

Organothiometalate Addition Reactions with Electronegative Alkynes.
The X-Ray Molecular Structures of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{FeC}(\text{O})\text{C}(\text{CF}_3)=\text{CHSMe}]$,
 $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{FeC}(\text{CF}_3)=\text{CHS}(\text{Me})\text{Fe}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)\text{SMe}]$, and
 $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{MoC}(\text{O})\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{C}(\text{O})\text{SMe}]$

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Summary Addition of $\text{F}_3\text{CC}=\text{CH}$ and $\text{F}_3\text{CC}\equiv\text{CCF}_3$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{FeSMe}(\text{CO})_2]$ gives mono- and bi-nuclear methylthio-alkenyl complexes, and with $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ and MeSSMe a novel six-membered metallocycle incorporating S-methyl thioester and η^3 -acryloyl functions is obtained.

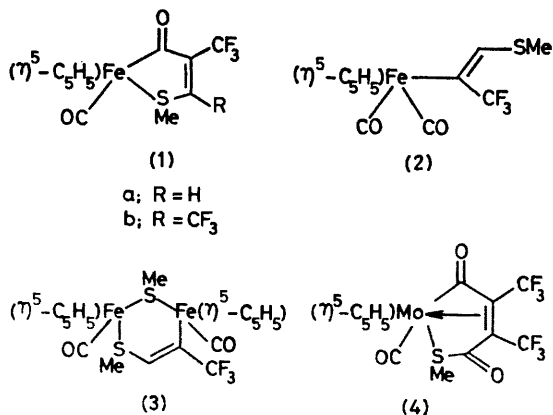
The complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{SMe})(\text{CO})_2]$ reacts with trifluoropropyne to give a species which is formulated as **(1a)** on the basis of an X-ray analysis.† The corresponding reaction with hexafluorobut-2-yne gives **(1b)**. The heterocycle in **(1a)** is formed by alkyne-bridging of the methylthio and carbonyl ligands of the parent complex and its structure supports the previous conclusion of Davidson *et al.*¹ regard-

ing initial formation of an $\text{M} \leftarrow \text{S}(\text{Me})\text{C}=\text{CC}(\text{O})$ species with molybdenum or tungsten derivatives. However, in contrast with the behaviour of the Group 6B heterocycles, on irradiation (Hanau TQ150, mercury vapour lamp) **(1a)** undergoes rearrangement in tetrahydrofuran to give the acyclic species **(2)** (characterised analytically and by ^1H , ^{13}C , and ^{19}F n.m.r. and mass spectroscopy). With an excess of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{SMe})(\text{CO})_2]$, **(2)** undergoes further reaction to yield the binuclear complex **(3)**, which may

REACTIONS between alkynes and $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{SMe})(\text{CO})_3]$ complexes (M = Mo or W) have recently been described. Initially, $\text{M} \leftarrow \text{S}(\text{Me})\text{C}=\text{CC}(\text{O})$ heterocycles are believed to be formed. These undergo a subsequent rearrangement of uncertain mechanism to give finally $\text{M} \leftarrow \text{S}(\text{Me})\text{C}(\text{O})\text{C}=\text{C}$ species.^{1,2} The chemical and crystallographic studies which we now report are pertinent to an understanding of the mechanism of this unusual rearrangement.

† *Crystal data:* **(1a)**, $\text{C}_{11}\text{H}_9\text{F}_3\text{FeO}_2\text{S}$, monoclinic, space group $P2_1/n$, $a = 8.573(2)$, $b = 14.263(2)$, $c = 10.355(2)$ Å, $\beta = 105.77(2)^\circ$, $Z = 4$; $R = 0.034$ for 2446 diffractometric intensities. **(3)**, $\text{C}_{17}\text{H}_{17}\text{F}_3\text{Fe}_2\text{O}_2\text{S}_2$, monoclinic, space group $P2/c$, $a = 7.866(1)$, $b = 26.242(5)$, $c = 9.288(2)$ Å, $\beta = 102.77(2)^\circ$, $Z = 4$; $R = 0.040$ for 1496 diffractometric intensities. **(4)**, $\text{C}_{13}\text{H}_8\text{F}_6\text{MoO}_3\text{S}$, orthorhombic, space group $Pcab$, $a = 13.711(3)$, $b = 14.353(3)$, $c = 15.268(3)$ Å, $Z = 8$; $R = 0.034$ for 2520 diffractometric intensities. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

also be obtained directly by irradiation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{SMe})(\text{CO})_2]$ in the presence of trifluoropropyne. The complex (3) is stable in solution and appears not to undergo further reaction readily. The structure of (3), which has been established *inter alia* by X-ray analysis,[†] contains a six-membered SFeSFeC_2 ring. Whilst it is formally the result of a mono-insertion of alkyne into one Fe-S bond of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{SMe})(\text{CO})_2]$ this simple reaction appears unlikely for the formation of (3), which seems to require the interaction of two monomeric species.



Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ with dimethyl disulphide and hexafluorobut-2-yne under irradiation gives an orange-red product (4) originally formulated as a vinyl derivative.³ However, X-ray analysis[†] indicates that (4) has the stereochemistry shown in the Figure. The metal atom is incorporated into a six-membered ring, formed by linking a methylthio group through a carbonyl to the alkyne, which is in turn attached to a second carbonyl group. An 18-electron configuration is completed by donation of a lone pair of electrons from sulphur and of three electrons from an $\eta^3\text{-C}_3$ unit. No simple description of the $\eta^3\text{-C}_3\text{-Mo}$ bonding appears possible. The molybdenum atom is *ca.* 0.1 Å closer to C(8) than to C(4) and C(6), suggesting the $\sigma + \pi$ formulation (4), though it should be noted that the C(4)-C(6) and C(6)-C(8) bonds are equal in length. The torsion angles about the C(4)-C(6)-C(8) bonds (see Figure) would seem to preclude a *quasi-π*-allylic structure. Such *quasi-acryloyl* functions have been previously mentioned in cobalt chemistry⁴ although they have apparently not been characterised crystallographically. The complex (4) is thus analogous to the tungsten heterocycle described by Davidson *et al.*¹ but with a further carbonyl insertion into the M-C(alkenyl) bond. Such multiple insertions of, *e.g.*, alkynes have been previously described, but the double insertion of a carbonyl appears to be novel. The ring configuration, which permits attachment of three adjacent

carbon atoms (and the terminal sulphur atom) to the metal, with retention of an 18-electron configuration, undoubtedly assists the insertion of the second carbonyl group.

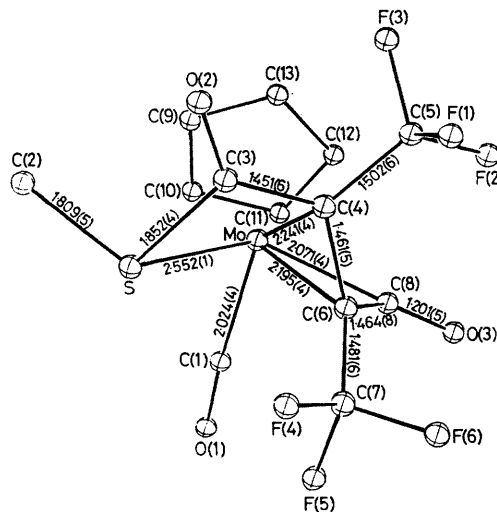


FIGURE. The molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{MoC}(\text{O})\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{C}(\text{O})\text{SMe}]$ (4) showing selected bond lengths (Å). The Mo-C(8)-O(3) and C(6)-C(8)-O(3) angles are, respectively, 147.0(3) and 137.8(4)°. The torsion angles C(7)-C(6)-C(4)-C(3) and C(7)-C(6)-C(8)-O(3) are -55(1) and -41(1)°.

The mass spectra of compounds (1a), (1b), and (4) show parent ions and ions derived from successive loss of up to two [in (1)] and three [in (4)] CO groups confirming that incorporation of carbonyl groups into heterocyclic functions is no barrier to their subsequent easy removal. In (1a) this result is in agreement with the ease of deacylation to form a terminal carbonyl group. In the present and recent work^{1,2} S-substituted thioesters are formed although such species do not result from reactions with trifluoromethane- and pentafluorobenzene-thiolate derivatives.⁵ The direction of insertion of trifluoropropyne in this work consistently occurs to give the trifluoromethyl group adjacent to the metal in accord with major interaction of the more electron-deficient end of the alkyne with the relatively electron-rich metal centre.

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¹ J. L. Davidson, M. Shiralian, Lj. Manojlović-Muir, and K. W. Muir, *J.C.S. Chem. Comm.*, 1979, 30.

² Lj. Manojlović-Muir and K. W. Muir, *J. Organometallic Chem.*, in the press; J. L. Davidson, M. Shiralian, Lj. Manojlović-Muir, and K. W. Muir, unpublished results.

³ F. Y. Petillon and D. W. A. Sharp, *J. Fluorine Chem.*, 1976, 8, 323.

⁴ G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. 2, Methuen, London, 1968, p. 57.

⁵ P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J.C.S. Dalton*, 1976, 241.