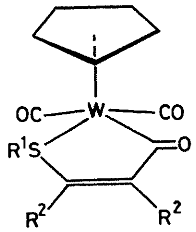
# Metal-promoted 1,3-Sulphur Shifts Leading to Novel Metallocycles. *X*-Ray Crystal and Molecular Structures of $[\overline{\mathrm{WC(CF_3)\cdot C}}\mathrm{(CF_3)\cdot C(O)SMe(\eta^5\text{-}C_5H_5)(CO)_2}]$ and $[\overline{\mathrm{WC(CO_2Me)C(CO_2Me)\cdot C(O)S}}\mathrm{Me(\eta^5\text{-}C_5H_5)(CO)_2}]$

By Jack L. Davidson* and Mahmoud Shiralian
(*Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh* EH14 4AS)
and Ljubica Manojlovic-Muir and Kenneth W. Muir*
(*Department of Chemistry, The University, Glasgow* G12 8QQ)

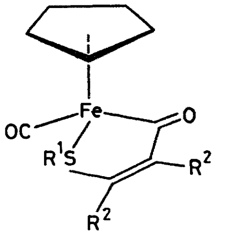
*Summary* The migration of an alkylthio group across an enone ligand co-ordinated to tungsten has been demonstrated; *X*-ray diffraction studies have established the structures of the two isomeric products, one of which contains a novel alkyl-carbene ligand which functions as a three-electron donor to the metal.

Reactions between acetylenes and organometallic complexes of the transition metals frequently lead to compounds containing unusual ligands which exhibit novel modes of attachment to the central metal or metals.[1] This is particularly true of reactions involving hexafluorobut-2-yne (hfb) but in previous investigations, reactions with organothiometallates $[\mathrm{M(\eta^5\text{-}C_5H_5)SR^1(CO)_3}]$ (M=Mo, W; R$^1$=CF$_3$, C$_6$F$_5$) only resulted in easy CO displacement to yield co-ordinatively unsaturated acetylene π-complexes $[\mathrm{M(\eta^5\text{-}C_5H_5)(SR^1)CO(hfb)}]$.[2] We now report that $[\mathrm{W(\eta^5\text{-}C_5H_5)SR^1(CO)_3}]$ (R$^1$=Me, Et,Pr$^i$) reacts with hfb or dimethyl acetylenecarboxylate to give complexes (**1**) while $[\mathrm{Fe(\eta^5\text{-}C_5H_5)SR^1(CO)_2}]$ (R$^1$=Me, Et, Pr$^i$) gives (**2**), structurally analogous to previously reported sulphur and nitrogen derivatives.[3] These structures are suggested on the basis of spectroscopic evidence and preliminary *X*-ray studies[4] which confirm that $[\overline{\mathrm{FeC(O)\cdot C(CF_3)\!:\!C(H)S}}\mathrm{Me(\eta^5\text{-}C_5H_5)CO}]$ obtained from the reaction of CF$_3$C≡CH with $[\mathrm{Fe(\eta^5\text{-}C_5H_5)SMe(CO)_2}]$ has structure (**2**). The incorporation of CO into the chelate ring with R$^1$ = Me, Et, or Pr$^i$ contrasts with the formation of simple insertion products $[\mathrm{FeC(CF_3)\!:\!C(CF_3)SR^1(\eta^5\text{-}C_5H_5)(CO)_2}]$ when R$^1$ = CF$_3$ or C$_6$F$_5$[5] which suggests that insertion of the acetylene into the metal–sulphur bond may precede sulphur co-ordination and CO migration on to the fluorocarbon ligand.



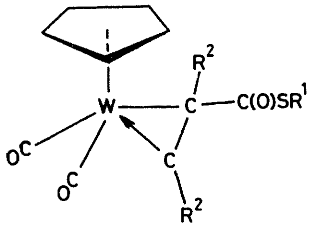
(1)

a; $R^1 = Me, R^2 = CF_3$
b; $R^1 = Et, R^2 = CF_3$
c; $R^1 = Me, R^2 = CO_2Me$
d; $R^1 = Et, R^2 = CO_2Me$
e; $R^1 = Pr^i, R^2 = CO_2Me$



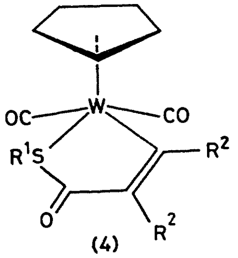
(2)

a; $R^1 = Me, R^2 = CF_3$
b; $R^1 = Me, R^2 = CO_2Me$
c; $R^1 = Pr^i, R^2 = CF_3$
d; $R^1 = Pr^i, R^2 = CO_2Me$



(3)

a; $R^1 = Me, R^2 = CF_3$
b; $R^1 = Et, R^2 = CF_3$
c; $R^1 = Pr^i, R^2 = CF_3$



(4)

a; $R^1 = Me, R^2 = CF_3$
b; $R^1 = Et, R^2 = CF_3$
c; $R^1 = Pr^i, R^2 = CF_3$
d; $R^1 = Me, R^2 = CO_2Me$

Complexes (**2**) are thermally stable in solution whereas complexes (**1**) rearrange to (**4**), reactions which, with $R^2 = CF_3$, proceed *via* heat and light sensitive intermediates (**3**). The structures of (**3a**) and (**4d**) have been established by single-crystal *X*-ray diffraction studies.

Complex (**3a**) is monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 7{\cdot}950(1)$, $b = 14{\cdot}416(2)$, $c = 14{\cdot}210(2)$ Å, $\beta = 105{\cdot}29(1)^\circ$; (**4d**) is also monoclinic, space group $P2_1/a$, $Z = 4$ with $a = 10{\cdot}323(2)$, $b = 16{\cdot}016(2)$, $c = 10{\cdot}437(2)$ Å, $\beta = 103{\cdot}56(2)^\circ$. Final values of *R* are 0·040 and 0·036 for 3282 and 3301 diffractometric intensities, respectively.†

Both (**3a**) and (**4d**) contain an $(\eta^5\text{-}C_5H_5)W(CO)_2$ unit and a ligand in which one of the acetylenic carbon atoms of the incoming alkyne is attached to a carbothiolic methyl ester function derived from MeS and CO groups in the original metal complex (Figure). In (**4d**) the integrity of the W–S bond is retained and a five-membered chelate ring is completed by a W–C ($\sigma$-alkenyl) linkage. The tungsten atom has a 'piano-stool' co-ordination. The S–W–C chelate angle [72·5(2)°] is only slightly more acute than the other angles at tungsten involving adjacent carbonyl or chelate donor atoms (75—82°). In (**3d**) the W–S bond has been ruptured (W · · · S 3·43 Å) and the tungsten co-ordination can be viewed as octahedral, with three facial sites occupied by two carbonyls and the midpoint of the bond between the central carbon atoms of the entering alkyne. The lengths of the W–C bonds in the $WC_2$ ring differ substantially. That of the longer bond, 2·193(7) Å, falls in the range expected for single W–C $\sigma$-bonds, such as is found in (**4d**). The shorter bond of 1·962(8) Å is comparable in length with the W–C(CO) bonds. We suggest that it should be formulated as a W–C(carbene) linkage which involves substantial W→C back-donation, arising from the electron-withdrawing nature of the substituents of the carbene carbon atom. Interestingly an $\eta^3$-vinylcarbene complex has recently been reported.[6] It then follows that in both (**3a**) and (**4d**) the tungsten atom attains an 18 e configuration, but in the former this has been achieved in a unique manner with a vinylic species functioning as an $\eta^2$ three-electron donor, an alkyl-carbene, and this rearranges to exhibit the 'normal' mode of bonding in the latter.

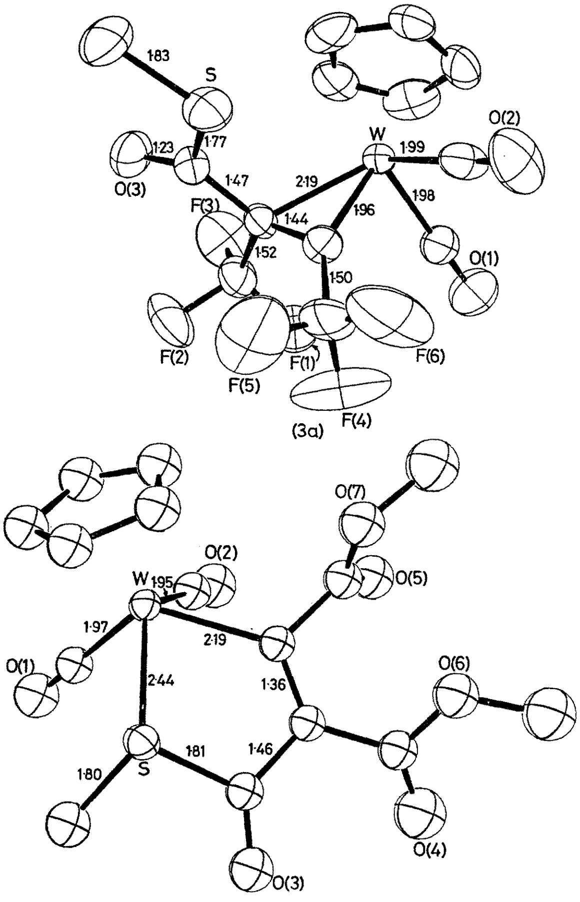


FIGURE. The molecular structures of (**3a**) and (**4d**) showing selected bond lengths (Å). Bond length standard deviations are < 0·01 Å. Labels for carbon atoms are omitted.

To our knowledge this represents the first reported example of a metal-promoted 1,3-shift of a mercapto

---

† 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.

substituent across an olefin and resembles metal promoted 1,3-hydrogen shifts in olefins and olefin complexes.[7] However, uncatalysed 1,3-sulphur shifts in allyl sulphides are known.[8] The currently accepted mechanism for metal promoted 1,3-hydride shifts involves stepwise pathways *via* allyl metal hydrides.[9] However, in the present case an analogous pathway, proceeding through a metallocyclobutenone[10] intermediate $[\overline{\mathrm{WC(CF_3)\!:\!C(CF_3)C}}(\mathrm{O})(\eta^5\text{-}\mathrm{C_5H_5})\text{-}\mathrm{SR(CO)_2}]$ containing a discrete SR ligand, seems unlikely since this would probably generate (**4**) directly. Concerted sulphur migration or a radical process, both of which would involve metal–sulphur bond cleavage, can more readily account for the initial formation of (**3**) in which the sulphur is no longer attached to the metal. The factors responsible for the stability of intermediate (**3**) sufficient to allow its isolation may be related to those which contribute to the stability of isostructural co-ordinatively unsaturated alkyne complexes $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{SR(CO)(hfb)}]$.[2]

We thank the S.R.C. for assistance in the purchase of the diffractometer (Enraf Nonius CAD-4F), the Pahlavi Foundation of Iran for a postgraduate scholarship (M. S.), and Miss Mary Macdonald for help with computing.

(*Received*, 18*th September* 1978; *Com.* 1003.)

[1] F. L. Bowden and A. B. P. Lever, *Organometallic Chem. Rev.* (*A*), 1968, **3**, 227.
[2] P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J.C.S. Dalton*, 1976, 241.
[3] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1966, **5**, 293 and references therein; A. T. Liu, W. Beck, G. Huttner, and H. Lorenz, *J. Organometallic Chem.*, 1977, **129**, 91 and references therein.
[4] F. Pétillon and A. N. Keith, personal communication.
[5] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2283.
[6] K. Nakatsu, T. Mitsudo, H. Nakanishi, Y. Watanabe, and Y. Takegami, *Chem. Letters*, 1977, 1447.
[7] M. Green and R. P. Hughes, *J.C.S. Dalton*, 1976, 1907 and references therein.
[8] P. Brownbridge and S. Warren, *J.C.S. Perkin I*, 1976, 2125.
[9] M. Green and R. P. Hughes, *J.C.S. Dalton*, 1976, 1907.
[10] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981.