Metal Perfluoroalkane- and Perfluoroarene-thiolates. Part V.† The Reactions of Tricarbonyl(π-cyclopentadienyl)-molybdenum and -tungsten Thiolates and Acetylenes ‡

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The thiolates $[(\eta^5\text{-}C_5H_5)M(CO)_3SR_F]$ (M = Mo or W; $R_F = CF_3$ or C_6F_5) react with acetylenes, RC≡CR (R = CF_3, Me, or Ph) to give the formally electron-deficient π-acetylene complexes $[(\eta^5\text{-}C_5H_5)M(CO)(RC_2R)SR_F]$. The bonding and isomerism in these complexes at low temperatures is discussed. On oxidation $[(\eta\text{-}C_5H_5)\text{-}MoO(CF_3C_2CF_3)SC_6F_5]$ can be isolated. Trifluoropropyne reacts with the thiolates to give the acetylene complex $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2H)SC_6F_5]$ and cyclopentadienone complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)\{(CF_3C_2H)_2CO\}\text{-}SCF_3]$ and $[\{(\eta^5\text{-}C_5H_5)[(CF_3C_2H)_2CO]SCF_3\}_2]$.

We have previously [1,2] described some reactions between tricarbonyl(π-cyclopentadienyl)molybdenum halides $[(\eta^5\text{-}C_5H_5)Mo(CO)_3X]$ (X = Cl, Br, or I) and acetylenes RC≡CR (R = Me, CF_3, or C_6H_5). In these reactions the products depend largely upon the acetylene substituent, being bis(alkyne) complexes, $[(\eta^5\text{-}C_5H_5)Mo(RC_2R)_2X]$ when R = Me or CF_3 or carbonyl alkyne, $[(\eta^5\text{-}C_5H_5)Mo\text{-}(CO)(RC_2R)X]$ or carbonyl cyclobutadienyl derivatives, $[(\eta^5\text{-}C_5H_5)Mo(CO)(RC_2R)_2X]$ when R = Ph. The reactions between metal perfluoroalkane- and perfluoroarene-thiolates and $CF_3C{\equiv}CF_3$ or $CF_3C{\equiv}CH$ have been shown [3] to give a range of types of product including many examples of insertion into either a metal–metal or a metal–sulphur bond. In the present paper we report on the products of the reactions between tricarbonyl(π-cyclopentadienyl)metal thiolates, $[(\eta^5\text{-}C_5H_5)M(CO)_3SR]$ (M = Mo or W) ($R_F = CF_3$ or C_6F_5), and some acetylenes.

The carbonyl thiolates react with the acetylenes MeC_2Me, $CF_3C_2CF_3$, and PhC_2Ph to give mono(alkyne) complexes $[(\eta^5\text{-}C_5H_5)M(CO)(RC_2R)SR_F]$ at moderate temperatures (see Table). Although trifluoropropyne gave a similar complex with the molybdenum pentafluorobenzenethiolate, reaction with the trifluoromethanethiolate gave a cyclopentadienone complex $[(\eta^5\text{-}C_5H_5)Mo(CO)\{(CF_3C_2CF_3)_2CO\}SCF_3]$. When attempts were made to increase the rates of reaction of the original metal carbonyl thiolates by using higher temperatures some decarbonylation occurred to give the dimers $[\{(\eta^5\text{-}C_5H_5)M(CO)_2SR_F\}_2]$ [4] or complete decomposition occurred rather than the formation of acetylene complexes, and it was subsequently found that the dimer $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_2SCF_3\}_2]$ did not react with hexafluorobut-2-yne even after 70 h at 360—370 K.

From stoicheiometry, crystallography, and spectral results § the alkyne carbonyl species are formulated to contain co-ordinated cyclopentadienyl, carbonyl, acetylene, and SR_F groups.

The similarity of these complexes to the carbonyl(diphenylacetylene)molybdenum(II) halides previously described [1,2] is emphasised by the conversion of $[(\eta^5\text{-}C_5H_5)MoCO(PhC_2Ph)Cl]$ into $[(\eta^5\text{-}C_5H_5)MoCO(PhC_2Ph)\text{-}SC_6F_5]$ by the use of thallium(I) pentafluorobenzenethiolate.[5]

Solutions of the alkyne carbonyl complexes when set aside in the air show spectral changes which it is considered are due, in all cases, to the formation of oxo-species, $[(\eta^5\text{-}C_5H_5)M(O)(RC_2R)SR_F]$; only in the case of $[(\eta^5\text{-}C_5H_5)Mo(O)(CF_3C_2CF_3)SC_6F_5]$, however, was it possible to isolate a pure complex since an excess of air causes further oxidation to unidentified species. Similar oxo-species were undoubtedly formed in other cases as evidenced by the mass spectra of the alkyne carbonyl complexes taken after exposure to air for varying periods of time; these showed spectra characteristic of the oxo-species, particularly molecular ions and prominent peaks from $[C_5H_5MoO(SR_F)]^+$ and from loss of O and F from the parent ions. The n.m.r. spectra of the oxo-complexes are also characteristic, all the resonances occurring downfield of the corresponding signals in the carbonyl

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[2] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 2531.

[3] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2283.

[4] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1972, 107.

[5] J. L. Davidson, unpublished work.

derivatives. The i.r. spectra of the oxo-complexes show C≡C modes at much higher frequencies than are observed for the alkyne carbonyl species. Oxo-species, $[(\eta^5\text{-}C_5H_5)MO(PhC_2Ph)Cl]$ (M = Mo or W) have been previously isolated when air is passed through solutions of $[(\eta^5\text{-}C_5H_5)M(CO)(PhC_2Ph)Cl]$ [1]; also $[(\eta^5\text{-}C_5H_5)WO(PhC_2Ph)Ph]$ is formed when diphenylacetylene reacts with tricarbonyl-(π-cyclopentadienyl)phenyltungsten apparently in the presence of air.[6]

The acetylene carbonyl thiolates $[(\eta^5\text{-}C_5H_5)M(CO)(RC{\equiv}CR)SR_F]$ are air and light sensitive to varying degrees, the molybdenum derivatives being more reactive than their tungsten analogues. The trifluoromethanethiolates have similar stabilities to the pentafluorobenzenethiolates; however in comparing the stabilities of the acetylene complexes the following order is found: $PhC_2Ph > MeC_2Me > CF_3C_2CF_3 \approx CF_3C_2H$.

TABLE

Product *	Reaction temp. (T/K)	Time (t/h)	Yield (%)	Colour	M.p. (t/K)	Analysis Found (Calc.) C (%)	H (%)	F (%)	S (%)	Metal (%)	M
$[(cp)Mo(CO)(CF_3C_2CF_3)SCF_3]$	303	90	36	Blue	384—386	30.3 (29.2)	1.2 (1.1)	36.2 (37.8)	6.6 (7.1)	21.0 (21.2)	452
$[(cp)W(CO)(CF_3C_2CF_3)SCF_3]$	313	200	30	Purple	347—349	26.2 (25.3)	1.0 (0.9)	31.0 (31.6)	5.4 (5.9)	32.9 (33.9)	540
$[(cp)Mo(CO)(CF_3C_2CF_3)SC_6F_5]$	303	240	75	Blue	399—401	35.1 (34.9)	1.0 (0.9)				550
$[(cp)Mo(CO)(MeC_2Me)SCF_3]$	303	20	77	Red-black	327—330	38.6 (38.4)	3.2 (3.2)	16.5 (16.6)	9.3 (9.3)	26.7 (27.9)	344
$[(cp)W(CO)(MeC_2Me)SCF_3]$	313	100	57	Red-black	351—353	31.4 (30.6)	2.2 (2.6)	12.9 (13.2)	7.1 (7.4)	41.0 (42.4)	432
$[(cp)Mo(CO)(MeC_2Me)SC_6F_5]$	323	10	70	Red-purple	375—377	43.1 (43.4)	2.6 (2.5)				442
$[(cp)Mo(CO)(PhC_2Ph)SCF_3]$	303	20	84	Blue	368—370	54.9 (53.9)	3.2 (3.2)	11.7 (12.2)	6.5 (6.8)	20.3 (20.5)	468
$[(cp)Mo(CO)(PhC_2Ph)SC_6F_5]$	333	3	91	Blue-black	447—449	54.8 (55.2)	2.6 (2.6)				566
$[(cp)Mo(CO)(CF_3C_2H)SC_6F_5]$	303	4	48	Purple	363—365	37.9 (37.3)	1.3 (1.2)				482
$[(cp)Mo(CO)\{(CF_3C_2H)_2CO\}SCF_3]$	308	120	32	Yellow	424 (dec.)	33.2 (33.2)	1.3 (1.4)	33.8 (32.4)	6.4 (6.3)	19.9 (19.0)	506
$[(cp)Mo\{(CF_3C_2H)_2CO\}SCF_3]_2$	$h\nu$/293	60	63	Red	488 (dec.)	33.0 (32.6)	1.3 (1.5)	34.3 (35.8)	6.9 (6.7)	21.3 (20.1)	956
$[(cp)MoO(CF_3C_2CF_3)SC_6F_5]$	393	96	70	Yellow	402—403	33.0 (33.5)	0.8 (0.9)				538

* cp = $\eta^5\text{-}C_5H_5$.

The mass spectra show monomeric molecular ions and species which have lost CO, RC_2R, R, and SR_F groups. All the compounds have high volatility and solubility suggesting that they are monomeric both in the solid state and in solution; the structures of $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)SC_6F_5]$ and $[(\eta^5\text{-}C_5H_5)MoO(CF_3C_2CF_3)SC_6F_5]$ confirm this.[7] The structures can be described as consisting of molecules of approximately octahedral coordination about the molybdenum with the cyclopentadienyl group occupying one face of the octahedron. Taking the molybdenum–sulphur bond as reference, the C≡C bond in the carbonyl derivative is at right angles to this bond whereas in the oxo derivative the C≡C bond is parallel to the Mo–S bond. The overall geometries of the complexes are similar to those of $[(\eta^5\text{-}C_5H_5)WO(PhC_2Ph)Ph]$ [6] and $[(\eta^5\text{-}C_5H_5)W(CO)(CF_3C_2CF_3)_2Cl]$.[1] Since many of the spectroscopic parameters of the complexes are comparable it is highly probable that all the complexes have structures which are generally similar to those described above and the n.m.r. and i.r. spectra can be explained in terms of these structures. The n.m.r. spectra of $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(HC_2H)]$ have been explained in terms of similar structures.[8]

The ^{19}F variable-temperature n.m.r. spectrum of $[(\eta^5\text{-}C_5H_5)M(CO)(CF_3C_2CF_3)SCF_3]$ (M = Mo or W) species are shown in Figure 2 for the temperature range 168—307 K. In the spectra of the molybdenum derivatives signals from the oxo-derivative are present. In the high-temperature spectra there are three signals of equal intensity; the low-field signal is assigned to the CF_3S group and the other two signals assigned to non-equivalent CF_3C groups as would be expected if the species present in solution had either of the geometries of Figure 1. At 168 K the high-field signal is virtually

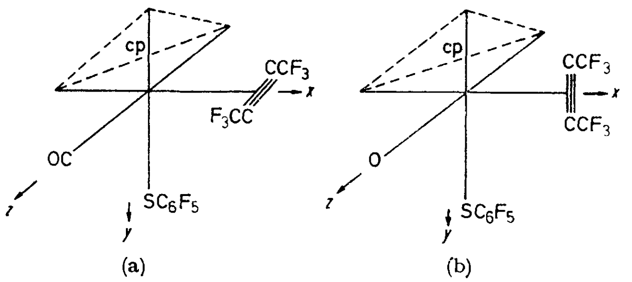

FIGURE 1 Structures of (a) $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)SC_6F_5]$ and (b) $[(\eta^5\text{-}C_5H_5)MoO(CF_3C_2CF_3)SC_6F_5]$ [7]

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[8] M. Herberhold, H. Alt, and C. G. Kreiter, *J. Organometallic Chem.*, 1972, **42**, 413.

unchanged but both the other CF_3C and the CF_3S signals are split, in accordance with the presence of two isomers at this temperature; coalescence of the CF_3C and CF_3S signals occurs simultaneously at 228 K (M = Mo) and 243 K (M = W). The CF_3S signal of $[(\eta^5\text{-}C_5H_5)Mo(CO)(MeC_2Me)SCF_3]$ is split at 183 K in a manner comparable with that observed for the hexafluorobut-2-yne complexes although the ^1H spectrum is apparently independent of temperature. The CF_3S signal of $[(\eta^5\text{-}C_5H_5)Mo(CO)(PhC_2Ph)SCF_3]$ becomes asymmetric at 183 K but again the ^1H spectrum is temperature independent. The variable-temperature spectra of $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)SC_6F_5]$ are very similar to those of the trifluoromethanethiolate derivatives with two isomers at 183 K and coalescence at 220 K. There was no evidence for isomers at low temperature in the spectra of the pentafluorobenzenethiolate derivatives with but-2-yne or diphenylacetylene.

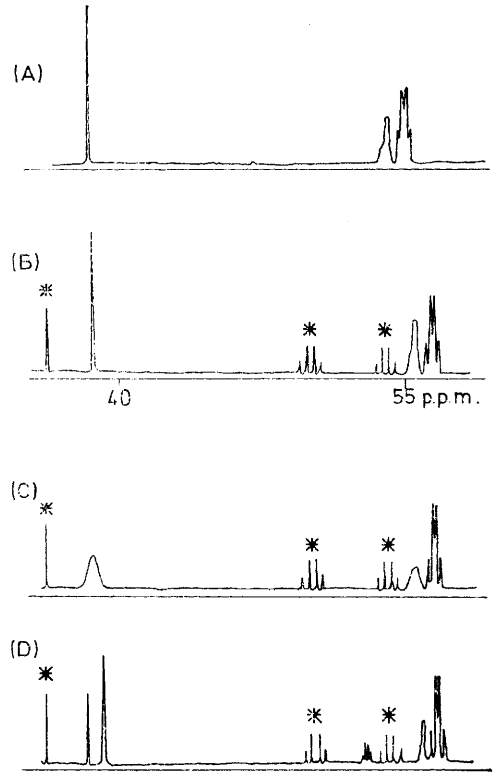

FIGURE 2 ^{19}F N.m.r. spectra (A) $[(\eta^5\text{-}C_5H_5)W(CO)(CF_3C_2CF_3)SCF_3]$ unoxidised measured at 307 K, (B),(C),(D) $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)SCF_3]$ partially oxidised with $[(\eta^5\text{-}C_5H_5)MoO(CF_3C_2CF_3)SCF_3]$ resonances marked *. Spectra recorded (B) at 307 K, (C) at 228 K, (D) at 168 K

It has been shown previously that the co-ordinated acetylenes in the complexes $[(\eta^5\text{-}C_5H_5)M(RC_2R)_2X]$ (R = Me or CF_3) undergo rotation at room temperature.[2] In the present carbonyl alkyne complexes rotation of the acetylenes would give equivalent R groups and hence is ruled out at all temperatures studied. The presence of isomers with the C≡C linkage parallel or perpendicular to the M–S linkage (*i.e.* interchange of the CO and SR groups or rotation of the acetylene through 90°) would not be entirely consistent with the n.m.r. spectra as it would seem likely that this situation would lead to complete non-equivalence of all four R groups of the two isomers and in practice only one of the substituents of an RC_2R group becomes split. If the cyclopentadienyl group is considered as a symmetrical substituent, isomerism cannot occur because of the relative positions of the other substituents. The remaining source of isomerism is the relative orientation of the SR group with respect to the C≡C bond. Molecular models of the $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)SC_6F_5]$ structure do not suggest significant steric interaction between the pentafluorobenzenethiolate group and the other substituents although in a model where the C≡C linkage is parallel to the Mo–S bond there is very significant interaction with one trifluoromethyl substituent of the acetylene. In the $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)SC_6F_5]$ molecule, however, specific orientations of the C_6F_5 substituent could occur which would depend upon *p–d* π-bonding between the sulphur and the molybdenum and at present this seems the most likely explanation for the isomerism observed at low temperatures in many of the $[(\eta^5\text{-}C_5H_5)M(CO)(RC_2R)SR_F]$ species.

The oxo and carbonyl compounds are formally d^2 and d^4 systems respectively, but in all cases give n.m.r. spectra characteristic of diamagnetic species with non-rotating acetylene ligands. These facts, the contrasting behaviour of the bis(alkyne) complexes, and the differing orientations of the acetylene ligands in the two series, can be understood using simple bonding arguments.

All the compounds may be represented as pseudo-octahedral in the axis systems of Figure 1, the C_5H_5 ligand occupying three sites. Then in the oxo-series ligand oxygen is in a position to π-donate into the $d(xz, yz)$ orbitals, provided these are empty, in much the same way as in vanadyl complexes, constraining the 'metal' electrons to occupy the $d(xy)$ orbital. In this situation, the acetylene can only act as a π-acceptor to the extent that it lies in the xy plane; π-donation from acetylene to $d(xz)$ will then also be possible.

In the carbonyl complexes the position is reversed. The 'metal' electrons will prefer $d(xz, yz)$ orbitals, from which they will be delocalised into the two CO $\pi^*(x,y)$ orbitals. In order to act as a π-donor to the vacant $d(xy)$ orbital ligand acetylene is constrained to lie in the xz plane; in this conformation it can also act as a π-acceptor towards the full $d(xz)$ orbital. In both series, rotation of the acetylenes would cause loss of all the metal–acetylene π-bonding and it is not surprising that such rotation is slow on the n.m.r. time-scale.

In the solid bis(alkyne) complexes, the acetylenes lie roughly parallel to the y axis, but free rotation is observed at relatively low temperatures. Efficient π-donation from both acetylenes at once is only possible in this conformation, the metal adopting the configuration $d(xy)^2d(yz)^2$ [more strictly, $d(a')^2\ d(a'')^2$, where a', a'' are $xy \pm yz$, but this does not affect the argument]. Rotation of one acetylene at a time will destroy π-bonding between that acetylene and metal, but both sorts of π-bonding between the other acetylene and metal will then be enhanced. Such orbital following can only lower the barrier to rotation. At equilibrium, $d(xz)$ accepts electrons from a linear combination of (acetylene)$_x\pi(z)$ and (acetylene)$_z\pi(x)$ orbitals, but even where one acetylene is passing through the xz plane, the other can still function as a π-donor, and the complex remains a quasi-18 electron system throughout.

The ^{19}F n.m.r. spectrum of $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2H)\text{-}SC_6F_5]$ at 293 K shows two signals ϕ_1 at 54.36 p.p.m. and ϕ_2 at 55.39 p.p.m. (with respect to CCl_3F) in a ratio of 10 : 1 in $CDCl_3$ solution and in a ratio of 3 : 1 in CD_3COCD_3 solution. These spectra are considered to arise because of the asymmetric nature of the acetylene. Because of the low intensity only single signals were detected by ^{1}H n.m.r. spectroscopy and distinct coupling between the CF_3 and H groups of the acetylene was not observed although the signals are broadened. At 178 K the most intense ^{19}F signal splits into two peaks without change in the signal due to the other isomer; on allowing the solution to warm the two new peaks merge at *ca.* 200 K and there is no significant change in the signal width as occurs at coalescence for the hexafluorobut-2-yne complexes. On exposure to oxygen the two isomers of $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2H)SC_6F_5]$ are oxidised at different rates and, further, the rate of oxidation is strongly solvent-dependent. All of these results on the trifluoropropyne complexes show clearly that the low-temperature isomerism is associated with interaction predominantly at one end of the acetylene and provide further evidence for the lack of rotation of the acetylenes in these complexes.

Variable-temperature n.m.r. studies of $[(\eta^5\text{-}C_5H_5)\text{-}MoO(CF_3C_2CF_3)SC_6F_5]$ and of the other oxo-alkyne complexes (studied as mixtures with the corresponding carbonyls) did not show the presence of isomers even at 173 K. At this temperature the pentafluorophenyl group shows all five fluorines as non-equivalent which would be associated with a fixed orientation of this group at this temperature resulting from a strong steric interaction with one trifluoromethyl group. Restricted rotation about an $S\text{-}C_6F_5$ linkage has been observed in $C_6F_5SF_3$ [9] and as mentioned previously the relative orientations of the acetylene and SC_6F_5 groups in the oxo-complex favour strong steric interaction.

The i.r. spectra of the carbonyl and oxo-complexes are consistent with the structures described above. The trifluoromethanethiolate groups show two C–F modes as is expected for terminal CF_3S groups [10] although the presence of isomers should cause further splitting. The trifluoromethanethiolate complexes each show two carbonyl peaks consistent with the presence of two isomers on an i.r. time scale. The $C\equiv C$ modes were not observed for all the complexes but where present they occurred near to 1 700 cm^{-1} in the carbonyl alkyne complexes and at 1 836 cm^{-1} in $[(\eta^5\text{-}C_5H_5)MoO(CF_3C_2CF_3)\text{-}SC_6F_5]$. The shift of the $C\equiv C$ mode to a higher frequency when the carbonyl is converted into the oxo-derivative is consistent with greatly reduced back bonding from the metal in its higher oxidation state. The very low frequencies observed for the $C\equiv C$ modes in the carbonyl alkyne complexes suggest that the acetylenes could be formally donating four electrons to the metal.[11] The observed $C\equiv C$ frequencies in the present complexes are appreciably lower than those observed (*ca.* 1 780 cm^{-1}) for the bis(alkyne) halides $[(\eta^5\text{-}C_5H_5)M(RC_2R)_2X]$.[2] If all these formally 16-electron complexes have 4-electron donation from the acetylenes this would be shared between two acetylenes in the bis(alkyne) complexes but would be confined to one acetylene in the present derivative. In the tris(alkyne)complexes $(RC_2R)_3WL$ four-electron bonding would be from two of the acetylenes; the $C\equiv C$ frequencies of these complexes are near to 1 700 cm^{-1},[11,12] which leaves the frequencies of the carbonyl complexes somewhat higher than might be expected but of the correct order of magnitude. The i.r. spectrum of the oxo-complex $[(\eta^5\text{-}C_5H_5)MoO(CF_3C_2CF_3)\text{-}SC_6F_5]$ has a band at 961 cm^{-1} which we assign to a Mo–O mode. The yellow crystalline complex obtained from the reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3SCF_3]$ and $CF_3C\equiv CH$ is formulated as a cyclopentadienone complex $[(\eta^5\text{-}C_5H_5)Mo(CO)\{(CF_3C_2H)_2CO\}SCF_3]$ on the basis of its i.r. spectrum which shows a C–O mode at 1690 cm^{-1} and its mass spectrum which shows only peaks resulting from the loss of one carbonyl group and also shows the presence of the $[(CF_3C_2H)_2CO]^+$ ion. It undergoes decarbonylation on photolysis in benzene solution to give the dimer $[\{(\eta^5\text{-}C_5H_5)Mo[(CF_3C_2H)_2CO]SCF_3\}_2]$ which still contains co-ordinated cyclopentadienone rings. The dimer has its CF_3S resonance at a very different field (+23.5 p.p.m. with respect to CCl_3F) than the monomer (+28.0 and +29.3 p.p.m.) suggesting that dimerisation is through sulphur bridges.

Condensation of two molecules of trifluoropropyne and carbon monoxide to a co-ordinated bis(trifluoromethyl)-cyclopentadienone could give various species depending upon differing positions of the trifluoromethyl groups (2,5; 3,4; or 2,4). Further, in a complex, trifluoromethyl groups which would be equivalent in a free ligand (2,5 or 3,4) can become non-equivalent because of the geometry of the complex. The i.r. spectrum of the carbonyl $[(\eta^5\text{-}C_5H_5)Mo(CO)\{(CF_3C_2H)_2CO\}SCF_3]$ contains two carbonyl peaks suggesting the presence of two isomeric complexes. The ^{19}F n.m.r. spectrum of this complex shows two sets of three resonances of equal intensity in a ratio of 4 : 1. The ^{1}H n.m.r. spectrum only shows peaks due to the predominant isomer because of the low intensity of the signals but the singlet at τ 4.34, attributed to the cyclopentadienyl protons, is slightly asymmetric suggesting that the cyclopentadienyl

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resonances of the two isomers are almost coincident. The ^{19}F signals from the trifluoromethyl substituents of the cyclopentadienone ring are exceedingly sharp singlets whereas the 3,4-bis(trifluoromethyl)cyclopentadienone would be expected to show strong FF coupling. The signals of the outermost protons of diene–metal complexes are shifted to much higher field on co-ordination than are the signals of the inner-protons [13] and the ^1H n.m.r. spectrum of the predominant isomer suggests non-equivalent 3,5 protons. The dimer $[\{(\eta^5\text{-}C_5H_5)Mo\text{-}[(CF_3C_2H)_2CO]SCF_3\}_2]$ has non-equivalent trifluoromethyl groups. All of this evidence points to the cyclopentadienone having non-equivalent 2,4-trifluoromethyl substituents with isomerism in the monomeric complexes being due to the relative orientations of the groups (the dimer could have non-equivalent but symmetrical substituted cyclopentadienones but this is considered a remote possibility). The formation of the non-symmetrically substituted cyclopentadienone is in contrast to the symmetrically 2,5-substituted derivative found in $[Fe(CO)_3\{(CF_3C_2H)_2CO\}]$.[13]

The present reactions between group VI metal thiolates and acetylenes are in contrast to studies with group VII and group VIII derivatives [3] where there is a great tendency for insertion of the acetylene into the metal–sulphur bond. It is clear that with the group VI metals there is a strong tendency to form π-acetylene complexes and the apparently low tendency for self-association of the acetylenes in the presence of derivatives of these metals may be associated with the very strong bonding between the acetylenes and the metals. In the formally electron-deficient acetylene complexes of niobium there is likewise very strong metal–acetylene bonding,[14] which is again associated with a reluctance for the acetylenes to undergo complexing or insertion reactions. The range of reactions between acetylenes and tricarbonyl $(\eta^5\text{-}C_5H_5)M(CO)_3X$ derivatives is not yet sufficient to fully allow the effect of X upon the products of the reaction to be evaluated but it is significant that in reactions with perfluorothiolates monocarbonyl monoalkyne complexes are formed with all the acetylenes studied whereas with the halides only diphenylacetylene forms this type of derivative.[2]

EXPERIMENTAL

The preparations of the trifluoromethanethiolate derivatives have been previously described.[4] $[(\eta^5\text{-}C_5H_5)Mo(CO)_3\text{-}SC_6F_5]$ [15] was prepared similarly. The method of carrying out the reactions with acetylenes has been described previously [3] and details are given in the Table. Products were purified by repeated fractional sublimation.

(π-Cyclopentadienyl)oxo(pentafluorobenzenethiolato)bis(trifluoromethyl)molybdenum.—This complex was formed by dissolving $[(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)SC_6F_5]$ (70 mg) in diethyl ether (20 ml) and sealing the solution in a tube containing some air for eight days until the colour of the solution changed from dark blue to pale yellow. Decomposition material was filtered off and hexane was added. After removal of some solvent, cooling to 253 K gave the oxo-compound in 70% yield.

N.m.r. spectra of the trifluoromethylthiolate complexes were recorded in CH_2Cl_2 (^{19}F) or $CDCl_3$ (^1H) solutions on a Jeol C60 spectrometer. Spectra of the pentafluorobenzenethiolate complexes were recorded in $[^2H_6]$acetone on a Jeol 1FT-100 spectrometer. Me_4Si and CCl_3F were used as internal references.

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