between the two groups. The fact that it does not occur in the other complexes of this type may suggest that there is some scope for variation in the geometry of the η^4-C(CF_3)C(CF_3)=CRCR′(SC_6F_5) ligand.

The ^1H NMR spectra of the MeC≡CH and PhC≡CH derivatives **4a** and **4b** provide additional structural information since the resonance due to the single proton appears at *ca.* δ 6 indicating that it is attached to the weakly co-ordinated C=C bond rather than to the metallated carbon bearing the thiolate group. A lower δ value would otherwise have been expected for attachment to an sp^3 carbon atom. This suggests that the more bulky group preferentially ends up adjacent to the thiolate substituent, a situation also observed with prone-[Mo{η^4-C(CF_3)C(CF_3)=CMeC(CO_2Me)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **2d** and in the reactions of PhC≡CMe with [M{η^3-C(CF_3)C(CF_3)(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] (M = Mo or W) where the structures of the products were confirmed by X-ray diffraction studies.[13]

Complexes of type **5** were only observed in two reactions, those where the alkyne contained at least one phenyl substituent, *viz.* PhC≡CMe and PhC≡CPh. This may reflect some particular feature or combination of features of the phenyl group or may simply be a steric effect involving both substituents R and R′. We favour the latter explanation in view of the fact that the reaction terminated at complex **4** with PhC≡CH. With both PhC≡CMe and PhC≡CPh the first observed reaction product on warming the reaction mixture from −20 °C is a η^3-C,C alkenyl complex of type **3**. This occurs at *ca.* −10 °C with PhC≡CMe and above 0 °C the resulting product [Mo{η^3-C(CF_3)C(CF_3)CMe=CPh(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3e** is converted into an equilibrium mixture containing **3e**, **4f** and **5a**, ratio 3.5:92:110. The ease with which these species interconvert prevented their individual isolation and consequently they were characterised as a mixture. Since the ^{19}F NMR spectrum of **5a** suggested the presence of a new structural type, attention was focused on the reaction with PhC≡CPh where a kinetic run followed by ^{19}F NMR spectroscopy established that at 20 °C a slow reaction produces **3f** initially followed by **5b** until a final equilibrium mixture of these two species is obtained. Several kinetic runs with different solvents at higher temperatures up to 60 °C eventually established the optimum synthetic conditions for isolating both products of the reaction. These involved heating the reactants **1** and PhC≡CPh in hexane at *ca.* 45 °C for 8 h when the main product [Mo{η^3-C(CF_3)C(CF_3)CPh=CPh(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3f** crystallised out and was isolated in 31% yield. A small quantity of [Mo{η^4-CPhCPh=C(CF_3)C(CF_3)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **5b** was also formed under these conditions but remained in solution which allowed separation in a pure form and subsequent characterisation by X-ray diffraction methods.[14]

The structure of [Mo{η^4-CPhCPh=C(CF_3)C(CF_3)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **5b** is related to that previously established for supine-[W{η^4-C(CF_3)C(CF_3)=CMeCMe(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] (structural type **4**), with η^5-C_5H_5, η^2-$F_3CC{\equiv}CCF_3$ and a η^4-butadienyl ligand, in this case CPhCPh=C(CF_3)C(CF_3)(SC_6F_5). The structure of the last moiety reveals that the thiolate ligand has undergone a 1,4 migration from the M–C(Ph) carbon in the precursor [Mo{η^4-C(CF_3)C(CF_3)=CPhCPh(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] to the M=C(CF_3) carbon. The orientation of the butadienyl ligand is virtually unchanged, *i.e.* it still adopts a supine orientation whilst the rest of the molecule also remains the same. Moreover, the thiolate substituent is still located towards the inside of the butadienyl ligand, a feature which has significance for the fluxional behaviour of the complex as will now be discussed.

The NMR spectra of complex **5b** can be interpreted in terms of the structure found in the solid state. The simplest peak in the spectrum is the quartet δ_3 which we assign to the alkyne CF_3 proximal to the CPhCPh moiety of the butadienyl ligand. The other alkyne CF_3 is close to the two CF_3 groups of the η^4-butadienyl ligand and on this basis should be a quartet of quartets of quartets. The butadienyl CF_3 groups will each couple to the proximal alkyne CF_3 and to each other also giving rise to a quartet of quartets of quartets. Unfortunately double-irradiation experiments did not distinguish between these peaks in view of the complexity of the couplings and complete spectral assignment was not possible. However, this did prove possible in the case of supine-[Mo{η^4-CPhCMe=C(CF_3)C(CF_3)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **5a** (and, by analogy, with **5b**) by an indirect route as will now be described.

This resulted from a detailed ^{19}F NMR study of the aforementioned equilibria between the PhC≡CMe derivatives **3e**, **4f** and **5a**. The equilibria **3e** ⇌ **4f** ⇌ **5a** are slow on the NMR time-scale at 18 °C but are sufficiently fast to prevent the isomers from being separated by crystallisation. Exchange between the three forms becomes rapid at higher temperatures and leads to coalescence of the three sets of CF_3 signals above *ca.* 90 °C. Details of the exchange between the major isomers **4f** and **5a** were obtained from ^{19}F NMR spin-saturation transfer experiments which established the following relationships: δ_1 **5a** exchanges with δ_1 **4f**, δ_2 **5a** exchanges with δ_4 **4f**, δ_3 **5a** exchanges with δ_2 **4f** and δ_4 **5a** exchanges with δ_3 **4f**. The small concentration of **3f** present prevented exchange connectivities being established for this isomer.

Since peak assignment in the ^{19}F NMR spectrum of complex **4** was carried out previously (for [Mo{η^4-C(CF_3)C(CF_3)=CEtCEt(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4e** the connectivities established enabled the peaks of isomer **5** to be assigned (see Fig. 4). As discussed earlier these could not be confirmed by double-resonance experiments on **5b** because of the complexity of the coupling patterns. However, the one peak in the spectrum of **5b** which can be assigned in this way is the quartet δ_3 and it is reassuring to note that this coincides with the assignment from the exchange connectivities.

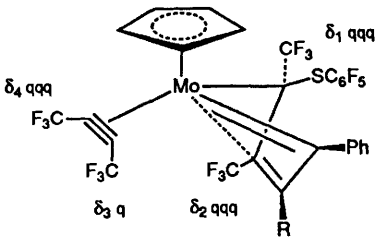
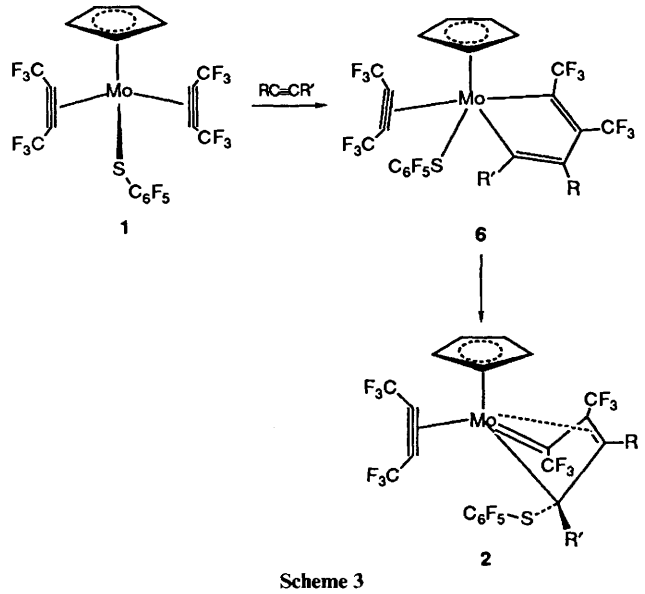


Fig. 4 Fluorine-19 NMR peak assignments for supine-[Mo{η^4-CPhCR=C(CF_3)C(CF_3)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **5**



Scheme 3

Discussion

The first observable stage in the reactions of [Mo(SC_6F_5)-($F_3CC{\equiv}CCF_3$)$_2$(η^5-C_5H_5)] with alkynes RC≡CR′ involves linkage of the incoming alkyne with SC_6F_5 and one of the $F_3CC{\equiv}CCF_3$ ligands to give the prone η^4-butadienyl complex **2**. The simplest explanation for this involves insertion of RC≡CR′ into the metal–sulfur bond followed by insertion of the second alkyne $F_3CC{\equiv}CCF_3$ into the Mo–C bond of the resulting σ-vinyl complex. However, insertions into M–S bonds do not readily occur unless the alkyne contains electron-withdrawing substituents such as CF_3. Precedent would suggest that one of the $F_3CC{\equiv}CCF_3$ ligands should preferentially insert before the incoming alkyne. To accommodate these and previous results we have proposed that such reactions proceed *via* initial formation of an intermediate metallacyclic species **6** which can undergo thiolate migration onto one of the two metallated carbons from a direction distal to the cyclopentadienyl ring, Scheme 3.[13]

Since migration clearly proceeds preferentially onto the carbon not bearing a CF_3 substituent this provides a logical explanation for the fact that η^2-C,C vinyl complexes [W{η^3-C(CF_3)C(CF_3)SR}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] containing a C(CF_3)–SR bond also react with alkynes to give complexes **3** and **4**.[13] Alternatively it is necessary to postulate that the incoming alkyne inserts into a carbon–sulfur bond in the η^2-C,C vinyl complexes, a process with little precedent. At present we are unable to distinguish between these possiblities but we have previously isolated and characterised 16-electron metallacyclic complexes [W{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SPr^i)}-(CNR)(η^5-C_5H_5)] (R = Me, Ph or 4-MeC_6H_4) which provide support for our first suggestion.[19] We further note that the formation of the prone isomeric form of the butadienyl complex, in particular with the thiolate on the inside of the metallaring, is a natural consequence of the sulfur migration proposed in Scheme 3, further supporting this proposal.

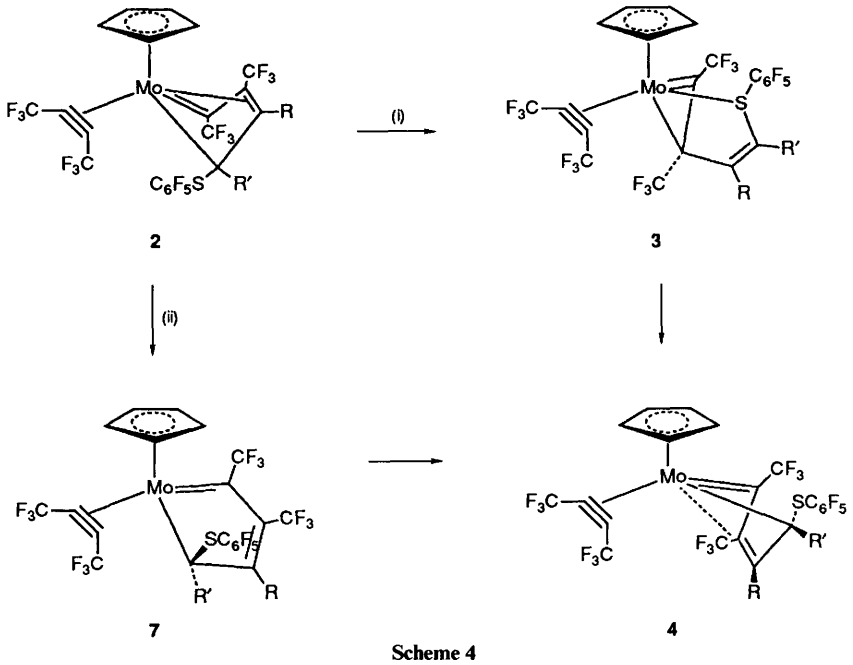
We noted earlier that these and related reactions[13] proceed regioselectively when unsymmetrically substituted alkynes are employed and the products **2**–**4** appear to have the bulky substituent on the same carbon as is the thiolate group. If the mechanism in Scheme 2 is valid it would appear that metallacyclisation occurs preferentially with the bulky group ending up on a metallated carbon of the ring. Metallacyclisations of this nature are well known in organometallic chemistry and in some cases regioselectivity of this type is observed. For example [Co(PPh_3)(PhC≡CPh)(η^5-C_5H_5)] reacts with alkynes RC≡CR′ to give a single isomer of [Co(CPh=CPhCR=CR′)(η^5-C_5H_5)] (R = H or Me, R′ = Ph or CO_2Me), that in which the more bulky substituent R′ also ends up on a terminal carbon of the metallacycle.[20]

Prone–supine isomerism in the relatively new class of compound containing η^4-butadienyl ligands, *i.e.* **2** and **4**, has not been observed previously. However, it has been studied extensively in η^4-diene complexes in recent years and when the bonding approaches the extreme 2σ-π mode a ring-flip mechanism is observed which interconverts the two forms.[21] Although butadienyl complexes **2** and **4** are related to 2σ-π diene derivatives, isomerisation proceeds *via* a totally different mechanism involving the η^2-vinyl intermediate [Mo{η^3-C(CF_3)C(CF_3)CR=CR′(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3** [Scheme 4, path (i)]. An interesting consequence of the ring-flip mechanism in butadiene complexes is inversion of stereochemistry at the two terminal carbons. Despite the intervention of a different isomerisation mechanism involving the η^2-vinyl intermediate **3**, inversion of stereochemistry is also observed in the conversion of **2** into **4**.

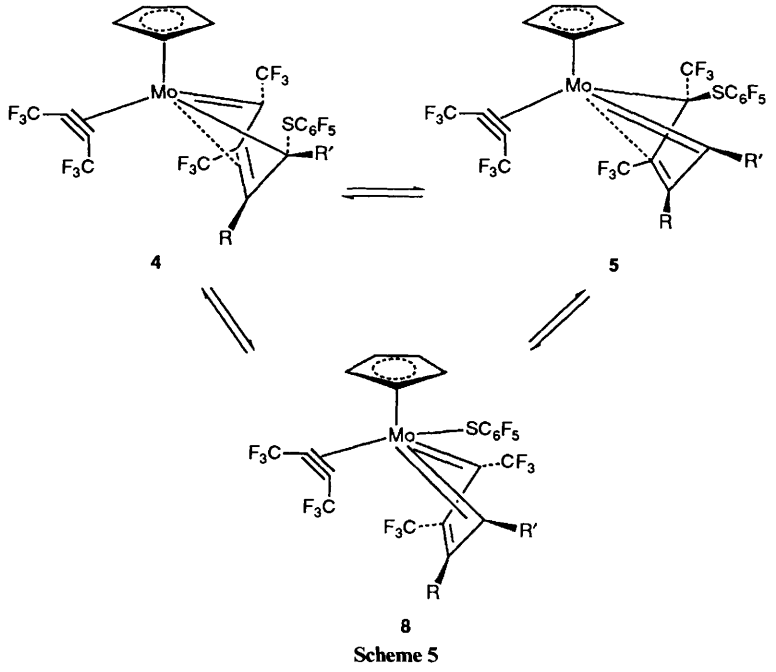
The fact that a ring-flip mechanism is not involved in the present case may reflect the fact that a thiolate substituent is present on the butadienyl ligand in **3** which allows the metal to maintain an 18-electron configuration throughout the isomerisation reaction. The alternative process [path (ii)] involving the 16-electron η^2-butadienyl intermediate **7** is presumably of higher energy. It is interesting that a butadienyl complex [Nb{η^2-CMeCMe=CMeCH(Me)}(η^5-C_5H_5)$_2$] exhibiting such a structure has been isolated from the reaction of but-2-yne with [NbH_3(η^5-C_5H_5)$_2$].[22] This clearly indicates that in the absence of a co-ordinating substituent such as a thiolate the interconversion of prone and supine η^4-butadienyl derivatives could proceed *via* an intermediate of this type.

The transformation of supine-[Mo{η^4-C(CF_3)C(CF_3)=CMe-CPh(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4f** into supine-[Mo{η^4-CPhCMe=C(CF_3)C(CF_3)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)-(η^5-C_5H_5)] **5a** provides an example of a novel new type of 1,4 migration across a metallacyclic ring. Migrations in organometallic complexes normally proceed *via* initial ligand transfer to the metal and in the present case an oxidative process, Scheme 5, proceeding *via* a metallacyclic intermediate of type **8** may be involved. The non-bonded metal–sulfur distance in both supine-[W{η^4-C(CF_3)C(CF_3)=CMeCMe(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] and **5b** is 326 pm, only 90–100 pm longer than typical Mo– and W–S covalent bond lengths. Thus thiolate transfer to the metal to give an intermediate of type **8** should be a facile process.

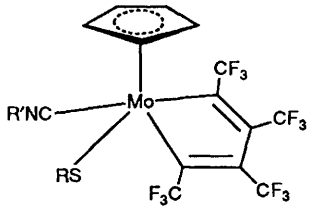
We have previously isolated related metallacyclic derivatives but with a co-ordinated isocyanide instead of an alkyne ligand.[19] Carbon-13 NMR evidence favours a more traditional metallacyclopentadiene mode of bonding for the latter species. Moreover, these are thought to have a four-legged piano-stool structure **9**, with *cis* isocyanide and thiolate ligands. However, this is not tenable for an intermediate in the fluxional process since to deliver the thiolate to the inner side of the metallacycle requires that the thiolate remains *trans* to the co-ordinated alkyne. An alternative proposal is available since molecular graphics studies of both [W{η^4-C(CF_3)C(CF_3)=CMeCMe-(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] and **5b** reveal that the non-bonded S···C(carbene) distances are only 298 and 289 pm respectively. Since the S–C bond distance in the two complexes is 182 and 183 pm we do not rule out the possibility that the 1,4



Scheme 4



Scheme 5



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thiolate migration can occur directly without intervention of the metallacycle **8**, a process which delivers the thiolate directly to the correct stereochemical site on the molecule.

The equilibrium between [Mo{η^3-C(CF_3)C(CF_3)CPh=CPh-(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3f** and [Mo{η^4-CPhCPh=C(CF_3)C(CF_3)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **5b** in contrast is very slow on the NMR time-scale and this fact enabled the isolation and hence characterisation of both species. The isomerisation appears to be solvent dependent since the reaction of [Mo(SC_6F_5)($F_3CC{\equiv}CCF_3$)$_2$(η^5-C_5H_5)] with PhC≡CPh in toluene at 50 °C gives mainly **3f** with only traces of **5b**. After 2 d in deuteriated acetone only a small amount of **3f** had been converted into **5b**, whereas after 24 h in CD_2Cl_2 a 1:1 equilibrium mixture of the two species was obtained. Whatever the mechanism of the thiolate shift it is reasonable to assume that the equilibrium between **3f** and **5b** proceeds *via* the mechanism which interconverts the PhC≡CMe derivatives **3e**, **4f** and **5a** except that in this case a species of type **4** is not present in sufficient quantity to be detected.

The reactions reported herein provide a detailed insight into the mechanisms by which alkynes link together under the influence and control of a transition metal. Previously we studied the reactions of non-activated alkynes with η^2-C,C vinyl complexes [M{η^3-C(CF_3)C(CF_3)SR}($F_3CC{\equiv}CCF_3$)(η^5-

C_5H_5)] (M = Mo or W)[13] and, as with the present reactions, complexes of type **3** or **4** were the dominant intermediates/products. A moderate steric effect of the alkyne substituents was noted since larger substituents inhibited the isomerisation of the kinetic product **3** into the thermodynamic isomer **4**. Some mobility of the thiolate group was also observed since thermolysis of the tungsten η^2-C,C vinyl derivative of type **3** [W{η^3-C(CF_3)C(CF_3)CMe=CPh(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] leads to thiolate transfer to the metal and concomitant alkyne oligomerisation to give the seven-membered metallacycle [W(SPr^i){η^5-C(CF_3)C(CF_3)C(CF_3)C(CF_3)CMe=CPh}(η^5-C_5H_5)]. In contrast [Mo{η^4-C(CF_3)C(CF_3)=CMeCR(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] gave the η^4-butadienyl derivatives [Mo{η^4-CMeCR=C(CF_3)CH(CF_3)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] (R = Me or Ph) as a result of thiolate loss and hydrogen transfer to the Mo=C(CF_3) carbon. The structure of the latter is therefore comparable with that of supine-[Mo{η^4-CR'CR=C(CF_3)C(CF_3)(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **5a**, **5b**. Interestingly, although these reactions were followed by ^{19}F NMR spectroscopy no evidence for 1,4 thiolate transfer to give supine-[Mo{η^4-CMeCR=C(CF_3)C(CF_3)(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] (structural type **5**) was found despite the structural similarity of these two types of complex. This may imply that **5** is not an intermediate in this reaction, *i.e.* the thiolate substituent in [Mo{η^4-C(CF_3)C(CF_3)=CMeCR(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] does not migrate onto the Mo=C(CF_3) carbon before substitution by hydrogen occurs.

An interesting aspect of the reactions reported here is that, following formation of the η^4-butadienyl complex of type **2**, isomerisation occurs to **3**–**5** rather than reaction of the remaining alkyne with the butadienyl ligand. This contrasts with Green's observation that the ruthenium complex [Ru{η^4-(*E*,*Z*)-CPhCPh=CPhCH(Ph)}(η^5-C_5H_5)] reacts with diphenylacetylene to give [Ru(η^5-*endo*-C_6Ph_6H)(η^5-C_5H_5)].[11] We previously noted that in reactions of [M{η^3-C(CF_3)C(CF_3)SR}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] with alkynes two mechanistic pathways are available. Both involve initial formation of an η^2-C,C vinyl derivative of type **3** [M{η^3-C(CF_3)C(CF_3)CMe=CPh(SPr^i)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] and this can undergo isomerisation to an η^4-butadienyl complex of type **4** or alternatively oligomerisation to give MC_6 metallacycles resulting from reaction of the η^3-C(CF_3)C(CF_3)SR ligand with co-ordinated $F_3CC{\equiv}CCF_3$. The present work appears to confirm that this preliminary conclusion is correct since formation of complexes of type **4** occurs in all cases reported here and **4** does not undergo reaction with the co-ordinated alkyne. Again we conclude that formation of the η^4-butadienyl complexes **4** prevents alkyne oligomerisation.

Finally we note that the isomerisation **4** ⟶ **5** may provide an explanation for a previous report of an unusual migration in ruthenium chemistry involving reaction of the σ-vinyl complex [Ru{σ-C(CF_3)=CH(CF_3)}(PPh_3)$_2$(η^5-C_5H_5)] with the alkyne $MeO_2CC{\equiv}CCO_2Me$. This gives a η^3-butadienyl complex [Ru{η^3-C(CF_3)=C(CF_3)C(CO_2Me)=CH(CO_2Me)}(PPh_3)(η^5-C_5H_5)] apparently as a result of $MeO_2CC{\equiv}CCO_2Me$ insertion into the C–H bond of the σ-vinyl ligand.[2a] However, a hydrogen migration proceeding *via* η^4-butadienyl intermediates of the type observed here for the thiolate group clearly provides a more logical explanation for this hitherto puzzling reaction.

Experimental

The NMR spectra were recorded on a Bruker WP 200SY spectrometer at 200.13 (^{1}H) and 188.13 MHz (^{19}F). Coupling constants are in Hertz and 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 9 spectrometer. 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 alkynes were obtained commercially and [Mo(SC_6F_5)($F_3CC{\equiv}CCF_3$)$_2$(η^5-C_5H_5)] was synthesised by published procedures.[23]

Reactions of [Mo(SC_6F_5)($F_3CC{\equiv}CCF_3$)$_2$(η^5-C_5H_5)] **1**.—*With* MeC≡CH (*NMR monitoring*). Intermediate **3'**: ^{19}F NMR [$(CD_3)_2CO$, −10 °C]: δ −52.98 (br, 3 F, CF_3), −53.57 (spt, 3 F, CF_3) and −56.80 (overlapping peaks, 6 F, CF_3).

With MeC≡CH. A solution of complex **1** (44 mg, 0.065 mmol) in diethyl ether–hexane (8 cm^3, 1:1) was treated with a slight excess (1:1.1 molar ratio) of MeC≡CH for 2 h at −30 °C. A change from deep purple to yellow was observed and a small quantity of yellow crystals separated. The solution was concentrated *in vacuo* to *ca.* 4 cm^3 and allowed to stand for 1 h. After this time the mother-liquor was transferred to a Schlenk tube and the crystals washed with several portions of cold hexane and dried *in vacuo*. Yield of [Mo{η^4-C(CF_3)C(CF_3)=CHCMe(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **2a**: 21 mg (50%) (Found: C, 36.6; H, 1.2. $C_{22}H_9F_{17}MoS$ requires C, 36.45; H, 1.25%). IR ($CDCl_3$): ν(C≡C) 1797wm cm^{-1}. NMR [$(CD_3)_2CO$]: ^{1}H (−60 °C), δ 2.48 (s, 3 H, Me), 5.75 (s, 5 H, C_5H_5) and 6.82 (s, 1 H); ^{19}F (−40 °C), δ −52.43 [q, J(F^1F^3) 1.7, 3 F, CF_3], −54.60 [qq, J(F^2F^3) 5.2, J(F^2F^4) 4.3, 3 F, CF_3], −55.70 [qq, J(F^3F^1) 1.6, J(F^3F^2) 5.2, 3 F, CF_3] and −64.43 [q, J(F^4F^2) 4.3 Hz, 3 F, CF_3].* The mother-liquor was allowed to warm slowly to room temperature and then concentrated further. Cooling to −15 °C gave yellow crystals of [Mo{η^4-C(CF_3)C(CF_3)=CHCMe(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4a** (11 mg, 26%) (Found: C, 35.1; H, 1.2. $C_{22}H_9F_{17}MoS$ requires C, 36.45; H, 1.25%). IR ($CDCl_3$): ν(C≡C) 1795wm cm^{-1}. NMR: ^{1}H (CD_2Cl_2), δ 2.33 (s, 3 H, Me), 5.95 (s, 5 H, C_5H_5), 6.01 (s, 1 H); ^{19}F ($CDCl_3$), δ −52.66 (q, J 5.7, 3 F, CF_3), −53.83 (q, J 4.7 Hz, 3 F, CF_3), −55.82 (m, 3 F, CF_3) and −60.30 (m, 3 F, CF_3).

With PhC≡CH (*NMR monitoring*). Compound **2b**: ^{19}F NMR [$(CD_3)_2CO$, −40 °C], δ −52.22 [q, J(F^1F^3) 3.9, 3 F, CF_3], −54.63 [qq, J(F^2F^3) 5.3, J(F^2F^4) 4.8, 3 F, CF_3], −55.30 [qq, J(F^3F^2) 5.2, J(F^3F^1) 3.9, 3 F, CF_3] and −63.00 [q, J(F^4F^2) 4.8 Hz, 3 F, CF_3].

With PhC≡CH *at* −20 °C. A solution of complex **1** (50 mg, 0.04 mmol) in diethyl ether–hexane (10 cm^3, 1:1) was treated with a slight excess (1:1.1 molar ratio) of PhC≡CH for 3 h at −20 °C. The solution was concentrated *in vacuo* and the temperature lowered to −25 °C when a small quantity of crystals separated. The mother-liquor was transferred to a Schlenk tube and the crystals washed with several portions of cold hexane and dried *in vacuo*. Yield of [Mo{η^3-C(CF_3)-C(CF_3)CH=CPh(SC_6F_5)}($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **3a**: 18 mg (31%) (Found: C, 40.9; H, 1.2. $C_{27}H_{11}F_{17}MoS$ requires C, 41.20; H, 1.40%). IR (KBr): ν(C≡C) 1808wm, ν(C=C) 1688wm and 1618(sh) cm^{-1}. NMR [$(CD_3)_2CO$, −30 °C]: ^{1}H, δ 6.12 (s, 5 H, C_5H_5) and 7.2–7.6 (m, 5 H, Ph); ^{19}F, δ −52.69 [br q, J(F^1F^2) 3.8, 3 F, CF_3], −53.28 [qq, J(F^2F^1) 3.8, J(F^2F^3) 4.5, 3 F, CF_3], −56.61 [qq, J(F^3F^2) 4.5, J(F^3F^4) 3.7, 3 F, CF_3], −57.06 [dq, J(F^4–C_6F_5) 8.0, J(F^4F^3) 3.7 Hz, 3 F, CF_3], −132.0 (m, 1 F), −134.4 (m, 1 F), −146.5 (m, 1 F), −157.3 (m, 1 F) and −158.7 (m, 1 F). The mother-liquor was allowed to warm slowly to room temperature, the temperature held for 2 h and the solution concentrated further. Cooling to −15 °C gave yellow crystals of [Mo{η^4-C(CF_3)C(CF_3)=CHPh(SC_6F_5)}-($F_3CC{\equiv}CCF_3$)(η^5-C_5H_5)] **4b** (16 mg, 28%) (Found: C, 41.6; H, 1.4. $C_{27}H_{11}F_{17}MoS$ requires C, 41.20; H, 1.40%); *m*/*z* 786 (M^+). IR ($CDCl_3$): ν(C≡C) 1793wm cm^{-1}. NMR (CD_2Cl_2: ^{1}H, δ 6.20 (s, 5 H, C_5H_5), 6.35 (s, 1 H) and 7.2–7.5 (m, 5 H, Ph); ^{19}F, δ −52.86 (q, J 6.1, 3 F, CF_3), −55.29 (q, J 4.0 Hz, 3 F, CF_3), −56.28 (m, 3 F, CF_3) and −60.65 (m, 3 F, CF_3).

With MeC≡CMe (*NMR*). Compound **3b**: ^{19}F NMR [$(CD_3)_2$-

* F^1–F^4 refer to CF_3 resonances observed at increasing field strength.

CO, −30 °C], δ −50.30 (br, 3 F, CF_3), −52.38 [qq, $J(F^2F^3)$ 3.8, $J(F^2F^1)$?, 3 F, CF_3], −53.24 [qq, $J(F^3F^1)$ 4.8, $J(F^3F^2)$ 3.7, 3 F, CF_3], −56.82 [dq, $J(F^4–C_6F_5)$ 6.0 Hz, $J(F^4F^1)$?, 3 F, CF_3], −131.9 (m, 1 F), −135.5 (m, 1 F), −148.4 (m, 1 F), −157.4 (m, 1 F) and −158.1 (m, 1 F).

With MeC≡CMe *at* −25 °C. A solution of complex **1** (35 mg, 0.05 mmol) in diethyl ether–hexane (4 cm^3, 1:1) was treated with a slight excess (1:1.1 molar ratio) of MeC≡CMe for 5 h at −25 °C. After this time the deep purple solution had turned yellow. It was concentrated *in vacuo* and after 2 h at −25 °C yellow crystals were obtained. These were washed with several portions of cold hexane and dried *in vacuo* to give [Mo{η⁴-C(CF_3)C(CF_3)=CMeCMe(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **2c** (27 mg, 71%) (Found: C, 36.9; H, 1.3. $C_{23}H_{11}F_{17}MoS$ requires C, 37.40; H, 1.50%). IR (KBr): ν(C≡C) 1792wm cm^{-1}. NMR: ^1H [$(CD_3)_2CO$, −30 °C], δ 2.49 (s, 3 H, Me), 2.68 (s, 3 H, Me) and 5.78 (s, 5 H, C_5H_5); ^{19}F ($CDCl_3$), δ −52.86 [br q, $J(F^1F^3)$ 3.0, 3 F, CF_3], −53.68 [qq, $J(F^2F^3)$ 5.2, $J(F^2F^4)$ 5.7, 3 F, CF_3], −55.62 [qq, $J(F^3F^1)$ 3.1, $J(F^3F^2)$ 5.2, 3 F, CF_3] and −57.76 [q, $J(F^4F^2)$ 5.7 Hz, 3 F, CF_3].

With MeC≡CMe *at* 20 °C. A solution of complex **1** (40 mg, 0.058 mmol) in diethyl ether–hexane (6 cm^3, 1:1) was treated with a slight excess (1:1.1 molar ratio) of MeC≡CMe for 15 min at 20 °C. After this time the deep purple solution had turned yellow. The solution was concentrated *in vacuo* to *ca.* 3 cm^3 and cooled to −15 °C to give yellow crystals. These were washed with several portions of cold hexane and dried *in vacuo* to give [Mo{η⁴-C(CF_3)C(CF_3)=CMeCMe(SC_6F_5)}(F_3CC≡CCF_3)-(η⁵-C_5H_5)] **4c** (32 mg, 75%) (Found: C, 36.8; H, 1.3. $C_{23}H_{11}F_{17}MoS$ requires C, 37.40; H, 1.50%). IR ($CDCl_3$): ν(C≡C) 1778wm cm^{-1}. NMR ($CDCl_3$): ^1H, δ 2.21 (br s, 3 H, Me), 2.25 (s, 3 H, Me) and 5.58 (s, 5 H, C_5H_5); ^{19}F, δ −50.30 (q, *J* 4.4, 3 F, CF_3), −51.29 (q, *J* 4.4 Hz, 3 F, CF_3), −56.31 (m, 3 F, CF_3) and −58.87 (m, 3 F, CF_3).

With MeC≡CCO_2Me (*NMR monitoring*). Compound **3c**: ^{19}F NMR [$(CD_3)_2CO$, +10 °C], δ −49.45 (br, 3 F, CF_3), −52.61 (m, 3 F, CF_3), −53.65 (spt, 3 F, CF_3) and −56.86 (m, 3 F, CF_3). Compound **4'**: ^{19}F NMR [$(CD_3)_2CO$, +10 °C], δ −50.99 (q, *J* 8.7, 3 F, CF_3), −53.48 (q, *J* 4.2 Hz, 3 F, CF_3), −55.86 (m, 3 F, CF_3) and −57.76 (br m, 3 F, CF_3).

With MeC≡CCO_2Me *at* −25 °C. A solution of complex **1** (60 mg, 0.09 mmol) in diethyl ether–hexane (6 cm^3, 2:1) was treated with a slight excess (1:1.1 molar ratio) of MeC≡CCO_2Me for 3 h at −25 °C. After this time the deep purple solution had turned yellow. It was concentrated *in vacuo* and cooled to −30 °C. After several hours yellow crystals formed and these were collected, washed with several portions of cold hexane and dried *in vacuo*. The mother-liquor which had been quickly transferred to another Schlenk tube at −30 °C was concentrated further to give a second batch of yellow crystals. Combined yield of [Mo{η⁴-C(CF_3)C(CF_3)=CMeC-(CO_2Me)(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **2d** (34 mg, 50%) (Found: C, 35.5; H, 1.2. $C_{24}H_{11}F_{17}MoO_2S$ requires C, 35.3; H, 1.40%). IR (KBr): ν(C≡C) 1803wm, 1783(sh), ν(C=O) 1715(sh) and 1700wm cm^{-1}. NMR [$(CD_3)_2CO$]: ^1H, δ 3.02 [br q, *J*(HF) 1.1, 3 H, Me], 3.70 (s, 3 H, CO_2Me) and 5.82 (s, 5 H, C_5H_5); ^{19}F, δ −53.70 [q, $J(F^1F^3)$ 3.2, 3 F, CF_3], −53.82 [qq, $J(F^2F^3)$ 5.4, $J(F^2F^4)$ 5.8, 3 F, CF_3], −55.52 [qq, $J(F^3F^1)$ 3.2, $J(F^3F^2)$ 5.4, 3 F, CF_3] and −58.07 [qq, $J(F^4F^2)$ 5.8, *J* 1.0 Hz, 3 F, CF_3].

With MeC≡CCO_2Me *at* 5 °C. A solution of complex **1** (50 mg, 0.07 mmol) in diethyl ether–hexane (8 cm^3, 1:1) was treated with a slight excess (1:1.1 molar ratio) of MeC≡CCO_2Me for 18 h at 5 °C. After this time the deep purple solution had turned orange-brown. It was concentrated *in vacuo* to *ca.* 3 cm^3 and cooled to −15 °C to give a yellow solid. This was recrystallised from diethyl ether–hexane and dried *in vacuo* to give [Mo{η⁴-C(CF_3)C(CF_3)=CMeC(CO_2Me)(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **4d** (9 mg, 16%) (Found: C, 36.7; H, 1.4. $C_{24}H_{17}F_{17}$-MoO_2S requires C, 35.3; H, 1.40%). IR ($CDCl_3$): ν(C≡C) 1784m, ν(C≡O) 1716m cm^{-1}. NMR: ^1H [$(CD_3)_2CO$], δ 2.45 [br q, *J*(HF) 0.7, 3 H, Me], 3.75 (s, 3 H, CO_2Me) and 6.35 (s, 5 H, C_5H_5); ^{19}F ($CDCl_3$), δ −49.95 (q, *J* 7.5, 3 F, CF_3), −52.42 (q, *J* 3.9 Hz, 3 F, CF_3), −56.29 (m, 3 F, CF_3) and −58.83 (br m, 3 F, CF_3).

With EtC≡CEt (*NMR monitoring*). Compound **3d**: ^{19}F NMR (CD_2Cl_2, −7 °C), δ −51.25 (br, 3 F, CF_3), −53.30 (m, 3 F, CF_3), −54.42 (spt, 3 F, CF_3) and −56.31 (m, 3 F, CF_3).

With EtC≡CEt *at* 20 °C. A solution of complex **1** (30 mg, 0.04 mmol) in diethyl ether–hexane (6 cm^3, 1:3) was treated with a slight excess (1:1.1 molar ratio) of EtC≡CEt for 24 h at 20 °C. After this time the deep purple solution had turned orange-yellow. It was concentrated *in vacuo*, centrifuged to remove flocculant material and cooled to −15 °C to give a yellow solid. This was recrystallised from diethyl ether–hexane and dried *in vacuo* to give [Mo{η⁴- C(CF_3)C(CF_3)=CEtCEt-(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **4e** (16 mg, 48%) (Found: C, 38.4; H, 2.1. $C_{25}H_{15}F_{17}MoS$ requires C, 39.15; H, 2.20%); *m/z* 766 (M^+). IR ($CDCl_3$): ν(C≡C) 1775wm cm^{-1}. NMR: ^1H ($CD_3C_6D_5$), δ 0.67 (t, 3 H, Me), 1.11 (t, 3 H, Me), 1.98 (m, 1 H, CH_2), 2.29 (m, 1 H, CH_2), 2.48 (m, 2 H, CH_2) and 5.35 (s, 5 H, C_5H_5); ^{19}F [$(CD_3)_2CO$], δ −49.92 [qt, $J(F^1F^4)$ 8.0, $J(F^1$–$C_6F_5)$ 2.0, 3 F, CF_3], −52.22 [q, $J(F^2F^3)$ 4.2, 3 F, CF_3], −56.22 [qq, $J(F^4F^3)$ 2.9, $J(F^3F^2)$ 4.2, 3 F, CF_3] and −56.73 [qq, $J(F^4F^1)$ 8.0, $J(F^4F^3)$ 2.9 Hz, 3 F, CF_3].

With PhC≡CMe (*NMR monitoring*). Compound **3e**: ^{19}F NMR (CD_2Cl_2, −20 °C), δ −51.06 (br, 3 F, CF_3), −53.26 (m, 3 F, CF_3), −54.38 (spt, 3 F, CF_3) and −56.10 (m, 3 F, CF_3).

With PhC≡CMe at 20 °C. A solution of complex **1** (50 mg, 0.07 mmol) in diethyl ether–hexane (8 cm^3, 1:1 was treated with a slight excess (1:1.1 molar ratio) of PhC≡CMe for 4 h at 20 °C. After this time the deep purple solution had turned orange. It was concentrated *in vacuo* and cooled to −15 °C to give orange crystals. These were washed with several portions of cold hexane and dried *in vacuo* to give an equilibrium mixture of [Mo{η³-C(CF_3)C(CF_3)CMe=CPh(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **3e**, [Mo{η⁴-C(CF_3)C(CF_3)=CMeCPh(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] (trace) **4f** and [Mo{η⁴-CPhCMe=C(CF_3)-C(CF_3)(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **5a** (36 mg, 62%) (Found: C, 42.5; H, 1.7. $C_{28}H_{13}F_{17}MoS$ requires C, 42.0; H, 1.65%); *m/z* 800 (M^+). IR ($CDCl_3$): ν(C≡C) 1783wm cm^{-1}. NMR: **4f**, ^1H ($CDCl_3$), δ 2.07 (br s, 3 H, Me), 6.16 (s, 5 H, C_5H_5) and 6.8–7.4 (m, 5 H, Ph); ^{19}F ($CD_3C_6D_5$), δ −50.37 (q, *J* 8.4, 3 F, CF_3), −53.12 (q, *J* 3.9 Hz, 3 F, CF_3), −56.42 (spt, 3 F, CF_3) and −59.30 (br m, 3 F, CF_3); **5a**, ^1H ($CDCl_3$), δ 1.92 (br q, *J* 1.8, 3 H, Me), 5.83 (s, 5 H, C_5H_5) and 6.8–7.4 (m, 5 H, Ph); ^{19}F ($CD_3C_6D_5$), δ −49.09 (br m, 3 F, CF_3), −54.11 (m, 3 F, CF_3), −54.52 (q, *J* 5.4 Hz, 3 F, CF_3) and −55.28 (m, 3 F, CF_3).

With PhC≡CPh *at* 45 °C. A solution of complex **1** (150 mg, 0.21 mmol) in hexane (15 cm^3) was treated with a slight excess (1:1.1 molar ratio) of PhC≡CPh for 8 h in a sealed tube at 45–50 °C when yellow crystals formed. The solution was allowed to cool slowly to room temperature and the mother-liquor transferred to another Schlenk tube. Recrystallisation of the yellow crystals from diethyl ether–hexane twice gave [Mo{η³-C(CF_3)C(CF_3)CPh=CPh(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **3f** (58 mg, 31%) (Found: C, 44.7; H, 1.6. $C_{33}H_{15}F_{17}MoS$ requires C, 45.95; H, 1.75%). IR ($CDCl_3$) ν(C≡C) 1810wm, ν(C=C) 1602w cm^{-1}. NMR ($CDCl_3$): ^1H, δ 5.79 (s, 5 H, C_5H_5) and 6.9–7.3 (m, 10 H, Ph); ^{19}F, δ −49.55 (br m, 3 F, CF_3), −53.09 (m, 3 F, CF_3), −54.56 (spt, 3 F, CF_3), −56.24 (m, 3 F, CF_3), −132.1 (m, 1 F), −132.3 (m, 1 F), −145.5 (m, 1 F), −157.5 (m, 1 F) and −158.2 (m, 1 F). The mother-liquor was concentrated slightly *in vacuo* and on cooling to −15 °C an impure solid was obtained. This was recrystallised twice from warm hexane to give orange-yellow crystals of [Mo{η⁴-CPhCPh=C(CF_3)C(CF_3)(SC_6F_5)}(F_3CC≡CCF_3)(η⁵-C_5H_5)] **5b** (10 mg, 5%) (Found: C, 46.4; H, 1.7. $C_{33}H_{15}F_{17}MoS$ requires C, 45.95; H, 1.75%). IR (hexane): ν(C≡C) 1762wm cm^{-1}. NMR [$(CD_3)_2CO$]: ^1H, δ 6.20 (s, 5 H, C_5H_5) and 7.0–7.6 (m, 10 H,

Ph); ^{19}F, δ −46.95 (br m, 3 F, CF_3), −48.82 (m, 3 F, CF_3), −53.07 (q, *J* 5.5 Hz, 3 F, CF_3) and −54.32 (m, 3 F, CF_3).

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