Molybdenum Promoted Alkyne Dimerisation Leading to Novel Metallacycles: The Crystal and Molecular Structures of *prone*-[Mo{η^4-C(CF_3)C(CF_3)C(Me)C(CO_2Me)(SC_6F_5)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] and *supine*-[Mo{η^4-C(CF_3)(SC_6F_5)C(CF_3)C(Ph)C(Ph)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)]

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Reactions of alkynes with [$MoSC_6F_5(CF_3C{\equiv}CCF_3)_2(\eta^5$-$C_5H_5)$] **1** gives the novel *prone* η^4-butadienyl complex [Mo{η^4-C(CF_3)C(CF_3)C(R′)C(R)(SC_6F_5)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)], which undergoes isomerisation *via* an η^2-vinyl intermediate to the *supine* isomer followed by a novel 1,4-thiolate migration to give *supine*-[Mo{η^4-C(CF_3)(SC_6F_5)C(CF_3)C(R)C(R′)}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)].

In recent years it has become apparent that metal–vinyl,[1] metal–butadienyl[2,3] and metallacyclopentadiene[4] complexes can adopt novel bonding modes that effectively stabilise coordinative unsaturation at the metal centre. We now report studies of the chemistry of the bis-alkyne derivative [$MoSC_6F_5(CF_3C{\equiv}CCF_3)_2(\eta^5$-$C_5H_5)$] **1**, that provide an insight into the interrelationships of these complex types and their role in alkyne insertion and dimerisation reactions.

Reactions of complex **1** with alkynes RC≡CR′ in diethyl ether–hexane were studied over the temperature range −40 to +50 °C and are summarised in Scheme 1. Previously we established that complexes of type **3** and **4** are obtained from reactions of alkynes with η^2-*C*,*C*-vinyl complexes [M{η^3-C(CF_3)C(CF_3)SPr^i}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] (M=Mo, W).[4] However, in the present case detailed ^{19}F NMR kinetic experiments established that the first detectable intermediate **2** is formed above *ca.* −35 °C. This isomerises at higher temperatures to **3** followed by **4** and ultimately **5**. The reactions appear to be sterically controlled in that **2** is only observed with alkynes bearing at least one small substituent, *e.g.* MeC≡CMe and MeC≡CH, whereas isomerisation to **5** is only observed when more bulky substituents are present as with PhC≡CMe and PhC≡CPh. Isolation of all four isomeric types proved possible† and **3** and **4** were identified by comparison of spectroscopic features with the SPr^i analogues previously characterised by X-ray methods.[2]

The structures of **2d** and **5b** have also been established by X-ray methods and the results are presented in Figs. 1 and 2.‡ Structurally the two complexes have much in common: both contain similar (η^5-C_5H_5)Mo($CF_3C{\equiv}CCF_3$) moieties with 2-electron donor alkyne ligands and in both an 18-electron configuration at the metal is completed by a 5-electron donor butadienyl ligand with a near-planar C_4 donor unit [C–C–C–C torsion angles respectively 9.0(5) and 15.0(6)°]. The geometric relationship of the Mo and S atoms to the C_4 butadienyl donor set is similar in both complexes; although the Mo and S atoms lie on opposite sides of the C_4 plane the non-bonded Mo···S

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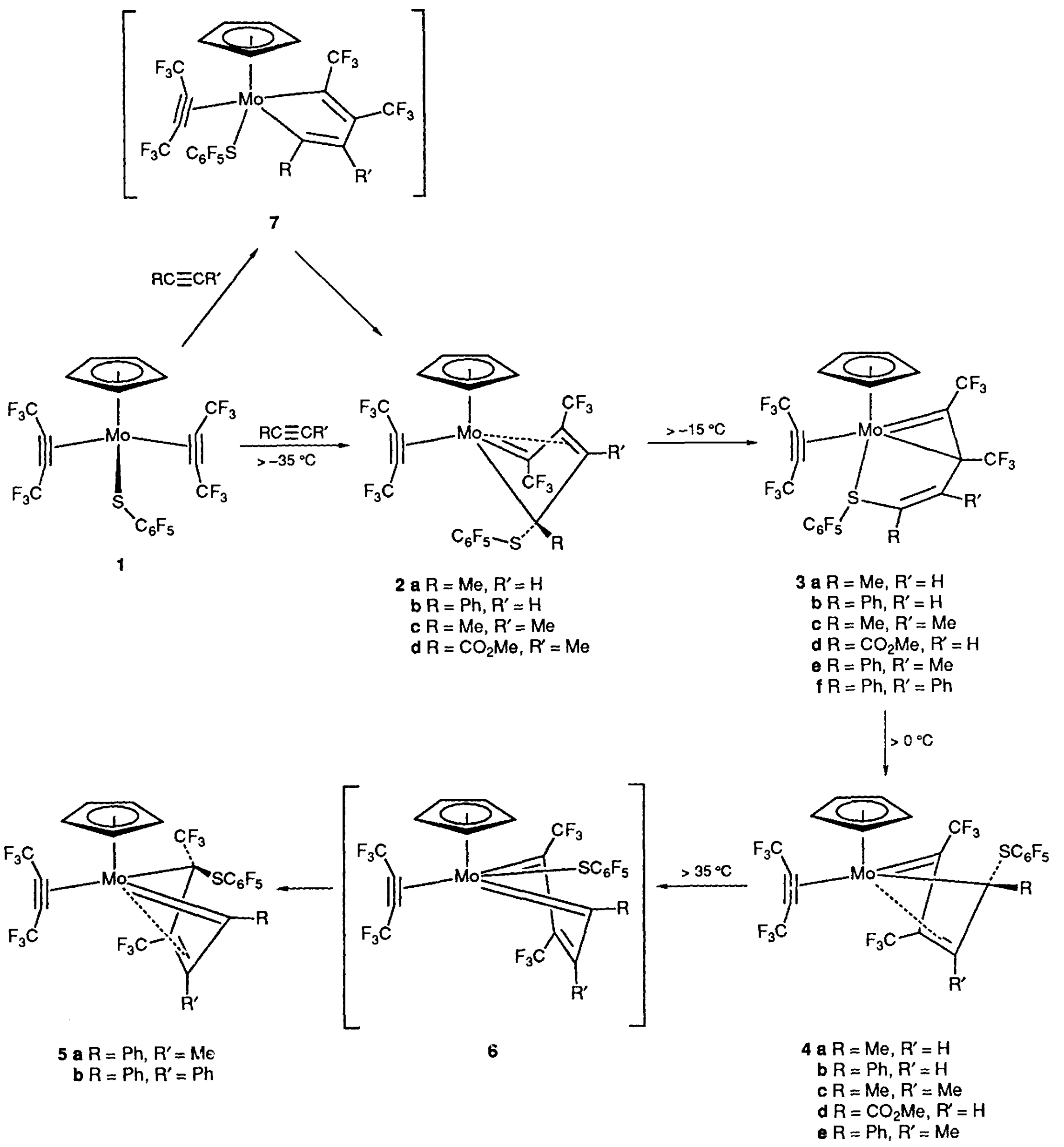
† Reactions were carried out under the following conditions, **2d** Et_2O–hexane, −20 °C; **3g** hexane, 45 °C; **4d** Et_2O–hexane, 10 °C. The complexes were crystallised from solution under the same conditions. **5b** was obtained by allowing **3f** to isomerise to an equilibrium mixture in CH_2Cl_2 at 20 °C and was then isolated by fractional crystallisation following addition of hexane.

‡ *Crystal data*: **2d** (R = CO_2Me, R′ = Me), $C_{24}H_{11}F_{17}MoO_2S$, M = 782.32, monoclinic, space group $P2_1/c$, a = 8.762(2), b = 15.962(1), c = 19.246(2) Å, β = 95.657(11)°, U = 2678.6(6) Å^3, Z = 4, D_c = 1.940 g cm^{-3}, μ(Mo-Kα) = 6.90 cm^{-1}, F(000) = 1528 electrons, $R(R_w)$ = 0.050 (0.063) after refinement of 407 parameters from 3787 independent reflections with $I \geqslant 3\sigma(I)$ and θ(Mo-Kα) <25°. **5b** (R = R′ = Ph), $C_{33}H_{15}F_{17}MoS$, M = 862.45, monoclinic, space group $P2_1/c$, a = 8.561(1), b = 18.927(4), c = 19.650(2) Å, β = 93.14(1)°, U = 3179.2(9) Å^3, Z = 4, D_c = 1.802 g cm^{-3}, μ(Mo-Kα) = 5.86 cm^{-1}, F(000) = 1696 electrons, $R(R_w)$ = 0.034 (0.030) after refinement of 469 parameters from 1968 independent reflections with $I \geqslant 2\sigma(I)$ and θ(Mo-Kα) <23°. Crystallographic measurements were made with an Enraf-Nonius CAD4F diffractometer and Mo-Kα radiation, λ = 0.71069 Å. Empirical absorption corrections were applied and allowance was made for all H-atoms. Each structure has been refined on F to convergence with $w = 1/\sigma^2(F)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

distances [both 3.26 Å] are only *ca.* 0.9 Å longer than typical Mo–S covalent bond lengths. In addition, the non-bonded S···C (carbene) distances [S···C(6) 2.81 Å in **2d**, S···C(10) 2.89 Å in **5b**] are appreciably shorter than S···C van der Waals contacts (3.55 Å according to Pauling).[5] The structures of **2d** and **5b** are thus consistent with easy mobility of the SC_6F_5 group.

Apart from the differing nature of the substituents the butadienyl ligands are oriented differently in the two complexes: the *prone* (*endo*) orientation in **2d** brings carbene C(6) nearly *trans* to C(R5) whereas the *supine* (*exo*) orientation in **5b** has carbene carbon C(10) nearly *trans* to C(2) and this is reflected in the lengthening of the Mo–C bond *trans* to C(carbene) in each case.

The following features are noteworthy. *Prone–supine* isomerism in the relatively new class of compound containing η^4-butadienyl ligands, *e.g.* **2** and **4**, has not been observed previously. However, *prone–supine* isomerism in η^4-diene complexes has been studied extensively in recent years and when the metal–ligand bonding approaches the extreme 2σ–π-mode a ring-flip mechanism is sometimes observed, which interconverts the two forms.[6] Butadienyl complexes **2**, **4** and **5** are related to 2σ–π-diene derivatives but clearly the isomerisation **2** → **4** proceeds *via* a totally different mechanism involving sulphur coordination to give a discrete η^2-vinyl intermediate **3**. Moreover, the ring-flip mechanism results in inversion of stereochemistry at the two metallated carbons of the diene complexes. Inversion at the butadienyl sp^3 carbon of

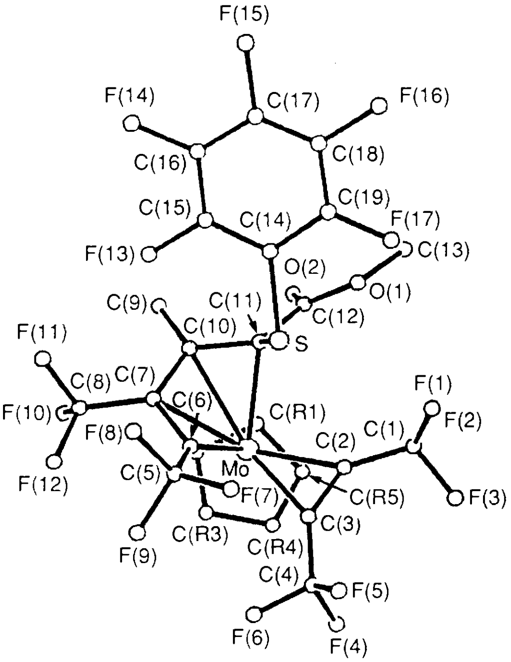


Fig. 1 The molecular structure of $[\mathrm{Mo}\{\eta^4\text{-C(CF}_3\text{)C(CF}_3\text{)C(Me)C(CO}_2\text{Me)(SC}_6\text{F}_5\text{)}\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$**2**. H-atoms are omitted for clarity. Selected distances are: Mo–C(2) 2.111(7), Mo–C(3) 2.106(7), Mo–C(6) 1.949(6), Mo–C(7) 2.313(6), Mo–C(10) 2.412(6), Mo–C(11) 2.291(6), Mo–C(R_n) = 2.365(7), 2.322(7), 2.315(7), 2.384(8) and 2.437(7) for n = 1 to 5, Mo···S 3.256(1), S···C(6) 2.810(5) Å

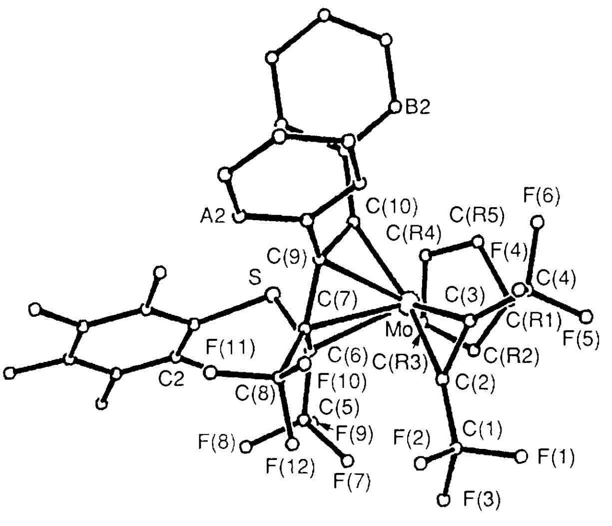


Fig. 2 The molecular structure of $[\mathrm{Mo}\{\eta^4\text{-C(CF}_3\text{)C(CF}_3\text{)(SC}_6\text{F}_5\text{)C(Ph)C(Ph)}\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$**5**. H-atoms are omitted for clarity. For phenyl rings A, B and C atoms are numbered 1–6 from the point of substitution and only the second atom is labelled. Selected distances are: Mo–C(2) 2.189(9), Mo–C(3) 2.070(10), Mo–C(6) 2.254(7), Mo–C(7) 2.381(7), Mo–C(9) 2.381(5), Mo–C(10) 1.965(6), Mo–C(R_n) = 2.335(9), 2.320(9), 2.336(8), 2.325(9) and 2.310(10) for n = 1 to 5, Mo···S 3.264(2), S···C(10) 2.891(7) Å

2 is also observed here despite the fact that a completely different mechanism is involved.

Secondly, ^{19}F NMR studies established that equilibria exist in solution between **3f** and **5b** and **4e** and **5a**. The equilibrium between **4e** and **5a** is slow on the NMR time scale at 18 °C but can be detected by ^{19}F NMR spin-saturation transfer experiments. However, exchange becomes rapid at higher temperatures and broadening and partial coalescence of the two sets of CF_3 signals are observed at *ca.* 90 °C. This reaction provides an example of an unusual type of 1,4-migration across a metallacyclic ring which has the additional feature that it is reversible on the NMR timescale. Migrations in organometallic complexes normally proceed *via* initial ligand transfer to the metal and in the present case a metallacyclic intermediate of type **6** may be involved. Formation of the *supine*-η^4-butadienyl complex **2** from **1** is also consistent with the formation of a related metallacyclic species **7** in which the thiolate ligand can undergo migration onto a metallated carbon from a direction distal to the cyclopentadienyl ring. Because migration in all cases 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 $[\mathrm{M}\{\eta^3\text{-C(CF}_3\text{)C(CF}_3\text{)SPr}^i\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{Cp})]$ (M=Mo, W) also react with alkynes to give complexes of types **3** and **4**[2] apparently as a result of alkyne insertion into a C–S bond. We have isolated derivatives of type **6** previously, but with a coordinated isocyanide instead of an alkyne ligand[7] whilst metallacycles related to **7** are also known.[4]

We also draw attention to the possibility that the isomerisation **4** → **5** may provide an explanation for an unusual result in ruthenium chemistry observed in the reaction of the σ-vinyl complex $[\mathrm{Ru}\{\sigma\text{-C(CF}_3\text{)=C(CF}_3\text{)H}\}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ with $\mathrm{MeO_2CC{\equiv}CCO_2Me}$. This gives an η^3-butadienyl complex $[\mathrm{Ru}\{\eta^3\text{-C(CF}_3\text{)=C(CF}_3\text{)C(CO}_2\text{Me)=C(CO}_2\text{Me)H}\}(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$ apparently as a result of $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ insertion into the C–H bond of the σ-vinyl ligand.[8] However, initial insertion of $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ into the metal–vinyl bond followed by a 1,4-hydrogen migration, *cf.* **4** → **5**, *via* a metallacyclic intermediate provides a more logical explanation for this hitherto puzzling reaction.

We thank the SERC for financial support.

Received, 29th May 1990; Com. 0/02397C

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