Co-ordinatively Unsaturated Alkyne Complexes of Molybdenum and Tungsten: Reactions and Dynamic Nuclear Magnetic Resonance Studies of $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) Complexes

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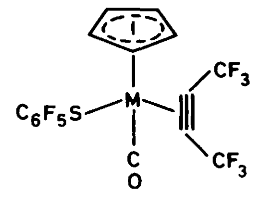
Variable-temperature ^{19}F n.m.r. studies of the hexafluorobut-2-yne complex $[W(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ reveal three distinct phases of fluxional behaviour between −90 and +80 °C, attributed to restricted rotation about (*a*) the S–C_6F_5 bond, (*b*) the W–SC_6F_5 bond, and (*c*) the CF_3CCCF_3–W bond ('propeller rotation'), in increasing order of energy. The oxo complex $[W(SC_6F_5)(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, obtained by air oxidation of the parent carbonyl in diethyl ether, in contrast shows only restricted rotation about the W-SC_6F_5 bond over the same temperature range. Reactions of the carbonyls $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with tertiary phosphines and phosphites (L) give carbonyl-substitution products $[M(SC_6F_5)(L)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ [M = Mo or W, L = $P(OMe)_3$, PMe_2Ph, or PEt_3; M = Mo, L = PPh_3 or $PMePh_2$] under unusually mild conditions which undergo alkyne propeller rotation according to ^{19}F n.m.r. studies. In the case of alkylphosphines, carbonyl substitution was observed to proceed *via* thermally unstable intermediates, $[M(SC_6F_5)(CO)\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(\eta^5\text{-}C_5H_5)]$, isolated and characterised for the case M = W, L = PEt_3. N.m.r. data indicate the presence of two isomeric forms containing an η^2-vinyl ligand $C(CF_3)C(CF_3)L$ resulting from attack of the phosphine at an alkyne carbon atom.

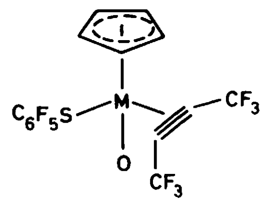
The ability of η^2-bonded alkyne ligands to stabilise co-ordinative unsaturation in complexes of the early transition metals has been substantiated by an increasing number of reports in recent years.[1–11] Extended Hückel calculations confirm that under appropriate circumstances both sets of filled π orbitals on an alkyne can participate in bonding with a metal, *i.e.* an alkyne can formally donate up to four electrons to a metal.[12–14] This usually results in the alkyne adopting specific orientations in a complex so as to maximise overlap of its π and π* orbitals with *d*π-type orbitals on the metal; *e.g.* in $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1a**) the C≡C axis lies perpendicular to the Mo–S bond, whereas in $[Mo(SC_6F_5)(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2a**) it lies parallel to this bond.[15] Since four-electron donation might also be expected to modify the chemistry of a co-ordinated alkyne a systematic study of the chemistry of molybdenum and tungsten alkyne complexes is currently being carried out with a view to determining the exact nature of these effects.[16] I now report some reactions of $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with oxygen, $P(OMe)_3$, and tertiary phosphines and dynamic n.m.r. studies of the products. Some of this work has been reported previously in a communication.[17]

Results and Discussion

The reaction of $[W(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1b**) with oxygen proceeds slowly in diethyl ether solution at room temperature to give the oxo complex $[W(SC_6F_5)(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2b**) as off-white crystals in 46% yield. This parallels the formation of $[Mo(SC_6F_5)(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ from (**1a**) under identical conditions,[2] while similar alkyne oxo complexes have been obtained previously by other workers apparently due to the presence of adventitious amounts of oxygen in reaction mixtures.[18,19] The reaction of trimethyl phosphite with both molybdenum and tungsten complexes (**1a**) and (**1b**) proceeds much more rapidly in diethyl ether at room temperature to give green solutions from which carbonyl substitution products $[M(SC_6F_5)\{P(OMe)_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ [M = Mo (**3a**), M = W (**4a**)] were obtained in good yield. No reaction was observed between $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ and triphenylphosphine under these conditions, but after 4 h at 60 °C complex (**3b**) was obtained. Addition of alkyl-substituted phosphines PEt_3, PMe_2Ph, and $PMePh_2$ to $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo) and PEt_3 and PMe_2Ph (M = W) at room temperature gave red-brown solutions immediately but on standing these turned green, rapidly in the case of $PMePh_2$ and more slowly in the case of PMe_2Ph and PEt_3. Again, green crystalline substitution products (**3**) and (**4**) were isolated but i.r. spectra of the red-brown solutions indicated the presence of a carbonyl complex. Consequently the reaction of $[W(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ with PEt_3 was repeated at 0 °C which resulted in the isolation of a red-brown crystalline complex (**5**), analysing as $[W(SC_6F_5)(CO)(C_4F_6)(PEt_3)(\eta^5\text{-}C_5H_5)]$.



(**1a**) M = Mo
(**1b**) M = W



(**2a**) M = Mo
(**2b**) M = W

The structures of both carbonyl and oxo molybdenum complexes (**1a**) and (**2a**) have previously been elucidated by *X*-ray diffraction studies.[15] Both exhibit the familiar 'three-legged piano-stool' geometry about the metal atom. This is based upon approximately octahedral co-ordination with the cyclopentadienyl ligand occupying a face and the other three ligands corners of the octahedron. The most interesting feature of the structures concerns the alkyne orientation since in (**1a**) the C≡C axis lies parallel to the M–CO axis and hence perpendicular to the M–S axis. In (**2a**) the alkyne adopts an orientation parallel

Table. N.m.r. data for the complexes

	^{1}H		^{19}F		
	C_5H_5	L[a]	CF_3	T/°C	T_c/°C[b]
(**2b**) $[W(SC_6F_5)(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	6.14 (s)		−53.22 (q, J_{FF} = 4, 3 F), −56.66 (q, J_{FF} = 4, 3 F)	21	>80[c]
(**3a**) $[Mo(SC_6F_5)\{P(OMe)_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	5.14 (s)	3.96 (d, J_{PH} = 11, 9 H, Me)	−55.17 (quintet, 3 F), −56.35 (quintet, 3 F)	−67	−10[d]
(**3b**) $[Mo(SC_6F_5)(PPh_3)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	4.90 (s)	7.45 (bm, 15 H, Ph)	−52.07 (bs, 3 F), −56.06 (bs, 3 F)	−90	+2[e]
(**3c**) $[Mo(SC_6F_5)(PMePh_2)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	4.92 (s)	7.54 (m, 10 H, Ph), 2.58 (d, J_{PH} = 9, 3 H, Me)	−52.36 (bs, 3 F), −55.96 (bs, 3 F)	−60	−4[d]
(**3d**) $[Mo(SC_6F_5)(PMe_2Ph)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	4.96 (s)	7.61 (m, 5 H, Ph), 2.12 (2d, J_{PH} = 9, 6 H, Me)	−51.80 (bs, 3 F), −56.0 (bs, 3 F)	−60	−28[d]
(**3e**) $[Mo(SC_6F_5)(PEt_3)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	5.08 (d, J_{PH} = 1)	2.10 (m, 6 H, CH_2), 1.13 (m, 9 H, Me)	−52.80 (bs, 3 F), −56.86 (bs, 3 F)	−80	−33[f]
(**4a**) $[W(SC_6F_5)\{P(OMe)_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	5.20 (s)	3.76 (d, J_{PH} = 11, 9 H, Me)	−54.95 (bs, 3 F), −56.39 (quintet, 3 F)	−66	10[e]
(**4b**) $[W(SC_6F_5)(PMe_2Ph)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	4.95 (d, J_{PH} = 1)	7.55 (m, 5 H, Ph), 2.31 (d, J = 9.5, 3 H, Me), 2.23 (d, J = 9, 3 H, Me)	−51.98 (apparent t, 3 F), −56.56 (bs, 3 F)	−65	4[d]
(**4c**) $[W(SC_6F_5)(PEt_3)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$	5.32 (s)	2.28 (m, 6 H, CH_2), 1.20 (m, 9 H, Me)	−52.10 (bs, 3 F), −56.68 (bs, 3 F)	−48	−5[e]
(**5**) $[W(SC_6F_5)(CO)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(\eta^5\text{-}C_5H_5)]$					
major isomer[g]	5.40 (s)	2.63, 2.12 (d, m, 6 H, CH_2), 1.25 (dt, 9 H, Me)	−51.68 (m, 3 F), −52.75 (bs, 3 F)	−20	
minor isomer[g]	5.28 (s)	h	−46.36 (bs, 3 F), −54.12 (bm, 3 F)		

[a] L = Phosphine, phosphite, CO, or O. [b] Recorded at 94.1 MHz. [c] $[^2H_8]$Toluene. [d] $CDCl_3$. [e] $[^2H_6]$Acetone. [f] CD_2Cl_2. [g] −10 °C, CD_2Cl_2. [h] Peaks obscured by resonances of major isomer.

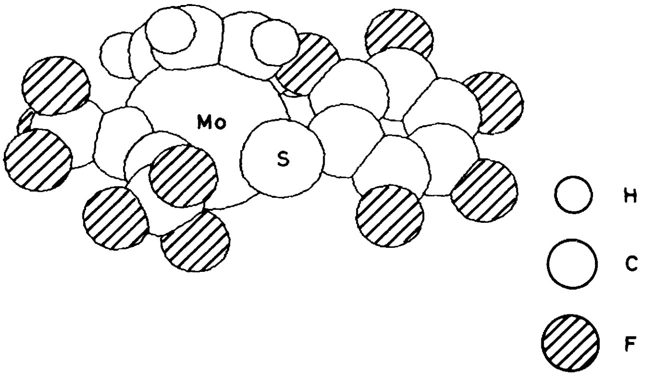


Figure 1. Space-filling diagram of (**2a**) [orientation (**2a**^{i})], showing the $C_5H_5 \cdots C_6F_5$ non-bonded contact

to the M–S axis and perpendicular to the M–O axis. This difference can be explained by simple bonding arguments[2,14] based on the fact that the metal in (**1**) has a d^4 configuration while (**2**) is a d^2 system. In (**1**) the carbonyl dominates the bonding by stabilising both filled $d\pi$ orbitals thus dictating that the alkyne must lie parallel to the M–CO axis to maximise back donation to the C≡C π^* orbitals. This allows the filled alkyne π perpendicular orbital to donate to the remaining empty metal $d\pi$-type orbital. However, in (**2**) the oxygen π-donates into the two empty metal $d\pi$ orbitals along the M–O axis leaving the third filled orbital to back-donate to the alkyne which must therefore lie parallel to the M–S axis. Thus the structural and, to some extent, spectroscopic properties of alkyne complexes of the type $[M(SR')(L)(RC{\equiv}CR)(\eta^5\text{-}C_5H_5)]$ ($R' = C_6F_5$, $R = CF_3$, L = O or CO) should depend crucially on the nature of the ligand L. The n.m.r. studies of (**1b**) and (**2b**) which will now be described clearly indicate that this is the case.

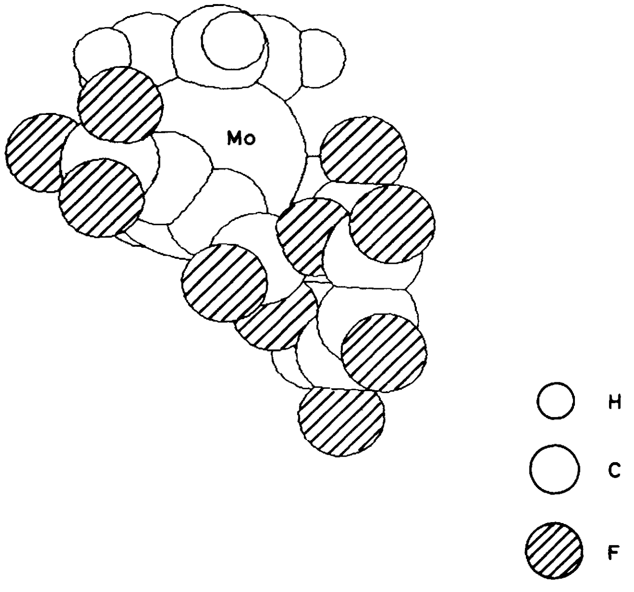
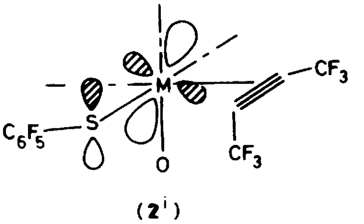
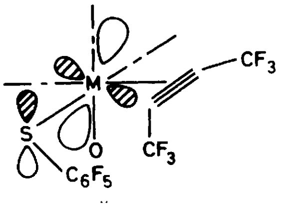


Figure 2. Space-filling diagram of (**2a**) [orientation (**2a**^{ii})], showing the $C_6F_5 \cdots CF_3C{\equiv}CCF_3$ non-bonded contact

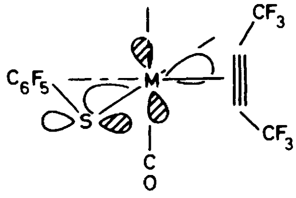
The spectroscopic features of (**2b**) (Table) are almost identical to those of (**2a**)[2] and consequently a similar structure is proposed. The ν(C≡C) mode in the i.r. spectrum at 1 798 cm^{-1} interestingly lies some 80 cm^{-1} to high frequency of that in the carbonyl (**1b**)[20] which may reflect (*a*) reduced metal–alkyne back donation due to the higher oxidation state, W^{IV} rather than W^{II}, (*b*) the fact that the alkyne acts as a two-electron donor since in (**2a**) the Mo–O distance is consistent with a metal–oxygen triple bond, *i.e.* the oxygen atom functions as a four-electron donor ligand.[15] The ^{19}F n.m.r. spectrum at 20 °C exhibits three C_6F_5 resonances and two CF_3 quartets as expected for the proposed structure. However, as with (**2a**)[2] the C_6F_5 *ortho*- and *meta*-fluorine signals each broaden and split into two separate resonances at lower temperatures, coalescence occurring at −51 (*o*-F) and −63 °C (*m*-F). No changes are observed in the CF_3 resonances down to −80 °C indicating that these effects result from restricted rotation about the S–C_6F_5 bond which leads to one preferred orientation for the C_6F_5 group at low temperatures. Evidence for restricted rotation about the S–C_6F_5 bond in $F_3SC_6F_5$ has also been obtained from dynamic ^{19}F n.m.r. studies[21] but it was not possible to eliminate the possibility of a concomitant intramolecular rearrangement at sulphur.



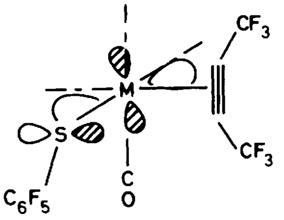
(**2**^{i})



(**2**^{ii})



(**1**^{i})



(**1**^{ii})

With a view to establishing the origin of the rotational barrier in (**2a**) and (**2b**) molecular graphics studies[22] were carried out using the atomic co-ordinates of (**2a**)[15] as the basis. The crucial factor involved appears to be the orientation of the S–C_6F_5 group. In the solid-state structure the alkyne lies virtually parallel to the Mo–S–C(C_6F_5) plane. Assuming that this orientation is retained in solution at low temperature free rotation about the S–C_6F_5 bond appears to be restricted by close contact between the *ortho* fluorines and the C_5H_5 ligand (Figure 1). With the C_6F_5 ligand set so as to interact fully with the cyclopentadienyl group, rotation of the latter results in the F–C distance oscillating between 1.36 Å in the staggered position and 0.99 Å in the eclipsed conformation. Although structural relaxation could reduce this effect, taking into account additional steric interactions with the C_5H_5 hydrogens and the absence of other short intramolecular contacts, the $C_5H_5 \cdots C_6F_5$ interaction appears to be the most likely source of restricted rotation.

The preference for the observed S–C_6F_5 orientation about the Mo–S bond can readily be explained by electronic effects since the d^2 configuration of the metal could conceivably allow sulphur ⟶ metal π-donation. In principle two conformations should be possible (**2**^{i}) and (**2**^{ii}) where π-donation would be maximised but we find that the latter is precluded by severe steric interaction between the C_6F_5 and one of the CF_3 groups of the alkyne (Figure 2), *i.e.* free rotation about the M–S bond is

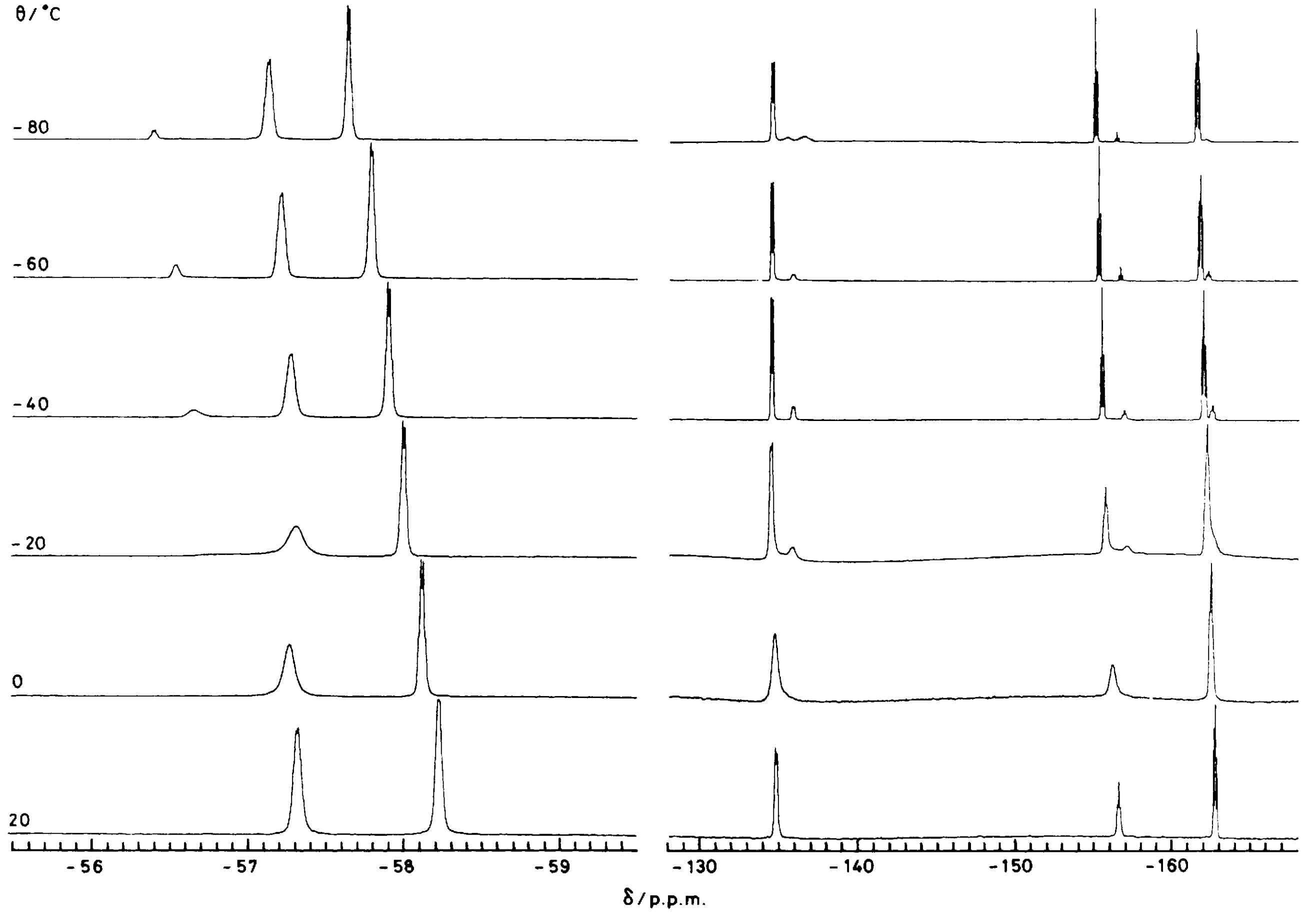


Figure 3. Variable-temperature ^{19}F n.m.r. spectra of (**1b**)

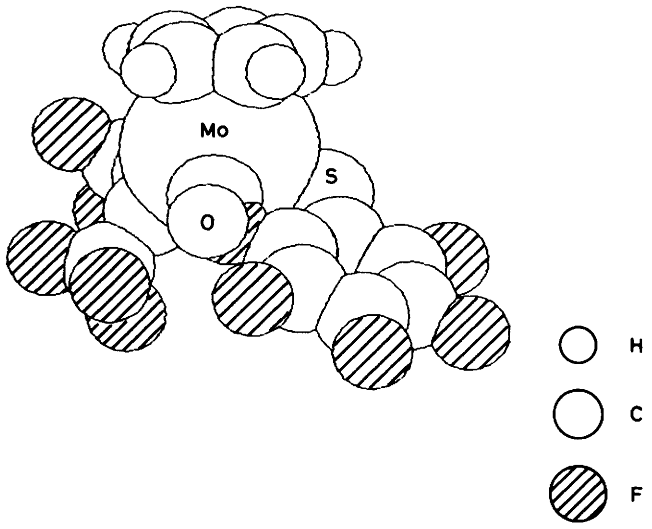


Figure 4. Space-filling diagram of **(1a)** [orientation **(1a^{ii})**], showing the $C_6F_5 \cdots CO$ non-bonded contact

prevented by steric effects. This could possibly be relieved by alkyne 'propeller rotation' about the metal–alkyne axis but no evidence was obtained for this in the ^{19}F n.m.r. spectrum of **(2b)** (at 188 MHz) up to 90 °C.

Previously it has been observed that the related carbonyl complex $[Mo(SCF_3)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ exists in two interconverting isomeric forms which are attributed to restricted rotation about the Mo–S bond.[2] This phenomenon was also indicated by the presence of two ν(CO) modes in the i.r. spectrum near 2 000 cm^{-1} while the i.r. spectrum of the recently reported complex $[Mo(SMe)(CO)(MeC{\equiv}CMe)(\eta^5\text{-}C_5H_5)]$ was interpreted similarly.[23] However, both SC_6F_5 derivatives **(1a)** and **(1b)** only show a single ν(CO) mode suggesting the presence of only one isomer or, alternatively, degeneracy of the two ν(CO) modes. The latter possibility was subsequently confirmed by variable-temperature ^{19}F n.m.r. studies of the tungsten derivative **(1b)** obtained at 188 MHz over the temperature range 0 to −90 °C.

The spectrum in the CF_3 region at 20 °C ([$^2H_8$]toluene) consists of two multiplets instead of the simple quartets expected, thus indicating coupling of both CF_3 groups to C_6F_5. This was confirmed by irradiating the C_6F_5 *ortho* fluorines which resulted in two CF_3 quartets, J_{FF} = 3.0 Hz, although one signal (δ −57.3) remained somewhat broader than the other at δ −58.2. It seems unlikely that discernible F–F coupling could occur through seven bonds and it is concluded that through-space coupling[24] is responsible for the observed $C_6F_5 \cdots CF_3$ interaction. Consequently it appears that the C_6F_5 *ortho* fluorines are sufficiently close to both CF_3 groups in the carbonyl complex **(1b)** to produce coupling, whereas in the oxo complex **(2b)** no $C_6F_5 \cdots CF_3$ interaction was observed. Molecular graphics studies indicate that in **(1a)** the *ortho* fluorines of C_6F_5 can approach to within 1.88 and 1.68 Å of the two alkyne CF_3 groups, assuming free rotation about the M–S and S–C_6F_5 bonds which appears to be the case at room temperature.

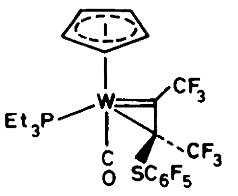
The ^{19}F n.m.r. spectrum of **(1b)** at lower temperatures in CD_2Cl_2 (see Figure 3) confirms that two isomeric forms exist since two sets of CF_3 and C_6F_5 signals are observed (ratio 6:1). One of the CF_3 signals of the minor isomer is apparently obscured by the major isomer peak at *ca.* δ −58 but can be observed as a distinct signal at −40 °C in $CDCl_3$. As for $[Mo(SCF_3)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[2] this isomerism is attributed to restricted rotation of the SR′ ligand about the M–S bond. Assuming that this interpretation is correct it is conceivable that either steric or electronic factors could be responsible for the conformational preferences of the thiolate group. The following argument is presented in favour of electronic control.

Since the metal in **(1b)** has a d^4 configuration one metal $d\pi$ orbital is empty and consequently can be stabilised by π-donation from both alkyne and sulphur ligands. Thus two SC_6F_5 orientations, **(1^{i})** and **(1^{ii})**, may be electronically stabilised in accord with the low-temperature n.m.r. data. This contrasts with the otherwise comparable situation in **(2a)** where steric restraints prevented one electronically favourable orientation being adopted. However, both alkyne and SC_6F_5 ligands in **(1a)** adopt conformations in the solid state which lie at 90° to those in **(2a)** as a consequence of the differing orbital occupancy and hence π-bonding possibilities. Thus orientation **(1^{i})** is adopted in the solid-state structure of $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ while recent *X*-ray diffraction studies reveal that this orientation is similarly adopted by two related alkyne thiolate complexes, $[Mo(SC_6H_4NO_2\text{-}4)\{P(OMe)_3\}(MeC{\equiv}CMe)(\eta^5\text{-}C_5H_5)]$ and $[Mo(SC_6H_4SPh\text{-}2)(CO)(MeC{\equiv}CMe)(\eta^5\text{-}C_5H_5)]$. The L–Mo–S–C(aryl) torsion angles of 178.6 and 179.3° respectively in these two complexes compare with 175.5° determined for **(1a)**.[15] It seems unlikely that such similar torsion angles would be found if steric factors were responsible for the thiolate ligand orientation, given the different steric interactions which will be present in the three different molecules. Consequently electronic factors appear to be dominant.

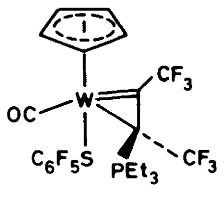
Computer graphics techniques were again employed to probe steric interactions in the two orientations. These revealed that when the SC_6F_5 ligand is rotated by 180° from the solid-state orientation **(1^{i})** to produce **(1^{ii})** no severe van der Waals contacts are present which would significantly destabilise the structure. This is in contrast to the oxo complex where free rotation is not possible.

Interestingly in both **(1a^{i})** and **(1a^{ii})** (M = Mo) the $(C_6F_5)o\text{-}F \cdots CF_3$ distances have increased markedly relative to the minimum distances of 1.85 and 1.68 Å found when the SC_6F_5 group is allowed to rotate about the Mo–S bond. Not surprisingly the $C_6F_5 \cdots CF_3$ coupling observed in the room-temperature ^{19}F n.m.r. spectrum all but disappears at lower temperatures and the CF_3 resonances become reasonably well resolved quartets. This effect serves to distinguish between restricted rotation about the M–S bond and the alternative isomerisation mechanism involving inversion at sulphur. In the latter case $C_6F_5 \cdots CF_3$ coupling would be unlikely at higher temperatures since the $o\text{-}F \cdots CF_3$ distance would tend to increase as the transition state between the two conformations was reached.

At still lower temperatures (< −50 °C) the spectrum of **(1b)** in the C_6F_5 region reveals a second mode of dynamic behaviour, but only with the minor isomer. At −90 °C two distinct *ortho*-fluorine resonances can be discerned while the *meta*-fluorine peak has broadened considerably, consistent with the adoption of a preferred C_6F_5 orientation as found in the oxo complexes **(2)**. This is not observed in the major isomer of **(1b)** implying that if steric effects are responsible they are less severe in the latter. Analysis of intramolecular contacts in orientation **(1a^{i})** as the C_6F_5 rotates reveals a minimum $(C_6F_5)o\text{-}F \cdots C(C_5H_5)$ distance of 1.37 Å. However, a 'cog-wheel rotation' may still be possible since the fluorine–carbon distance can rise to 1.715 Å (at which point the $F \cdots H$ distance is 1.59 Å) as the C_5H_5 ring rotates to a staggered position. This is somewhat larger than the corresponding $F \cdots C$ distance of 1.36 Å in **(2a)**. In contrast, free rotation of the C_6F_5 about the C–S bond is much less likely with conformation **(1^{ii})** where a minimum $(C_6F_5)F \cdots C(CO)$



(**5a**)



(**5b**)

distance of 0.66 Å is found (Figure 4). It is therefore concluded that the carbonyl ligand is responsible for restricted rotation in the minor isomer at low temperatures. Consequently by implication the minor isomer must have orientation (**1**$^{\text{ii}}$), the opposite of that adopted by (**1a**) in the solid state, *i.e.* (**1**$^{\text{i}}$) which is presumably that favoured by the major isomer.

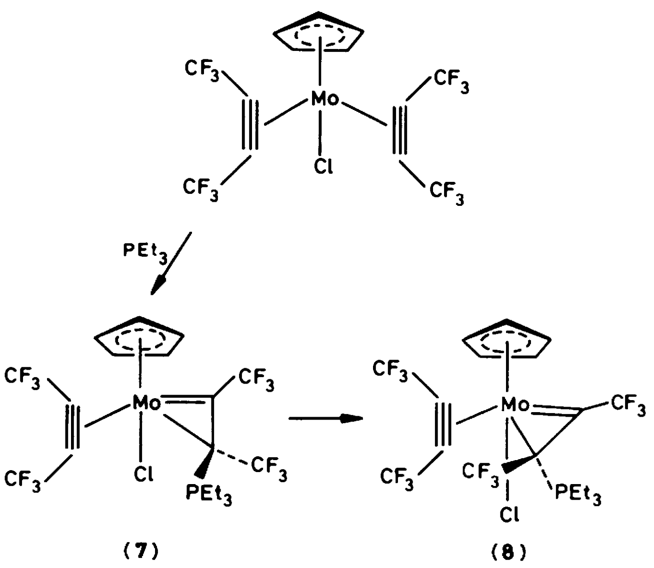
The ^{19}F n.m.r. spectrum of [W(SC$_6$F$_5$)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] above ambient temperature indicates a third phase of dynamic behaviour. Spectra were taken at 94.6 MHz to reduce coalescence temperatures and hence decomposition and under these conditions the two alkyne CF$_3$ signals broaden and collapse to a single peak above 80 °C in CD$_3$C$_6$D$_5$. Similar behaviour was observed with (**1a**) where coalescence occurred at 72 °C. This is attributed to the onset of alkyne propeller rotation but further discussion is deferred to a later stage.

The ultimate products of reactions between [M(SC$_6$F$_5$)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (M = Mo or W) and phosphines or phosphites (L) are simple alkyne derivatives [M(SC$_6$F$_5$)(L)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] according to elemental analyses and spectroscopic data (see Table). Apart from the absence of a ν(CO) mode in the i.r. spectrum, the i.r. and ^{1}H and ^{19}F n.m.r. data are in several respects comparable with those of the monocarbonyl precursors (**1**). Interestingly the ν(C≡C) mode in the i.r. spectra is observed at *ca.* 1 670—1 690 cm^{-1} in the molybdenum derivatives (**3**) while even lower values are observed for the tungsten complexes (**4**) [1 665 cm^{-1}, L = P(OMe)$_3$; 1 650 cm^{-1}, L = PEt$_3$; 1 640 cm^{-1}, L = PMe$_2$Ph]. These represent, to my knowledge, the largest reductions in ν(C≡C) from the free ligand (2 300 cm^{-1})[25] yet observed on coordination of an alkyne to a single metal centre and contrast with values of 1 919 cm^{-1} in [Mn(CO)$_2$(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)][26] and 1 790 cm^{-1} in [Ni(CF$_3$C≡CCF$_3$)(PPh$_3$)$_2$][27] where the alkyne acts as a simple two-electron donor ligand. Values of 1 600 and 1 597 cm^{-1} are found for the μ-η^2-bonded CF$_3$C≡CCF$_3$ ligand in [Co$_2$(CO)$_6$(μ-CF$_3$C≡CCF$_3$)] and [Ni$_2$(η^5-C$_5$H$_5$)$_2$(μ-CF$_3$≡CCF$_3$)][28] respectively, where both sets of mutually orthogonal C≡C π orbitals are involved in bonding to a metal, which suggests a similar situation in (**3**) and (**4**) but in these complexes only one metal is involved. The greater σ-electron-donor and poorer π-electron-acceptor abilities of phosphines and phosphites relative to CO will also lead to greater metal to alkyne π back-donation and thus account for the even lower values of ν(C≡C) in (**3**) and (**4**) relative to (**1**).

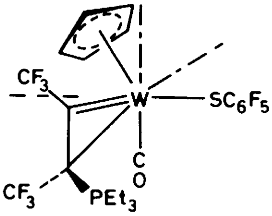
Complexes (**3**) and (**4**) can be compared with recently reported hydrocarbon alkyne thiolate derivatives [Mo(SR′){P(OMe)$_3$}(MeC≡CMe)(η^5-C$_5$H$_5$)] (R′ = C$_6$H$_4$NH$_2$-4, C$_6$H$_4$OMe-4, C$_6$H$_4$Me-4, C$_6$H$_4$NO$_2$-4, or C$_6$H$_5$) isolated from the reactions of NaSR′ with [Mo{P(OMe)$_3$}$_2$(MeC≡CMe)(η^5-C$_5$H$_5$)][BF$_4$].[23] An *X*-ray diffraction study of the SC$_6$H$_4$NO$_2$-4 derivative revealed a structure similar to that of [Mo(SC$_6$F$_5$)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] with the but-2-yne C≡C axis lying parallel to the Mo–P axis so as to maximise metal to alkyne π back-donation. The ^{19}F n.m.r. data for complexes (**3**) and (**4**) are consistent with such a structure at low temperatures. It is therefore not surprising to find evidence of C$_6$F$_5$ ··· CF$_3$ spin–spin coupling in the spectra of some complexes [*cf.* (**1b**)] as well as ^{31}P–^{19}F coupling. This is most readily observed with the trimethyl phosphite complexes and consequently homodecoupling experiments were carried out on [Mo(SC$_6$F$_5$){P(OMe)$_3$}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] at −67 °C where two CF$_3$ quintets are observed at δ_1 −55.17 and δ_2 −56.35. On decoupling δ_1, δ_2 collapsed to an apparent quartet whereas on irradiation of δ_2, δ_1 collapsed to a broad doublet (J = 2.7 Hz). This can be explained in terms of both CF$_3$ groups coupling to phosphorus (although fine structure is not evident in the broad ^{31}P-{^{1}H} singlet, δ 174.04), while δ_2 also appears to be coupled to the *ortho* fluorines of the C$_6$F$_5$ group. The latter conclusion was confirmed by irradiating δ_2 and observing the *ortho*-fluorine signal. In the absence of decoupling this appears as a broad doublet but on irradiation of δ_2 the expected doublet of doublets is observed.

Unlike (**1b**), no evidence was obtained for two rotamers of (**3**) and (**4**) at low temperatures in accord with computer graphics studies which indicate that conformation (**1**$^{\text{ii}}$) would be sterically impossible if a carbonyl is replaced by a phosphine. However, broadening of the C$_6$F$_5$ *ortho*-fluorine resonance of (**4b**) at −90 °C indicates that restricted rotation about the S-C$_6$F$_5$ bond occurs. Moreover, as with the carbonyls (**1a**) and (**1b**), alkyne propeller rotation was observed in every case as indicated by the broadening and coalescence of the two CF$_3$ resonances in the ^{19}F n.m.r. spectra at higher temperatures. Despite the fact that for practical reasons the same solvent could not be employed for each complex, marked differences in coalescence temperature (T_c) are observed depending on the nature of the ligand L (Table), in [M(SC$_6$F$_5$)(L)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)]. A rough correlation between T_c values and the π-acceptor ability of the ligand L is observed as higher values (and hence higher energy barriers) are found with better π acceptors such as CO and P(OMe)$_3$. In the present case quantitative data were not obtained for the rotational barriers due to the complexity of the coupling in the CF$_3$ signals. In cases where this has proved possible, *e.g.* [Mo(SC$_6$H$_4$R″-4)(L)(MeC≡CMe)(η^5-C$_5$H$_5$)] [R″ = NH$_2$, OMe, Me, H, or NO$_2$; L = P(OMe)$_3$] and [Mo(SMe)(L)(MeC≡CMe)(η^5-C$_5$H$_5$)] [L = CO or P(OMe)$_3$][23] higher energy barriers are observed where differences in the π-acceptor ability between ligands L and SR′ are greatest, in accord with my observations. This can be traced to electronic stabilisation of the alkyne orientation parallel to the M–L bond by the π-acceptor ligand L.[12,14]

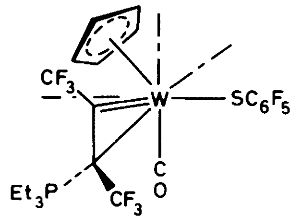
Due to the thermal instability of complex (**5**) in solution the i.r. spectrum was obtained as a Nujol mull while ^{1}H, ^{19}F, and ^{31}P n.m.r. spectra were observed at −10 °C or below. The i.r. spectrum contains a single ν(CO) mode at 1 915 cm^{-1}, *ca.* 100 cm^{-1} lower in energy than the comparable band in [W(SC$_6$F$_5$)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)], but, significantly, a ν(C≡C) band, observed for the latter at 1 720 cm^{-1}, is absent. This and n.m.r. evidence (see below) suggest the presence of a modified fluorocarbon moiety and in particular an η^2-vinyl ligand. Structure (**5a**) was originally proposed for this compound[17] but the recent isolation of η^2-vinyl complexes, *e.g.* [W(SC$_6$H$_4$Me-4){η^2-C(CF$_3$)C(CF$_3$)PEt$_3$}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**6**), resulting from addition of a phosphine to a co-ordinated CF$_3$C≡CCF$_3$ in [W(SC$_6$H$_4$Me-4)(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)],[16b] now suggests an alternative structure (**5b**) more consistent with n.m.r. data obtained subsequently. The ^{1}H n.m.r. spectrum of (**5**) exhibits CH$_3$ and CH$_2$ group signals in addition to two η^5-C$_5$H$_5$ singlets (ratio 11:1), suggesting the presence of two isomeric forms in solution. This is confirmed by the ^{19}F n.m.r. spectrum where two sets of CF$_3$ and C$_6$F$_5$ multiplets are observed while two resonances similarly are observed in the ^{31}P-{^{1}H} spectrum. The minor ^{31}P n.m.r. resonance is broad and relatively featureless while the major peak is a well resolved septet presumably reflecting coupling between the ^{31}P nucleus and both CF$_3$ groups. This was confirmed by broad-band de-



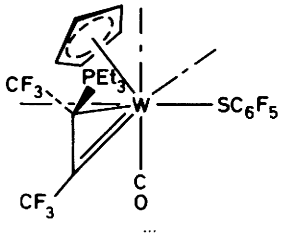
Scheme 1.



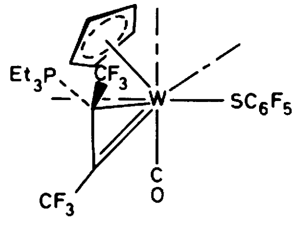
(5^{i})



(5^{ii})



(5^{iii})



(5^{iv})

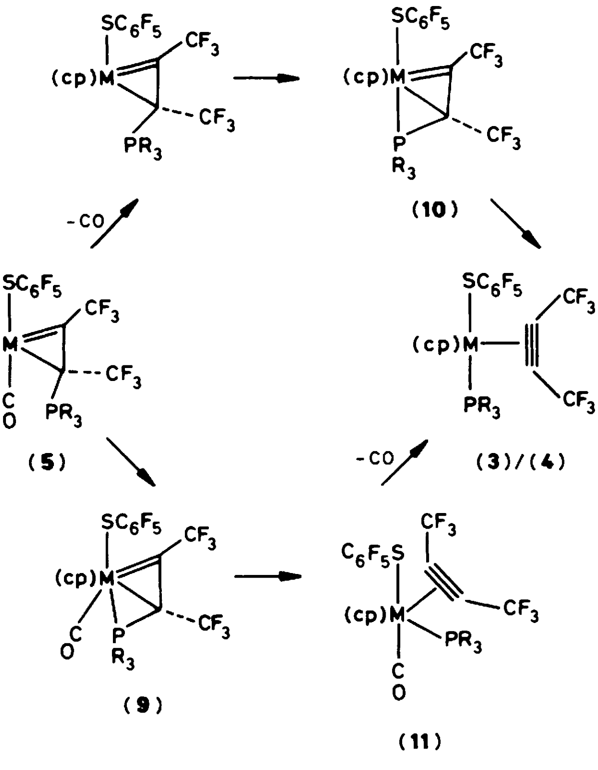
coupling of the two CF_3 resonances, when the phosphorus resonance collapsed to a singlet accompanied by tungsten-183 satellites, J_{P-W} = 25.5 Hz.

The following conclusions are therefore suggested. The phosphine ligand is attached to a carbon atom of the fluorocarbon moiety as in (**5b**) since the phosphorus–tungsten coupling constant is similar to that in (**6**) (J_{WP} = 20.5 Hz), where the presence of an identical η^2-vinyl ligand has been confirmed by single-crystal *X*-ray diffraction studies.[16b] A significantly larger J_{WP} value (247 Hz) is found with the ^{31}P-{^1H} resonance of the alkyne complex (**4c**) consistent with the direct co-ordination of the phosphine to tungsten.[29] Chemical shift differences are also observed between the latter (δ −0.10) and (**6**) (δ 37.85) and significantly the phosphorus chemical shift in (**5**) (δ 44.76; CD_2Cl_2, −20 °C) is close to that of (**6**), again implying similar structures. Although decoupling experiments were not carried out on the minor isomer of (**5**) the ^{31}P chemical shift (δ 39.08) similarly suggests an η^2-vinyl structure with the phosphine co-ordinated to the fluorocarbon ligand. Previously two isomeric forms (**7**) and (**8**) (Scheme 1) of the η^2-vinyl complex $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)PEt_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ have been isolated, where *X*-ray diffraction studies revealed that isomerism arises from (*a*) differing orientations of the η^2-vinyl ligand and (*b*) inversion of stereochemistry at the chiral carbon of the η^2-vinyl ligand which bears the phosphine ligand.[16d] Both sources of isomerism are clearly possible in (**5b**). However, Green and co-workers[19] have isolated two isomeric forms of the η^2-vinyl complex $[Mo\{\eta^2\text{-}C(CH_2Ph)C(H)Ph\}\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ which differ only in the orientation of the η^2-vinyl ligand by *ca.* 90°.

Extended Hückel molecular orbital calculations on such complexes suggest that the orientational preferences of the η^2-vinyl ligand parallel those of related alkyne complexes.[19] Thus the structure of (**5b**) may be assumed to resemble that of the precursor (**1b**) in which the metal has an idealised octahedral co-ordination geometry with the cyclopentadienyl ligand occupying a face and the CO, SC_6F_5, and $CF_3C{\equiv}CCF_3$ ligands occupying corners of the octahedron. It therefore seems probable that the η^2-vinyl ligand will adopt an orientation such that the C–C axis lies approximately parallel to the M–CO axis so as to maximise metal-η^2-vinyl π bonding. Thus four isomeric forms, (**5^{i}**), (**5^{ii}**), (**5^{iii}**), and (**5^{iv}**), are possible depending upon the direction of attack by the phosphine on the alkyne. In view of the conditions used in the preparation, isolation, and study of (**5**) I assume that the major isomer is the kinetic form, *i.e.* that no subsequent rearrangement has occurred following the co-ordination of the phosphine. Addition of PEt_3 to $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ to give an η^2-vinyl complex has been observed to proceed *via* a kinetic isomer which rearranges to the thermodynamic form (**6**) above 0 °C.[30] In contrast, isomerisation of the kinetic form of the chloro η^2-vinyl complex $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)PEt_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**7**) into the thermodynamic form (**8**) (Scheme 1) only proceeds at a reasonable rate in hexane at temperatures above 60 °C.[16d]

In an attempt to distinguish between the isomeric possibilities in (**5**), ^{19}F homodecoupling experiments were carried out on the major isomer. Irradiation of δ_2 at −52.75 p.p.m. transformed the poorly resolved peak δ_1 −51.68 into a doublet, J = 3.5 Hz, indicating coupling between $\delta_1(CF_3)$ and the phosphine. However, irradiation of δ_1 transformed δ_2 into a poorly resolved apparent quartet suggesting coupling both to the phosphine and, as in (**2b**), to the C_6F_5 *ortho* fluorines. This was confirmed by irradiating the peak due to the latter at −135.0 p.p.m. and observing δ_1 and δ_2. Little change was observed in the former whereas δ_2 was transformed into an apparent quintet (probably a doublet of quartets). Assuming that through-space coupling is involved $\delta_1(CF_3)$ appears to be remote from the C_6F_5 group while $\delta_2(CF_3)$ is sufficiently close to undergo spin–spin coupling. This tentatively eliminates (**5^{ii}**) and (**5^{iv}**) where both CF_3 groups should be relatively close to the C_6F_5 group. In view of the fact that phosphine attack at a co-ordinated hexafluorobut-2-yne in $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ occurs preferentially from a direction distal to the cyclopentadienyl group to give complex (**7**) (Scheme 1),[16d] I tentatively assign the major isomeric form to (**5^{i}**). Support for such a proposal is obtained from the reaction of $[Mo(Bu^tC{\equiv}CH)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)][BF_4]$ with $Li[CuPh_2]$ where the incoming phenyl group attacks distal to the C_5H_5 group to give the η^2-vinyl complex $[Mo\{\eta^2\text{-}CBu^tC(H)Ph\}\{POMe)_3\}_2(\eta^5\text{-}C_5H_5)]$[19] which is structurally analogous to (**5^{i}**).

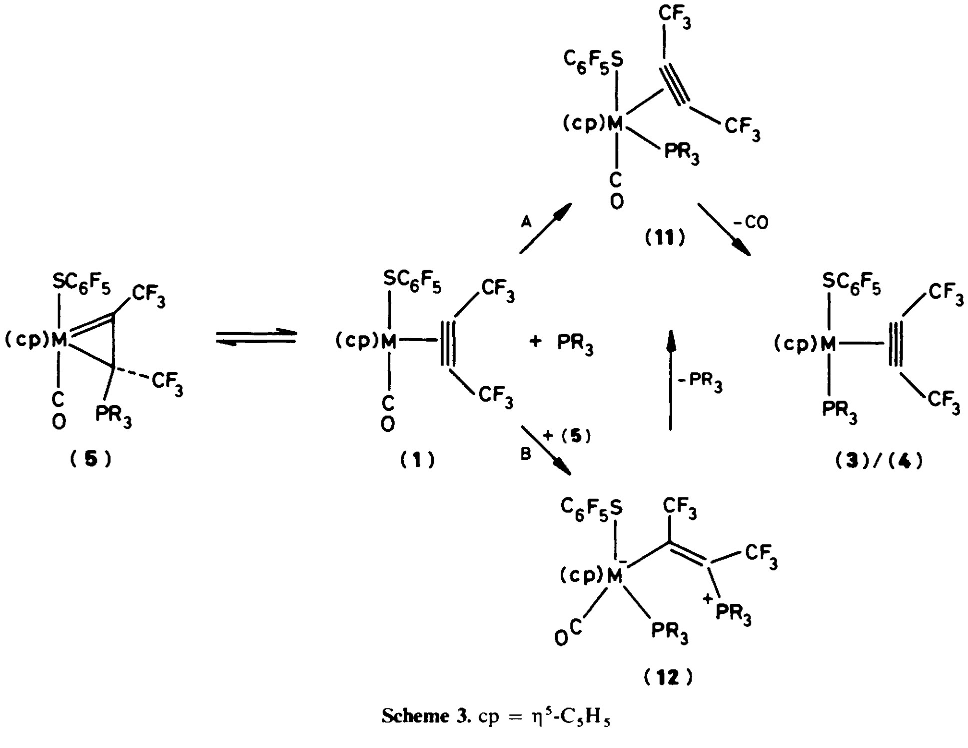
Two points of interest emerge from the substitution reactions (**1**) ⟶ (**3**) or (**4**) described herein, the first concerning the mechanism of carbonyl displacement. Such reactions usually involve dissociative mechanisms although associative and radical processes are also possible in appropriate circumstances.[31] In the present case initial attack of PEt_3, PMe_2Ph, and $PMePh_2$ at the alkyne is not entirely surprising in view of previous observations that nucleophilic attack by phosphines on co-ordinated hexafluorobut-2-yne occurs readily in bis(alkyne) complexes $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, X = Cl or SC_6F_5; M = W, X = Cl, SC_6F_5, or SC_6H_4Me-4), as described earlier.[16b,d] Preference for attack at the alkyne rather than the metal may result in part from the fact that in these complexes both sets of alkyne π electrons are apparently donated to the metal centre thus leading to electron-deficient alkyne carbons which presumably increases the π-acidity of the ligand. The latter effect is no doubt enhanced by the presence of CF_3 groups on the alkyne.



Scheme 2. cp = $\eta^5\text{-}C_5H_5$

The simplest process by which the conversion of (5) into (3c) can be accomplished involves intramolecular migration of PEt_3 from carbon to metal preceded or followed by carbonyl dissociation (Scheme 2). Such reactions could proceed *via* (9) or (10), containing a bridging phosphine, and it is pertinent to note that a related species $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ containing a bridging thiolate group has been characterised previously. Interestingly, analogous SPr^n, SEt, and SMe derivatives undergo reversible total migration of the SR′ group onto the metal as a result of carbon–sulphur bond fission, a reaction which parallels the transformation: (9) or (10) ⟶ (3). More recently it has been shown that addition of one molar equivalent of t-butyl isocyanide to the bis(alkyne) complex $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ gives the η^2-vinyl complex $[Mo(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)CNBu^t\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, which on addition of a second molar equivalent is transformed into a metallocyclic complex $[Mo\{C(CF_3){=}C(CF_3){-}C(CF_3){=}C(CF_3)\}(SC_6F_5)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ containing two isocyanides co-ordinated to the metal.[16f] This clearly involves an η^2-vinyl ⟶ alkyne transformation analogous to the reaction (5) ⟶ (3).

An alternative mechanism for the conversion of (5) into (3) which cannot be totally excluded involves phosphine dissociation followed by nucleophilic attack at the metal of either the resulting alkyne complex (1) (Scheme 3, path A) or of the η^2-vinyl complex (5) (Scheme 3, path B). The former produces the intermediate alkyne carbonyl complex (11) directly whereas the latter proceeds *via* a zwitterionic σ-vinyl derivative (12) similar to structurally characterised chromium, $[Cr\{\sigma\text{-}C(OSiMe)_3{=}C(PMe_3)H\}(CO)_5]$,[32] and manganese, $[Mn\{\sigma\text{-}C(CO_2Me){=}C(PPh_3)H\}(CO)_2(\eta^5\text{-}C_5H_5)]$,[33] complexes. Subsequent dissociation of CO will then be accompanied by the conversion of the alkyne from a two-electron donor ligand in (11) into a formal four-electron donor in (3). I note that in the reaction of diaryl-



Scheme 3. cp = $\eta^5\text{-}C_5H_5$

or dimethyl-cuprates with cationic molybdenum alkyne complexes, such as $[Mo\{P(OMe)_3\}_2(PhC\equiv CPh)(\eta^5\text{-}C_5H_5)]^+$ attack at metal or an alkyne carbon can occur to give alkyne complexes, *e.g.* $[MoMe(PhC\equiv CPh)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]$, or η^2-vinyl products, *e.g.* $[Mo\{\eta^2\text{-}C(Ph)CPh_2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$.[19] Moreover, nucleophilic attack by substituted pyridines (L) on platinum ethylene complexes $[PtCl_2(H_2C{=}CH_2)L]$ has been observed to occur, either at the metal, leading to pyridine exchange, or at the alkene, giving zwitterionic complexes $[PtCl_2(\sigma\text{-}CH_2CH_2L)L]$.[34] Interestingly the latter reaction is only observed with more basic ligands such as 4-methylpyridine and 3,5-dimethylpyridine. Since intermediates were not detected in the reactions of PPh_3 and $P(OMe)_3$ with (**1a**) or (**1b**) a similar situation may be operative here in which stronger nucleophiles, *e.g.* PEt_3, undergo kinetically controlled attack on the alkyne, whereas the thermodynamically favoured reaction is attack on the metal leading to carbonyl substitution. The absence of full kinetic data does not allow firm conclusions to be reached concerning the thermal rearrangement (**5**) $\longrightarrow$ (**3c**) but some information was obtained from n.m.r. studies carried out at ambient temperature. No intermediates were detected during the course of the reaction while addition of triethylphosphine produced no significant affect on the rate. Consequently it appears that the phosphine plays no part in the rate-determining step.

The second point of interest emerging from this work concerns the ease with which carbonyl substitution occurs in the complexes $[M(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$. This contrasts with most situations where successive substitution of carbonyls by other ligands leads to increased difficulties in subsequent substitutions due to increased $M \longleftarrow CO$ π back-donation and hence stronger M–CO bonding. Substitution of the final CO in metal carbonyls is usually only possible when stronger π acceptors than CO are present in the molecule, *i.e.* PF_3. Previously we have isolated the bis(hexafluorobut-2-yne) complex $[WBr_2(CO)(CF_3C\equiv CCF_3)_2]$ from the reaction of $[\{WBr_2(CO)_4\}_2]$ with $CF_3C\equiv CCF_3$ and noted that the remaining CO exhibits a ν(CO) mode in the i.r. spectrum at 2 172 cm^{-1}, 30 cm^{-1} to high frequency of that for free carbon monoxide.[16b] This implies that the CO ligand is functioning almost exclusively as a σ-bonding ligand and hence that the η^2-bonded $CF_3C\equiv CCF_3$ ligands are the dominant π-acceptor ligands in the molecule. If indeed $CF_3C\equiv CCF_3$ can function as a superior π-acceptor ligand to CO it is perhaps not surprising that the remaining CO ligand in $[M(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ is so readily substituted. This explanation applies both to the intra- and inter-molecular mechanisms in Schemes 2 and 3 since in each case an intermediate alkyne carbonyl complex (**11**) is involved.

Experimental

Hydrogen-1, ^{19}F, and ^{31}P n.m.r. spectra were recorded on a Bruker WP-200 SY instrument operating at 200.13, 188.31, and 81.02 MHz respectively; some variable-temperature ^{19}F n.m.r. spectra were recorded on a Varian XL 100 instrument at 94.1 MHz (Table). I.r. spectra were recorded as solutions in $CHCl_3$ (unless stated otherwise) on a Perkin-Elmer 580 spectrophotometer. Reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents (diethyl ether and hexane) were dried by refluxing over powdered calcium hydride and distilled under nitrogen prior to use. Hexafluorobut-2-yne complexes $[M(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) were prepared as described previously.[2,20] Phosphines and phosphites were obtained commercially (Strem) and used as supplied.

Oxidation of $[W(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1b**).—The complex (20 mg) was dissolved in diethyl ether (5 cm^3) in air and sealed in a tube until the red-purple solution became almost colourless. The solution was filtered, concentrated, hexane (1 cm^3) added, and on cooling to -15 °C off-white crystals (9 mg, 46%) of $[W(SC_6F_5)(O)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2b**) were obtained (Found: C, 28.5; H, 0.7. Calc. for $C_{15}H_5F_{11}OSW$: C, 28.75; H, 0.80%). I.r.: $\nu(C\equiv C)$ 1 798wm cm^{-1}.

Reaction of $[W(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* PEt_3.—Complex (**1b**) (30 mg) was dissolved in diethyl ether (10 cm^3) at 0 °C and triethylphosphine added slowly with stirring until no further colour change occurred. The resulting orange-brown solution was kept at 0 °C and reduced in volume (*in vacuo*) to *ca.* 3 cm^3 when ice-cold hexane (*ca.* 5 cm^3) was added slowly. The solution was then cooled to -15 °C when orange-brown crystals were obtained. These were collected and washed with cold hexane to give 25 mg (70%) of $[W(SC_6F_5)(CO)\{\eta^2\text{-}C(CF_3)C(CF_3)PEt_3\}(\eta^5\text{-}C_5H_5)]$ (**5**) (Found: C, 34.6; H, 2.4; P, 3.7; S, 4.0. Calc. for $C_{22}H_{20}F_{11}OPSW$: C, 34.9; H, 2.65; P, 4.10; S, 4.25%). I.r.: ν(CO) 1 915s cm^{-1}.

Reaction of $[Mo(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1a**) *with* PEt_3.—The complex (30 mg) was treated as above with PEt_3 at ambient temperature giving a red-brown solution which was refluxed gently until a green solution was obtained, which was filtered and the ether removed *in vacuo* to give a green oil. This was extracted with *ca.* 2—3 cm^3 of warm hexane and after filtration cooled to -15 °C to give green crystals which were crystallised a second time from diethyl ether–hexane to give $[Mo(SC_6F_5)(PEt_3)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3e**). Yield 14 mg, (40%) (Found: C, 39.0; H, 3.0. Calc. for $C_{21}H_{20}F_{11}MoPS$: C, 39.4; H, 3.15%). I.r.: $\nu(C\equiv C)$ 1 675wm cm^{-1}.

Reaction of $[W(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* PEt_3.—Complex (**1b**) (30 mg) was treated with triethylphosphine as above to give $[W(SC_6F_5)(PEt_3)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**4c**) as green crystals in 35% yield (Found: C, 34.3; H, 2.5; P, 3.9; S, 4.5. Calc. for $C_{21}H_{20}F_{11}PSW$: C, 34.6; H, 2.75; P, 4.25; S, 4.40%). I.r.: $\nu(C\equiv C)$ 1 650wm cm^{-1}.

Reaction of $[Mo(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* $P(OMe)_3$.—Trimethyl phosphite was added slowly to a stirred solution of (**1a**) (70 mg) in diethyl ether (15 cm^3) until the solution just turned green. The mixture was stirred for 25 min and volatiles removed to give a green oil. This was extracted with warm hexane (15 cm^3) and the resulting solution filtered, reduced in volume, and cooled to -15 °C to give green crystals. A second recrystallisation from diethyl ether–hexane gave 50 mg (61%) of $[Mo(SC_6F_5)\{P(OMe)_3\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3a**) (Found: C, 33.7; H, 2.3; F, 31.9; P, 4.4. Calc. for $C_{18}H_{14}F_{11}MoO_3PS$: C, 33.45; H, 2.15; F, 32.35; P, 4.80%). I.r.: $\nu(C\equiv C)$ 1 690wm cm^{-1}.

Reaction of $[W(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* $P(OMe)_3$.—Complex (**1b**) (50 mg) was similarly reacted with trimethyl phosphite to give green crystals of $[W(SC_6F_5)\{P(OMe)_3\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**4a**) in 57% yield (Found: C, 29.5; H, 4.4. Calc. for $C_{18}H_{14}F_{11}O_3PSW$: C, 29.45, H, 4.35%). I.r.: $\nu(C\equiv C)$ 1 665wm cm^{-1}.

Reaction of $[Mo(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* PMe_2Ph.—The complex (70 mg) in diethyl ether (15 cm^3) was reacted with dimethylphenylphosphine to give a red-brown solution at room temperature. On standing the reaction mixture slowly turned green and after 2 h the solution was filtered, reduced in volume, hexane (5 cm^3) added, and cooled to -15 °C to give green crystals. A second crystallisation from diethyl ether–hexane gave 45 mg (54%) of $[Mo(SC_6F_5)$-

$(PMe_2Ph)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3d**) (Found: C. 41.6; H, 2.6. Calc. for $C_{23}H_{16}F_{11}MoPS$: C, 41.8, H, 2.40%). I.r.: $\nu(C{\equiv}C)$ 1 675wm cm^{-1}.

Reaction of $[W(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* PMe_2Ph.—The complex (30 mg) was treated with PMe_2Ph as above to give dark green crystals of $[W(SC_6F_5)(PMe_2Ph)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**4b**) (18 mg, 51%) (Found: C, 36.7; H, 2.1. Calc. for $C_{23}H_{16}F_{11}PSW$: C, 36.90; H, 2.15%). I.r.: $\nu(C{\equiv}C)$ 1 640wm cm^{-1}.

Reaction of $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* $PMePh_2$.—The complex (100 mg) in diethyl ether (15 cm^3) was treated with methyldiphenylphosphine at room temperature, when a brown solution formed but rapidly turned green. Hexane (5 cm^3) was added and, following filtration, partial removal of solvent, and cooling to -15 °C, green crystals were obtained. A second crystallisation from diethyl ether–hexane gave 115 mg (88%) of $[Mo(SC_6F_5)(PMePh_2)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3c**) (Found: C, 46.8; H, 2.6. Calc. for $C_{28}H_{18}F_{11}MoPS$: C, 46.5; H, 2.50%). I.r.: $\nu(C{\equiv}C)$ 1 678wm cm^{-1}.

Reaction of $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *with* PPh_3.—The complex (60 mg) in diethyl ether (30 cm^3) was treated with PPh_3 (65 mg) for 1 h at 20 °C; no reaction occurred. The reaction solution was transferred to a thick glass tube fitted with a Rotaflo Teflon stopcock and heated at 60 °C for 4 h; a pale green solution was obtained. Hexane (*ca.* 10 cm^3) was added and the solution reduced in volume, with formation of green crystals. These were collected and recrystallised from diethyl ether–hexane to give 60 mg (70%) of $[Mo(SC_6F_5)(PPh_3)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3b**) (Found: C, 50.8; H, 3.7. Calc. for $C_{33}H_{20}F_{11}MoPS$: C, 50.5; H, 3.95%). I.r.: $\nu(C{\equiv}C)$ 1 678wm cm^{-1}.

Acknowledgements

I thank the S.E.R.C. for generous support.

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Received 9th *December* 1985; *Paper* 5/2147