Reactions of Some Iron and Tungsten Mercapto-complexes with Electrophilic Acetylenes leading to Novel Metallacycles. The Crystal and Molecular Structure of the η^2-Vinyl Complex [W{η^2-C(CF$_3$)C(CF$_3$)-C(O)SMe}(CO)$_2$(η^5-C$_5$H$_5$)] †

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Reactions of $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ with activated alkynes $CF_3C{\equiv}CCF_3$ and $MeO_2CC{\equiv}CCO_2Me$ give heterocyclic complexes $[Fe\{C(O)C(R){=}C(R)SR'\}(CO)(\eta^5\text{-}C_5H_5)]$ (R′ = alkyl or aryl, R = CF$_3$ or CO$_2$Me). Related derivatives $[W\{C(O)C(R){=}C(R)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (R′ = Me or Et) obtained from $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ and the alkynes in hexane at 20 °C undergo a sequence of thermal isomerisations above 25 °C involving initially a novel 1,3 shift of the SR′ ligand across the eneone ligand to give the η^2-vinyl complex $[W\{\eta^2\text{-}C(R)C(R)C(O)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (R = CF$_3$ only) followed by S-bonded vinyl ketone complexes $[W\{C(R){=}C(R)C(O)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ and ultimately O-bonded vinyl ketone derivatives $[W\{C(R){=}C(R)C(SR')O\}(CO)_2(\eta^5\text{-}C_5H_5)]$ and co-ordinatively unsaturated alkyne complexes $[W(SR')(CO)(RC{\equiv}CR)(\eta^5\text{-}C_5H_5)]$ (R = CF$_3$ only). An *X*-ray structure determination of the η^2-vinyl complex $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ reveals the first example of a vinyl group bonded to a metal *via* both carbon atoms and therefore acting as a three-electron donor ligand. The structure consists of an approximately octahedrally co-ordinated tungsten atom bonded to an η^5-C$_5$H$_5$ ligand which occupies one face of the octahedron. Two carbonyl ligands occupy two octahedral sites while the third is occupied by the η^2-C(CF$_3$)C(CF$_3$)C(O)SMe ligand which adopts an orientation such that the vinylic C–C axis lies approximately parallel to one of the W–CO axes.

The possibility that insertion (ligand-migration) reactions are involved in transition-metal-catalysed hydrogenation, polymerisation, and isomerisation of unsaturated hydrocarbons has prompted extensive studies of this fundamental organometallic process. With olefins and acetylenes attention has focused primarily on insertions into metal–carbon and metal–hydrogen bonds whereas we have previously reported that hexafluorobut-2-yne also inserts into metal–sulphur bonds.[1] In contrast $CF_3C{\equiv}CCF_3$ does not insert into the metal–sulphur bond of $[M(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, R′ = CF$_3$; M = Mo, R′ = C$_6$F$_5$), and an alternative reaction pathway is observed leading to co-ordinatively unsaturated alkyne complexes $[M(SR')(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$.[2] Similar complexes are also obtained from the reactions of diphenylacetylene and phenylpropyne with $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$ (X = Cl, Br, or I).[3]

In an effort to rationalise such diverse modes of reactivity we have carried out a systematic study of the reactions of the activated acetylenes $CF_3C{\equiv}CCF_3$ and dimethyl acetylenedicarboxylate ($MeCO_2C{\equiv}CCO_2Me$) with thiolates $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R′ = Me, Et, Ph, *p*-MeC$_6$H$_4$, or C$_6$F$_5$) and $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ (R′ = Me, Et, Pr^i, Ph, *p*-MeC$_6$H$_4$, CH$_2$Ph, or Bu^t). During the course of this work similar studies were reported by Sharp and Petillon.[4] However, the use of milder reaction conditions has enabled us to isolate unstable intermediates in some of these reactions which provide more definitive information about the mechanisms of the processes studied. Part of this work has been published in earlier communications.[5]

Results

(*a*) *Reactions of* $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ *with* $CF_3C{\equiv}CCF_3$ *and* $MeCO_2C{\equiv}CCO_2Me$.—Iron thiolates $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ (R′ = Me, Et, Ph, *p*-MeC$_6$H$_4$, Pr^i, CH$_2$Ph, or Bu^t) undergo thermal reactions (room temperature in diethyl ether solution) with $CF_3C{\equiv}CCF_3$ or $MeCO_2C{\equiv}CCO_2Me$ (L) to give moderate to good yields (45—80%) of brown crystalline complexes which according to elemental analyses (Table 1) have the stoicheiometry $[Fe(SR')(CO)_2L(\eta^5\text{-}C_5H_5)]$. This is confirmed by the mass spectra which exhibit a molecular ion M^+ and ions $[M - CO]^+$, $[M - 2CO]^+$, and $[M - L]^+$. The i.r. spectra in all cases exhibit a single ν(CO) band around 1 965 cm^{-1} while a strong band at *ca.* 1 625 cm^{-1} is characteristic of a metal–acyl ν(CO) mode. The ^{19}F n.m.r. spectra of the $CF_3C{\equiv}CCF_3$ derivatives exhibit two equal-intensity quartets near δ 55 and 59 with coupling constants *J*(FF) *ca.* 11–11.9 Hz characteristic of a *cis* C(CF$_3$)=C(CF$_3$) moiety.[6] The ^{1}H n.m.r. spectra in all cases exhibit a sharp singlet near δ 4.5 due to the η^5-C$_5$H$_5$ ligand and other resonances typical of the organic group attached to sulphur, while the $MeCO_2C{\equiv}CCO_2Me$ derivatives also exhibit two singlets around δ 6.5 due to two inequivalent CO(OMe) substituents. On this basis the complexes are assigned structure (1), a proposal supported by the results of an *X*-ray diffraction study of the related complex $[Fe\{C(O)C(CF_3){=}C(H)SMe\}(CO)(\eta^5\text{-}C_5H_5)]$ isolated from the reaction of trifluoropropyne with $[Fe(SMe)(CO)_2(\eta^5\text{-}C_5H_5)]$.[4b]

(*b*) *Reactions of* $[W(SR')(CO)_3(\eta\text{-}C_5H_5)]$ *with* $CF_3C{\equiv}CCF_3$ *and* $MeCO_2C{\equiv}CCO_2Me$.—The tungsten complexes $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R′ = Me or Et) react with $CF_3C{\equiv}CCF_3$ and $MeCO_2C{\equiv}CCO_2Me$ (L) at 20 °C in hexane to give brown crystalline 1 : 1 adducts $[W(SR')(CO)_3L(\eta^5\text{-}C_5H_5)]$ which exhibit similar spectroscopic features (Table 2) to the iron

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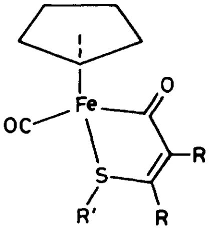
† Dicarbonyl(η-cyclopentadienyl)[3-methylthio-3-oxo-1,2-bis(trifluoromethyl)propen-2-yl-1-ylidene]tungsten.

Supplementary data available (No. SUP 23994, 16 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Transactions*, 1984, Issue 1, pp. xvii—xix.

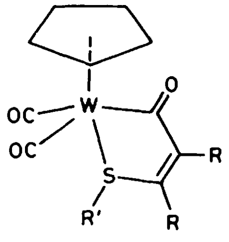
Table 1. Analytical data for the complexes [a]

	Compound	Analysis (%)				
		C	H	S	F	M [b]
(1a)	[Fe{C(O)C(CF$_3$)=C(CF$_3$)SMe}(CO)(η^5-C$_5$H$_5$)]	38.0 (37.3)	2.1 (2.1)			386 (386)
(1b)	[Fe{C(O)C(CF$_3$)=C(CF$_3$)SEt}(CO)(η^5-C$_5$H$_5$)]	38.9 (39.0)	2.3 (2.5)	7.7 (8.0)	28.0 (28.5)	400 (400)
(1c)	[Fe{C(O)C(CF$_3$)=C(CF$_3$)SPr^i}(CO)(η^5-C$_5$H$_5$)]	41.0 (40.6)	3.1 (2.9)			414 (414)
(1d)	[Fe{C(O)C(CF$_3$)=C(CF$_3$)SPh}(CO)(η^5-C$_5$H$_5$)]	45.0 (45.5)	2.3 (2.2)			448 (448)
(1e)	[Fe{C(O)C(CF$_3$)=C(CF$_3$)SC$_6$H$_4$Me-*p*}(CO)(η^5-C$_5$H$_5$)]	47.5 (46.8)	2.8 (2.6)			462 (462)
(1f)	[Fe{C(O)C(CO$_2$Me)=C(CO$_2$Me)SMe}(CO)(η^5-C$_5$H$_5$)]	45.4 (45.9)	3.9 (3.8)			366 (366)
(1g)	[Fe{C(O)C(CO$_2$Me)=C(CO$_2$Me)SEt}(CO)(η^5-C$_5$H$_5$)]	47.1 (47.4)	4.5 (4.2)			380 (380)
(1h)	[Fe{C(O)C(CO$_2$Me)=C(CO$_2$Me)SCH$_2$Ph}(CO)(η^5-C$_5$H$_5$)]	53.7 (54.3)	4.3 (4.1)			442 (442)
(1i)	[Fe{C(O)C(CO$_2$Me)=C(CO$_2$Me)SBu^t}(CO)(η^5-C$_5$H$_5$)]	49.4 (50.0)	4.9 (4.9)			408 (408)
(1j)	[Fe{C(O)C(CO$_2$Me)=C(CO$_2$Me)SC$_6$H$_4$Me-*p*}(CO)(η^5-C$_5$H$_5$)]	54.5 (54.3)	4.1 (4.1)			442 (442)
(2a)	[W{C(O)C(CF$_3$)=C(CF$_3$)SMe}(CO)$_2$(η^5-C$_5$H$_5$)]	29.0 (28.8)	1.7 (1.5)	5.6 (5.9)	20.5 (21.0)	540 (540)
(2b)	[W{C(O)C(CF$_3$)=C(CF$_3$)SEt}(CO)$_2$(η^5-C$_5$H$_5$)]	30.0 (30.3)	1.8 (1.8)			554 (554)
(2c)	[W{C(O)C(CO$_2$Me)=C(CO$_2$Me)SMe}(CO)$_2$(η^5-C$_5$H$_5$)]	35.0 (34.5)	3.0 (2.7)	6.4 (6.1)		520 (520)
(2d)	[W{C(O)C(CO$_2$Me)=C(CO$_2$Me)SEt}(CO)$_2$(η^5-C$_5$H$_5$)]	35.2 (35.8)	3.3 (3.0)			534 (534)
(3)	[W{η^2-C(CF$_3$)C(CF$_3$)C(O)SMe}(CO)$_2$(η^5-C$_5$H$_5$)]	29.2 (28.8)	1.6 (1.5)	6.2 (5.9)	22.3 (21.0)	540 (540)
(4a)	[W{C(CF$_3$)=C(CF$_3$)C(O)SMe}(CO)$_2$(η^5-C$_5$H$_5$)]	28.3 (28.8)	1.3 (1.5)	5.8 (5.9)		540 (540)
(4b)	[W{C(CF$_3$)=C(CF$_3$)C(O)SEt}(CO)$_2$(η^5-C$_5$H$_5$)]	30.6 (30.2)	2.0 (1.8)			554 (554)
(4c)	[W{C(CO$_2$Me)=C(CO$_2$Me)C(O)SMe}(CO)$_2$(η^5-C$_5$H$_5$)]	34.8 (34.5)	2.5 (2.7)			520 (520)
(5a)	[W{C(CF$_3$)=C(CF$_3$)C(SMe)O}(CO)$_2$(η^5-C$_5$H$_5$)]	28.7 (28.8)	1.3 (1.5)	6.3 (5.9)		540 (540)
(5b)	[W{C(CO$_2$Me)=C(CO$_2$Me)C(SMe)O}(CO)$_2$(η^5-C$_5$H$_5$)]	34.0 (34.5)	3.0 (2.7)			520 (520)
(6a)	[W(SMe)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)]	27.0 (27.2)	1.7 (1.6)			484 (484)
(6b)	[W(SPh)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)]	35.4 (35.0)	1.9 (1.8)			546 (546)
(6c)	[W(SC$_6$H$_4$Me-*p*)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)]	36.6 (36.3)	2.1 (2.1)			560 (560)
(6d)	[W(SC$_6$F$_5$)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)]	30.3 (30.1)	1.0 (0.8)			636 (636)

[a] Calculated values in parentheses. [b] Molecular ion in mass spectrum. For tungsten isotope *m*/*e* = 182.



(1)

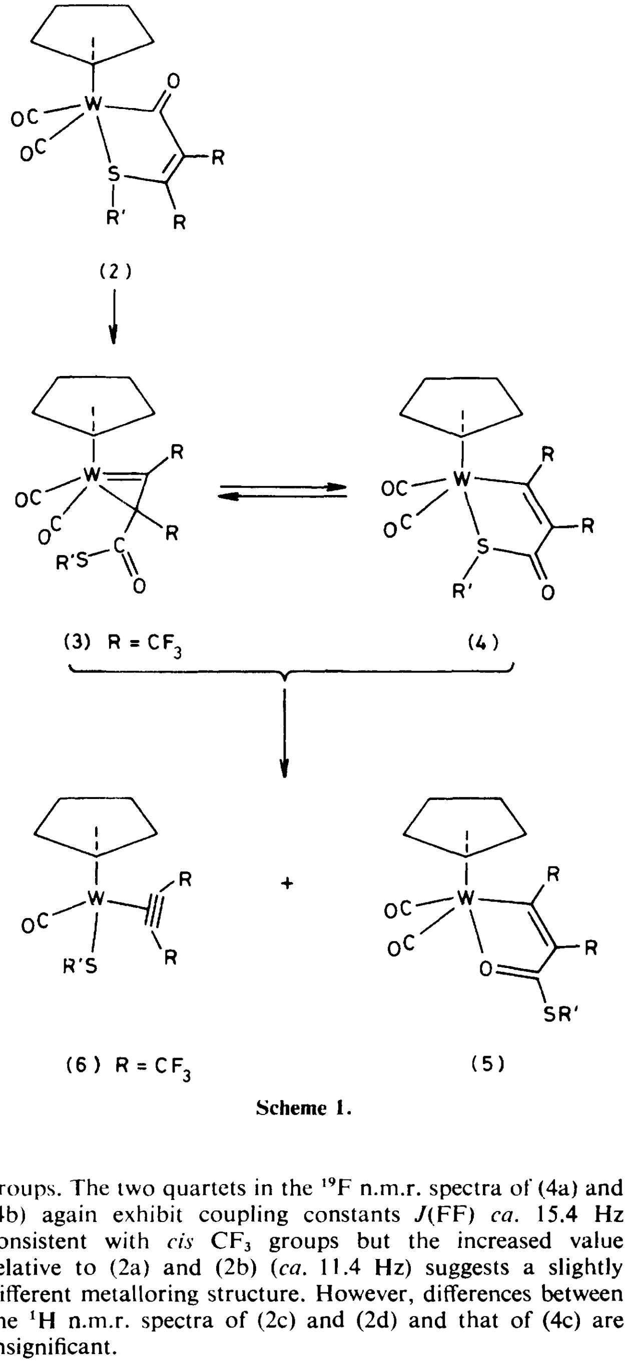


(2)

R = CF$_3$ or CO$_2$Me

derivatives (1) and a related structure (2) is proposed. This structure is also favoured by Petillon *et al.*[4a] who have prepared the SMe complexes of both molybdenum and tungsten, while related complexes have been isolated from the insertion of PhSC≡CNEt$_2$ into the M–H bonds of [MH(CO)$_3$(η^5-C$_5$H$_5$)] (M = Mo or W).[7]

(*c*) *Thermal Rearrangement of* [W{C(O)C(R)=C(R)SR′}(CO)$_2$(η^5-C$_5$H$_5$)].—The thermal rearrangements of complexes (2a)—(2c) are summarised in Scheme 1. Thus complex (2a) undergoes thermal reactions at 30 °C in hexane in a sealed tube to give yellow-orange crystals of (3) and small amounts of dark brown crystalline (4a), while (2b) undergoes rearrangement to give (4b) only. Thermal isomerisation of the MeCO$_2$C≡CCO$_2$Me complex (2c) only occurs above 50 °C in hexane giving a single product (4c). At higher temperatures (above 80 °C, hexane) (4c) isomerises to (5c). The thermal rearrangements of the secondary CF$_3$C≡CCF$_3$ adducts are more complex since (3) rearranges to (5a) and (6a), while (4a) can be detected (i.r. monitoring) and isolated in the early stages of the reaction. Similarly (4a) rearranges to (5a) and (6a) while (3) is detected in the early stages of the rearrangement. Thermolysis of the ethyl complex (2b) follows a similar route to that of (2a), but due to differing stabilities only (4b) was isolated although analogues of (3), (5a), and (6a) were detected by i.r. spectroscopy. Elemental analyses and mass spectrometry established that complexes (3)—(5) have the same stoicheiometry as (2) but spectroscopic data (Table 2) indicated differing isomeric forms. The spectroscopic data for (2a) and (2b) and (4a) and (4b) are similar indicating the presence of related structural features. Detailed differences include the ketonic ν(CO) mode in the i.r. spectra of (4a) and (4b) near 1 730 cm^{-1} instead of an acyl band near 1 550 cm^{-1}, indicating that the ketonic CO is no longer attached to the metal. This band is partially obscured in the MeCO$_2$C≡CCO$_2$Me derivative (4c) by absorptions of the COOMe



Scheme 1.

groups. The two quartets in the ^{19}F n.m.r. spectra of (4a) and (4b) again exhibit coupling constants *J*(FF) *ca.* 15.4 Hz consistent with *cis* CF$_3$ groups but the increased value relative to (2a) and (2b) (*ca.* 11.4 Hz) suggests a slightly different metalloring structure. However, differences between the ^{1}H n.m.r. spectra of (2c) and (2d) and that of (4c) are insignificant.

In contrast, although the gross spectroscopic features of complex (3) exhibit similarities to those of (2a) and (2b) and (4a) and (4b), quite marked differences are observed in some of the details. The band at 1 666 cm^{-1} in the i.r. spectrum suggests that as with (4a) and (4b) the ketonic CO is no longer attached to the metal. However, the two terminal ν(CO) modes at 2 058 and 1 994 cm^{-1} are *ca.* 100 cm^{-1} higher in frequency than those of either (2a) and (2b) or (4a) and (4b) suggesting a markedly different mode of attachment of the C(CF$_3$)C(CF$_3$)COSMe moiety to the metal. This is further suggested by the coupling constant of the two quartets in the ^{19}F n.m.r. spectrum, 2.70 Hz. Since these data did not allow unequivocal structural assignments to be carried out, single-crystal *X*-ray diffraction studies of complexes (3) and (4c) (Figure 1, Tables 3 and 4) were undertaken. The structure of (4c) has been described elsewhere.[8]

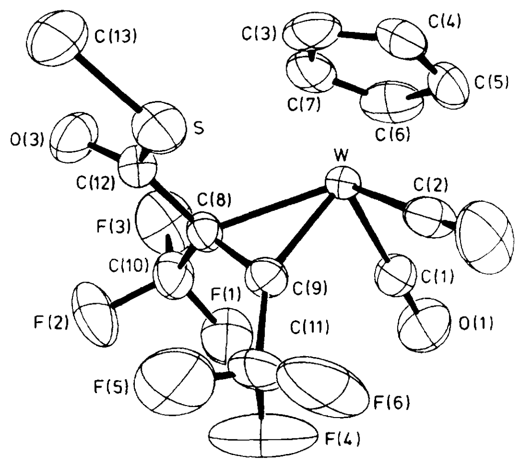


Figure 1. A perspective view of the molecular structure of [W{η^2-C(CF$_3$)C(CF$_3$)C(O)SMe}(CO)$_2$(η^5-C$_5$H$_5$)] (3) showing the atomic numbering scheme. Hydrogen atoms are omitted and 50% probability ellipsoids are displayed

The crystals of complex (3) contain discrete molecules in which the tungsten atom of a (C$_5$H$_5$)W(CO)$_2$$^+$ moiety completes an 18-electron configuration by interaction with a vinyl anion C(CF$_3$)C(CF$_3$)C(O)SMe$^-$. This ligand is η^2-bonded to the tungsten atom through C(8) and C(9), originally the unsaturated carbon atoms of an incoming hexafluorobut-2-yne molecule. The carbothiolic ester function on C(8) is derived from CO and SMe$^-$ groups in the starting complex. There is thus an interesting structural comparison to be made with (4c), which is also a complex of (C$_5$H$_5$)W(CO)$_2$$^+$ with a vinyl anion C(CO$_2$Me)C(CO$_2$Me)C(O)SMe$^-$.[5a,8] However, in (4c) the attachment of the anion to the metal is through conventional W–S and σ-W–C(alkenyl) linkages.

The (C$_5$H$_5$)W(CO)$_2$ unit in complex (3) possesses approximate C_s symmetry: the mirror plane is normal to the C$_5$ ring and passes through the atoms W and C(5). The C$_5$ ring is a pentagon of side 1.411(5) Å, from which the metal is displaced by 2.002(1) Å. Individual W–C(ring) distances [2.310(9)—2.373(9) Å] are slightly irregular. They, and the W–CO bond lengths [1.975(8) and 1.994(8) Å] agree well with corresponding values in complex (4c).[8] Nevertheless, the tungsten co-ordination in (3) is significantly different from that in (4c): the latter complex displays the well established 3 + 4 piano-stool arrangement,[9] whereas the co-ordination in (3) is less easily characterised. It may most simply be described as octahedral, with three facial sites occupied by the C$_5$ ring and the remaining three by the two carbonyl ligands and by the midpoint of C(8)–C(9). Alternatively, the metal could be regarded as seven-co-ordinate, with C(8) capping an octahedron defined by C(1), C(2), C(9), and the C$_5$ ring. The differences in metal co-ordination between complexes (3) and (4c) are nicely illustrated by the respective OC–W–CO angles of 88.2(3) and 75.2(3)°.

The orientation of the vinyl anion in complex (3) relative to the metal co-ordination polyhedron is such as to make the C(8)–C(9) and W–C(2) vectors almost coplanar, the C(9)–C(8)–W–C(1) and –C(2) torsion angles are respectively 76.3(4) and −16.4(5)°. Theoretical considerations suggest that the most favourable orientation for multiple bonding between the tungsten atom and the *sp*^{2}-carbon atom C(9) is that in which the nodal plane of the carbon *p* orbital coincides with the symmetry plane of the (C$_5$H$_5$)W(CO)$_2$ fragment.[10] In (3) the C(8)–C(9) bond is rotated by about 30° around the vector from the tungsten atom to the C(8)–C(9) centroid from this

Table 2. I.r. and n.m.r. data for the complexes

	I.r. (cm^{-1})		^{1}H N.m.r. [a]			^{19}F N.m.r. [b]	
Complex	ν(CO)	ν(C=O)	δ(C_5H_5)	δ(SR)	δ[C(O)OMe]	δ(CF_3)	^{5}J(FF)/Hz
(1a)	1 970vs	1 642m	4.40(s)	2.70(s, Me)		−54.4(q), −59.55(q)	11.25
(1b)	1 971vs	1 642m	4.70(s)	1.40(t, Me), 2.46(m, H), 3.40(m, H)		−54.70(q), −59.55(q)	11.45
(1c)	1 965vs	1 638m	4.70(s)	1.15(d, Me), 1.30(d, Me), 3.85(m, H)		−55.0(q), −59.10(q)	11.90
(1d)	1 960vs	1 633m	4.70(s)	7.70(br m, Ph)		−56.0(q), −59.10(q)	11.75
(1e)	1 970vs	1 631m	4.65(s)	2.35(s, Me), 7.25(m, C_6H_4)		−55.0(q), −59.30(q)	11.50
(1f)	1 960vs	1 620m	4.70(s)	2.65(s, Me)	3.90(s), 3.85(s)		
(1g)	1 965vs	1 610m	4.70(s)	1.35(t, Me), 2.40(m, H), 3.50(m, H)	3.90(s), 3.75(s)		
(1h)	1 952vs	1 613m	4.30(s)	4.0(m, CH_2), 7.45(s, Ph)	3.90(s), 3.85(s)		
(1i)	1 955vs	1 618m	4.60(s)	1.25(s, Bu^t)	3.70(s), 3.70(s)		
(1j)	1 966vs	1 620m	4.65(s)	2.35(s, Me), 7.25(m, C_6H_4)	3.90(s), 3.65(s)		
(2a)	1 969vs, 1892vs	1 593m	5.40(s)	3.15(s, Me)		−54.70(q), −59.95(q)	11.10
(2b)	1 965vs, 1 899vs	1 592m	5.40(s)	1.15(t, Me), 3.15(m, H), 3.65(m, H)		−54.30(q), −58.90(q)	11.40
(2c)	1 961vs, 1 886s	1 551m, 1 565m	5.40(s)	3.10(s, Me)	3.85(s), 3.80(s)		
(2d)	1 960vs, 1 883s	1 551m, 1 565m	5.40(s)	1.15(t, Me), 3.15(m, H), 3.85(m, H)	3.85(s), 3.80(s)		
(3)	2 058vs, 1 994vs	1 666m	5.60(s)	2. 10(s, Me)		−54.9(br s), −58.75(q)	2.70
(4a)	1 971vs, 1 889s	1 730m	5.60(s)	2.75(s, Me)		−51.0(q), −58.65	15.40
(4b)	1 969vs, 1 884s	1 728m	5.60(s)	1.45(t, Me), 2.95(m, H), 3.45(m, H)		−51.0(q), −58.60(q)	15.30
(4c)	1 965vs, 1 883s	1 725br, m	5.60	2.80(s, Me), 3.75(s, Me), 3.90(s, Me)			
(5a)	1 994vs, 1 926s	1 465m	5.60(s)	2.50(s, Me)		−50.75(q), −53.60(q)	14.10
(5b)	1 983vs, 1 912s	1 708s, 1 462wm	5.55(s)	2.45(s, Me)	3.90(s), 3.80(s)		
(6a)	1 999vs	1 720w [c]	5.35	1.95(s, Me)		−55.25(q), −56.85	2.90
(6b)	1 999vs	1 718w [c]	5.30(s)	7.10(br s, Ph)		−54.75(q), −56.85(q)	3.30
(6c)	1 998vs	1 717w [c]	5.40(s)	2.30(s, Me), 7.0(br s, C_6H_4)		−54.70(q), −56.90(q)	3.20
(6d)	2 001vs	1 720w [c]	5.65(s)	—		−56.35(br s), −57.25(s)	2.60

[a] δ(SiMe) = 0 p.p.m. [b] δ(CCl_3F) = 0 p.p.m.: chemical shifts are positive to high frequency. [c] ν(C≡C).

Table 3. Fractional co-ordinates (× 10^4) for [W{η^2-C(CF_3)C(CF_3)C(O)SMe}$(CO)_2$(η^5-C_5H_5)]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 914(1)	861(1)	2 799(1)	C(2)	1 737(10)	−439(5)	2 303(6)
S	−690(3)	1 679(2)	635(1)	C(3)	−618(12)	1 455(8)	3 090(6)
F(1)	5 443(6)	2 258(4)	2 730(4)	C(4)	−541(12)	485(7)	3 298(7)
F(2)	4 271(8)	3 228(4)	1 613(4)	C(5)	913(13)	317(6)	4 090(7)
F(3)	3 637(9)	3 269(4)	2 979(4)	C(6)	1 709(13)	1 182(8)	4 403(6)
F(4)	5 403(10)	846(7)	1 283(7)	C(7)	787(13)	1 867(6)	3 781(7)
F(5)	3 324(15)	1 154(8)	146(6)	C(8)	2 456(9)	2 008(5)	1 907(5)
F(6)	3 542(13)	−143(5)	788(7)	C(9)	2 794(9)	1 071(5)	1 650(5)
O(1)	5 722(8)	433(5)	3 955(5)	C(10)	3 930(10)	2 685(5)	2 305(6)
O(2)	1 604(12)	−1 188(5)	2 018(6)	C(11)	3 714(14)	699(6)	933(7)
O(3)	546(8)	3 296(4)	1 377(5)	C(12)	847(9)	2 464(5)	1 347(5)
C(1)	4 339(10)	589(6)	3 532(6)	C(13)	−2 445(12)	2 512(8)	142(7)

favourable parallel position. Thus the structural features of complexes (3) and (4c) in the solid state are clearly consistent with the spectroscopic features exhibited in solution and the contrasting i.r. and n.m.r. data of (3) and (4a) and (4b) are therefore explicable in terms of the differing co-ordination modes of the C(CF_3)C(CF_3)(CO)SMe ligand.

Elucidation of the structure of (4c) also allows us to propose a plausible structure for complexes (5a) and (5b) since the spectral features are very similar except that a ketonic ν(CO) mode near 1 730 cm^{-1} due to the C(O)SR moiety is absent from the i.r. spectra of the latter. This can be explained in terms of the illustrated structure in which the ketonic oxygen is co-ordinated to tungsten instead of the sulphur atom. Keto-vinyl complexes of this type have been isolated previously from the reactions of [MR$(CO)_3$(η^5-C_5H_5)] (M = Mo or W, R = alkyl) with acetylenes [11,12] and the ketonic ν(CO) mode is generally observed at lower frequencies *ca.* 1 400—1 500 cm^{-1}. Consequently the presence of a weak-to-medium intensity band near 1 460 cm^{-1} in the spectra of (5a) and (5b) supports the proposed structure. Further support is provided by the similarity in the *J*(FF) coupling constants in the ^{19}F n.m.r. spectra of (4a) and (4b), *ca.* 15.4 Hz, and (5a), 14.1 Hz, since little alteration to the chelate ring geometry is to be expected.

(*d*) *Reactions of* [W(SR′)$(CO)_3$(η^5-C_5H_5)] (R′ = Ph, *p*-MeC_6H_4, *or* C_6F_5) *with* $CF_3C{\equiv}CCF_3$.—The phenyl- and tolylthio-complexes reacted with $CF_3C{\equiv}CCF_3$ at 60 °C in hexane to give only monoacetylene complexes (6b) and (6c) in reasonable yield. Complex (6b) has been prepared previously

Table 4. Selected interatomic distances (Å) and angles (°)

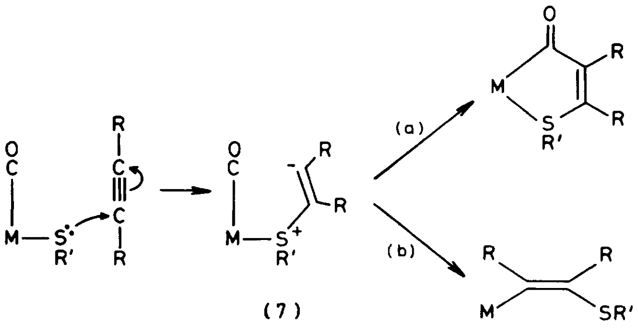
W–C(1)	1.975(8)	W–C(9)	1.962(7)	F(4)–C(11)	1.321(13)	C(3)–C(7)	1.409(14)
W–C(2)	1.994(8)	S–C(12)	1.773(7)	F(5)–C(11)	1.263(13)	C(4)–C(5)	1.406(13)
W–C(3)	2.323(9)	S–C(13)	1.834(10)	F(6)–C(11)	1.233(12)	C(5)–C(6)	1.416(14)
W–C(4)	2.310(9)	F(1)–C(10)	1.344(9)	O(1)–C(1)	1.128(10)	C(6)–C(7)	1.396(14)
W–C(5)	2.321(9)	F(2)–C(10)	1.341(10)	O(2)–C(2)	1.149(10)	C(8)–C(9)	1.443(10)
W–C(6)	2.373(9)	F(3)–C(10)	1.341(10)	O(3)–C(12)	1.227(9)	C(8)–C(10)	1.516(10)
W–C(7)	2.348(10)	C(9)–C(11)	1.501(21)	C(3)–C(4)	1.427(14)	C(8)–C(12)	1.471(10)
W–C(8)	2.193(7)						

C(1)–W–C(2)	88.2(3)	C(6)–C(7)–C(3)	109.3(9)	F(1)–C(10)–F(2)	105.5(6)
C(1)–W–C(8)	98.1(3)	W–C(8)–C(9)	61.3(4)	F(1)–C(10)–F(3)	105.7(7)
C(1)–W–C(9)	87.5(3)	W–C(8)–C(10)	121.4(5)	F(2)–C(10)–F(3)	105.3(6)
C(2)–W–C(8)	120.7(3)	W–C(8)–C(12)	112.0(5)	C(9)–C(11)–F(4)	108.4(8)
C(2)–W–C(9)	81.9(3)	C(9)–C(8)–C(10)	121.3(6)	C(9)–C(11)–F(5)	111.4(9)
C(8)–W–C(9)	40.2(3)	C(9)–C(8)–C(12)	118.3(6)	C(9)–C(11)–F(6)	114.4(9)
C(12)–S–C(13)	98.1(4)	C(10)–C(8)–C(12)	113.0(6)	F(4)–C(11)–F(5)	103.7(10)
W–C(1)–O(1)	179.6(7)	W–C(9)–C(8)	78.6(4)	F(4)–C(11)–F(6)	106.2(10)
W–C(2)–O(2)	178.8(8)	W–C(9)–C(11)	148.6(6)	F(5)–C(11)–F(6)	112.0(10)
C(7)–C(3)–C(4)	106.6(8)	C(8)–C(9)–C(11)	131.6(7)	S–C(12)–O(3)	122.2(6)
C(3)–C(4)–C(5)	108.4(8)	C(8)–C(10)–F(1)	112.6(6)	S–C(12)–C(8)	113.2(5)
C(4)–C(5)–C(6)	107.7(8)	C(8)–C(10)–F(2)	112.9(6)	O(3)–C(12)–C(8)	124.6(6)
C(5)–C(6)–C(7)	107.9(8)	C(8)–C(10)–F(3)	114.1(7)		

by a different route.[13] I.r. monitoring of the reactions indicated that an intermediate with spectral features similar to those of (3) is produced initially but this was not isolated. Thus two ν(CO) modes are observed (2 050 and 1 999 cm^{-1}, R = Ph; 2 045 and 1 995 cm^{-1}, R = p-C_6H_4Me) while a weaker band at *ca.* 1 690 cm^{-1} compares with 1 666 cm^{-1} for the ν(CO) mode of the C(O)SMe group in complex (3). The high frequencies of the two terminal CO modes strongly suggest a similar structure to (3). The complex $[W(SC_6F_5)(CO)_3(\eta^5\text{-}C_5H_5)]$ in contrast did not react thermally with $CF_3C{\equiv}CCF_3$ in hexane up to 90 °C when extensive decomposition was observed. However, the photochemical reaction proceeds smoothly in diethyl ether solution at 20 °C and the sole product $[W(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (6d) was isolated in moderate yield (45%). The spectroscopic features of (6a)—(6d) are similar to those of $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ the structure of which has been established by *X*-ray diffraction studies.[14] The mass spectra exhibit molecular ions M^+ and an ion $[M\text{–}CO]^+$ while a strong ν(CO) mode is observed in the i.r. spectrum near 2 000 cm^{-1} and a band near 1 720 cm^{-1} is assigned as the ν(C≡C) mode of the co-ordinated alkyne. The ^{19}F n.m.r. shows two quartets $^5J(FF)$ *ca.* 3 Hz due to two inequivalent CF_3 groups as expected for structures similar to that of $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$.[2,14]

Discussion

A comparison of the results of the present work with those described previously illustrates that reactions of iron and tungsten thiolates $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ with activated alkynes exhibit a marked dependency on the substituent R′ attached to sulphur. Thus, electron-withdrawing substituents, *e.g.* R′ = CF_3 or C_6F_5, lead to σ-vinyl complexes $[Fe\{C(CF_3){=}C(CF_3)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ [1] and monoacetylene derivatives (6) [2] as the sole products, whereas with electron-releasing substituents, *e.g.* R = Me, Et, or Ph, complexes (1) and (2) containing a chelate ring MC(O)CR=CR(SR′) are obtained. Previously it has been shown that the ease with which sulphur, nitrogen, phosphorus, and arsenic nucleophiles ER_nH (n = 1 or 2) add across $CF_3C{\equiv}CCF_3$ to give vinylic products $R_nEC(CF_3){=}C(CF_3)H$ reflects the nucleophilic character of the atom E, stronger nucleophiles adding more readily.[15] The proposed mechanism for such reactions, which involves initial nucleophilic attack at an acetylenic carbon to give a dipolar intermediate $HR_nE^+C(CF_3){=}C^-(CF_3)$, leads us to suggest a similar mechanism for the formation of complexes (1) and (2) in which the sulphur atom acts as the nucleophilic centre (Scheme 2). The formation of (1) and (2) can therefore be explained in terms of intermediate (7) which collapses *via* attack of the anionic carbon on a co-ordinated carbonyl ligand, route (a), while vinyl complexes result from attack at the metal [route (b)]. Alternatively, the latter could be formed by a completely different mechanism, *e.g.* a concerted *cis* insertion process. Significantly, no intermediates were detected in reactions of $[M(SC_6F_5)(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with $CF_3C{\equiv}CCF_3$ which lead to simple adducts $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ rather than heterocycles (2), implying that with fluorocarbon thiolates the sulphur atoms may not be sufficiently nucleophilic to attack the alkyne and as a result an alternative process occurs. This finds support in the fact that similar η^2-acetylene adducts $[MX(CO)(R^1C{\equiv}CR^2)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, Br, I, or SR) are the first products isolated from reactions of $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$ with unactivated acetylenes, *e.g.* PhC≡CPh, MeC≡CMe, or PhC≡CMe where attack by the ligand X at an acetylenic carbon is only a remote possibility.[3] Moreover, Petillon and co-workers [13] have recently shown that the binuclear mercapto-bridged complexes $[(\eta^5\text{-}C_5H_5)\text{-}$

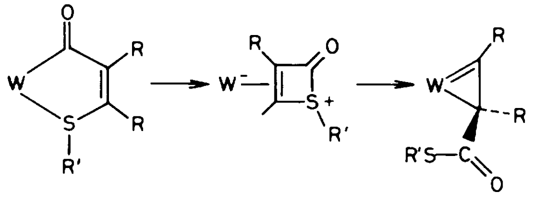


Scheme 2.

Table 5. Selected distances (Å) and angles (°) in η^2-vinyltungsten complexes

Complex	W–C$_\alpha$	W–C$_\beta$	C$_\alpha$–C$_\beta$	C$_\beta$–C$_\alpha$–CF$_3$	C–C$_\alpha$–C$_\beta$–CF$_3$	C–C$_\beta$–C$_\alpha$–W	Ref.
$[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$	1.962(7)	2.193(7)	1.443(10)	131.6(7)	−59.1(11)	−170.2(9)	This work
$[W\{C(CF_3)C(CF_3)PEt_3\}(SC_6H_4Me)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	1.910(4)	2.330(4)	1.448(6)	124.8(4)	62.9(7)	169.2(6)	12
$[W\{C(CF_3)C(CF_3)SPr^i\}\{(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	1.905(7)	2.178(8)	1.417(11)	127.7(8)	53.8(10)	176.5(10)	*
$[W\{C(CF_3)(CF_3)CNBu^t\}(CF_3C{\equiv}CCF_3)Cl(\eta^5\text{-}C_5H_5)]$	1.894(8)	2.304(9)	1.410(12)	123.3(8)	59.5(12)	173.2(10)	12

* L. Carlton, J. L. Davidson, J. C. Miller and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1984, 11.

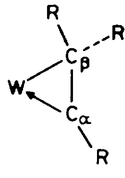


Scheme 3.

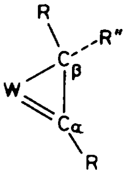
$(OC)_3W(\mu\text{-}SR')M(CO)_5]$ (M = Cr, Mo, or W; R' = Me or Ph), in which a sulphur lone pair is already co-ordinated to the second metal, also give η^2-alkyne complexes $[(\eta^5\text{-}C_5H_5)(OC)(CF_3C{\equiv}CCF_3)W(\mu\text{-}SMe)M(CO)_5]$ (M = Cr, Mo, or W) on reaction with hexafluorobut-2-yne.

These workers have also studied the reaction of $[W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$ with $CF_3C{\equiv}CCF_3$ but under more severe conditions (photolysis) than used in the present work.[4] Not surprisingly, in view of the instability of complexes (2a) and (3), the only products isolated were those formed in the later stages of the thermolysis, *i.e.* (4a), (5a), (see below), and a complex $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(SMe)OC(O)\}(CO)_2(\eta^5\text{-}C_5H_5)]$ containing a η^3-lactone ring not isolated in the present work. Since the photolysis did not lead to complex (6) the reaction is obviously quite sensitive to experimental conditions.

The novel isomerisation of complex (2) into (3) is to our knowledge the first observed [1,3] shift of a mercapto-group across an olefin promoted by a transition metal. Substituted allyl phenyl sulphides undergo [1,3] allylic phenylthio-shifts, probably *via* radical-chain mechanisms,[16] while the well established [1,3] hydride-shift reaction in metal–olefin complexes is generally thought to proceed *via* an oxidative pathway involving allylhydride intermediates.[17] Both radical and oxidative mechanisms can readily explain the 1,3 shift described herein but several facts lead us to favour the third alternative illustrated in Scheme 3. This involves attack of sulphur on the electron-deficient acyl carbon atom with concomitant co-ordination of the olefinic C=C bond leading to an intermediate zwitterionic oxothiete complex (8) which can ring-open to produce the η^2-vinyl complex. The initial ring-forming process finds precedent in our previous report that the heterometallocycle $[Mn\{C_4(CF_3)_2H_2SC_6F_5\}(CO)_4]$ structurally related to (2) undergoes ring closure to give a zwitterionic sulphur heterocycle $[\overset{-}{Mn}\{C_4(CF_3)_2H_2\overset{+}{S}C_6F_5\}(CO)_3]$.[1] The stability of the latter relative to the proposed intermediate (8) can be attributed to reduced strain in the five-membered ring accompanied by the well known ability of cyclic 1,3-dienes to co-ordinate strongly to transition metals. We also note that oxidation of a saturated nitrogen analogue of (2), *viz.* $[Mo\{C(O)CH_2CH_2NHCH_2Ph\}(CO)_2(\eta^5\text{-}C_5H_5)]$ with Ag_2O gives a four-membered β-lactam ring analogous to the oxothiete ring in (8).[18] The crucial ring-closure reaction is thought to involve attack by nitrogen on the acyl carbon in a manner related to that in Scheme 3. Further support for the proposal that an oxothiete ring is the precursor to the η^2-vinyl ligand is provided by the *X*-ray structure of (3). The rather shallow C(9)–C(8)–C(12)–S torsion angle of −16.5(8)° in the η^2-vinyl ligand is accompanied by an extremely short non-bonded S ··· C(9) distance of 2.90 Å, *ca.* 0.7 Å less than the sum of the van der Waals radii. This may be significant in view of the fact that the four-membered ring in complex (8) would involve a direct carbon–sulphur bond between S and C(9).



(9a)



(9b)

Our preliminary report [5a] of the structure of (3) has been followed by several other structural characterisations of complexes containing η^2-vinyl ligands derived, in these cases, by nucleophilic attack on an alkyne.[19–22] The geometries of the tungsten complexes which have been studied are summarised in Table 5; in every case the η^2-vinyl ligand has been formed from a hexafluorobut-2-yne molecule. Molybdenum complexes of η^2-vinyls derived either from hexafluorobut-2-yne [19,20] or from less electronegative alkynes [21,22] show broadly similar structural features to the complexes in Table 5. The data in Table 5 indicate that η^2-vinyl–tungsten interactions should be described in terms of the cyclocarbene structure (9a) which becomes (9b), a metallated cyclopropene, in the limiting case of maximum W→C$_\alpha$ back donation. This view is consistent with (*i*) the near coplanarity of the three bonds radiating from C$_\alpha$, as shown by the nearness of the pseudo-torsion angles C–C$_\alpha$–C$_\beta$–W to 180°, (*ii*) the torsion angles about the C$_\alpha$–C$_\beta$ bonds, which are comparable with C(*exo*)–C–C–C(*exo*) angles of 70—80° found in substituted cyclopropenes,[23] and (*iii*) the shortness of the W–C$_\alpha$ bonds compared with the W–C$_\beta$ bonds. The complexes in Table 5 appear close to structure (9b) since the W—C$_\alpha$ bonds are all shorter than the value of 1.967(6) Å in $[PtW(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(PMe_2Ph)_2(\eta^5\text{-}C_5H_5)]$ which is thought to represent a W–C bond order close to two.[24] Of the W–C$_\alpha$ bonds, that in complex (3), where the metal carries two π-acidic carbonyl ligands, is the longest. Bigger variations are found in the longer, and presumably weaker W–C$_\beta$ bonds. Electronic factors are presumed to be responsible and, in this connection, it may be significant that the longer W–C$_\beta$ bonds occur when molecules, such as PEt_3 or $CNBu^t$, rather than anions add to the alkyne. The shorter W–C$_\beta$ bonds are comparable in length with the σ-W–C(vinyl) distance of 2.194(7) Å in complex (4c).[8] The C$_\alpha$–C$_\beta$ bond lengths in Table 5 are fairly constant: they show a substantial increase on corresponding distances in η^2-$CF_3C{\equiv}CCF_3$ tungsten complexes (*ca.* 1.29 Å),[19] but are shorter than C–C single bond lengths in

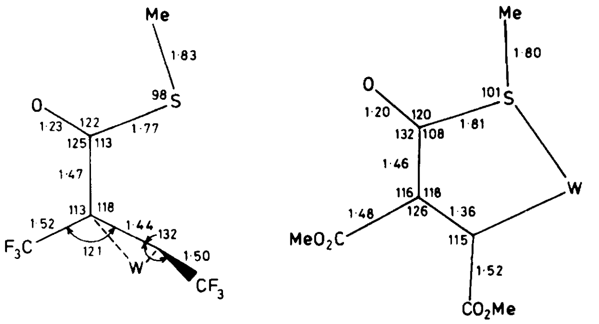
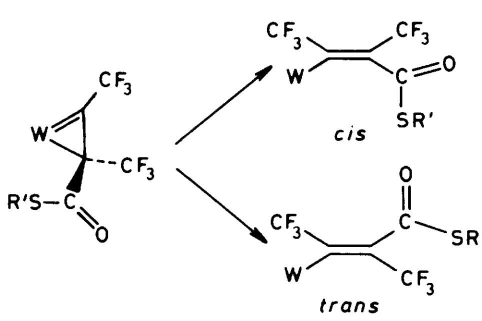


Figure 2. A comparison of bond lengths (Å) and angles (°) of the C(R)C(R)C(O)SMe ligands in the complexes [W{C(R)C(R)C(O)-SMe}(CO)$_2$(η^5-C$_5$H$_5$)], R = CF$_3$ and CO$_2$Me. In each case the direction of view is normal to the C–C(O)SC(methyl) plane. The standard deviation of each quantity is $\leqslant 1$ in units of the least significant digit. Relevant torsion angles, for R = CF$_3$ and CO$_2$Me respectively, are O–C–S–C(methyl) −1(1) and −29(1), and C(R)–C(R)–C–S 15(1) and −17(1)°



Scheme 4.

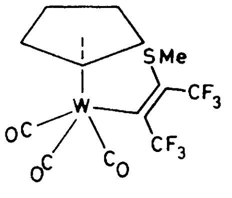
cyclopropenes [1.517(2)—1.527(2) Å].[23,25] A more exact description of the bonding than (9a) or (9b) would probably invoke some slight delocalisation.

Comparison of the bond lengths and angles in the C(R)C(R)C(O)SMe$^-$ ligands of complexes (3) and (4c) enables the effects of the different modes of attachment to tungsten to be assessed (see Figure 2). In complex (4c) the MeO$_2$C–C–C–CO$_2$Me torsion angle of −0.3(10)° allows good π overlap between the central carbon atoms, the MeO$_2$CC–CCO$_2$Me bond length 1.358(9) Å being as expected for a C=C bond. The F$_3$C–C–C–CF$_3$ and −C(O)SMe torsion angles in (3) of −59.1(11) and 88.9(10)° would appear to permit only very limited π overlap between C(8) and C(9), as one would also expect from the C(8)–C(9) bond length 1.443(10) Å. Otherwise the structural differences between the two ligands in Figure 2 are remarkably slight and seem to stem almost entirely from the varying sulphur environments.

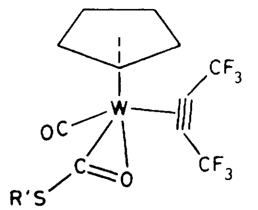
The closest parallel to the behaviour of the vinyl ligands in complexes (3) and (4c) appears to be that of the σ- and η^2-bonding modes of the $^-$C(R)=C=O ketenyl system in [W{σ-C(C$_6$H$_4$Me)=C=O}(CO)(PMe$_3$)$_2$(η^5-C$_5$H$_5$)] and [W{η^2-C(C$_6$H$_4$Me)C=O}(CO)(PMe$_3$)(η^5-C$_5$H$_5$)] respectively.[26] The ketenyl ligand in the former has been observed to undergo a reversible transformation to the η^2 form on loss of trimethylphosphine. This compares with the isomerisation (3)$\rightleftarrows$(4) which also appears to be reversible although the subsequent formation of complexes (5) and (6) is not. However, the $\eta^2 \longrightarrow \sigma$ vinyl transformation, unlike its ketenyl counterpart, has interesting stereochemical consequences since co-ordination of the sulphur atom of the C(O)SR moiety leads to a *cis* arrangement of the CF$_3$ substituents in (4). It is clear that should the $\eta^2 \longrightarrow \sigma$ transformation proceed *via* the alternative movement of the CF$_3$ on C(8) towards the metal a *trans*-vinyl complex would result. σ-Vinyl complexes, *cis* and/or *trans*, are frequently isolated from the insertion reactions of alkynes with metal hydrides and alkyls and from nucleophilic and electrophilic additions to co-ordinated alkynes. The factors controlling the stereochemistry of these reactions have been studied extensively in recent years but the mechanisms are still not properly understood. Recently [20,27] we suggested that η^2-vinyl complexes might act as precursors to σ-vinyl derivatives and thus it may be possible to rationalise the stereochemistry of σ-vinyl formation in terms of the ring-opening processes illustrated in Scheme 4.

With respect to the $\eta^2 \longrightarrow \sigma$ transformation (3) $\longrightarrow$ (4), it is informative to compare the CF$_3$CC–CF$_3$ and –C(O)SMe torsion angles of −59.1 and 88.9° in complex (3). This illustrates that in the η^2-vinyl ligand the COSMe group is already oriented in the direction in which it finally ends up in the *cis* σ-vinyl complex (4a), *i.e.* there is already a structural preference for the *cis* vinyl ligand while still bonded in the η^2 mode. Arguably such a preference, although small, might be expected in this particular case in view of the presence of a nucleophilic MeS group since the sulphur atom ultimately becomes bonded to the metal. However, the W–S distance of 3.43 Å in (3) does not support the presence of an embryonic W–S bond which might account for the distortion of the COSMe group towards the metal. Thus, in general terms it is conceivable that the differing electronic (and possible steric) properties of substituents on η^2-vinyl ligands may determine the stereochemical preference for *cis* or *trans* σ-vinyl formation by altering the torsion angles on the η^2-vinyl such as to generate a distinct orientational preference. Moreover, we have recently established that the η^2-vinyl ligand in complexes [MCl{η^2-C(CF$_3$)C(CF$_3$)R}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (M = Mo or W, R = tertiary phosphine) exhibits distinct orientational as well as configurational preferences.[27] This could indicate that the stereochemistry of η^2—σ vinyl transformations is also controlled by such influences. Previously, Huggins and Bergman [28] demonstrated that addition of alkynes RC≡CR to [NiR″-(acac)(PPh$_3$)] (acac = acetylacetonate) gives both *cis* and *trans* vinyl complexes [Ni(CR=CR″R)(acac)(PPh$_3$)] and it was postulated that a key step in the reaction was the conversion of an initially formed *cis* σ-vinyl complex into the *trans* isomer. If true, such an isomerisation could proceed *via* an η^2-vinyl species by analogy with Scheme 4 and thus account for the stereochemical features of the reaction. Studies currently being conducted in these laboratories into the synthesis and reactions of η^2-vinyl complexes related to (3) will hopefully throw further light on these proposals.

The formation of the O-metallated vinyl ketone complexes (5) from the S-metallated form (4) on heating suggest that the former are the thermodynamically favoured isomeric forms whereas the latter are the products of kinetic control. Isomerisation presumably occurs *via* M–S bond cleavage and rotation of the C(O)SR group about the appropriate C–C bond of the intermediate η^2-vinyl complex (3). O-Metallated vinyl ketone complexes have been isolated previously from reactions of alkylmetal carbonyls with acetylenes [11,12] and are also implicated in the tetracarbonylnickel-catalysed reactions of acetylenes and carbon monoxide with alkyl, allyl, or aryl halides which give free lactones.[29] The methyl vinyl ketone analogue of (5) on reaction with phosphines and isocyanides is readily converted into η^3-lactone complexes as a result of CO insertion followed by ring closure.[11] Petillon *et al.*[4a] have isolated such a species [W{η^3-C(CF$_3$)C(CF$_3$)C(SMe)OC(O)}-CO)$_2$(η^5-C$_5$H$_5$)] from the photolytic reaction of [W(SMe)-



(10)



(11)

$(CO)_3(\eta^5\text{-}C_5H_5)]$ with $CF_3C\equiv CCF_3$ in tetrahydrofuran in a sealed tube but this complex was not detected under the conditions employed in the present work. It is therefore conceivable that the lactone complex results from the reaction of (5) with CO, although other possible precursors are the isomeric complexes (3) and (4). Interestingly, (5) was apparently not detected in the photolytic reaction described above, but we note that a complex with virtually identical spectral features was isolated but assigned structure (10) on the basis of the i.r. spectrum which exhibited three bands in the ν(CO) region. The weak high-frequency band near 2 060 cm^{-1} was occasionally observed in samples of complex (5) obtained in the present work but careful chromatographic work established the presence of impurities and pure samples of (5) exhibited only the two ν(CO) modes expected for the proposed structure.

Finally we note that the formation of the monoacetylene complex (6a) from $[W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$ *via* (2) and the η^2-vinyl species (3) constitutes a remarkable rearrangement process in which CO, SMe, and $CF_3C\equiv CCF_3$ combine initially to form an olefinic ligand which under the influence of the metal rearranges ultimately to regenerate the separate components again. It is not clear whether the η^2-vinyl complex (3) or the vinyl ketone derivative (4), or both, function as the immediate precursor of the acetylene complex in view of the ease with which these species interconvert, but studies currently in progress on a variety of related complexes may help resolve this question. Clearly the mercapto-group migrates onto the metal at some stage in the process, either directly *via* (4) or perhaps *via* an intermediate thioester complex (11) which undergoes decarbonylation to give (6). An acyl complex $[M\{C(O)Me\}(CO)(HC\equiv CH)(\eta^5\text{-}C_5H_5)]$ structurally analogous to (11) has been isolated previously [20] from the reaction of the acetylene complex $[WMe(CO)(HC\equiv CH)(\eta^5\text{-}C_5H_5)]$ [*cf.* (6)] with carbon monoxide, *i.e.* the reverse of the reaction (11) $\longrightarrow$ (6). Structurally analogous η^2-vinyl complexes $[M(X)\{\eta^2\text{-}C(CF_3)C(CF_3)R\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ are also known which have been characterised by *X*-ray diffraction methods for M = W, X = Cl, R = $CNBu^t$; X = SC_6H_4Me-*p*, R = PEt_3 [19] and M = Mo, X = Cl, R = PEt_3. [21]

Experimental

Proton n.m.r. studies were carried out in $CDCl_3$ solution on a JEOL MH 100 spectrometer at 100 MHz and a Bruker WP-200 SY at 200 MHz, and ^{19}F n.m.r. on a Bruker WP-200 SY operating at 188 MHz. I.r. spectra were recorded on Perkin-Elmer 457 and 580 spectrophotometers, mass spectra on an A.E.I. MS 9. Reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. Solvents were refluxed over $LiAlH_4$ and distilled under nitrogen prior to use. The complexes $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ were prepared from the methathetical reactions of $[FeCl(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with Tl(SR') in tetrahydrofuran (thf) at room temperature, apart from $[W(SC_6F_5)(CO)_3(\eta^5\text{-}C_5H_5)]$ which was obtained from the photolytic reaction of $C_6F_5SSC_6F_5$ with $[\{W(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ in benzene.

Reactions of $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$.—(*a*) *With hexafluorobut-2-yne.* In a typical reaction the thiolate $[Fe(SR')(CO)_2(\eta\text{-}C_5H_5)]$ (*ca.* 0.3 g) was dissolved in diethyl ether (40 cm^3). The mixture was transferred to a thick glass tube (100 cm^3) fitted with a Westef stopcock and the solution degassed several times by the freeze–thaw method. Excess of $CF_3C\equiv CCF_3$ (*ca.* 1.0 g) was condensed (*ca.* 96 °C) into the tube which was then kept at room temperature for *ca.* 6 h. The volatile material and solvent were removed *in vacuo* and the product $[Fe\{C(O)C(CF_3)=C(CF_3)SR'\}CO(\eta^5\text{-}C_5H_5)]$ (1) recrystallised from diethyl ether–hexane and washed with hexane. A further recrystallisation gave analytically pure dark brown crystals in 60—80% yield. In some cases, *e.g.* R = Bu^t or CH_2Ph, an oily product was obtained initially which was chromatographed over a Florisil packed column, using hexane–diethyl ether (1 : 2) as eluant. Pure crystals were then obtained by crystallisation at −20 °C.

(*b*) *With dimethyl acetylenedicarboxylate.* In a typical reaction, thiolate $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ (0.30 g) and an equimolar amount of $MeCO_2C\equiv CCO_2Me$ were stirred in diethyl ether (40 cm^3) in a Schlenk tube. After *ca.* 4 h at room temperature the mixture was filtered and after reducing the volume of solvent the crude product was crystallised at −20 °C following addition of hexane. The solid was recrystallised several times in this manner to give pure dark brown crystals of $[Fe\{C(O)C(CO_2Me)=C(CO_2Me)SR'\}(CO)(\eta^5\text{-}C_5H_5)]$ (1) which were dried *in vacuo* and collected. In some cases, due to the presence of excess of unreacted dimethyl acetylenedicarboxylate, an oily material formed, which was chromatographed over a Florisil packed column using diethyl ether–hexane (1 : 2) as eluant, and the product recrystallised from diethyl ether–hexane at −20 °C. Yields of 45—75% were obtained.

Reaction of Hexafluorobut-2-yne with $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R' = Me *or* Et).—The complex (0.5 g) dissolved in hexane (40 cm^3) was transferred to a thick glass reactor fitted with a Westef stopcock (100 cm^3) and the solution degassed several times by the freeze–thaw method. Excess of $CF_3C\equiv CCF_3$ (2 g) was condensed in at −196 °C and the sealed tube then allowed to warm slowly to room temperature. After *ca.* 8 h dark needles formed. Following removal of unreacted $CF_3C\equiv CCF_3$ *in vacuo*, these were collected and recrystallised from diethyl ether–hexane at −20 °C to give dark brown crystals of $[W\{C(O)C(CF_3)=C(CF_3)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (2a), yield 89%. Complex (2b) was obtained similarly in 82% yield from $[W(SEt)(CO)_3(\eta^5\text{-}C_5H_5)]$.

Reaction of Dimethyl Acetylenedicarboxylate with $[W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$.—The complex (0.5 g) was dissolved in hexane (50 cm^3) in a Schlenk tube under nitrogen and an equimolar amount of $MeCO_2C\equiv CCO_2Me$ in diethyl ether (10 cm^3) was added dropwise with stirring and the mixture allowed to react for 20 h, when dark brown crystals formed. These were filtered off and recrystallised from dichloromethane–hexane to give $[W\{C(O)C(CO_2Me)=C(CO_2Me)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (2c) in 84% yield. Complex (2d) was obtained similarly in 76% yield from $[W(SEt)(CO)_3(\eta^5\text{-}C_5H_5)]$.

Thermolyses.—$[W\{C(O)C(CF_3)=C(CF_3)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (2a). The complex (0.3 g) and hexane (40 cm^3) were transferred to a reaction tube (under nitrogen) which was then sealed and held at 30—35 °C for 60 h. After this time large orange crystals and small quantities of dark red-brown crystals had formed. These were separated by hand and the former recrystallised from CH_2Cl_2–hexane to give $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (3) in 63% yield. Recrystallisation of the dark red-brown crystals from diethyl ether–hexane gave $[W\{C(CF_3){=}C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (4a) in 6% yield. Thermolysis of $[W\{C(O)C(CF_3){=}C(CF_3)SEt\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (2b) under the same conditions gave $[W\{C(CF_3){=}C(CF_3)C(O)SEt\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (4b) as the sole product in 43% yield. The latter was also obtained in good yield when solid samples of (2b) were kept at 20—25 °C under nitrogen for several months.

$[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (3) *at* 45 °C. The complex (0.2 g) in diethyl ether (30 cm^3) was heated in a sealed tube at *ca.* 45 °C for 6 d. The dark red product solution was chromatographed over Florisil with diethyl ether–hexane (1 : 1) as eluant. Two bands, red and purple, developed and these were collected and recrystallised to give dark red-brown crystals of complex (5a) in 15% yield and purple crystals of (6a) in 6% yield.

$[W\{C(CF_3){=}C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (4a). The complex (0.05 g) was treated as above and gave (5a) and (6a) in similar yields.

$[W\{C(O)C(CO_2Me){=}C(CO_2Me)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (2c) *at* ca. 60 °C. The complex (0.2 g) in hexane (40 cm^3) was heated at 60—70 °C for 48 h when a red solution developed. Volatiles were removed *in vacuo* and the residue extracted with dichloromethane and filtered. Recrystallisation from dichloromethane twice gave dark red crystals of complex (4c) in 29% yield.

$[W\{C(O)C(CO_2Me){=}C(CO_2Me)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (2c) *at* ca. 90 °C. The complex (0.1 g) was heated in hexane as above but at 90 °C. I.r. monitoring indicated the formation of (4c) as an intermediate but after *ca.* 20 h only the final product (5c) could be detected. This was recrystallised from dichloromethane–hexane to give dark red crystals in 21% yield.

Reactions of Hexafluorobut-2-yne.—(*a*) *With* $[W(SPh)(CO)_3(\eta^5\text{-}C_5H_5)]$. The complex (0.14 g) in diethyl ether and alkyne (1 g) were allowed to react at 60 °C for 24 h. Recrystallisation of the product from Et_2O–hexane at −20 °C gave red-purple crystals of $[W(SPh)(CO)(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ (6b) in 54% yield. Similarly, $[W(SC_6H_4Me\text{-}p)(CO)_3(\eta^5\text{-}C_5H_5)]$ and $CF_3C{\equiv}CCF_3$ gave red-purple crystals of $[W(SC_6H_4Me\text{-}p)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (6c) in 45% yield.

(*b*) *With* $[W(SC_6F_5)(CO)_3(\eta^5\text{-}C_5H_5)]$. The complex (60 mg) in hexane–diethyl ether (1 : 1, 40 cm^3) was photolysed in a sealed tube for 48 h. The solution was filtered and volatiles removed. Recrystallisation of the product from diethyl ether–hexane at −20 °C gave dark red crystals of complex (6d) in 46% yield. A thermal reaction (up to 90 °C) only resulted in decomposition of the starting material.

X-Ray Crystal Structure of $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (3).—*Crystal data.* $C_{13}H_8F_6O_3SW$, M = 542.1, monoclinic, a = 7.950(2), b = 14.416(2), c = 14.210(2) Å, β = 105.29(2)°, U = 1 571 $Å^3$, Z = 4, D_c = 2.292 g cm^{-3}, $F(000)$ = 1 016, space group $P2_1/c$, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 77.1 cm^{-1}.

Measurements. An Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator was used. The cell dimensions were obtained by a least-squares fit to the setting angles of 25 automatically centred reflections. The integrated intensities of all independent reflections in the range $2 \leqslant \theta \leqslant 30°$ were estimated from continuous θ—2θ scans of 0.98° in θ, the scan speed being adjusted to give $\sigma(I)/I \leqslant 0.02$ subject to a maximum scan time of 70 s. Correction for background and Lorentz polarisation effects yielded 3 282 reflections with $I \geqslant 3\sigma(I)$.

Structure analysis. The structure was solved and refined using conventional Patterson, Fourier difference, and least-squares techniques. Hydrogen atoms were not included in the structure-factor calculations. In the later stages anisotropic thermal parameters were refined for all non-hydrogen atoms. Minimisation of $\Sigma w(|F_o| - |F_c|)^2$ [$w = 1/(\sigma^2 + 0.0004F_o^2)$, σ being the standard deviation of $|F_o|$ derived from counting statistics] with respect to 217 structural parameters converged with R 0.040 and R' 0.051. The final difference synthesis showed random fluctuations ($|\Delta\rho| \leqslant 1.0$ e $Å^{-3}$) except near the tungsten atom where the extreme values were −2.9 and +3.8 e $Å^{-3}$, probably reflecting our failure to correct for absorption. Scattering factors and anomalous dispersion corrections were taken from ref. 30. Programs used were CAD4 (M. B. Hursthouse), *X*-RAY 76 (J. M. Stewart), ORTEP (C. K. Johnson), and GEOM (P. R. Mallinson).

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