Synthesis, Reactions, and Dynamic Nuclear Magnetic Resonance Studies of η^2-Vinyl Complexes of Tungsten, $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SR)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (R = Me, Et, Pr^n, Pr^i, or Bu^t)

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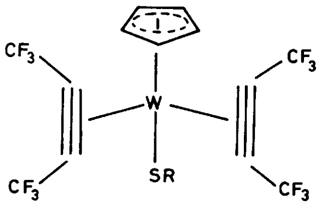
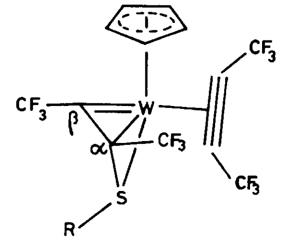
Reactions of the hexafluorobut-2-yne complex $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with thallium(I) thiolates Tl(SR) give the bis-alkyne derivative $[W(SR)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ when R = C_6H_4Me-4 whereas an isomeric η^2-vinyl form $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SR)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, resulting from migration of the SR ligand to a bridging mode between the metal and a fluorocarbon ligand, is obtained when R = Me, Et, Pr^n, Pr^i, or Bu^t. When R = Pr^i or Bu^t one isomeric form is observed which undergoes fluxional behaviour involving total CF_3 group scrambling, indicating reversible fission of the C–S bond of the η^2-vinyl ligand. With R = Me, Et, or Pr^n two isomeric η^2-vinyl forms are observed, both of which undergo CF_3 group exchange in addition to isomer exchange, according to ^{19}F n.m.r. studies. Reactions of both bis-alkyne (R = C_6H_4Me-4) and η^2-vinyl complexes (R = Pr^i or Bu^t) with tertiary phosphines and phosphites (L) give η^2-vinyl complexes $[W(SR)\{\eta^2\text{-}C(CF_3)C(CF_3)(L)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ the stability of which increases with the nucleophilic character of the phosphorus ligand. ^{19}F N.m.r. studies have established that in some cases the reactions proceed *via* two unstable kinetic isomers which undergo thermal rearrangement to a thermodynamically more stable form.

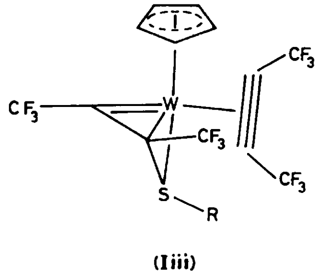
The insertion of alkenes and alkynes into metal–hydrogen and metal–carbon bonds has been widely studied in recent years in view of the probable role of such reactions in homogeneous catalysis.[1] In many insertion reactions metal–alkene or metal–alkyne π complexes are postulated as intermediates but in relatively few cases has this been demonstrated unequivocally. Previously we have reported the isolation of mono-and bis-alkyne complexes $[MX(CO)(RC{\equiv}CR')(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, Br, or I; R = R′ = Ph; R = Me, R′ = Ph) and $[MX(RC{\equiv}CR')_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, Br, or I; R = R′ = Me, CF_3, or Ph; R = Me, R′ = Ph)[2,3] which could function as suitable species for studies into the mechanisms of alkyne insertion reactions. The starting point for our investigation was the observation that the electrophilic alkyne $CF_3C{\equiv}CCF_3$ forms simple mono- and bis-alkyne perfluorobenzenethiolate complexes, $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[4] and $[M(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$[5] (M = Mo or W), but undergoes insertion reactions with hydrocarbon thiolate complexes such as $[W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$.[6,7] This suggested a potentially fruitful area of study involving synthesis of complexes containing both co-ordinated $CF_3C{\equiv}CCF_3$ and hydrocarbon thiolate ligands where the possibility existed of alkyne insertion into the M–SR bond. We now report the results of these studies, some of which have been communicated previously.[8,9]



(Ii)



(Iii)



(Iiii)

Results and Discussion

Reactions of the bis-alkyne complex $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with thallium(I) thiolates Tl(SR) (R = C_6H_4Me-4, Me, Et, Pr^n, Pr^i, or Bu^t), in diethyl ether at room temperature, gives crystalline complexes (**1a**)—(**1f**) of stoicheiometry '$[W(SR)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$' according to mass spectral and analytical data in yields ranging from 38 (**1c**; R = Et) to 79% (**1a**; R = C_6H_4Me-4). Perfluorobenzenethiolate complexes $[M(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W), previously synthesised by similar methods,[5] have been shown by spectroscopic methods to be structurally analogous to $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ the structure of which has been confirmed by *X*-ray diffraction studies.[3] This exhibits an approximately octahedral co-ordination geometry for the metal with the $\eta^5\text{-}C_5H_5$ group occupying a face and the other three ligands corners of the octahedron. The alkyne C≡C axes lie approximately parallel to each other and to the M–Cl bond.

The spectroscopic features of compound (**1a**) (R = C_6H_4Me-4) are similar to those of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ and a similar bis-alkyne structure (**Ii**) is therefore proposed. Thus, two ν(C≡C) modes are observed in the i.r. spectrum at 1 779 and 1 743 cm^{-1} while a single CF_3 resonance is observed in the ^{19}F n.m.r. spectrum at δ −56.4 down to −90 °C in CD_2Cl_2 and $CDCl_3$. Two CF_3 peaks would be expected for the proposed structure but variable-temperature ^{19}F n.m.r. studies of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ and related complexes[2,4] indicate fluxional behaviour involving alkyne propeller rotation and the single peak observed at 20 °C splits into two resonances at lower temperature. The absence of such

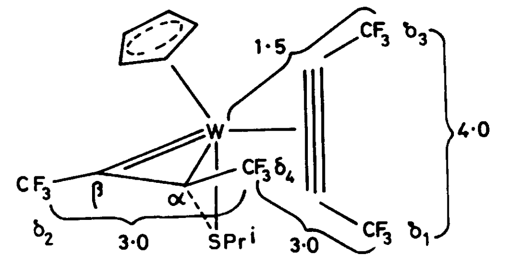


Figure 1. ^{19}F N.m.r. spectral assignments for $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SPr^i)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1e**); couplings in Hz

splitting in the case of (**1a**) we assume to be due to a lower rotational barrier resulting from the replacement of Cl by SC_6H_4Me-4. Significantly the perfluorobenzenethiolate derivatives $[M(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) exhibit similar features in the ^{19}F n.m.r. spectra.[5]

Quite different spectroscopic properties are found with Pr^i and Bu^t derivatives (**1e**) and (**1f**) respectively, suggesting a different structural form. Thus, only one ν(C≡C) mode is observed in the i.r. spectrum near 1 760 cm^{-1} while four CF_3 resonances are observed in the ^{19}F n.m.r. spectrum. This, in conjunction with the presence of diastereotopic isopropyl methyl groups in (**1e**), which give rise to two doublets in the ^1H n.m.r. spectrum, originally suggested a dimeric structure with bridging thiolate groups.[10] However, our subsequent isolation of η^2-vinyl complexes (**2**), resulting from nucleophilic attack of a phosphine at an alkyne carbon in $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$[8] (see later), which exhibited similar ^{19}F n.m.r. spectra, suggested an alternative η^2-vinyl structure for (**1e**) and (**1f**). This was confirmed by a single-crystal *X*-ray diffraction study of (**1e**) which revealed structure (**Iii**), in which the sulphur ligand has apparently undergone intramolecular nucleophilic attack on an alkyne carbon.[9] The result is a novel five-electron donor η^3 ligand bound to the metal *via* sulphur and an adjacent η^2-vinyl moiety of a type now well established.[6,8,11–14] The structure is closely related to that of the pyridine-2-thiolate complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)NC_5H_4S\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[15] but the replacement of the three-atom bridge of the SC_5H_4N moiety by a SPr^i group results in detailed changes such as the orientations of both the η^2-bonded alkyne and the η^2-vinyl function with respect to each other and to the M–S bond. This probably reflects the constraints imposed by replacing a three-atom chain by a single atom.

The ^{19}F n.m.r. spectrum of (**1e**) can be interpreted in terms of the solid-state structure as follows. A two-dimensional ^{19}F COSY spectrum in conjunction with homodecoupling experiments established the following connectivities: δ_1 (qq, J_{13} 4.0, J_{14} 3.0), δ_2 (q, J_{24} 3.0), δ_3 (qq, J_{31} 4.0, J_{34} 1.5), and δ_4 (qqq, J_{41} 3.0, J_{42} 3.0, J_{43} 1.5 Hz) (Figure 1). Thus three CF_3 groups couple to δ_4, two of which couple to one other CF_3 group. Since a through-bond mechanism involves coupling over six bonds it seems probable that coupling between CF_3 groups on different ligands involves a through-space mechanism.[16] Moreover the CF_3 on the sp^2 β carbon of the η^2-vinyl is remote from both alkyne CF_3 groups and consequently this can be assigned to the quartet δ_2 which couples only with δ_4, the other η^2-vinyl CF_3. On the basis that δ_4 CF_3 is 4.44 Å from one alkyne CF_3 but only 4.14 Å from the other, measured in terms of the C–C distance, we associate the larger of the two remaining couplings (3.0 Hz) with the latter and hence the other assignments follow. Variable-temperature ^{19}F n.m.r. studies were also carried out on (**1e**) in $[^2H_8]$toluene between 20 and 100 °C. The spectrum at 20 °C contains four CF_3 peaks as with the $CDCl_3$ spectrum but less well resolved, Figure 2. At higher temperatures all four peaks broaden and collapse to a single peak at 80 °C. This indicates that complete exchange of all four CF_3 environments is occurring as observed for the bis-alkyne complex (**1a**). This suggests that C–S bond fission occurs in (**1e**) at higher temperatures to generate a bis-alkyne intermediate or transition state in which alkyne rotation can occur thus leading to total CF_3 exchange.

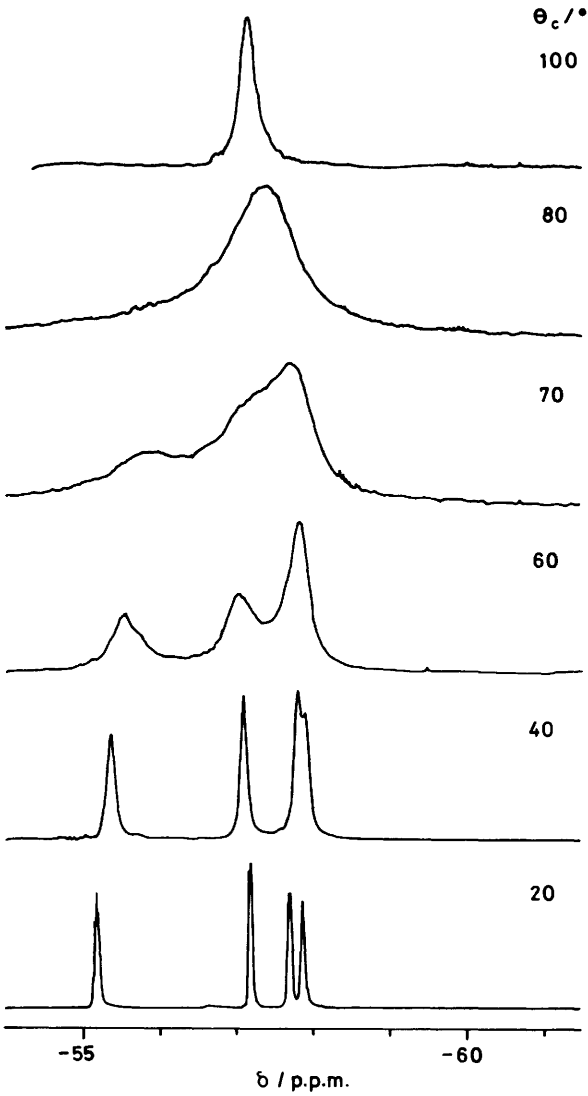


Figure 2. Variable-temperature ^{19}F n.m.r. spectra for $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SPr^i)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1e**)

It is therefore apparent that with electron-donating groups R = Pr^i or Bu^t the most stable isomeric form for complexes (**1e**) and (**1f**) is (**Iii**), containing an η^2-vinyl ligand formed by intramolecular attack of the SR ligand on a co-ordinated alkyne. At higher temperatures the migration process is reversed and C–S bond fission occurs to give the bis-alkyne structure (**Ii**). The latter structure is thermodynamically more favourable at lower temperatures when the thiolate substituent R is sufficiently electron withdrawing, *e.g.* R = C_6F_5 or C_6H_4Me-4. However, more complex behaviour is observed with the Me, Et, and Pr^n derivatives (**1b**)—(**1d**) respectively, where the organic group lies between these extremes in electron-donor ability. This is most readily demonstrated by discussion of the spectroscopic properties of (**1c**) although (**1b**) and (**1d**) exhibit qualitatively similar features. The i.r. spectrum in Nujol mull is similar to that of (**1e**) and (**1f**) giving a single $\nu(C{\equiv}C)$ mode at 1 759 cm^{-1} indicative of the η^2-vinyl structure. However, a second band at 1 782 cm^{-1} is observed in a hexane solution spectrum. The ^{19}F n.m.r. spectrum at 60 °C consists of a single resonance similar to that of (**1e**) suggesting structure (**Iii**) which is fluxional. However, at lower temperatures *e.g.* <0 °C (see Figure 3) this resonance broadens and separates out into two sets of peaks due to two isomeric forms (**A**) and (**B**). Isomer (**A**) exhibits three resonances (ratio 1:2:1) consistent with an η^2-vinyl structure (**Iii**) with two overlapping CF_3 resonances. This is substantiated by the appearance of the spectrum of isomer (**A**) for (**1d**) at -30 °C which is almost identical to that of (**1e**). The CF_3 groups of isomer (**B**) are equivalent at 0 °C giving rise to a singlet but at lower temperatures this collapses and eventually separates into four distinct peaks indicative of a second η^2-vinyl form. Thus two η^2-vinyl forms apparently exist at low temperatures, one of which [(**B**)] undergoes total CF_3 exchange at intermediate temperatures, while exchange between the two isomers which occurs at higher temperatures leads to total CF_3 group scrambling. This can be explained in terms of the mechanism shown in Scheme 1 in which, as with (**1e**), C–S bond fission in the η^2-vinyl ligand leads to an intermediate bis-alkyne complex (**Ii**) where alkyne rotation results in CF_3 exchange.

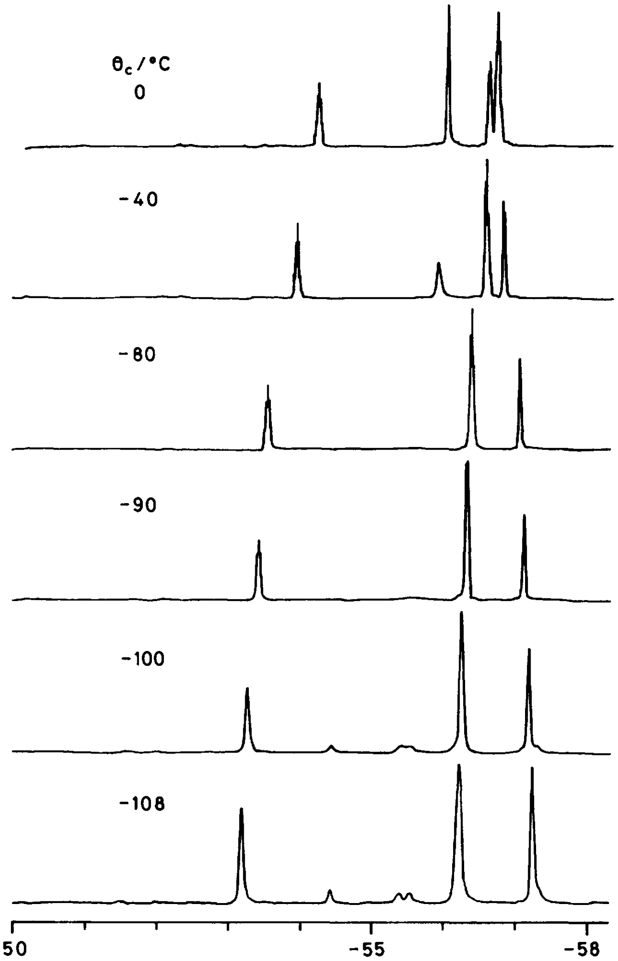
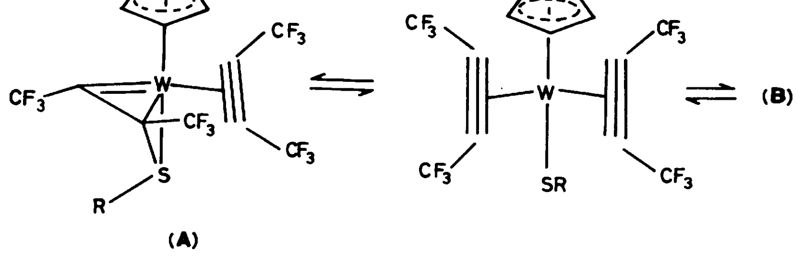


Figure 3. Variable-temperature ^{19}F n.m.r. spectra for $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SEt)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1c**)

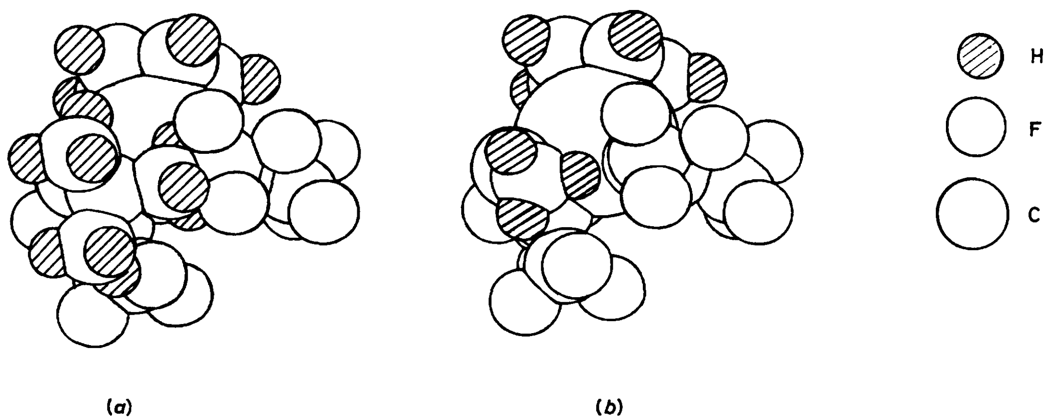
Since isomer (**A**), structure (**Iii**) does not become fluxional until substantially higher temperatures are reached it is evident that the C–S bond in this isomer is not cleaved as readily as that in (**B**). It is therefore of interest to compare the isomer ratio (**A**):(**B**) as the thiolate substituent and the temperature are varied. This changes from 1:3 at 20 °C to 1:1.6 at -100 °C (R = Me), from 3:1 at 20 °C to 9:1 at -110 °C (R = Et), and from 3.3:1 at 20 °C to 7:1 at -104 °C (R = Pr^n). These data reveal an increasing preference for (**A**) as the temperature decreases. Moreover the preference for isomer (**A**) also increases in the order R = Me < Et < Pr^n in line with the observation that with R = Pr^i and Bu^t only this isomer is observed.

A possible explanation for this derives from consideration of the source of isomerism. Isomerism in mercapto complexes containing a bridging sulphur is well established and results from the possibility of two orientations of the thiolate substituent. The solid-state structure of (**1e**) establishes that the Pr^i group is orientated towards the cyclopentadienyl ligand and away from the hexafluorobut-2-yne. Inversion at sulphur would result in a second isomer (**Iiii**), with the Pr^i group pointing towards the alkyne. Molecular graphics studies[17] established that with R = Pr^i or Bu^t this isomer would be unfavourable due to steric interaction between the thiolate R group and one of the CF_3 groups on the alkyne (see Figure 4). However with R = Me no severe steric interactions exist in line with the observation that two isomers of (**1b**) are found. Thus the increased preference for isomer (**A**) in the order Me < Et < Pr^n < Pr^i could reflect steric destabilisation of isomer (**B**) by bulkier substituents on sulphur.

Despite the attractive simplicity of this explanation we cannot rule out an alternative source of isomerism based on consideration of the origin of the η^2-vinyl ligand. Formally it is derived from the bis-alkyne structure by nucleophilic attack of sulphur on one of the alkyne C≡C carbons. Since the alkynes can undergo propeller rotation, attack at any of the four carbon atoms is possible. Focusing attention on one alkyne (since attack at the other merely leads to enantiomers) C–S bond formation can occur in four different ways as Scheme 2 shows. However, rotational equivalence means that only two distinct isomeric forms can be obtained. Thus attack at sites $C^{\ddagger}$ leads to structure (**Iii**) [isomer (**A**)] whereas attack at C^{*} gives isomer (**Iiv**). The two species therefore differ with respect to (*a*) the orientation of the CF_3C–CCF_3 bond of the η^2-vinyl ligand and

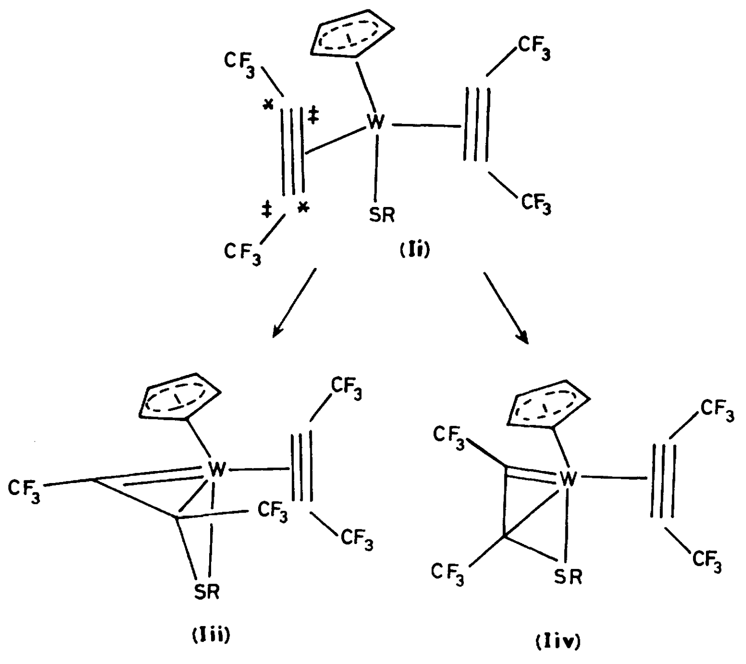


Scheme 1.



(a) (b)

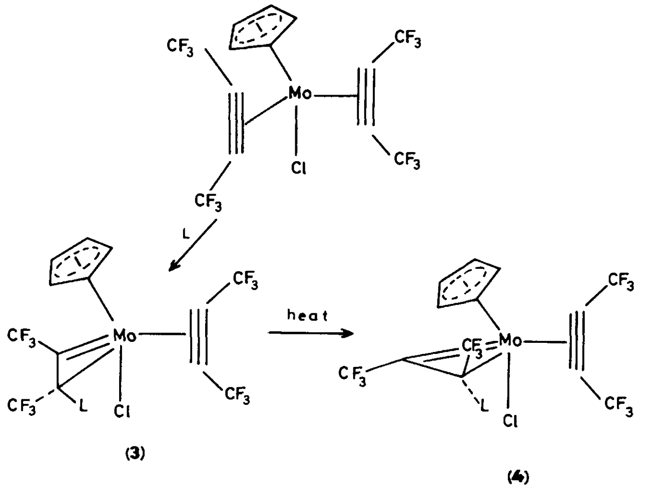
Figure 4. Space filling diagrams of (*a*) $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SBu^t)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1f**) and (*b*) $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SMe)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1b**) structure (**Iiii**)



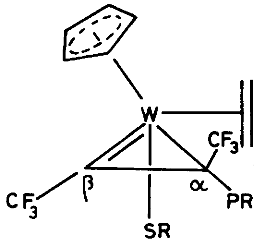
Scheme 2.

(*b*) the stereochemistry of the chiral carbon atom attached to sulphur. Interestingly we have previously reported that η^2-vinyl complexes $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)(L)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3**), formed by attack of L (PEt_3 or PMe_2Ph) on $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$, undergo thermal isomerisation in solution into a thermodynamically more stable form (**4**), Scheme 3.[12] Significantly these two isomers also differ with respect to both the orientation of the η^2-vinyl ligand and the stereochemistry of the chiral carbon. Moreover the thermodynamically more stable form is the structural analogue of (**Iii**) while steric factors appear to control the stability of (**3**) (see later). Thus steric factors may also control isomer equilibria in complexes (**1b**)—(**1d**) if the source of isomerism is the η^2-vinyl ligand, *i.e.* if isomer (**B**) has structure (**Iiv**).

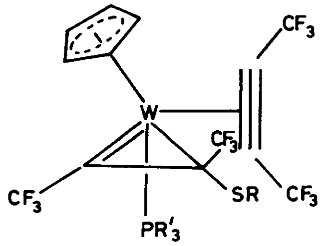
The existence of two structural isomers of complexes $[W(SR)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$, a bis-alkyne form and an η^2-vinyl form, has implications for other ligand migration reactions in organometallic chemistry involving for example hydrido or alkyl ligands. In the case of the mercapto complexes the presence of lone-pair electrons on sulphur enables structure (**5**)



Scheme 3. L = PEt_3 or PMe_2Ph



(IIi)



(IIii)

to exist as a stable isolable entity whereas with one-electron donors equivalent structures (**6**) and (**7**) are more likely to function as transition states in migration reactions. However, the existence of bridging hydrogen[18] and alkyl[19] groups in transition-metal complexes raises the interesting possibility that in favourable circumstances such species may be isolable. Interestingly the recent report that the β-hydrogen of the dimetallated η^2-vinyl ligand in $[(\eta^5\text{-}C_5H_4Me)_2ZrCl(CH{=}CMe)ZrCl(\eta^5\text{-}C_5H_5)_2]$ interacts with the adjacent metal in an agostic manner provides evidence that this is possible with hydrogen.[20]

A second point of interest concerns the effect of the thiolato substituent on the stability of the η^2-vinyl product. The observation that migration of the SR ligand onto the co-ordinated alkyne is promoted by electron-donating substituents may have more general significance. For example migration of hydrogen or alkyl groups onto co-ordinated alkenes and alkynes may be controlled to some extent by the degree of polarisation of the M–H or M–C bond. Moreover this may also affect the reversibility of the migration reaction as illustrated in Scheme 1. Reactions of σ-vinyl $[Ru\{C(CO_2Me){=}C(H)(CO_2Me)\}(PPh_3)_2(\eta^5\text{-}C_5H_5)]$[21] and η^2-vinyl, (**1e**),[22] complexes with $CF_3C{\equiv}CCF_3$ give insertion products $[Ru\{C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)H\}(PPh_3)(\eta^5\text{-}C_5H_5)]$ and $[W\{{=}C(CF_3)C(CF_3){=}C(Me)C(Me)(SPr^i)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ respectively which can only reasonably be explained in terms of hydrogen or thiolate transfer back to the metal at some stage in the reaction.

The observation that $CF_3C{\equiv}CCF_3$ undergoes insertion into the metal–sulphur bond of a wide range of organothiolate complexes[6,7,23,24] also prompted us to carry out reactions of $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1a**) with phosphines in an attempt to promote co-ordination induced migration of the thiolate ligand onto one of the alkynes. Addition of PEt_3, PMe_2Ph, $P(OMe)_3$, or $P(OEt)_3$ to a stirred solution of complex (**1a**) in diethyl ether at 20 °C resulted in an immediate colour change from purple to yellow and crystalline adducts (**2**) [PR'_3 = PEt_3 (**2a**), PMe_2Ph (**2b**), $P(OMe)_3$ (**2d**), $P(OEt)_3$ (**2e**)] were obtained in good yield on addition of hexane. No reaction was observed with PPh_3 whereas with $PMePh_2$ only a slight colour change was observed. On cooling the 1:1 mixture to −15 °C the solution turned yellow (reversibly) and on adding hexane at this temperature yellow-orange crystals of a 1:1 adduct (**2c**) were obtained. On redissolving the crystals in polar organic solvents red-purple solutions were again obtained indicating dissociation of the complex. This was readily confirmed by n.m.r. spectroscopy where peaks due to both (**2c**) and (**1a**) are observed at 20 °C indicating an equilibrium between the two species.

The i.r. spectra of the phosphine adducts are somewhat similar to those of the η^2-vinyl complexes (**1e**) and (**1f**) while the ^{19}F n.m.r. spectrum similarly in each case exhibits four distinct CF_3 resonances. Originally we interpreted this in terms of a bis-alkyne structure with the phosphine co-ordinated to the metal[10] but the subsequent isolation of the pyridine-2-thiolate complex $[W\{\eta^3\text{-}C(CF_3)C(CF_3)NC_5H_4S\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, containing an η^2-vinyl ligand resulting from attack of the pyridine nitrogen at a co-ordinated alkyne,[11,15] suggested an alternative η^2-vinyl formulation. This was subsequently confirmed by *X*-ray diffraction studies of (**2a**)[8] which revealed structure (**IIi**) (R' = Et, R = C_6H_4Me-4) containing an η^2-$C(CF_3)C(CF_3)(PEt_3)$ ligand derived from nucleophilic attack of the phosphine on one of the alkyne carbon atoms. The structure is somewhat similar to that of (**1e**) (Figure 1) except that the independence of the η^2-vinyl and thiolate ligands produces a co-ordination geometry in some respects more akin to that of the bis-alkyne complex $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$. For example the alkyne lies virtually parallel to the W–S bond whereas in (**1e**) a torsion angle of −35.4° is found. The $SWC_\alpha C_\beta$ torsion angles of 105 [(**2a**)] and 130° [(**1e**)] are also quite different illustrating that when free from constraint the C–C axis of the η^2-vinyl can be rotated to a position almost normal to the alkyne. This constitutes a rotation of almost 90° from that adopted by the two alkynes in $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$.

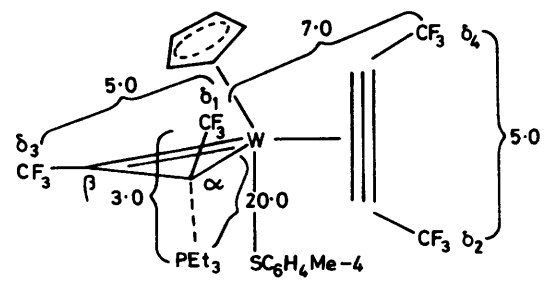


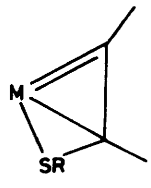
Figure 5. ^{19}F N.m.r. spectral assignments for $[W(SC_6H_4Me\text{-}4)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2a**); couplings in Hz

The n.m.r. spectra of (**2a**) are readily interpreted in terms of the solid-state structure. For example the phosphorus atom on attachment to the alkyne carbon probably has some phosphonium ion character as in canonical form (**8**) and this is reflected in the ^{31}P-{^1H} n.m.r. chemical shift at δ 37.85 which compares with δ 19.7 in $PEt_3H^+Br^-$ and δ −20.4 for the free ligand.[25] A similar but less dramatic shift is observed on co-ordination to a metal as in $[W(SC_6F_5)(PEt_3)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, δ = 0.1.[26] The ^{19}F n.m.r. spectrum of (**2a**)—(**2e**) in each case consists of a broad almost featureless resonance at *ca.* δ −46 to −48 separated by *ca.* 5 p.p.m. from a cluster of three other peaks at δ −52 to −54, comprising two quartets and a well resolved multiplet. Extensive decoupling experiments were carried out on (**2a**) with the following results (Figure 5). A two-dimensional ^{19}F COSY experiment established that the broad peak at δ_1 −46.93 was coupled to the quartet at δ_3 −53.31 and multiplet at δ_4 −54.34 while the quartet at δ_2 −52.81 was coupled to δ_4. ^{19}F Homodecoupling experiments confirmed the above conclusions and provided the coupling constants J_{13} 5.0, J_{14} 7.0, and J_{24} 5.0 Hz. Interestingly irradiation of δ_3 or δ_4 produced a slightly better resolved multiplet rather than a quartet thus indicating coupling between δ_1 and phosphorus. The ^{31}P-{^1H} signal consists of a broad quartet (J_{PF} 3.0 Hz) with tungsten satellites (J_{WP} 20.0 Hz) consistent with this conclusion. This was confirmed by decoupling phosphorus while observing fluorine where the only change occurred in δ_1 which showed increased fine structure relative to the undecoupled ^{19}F spectrum, suggesting that δ_1CF_3 is attached to the same carbon as the phosphine ligand. Since δ_1 is coupled to two other CF_3 groups, as with (**1e**), coupling between fluorines on different ligands is likely to occur *via* a through-space rather than a through-bond mechanism since a separation of six bonds is again involved. On the basis that δ_1CF_3 is significantly closer to one alkyne CF_3 than the other, the C–C distances being 3.82 and 4.83 Å, we assign the CF_3 resonances as shown in Figure 5. Molecular graphics studies[17] reveal a minimum F–F distance of 1.69 Å between δ_1CF_3 and δ_4CF_3 as the CF_3 groups rotate, thus accounting for the substantial J_{FF} value of 7 Hz.

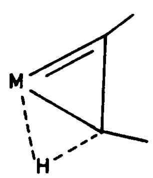
As mentioned earlier we have previously isolated two isomeric forms of similar η^2-vinyl complexes from reactions of phosphines and phosphites with $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$. *X*-Ray diffraction studies reveal that the thermodynamically more stable form of $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$, (**4**),[12] is structurally comparable to (**2a**). Since the ^{19}F n.m.r. spectra of (**2a**) and (**4**) are similar to those of (**2b**)—(**2e**) we assign similar structures. However, this raised the possibility that unstable kinetic isomers equivalent to (**3**) may also exist which were not observed in the original synthesis of (**2a**)—(**2e**) carried out at room temperature. Consequently the reactions of (**1a**) with PEt_3 and $P(OMe)_3$ were repeated at −20 °C in diethyl ether and crystallisation carried out by addition of cold hexane at this temperature. The ^{19}F n.m.r. spectra of the crystalline products obtained were taken at −20 °C to minimise thermal isomerisation. In both cases the spectra exhibited three sets of CF_3 peaks, due to the thermodynamic isomer (**2**) (**A**) and two additional kinetic forms (**2**) (**B**) and (**2**) (**C**), isomer ratios being (**A**):(**B**):(**C**) = 16:13:1 for (**2a**) and 10:18:1 for (**2d**). On warming to room temperature a clean and rapid isomerisation occurred in both cases giving the thermodynamic form (**2**) (**A**) only.

The isomerisation process was also observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum where initially (**2d**) exhibited a well resolved quartet at δ 47.87 (J_{PF} 1.5) with tungsten satellites (J_{WP} 21.5 Hz) due to (**2d**) (**A**) and a substantially broader quartet at δ 43.94 (J_{PF} 7.5 Hz) due to (**2d**) (**B**). In the case of (**2a**) a single broad peak was observed suggesting coincidence of the ^{31}P resonances. A peak due to isomer (**2**) (**C**) was not observed in either case due to the small quantity of this species present in solution. Subsequent isomerisation resulted in the formation of one quartet signal in each case due to isomer (**2**) (**A**).

Previously we have observed that the ^{19}F n.m.r. resonances of the kinetic and thermodynamic isomers of η^2-vinyls such as (**3**) and (**4**) exhibit distinctive chemical shift patterns.[27] Thus the kinetic isomers have four symmetrically distributed peaks whereas the thermodynamic isomers have one peak near δ −47 separated by *ca.* 5 p.p.m. from a cluster of three higher field peaks. As already described the latter distribution is found with complexes (**2a**)—(**2e**) when isolated at room temperature, whereas isomers (**2a**) (**C**) and (**2d**) (**C**) exhibited patterns similar to the kinetic isomers as did isomer (**2a**) (**B**). In contrast the major kinetic isomer (**B**) of (**2d**) shows peaks at δ −46.71, −53.70, −54.14, and −55.15, a pattern more characteristic of the thermodynamic form (**A**). This may indicate that chemical shift differences are not always a reliable criterion for distinguishing between isomers, particularly when different phosphorus ligands are involved, or alternatively that structures (**2a**) (**B**) and (**2d**) (**B**) are different. However, we are unable to resolve this question at the present time.



(**5**)



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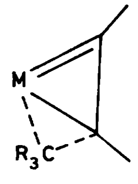
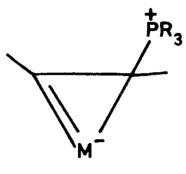


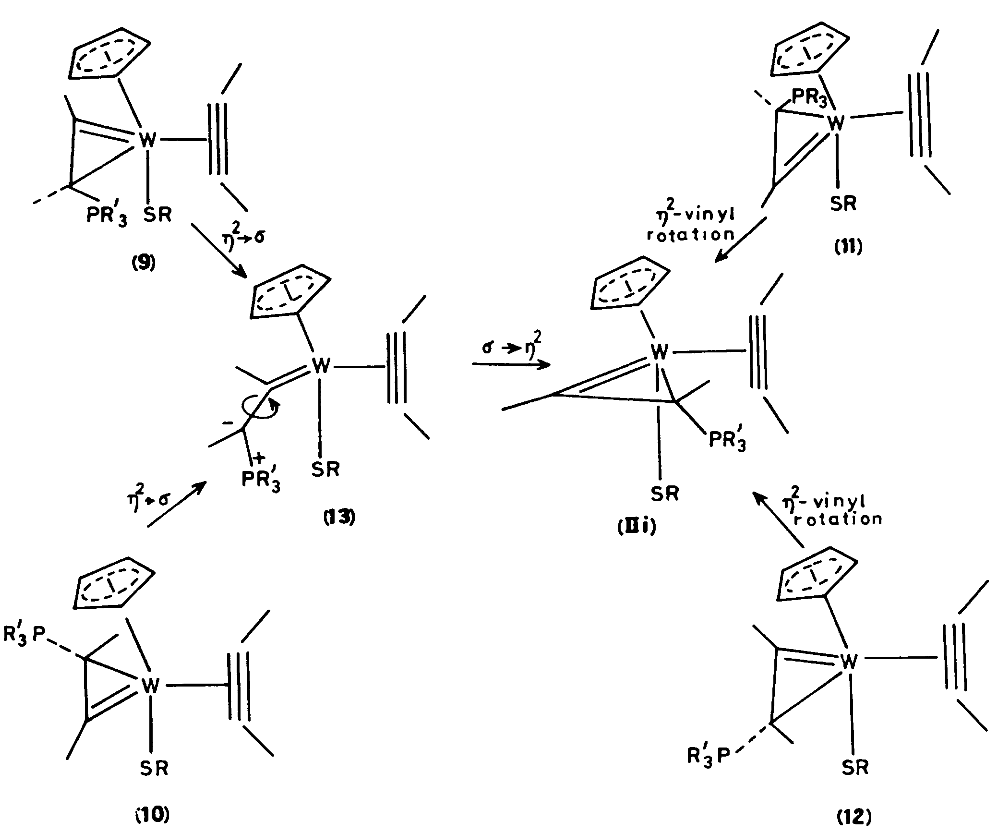
(**7**)



(**8**)

Three potential sources of isomerism exist in η^2-vinyl complexes of this type, the first involving the alkyne orientation which in (**2a**) lies approximately parallel to the W–S bond. This orientation is also found in four other η^2-vinyl complexes derived from $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ [8,12,15] and in the parent complex $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ [3] where both alkynes are approximately parallel to the M–Cl bond. Only in (**1e**) has a different orientation been found (rotated by *ca.* 35°), possibly because co-ordination of the sulphur atom to an alkyne carbon results in reorientation of the M–S bond. Consequently we rule out the alkyne orientation as a source of isomerism. The two remaining sources of isomerism are clearly the stereochemistry of the chiral carbon atom and the orientation of the η^2-vinyl ligand as previously discussed with (**Iii**) and (**Iiv**). As with internal nucleophilic attack four sites are accessible leading to four kinetic isomers (**9**), (**10**), (**11**), and (**12**) (neglecting enantiomeric pairs) based upon the direction of attack by the phosphorus ligand (Scheme 4). This assumes that the η^2-vinyl ligand adopts an orientation similar to that of the alkyne from which it is derived, *i.e.* parallel to the M–SR bond. In this case the attacking nucleophile is not constrained by simultaneous co-ordination to the metal and although the four isomers initially can be considered distinct, (**9**) and (**10**) are related by rotation of the vinyl by 180° as are (**11**) and (**12**). However, molecular graphics studies of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ suggest that sterically the most favourable route for attack is from a direction distal to the cyclopentadienyl ligand, leading preferentially to isomers (**9**) and (**11**). This would appear to be substantiated by the solid-state structure of complex (**3**) the kinetic isomer of $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{–}C_5H_5)]$ which is the equivalent of (**9**). This fact in conjunction with the ^{19}F n.m.r. data leads to the conclusion that one of the two kinetic forms of (**2a**) and (**2d**) has structure (**9**) although it is not possible to decide which. We tentatively assign structure (**11**) to the other kinetic isomer.

Isomerisation to the thermodynamic form (**2**) (**A**) which has structure (**IIi**) is a relatively simple process for kinetic isomers (**11**) or (**12**), merely requiring rotation of the η^2-vinyl ligand by *ca.* 90° (Scheme 4). Recently it has been reported that an analogous rotation of the η^2-vinyl ligand by *ca.* 90° converts the kinetic isomer of $[Mo\{\eta^2\text{-}C(CH_2Ph)C(H)(Ph)\}\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ into the thermodynamically more stable form.[14] Moreover analysis of η^2-vinyl orientations in (**2a**) (**A**) and a series of complexes derived from $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, X = Cl)[8,15] reveals a range of orientations in agreement with extended-Hückel calculations[14] that the energy surface for η^2-vinyl rotation should be relatively flat. In contrast, isomerisation of the kinetic isomer (**9**) [or (**10**)] into (**IIi**) involves a combination of η^2-vinyl rotation and inversion of stereochemistry at the chiral carbon, possibly *via* an intermediate (**13**) as suggested previously[12] for the conversion of (**3**) into (**4**). Since two chiral centres are present in (**2**) an alternative process involves inversion at the metal centre but the isolation of stable phosphonium ylide complexes analogous to (**13**)[28] (see later) suggests that inversion at carbon may be more probable. Since inversion at carbon requires metal–carbon



Scheme 4. CF_3 groups omitted

bond fission it is conceivable that isomerisation of (**9**) may involve a higher energy barrier and therefore occur less readily than simple rotation of the vinyl ligand in (**11**). The very small percentage of (**2**) (**C**) present in solution did not allow us to observe accurately relative rates of isomerisation of (**2**) (**B**) and (**2**) (**C**) and therefore we are unable to confirm that two different processes are involved. However, studies of isomerisation in η^2-vinyl complexes $[MX\{\eta^2\text{-}C(CF_3)C(CF_3)(PR_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, X = Cl or SC_6F_5) designed to throw light on this problem are currently in progress and will hopefully resolve the situation.

Whatever the structures of the isomer (**2**) (**B**) and (**2**) (**C**) and the mechanism of the rearrangement process it is clear that isomerisation occurs much more readily with SC_6H_4Me-4 derivatives (**2a**) and (**2d**) than with $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ which requires several hours in hexane at 80 °C.[12] Although electronic factors may contribute to the relative stabilities of the isomers, a rough correlation was observed between the stability of kinetic isomers (**3**) and the cone angle of the phosphorus ligand, *i.e.* ligands with smaller core angles such as PEt_3 and $P(OMe)_3$ gave more stable kinetic isomers.[12] This implies that steric factors are important in determining the stability of η^2-vinyl complexes of this type. Similar conclusions have been reached concerning isomerisations of η^2-vinyl complexes derived from cationic monoalkyne complexes $[Mo(RC{\equiv}CR')\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)][BF_4]$ (R = Ph or Me, R' = Ph; R = Bu^t or Pr^i, R' = H).[14] Thus the rapid isomerisations (**2**) (**A**) and (**2**) (**C**)→(**2**) (**A**) may reflect the increased steric requirements of the SC_6H_4Me-4 ligand relative to the chlorine atom in complex (**3**).

The formation of η^2-vinyl complexes (**2**) rather than insertion products from the reactions of phosphines and phosphites with $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ prompted us to carry out similar reactions with the η^2-vinyl complexes (**1e**) and (**1f**) since the mercapto ligand has already become bonded to the alkyne ligand and complete migration might therefore be more likely. The reaction of (**1f**) with triethylphosphine at 0 °C gave orange-brown crystals of $[W(SBu^t)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2f**) on slow crystallisation from diethyl ether–hexane at −15 °C. The reaction of (**1f**) with PMe_2Ph similarly gave a 1:1 adduct (**2g**) but attempts to obtain such a product from the reaction of (**1e**) with PMe_2Ph were not totally successful since the orange crystals of $[W(SPr^i)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMe_2Ph)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2h**) which were isolated could not be obtained in a pure form. The explanation for this was provided by variable-temperature ^{19}F n.m.r. studies which revealed that although all three adducts (**2f**)—(**2h**) are stable in solution at low temperatures (< −20 °C) phosphine dissociation occurs at higher temperatures to give an equilibrium mixture similar to that observed between $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1a**) and $PMePh_2$, and in the case of (**2h**) dissociation occurs more readily.

The ^1H and ^{19}F n.m.r. data of (**2f**)—(**2h**) obtained at 0 °C or below are similar to those of η^2-vinyl adducts (**2a**)—(**2e**). In the case of (**2g**) and (**2h**) only one isomeric form was observed whereas the more stable adduct (**2f**) exhibited two forms at 0 °C (ratio 7.5:1) but on warming to room temperature the minor (kinetic ?) isomer disappeared prior to dissociation. This behaviour is reminiscent of that observed with (**2a**) and (**2d**). Despite this, and the fact that the number and chemical shift distribution of the ^{19}F n.m.r. peaks of (**2f**)—(**2h**) are similar to those of the thermodynamic isomer of (**2a**)—(**2e**), the multiplet structure of the resonances is different. Thus an alternative structure (**IIii**) was originally considered possible for (**2f**)—(**2h**). However the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**2f**) which consists of

Table. N.m.r. spectral data for the complexes[a]

Complex	θ_c/°C	Isomer	^1H (δ/p.p.m.)	^{19}F (δ/p.p.m.)
(1a)	20		2.37 (s, 3 H, Me-4), 6.32 (s, 5 H, C_5H_5), 7.30 (m, 4 H, C_6H_4)	−56.40 (s)
(1b)[b]	−50	(A)	3.29 (s, 3 H, Me), 5.65 (s, 5 H, C_5H_5)	−32.67 (spt, 3 F), −56.16 (br m, 3 F), −56.24 (m, 3 F), −56.31 (q, *J* 3.0, 3 F)
		(B)	3.43 (s, 3 H, Me), 5.61 (s, 5 H, C_5H_5)	−55.55 (s)
(1c)[c]	−20	(A)	4.85 (s, 5 H, C_5H_5)	−53.88 (spt, 3 F), −56.25 (m, 3 F), −56.38 (br m, 6 F)
			3.25 (q) 1.25 (t) 0.75 (m) −0.1 (m) Et	
		(B)	4.60 (s, 5 H, C_5H_5)	−55.68 (s)
(1d)[b]	−25	(A)	4.91 (s, 5 H, C_5H_5)	−54.87 (spt, 3 F), −57.38 (br m, 3 F), −57.44 (q, *J* 4.0, 3 F), −57.59 (q, *J* 3.0, 3 F)
			3.35 (br t) 1.75 (m) 1.25 (m) 1.05 (m) 0.8 (m) 0.62 (t) 0.17 (m) Pr^n	
		(B)	4.68 (s, 5 H, C_5H_5)	−56.72 (s)
(1e)	−30		1.25 (m, 1 H, Pr^i methine), 1.33 (d, 3 H, Me), 1.50 (d, 3 H, Me), 5.94 (s, 5 H, C_5H_5)	−55.48 (qq, 3 F), −57.79 (q, 3 F), −57.96 (qq, 3 F), −58.35 (qqq, 3 F)
(1f)	20		1.20 (s, 9 H, Bu^t), 5.86 (s, 5 H, C_5H_5)	−54.46 (q, *J* 4.0, 3 F), −54.96 (spt, 3 F), −57.63 (m, 3 F), −57.78 (m, 3 F)
(2a)[d]	−20	(A)	1.0 (dt, 9 H, Me), 2.15 (m, 6 H, CH_2), 2.30 (s, 3 H, Me-4), 5.80 (s, 5 H, C_5H_5), 7.07 (m, 4 H, C_6H_4)	−46.93 (dqq, 3 F), −52.81 (q, 3 F), −53.31 (q, 3 F), −54.34 (qq, 5 F)
		(B)		−46.65 (br q, *J* 3.5, 3 F), −51.54 (q, *J* 4.5, 3 F), −53.46 (br m, 3 F), −57.89 (m, 3 F)
		(C)		−48.40 (m, 3 F), −51.86 (m, 3 F), −54.64 (m, 3 F), −58.26 (m, 3 F)
(2b)	20		1.88 (d, 3 H, Me), 2.30 (s, 3 H, Me-4), 2.40 (d, 3 H, Me), 5.70 (s, 5 H, C_5H_5), 7.40 (m, 9 H, C_6H_5, C_6H_4)	−46.67 (m, 3 F), −51.77 (q, *J* 5.0, 3 F), −52.64 (q, *J* 4.5, 3 F), −53.82 (m, 3 F)
(2c)	20		2.27 (s, 3 H, Me-4), 2.33 (d, 3 H, Me), 5.91 (s, 5 H, C_5H_5), 7.40 (m, 14 H, C_6H_5, C_6H_4)	−45.63 (m, 3 F), −50.95 (br q, *J* 4.5, 3 F), −52.24 (q, *J* 5.0, 3 F), −54.81 (m, 3 F)
(2d)[e]	−20	(A)	2.25 (s, 3 H, Me-4), 3.70 (d, 9 H, Me), 5.78 (s, 5 H, C_5H_5), 7.08 (apparent q, 4 H, C_6H_4)	−49.98 (m, 3 F), −53.57 (q, *J* 4.5, 3 F), −54.49 (m, 3 F), −55.74 (q, *J* 3.5, 3 F)
		(B)		−46.71 (br s, 3 F), −53.70 (br q, *J* 4.5, 3 F), −54.14 (q, *J* 4.5, 3 F), −55.15 (br s, 3 F)
		(C)		−48.75 (m, 3 F), −53.18 (m, 3 F), −55.91 (m, 3 F), −57.93 (m, 3 F)
(2e)	20		1.20 (t, 9 H, Me), 2.30 (s, 3 H, Me-4), 4.10 (qnt, 6 H, CH_2), 5.75 (s, 5 H, C_5H_5), 7.05 (m, 4 H, C_6H_4)	−48.80 (m, 3 F), −52.61 (q, *J* 5.0, 3 F), −53.97 (m, 3 F), −54.66 (q, *J* 4.0, 3 F)
(2f)	−20	(A)	1.18 (dt, 9 H, Me), 1.40 (s, 9 H, Bu^t), 2.28 (dm, 6 H, CH_2), 6.0 (s, 5 H, C_5H_5)	−47.05 (br s, 3 F), −52.58 (qq, 3 F), −53.52 (q, 3 F), −54.69 (qq, 3 F)
		(B)		−45.60 (m, 3 F), −50.44 (m, 3 F), −52.97 (m, 3 F), −58.27 (m, 3 F)
(2g)[b]	−20			−45.78 (br s, 3 F), −50.96 (br q, *J* 2.0, 3 F), −51.90 (q, *J* 3.5, 3 F), −53.89 (q, *J* 4.0, 3 F)
(2h)	−50		1.25 (dd, 6 H, Me), 1.96 (d, 3 H, Me), 2.38 (d, 3 H, Me), 2.88 (m, 1 H, Pr^i methine), 5.95 (s, 5 H, C_5H_5), 7.55 (m, 5 H, C_6H_5)	−47.20 (br s, 3 F), −52.40 (q, *J* 5.0, 3 F), −54.30 (br q, *J* 3.5, 3 F), −54.72 (spt, 3 F)

[a] In $CDCl_3$ unless stated otherwise; *J* values in Hz. [b] In $(CD_3)_2CO$. [c] In $CD_3C_6D_5$. [d] ^{31}P-$\{^1H\}$: isomer (A), 37.97 (q, J_{PF} 3.0, J_{PW} 20.0); isomer (**B**), 37.85. [e] ^{31}P-$\{^1H\}$: isomer (A), 47.87 (q, J_{PF} 1.5, J_{PW} 21.5); isomer (**B**), 43.94 (br q, J_{PF} 7.5).

a quartet at δ 36.79 (J_{PF} 2 Hz) exhibits ^{31}P—^{183}W coupling (20 Hz) similar to that of (**2a**) thus indicating a similar structure (**IIi**). In contrast one bond W–P coupling constants are usually an order of magnitude larger than this, a typical value for J_{WP} of 247 Hz being observed in the related alkyne complex $[W(SC_6F_5)(PEt_3)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$.[26] The ^{19}F n.m.r. spectrum of (**2f**) (major isomer) consists of four CF_3 resonances including a broad featureless peak at δ −47.05 and when this was irradiated the ^{31}P-$\{^1H\}\{^{19}F\}$ resonance collapsed to a singlet thus indicating that the phosphine is attached to the same carbon atom [*cf.* (**2a**)]. Subsequent ^{19}F double-resonance experiments are summarised in Figure 6 where peak assignments are provided. The differences between the ^{19}F n.m.r. spectra of (**2a**)—(**2e**) and (**2f**)—(**2h**) therefore do not appear to arise from fundamental structural differences, but possibly from small changes in the orientation of the η^2-vinyl ligand which results in different interligand coupling constants.

The conversion of a sulphur-bonded η^2-vinyl [(**Iii**)] into the

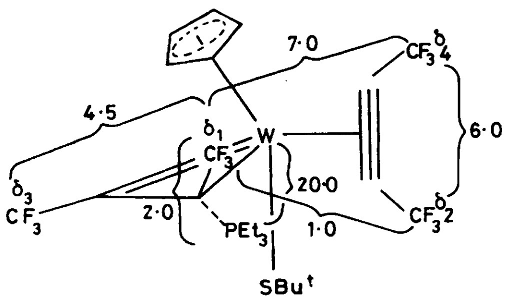


Figure 6. ^{19}F N.m.r. spectral assignments for $[W(SBu^t)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2f**); couplings in Hz

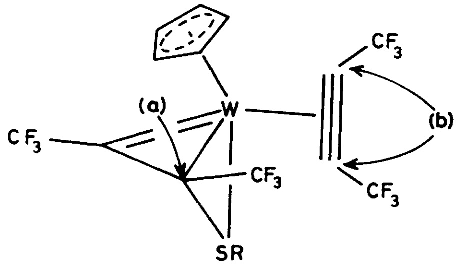
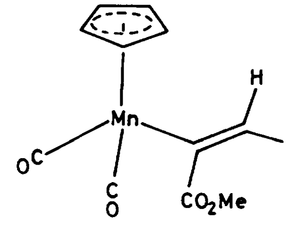


Figure 7. Sites for nucleophilic attack by phosphines in $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SR)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ [*R* = Pr^i or Bu^t]

phosphorus-bonded form (**2**) involves carbon–sulphur bond cleavage promoted by co-ordination of the phosphine to carbon. This could occur either *via* phosphine attack at the η^2-vinyl carbon in an S_N2 nucleophilic substitution [Figure 7, path (a)] or *via* direct attack on the co-ordinated alkyne [path (b)]. Although path (a) would lead to only two kinetic isomers (**9**) and (**10**) while path (b) could lead to four, (**9**), (**10**), (**11**), and (**12**) the isolation of predominantly the thermodynamic isomer in all three reactions does not allow us to distinguish between these two mechanisms on the basis of product stereochemistry. Moreover it is conceivable that the reaction proceeds *via* both routes simultaneously.

Conclusions

The formation of η^2-vinyl complexes either *via* intra- [(**1b**)—(**1f**)] or inter-molecular [(**1**)→(**2**)] nucleophilic attack on a co-ordinated alkyne raises interesting questions concerning a possible relationship between the reactivity of a co-ordinated alkyne and its bonding with the metal. Unco-ordinated hexafluorobut-2-yne readily undergoes nucleophilic[29] attack whereas in the co-ordinated state, when it functions as a two-electron donor, it is reactive towards electrophiles.[30] However the observation that the alkynes in $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, X = Cl or SR) and $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ are reactive towards nucleophiles previously led us to suggest that this change in reactivity may be associated with the involvement of the π-perpendicular orbitals of the alkyne in bonding with the metal.[8,15,26] This proposal appears to be substantiated by the recent report that phosphines and phosphites also attack the unactivated four-electron donor alkyne in $[M(PhC{\equiv}CH)(ma)(S_2CNR_2)_2]$ (M = Mo or W, R = Me; M = W, R = Et; ma = maleic anhydride)[31] to give η^2-vinyl complexes $[M\{\eta^2\text{-}C(Ph)C(H)(PR_3)\}(ma)(S_2CNR_2)_2]$. Alkynes can also be activated towards nucleophilic attack by co-ordination to a positively charged metal centre as in $[Mo(PhC{\equiv}CPh)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)][BF_4]$[14] and by multisite co-ordination to two or more metal atoms in metal clusters.[32] The latter method has also enabled Mott and Carty[33] to develop an extensive chemistry of alkynyl ligands by μ-η^2-co-ordination as in $[Fe_2(CO)_6(C{\equiv}CR)(PPh_2)]$ (R = alkyl or aryl).[33] However it is significant that the two-electron donor alkyne ligand in $[Mn(HC{\equiv}CCO_2Me)(CO)_2(\eta^5\text{-}C_5H_5)]$ reacts with triphenylphosphine yielding an σ-phosphonium ylide complex (**14**), the σ-equivalent of the η^2-vinyl ligands in complexes (**2a**)—(**2h**).[28] This indicates that although three- or four-electron donation to a metal may contribute in activating a co-ordinated alkyne towards nucleophilic attack, under appropriate circumstances it is not necessarily a prerequisite. It is therefore interesting to speculate on the role that Hoffmann's 'slippage' mechanism, *i.e.* deformation towards σ-co-ordination of the alkyne, may play in the formation of η^2-vinyl complexes.[34]



(**14**)

Experimental

Proton, ^{19}F, and ^{31}P n.m.r. spectra were recorded on a Bruker WP-200 SY n.m.r. spectrometer operating at 200.13, 188.31, and 81.02 MHz respectively using $SiMe_4$, CCl_3F, and H_3PO_4 (δ = 0 p.p.m.) as references. The n.m.r. data are presented in the Table. I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer and mass spectra on a Vacuum Generator's updated A.E.I. MS9 at 70 eV (*ca.* 11.2 × 10^{-18} J). 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. Tetrahydrofuran was dried over sodium–benzophenone. The hexafluorobut-2-yne complex $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ was prepared as described previously[3] while phosphines PEt_3, $PMePh_2$ and phosphites $P(OMe)_3$ and $P(OEt)_3$ were obtained commercially (Strem and Maybridge). Thallium(I) thiolates were prepared by adding a methanol solution of the thiol to a stirred solution of thallium(I) acetate in aqueous methanol containing a few pellets of KOH. The resulting yellow solid was filtered off and washed successively with water, methanol, and diethyl ether before drying under vacuum.

Reactions of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$.—(*a*) *With* $Tl(SC_6H_4Me\text{-}4)$. A mixture of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (300 mg) and $Tl(SC_6H_4Me\text{-}4)$ (200 mg) in diethyl ether (40 cm^3) was stirred for 3 h giving a deep purple solution. This was centrifuged, reduced in volume *in vacuo*, and hexane (15 cm^3) added. On cooling to −15 °C deep purple crystals of $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1a**) were obtained. These were recrystallised a second time from diethyl ether–hexane. Yield: 180 mg, 79%; M^+, 696 (Found: C, 34.8; H, 1.5; F, 33.5; S, 4.3. Calc.: C, 34.5; H, 1.7; F, 32.8; S, 4.6%). I.r. (CH_2Cl_2): ν(C≡C) at 1 779wm and 1 743wm cm^{-1}.

(*b*) *With* Tl(SMe). A mixture of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (20 mg) and Tl(SMe) (14 mg) in diethyl ether (3 cm^3) was stirred for 20 min. Work-up as above gave red crystals of $[W(SMe)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1b**) (13 mg, 67%); M^+, 620

(Found: C, 27.1; H, 1.4. Calc.: C, 27.1; H, 1.3%). I.r. (hexane): $\nu(C\equiv C)$ at 1 789wm and 1 755wm cm^{-1}.

(*c*) *With* Tl(SEt). A mixture of $[WCl(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (100 mg) and Tl(SEt) (60 mg) in diethyl ether (15 cm^3) was stirred at room temperature for 90 min. Work-up as above gave orange crystals of $[W(SEt)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1c**) (40 mg, 38%); M^+, 634 (Found: C, 28.8; H, 1.3. Calc.: C, 28.4; H, 1.6%). I.r. (hexane): $\nu(C\equiv C)$ at 1 782wm and 1 762wm cm^{-1}.

(*d*) *With* Tl(SPr^n). A mixture of $[WCl(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (26 mg) and Tl(SPr^n) (16 mg) in diethyl ether (10 cm^3) was stirred at room temperature for 30 min. Work-up as above gave orange crystals of $[W(SPr^n)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1d**) (16 mg, 58%); M^+, 648 (Found: C, 29.5; H, 1.6. Calc.: C, 29.7; H, 1.9%). I.r. (hexane): $\nu(C\equiv C)$ at 1 784wm and 1 764wm cm^{-1}.

(*e*) *With* Tl(SPr^i). A mixture of $[WCl(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (100 mg) and Tl(SPr^i) (60 mg) in diethyl ether (15 cm^3) was stirred at room temperature for 4 h. Work-up as above gave yellow-orange crystals of $[W(SPr^i)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1e**) (81 mg, 76%); M^+, 648 (Found: C, 29.2; H, 1.7. Calc.: C, 29.6; H, 1.9%). I.r. ($CHCl_3$): $\nu(C\equiv C)$ at 1 760wm cm^{-1}.

(*f*) *With* Tl(SBu^t). A mixture of $[WCl(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (300 mg) and Tl(SBu^t) (150 mg) in diethyl ether (40 cm^3) was stirred at room temperature for 4 h. Work-up as above gave yellow-orange crystals of $[W(SBu^t)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1f**) (195 mg, 60%); M^+, 660 (Found: C, 31.1; H, 2.0. Calc.: C, 30.8; H, 2.10%). I.r. (CCl_4): $\nu(C\equiv C)$ at 1 757wm cm^{-1}.

Reactions of $[W(SC_6H_4Me\text{-}4)(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1a**).—*With* P(OMe)$_3$. A solution of P(OMe)$_3$ (100 mg) in diethyl ether (2 cm^3) was added dropwise to a stirred solution of complex (**1a**) (80 mg) in diethyl ether (15 cm^3) until the purple mixture just turned pale yellow. Hexane (10 cm^3) was added and the solution concentrated to *ca.* 15 cm^3 *in vacuo*. On cooling to −15 °C yellow crystals were obtained which were recrystallised a second time from CH_2Cl_2–hexane to give $[W(SC_6H_4Me\text{-}4)\{\eta^2\text{-}C(CF_3)C(CF_3)[P(OMe)_3]\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2d**) (65 mg, 69%) (Found: C, 33.2; H, 2.6. Calc.: C, 33.7; H, 2.6%). I.r. (CCl_4): $\nu(C\equiv C)$ at 1 761wm cm^{-1}.

(*b*) *With* PEt$_3$. Similarly to (*a*) above complex (**1a**) (80 mg) gave $[W(SC_6H_4Me\text{-}4)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2a**) (55 mg, 59%) (Found: C, 38.7; H, 3.5. Calc.: C, 38.4; H, 3.35%). I.r. (CCl_4): $\nu(C\equiv C)$ at 1 768wm cm^{-1}.

(*c*) *With* PMe$_2$Ph. Similarly to (*a*) above complex (**1a**) (50 mg) gave $[W(SC_6H_4Me\text{-}4)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMe_2Ph)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2b**) (38 mg, 63%) (Found: C, 40.1; H, 2.5. Calc.: C, 40.4; H, 2.8%). I.r. (CCl_4): $\nu(C\equiv C)$ at 1 762wm cm^{-1}.

(*d*) *With* P(OEt)$_3$. Similarly to (*a*) above complex (**1a**) (50 mg) gave $[W(SC_6H_4Me\text{-}4)\{\eta^2\text{-}C(CF_3)C(CF_3)[P(OEt)_3]\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2e**) (35 mg, 56%) (Found: C, 36.6; H, 3.0. Calc.: C, 36.30; H, 3.15%). I.r. (CCl_4): $\nu(C\equiv C)$ at 1 762wm cm^{-1}.

(*e*) *With* PMePh$_2$. PMePh$_2$ (20 mg) in diethyl ether (5 cm^3) was added to complex (**1a**) (60 mg) in diethyl ether (10 cm^3). Hexane (15 cm^3) was added and the solution concentrated and cooled to −15 °C when the colour changed from red-purple to yellow and yellow crystals of $[W(SC_6H_4Me\text{-}4)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMePh_2)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2c**) were obtained (35 mg, 45%) (Found: C, 44.8; H, 2.5. Calc.: C, 44.3; H, 2.8%). I.r. (Nujol mull): $\nu(C\equiv C)$ at 1 760wm cm^{-1}.

Reactions of $[W\{\eta^3\text{-}C(CF_3)=C(CF_3)(SBu^t)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1f**).—(*a*) *With* PEt$_3$. Triethylphosphine (15 mg) was added to complex (**1f**) (40 mg) in diethyl ether (10 cm^3) at 0 °C. Ice-cold hexane (5 cm^3) was added and the solution concentrated *in vacuo* at 0 °C. The solution was then cooled slowly to −15 °C when orange-brown crystals of $[W(SBu^t)\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2f**) were obtained (21 mg, 47%) (Found: C, 39.6; H, 3.8; P, 3.0. Calc.: C, 36.9; H, 3.9; P, 4.15%). I.r. (Nujol mull): $\nu(C\equiv C)$ at 1 760wm cm^{-1}.

(*b*) *With* PMe$_2$Ph. PMe$_2$Ph (15 mg) and complex (**1f**) (30 mg) were reacted similarly to give impure orange-brown crystals of $[W(SBu^t)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMe_2Ph)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2g**) (12 mg). I.r. (Nujol mull): $\nu(C\equiv C)$ at 1 750wm cm^{-1}.

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)(SPr^i)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1e**) *with* PMe$_2$Ph.—PMe$_2$Ph (10 mg) and complex (**1e**) (30 mg) were treated similarly to give $[W(SPr^i)\{\eta^2\text{-}C(CF_3)C(CF_3)(PMe_2Ph)\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2h**) (12 mg, 34%) as a yellow microcrystalline powder (Found: C, 37.0; H, 2.7. Calc.: C, 36.6; H, 2.9%). I.r. (Nujol mull): $\nu(C\equiv C)$ at 1 756wm cm^{-1}.

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