Formation of Novel η^2-Vinyl Complexes by Nucleophilic Attack at Co-ordinated Hexafluorobut-2-yne: Implications for the Stereochemistry of Addition and Insertion Reactions of Co-ordinated Acetylenes. Crystal and Molecular Structure of $[Mo\{SC_5H_4NC(CF_3)\cdot C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$

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Summary Reactions of Tl(LL) (LL^- = pyridine-2-thiolato, pyrimidine-2-thiolato, or thiazoline-2-thiolato) with the bis-hexafluorobut-2-yne complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W), give products $[M\{(LL)C(CF_3)\cdot C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ containing a novel η^2-vinyl ligand resulting from nucleophilic attack of LL^- on an alkyne ligand whereas with $[WCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ the thallium(I) salt of 2-mercaptopyridine *N*-oxide unexpectedly promotes cyclopentadienyl group displacement to give the co-ordinatively unsaturated bis-hexafluorobut-2-yne complexes $[W(SC_5H_4NO)_2(CF_3C{\equiv}CCF_3)_2]$ and $[W(SC_5H_4N)(SC_5H_4NO)(CF_3C{\equiv}CCF_3)_2]$; the structure of $[Mo\{SC_5H_4NC(CF_3)\cdot C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ has been determined by *X*-ray crystallography.

IT has been suggested that acetylenes under certain circumstances may stabilise co-ordinative unsaturation in transition-metal complexes by involving both sets of π-orbitals in bonding with the transition metal.[1] We now report reactions of co-ordinatively unsaturated hexafluorobut-2-yne complexes, $[MCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (**1**), with nucleophiles which illustrate that either an acetylene ligand or the metal can function as an electrophilic centre.†

Complexes (**1**) (M = Mo or W) react with thallium(I) salts Tl(LL) (LL^- = pyridine-2-thiolato, pyrimidine-2-thiolato, or thiazoline-2-thiolato) in Et_2O or tetrahydrofuran (thf) at 20 °C to give the complexes (**2a**—**d**). To establish the structure of these complexes *X*-ray diffraction studies were carried out on the pyridine-2-thiolato-derivative (**2a**).

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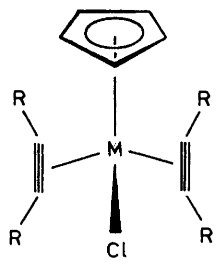
† Satisfactory elemental analyses were obtained for all complexes.

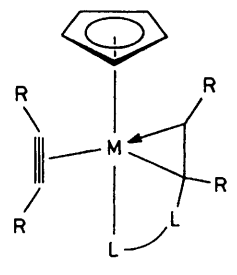
Crystal data: $C_{18}H_{9}F_{12}MoNS$, $M = 595$; monoclinic, space group $P2_1/n$, $a = 9{\cdot}475(1)$, $b = 24{\cdot}856(4)$, $c = 8{\cdot}657(2)$ Å, $\beta = 94{\cdot}50(1)°$, $U = 2033$ Å^3, $Z = 4$, $D_c = 1{\cdot}945$ g cm^{-3}. Intensity measurements were made to $\theta(\text{Mo-}K_\alpha) = 30°$ on an Enraf Nonius CAD4F diffractometer. The structure (Figure) was solved by the heavy-atom method and refined by full-matrix least-squares techniques (307 structural parameters) to R 0·029 and R_w 0·038 for 3341 independent reflections with $I > 3\sigma(I)$.‡



(1)

a; M = Mo

b; M = W



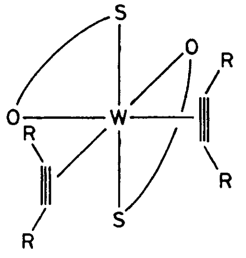
(2)

a; LL = 2-SC_5H_4N, M = Mo

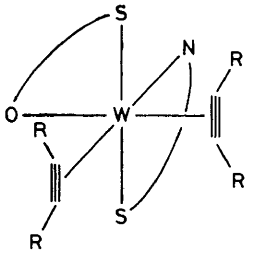
b; LL = 2-SC_5H_4N, M = W

c; LL = 2-$SC_4H_3N_2$, M = Mo

d; LL = 2-SC_3H_2NS, M = Mo



(3)



(4)

R = CF_3

S⌒O = 2-SC_5H_4NO

S⌒N = 2-SC_5H_4N

The molybdenum atom in (**2a**) attains an 18-electron configuration by attachment to an η^5-cyclopentadienyl ring, a conventional 2-electron-donor η^2-hexafluorobut-2-yne ligand, and a novel η^3-ligand derived by condensation of the pyridine-2-thiolato-nitrogen atom on the second hexafluorobut-2-yne (Figure). This new ligand is attached to molybdenum through sulphur and through a novel η^2-vinyl linkage. Previously we have established the presence of an η^2-vinyl ligand in $[W\{C(CF_3){\cdot}C(CF_3)C(O)SMe\}(CO)_2(\eta\text{-}C_5H_5)]$[2] and reported evidence for the intermediacy of related complexes in the reactions of $[M(SC_6F_5)CO(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ (M = Mo, W) with tertiary phosphines.[3]

Hexafluorobut-2-yne readily undergoes addition reactions with nucleophiles ER_2H (E = N, P, or As) to give vinylic products $R_2EC(CF_3){=}C(CF_3)H$[4] whereas co-ordination to metals normally results in activation towards electrophilic attack.[5] We tentatively attribute the reactivity towards nucleophiles observed in the present case to the involvement of both sets of filled acetylenic π-orbitals with the metal, an interaction which might be expected to reduce considerably the electron density in the vicinity of the acetylenic carbons.

Complex (**2a**) is also obtained as the major product (57%) from the reaction of (**1a**) with the thallium salt of 2-mercaptopyridine *N*-oxide ($TlSC_5H_4NO$) in ether at 20 °C. The tungsten analogue (**2b**) is similarly formed but in trace amounts only from the reaction of (**1b**) with $TlSC_5H_4NO$. The major products of this reaction are the bis-acetylene complexes $[W(SC_5H_4NO)_2(CF_3C{\equiv}CCF_3)_2]$ (**3**) (4%), and $[W(SC_5H_4NO)(SC_5H_4N)(CF_3C{\equiv}CCF_3)_2]$ (**4**) (29%), in which the thiolato-ligands have unexpectedly displaced both the cyclopentadienyl and the chloride ligands. The ^{19}F n.m.r. spectrum of (**3**) is temperature-independent between −63 and 25 °C whereas the spectrum of (**4**) exhibits four CF_3 multiplets at −63 °C two of which (δ −55·96 and −57·17 p.p.m.) coalesce to a singlet above 20 °C; coalescence of the other two peaks (δ −56·17 and −58·10 p.p.m.) to a singlet is only observed above 70 °C. Thus both acetylenes appear to undergo propeller rotation but with significantly different barriers to rotation. These data are explicable in terms of structures (**3**) and (**4**) {related to that of $[Mo(S_2CNEt_2)_2(PhC{\equiv}CPh)_2]$},[1b] although we are unable to distinguish between the structures illustrated and a number of related *cis*-isomers. The observation of two distinct rotational barriers in (**4**) has not been observed previously in bis-acetylene complexes and may reflect the differing π-bonding abilities of the donor groups *trans* to the acetylenes. Com-

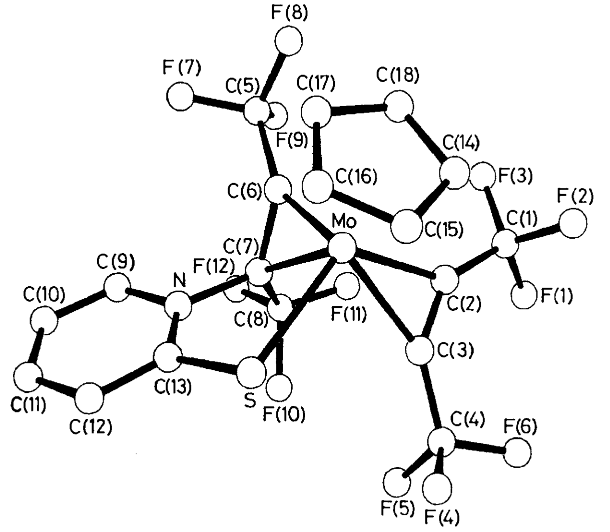


FIGURE. The molecular structure of (**2a**). Atoms are represented by spheres of arbitrary size and hydrogen atoms are omitted. Selected bond lengths are Mo–S 2·468(1), Mo–C(2) 2·092(3), Mo–C(3) 2·132(3), Mo–C(6) 1·914(4), Mo(C–7) 2·120(3), Mo–C(C_5H_5) 2·337(4)—2·385(3), C(6)–C(7) 1·390(5), N–C(7) 1·504(4), and C(2)–C(3) 1·255(7) Å.

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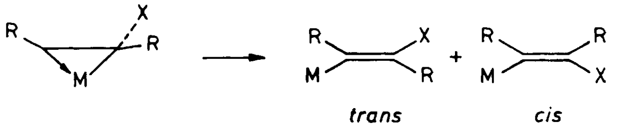
‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

plexes structurally related to (**3**) and (**4**), *e.g.* [Mo(S_2CNEt_2)$_2$(PhC≡CPh)$_2$], have been isolated previously *via* conventional routes.[1b] This alternative method involving displacement of a cyclopentadienyl ligand appears to be unique to the 1-oxopyridine-2-thiolato-ligand. Recently attention has focused on the ability of trialkyl *N*-oxides to promote CO substitution in metal carbonyls.[6] The conversion of (**1b**) into (**3**) and (**4**) suggests that other ligands normally inert to substitution may also be readily displaced by *N*-oxides.



SCHEME

The isolation of complexes (**2**) raises the possibility that reactions of acetylenes leading to η^1-vinyl complexes, *e.g.* insertions or reactions with electrophiles or nucleophiles, may proceed in some cases *via* η^2-vinyl intermediates. Consequently the stereochemistry of the η^1-vinyl product (*cis* or *trans*) will depend on the mode of ring opening in the η^2-vinyl intermediate (see Scheme). This proposal is supported by our previous observation that an η^2-vinyl complex can act as precursor to a *cis* η^1-vinyl compound.[2] Moreover η^2-vinyl species can conceivably serve as intermediates in the interconversion of *cis*- and *trans*-η^1-vinyl complexes, a process which is thought to occur in the reactions of acetylenes with nickel alkyls and aryls.[7] We hope that studies currently in progress will provide further information about the stereochemistry of $\eta^2 \rightleftharpoons \eta^1$ vinyl interconversions and and thus lead to a more detailed mechanistic insight into the addition and insertion reactions of co-ordinated acetylenes.

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