

**Molybdenum Promoted Alkyne Dimerisation Leading to Novel Metallacycles: The Crystal and Molecular Structures of *prone*-[Mo{ $\eta^4$ -C(CF<sub>3</sub>)C(CF<sub>3</sub>)C(Me)C(CO<sub>2</sub>Me)-(SC<sub>6</sub>F<sub>5</sub>)}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] and *supine*-[Mo{ $\eta^4$ -C(CF<sub>3</sub>)(SC<sub>6</sub>F<sub>5</sub>)C(CF<sub>3</sub>)C(Ph)C(Ph)}-(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)]**

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Reactions of alkynes with [MoSC<sub>6</sub>F<sub>5</sub>(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] **1** gives the novel *prone*  $\eta^4$ -butadienyl complex [Mo{ $\eta^4$ -C(CF<sub>3</sub>)C(CF<sub>3</sub>)C(R')C(R)(SC<sub>6</sub>F<sub>5</sub>)}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)], which undergoes isomerisation via an  $\eta^2$ -vinyl intermediate to the *supine* isomer followed by a novel 1,4-thiolate migration to give *supine*-[Mo{ $\eta^4$ -C(CF<sub>3</sub>)(SC<sub>6</sub>F<sub>5</sub>)C(CF<sub>3</sub>)C(R)C(R')}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)].

In recent years it has become apparent that metal-vinyl,<sup>1</sup> metal-butadienyl<sup>2,3</sup> and metallacyclopentadiene<sup>4</sup> 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<sub>6</sub>F<sub>5</sub>(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] **1**, that provide an insight into the interrelationships of these complex types and their role in alkyne insertion and dimerisation reactions.

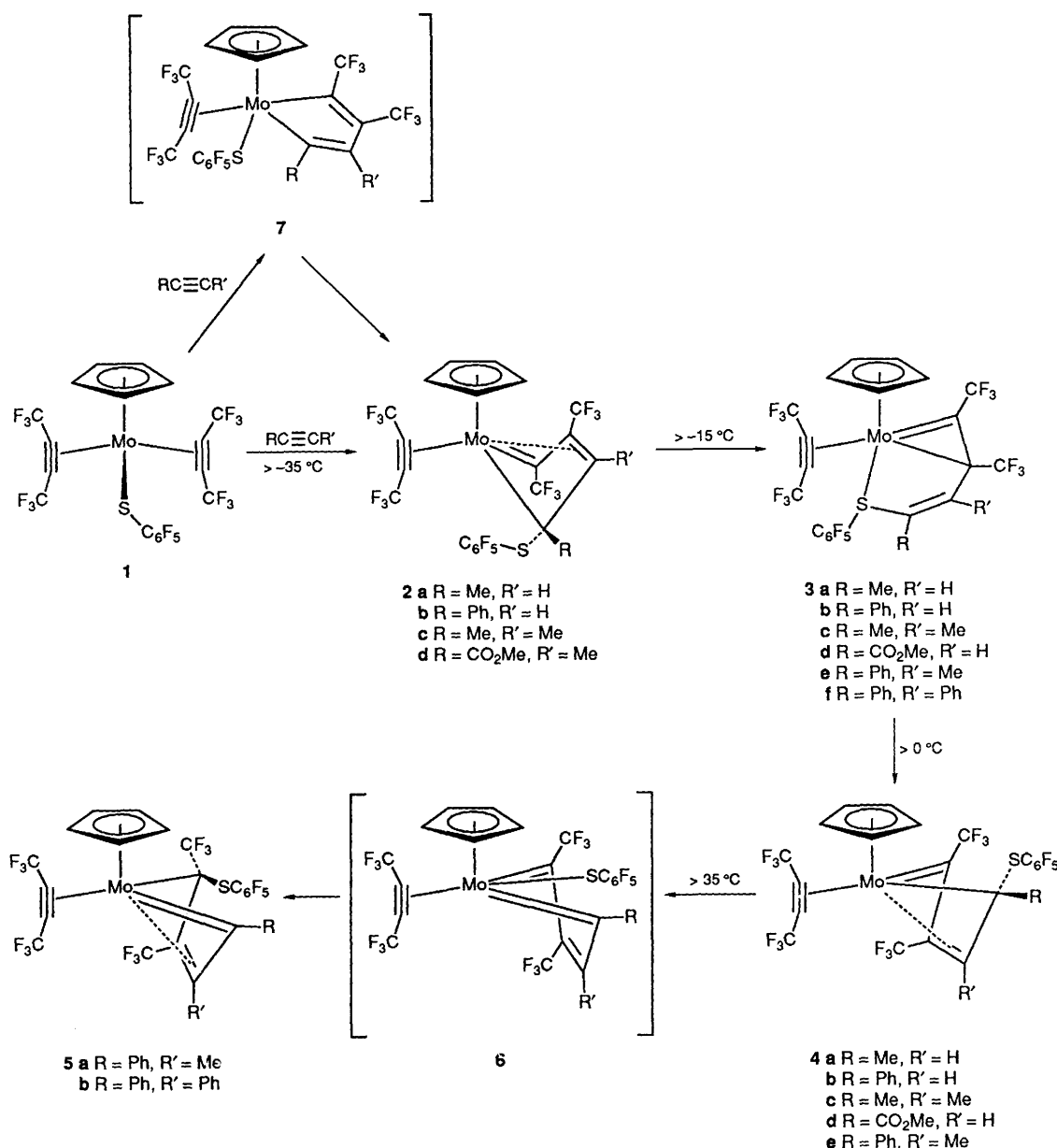
Reactions of complex **1** with alkynes RC $\equiv$ CR' in diethyl ether-hexane were studied over the temperature range -40 to +50 °C and are summarised in Scheme 1. Previously we established that complexes of type **3** and **4** are obtained from reactions of alkynes with  $\eta^2$ -C,C-vinyl complexes [M{ $\eta^3$ -C(CF<sub>3</sub>)C(CF<sub>3</sub>)SPri}(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] (M=Mo, W).<sup>4</sup> However, in the present case detailed <sup>19</sup>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 $\equiv$ CMe and MeC $\equiv$ CH, whereas isomerisation to **5** is only observed when more bulky substituents are present as with PhC $\equiv$ CMe and PhC $\equiv$ CPh. Isolation of all four isomeric types proved possible† and **3** and **4** were identified by

comparison of spectroscopic features with the SPri analogues previously characterised by X-ray methods.<sup>2</sup>

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 ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mo(CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub>) 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<sub>4</sub> 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<sub>4</sub> butadienyl donor set is similar in both complexes; although the Mo and S atoms lie on opposite sides of the C<sub>4</sub> plane the non-bonded Mo...S

† Reactions were carried out under the following conditions, **2d** Et<sub>2</sub>O-hexane, -20 °C; **3g** hexane, 45 °C; **4d** Et<sub>2</sub>O-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<sub>2</sub>Cl<sub>2</sub> at 20 °C and was then isolated by fractional crystallisation following addition of hexane.

‡ Crystal data: **2d** (R = CO<sub>2</sub>Me, R' = Me), C<sub>24</sub>H<sub>11</sub>F<sub>17</sub>MoO<sub>2</sub>S, *M* = 782.32, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 8.762(2), *b* = 15.962(1), *c* = 19.246(2) Å,  $\beta$  = 95.657(11)°, *U* = 2678.6(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.940 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 6.90 cm<sup>-1</sup>, *F*(000) = 1528 electrons, *R*(*R*<sub>w</sub>) = 0.050 (0.063) after refinement of 407 parameters from 3787 independent reflections with *I*  $\geq$  3 $\sigma$ (*I*) and  $\theta$ (Mo-K $\alpha$ ) < 25°. **5b** (R = R' = Ph), C<sub>33</sub>H<sub>15</sub>F<sub>17</sub>MoS, *M* = 862.45, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 8.561(1), *b* = 18.927(4), *c* = 19.650(2) Å,  $\beta$  = 93.14(1)°, *U* = 3179.2(9) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.802 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 5.86 cm<sup>-1</sup>, *F*(000) = 1696 electrons, *R*(*R*<sub>w</sub>) = 0.034 (0.030) after refinement of 469 parameters from 1968 independent reflections with *I*  $\geq$  2 $\sigma$ (*I*) and  $\theta$ (Mo-K $\alpha$ ) < 23°. Crystallographic measurements were made with an Enraf-Nonius CAD4F diffractometer and Mo-K $\alpha$  radiation,  $\lambda$  = 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.

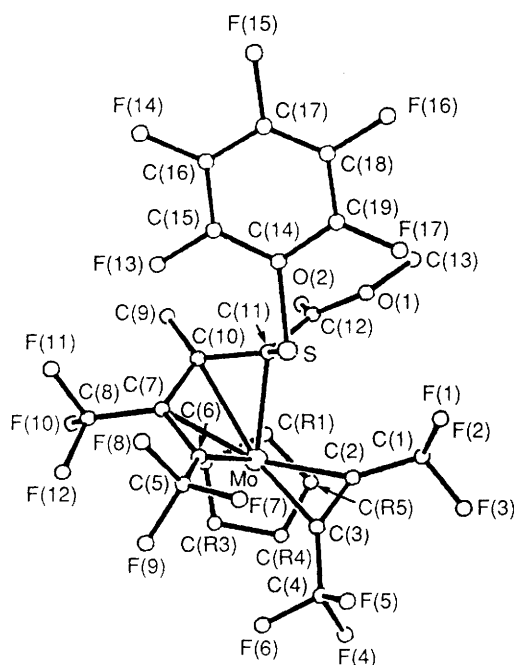


Scheme 1

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).<sup>5</sup> The structures of **2d** and **5b** are thus consistent with easy mobility of the SC<sub>6</sub>F<sub>5</sub> 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  $\eta^4$ -butadienyl ligands, *e.g.* **2** and **4**, has not been observed previously. However, *prone-supine* isomerism in  $\eta^4$ -diene complexes has been studied extensively in recent years and when the metal–ligand bonding approaches the extreme  $2\sigma$ - $\pi$ -mode a ring-flip mechanism is sometimes observed, which interconverts the two forms.<sup>6</sup> Butadienyl complexes **2**, **4** and **5** are related to  $2\sigma$ - $\pi$ -diene derivatives but clearly the isomerisation **2**  $\rightarrow$  **4** proceeds via a totally different mechanism involving sulphur coordination to give a discrete  $\eta^2$ -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  $\text{sp}^3$  carbon of

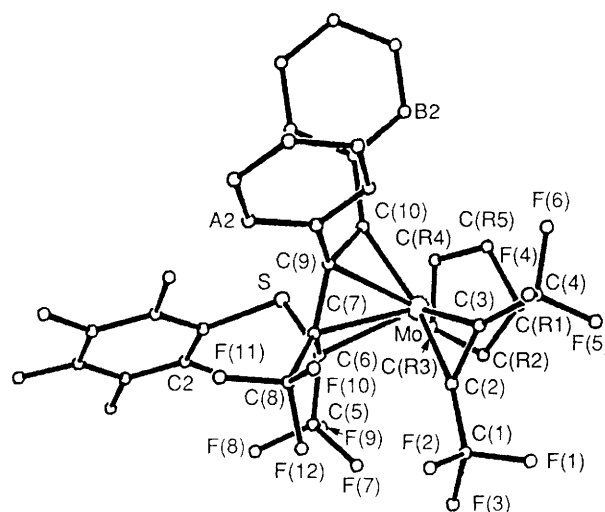


**Fig. 1** The molecular structure of  $[\text{Mo}\{\eta^4\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{C}(\text{Me})\text{C}(\text{CO}_2\text{Me})(\text{SC}_6\text{F}_5)\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]\mathbf{2}$ . H-atoms are omitted for clarity. Selected distances 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 $\cdots$ S 3.256(1), S $\cdots$ C(6) 2.810(5) Å

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

Secondly,  $^{19}\text{F}$  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  $^{19}\text{F}$  NMR spin-saturation transfer experiments. However, exchange becomes rapid at higher temperatures and broadening and partial coalescence of the two sets of  $\text{CF}_3$  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*- $\eta^4$ -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  $\text{CF}_3$  substituent this provides a logical explanation for the fact that  $\eta^2\text{-C,C-vinyl}$  complexes  $[\text{M}\{\eta^3\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{SPri}\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{Cp})]$  ( $\text{M}=\text{Mo}, \text{W}$ ) also react with alkynes to give complexes of types **3** and **4**<sup>2</sup> 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<sup>7</sup> whilst metallacycles related to **7** are also known.<sup>4</sup>

We also draw attention to the possibility that the isomerisation **4**  $\rightarrow$  **5** may provide an explanation for an unusual result in ruthenium chemistry observed in the reaction of the  $\sigma$ -vinyl



**Fig. 2** The molecular structure of  $[\text{Mo}\{\eta^4\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)(\text{SC}_6\text{F}_5)\text{-C}(\text{Ph})\text{C}(\text{Ph})\}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]\mathbf{5}$ . 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 $\cdots$ S 3.264(2), S $\cdots$ C(10) 2.891(7) Å

complex  $[\text{Ru}\{\sigma\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$  with  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ . This gives an  $\eta^3$ -butadienyl complex  $[\text{Ru}\{\eta^3\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H}\}(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$  apparently as a result of  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  insertion into the C–H bond of the  $\sigma$ -vinyl ligand.<sup>8</sup> However, initial insertion of  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  into the metal–vinyl bond followed by a 1,4-hydrogen migration, *cf.* **4**  $\rightarrow$  **5**, *via* a metallacyclic intermediate provides a more logical explanation for this hitherto puzzling reaction.

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## References

- 1 J. L. Templeton, *Adv. Organomet. Chem.*, eds. F. G. A. Stone and R. West, 1989, **29**, 1.
- 2 N. M. Agh-Atabay, J. L. Davidson, G. Douglas and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1989, 549; L. Carlton, J. L. Davidson, P. Ewing, Lj. Manojlović-Muir and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1985, 1474.
- 3 G. C. Conole, M. Green, M. McPartlin, C. Reeve and C. M. Woolhouse, *J. Chem. Soc., Chem. Commun.*, 1988, 1310; J. R. Tonker and J. L. Templeton, *J. Am. Chem. Soc.*, 1985, **107**, 5004; S. G. Feng, A. S. Gamble and J. L. Templeton, *Organometallics*, 1989, **8**, 2024.
- 4 M. O. Albers, D. J. A. de Waal, D. C. Liles, D. J. Robinson, E. Singleton and M. B. Wiege, *J. Chem. Soc., Chem. Commun.*, 1986, 1680; W. Hirpo and M. D. Curtis, *J. Am. Chem. Soc.*, 1988, **110**, 5218.
- 5 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960, 3rd edn., p. 260.
- 6 H. Yasuda and A. Nakamura, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 723.
- 7 L. J. Canoira, J. L. Davidson, G. Douglas and K. W. Muir, *J. Organomet. Chem.*, 1989, **362**, 135.
- 8 T. Blackmore, M. I. Bruce and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 106.