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Reversible insertion of alkynes into molybdenum– and tungsten–sulphur bonds *

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Abstract

Reactions of the bis-hexafluorobut-2-yne complex $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with thallium salts TlSR give η^2-*C,C* vinyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1**), fully characterised in the cases M = Mo, R = Pr^i, Bu^t, but only partially so in the case M = Mo, R = 4-MeC_6H_4. Air oxidation of η^2-*C,C* vinyls **1** (M = Mo, R = 4-MeC_6H_4; M = W, R = Pr^i) and the isomeric bis-alkyne derivatives $[MSR(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**2**) (M = Mo, R = C_6F_5; M = W, R = 4-MeC_6H_4) gives *cis* σ-alkenyl-oxo derivatives $[M\{C(CF_3){=}C(CF_3)SR\}(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3**). With **1** (M = Mo, R = Pr^i) a *cis-cis* η^2-butadienyl complex $[Mo\{\eta^2\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i\}(O)(\eta^5\text{-}C_5H_5)]$ **4** is obtained instead, whereas air oxidation of $[WSC_6F_5(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ gives a dimeric alkyne derivative $[W_2(CF_3C{\equiv}CCF_3)_4(O)_n(\eta^5\text{-}C_5H_5)_2]$ (n = 1 or 2) (**5**) resulting from loss of the thiolate ligand. Reactions of σ-alkenyl-oxo complexes **3** (M = Mo, R = C_6F_5; M = W, R = 4-MeC_6H_4) with tertiary phosphines L give η^2-vinyl complexes $[MSR\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, R = C_6F_5, L = PEt_3 or PMe_2Ph; M = W, R = 4-MeC_6H_4, L = PEt_3, PMe_2Ph or $PMePh_2$) (**6**) as a result of reduction of the metal $M^{IV} \rightarrow M^{II}$ and thiolate migration to the metal.

Introduction

The fundamental role of ligand migration (insertion) reactions in organometallic chemistry and transition metal catalysis has prompted many studies of such reactions in recent years. It has generally been assumed that insertion reactions involving alkynes should resemble those of alkenes, an assumption which is to some

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* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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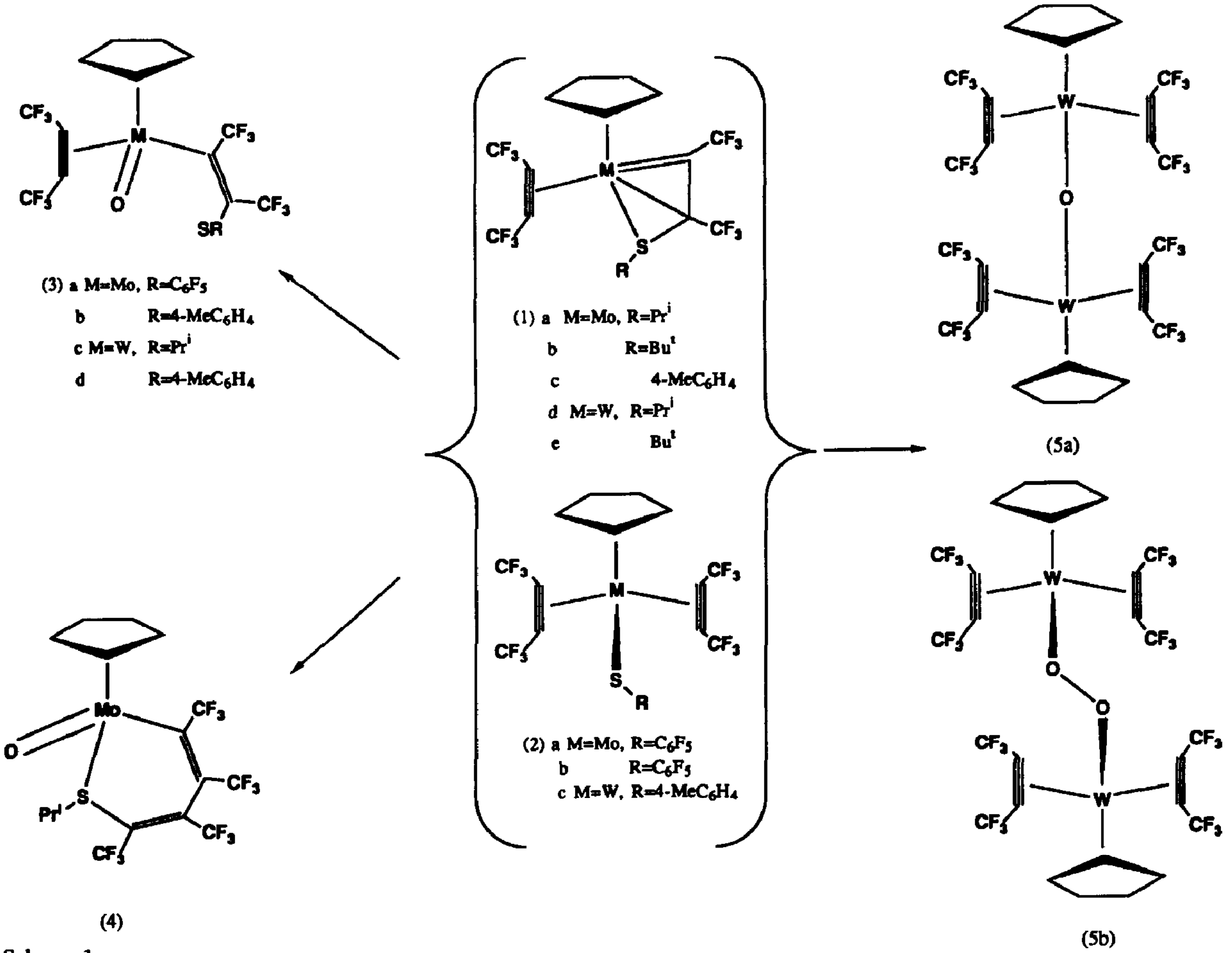
extent valid provided that the additional π,π^* orbitals on the alkyne do not participate in the insertion process [1]. However, a wide range of alkyne complexes have been isolated in the last few years in which both sets of filled π orbitals of the alkyne are thought to participate in bonding with a metal [2]. Addition reactions of such complexes give novel η^2-vinyl derivatives [2,3] which contrasts with the formation of σ-vinyl complexes from normal alkyne derivatives. This led us to suggest that, in certain circumstances, η^2-vinyl intermediates might play an important role in insertion reactions and, as a consequence, have a significant effect on the stereochemistry of the products [3]. This prompted us to attempt the synthesis of a range of η^2-*C,C* vinyl molybdenum thiolate complexes $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1**) and compare their reactions with those of (a) related tungsten derivatives [4a], (b) isomeric bis-alkyne derivatives $[MSR(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**2**) ($M = Mo, W, R = C_6F_5$ [4b]; $M = W, R = 4\text{-}MeC_6H_4$ [4d]), reported previously

Results and discussion

Reactions of the bis-alkyne complex $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with thallium(I) thiolates TlSR ($R = Pr^i, Bu^t$) in diethyl ether at room temperature gave yellow-orange crystalline complexes of stoicheiometry $[MoSR(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1l**; $R = Pr^i$; **1b**: $R = Bu^t$) as indicated by their elemental analyses. Attempts to obtain similar SMe and $S(4\text{-}Me)C_6H_4$ (**1c**) derivatives were unsuccessful owing to the extreme air sensitivity of the product in the case $R = 4\text{-}MeC_6H_4$ or, for R = Me, competing side reactions that led to a complex mixture of products. This contrasts with the outcome of analogous tungsten reactions, from which both methyl and $4\text{-}MeC_6H_4$ complexes were isolated in reasonable yield [4a]. Spectroscopic data for complexes **1a,b** are, in each case, similar to those of tungsten derivatives **1d** ($R = Pr^i$) and **1e** ($R = Bu^t$) whose structure has been confirmed by X-ray diffraction studies in the case of **1d** [5]. A similar structure (see Scheme 1) is therefore proposed for **1a** and **1b**. In the case of the tungsten derivatives two interconverting isomeric forms were detected in solution for R = Me, Et or Pr^n, but only one form for $R = Pr^i$ or Bu^t. The molybdenum derivatives isolated similarly exist in only one isomeric form and are stereochemically rigid at room temperature.

As mentioned earlier the $4\text{-}MeC_6H_4$ derivative (**1c**) could not be isolated in a pure form owing to its high sensitivity to air in solution. However, it was partially characterised by ^{19}F NMR spectroscopy at −50 °C, which revealed four distinct CF_3 environments, as found with **1a** and **1b**. This indicates that the complex adopts the η^2-*C,C* vinyl structure **1**, unlike the analogous tungsten derivative, which shows one CF_3 resonance down to −90 °C. This is consistent with the bis-alkyne form **2** which undergoes alkyne propeller rotation. We therefore conclude that the η^2-*C,C* vinyl form is more stable for the molybdenum than the tungsten complexes. This is in accord with previous observations [3a, 6] of the stability of η^2-vinyl complexes $[MCl\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ obtained from the reactions of tertiary phosphines L with bis-alkyne derivatives $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, W). For example, with $L = PPh_3$ a stable complex is obtained when M = Mo, but with M = W an equilibrium mixture of all three components is obtained. It appears that the alkyne carbons in the tungsten derivatives are less electrophilic than in the corresponding molybdenum derivatives.



(3) a M=Mo, $R=C_6F_5$
b $R=4\text{-}MeC_6H_4$
c M=W, $R=Pr^i$
d $R=4\text{-}MeC_6H_4$

(1) a M=Mo, $R=Pr^i$
b $R=Bu^t$
c $4\text{-}MeC_6H_4$
d M=W, $R=Pr^i$
e Bu^t

(2) a M=Mo, $R=C_6F_5$
b $R=C_6F_5$
c M=W, $R=4\text{-}MeC_6H_4$

(5a)

(4)

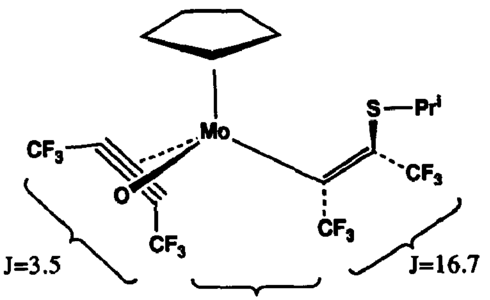
(5b)

Scheme 1

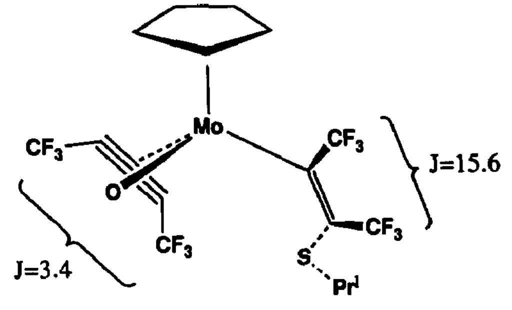
Previously we reported that mono- and bis-alkyne complexes [MCl(L)(PhC≡CPh)(η^5-C_5H_5)] (M = Mo, L = CO [7], PhC≡CPh [6]; M = W, L = CO [7]) and [MSC_6F_5(CO)(CF_3C≡CCF_3)(η^5-C_5H_5)] (M = Mo, W) [8] readily undergo air oxidation to give oxo-alkyne derivatives [MCl(O)(PhC≡CPh)(η^5-C_5H_5)] and [MSC_5F_5(O)(CF_3C≡CCF_3)(η^5-C_5H_5)]. This fact, and the sensitivity of **1c** to oxygen, prompted us to investigate the reactions of η^2-vinyl and bis alkyne derivatives **1** and **2** with oxygen. The results, summarised in Scheme 1, show that the products of oxidation are sensitive to the nature of the metal and the thiolate group SR. For example, the bis-alkyne derivatives **2a,c** and the η^2-*C,C* vinyl complexes **1c,d** react in diethyl ether to give white, yellow, or orange crystalline solids **3a–d** which, according to elemental analyses and mass spectrometry, have the stoicheiometry [MSR(O)($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)]. The IR spectrum in each case shows a single ν(C≡C) band near 1800 cm^{-1} consistent with the presence of a coordinated hexafluorobut-2-yne. The ^1H and ^{19}F NMR spectra did not uniquely define the structure of the complexes, and a single crystal X-ray diffraction study of [$MoSC_6F_5$(O)($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)] (**3a**) was carried out by Muir and Manojlovic-Muir (University of Glasgow), the results of which are reported elsewhere [9].

These studies revealed that oxidation had resulted in complete transfer of the SC_6F_5 group to an alkyne carbon to generate a *cis* alkenyl group C(CF_3)=C(CF_3)-SC_6F_5 σ-bonded to molybdenum. As such, **3a** is formally derived by *cis* insertion of CF_3C≡CCF_3 into the molybdenum–sulphur bond of the previously reported oxo complex [$MoSC_6F_5$(O)(CF_3C≡CCF_3)(η^5-C_5H_5)] [10]. Not surprisingly these two complexes share common structural features, in particular the alkyne orientation, in which the C≡C bond lies normal to the M–O bond axis. This enables two empty metal $d\pi$ orbitals to accept π-electron density from the oxygen $p\pi$ orbitals such that the Mo–O linkage is formally a triple bond. The third $d\pi$ orbital on the metal therefore functions as a π-donor to the remaining, empty π^* orbital on the alkyne. The alkyne can therefore be formally regarded as a two electron donor under these circumstances. Interestingly a range of vinyl thiolate complexes have been obtained from insertion reactions of activated alkynes (including CF_3C≡CCF_3) into metal–SR bonds [11]. Related complexes have also been obtained on addition of RS^- to cationic alkyne complexes, such as [Fe(CO){$P(OPh)_3$}(MeC≡CH_2OMe)(η^5-C_5H_5)]$^+$ [12].

The NMR spectra of **3a–d** can be interpreted in terms of the solid state structure of **3a** with the additional feature that in solution two isomeric forms, **A** and **B**, are present in ratios of 5.5/1 (**3a**), 1/3.6 (**3b**), 1/1.2 (**3c**) and 1/1.8 (**3d**). The source of isomerism in the complexes was probed by molecular graphics [13] studies of **3a**, which revealed that the σ-alkenyl ligand can adopt two preferred orientations about the Mo–C (alkenyl) bond (Fig. 1). It appears that free rotation about the Mo–C bond is prevented by steric interactions of both the sulphur atom and the α CF_3 of the alkenyl ligand with one of the alkyne CF_3 groups and, to a lesser extent, with the η^5-C_5H_5 ligand. A related situation exists in [$MoSC_6F_5$(O)(CF_3C≡CCF_3)(η^5-C_5H_5)], in which free rotation about Mo–S bond is prevent in **4d** by interaction of the C_6F_5 group with an alkyne CF_3 [8]. Thus, as illustrated in Fig. 1, two alkenyl group conformations are possible in **3**, the first as found in the solid state (**A**), and the second related to the first by rotation of the alkenyl ligand about the M–C bond by ca. 180° to give structure **B**. Rotational isomerism in σ-alkenyl complexes derived from alkyne insertion reactions is well known and, in several cases, NMR spectro-



Isomer A



Isomer B

Fig. 1. Isomeric structures and ^{19}F NMR data for [W{C(CF$_3$)=C(CF$_3$)SPr^i}(O)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (3c).

scopic studies have established quite high barriers to rotation [14]. This contrasts with the low barrier in *cis* σ-alkenyl complexes of iron [Fe{C(CF$_3$)=C(CF$_3$)SR}(CO)$_2$(η^5-C$_5$H$_5$)] (R = CF$_3$, C$_6$F$_5$), for which the isomerism could not be detected by NMR methods, but was observed in the IR spectra [11c]. In the present case the barriers to rotation must be quite large, since no changes were observed in the ^{19}F NMR spectrum of **3a** up to 80 ° C.

The ^{19}F NMR spectrum of **3c** (see Fig. 2) will be interpreted in detail since, in this particular case, the situation is not complicated by signal overlap and second order effects. As Fig. 2 illustrates, each isomer gives rise to four CF$_3$ peaks (isomer A, A1–A4, isomer B, B1–B4), two of which exhibit a large CF$_3$–CF$_3$ coupling J(A1–A3) 16.7 and J(B1–B2) 15.6 Hz. These can be assigned to the *cis* σ-C(CF$_3$)=C(CF$_3$)SPr^i group on the basis that *cis* CF$_3$C=CCF$_3$ groups exhibit J(F–F) values in the range 11–18 Hz [15]. However, coordinated CF$_3$C≡CCF$_3$ ligands show J(F–F) values of ca. 3–5 Hz [8], in accord with observed values J(A2–A4) 3.5 and J(B3–B4) 3.4 Hz. Interestingly, inter-ligand coupling is also observed, but only for isomer A for which J(A1–A2) 6.0 Hz. These features are common to all four complexes **3a–d**, although in the case of **3a** the CF$_3$ resonance A3 also shows triplet splitting, with J = 2.0 Hz, due to coupling to the two *ortho* fluorines of the C$_6$F$_5$ group. The last feature identifies A3 as being due to the β CF$_3$ of the C(CF$_3$)=C(CF$_3$)SC$_6$F$_5$ moiety. Moreover, molecular graphics studies of **3a** indicate

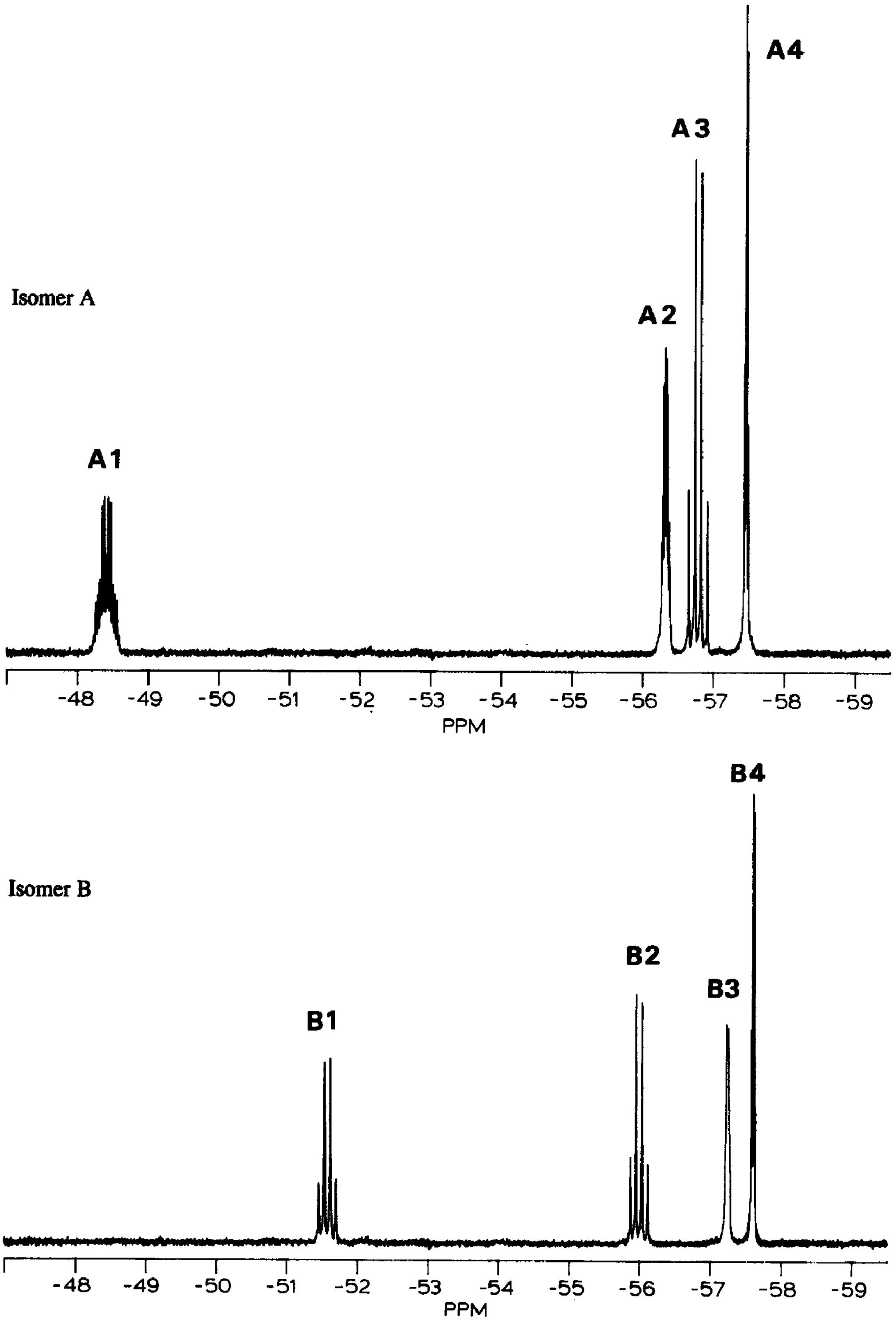


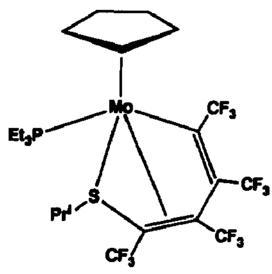
Fig. 2. ^{19}F NMR spectrum of $[W\{C(CF_3)=C(CF_3)SPr^i\}(O)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (3c). The peaks for each isomer (*A* and *B*) have been plotted separately for clarity.

that the α CF_3 is close to one particular alkyne-CF_3 group. Since the inter-ligand coupling of 6.0 Hz is likely to be through-space rather than through six bonds, the overall assignments can be summarised as shown in Fig. 2. The assumption is that the solid state structure is isomer **A** and not **B**. We note that molecular graphics studies of isomer **B** reveal that no close CF_3–CF_3 contacts are possible, thus accounting for the absence of significant inter ligand coupling in this case.

The reaction of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1a**) with oxygen follows a different course from that observed with **1c,d** and **2a,c** in that the dark green lustrous product **4** does not exhibit a $\nu(C{\equiv}C)$ band in the IR spectrum, although the empirical formula is similar to that of **3c**. The proposed structure for **4**, containing a $\eta^2\text{-}C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i$ ligand, is consistent with the spectroscopic data, in particular with the ^{19}F NMR spectrum. This, as with **3**, provides evidence for two isomeric forms in solution, each exhibiting four CF_3 multiplets. Significantly however, every peak exhibits a large quartet splitting, with $J(CF_3\text{–}CF_3)$ ca. 13–16 Hz, indicating the presence of two *cis* $CF_3C{=}CCF_3$ groups [15]. Weak coupling, ca. 3 Hz, is also observed between two of the four CF_3 groups in each isomer. This weak coupling can be accounted for if the Mo–C=C–C=C–S ring is assumed to adopt a non-planar arrangement, as seems likely from studies of molecular models. We assume that, as with oxo complexes $[MoSC_6F_5(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ and **3a**, the structure is based upon an octahedral-coordinated metal with the η^5-C_5H_5 group occupying a face and the other coordinated atoms the corners of the octahedron. On this basis it appears to be necessary to twist the butadienyl ligand about the central C–C bond of the Mo–C=C–C=C–S ring. This generates a non-zero dihedral angle between the planes of the two $CF_3C{=}CCF_3$, so that the two internal CF_3 groups twist away from each other. Consequently through space F–F coupling will be reduced considerably, as is observed. The proposed non-planarity of the six membered ring also provides an explanation for the presence of two isomers, since this may arise from the existence of two preferred metalla-ring conformations. Alternatively, inversion at sulphur may produce two isomers. It is also conceivable that these possibilities are not mutually exclusive, i.e. that the isomerism involves a combination of the two.

The proposed structure of **4**, which results from linking of two $CF_3C{\equiv}CCF_3$ ligands and a thiolate group, can be compared with those of variety of complexes containing related butadienyl groups. The closest comparison is with **7**, obtained from the reaction of PEt_3 with **1a** [9]. Since the phosphine is a two electron donor, the butadienyl ligand in **7** is required to bond in a η^4-mode in order that the stable 18-electron configuration is attained. The ability of O^{2-} to function as a six electron donor in **4** eliminates this requirement and hence the η^2-mode of coordination is found. Other modes of coordination are known for butadienyl ligands, as in **8** [16], **9** [3b], **10** [17] and **11** [18]. However, none of these would give rise to the ^{19}F NMR spectrum exhibited by **4**. It is nontheless interesting to note the increasing range of isomeric forms exhibited by such ligands, which illustrates their ability to alter their coordination mode in response to the steric and electronic requirements of the metal

Previously it has been suggested that complexes containing both σ-alkenyl and η^2-alkyne ligands, e.g. $[Ir\{C(CF_3){=}C(CF_3)H\}(CF_3C{\equiv}CCF_3)(CO)(PPh_3)_2]$ may, in appropriate circumstances, function as intermediates in metal-promoted alkyne oligomerisation reactions [19]. The isolation of **3** and **4** would seem to support this proposal in that logically the formation of **4** would be expected to result from



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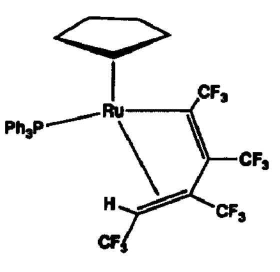

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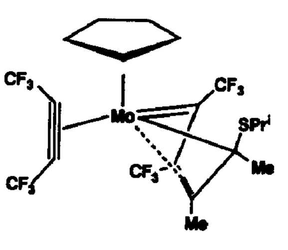

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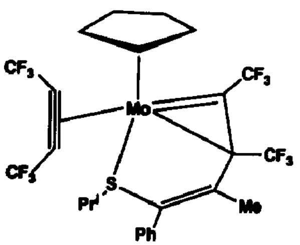

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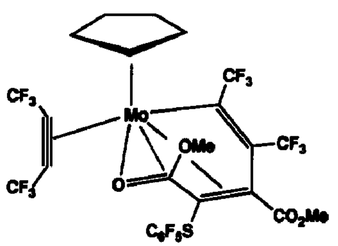

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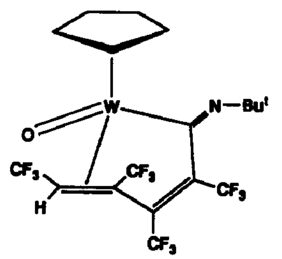


(12)

insertion of the alkyne into the M–C alkenyl bond of an intermediate of structure **3**. Interestingly, however, attempts to induce such a reaction by heating a solution of **3a** in toluene for several hours at 70 ° C gave an intractable mixture of products with no evidence for the SC_6F_5 analogue of **4**. This does not necessarily rule out the intermediacy of a species of type **3** in the formation of **4**. Nonetheless, alternative pathways are possible, as demonstrated by our recent observation that metallacyclopentadiene complexes $[WC(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)(SR)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ ($R = Pr^i$, Bu^t, $4\text{-}MeC_6H_4$) on hydrolysis give the iminoacyl oxo derivative **12** with strong structural similarities to **4** [20].

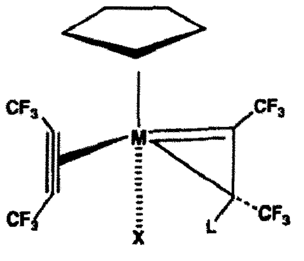
The third type of product obtained on oxidation of the alkyne thiolate complexes apparently results from loss of the SC_6F_5 group from $[WSC_6F_5(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$, according to analytical and spectroscopic data. However, the exact formula of the yellow crystalline product **5** is not clear, since C and H analysis are in accord with either of two stoicheiometries $[W_2(O)(CF_3C_2CF_3)_4(\eta^5\text{-}C_5H_5)_2]$ or $[W_2(O)_2(CF_3C_2CF_3)_4(\eta^5\text{-}C_5H_5)_2]$. Moreover, satisfactory analysis for fluorine was not obtained, as is sometimes the case with fluoro-organometallic compounds. The mass spectrum did not exhibit a molecular ion, the highest peak at $m/z = 587$ corresponding to $[W(O)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]^+$, whilst other metal containing ions are observed that result from loss of O, F and CF_3 from this ion. The IR spectrum shows two bands at 1782 and 1762 cm^{-1} assigned as $\nu(C{\equiv}C)$ stretching modes, and as such can be compared with those of bis-alkyne complexes, $[W(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ ($X = Cl$ [21], $S\text{-}4\text{-}MeC_6H_4$ [4a], SC_6F_5 [4b]). No C_6F_5 absorptions are observed, confirming the loss of this group on oxidation, while the C–F stretching region (1100–1300 cm^{-1}) contains a similar pattern of peaks to that from the precursor $[WSC_6F_5(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$.

The ^1H NMR spectrum contains a η^5-C_5H_5 singlet at δ 6.12, whilst the ^{19}F NMR spectrum is temperature dependent, thus indicating fluxional behaviour. At ambient temperature a single resonance is observed at δ–58.19, but at lower temperatures this peak broadens, and separates into two peaks at −60 ° C, the coalescence temperature being ca. −20 ° C. Almost identical behaviour has been observed previously with [MX($CF_3C{\equiv}CCF_3$)$_2$(η^5-C_5H_5)] (M = Mo, W; X = Cl, Br, I), and this was attributed to alkyne propeller rotation. The frozen spectrum at low temperature indicates two CF_3 environments, in accord with the solid state structure established for [WCl($CF_3C{\equiv}CCF_3$)$_2$(η^2-C_5H_5)] [21]. At higher temperatures, the two inequivalent sets of two CF_3 groups at the ends of the equivalent alkynes undergo exchange as alkyne rotation commences. The coordination geometry in **5** is clearly similar to that in [WCl($CF_3C{\equiv}CCF_3$)$_2$(η^5-C_5H_5)], and on this basis two structures **5a** and **5b** are possible, based on a bridging oxo or peroxo linkage, respectively. The difficulties presented by oxygen analysis in fluorine-containing species unfortunately do not allow us to distinguish between the two species. However, oxygen-bridged dimers are well-known in Group VI metal chemistry [22], whereas peroxo linkages as in **5b** are more prevalent in iron and cobalt systems [23]. On this basis structure **5a** is tentatively preferred, but clearly the situation needs to be resolved by X-ray diffraction studies. Unfortunately attempts to obtain suitable crystals were unsuccessful.

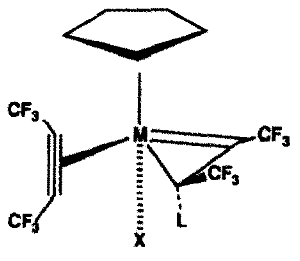
σ-Vinyl complexes have frequently been isolated from reactions of alkynes with metal complexes [11,14,24,25] or from nucleophilic or electrophilic addition to coordinated alkynes [25,26]. However, few complexes similar to **3** are known in which a σ-vinyl ligand and an alkyne are both coordinated to the same metal. In the past few years a variety of complexes has been synthesised in these laboratories containing both η^2-vinyl and alkyne ligands [3,4a,5,17] which are plausible intermediates in alkyne oligomerisation reactions. Consequently, initial studies were carried out designed to investigate the possibility of promoting insertion of the coordinated alkyne into the M–C alkenyl bond in **3a** and **3d**. This involved addition of phosphines PEt_3, PMe_2Ph or $PMePh_2$ to the vinyl complexes in the expectation that alkyne insertion might be promoted by phosphine coordination.

Reactions were carried out in diethyl ether at room temperature with an excess of phosphine present, and, in all cases except that of the reaction of (3a) with $PMePh_2$, which will be described in a separate publication, yellow or yellow-orange crystalline complexes (**6a–c**) were obtained in yields ranging from 53% (**6b**) to 91% (**6a**). Elemental analyses are consistent with the stoicheiometry [MSR($CF_3C_2CF_3$)$_2$L(η^5-C_5H_5)} (L = phosphine), and it was subsequently established that the tungsten derivatives **6c**, **6d** and **6e** have identical spectroscopic features of those of previously reported η^2-vinyl complexes isolated from the reactions of [W(S4-MeC_6H_4)($CF_3C{\equiv}CCF_3$)$_2$(η^5-C_5H_5)] with tertiary phosphines [4]. In a wide-ranging parallel study involving reactions of phosphines with complexes of types **1** and **2** it was found that that PEt_3 and PMe_2Ph also react with [$MoSC_6F_5$($CF_3C{\equiv}CCF_3$)$_2$(η^5-C_5H_5)] to give complexes **6a** and **6b**. These studies will be described in a future publication.

Complexes **6a** and **6b** have similar spectroscopic features to those of **6c,d,e**, and consequently an η^2-vinyl structure is also proposed for them. Before describing the spectroscopic data, it is pertinent to point out that X-ray structure studies of a range of η^2-vinyl complexes have been carried out in the last five or six years, including complex **6c** [2]. Of particular relevance are the structures of two isomeric complexes



(6i)

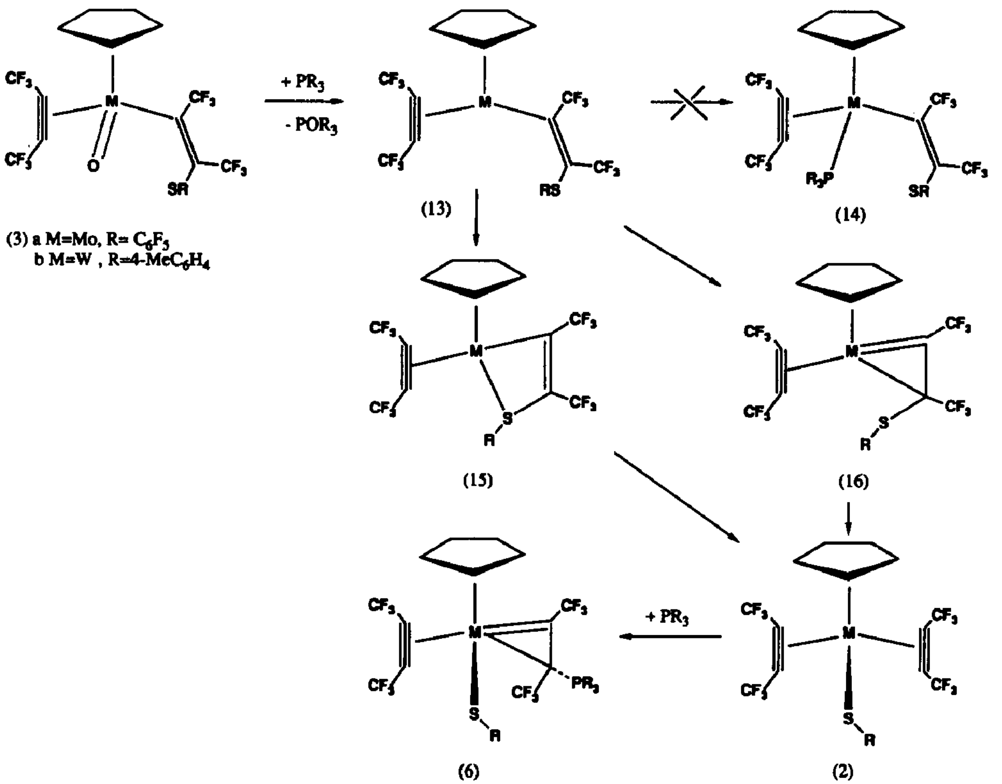


(6ii)

isolated from reactions of [MoCl(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] with PEt$_3$ [3a]. The first, **6i**, is a kinetic isomer, which was transformed when its solution in hexane was heated at 90 °C into the thermodynamically more stable form **6ii**. The S(4-Me)C$_6$H$_4$ derivative **6c** is the structural analogue of the thermodynamic form **6ii**. Isomer **6i** results from attack of PEt$_3$ at the least sterically hindered of the alkyne carbons to give a three electron donor η^2-vinyl ligand. Interestingly, apart from modifications to the coordination geometry around this carbon, the structure of the molecule remains virtually unchanged relative to that of the bis-alkyne precursor. However, in isomer **6ii** the η^2-vinyl ligand has changed its orientation, and the chiral carbon of the η^2-vinyl ligand has undergone inversion of stereochemistry. These structural changes result in differences between the spectroscopic data of the two isomers which allow structural assignment of the new complexes **6a,b** reported herein.

The IR spectra in both cases exhibit ν(C≡C) bands (at 1805 and 1795 cm^{-1} respectively) some 30–40 cm^{-1} to high frequency of those for the equivalent S(4-Me)C$_6$H$_4$ derivatives. This frequency difference is also found with the bis-alkyne precursors, and appears to reflect the influence of the metal rather than the substituent on sulphur. The ^{1}H and ^{19}F NMR spectra of **6a** and **6b** both show two sets of peaks, consistent with two isomeric forms in solution in ratios of 10/1 and 17/1. The ^{19}F NMR data are particularly revealing in respect of isomer identification. In each case a major isomer is present, with four CF$_3$ resonances exhibiting a distinctive chemical shift pattern of one peak near δ −45 and three peaks in the region δ −52 to δ −56. This pattern is also found with the thermodynamic isomers of [MCl{η^2-C(CF$_3$)C(CF$_3$)L}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (M = Mo, W; L = PEt$_3$, PMe$_2$Ph or PMePh$_2$) [3a,3b] and with the S-4-MeC$_6$H$_4$ derivatives **6c,d,e** [4] and similar structures to **6ii** are proposed. The minor isomers of **6a,b** also exhibit a characteristic chemical shift pattern, with a more symmetrical distribution of the four CF$_3$ peaks, similar to that for the kinetic isomer **6i**. The situation is therefore comparable to that found with η^2-vinyl isomers of [MoCl{η^2-C(CF$_3$)C(CF$_3$)L}-(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)], except that isomerism of the kinetic form of the SC$_6$F$_5$ derivatives appears to occur more readily, even with significantly milder reaction conditions.

The formation of η^2-vinyl complexes **6a–e** on addition of excess phosphine to oxo-complexes **3a** and **3d** clearly results from oxygen loss, reduction of the metal to the divalent state, and transfer of the SR group back to the metal. A possible



Scheme 2

mechanism for this transformation is illustrated in Scheme 2. It seems likely that removal of oxygen and reduction of the metal is effected by the first mole of phosphine which is oxidised to the phosphine oxide. Phosphine oxides have previously been obtained from reactions of metal phosphine complexes with oxygen [27] whilst phosphines have also been used to remove a sulphur atom from sulphur-containing metal derivatives by forming the phosphine sulphide [28]. If this postulate is correct, in the present case formation of the coordinatively unsaturated intermediate **13** will occur. It is clear that this is not intercepted by a phosphine to give the σ-alkenyl derivative **14** and an extremely rapid transformation to the bis-alkyne complex **2** must occur, possibly via the sequence **13** → **15** → **2**, or alternatively **13** → **16** → **2**. Subsequently, reaction of **2** with the second mole of phosphine gives the final η^2-vinyl complexes **6**.

Whatever the mechanistic details of the reaction we note that addition of phosphines to complexes **3** gives η^2-vinyl complexes **6** that are also obtained by addition of phosphines to alkyne complexes **1** and **2**. This illustrates that reduction of the metal from M^{IV} to M^{II} reverses the insertion process so that the thiolate ligand is transferred back to the metal. These results not only demonstrate that oxidation of the metal leads to migration of thiolate from metal to alkyne, but also the reverse is possible.

Conclusions

It is clear from the reactions described that, although air oxidation of alkyne thiolate complexes **1** and **2** produces oxo complexes in all cases studied, the reaction is sensitive to the metal and the thiolate substituent. The most significant feature of the reactions is that oxidation leads to migration of the thiolate onto an alkyne carbon, i.e. **2** → **3** or alternatively, transformation of an η^2-into a σ-vinyl ligand, i.e. **1** → **3**. In the case of **1a** the η^2-butadienyl complex **4** is formed, possibly via an intermediate α-alkenyl derivative of type **3**, although we have no clear evidence for this. Interestingly, the formation of complexes **3** can be compared with the reactions of $[Mo(O)(RC{\equiv}CR^1)(S_2CNMe_2)_2]$ with trifluoroacetic acid which stereospecifically yield σ-vinyl complexes $[Mo\{C(R){=}C(R^1)H\}(CF_3CO_2)(O)(S_2CNMe_2)_2]$ (R^1 = CO_2Me; R = H, CO_2Me), [29]. Moreover, protonation of the bis alkyne complex $[W(PhC{\equiv}CPh)_2(S_2CNEt_2)_2]$ followed by hydrolysis gives the η^4-butadienyl oxo complex $[W(S_2CNEt_2)(O)\{\eta^4\text{-}C(Ph)C(Ph)C(Ph)C(H)(Ph)\}]$ [30]. Despite differences in the ligands coordinated to the Group 6 metal the bis-dithiocarbamate and cyclopentadienyl alkyne complexes exhibit some similarities in the chemistry of the coordinated alkynes. As reported in a recent communication [9], migratory insertion reactions in η^2-*C*,*C* vinyl and bis-alkyne complexes of type **1** and **2** can also be induced by addition of Lewis basis such as tertiary phosphines when complexes **7** related to **4** are obtained. Alternatively, cyclobutadiene products e.g. $[MoSC_6F_5(PMe_2Ph)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ have been isolated, pointing towards the intermediacy of metallacyclopentadiene complexes of the type obtained previously on addition of isocyanides to complexes **1** and **2** [20]. These diverse results indicate that a variety of factors control the reactivity of coordinated alkynes, an observation we will amplify in forthcoming publications concerning complexes of type **1** and **2**.

Experimental

NMR spectra were recorded on a Bruker WP200 SY spectrometer at 200.13 MHz (^1H) and 188.31 MHz (^{19}F); chemical shifts are referred to $SiMe_4$ and CCl_3F respectively ($\delta = 0$ ppm). Coupling constants are in Hz. IR spectra were recorded on Perkin Elmer 580 spectrometer and mass spectra on a Vacuum Generator's updated AE1 MS9 spectrometer at 70 eV. Reactions were carried out under nitrogen (unless stated otherwise) by standard Schlenk techniques. Solvents were dried by refluxing over powdered calcium hydride (hexane, diethyl ether) or P_2O_5 (dichloromethane) and distilled under nitrogen just before use. Complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) were synthesised by published procedures [21].

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $TlSPr^i$

A mixture of the complex (155 mg, 0.3 mmol) and $TlSPr^i$ (120 mg, 0.43 mmol) in diethyl ether (20 cm^3) was stirred vigorously for 2 h at 20 °C. The mixture was centrifuged to give a yellow-orange solution, which was concentrated in vacuo. Hexane (ca. 5 cm^3) was added, and cooling to −15 °C gave orange-yellow crystals. These were removed and the mother liquor concentrated further to give a second crop. Total yield of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1a**), (110 mg, 65%). MS *m/z* 560 (M^+). Anal. Found: C, 34.2; H, 2.1; S, 5.9. $C_{16}H_{12}F_{12}MoS$ calcd.: C, 34.3; H, 2.2; S, 5.7%. IR ($CDCl_3$) $\nu(C{\equiv}C)$ 1784 (wm) cm^{-1}. ^1H NMR

(C_6D_6) δ 5.06 (s, 5H, C_5H_5), 1.3 (m, 1H, Pr^i), 0.93 (d, *J* 6.3, 3H, Pr^i), 0.31 (d, *J* 6.7, 3H, Pr^i); ^{19}F NMR (C_6D_6) δ −53.96 (qq, *J* 3.5, 3.3, 3F), −56.46 (q, *J* 3.5, 3F), −56.78 (q, *J* 3.6, 3F), −57.84 (qq, *J* 3.6, 3.3 Hz, 3F).

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $TlSBu^t$

A mixture of the complex (160 mg, 0.31 mmol) and $TlSBu^t$ (120 mg, 0.4 mmol) in diethyl ether (30 cm^3) was stirred vigorously for 3 h at 20 °C. The mixture was centrifuged and concentrated in vacuo. Hexane (ca. 10 cm^3) was added and the solution cooled to −15 °C to give orange-yellow crystals. These were removed and the mother liquor concentrated further to give a second batch. Total yield of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SBu^t\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**1b**), (100 mg, 56%). MS *m/z* 574 (M^+). Anal Found: C, 35.2; H, 2.6. $C_{17}H_{14}F_{12}$ MoS calcd.: C, 35.5; H, 2.4%. IR ($CDCl_3$) η(C≡C) 1786 (wm) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.85 (s, 5H, C_5H_5), 1.20 (s, 9H, Bu^t). ^{19}F NMR ($CDCl_3$), δ −53.43 (qq, *J* 3.5, 3.4, 3F), −53.94 (q, *J* 3.8, 3F), −56.32 (qq, *J* 3.6, 1.0, 3F), −57.41 (qqq, *J* 3.8, 3.4, 1.0 Hz, 3F).

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $TlS(4\text{-}Me)C_6H_4$

A mixture of the complex (4 mg, 0.007 mmol) and $TlS(4\text{-}Me)C_6H_4$ (5 mg, 0.015 mmol) in $CD_3C_6D_5$ (ca. 1 cm^3) was stirred vigorously at 20 °C for 5 min and centrifuged quickly to give a yellow solution. This was transferred to an NMR tube under nitrogen and cooled to −50 °C for recording of the NMR spectra. The following data were obtained for complex **1c**, $[Mo(\eta^3\text{-}C(CF_3)C(CF_3)S(4\text{-}Me)\text{-}C_6H_4)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$. ^1H NMR δ 6.37 (m, 4H, C_6H_4Me), 4.76 (s, 5H, C_5H_5), 1.68 (s, 3H, C_6H_4Me). ^{19}F NMR δ −53.10 (qq, *J* 4.5, 3.5, 3F), −55.15 (q, *J* 3.0, 3F), −56.0 (q, *J* 4.5, 3F), −57.41 (qq, *J* 3.3, 3.0 Hz, 3F). Weak signals due to the oxo complex **3b** were also observed.

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ *with* $TlS(4\text{-}Me)C_6H_4$ *in air*

A solution of of the complex (100 mg, 0.19 mmol) and $TlS(4\text{-}Me)C_6H_4$ (80 mg, 0.24 mmol) in diethyl ether (30 cm^3) was stirred in a sealed Schlenk tube under air for 2 h. The resulting solution was centrifuged and concentrated and hexane (ca. 5 cm^3) was added. The solution was cooled to −15 °C to give orange-yellow crystals of $[Mo\{C(CF_3){=}C(CF_3)S(4\text{-}Me)C_6H_4\}(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3b**) (35 mg, 30%). MS *m/z* 608 ($[M-O]^+$). Anal. Found: C, 38.7; H, 1.6. $C_{20}H_{12}F_{12}OMoS$ calcd.: C, 38.5; H, 1.9%. IR (nujol) ν(C≡C) 1808 (wm), ν(C=C) 1559 (w) cm. ^1H NMR ($CDCl_3$, −25 °C) δ 7.23–6.94 (m, 4H, C_6H_4Me), 6.51, 6.47 (s, 5H, C_5H_5), 2.30 (s, 3H, C_6H_4Me). ^{19}F NMR ($CDCl_3$, 20 °C) isomer A δ −49.82 (qq, *J* 14.9, 5.5, 3F), −54.66 (qq, *J* 5.5, 2.9, 3F), −55.64 (q, *J* 15.7, 3F), −56.19 (q, *J* 2.9, 3F); isomer *B* δ − 53.45 (bq, *J* 14.6, 3F), −54.19 (bq, *J* 14.6, 3F), −55.43 (br.s, 3F), −56.11 (q, *J* 3.0 Hz, 3F).

Reaction of $[WS(4\text{-}Me)C_6H_4(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)$ *(2) with air*

A solution of complex **2c** (140 mg, 0.2 mmol) in diethyl ether (30 cm^3) was kept under air at 20 °C for 5 h, during which it turned yellow. The solution was filtered and concentrated in vacuo and hexane (ca. 10 cm^3) was added. The solution was cooled to −15 °C to give yellow crystals of $[W\{C(CF_3){=}C(CF_3)S(4\text{-}Me)C_6H_4\}(O)\text{-}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3d**), (62 mg, 43%). MS *m/z* 712 (M^+). Anal. Found: C, 33.8; H, 1.60. $C_{20}H_{12}F_{12}OSW$ calcd.: C, 33.7; H, 1.7%. IR ($CHCl_3$) ν(C≡C) 1790 (wm), ν(C=C) 1555 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.16 (m, 4H, C$_6$$H_4$Me), 6.53, 6.51 (s, 5H, C$_5$H$_5$), 2.32, 2.29 (s, 3H, C$_6$H$_4$$Me$). ^{19}F NMR (CDCl$_3$) isomer **A** δ −48.66 (m, 3F), −55.46 (q, J 16.0, 3F), −56.08 (m, 3F), −57.42 (q, J 3.5, 3F); isomer **B** δ −53.98 (br.q, J 14.5, 3F), −54.46 (br.q, J 14.0 Hz, 3F), −56.88 (m, 3F), −57.29 (m, 3F).

*Reaction of [MoSC$_6$F$_5$(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] (**2a**) with air*

A solution of complex **2a** (140 mg, 0.20 mmol) in diethyl ether (30 cm^3) was left exposed to the air at 20 °C for 4 h, during which the purple solution turned pale brown. The mixture was filtered and concentrated in vacuo, and hexane (ca. 10 cm^3) was added. The solution was cooled to −15 °C to give off-white crystals of [Mo{C(CF$_3$)=C(CF$_3$)SC$_6$F$_5$}(O)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**3a**) (60 mg, 42%). MS m/z 684 ([M − O]$^+$). Anal. Found: C, 32.9; H, 0.5; S 4.3. C$_{19}$H$_5$F$_{17}$MoOS calcd.: C, 3.26; H, 0.7; S 4.6%. IR (CCl$_4$) ν(C≡C) 1818 (wm) ν(C=C) 1555 (w) cm^{-1} (CDCl$_3$) isomer A, δ 6.55 (s, 5H, C$_5$H$_5$); isomer **B**, 6.65 (s, 5H, C$_5$H$_5$). ^{19}F NMR (CDCl$_3$) isomer **A** δ −49.02 (qq, J 16.1, 6.8, 3F), −55.24 (qq, J 6.8, 2.9, 3F), −55.61 (qt, J 16.2, 2.1, 3F), −56.12 (q, J 2.9, 3F); isomer **B** * δ 51.07 (br.q, J 15.2, 3F), −55.8 (br.s, 3F), −56.29 (q, J 2.9 Hz, 3F).

*Reaction of [WSC$_6$F$_5$(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] (**2b**) with air*

A solution of complex **2b** (210 mg, 0.27 mmol) in thf (30 cm^3) was left in air at 20 °C for 24 h during which the orange solution turned yellow. Solvent was removed and the residue extracted with diethyl ether (30 cm^3) and the extract then filtered concentrated in vacuo. Hexane (10 cm^3) was added and the solution cooled to −15 °C to give yellow crystals. These were recrystallised from dichloromethane/hexane to give 45 mg (28%) of [W$_2$(O)$_n$(CF$_3$C≡CCF$_3$)$_4$ (η^5-C$_5$H$_5$)$_2$] (**5**). MS m/z 587 ([WO(C$_4$F$_6$)$_2$(C$_5$H$_5$)]$^+$). Anal. Found: C, 25.7; H, 0.8. C$_{13}$H$_5$F$_{12}$OW calcd.: C, 26.9; H 0.9%. IR (CDCl$_3$) ν(C≡C) 1782 (wm), 1762 (wm) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.12 (s, C$_5$H$_5$). ^{9}F NMR (CDCl$_3$, 20 °C) δ −58.19 (s, CF$_3$).

*Reaction of [Mo{η^3-C(CF$_3$)C(CF$_3$)SPr^i}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**1a**) with air*

A solution of complex **1a** (80 mg, 0.14 mmol) in diethyl ether (25 cm^3) was kept under air in a sealed tube for 25 h, to give a black solid and a deep purple solution. The solvent was removed in vacuo and the residue extracted with dichloromethane (ca. 10 cm^3) and the extract centrifuged. Addition of hexane (ca. 5 cm^3), concentration in vacuo, and cooling to −15 °C gave a lustrous deep green/purple microcrystalline solid [Mo{η^2-C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)SPr^i}(O)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**4**), (22 mg, 27%). Anal. Found: C, 32.8; H, 2.1; S, 6.0. C$_{16}$H$_{12}$F$_{12}$OMoS calcd.: C, 33.3; H, 2.1; S, 5.6%. IR (CDCl$_3$) ν(C≡C) 1601 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.38, 6.18 (s, 5H, C$_5$H$_5$), 3.60 (m, 1H, Pr^i), 1.32 (overlapping signals, 6H, Pr^i). ^{19}F NMR (CDCl$_3$) δ −49.48 (q, J 16.3, 3F), −49.79 (q, J 16.2, 3F), −54.43 (q, J 16.7, 3F), −55.0 (qq, J 16.4, 3.3, 3F), −55.19 (qq, J 13.9, 1.7, 3F), −55.47 (qq, J 13.8, 3.3, 3F), −58.18 (q, J 13.8, 3F), −58.33 (q, 13.6 Hz, 3F).

*Reaction of [W{η^3-C(CF$_3$)C(CF$_3$)SPr^i}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**1d**) with air*

A solution of complex **1d** (30 mg, 0.05 mmol) in diethyl ether (15 cm^3) was kept for 24 h under air. The mixture was concentrated and washed through Florisil with

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* One CF$_3$ signal obscured by isomer A peak at δ −55.61.

diethyl ether/hexane (1/1) to give a pale brown solution. This was concentrated in vacuo and on cooling an impure light brown solid was obtained. This was recrystallised several times from diethyl ether/hexane to give yellow crystals of $[W\{C(CF_3)=C(CF_3)SPr^i\}(O)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3c**) (9 mg, 29%). MS *m/z* 644 ($[M-O]^+$). Anal. Found: C, 29.3; H, 1.9. $C_{16}H_{12}F_{12}OSW$ calcd.: C, 28.9; H, 1.8%. IR ($CDCl_3$) $\nu(C\equiv C)$ 1788 (wm) $\nu(C=C)$ 1555 (w) cm^{-1}. ^1H NMR ($CDCl_3$) isomer **A** δ 6.52 (s, 5H, C_5H_5), ~ 3.5 * (m, 1H, Pr^i), 1.25 (d, *J* 6.7, 3H, Pr^i), 1.18 (d, *J* 6.6, 3H, Pr^i); isomer **B** δ 6.59 (s, 5H, C_5H_5) ~ 3.5 * (m, 1H, Pr^i), 1.27 (d, *J* 6.6, 3H, Me), 1.07 (d, *J* 6.9, 3H, Pr^i). ^{19} F NMR ($CDCl_3$) isomer **A** δ −48.42 (qq, *J* 16.7, 6.0, 3F), −56.33 (qq, *J* 6.0, 3.5, 3F), −56.79 (q, *J* 16.7, 3F), −57.47 (q, *J* 3.5, 3F); isomer **B** δ −51.58 (q, *J* 15.6, 3F), −55.99 (q, *J* 15.6, 3F), −57.25 (q, *J* 3.4, 3F), −57.61 (*q*, *J* 3.4 Hz, 3F). Ratio **A/B** = 3/2.

Reaction of $[Mo\{C(CF_3)=C(CF_3)SC_6F_5\}(O)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *(3a) with* PEt_3

A solution of complex (**3a**) (50 mg, 0.07 mmol) in diethyl ether (15 cm^3) was treated with three molar equivalents of PEt_3 upon which the colourless solution immediately turned yellow. The solution was concentrated in vacuo, hexane (ca. 5 cm^3) was added, and the solution cooled to −15 °C to give yellow crystals. These were recrystallised from dichloromethane/hexane to give 52 mg (91%) of $[MoSC_6F_5\{\eta^2\text{-}C(CF_3)C(CF_3)PEt_3\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**6a**). MS *m/z* 684 ($[M-PEt_3]^+$). Anal. Found: C, 37.5; H, 2.4. $C_{25}H_{20}F_{17}MoPS$ calcd.: C, 37.40; H, 2.30%. IR ($CDCl_3$) $\nu(C\equiv C)$ 1805 (wm) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.73 (kinetic isomer) 5.57 (thermodynamic isomer) (s, 5H, C_5H_5), 2.64–2.22 (complex m, 6H, CH_2) 1.24 (dt *J*(P–H) 17.5, *J*(H–H) 7.5 9H, CH_3); ^{19}F NMR ($CDCl_3$) (kinetic isomer) δ −46.90 (q, *J* 3.5, 3F), −49.89 (br.q, *J* 5.0, 3F), −55.33 (br.s, 3F), −56.85 (m, 3F); (thermodynamic isomer), −45.43 (m, 3F), −52.67 (sept, 3F), −53.61 (br.q, *J* 4.0 Hz, 3F), −55.39 (sept, 3F).

Reaction of $[Mo\{C(CF_3)=C(CF_3)SC_6F_5\}(O)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *(3a) with* PMe_2Ph

When a solution of complex **3a** (50 mg 0.07 mmol) in diethyl ether (15 cm^3) was treated with three molar equivalents of PMe_2Ph it turned yellow. The mixture was concentrated in vacuo, hexane (ca. 5 cm^3) was added and the solution cooled to −15 °C to give yellow crystals. These were recrystallised from hexane to give 31 mg (53%) of $[MoSC_6F_5(\eta^2\text{-}C(CF_3)C(CF_3)PMe_2Ph\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**6b**). MS *m/z* 684 ($[M-PMe_2Ph]^+$). Anal. Found: C, 38.8,; H, 1.7. $C_{27}H_{16}H_{17}MoPS$ calcd.: C, 39.40; H, 1.0 %. IR ($CDCl_3$) $\nu(C\equiv C)$ 1795 (wm) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.79 (kinetic isomer) δ 5.57 (thermodynamic isomer) (s, 5H, C_5H_5) 7.8–15 (m, H, Ph), 2.34 (d, *J*(P–H) 13.1, 3H, Me): ^{19}Fe NMR ($CDCl_3$) (kinetic isomer) δ −46.93 (m, 3F), −49.32 (br.q, *J* 4.5 Hz, 3F), −54.72 (br.m, 3F), 56.87 (m, 3F); (thermodynamic isomer) δ −45.66 (br.s, 3F), −51.62 (sept., 3F), −53.79 (br.s, 3F), −55.48 (m, 3F).

Reaction of $[W\{C(CF_3)=C(CF_3)S(4\text{-}Me)C_6H_4\}(O)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ *(3d) with* PEt_3

When a solution of complex **3d** (17 mg, 0.02 mmol) in diethyl ether (10 cm^3) was treated with three molar equivalents of PEt_3 the colourless solution turned yellow.

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* Overlapping signals.

The mixture was concentrated in vacuo, hexane (ca. 4 cm^3) was added and the solution cooled to $-15\,^\circ$C to give orange crystals. These were recrystallised from dichloromethane/hexane to give $[\mathrm{WS\text{-}4\text{-}MeC_6H_4\{\eta^2\text{-}C(CF_3)C(CF_3)PEt_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$ (**6c**) (14 mg, 72%). MS *m/z* 696 ($[M-\mathrm{PEt_3}]^+$).

Reaction of $[\mathrm{W\{C(CF_3){=}C(CF_3)S(4\text{-}Me)C_6H_4\}(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$ *(3d) with* $\mathrm{PMe_2Ph}$

A solution of complex **3d** (16 mg, 0.02 mmol) in diethyl ether (10 cm^3) was treated with three molar equivalents of $\mathrm{PMe_2Ph}$ to give a yellow solution. This was concentrated in vacuo, hexane (ca. 4 cm^3) was added and the solution cooled to $-15\,^\circ$C to give orange-yellow crystals. These were recrystallised from dichloromethane/hexane to give 11 mg (59%) of $[\mathrm{WS(4\text{-}Me)C_6H_4\{\eta^2\text{-}C(CF_3)C(CF_3)PMe_2Ph\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$ (**6d**). MS *m/z* 969 ($[M-\mathrm{PMe_2Ph}]^+$).

Reaction of $[\mathrm{W\{C(CF_3){=}C(CF_3)S(4\text{-}Me)C_6H_4\}(O)(CF_3C{\equiv}CCF_3)(\eta^5 - C_5H_5)}]$ *(3d) with* $\mathrm{PMePh_2}$

A solution of complex **3d** (26 mg, 0.04 mmol) in diethyl ether (10 cm^3) was treated with three molar equivalents of $\mathrm{PMePh_2}$ to give a yellow solution. The mixture was concentrated in vacuo, hexane (ca. 5 cm^3) was added and the solution cooled to $-15\,^\circ$C to give orange-yellow crystals. These were recrystallised from dichloromethane/hexane at to give 17 mg (52%) of $[\mathrm{WS(4\text{-}Me)C_6H_4\{\eta^2\text{-}C(CF_3)C(CF_3)PMePh_2\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$ (**6e**). MS *m/z* 969 ($[M-\mathrm{PMePh_2}]^+$).

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