Reactions of Electrophilic Alkynes with Some Iron and Tungsten Sulphur, Selenium, and Arsenic Complexes†

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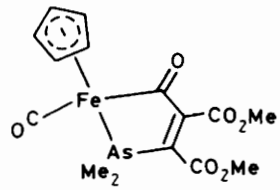
Reactions of $[Fe(AsMe_2)(CO)_2(\eta^5\text{-}C_5H_5)]$, $[W(AsMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]$, and $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ with activated alkynes $CF_3C{\equiv}CCF_3$ and/or $MeO_2CC{\equiv}CCO_2Me$ afford metallacyclic complexes $[Fe\{C(O)C(CO_2Me){=}C(CO_2Me)AsMe_2\}(CO)(\eta^5\text{-}C_5H_5)]$, $[W\{C(O)C(R){=}C(R)AsMe_2\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (R = CF_3 or CO_2Me), and $[W\{C(O)C(R){=}C(R)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (R = CF_3, R' = Pr^n; R = CO_2Me, R' = Pr^i or Pr^n) or the η^2-vinyl complex $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ when R' = Pr^i. The photolytic reaction of $[W(SePh)(CO)_3(\eta^5\text{-}C_5H_5)]$ with $CF_3C{\equiv}CCF_3$ gives an alkyne derivative $[W(SePh)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$. A similar species $[W(SC_6H_4Me\text{-}4)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ was obtained from the thermal reaction of $[W(SC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ with $CF_3C{\equiv}CCF_3$ *via* metallacyclic $[W\{C(O)C(CF_3){=}C(CF_3)SC_6H_4Me\text{-}4\}(CO)_2(\eta^5\text{-}C_5H_5)]$ and η^2-vinyl $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SC_6H_4Me\text{-}4\}(CO)_2(\eta^5\text{-}C_5H_5)]$ intermediates. In contrast, $[W\{C(O)C(CF_3){=}C(CF_3)SPr^n\}(CO)_2(\eta^5\text{-}C_5H_5)]$ isomerises *via* an η^2-vinyl analogue into the S-bonded vinyl ketone complex $[W\{C(CF_3){=}C(CF_3)C(O)SPr^n\}(CO)_2(\eta^5\text{-}C_5H_5)]$ as a result of a 1,3 SR' shift across the metallacyclic ring. Such a shift is also observed on thermal isomerisation of $[W\{C(O)C(CO_2Me){=}C(CO_2Me)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (R' = Me or Pr^i) but this proceeds *via* a σ-vinyl intermediate $[W\{C(CO_2Me){=}C(CO_2Me)SR'\}(CO)_3(\eta^5\text{-}C_5H_5)]$ to give both S- and O-metallated isomeric vinyl ketone derivatives. The mechanism of the shift is discussed in terms of three alternative pathways which are determined by the nature of the group R on the alkyne. The η^2-vinyl complexes $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (R' = Me or Pr^i), on reaction with two-electron donor ligands L = CO, $CNBu^t$, PMe_2Ph, or $P(OMe)_3$, afford η^3-lactone derivatives $[W\{\eta^3\text{-}C(CF_3)C(CF_3)C(SR')OC(O)\}(CO)L(\eta^5\text{-}C_5H_5)]$ as a result of cyclisation of the η^2-vinyl ligand with a co-ordinated carbonyl group.

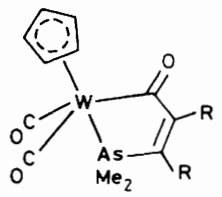
It is now well established that a wide range of alkynes insert into metal–hydrogen[1,2] and to a lesser extent into metal–carbon[1,3] bonds whereas insertion into metal–sulphur bonds is generally observed only with activated alkynes such as hexafluorobut-2-yne (hfb) and dimethyl acetylenedicarboxylate (dmad).[1,4] Previously we reported that alkyne insertions into the tungsten–sulphur bond of $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ are promoted by electron-donating substituents, *e.g.* Me or Et,[5] on the sulphur whereas electron-withdrawing substituents, *e.g.* C_6F_5, inhibit such reactions.[6] Moreover metallacyclic complexes $[W\{C(O)C(R){=}C(R)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$, the primary products of insertions into the W–S bond of $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R' = Me or Et), were found to undergo a novel 1,3 SR' shift reaction leading to η^2-vinyl and vinyl ketone complexes.[5] Related studies by Sharp and Petillon[7] illustrated broadly similar features although differences were observed which can be attributed to the different reaction conditions employed.

With two objectives in mind, (*a*) obtaining a clearer understanding of insertion reactions involving alkynes and metal–heteroatom bonds and (*b*) establishing a plausible mechanism for the 1,3 sulphur shift reaction, we have extended our investigations into reactions between activated alkynes and mercapto complexes. In addition, limited studies involving metal–selenium and –arsenic derivatives have also been carried out. The more novel aspects of this work have been reported in communication form.[8]

† *Non-S.I. unit employed:* atm = 101 325 Pa.



(1)



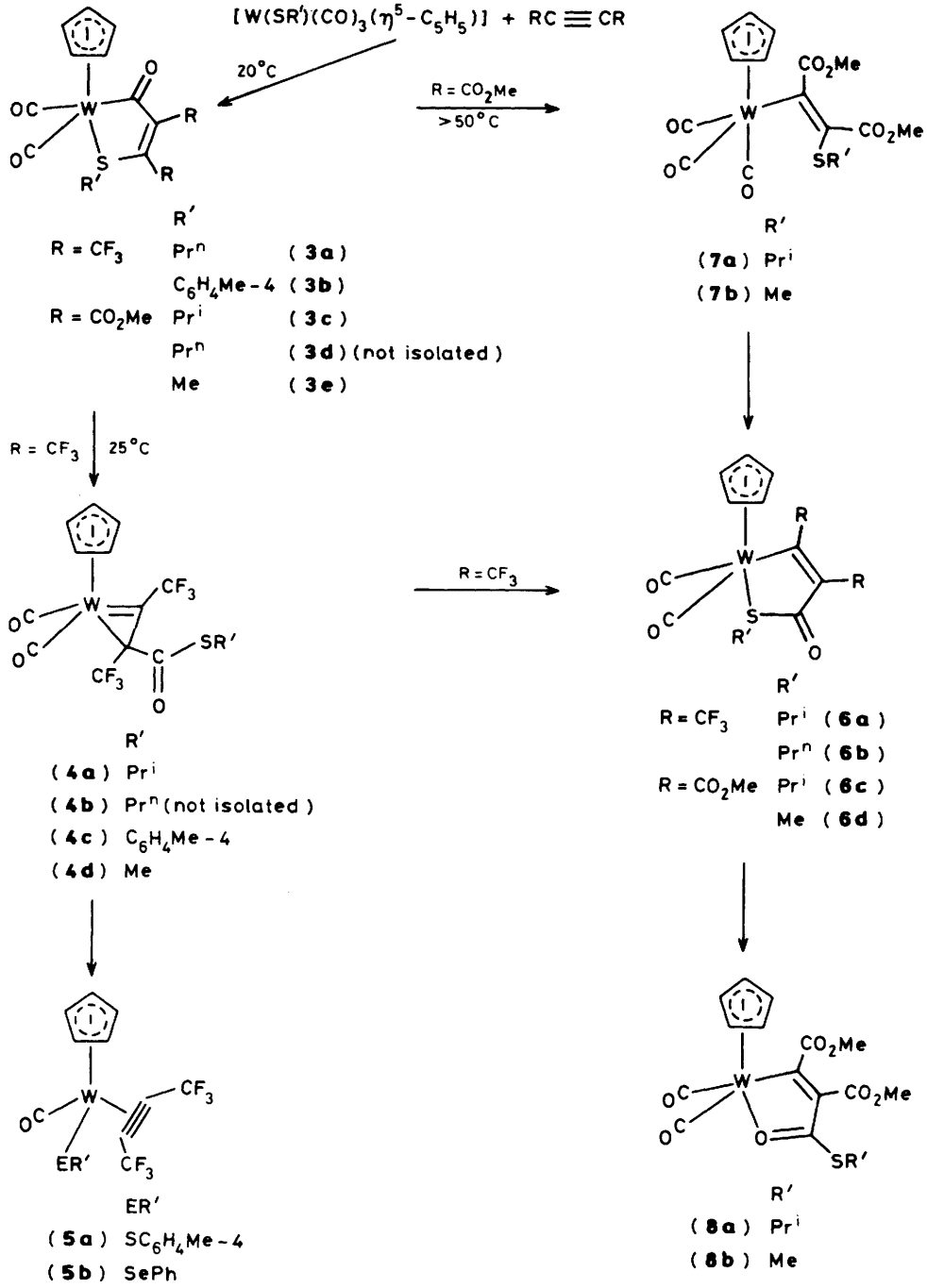
R

(2a) CF_3

(2b) CO_2Me

Results

Reactions of Iron and Tungsten Complexes with hfb ($CF_3C{\equiv}CCF_3$) *and dmad* ($MeO_2CC{\equiv}CCO_2Me$).—The dimethylarsenido complexes $[Fe(AsMe_2)(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[W(AsMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]$ react with dmad in cyclohexane at room temperature to give 1:1 adducts (**1**) and (**2b**) respectively while hfb and $[W(AsMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]$ similarly give (**2a**) under these conditions. Spectroscopic features of (**1**) and (**2**) are similar to those of related mercapto complexes $[Fe\{C(O)C(CF_3){=}C(CF_3)SR'\}(CO)(\eta^5\text{-}C_5H_5)]$ and $[W\{C(O)C(CF_3){=}C(CF_3)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ reported previously.[5,7,8] Thus a strong band in the i.r. spectrum near 1 600 cm^{-1} is assigned as an acyl CO stretching mode while the ^{19}F n.m.r. spectrum of (**2a**) exhibits two quartets with coupling constant J_{FF} = 10.5 Hz consistent with a *cis*-$C(CF_3){=}C(CF_3)$ moiety.[9] Accordingly similar structures are proposed. However,



Scheme 1.

unlike the tungsten mercapto derivatives (**3**) (see below), (**2a**) and (**2b**) do not undergo thermal isomerisation in benzene even after several days at 90—110 °C.

Reactions of mercapto complexes $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R′ = Me or Et) with alkynes RC≡CR (R = CF_3 or CO_2Me) have previously been shown to give metallacyclic derivatives of type (**3**) at room temperature in hexane.[5] Subsequent isomerisation of (**3**) was observed at higher temperatures to give products of a 1,3 sulphur shift, (**4**)—(**6**) and (**8**) when R = CF_3 or (**6**) and (**8**) when R = CO_2Me. Broadly similar reactions were observed in the present work with SPr^i and SPr^n tungsten derivatives (see Scheme 1) but with important detailed differences as will now be described. Thus $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R′ = Pr^n) reacts with hfb in hexane at 4 °C to give (**3a**) the analogue of (**2**) in 53% yield, whereas the product of thermal rearrangement of such a species, the η^2-vinyl complex (**4a**), was isolated in the case of the isopropyl mercapto complex (R′ = Pr^i). However, $[W(SPr^i)(CO)_3(\eta^5\text{-}C_5H_5)]$ and dmad react smoothly in hexane at 20 °C to give the primary product (**3c**) in 45% yield whereas the SPr^n complex did not give isolable products although (**3d**) was detected in the product mixture by i.r. spectroscopy.

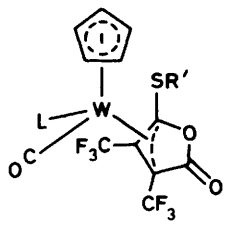
Previously we have observed that $[W(SC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ and hfb react at 60 °C in diethyl ether to give the alkyne complex (**5a**),[5] but only spectroscopic evidence for the intermediate η^2-vinyl complex (**4c**) was obtained.[5] This reaction

was repeated at 20 °C which led to the isolation of two intermediates (**3b**) and (**4c**) in approximately equal quantities but low overall yield due to the ease with which thermal rearrangement occurs to give (**5a**). Consequently analytical data were not obtained and the structures of (**3b**) and (**4c**) are assigned on the basis of i.r., n.m.r., and mass spectroscopic data which are similar to those of fully characterised species (**3a**) and (**4a**). Intermediates of type (**3**) and (**4**) were not detected in the photochemical reaction of $[W(SePh)(CO)_3(\eta^5\text{-}C_5H_5)]$ with hfb in diethyl ether which yielded dark red crystals of $[W(SePh)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**5b**) as the sole product (43%) following chromatography of the product solution. In contrast, attempts to isolate adducts of $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R' = Bu^t or CH_2Ph) with hfb or dmad (R' = Bu^t) were unsuccessful due to extensive decomposition.

The structures of complexes (**3**)—(**5**) are proposed on the basis of spectroscopic data which are similar to those of related MeS, EtS, or C_6F_5S derivatives reported previously.[5,6] The structures of (**4d**)[5] and (**5**) (M = Mo, R' = C_6F_5)[10] have previously been confirmed by single-crystal *X*-ray diffraction studies. In the case of $[W(SePh)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ the two quartets in the ^{19}F n.m.r. spectrum at 20 °C confirm that the alkyne ligand adopts a fixed orientation probably with the C≡C axis parallel to the M–CO bond as found in $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$.[10] However fluxional behaviour is observed at higher temperatures as evidenced by the gradual broadening of the two resonances and their ultimate coalescence to a singlet above 115 °C. We attribute this to alkyne propeller rotation, a well known phenomenon in mono- and bis-alkyne complexes of this type.[11]

Thermal Isomerisation Reactions.—The metallacyclic complex (**3a**) was converted in low yield (13%) to the S-bonded vinyl ketone complex (**6b**) by the action of gentle heat (30 °C) on a suspension of the solid in hexane in a sealed tube. An η^2-vinyl complex (**4b**) was detected by i.r. spectroscopy (but not isolated) in low concentration during the reaction and not surprisingly the η^2-vinyl SPr^i complex (**4a**) was also found to undergo isomerisation to the vinyl ketone derivative (**6a**) under similar conditions. The dmad metallacycle (**3c**) as with (**3e**)[5] requires higher temperatures for isomerisation and at 90 °C reacts in hexane to produce a mixture which was separated by chromatography over Florisil giving red crystals of (**8a**), an impure red product (**6c**), and a third red solid in quantities too small for characterisation. Attempts to purify (**6c**) for analytical purposes were unsuccessful and identification is based on a comparison of spectroscopic data with those of (**6d**).[5] In the early stages of thermolysis a yellow solid crystallised out from the reaction mixture but this gradually disappeared as the reaction continued and was not observed in the final product mixture. Consequently the reaction was repeated at lower temperatures (*ca.* 60 °C) when yellow crystals of (**7a**) were obtained in 15% yield. Thermolysis of complex (**3e**) which was originally observed to give (**6d**) followed by (**8b**),[5] was subsequently repeated and after 18 h at 65 °C in hexane small quantities of (**7b**) and red crystals of (**8b**) were isolated in 5 and 20% yield respectively. Small amounts of (**6d**) were detected during this reaction but not isolated.

Complexes (**6a**)—(**6c**) and (**8a**) are assigned isomeric vinyl ketone structures by comparison of spectroscopic data with those of methyl and ethyl derivatives reported previously[5] and structurally characterised by *X*-ray diffraction methods in the case of (**6d**).[12] Complexes (**7a**) and (**7b**), analogues of which were not detected on thermolysis of hfb adducts of type (**3**), are assigned a σ-vinyl structure on the basis of spectroscopic data. The mass spectra exhibit molecular ions $[M]^+$ which undergo sequential loss of CO giving rise to ions $[M - CO]^+$, $[M - 2CO]^+$, and $[M - 3CO]^+$. Significantly, the i.r. spectra



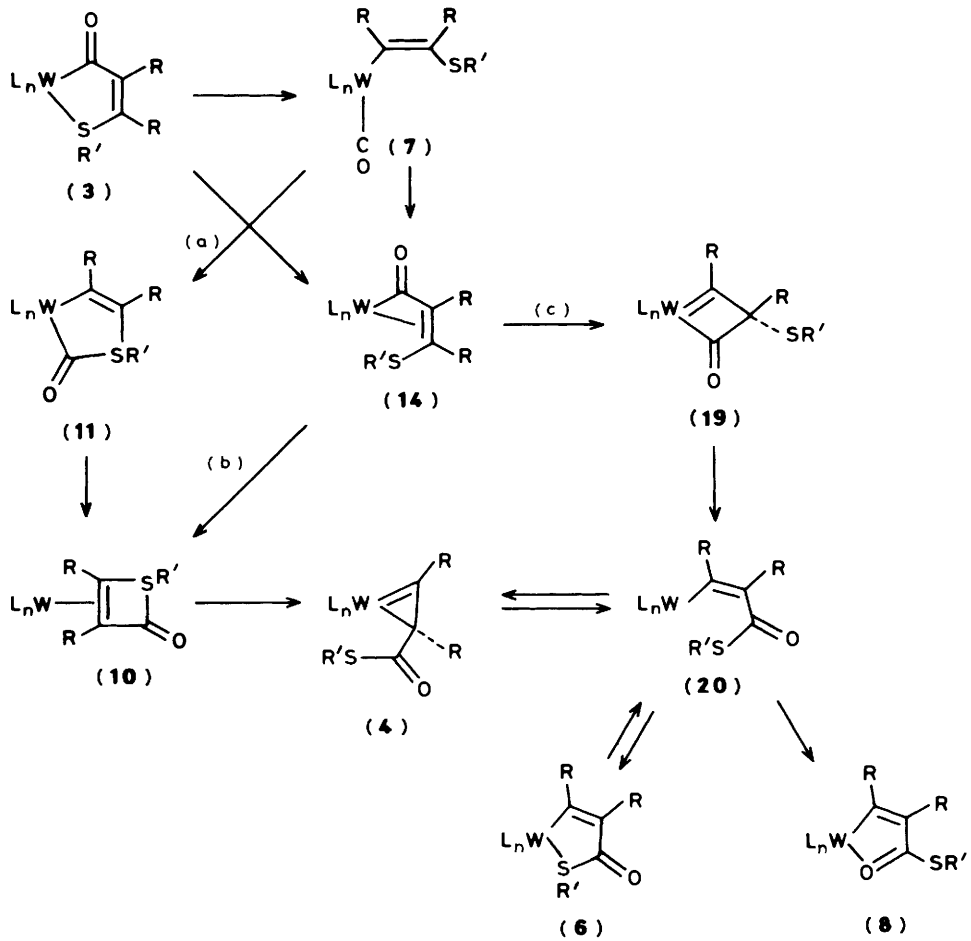
L	R' = Me	R' = Pr^i
PMe_2Ph	(**9a**)	(**9e**)
$P(OMe)_3$	(**9b**)	(**9f**)
$CNBu^t$	(**9c**)	(**9g**)
CO	(**9d**)	(**9h**)

exhibit the familiar group of three CO stretching modes ($2a' + a''$) near 2 000 cm^{-1} expected of a metal tricarbonyl system with C_s symmetry.[13] The frequencies exhibit a shift of *ca.* 15—20 cm^{-1} to higher energy relative to those of $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$, consistent with the attachment of a more electronegative group to the tungsten centre. The ^1H n.m.r. spectra exhibit peaks due to an $\eta^5\text{-}C_5H_5$ ligand, an SR' group, and two inequivalent CO_2Me groups. Unfortunately, this does not provide information concerning the stereochemistry of the vinyl ligand but we assume a *cis* disposition of CO_2Me groups in view of this arrangement in the precursor (**3**) and product (**6**). We note that σ-mercapto vinyl complexes $[Fe\{C(CF_3){=}C(CF_3)SR'\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (R' = CF_3 or C_6F_5) previously isolated from reactions of $[Fe(SR')(CO)_2(\eta^5\text{-}C_5H_5)]$ with hfb[4c] have been shown by ^{19}F n.m.r. spectroscopy to exhibit a *cis* geometry. More detailed inspection of the n.m.r. spectrum of the isopropyl derivative (**7a**) provides further support for the proposed structure. For complexes (**3c**) and (**6c**) where co-ordination of the sulphur results in two methyl groups becoming inequivalent and hence diastereotopic, two doublets are observed. In contrast only one doublet is observed in the spectrum of (**7a**), consistent with the absence of a chiral centre. This feature also serves to distinguish between the isomeric vinyl ketones (**6c**) and (**8a**), the former in which the sulphur is co-ordinated to the metal giving two doublets, the latter one doublet consistent with the removal of the SPr^i group from a chiral centre.

Reactions of η^2*-Vinyl Complexes* (**4a**) *and* (**4d**) *with Nucleophiles.*—The η^2-vinyl complexes react with two-electron donors L = PMe_2Ph, $P(OMe)_3$, or $CNBu^t$ in diethyl ether at 20 °C to give yellow crystalline adducts (**9**) in yields ranging from poor (L = $CNBu^t$) to good (L = PMe_2Ph). In each case the i.r. spectrum exhibits a terminal ν(CO) band near 1 980 cm^{-1} and a ketonic ν(CO) mode near 1 740 cm^{-1}, while the ^{19}F n.m.r. spectrum exhibits two quartets with coupling constants J_{FF} = *ca.* 8—9 Hz characteristic of *cis* CF_3 groups.[9] It was subsequently found that carbonylation of (**4a**) and (**4d**) (CO, 4 atm, 20 °C) gave dicarbonyls (**9d**) and (**9h**) with similar spectroscopic features. Significantly, the methyl derivative (**9d**) was found to exhibit identical features to those of $[W(CO)_2\{\eta^3\text{-}C(CF_3)C(CF_3)C(SMe)OC(O)\}(\eta^5\text{-}C_5H_5)]$ isolated from the photolytic reaction of $[W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$ with hfb in a sealed system.[7a] This was shown by *X*-ray diffraction studies to contain a lactone ring resulting from condensation of two CO ligands, one $CF_3C{\equiv}CCF_3$ and one SMe group and on this basis we assign a similar structure to complexes (**9**).

Discussion

The reactions of $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (R' = Pr^n, Pr^i, or C_6H_4Me-4) with electrophilic alkynes hfb and/or dmad are broadly similar to those of analogous methyl- and ethyl-thio

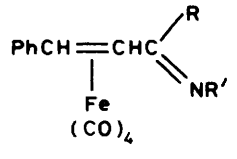


Scheme 2. R = CF_3 or CO_2Me, L_n = $(\eta^5\text{-}C_5H_5)(CO)_2$

complexes described previously.[5,7] The key step in these reactions appears to be carbon–sulphur bond formation resulting in the initial formation of metallacyclic derivatives (**3**). To account for this we previously proposed a mechanism involving nucleophilic attack by the mercapto ligand of $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ at an alkyne carbon.[5] In contrast, selenium ligands RSe are generally considered to have reduced nucleophilic character relative to RS groups,[14] and it is perhaps not surprising to find that, as with $[M(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; R′ = CF_3 or C_6F_5),[5,6] reaction of $[W(SePh)(CO)_3(\eta^5\text{-}C_5H_5)]$ with hfb gives (**5b**) rather than a selenium analogue of (**3**). However, the Me_2As ligand appears to be sufficiently nucleophilic to promote attack on hfb and dmad, although not as readily as the SR′ group since the yields of metallacyclic products (**1**) and (**2**) were much lower than those of (**3**).

In previous publications describing the formation of metallacyclic mercapto complexes (**3**) (R′ = Me or Et) we also reported the novel isomerisation of (**3**) into (**4**) (R = CF_3, R′ = Me) which involves the 1,3 shift of the SR′ group across the eneone portion of the metallacycle.[5] This reaction proceeds readily under mild conditons (*ca.* 30 °C) whereas in contrast isomerisation of $[W\{C(O)C(CF_3)=C(CF_3)AsMe_2\}(CO)_2(\eta^5\text{-}C_5H_5)]$ could not be effected even after several days at *ca.* 100 °C. Moreover the 1,3 sulphur shift appears to be promoted by electron-donating substituents since (**3**; R = CF_3) undergoes thermal rearrangement above 25 °C at a rate which increases in the order R′ = Me < Et < Pr^n. Moreover with R′ = Pr^i, (**3**) was not even detected in the reaction of $[W(SPr^i)(CO)_3(\eta^5\text{-}C_5H_5)]$ with hfb which gives the 1,3 shift products (**4a**) and (**6a**) directly. These features are explicable in terms of the previously proposed mechanism in Scheme 2 involving ring contraction to produce the intermediate zwitterion (**10**) which undergoes C–S bond fission to yield the η^2-vinyl (**4**). The effect of electron-donating groups R′ on sulphur will be two fold: (*a*) to increase the nucleophilicity of sulphur in (**3**) so as to promote attack on the electron-deficient acyl carbon; (*b*) to stabilise the resulting positive charge on sulphur in the intermediate zwitterion (**10**). An alternative explanation for the observed order of reactivity of complexes (**3**) is based on increased steric destabilisation of (**3**) in the order R′ = Me < Et < Pr^n < Pr^i. Although this argument is tenable in the case of the mercapto complexes, the fact that the arsenic derivative (**2a**) does not undergo a 1,3 shift under much more extreme conditions, despite the presence of two CH_3 groups on the co-ordinated arsenic atom, argues in favour of electronic control. Conceivably the absence of a lone pair on the arsenic atom in (**2**) hinders the initial cyclisation reaction and as a consequence a zwitterionic intermediate (**10**) cannot be formed.

A third feature of the 1,3 shift reaction is its sensitivity to the substituent R on the alkyne-derived portion of the metallacyclic ring of (**3**) since adducts derived from dmad are thermally more stable than their hfb analogues and do not undergo significant isomerisation below *ca.* 50 °C. A 1,3 sulphur shift is again observed as illustrated by the isolation of vinyl ketone complexes (**6**) with R′ = Me[5] or Pr^i in addition to the thermodynamically more stable O-metallated isomer (**8**) at higher temperatures. However η^2-vinyl intermediates, *cf.* (**4**), were not detected in this case which may, in view of the higher



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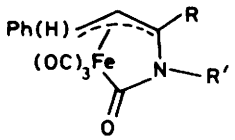

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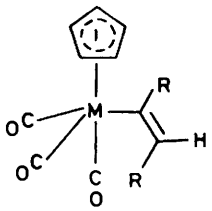
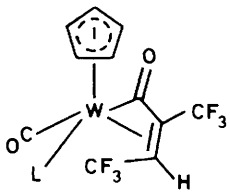


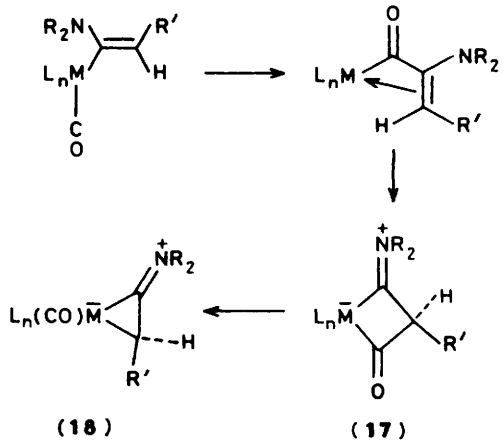


	M	R	L
(15a)	W	CF_3	(16a) CO
(15b)	W	CO_2Me	(16b) $P(OMe)_3$
(15c)	Mo or W	CN	

temperatures required, be explained by the observed thermal instability of such species. Alternatively this may indicate that different mechanistic routes are available for the 1,3 shift process, depending on the nature of R in (3). This follows from the observation that only with R = CO_2Me are σ-vinyl intermediates (7) observed in the isomerisation (3) ⟶ (6) where η^2-vinyl species (4) are observed when R = CF_3. It can therefore be concluded that although the 1,3 shift mechanism we previously proposed,[5] *i.e.* (3) ⟶ (10) ⟶ (4) ⟶ (6) (Scheme 2), can adequately account for the isomerisation of complex (3) when R = CF_3, the results obtained with R = CO_2Me indicate that more complex processes are involved. Clearly in this case at least, transfer of the acyl CO in (3) back to the metal to give (7) precedes the sulphur shift. The subsequent transformation (7) ⟶ (6) can then be accomplished in three different ways, Scheme 2, paths (a), (b), or (c), which may or may not involve η^2-vinyl intermediates.

Path (a) involves nucleophilic attack by sulphur on a co-ordinated carbonyl ligand in complex (7) to give zwitterion (11) which undergoes ring contraction to (10) followed by ring opening giving the η^2-vinyl (4), and subsequently the vinyl ketone complexes (6) and (8), depending on the reaction conditions. This pathway is suggested by the observation that azadiene complexes of iron (12) can be transformed into isomeric carbamoyl derivatives (13) as a result of nucleophilic attack by nitrogen at a co-ordinated CO.[15] Alternative pathways (b) and (c) could involve an acryloyl intermediate (14) resulting from migration of the σ-vinyl ligand onto an adjacent carbonyl group. We note that σ-vinyl complexes (15) have previously been isolated from reactions of $[WH(CO)_3(\eta^5\text{-}C_5H_5)]$ with hfb,[16] dmad,[2b] and dicyanoacetylene[2d] and significantly the hfb adduct (15a) on photolysis could be isomerised to the η^3-acryloyl complex (16a) which was characterised by single-crystal *X*-ray diffraction studies. In the present case we also recognise that (14) could well be formed directly from complex (3). Assuming that (14) is a plausible intermediate in the reaction, the mercapto group is nicely set up for nucleophilic attack on the acryloyl carbonyl, path (b), thus leading to zwitterion (10) and hence (4).

However a third possibility, path (c), is equally plausible based on the report that σ-vinyl complexes obtained from the insertion reactions of $[MH(CO)_2L(\eta^5\text{-}L')]$ (M = Mo or W; L = CO or phosphite; L′ = C_5H_5, C_5H_4Me, or indenyl) have



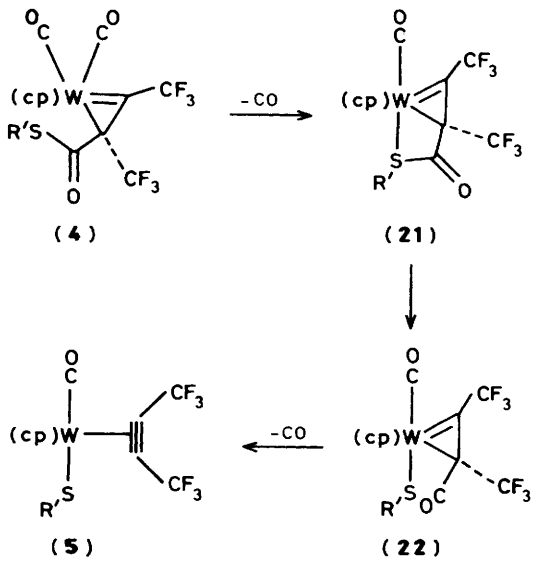
(18) (17)

Scheme 3. $L_n = (\eta^5\text{-}C_5H_5)(CO)_2$

been shown to undergo isomerisation *via* acryloyl complexes into aminocarbenes (17) (Scheme 3).[17] Moreover all of these species can be transformed into η^2-vinyl-like complexes (18). In the same way the acryloyl intermediate (14) in Scheme 2 could rearrange to (19), *cf.* (17), and then, as a result of 1,2 sulphur shift, give the σ-vinyl ketone (20). Ultimately this can undergo an η^2 ⟶ σ transformation giving (4) when R = CF_3 or alternatively chelate-ring formation giving (6) and/or (8). Clearly (20) could also function as an intermediate in the observed isomerisation of complex (4) into (6) and (6) into (8)[5] since it is accessible from (4) and (6) by ring opening. Thus all products which result from the 1,3 sulphur shift can in principle be accounted for in terms of kinetically and thermodynamically controlled rearrangement of (20). Attractive and simple as this proposal may be we have no evidence which favours this mechanism over the alternatives already discussed.

The results of the present work also allow us to reach more detailed conclusions concerning mechanistic pathways leading to the alkyne complexes (5). Thermal rearrangement of the η^2-vinyl derivative (4; R = CF_3, R′ = Me) has previously been shown to produce two products (5) and (6) and we could not eliminate the possibility that the S-metallated vinyl ketone (6), which isomerises to the O-metallated form (8), could also function as the immediate precursor to the alkyne derivative (5).[5] This would merely require C–S bond fission and CO dissociation. However, the observation that thermolysis of the SC_6H_4Me-4 derivative (3b) initially gives the η^2-vinyl complex (4c), which subsequently isomerises to (5a) exclusively, argues in favour of two distinct pathways for the transformation of (4) into (5) and (6). This conclusion is reinforced by the fact that the dmad derivatives (3) do not produce alkyne complexes (5); instead the alternative sequence (3) ⟶ (6) ⟶ (8) is observed exclusively. The transformation of complex (4) into (6) involves a simple η^2 ⟶ σ vinyl rearrangement with concomitant metal–sulphur bond formation. The latter process is also involved in the alternative production of (5) but CO dissociation from the metal and CO extrusion from the η^2-vinyl ligand are also required. This could occur *via* intermediates (21) and (22) in Scheme 4 which are related to structurally characterised η^2-vinyl complexes $[Mo\{C(CF_3)C(CF_3)C_5H_4NS\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[18] and $[WCl\{\eta^2\text{-}C(CF_3)C(CF_3)CNBu^t\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[19] reported previously.

Following our initial publication of the synthesis and *X*-ray diffraction study of complex (4d) containing the first example of a vinyl ligand bonded in an η^2 manner to the metal atom, further examples of such species have been reported. Most have been isolated from the addition of nucleophiles to neutral, *e.g.* $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W),[18] or

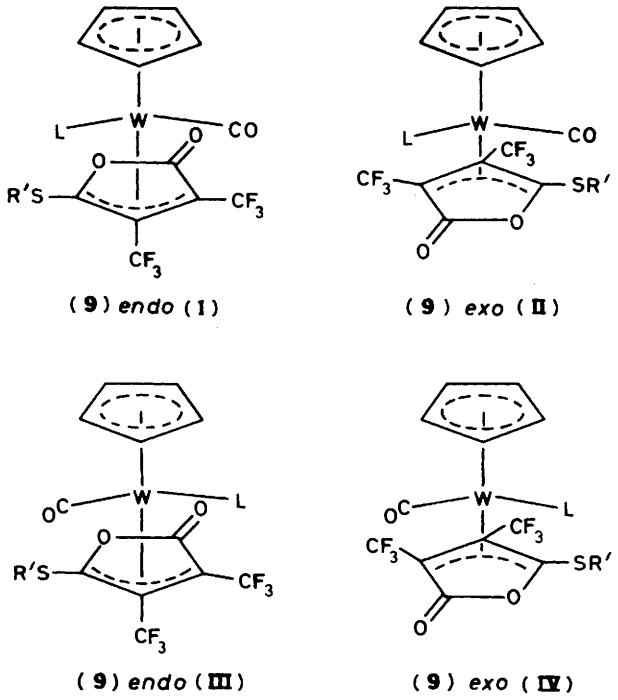


Scheme 4. cp = η^5-C_5H_5

cationic alkyne complexes, *e.g.* $[Mo\{P(OMe)_3\}_2(RC{\equiv}CR)(\eta^5\text{-}C_5H_5)]^+$ (R = Me or Ph),[20] although, as pointed out earlier, insertion of alkynes into the M–H bond of $[MH(CO)_2L(\eta^5\text{-}C_5H_5)]$ [M = Mo or W; L = CO or $P(OR)_3$] also leads directly or indirectly to related species (Scheme 3).[17] Previously we have suggested that η^2-vinyls might be involved in the addition, insertion, and polymerisation reactions of alkynes promoted by transition metals[18,19,21,22] and more recently have presented evidence for $\eta^2 \longrightarrow \sigma \longrightarrow \eta^2$ vinyl group rearrangements.[21] Transformations $\eta^2 \longrightarrow \sigma$ have also been reported for metal–η^2-acyl[23] and η^2-ketenyl[24] systems which are structurally related to metal–η^2-vinyls. This prompted us to carry out reactions of complexes (**4a**) and (**4d**) with two-electron donors L = PMe_2Ph, $P(OMe)_3$, Bu^tNC, and CO, anticipating that co-ordination of such ligands would promote formation of stable σ-vinyl complexes. However, the isolation of lactone complexes (**9**) from these reactions suggests that if such a reaction is involved initially this is followed by CO insertion and subsequent cyclisation to give the final product

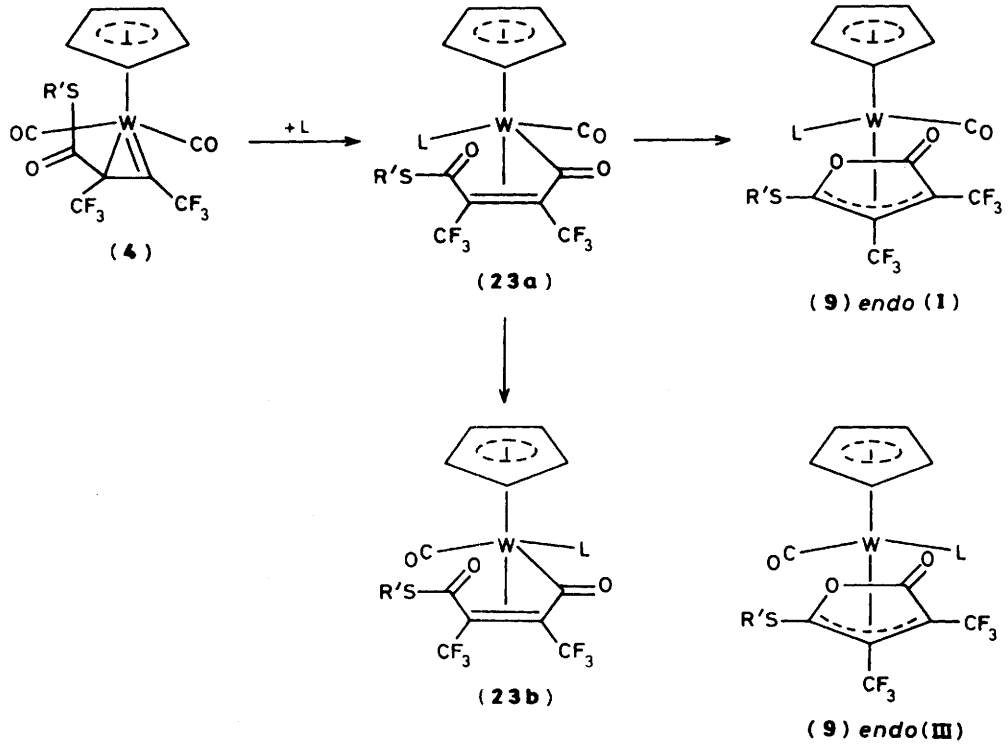
The structure of complex (**9d**) confirmed by *X*-ray diffraction studies[7a] is similar to that of $[Mo\{\eta^3\text{-}C(O)OC(Me)C(Me)C(Me)\}(CO)(CNBu^t)(\eta^5\text{-}C_5H_5)]$ obtained from the Bu^tNC-promoted cyclisation of the vinyl ketone $[Mo\{C(Me){=}C(Me)C(O)Me\}(CO)_2(\eta^5\text{-}C_5H_5)]$.[25] This originally led us to suggest[5] that complexes (**6**) or (**8**) containing S- and O-bonded vinyl ketone ligands could conceivably function as precursors to (**9**). Complex (**9d**) was originally isolated from the photochemical reaction of $[W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$ with hfb in a sealed tube[7a] and a plausible route involved attack by adventitious carbon monoxide (formed during the reaction) on (**6**) or (**8**). However the observation that the η^2-vinyl complex (**4d**) was not isolated from the photochemical reaction, coupled with our subsequent observation that carbonylation of (**4a**) and (**4d**) yields (**9h**) and (**9d**) respectively, suggests that the η^2-vinyl derivative is a more likely precursor to the lactone complex than (**6**) or (**8**).

The co-ordination geometry in η^3-lactone complexes of this type has been discussed in detail and the tentative conclusion reached that it may be represented by a monocapped trigonal prism.[25] A more useful description for our purposes is that it approximates to the familiar 4:3 piano-stool arrangement with the C_5H_5 ligand occupying three co-ordination sites and the other ligands the tetragonal base. Disregarding enantiomeric

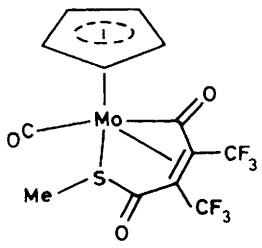


pairs, four distinct isomers of complex (**9**) could exist in principle arising from the relative disposition of the lactone ring with respect to the other ligands on the metal.[25] Thus two *endo* and two *exo* forms are possible which are related pairwise by rotation of the lactone about the metal–η^3-allyl axis, *i.e. endo* (**I**) ⇌ *exo* (**II**) and *endo* (**III**) ⇌ *exo* (**IV**). In the case of the dicarbonyls (**9d**) and (**9h**) obviously only one *endo* and one *exo* form can exist. Previously two isomeric forms of $[Mo\{\eta^3\text{-}C(O)OC(R)C(Me)C(Me)\}L(\eta^5\text{-}C_5H_5)]$ (R = Me or CF_3; L = PPh_3, $CNBu^t$, or CNC_6H_{11}[1]) have been observed in solution by n.m.r. spectroscopy, in 10:1 ratio suggesting a certain degree of stereoselectivity in the cyclisation reaction.[25] This was explained in terms of a mechanism involving opening in the vinyl ketone chelate ring, CO insertion, and stereoselective ring formation *via* nucleophilic attack of the oxygen of the terminal RC(O) group on the acyl carbon attached to the metal. This mechanism could also apply to the formation of complex (**9**) from (**4**) assuming an initial $\eta^2 \longrightarrow \sigma$ vinyl transformation. However the observation that all lactone complexes isolated in the present work adopt only a single isomeric form prompts us to propose an alternative mechanism illustrated in Scheme 5.

We start from the premise that the structure in solution has the *endo* form in view of the fact that both complex (**9d**)[7a] and $[Mo\{\eta^3\text{-}C(O)OC(Me)C(Me)C(Me)\}(CO)(CNBu^t)(\eta^5\text{-}C_5H_5)]$ (ref. 25) adopt such a structure in the solid state [in the latter case *endo* (**I**)]. The key step we suggest may involve transformation of the η^2-vinyl into an acryloyl derivative (**23a**) or (**23b**) as a result of a co-ordination induced CO migration, either by direct insertion into the M=C bond of (**4**) or *via* a σ-vinyl intermediate (**20**). This suggestion is prompted by (*a*) the previously described isomerisation of the σ-vinyl (**15a**) into the acryloyl derivative (**16a**)[16] and (*b*) the isolation of (**24**) containing an acryloyl ligand bearing a sulphur-co-ordinated COSMe substituent on the γ-carbon.[7b] The latter was obtained from the reaction of $[Mo(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$ (prepared *in situ*) with $CF_3C{\equiv}CCF_3$, a reaction which, by analogy with that of $[W(SMe)(CO)_3(\eta^5\text{-}C_5H_5)]$, may proceed *via* a molybdenum η^2-vinyl complex of type (**4**). We note that two geometrical isomers of (**23**) are possible in which the ligand L is either *trans*, (**23a**), or *cis*, (**23b**), with respect to the carbonyl function of the



Scheme 5.



(24)

acryloyl moiety. It may be significant that the reaction of the σ-vinyl complex (**15a**) with $P(OMe)_3$ stereospecifically produces (**16b**) in which the $P(OMe)_3$ lies *trans* to the carbonyl function.[15] This suggests that isomer (**23a**) in Scheme 5 might be formed preferentially, particularly in view of the mild conditions employed in the reactions described. *X*-Ray diffraction studies of the two acryloyl complexes (**16a**) and (**16b**)[15] indicate that in intermediate (**23a**) the COSMe on the γ-carbon of the acryloyl ligand could adopt an orientation such that the carbonyl oxygen would be nicely set up for attack on the acryloyl acyl carbon, a reaction which would lead to lactone-ring formation. Moreover the orientation of the acryloyl group would be such as to produce directly, *i.e.* without subsequent rotation, the desired *endo* configuration. This in conjunction with the stereoselectivity imposed by the preferential formation of a specific form of the acryloyl complex (**23a**) could conceivably account for the isolation of only a single isomer of the final η^3-lactone product (**9**).

We note that this mechanism may also operate in the formation of lactone complexes from vinyl ketone derivatives.[25,26] It is encouraging in this respect that the structure of $[Mo\{\eta^3\text{-}C(O)OC(Me)C(Me)C(Me)\}(CO)(CNBu^t)(\eta^5\text{-}C_5H_5)]$ found in the solid state, *endo* (**I**),[25] is exactly that which would be expected from cyclisation of (**23a**) which we predict to be the favoured isomeric form if acryloyl intermediates are involved.

The formation of small quantities of a second isomeric lactone complex in such reactions can readily be explained by partial isomerisation, *cf.* (**23a**) ⟶ (**23b**) (Scheme 5), which might occur more readily with molybdenum complexes or, in the case of the tungsten derivatives isolated, be a consequence of the more vigorous reaction conditions employed.[15] We note that isomerisation of complex (**16b**) to the alternative form in which the phosphite ligand lies *cis* to the acryloyl carbonyl group, *cf.* (**23b**), does occur on prolonged photolysis[15] and such a structure would be predicted to produce the isomeric lactone species *endo* (**III**). Studies currently in progress will hopefully provide information concerning the possible role of acryloyl complexes in lactonisation reactions of this type.

Experimental

Proton and ^{19}F n.m.r. spectra were recorded in $CDCl_3$ (unless stated otherwise) on a Bruker WP-200SY instrument operating at 200.13 and 188.31 MHz. Mass spectra were obtained on a V.G. updated A.E.I. MS9 spectrometer and i.r. spectra on a Perkin-Elmer 580 spectrophotometer. Reactions were carried out under a dry oxygen-free nitrogen atmosphere using standard Schlenk techniques. Reactions involving hfb were carried out in thick glass reaction tubes (capacity *ca.* 100 cm^3) fitted with a Westef stopcock. Carbonylations were carried out in a Berghof autoclave (capacity 100 cm^3). Solvents were refluxed over powdered calcium hydride (hexane, diethyl ether), sodium–benzophenone (tetrahydrofuran, thf), or P_2O_5 (dichloromethane) and distilled under nitrogen just before use. Hexafluorobut-2-yne (Fluorochem) and dimethyl acetylenedicarboxylate (Aldrich) were obtained commercially and used as supplied. Thiolates $[W(SR')(CO)_3(\eta^5\text{-}C_5H_5)]$ were prepared from stirred mixtures of $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ and Tl(SR') (10% excess) in thf at room temperature. The complexes $[W(SePh)(CO)_3(\eta^5\text{-}C_5H_5)]$,[27] $[W(AsMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]$,[28] and $[Fe(AsMe_2)(CO)_2(\eta^5\text{-}C_5H_5)]$[28] were prepared by published methods.

Reaction of $[Fe(AsMe_2)(CO)_2(\eta^5\text{-}C_5H_5)]$ *with dmad.*—A solution of the complex (0.20 g, 0.07 mmol) in cyclohexane (15 cm^3) was treated with dmad (0.1 g, 0.7 mmol) to give a yellow-brown precipitate. This was dissolved in CH_2Cl_2 (1 cm^3), and chromatographed on Florisil with Et_2O; evaporation of the eluate gave complex (**1**) as a red-brown oil (0.05 g, 17%) (Found: C, 42.9; H, 3.8. $C_{15}H_{17}FeO_6$ requires C, 42.45; H, 4.0%); M^+ at *m/z* 424. I.r. (CCl_4): ν(CO) 1 947vs, ν(C=O) 1 741s, 1 730 (sh), 1 710s, 1 598s, ν(C=C) 1 623m-w cm^{-1}. ^1H N.m.r.: δ 1.79 (s, 3 H, AsMe), 1.84 (s, 3 H, AsMe), 3.80 (s, 3 H, CO_2Me), 3.82 (s, 3 H, CO_2Me), and 4.60 (s, 5 H, C_5H_5).

Reaction of $[W(AsMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]$ *with hfb.*—A solution of the complex (0.35 g, 0.8 mmol) in cyclohexane (20 cm^3), was treated with an excess of hfb in a sealed tube and allowed to stand at room temperature for 18 h. The excess of hfb was removed and the resulting orange solution filtered, concentrated to *ca.* 1 cm^3, and chromatographed over Florisil with Et_2O as eluant to give a red solution. Concentration of this solution and treatment with hexane gave red crystals of complex (**2a**) (0.12 g, 12.5%) (Found: C, 28.6; H, 1.5. $C_{14}H_{11}AsF_6O_3W$ requires C, 28.0; H, 1.8%); M^+ at *m/z* 600. I.r. (CCl_4): ν(CO) 1 965s, 1 891s, ν(C=O) 1 599m, ν(C=C) 1 630w cm^{-1}. N.m.r.: ^1H, δ 1.92 (s, 3 H, AsMe), 2.14 (s, 3 H, AsMe), and 5.49 (s, 5 H, C_5H_5); ^{19}F, −53.85 (q, J_{FF} 10.5) and −60.22 (q, J_{FF} 10.5 Hz).

Reaction of $[W(AsMe_2)(CO)_3(\eta^5\text{-}C_5H_5)]$ *with dmad.*—A solution of the complex (0.48 g, 1.1 mmol) in cyclohexane (10 cm^3) was treated with dmad (0.16 g, 1.1 mmol) and allowed to stand at room temperature for 2 h to give a red-brown precipitate. This was recrystallised from CH_2Cl_2–hexane to give red crystals of complex (**2b**) (0.082 g, 13%) (Found: C, 33.4; H, 3.0; As, 13.4. $C_{16}H_{17}AsO_2W$ requires C, 33.1; H, 3.0; As, 12.9%); M^+ at *m/z* 580. I.r. ($CHCl_3$): ν(CO) 1 956s, 1 878s, ν(C=O) 1 732m, 1 712m, 1 565m, ν(C=C) 1 630w cm^{-1}. ^1H N.m.r.: δ 1.90 (s, 3 H, AsMe), 2.05 (s, 3 H, AsMe), 3.82 (s, 3 H, CO_2Me), 3.85 (s, 3 H, CO_2Me), and 5.38 (s, 5 H, C_5H_5).

Reaction of $[W(SePh)(CO)_3(\eta^5\text{-}C_5H_5)]$ *with hfb.*—A solution of the complex (0.20 g, 0.41 mmol) in diethyl ether (30 cm^3) was transferred to a glass tube fitted with a Westef stopcock. Hexafluorobut-2-yne (1 g, 6 mmol) was condensed in at −196 °C and the tube sealed. The mixture was irradiated with a 500-W visible-light source for 2 h. Volatiles were removed and the residue chromatographed over Florisil using diethyl ether–hexane (1:1) as eluant to give dark red crystals of complex (**5b**) (0.10 g, 43%) (Found: C, 33.3; H, 1.9; F, 18.7. $C_{16}H_{10}F_6OSeW$ requires C, 32.3; H, 1.7; F, 19.2%); M^+ at *m/z* 596. I.r. (CCl_4): ν(CO) 1 990s and ν(C≡C) 1 712w-m cm^{-1}. N.m.r.: ^1H, δ 5.41 (s, 5 H, C_5H_5) and 7.24 (m, 5 H, Ph); ^{19}F, −55.56 (q, J_{FF} 3.0) and 57.66 (q, J_{FF} 3.0 Hz).

Reaction of $[W(SPr^n)(CO)_3(\eta^5\text{-}C_5H_5)]$ *with hfb.*—A solution of the complex (0.52 g, 1.3 mmol) in hexane (50 cm^3) was treated with an excess of hfb and allowed to stand at 4 °C for 18 h. The dark red solution was filtered, evaporated to dryness, and the residue recrystallised from Et_2O–hexane to give dark red crystals of complex (**3a**) (0.39 g, 53%) (Found: C, 31.8; H, 2.0. $C_{15}H_{12}F_6O_3SW$ requires C, 31.6; H, 2.1%); M^+ at *m/z* 571. I.r. (CCl_4): ν(CO) 1 968s, 1 891s, ν(C=O) 1 597m cm^{-1}. N.m.r.: ^1H, δ 1.1 (t, 3 H, *J* 7.2, Pr^n methyl), 1.5 (m, 2 H, Pr^n β-methylene), 3.2 (m, 1 H, Pr^n α-methylene), 3.5 (m, 1 H, Pr^n α-methylene), and 5.5 (s, 5 H, C_5H_5); ^{19}F, −54.7 (q, J_{FF} 11.5) and −59.6 (q, J_{FF} 11.5 Hz).

Reaction of $[W(SPr^i)(CO)_3(\eta^5\text{-}C_5H_5)]$ *with hfb.*—A solution of the complex (0.48 g, 1.2 mmol) in hexane (60 cm^3) was treated with an excess of hfb and allowed to stand at room temperature for 18 h to give light brown crystals of complex (**4a**) (0.14 g, 21%) (Found: C, 32.4; H, 2.3. $C_{15}H_{12}F_6O_3SW$ requires C, 31.7; H, 2.1%); M^+ at *m/z* 568. I.r. (CCl_4): ν(CO) 2 058s, 1 993s, ν(C=O) 1 676m cm^{-1}. N.m.r.: ^1H, δ 1.22 (d, 6 H, *J* 6.5, 2Me), 3.42 (spt, 1 H, *J* 6.5 Hz), and 5.72 (s, 5 H, C_5H_5); ^{19}F, −54.74 (br s) and −58.45 (br s).

Reaction of $[W(SC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)]$ *with hfb.*—The complex (0.071 g, 0.16 mmol) in Et_2O (20 cm^3) was treated with an excess of hfb and allowed to stand at room temperature for 40 h. Concentration of the solution (to *ca.* 10 cm^3) followed by addition of hexane (10 cm^3) and cooling to 0 °C gave after 2 h a red-brown crystalline solid (0.01 g). This was dissolved in CH_2Cl_2 (0.2 cm^3) and chromatographed over Florisil eluting first with Et_2O–hexane (5:1) to remove unreacted starting material and then with CH_2Cl_2 to give a yellow-orange solution. The solution was concentrated and treated with hexane to give yellow crystals of complex (**4c**) (0.001 g, 1%); M^+ at *m/z* 618. I.r. (CCl_4): ν(CO) 2 058s, 1 993s, ν(C=O) 1691m cm^{-1}. N.m.r.: ^1H, δ 2.33 (s, 3 H, Me), 5.81 (s, 5 H, C_5H_5), and 7.14 (br s, 4 H, C_6H_4); ^{19}F, −55.64 (br s) and −59.34 (q, *J* 3.0 Hz). Careful crystallisation gave red crystals of complex (**3b**) (0.005 g, 5%); M^+ at *m/z* 618. I.r. ($CHCl_3$): ν(CO) 1 970s, 1 896s, ν(C=O) 1 592 s cm^{-1}. N.m.r.: ^1H, δ 2.41 (s, 3 H, Me), 5.71 (s, 5 H, C_5H_5), and 6.9—7.3 (m, 4 H, C_6H_4); ^{19}F, −54.0 (br m) and −59.60 (q, J_{FF} 11.0 Hz).

Reaction of $[W(SPr^i)(CO)_3(\eta^5\text{-}C_5H_5)]$ *with dmad.*—A solution of the complex (0.15 g, 0.38 mmol) in hexane (50 cm^3) was treated with dmad (0.058 g, 0.41 mmol) at 20 °C for 48 h to give red-brown crystals. These were recrystallised from CH_2Cl_2–hexane to give complex (**3c**) (0.095 g, 45%) (Found: C, 36.6; H, 3.3. $C_{17}H_{18}O_7SW$ requires C, 37.2; H, 3.3%); M^+ at *m/z* 547. I.r. ($CHCl_3$): ν(CO) 1 959s, 1 881s, ν(C=O) 1 752s, 1 730s, 1 565 cm^{-1}. ^1H N.m.r.: δ 1.28 (2 overlapping d, 6 H, *J* 6.0 Hz, Pr^i methyl), 3.82 (m, 1 H, Pr^i methine), 3.82 (s, 3 H, CO_2Me), 3.89 (s, 3 H, CO_2Me), and 5.44 (s, 5 H, C_5H_5).

Thermal Rearrangement of $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SPr^i\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (**4a**).—The complex (0.16 g, 0.28 mmol) in hexane was heated at 30 °C in a sealed tube for 40 h to give black crystals which were recrystallised from CH_2Cl_2–hexane to give 0.096 g (60%) of complex (**6a**) (Found: C, 32.0; H, 2.3. $C_{15}H_{12}F_6O_3SW$ requires C, 31.6; H, 2.1%); M^+ at *m/z* 570. I.r. ($CHCl_3$): ν(CO) 1 973s, 1 882s, ν(C=O) 1 735m cm^{-1}. N.m.r.: ^1H, δ 1.45 (d, *J* 7.0, 3 H, Me), 1.62 (d, *J* 7.0, 3 H, Me), 3.64 (m, 1 H), and 5.68 (s, 5 H, C_5H_5); ^{19}F, −51.18 (q, J_{FF} 15.0) and −58.39 (q, J_{FF} 15.0 Hz).

Thermal Rearrangement of $[W\{C(O)C(CF_3)=C(CF_3)SPr^n\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (**3a**).—A suspension of complex (**3a**) (0.095 g, 0.17 mmol) in hexane (15 cm^3) in a tube was warmed to 30 °C for 18 h to give black crystals of (**6b**) (0.012 g, 13%) (Found: C, 31.7; H, 2.0. $C_{15}H_{12}F_6O_3SW$ requires C, 31.6; H, 2.1%); M^+ at *m/z* 570. I.r. (CCl_4): ν(CO) 1 970s, 1 886s, ν(C=O) 1 729m cm^{-1}. N.m.r.: ^1H, δ 1.1 (t, 3 H, *J* 7, Pr^n methyl), 1.8 (sxt, 2 H, *J* 7.5, Pr^n β-methylene), 2.9 (d, *J* 12.8, of triplets, 1 H, *J* 7.4, α-methylene), 3.5 (d, *J* 13.0, of triplets, 1 H, *J* 7.5, Pr^n β-methylene), and 5.7 (s, 5 H, C_5H_5); ^{19}F, −51.6 (q, J_{FF} 15.5) and −59.3 (q, J_{FF} 15.5 Hz). Complex (**4b**) was detected by i.r. spectroscopy during the reaction but could not be isolated in a pure form.

Thermal Rearrangement of $[W\{C(O)C(CO_2Me)=C(CO_2Me)SMe\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (**3e**).—Crystals of complex (**3e**) (0.02 g, 0.04 mmol) in hexane (20 cm^3) were heated to 65 °C for 18 h. The resulting solution was decanted from undissolved solid, concentrated to *ca.* 5 cm^3, and allowed to stand at 4 °C for 24 h

to give red crystals of the previously characterised complex (**8b**)[5] (0.004 g, 20%). I.r. (CCl_4): ν(CO) 1 982s, 1 910s, ν(C=O) 1 722 (sh), 1 706m cm^{-1}. An orange solid was also formed. It was recrystallised from CH_2Cl_2–hexane to give yellow crystals of complex (**7b**) (0.001 g, 5%); M^+ at *m/z* 522. I.r. ($CHCl_3$): ν(CO) 2 040s, 1 959s, 1 939s, ν(C=O) 1 710m, 1 698 (sh) cm^{-1}. ^1H N.m.r.: δ 2.29 (s, 3 H, SMe), 3.74 (s, 6 H, CO_2Me), and 5.58 (s, 5 H, C_5H_5).

Thermal Rearrangement of [W{C(O)C(CO_2Me)=C(CO_2Me)-SPr^i}(CO)$_2$(η^5-C_5H_5)] (**3c**).—*At* 60 °C. Crystals of complex (**3c**) (0.048 g, 0.087 mmol) in hexane (13 cm^3) were heated to 60 °C for 7 d to give a mixture of red and yellow solids and an orange solution. The solid material was extracted with ether and crystallised with hexane. The resulting yellow-orange solid was recrystallised from CH_2Cl_2–hexane to give yellow crystals of complex (**7a**) (0.007 g, 15%) (Found: C, 37.0; H, 3.3; S, 5.5. $C_{17}H_{18}O_7SW$ requires C, 37.1; H, 3.3; S, 5.8%); M^+ at *m/z* 550. I.r. ($CHCl_3$): ν(CO) 2 040s, 1 960s, 1 936s, ν(C=O) 1 711m, 1 698 (sh) cm^{-1}. ^1H N.m.r.: δ 1.24 (d, 6 H, *J* 6.5, Pr^i methyl), 3.30 (spt, 1 H, *J* 6.5 Hz, Pr^i methine), 3.71 (s, 3 H, CO_2Me), 3.73 (s, 3 H, CO_2Me), and 5.56 (s, 5 H, C_5H_5).

At 90 °C. Crystals of complex (**3c**) (0.088 g, 0.16 mmol) in hexane (15 cm^3) were heated to 90 °C for 46 h to give a red solution. Yellow crystals of complex (**7a**) (moderate-to-good yield) observed after 18 h had disappeared after 48 h. The solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (1 cm^3) and chromatographed on Florisil, eluting first with Et_2O–hexane (1:1), then with Et_2O–hexane (4:1), and finally with thf to give orange-red solutions. These were concentrated and treated with hexane to give (in order of elution from the column): a red solid which due to the low yield was not investigated further; red crystals of complex (**8a**) (0.004 g, 4.5%) (Found: C, 37.5; H, 3.2. $C_{17}H_{18}O_7SW$ requires C, 37.1; H, 3.3%); M^+ at *m/z* 550; i.r. (CCl_4): ν(CO) 1 981s, 1 910s, ν(C=O) 1 720 (sh), 1 706m cm^{-1}; ^1H n.m.r.: δ 1.34 (d, 6 H, *J* 7.0 Hz, Pr^i methyl), 3.77 (s, 3 H, CO_2Me), 3.91 (s, 3 H, CO_2Me), and 5.54 (s, 5 H, C_5H_5) (*NB.* Pr^i CH multiplet obscured by singlet at δ 3.77); an impure red oily solid (**6c**) (0.003 g, 6 × 10^{-6} mol, 4%); M^+ at *m/z* 550; i.r. (CCl_4): ν(CO) 1 964s, 1 882s, ν(C=O) 1 742m, 1 722m, 1 710m cm^{-1}; ^1H n.m.r.: δ 1.47 (d, *J* 7.0 Hz, 3 H, Pr^i methyl), 1.54 (d, 3 H, *J* 7.0, Pr^i methyl), 3.76 (s, 3 H, CO_2Me), 3.91 (s, 3 H, CO_2Me), and 5.60 (s, 5 H, C_5H_5) (*NB.* Pr^i CH multiplet obscured by singlet at δ 3.76).

Reactions of [W{η^2-C(CF_3)C(CF_3)C(O)SMe}(CO)$_2$(η^5-C_5H_5)] (**4d**).—*With* PMe_2Ph. A solution of complex (**4d**) 0.028 g, 0.052 mmol) in Et_2O (5 cm^3) was treated with PMe_2Ph (*ca.* 0.4 mmol) and allowed to stand at room temperature for 3 h to give a red solution. The solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–hexane to give a mixture (separated by hand) of yellow crystals of complex (**9a**) (0.007 g, 20%) [*i.r.* ($CHCl_3$): ν(CO) 1 967s, ν(C=O) 1 740s, 1 730 (sh) cm^{-1}. N.m.r.: ^1H, δ 1.97 (d, 3 H, J_{PH} 9.0, PMe_2Ph methyl), 2.00 (d, 3 H, J_{PH} 9.0, PMe_2Ph methyl), 2.6 (s, 3 H, SMe), 4.97 (d, 5 H, J_{PH} 1.5, C_5H_5), and 7.46 (m, 5 H, Ph); ^{19}F, −53.15 (q, J_{FF} 5.0) and −57.13 (q, J_{FF} 8.0 Hz)] and trace amounts of red crystals which were not investigated further.

With $P(OMe)_3$. A solution of complex (**4d**) (0.015 g, 0.028 mmol) in Et_2O (4 cm^3) was treated with $P(OMe)_3$ (*ca.* 0.4 mmol) and allowed to stand at room temperature for 48 h to give a yellow solution. Concentration of the solution followed by addition of hexane gave yellow crystals of complex (**9b**) (0.006 g, 32%); M^+ at *m/z* 666. I.r. ($CHCl_3$): ν(CO) 1 998 (sh), 1 977s, ν(C=O) 1 741s, 1 730 (sh) cm^{-1}. N.m.r.: ^1H, δ 2.22 (s, 3 H, SMe), 3.71 [d, 9 H, J_{PH} 11.0, $P(OMe)_3$], and 5.28 (d, J_{PH} 1.5, 5 H, C_5H_5); ^{19}F, −55.3 (q, J_{FF} 8.0) and −56.9 (q, J_{FF} 8.0 Hz).

With Bu^{t}NC. The complex (0.037 g, 0.068 mmol) in Et_2O (5 cm^3) was treated with Bu^{t}NC (*ca.* 0.4 mmol) and allowed to stand at room temperature for 18 h to give a red solution. This was concentrated to *ca.* 0.5 cm^3, hexane (2 cm^3) was added, and the mixture allowed to stand at room temperature for 48 h to give an orange solid and a red oil. The solid was recrystallised four times from CH_2Cl_2–hexane to give yellow crystals of complex (**9c**) (0.002 g, 5%); M^+ at *m/z* 625. I.r. (CCl_4): ν(C≡N) 2 160s, ν(CO) 1 998s, ν(C=O) 1 768s cm^{-1}. N.m.r.: ^1H, δ 1.50 (s, 9 H, CNBu^t), 2.26 (s, 3 H, SMe), and 5.31 (s, 5 H, C_5H_5); ^{19}F, −55.76 (q, J_{FF} 8.0) and −56.77 (q, J_{FF} 8.0 Hz).

Reactions of [W{η^2-C(CF_3)C(CF_3)C(O)SPr^i}(CO)$_2$(η^5-C_5H_5)] (**4a**).—*With* $P(OMe)_3$. A solution of complex (**4a**) (0.009 g, 0.016 mmol) in Et_2O (4 cm^3) was treated with $P(OMe)_3$ (*ca.* 0.4 mmol) and allowed to stand at room temperature for 48 h. After concentrating the solution and adding hexane a yellow solid was obtained which on recrystallisation from CH_2Cl_2–hexane gave yellow crystals of complex (**9f**) (0.009 g, 82%) (Found: C, 31.0: H, 3.0. $C_{18}H_{21}F_6O_6PSW$ requires C, 31.1; H, 3.0%); M^+ at *m/z* 668. I.r. (CCl_4): ν(CO) 1 968s, ν(C=O) 1 760 (sh), 1 752s, 1 735 (sh) cm^{-1}. N.m.r.: ^1H, δ 1.21 (d, 3 H, *J* 7.0, Pr^i methyl), 1.31 (d, 3 H, *J* 7.0, Pr^i methyl), 3.22 (spt, 1 H, *J* 7.0, Pr^i methine), 3.71 [d, 9 H, J_{PH} 11.0, $P(OMe)_3$], and 5.27 (d, 5 H, J_{PH} 1.5, C_5H_5); ^{19}F, −54.69 (q, J_{FF} 8.5) and −56.78 (q, J_{FF} 8.5 Hz).

With Bu^{t}NC. A solution of complex (**4a**) (0.021 g, 0.037 mmol) in Et_2O (5 cm^3) was treated with Bu^{t}NC (*ca.* 0.4 mmol), and allowed to stand at room temperature for 2 h before concentrating to 0.5 cm^3. A red oil was obtained which was recrystallised three times from CH_2Cl_2–hexane to give yellow crystals of complex (**9g**) (0.002 g, 8%) (Found: C, 36.9; H, 3.1; N, 2.2. $C_{20}H_{21}F_6NO_3SW$ requires C, 36.8; H, 3.2; N, 2.1%); M^+ at *m/z* 652. I.r. ($CDCl_3$): ν(CN) 2 172s, ν(CO) 1 990s, ν(C=O) 1 742s cm^{-1}. N.m.r.: ^1H, δ 1.21 (d, 3 H, *J* 7.0, Pr^i methyl), 1.32 (d, 3 H, *J* 7.0, Pr^i methyl), 1.48 (s, 9 H, Bu^{t}NC methyl), 3.26 (spt, 1 H, *J* 7.0, Pr^i methine), and 5.28 (s, 5 H, C_5H_5); ^{19}F, −55.42 (q, J_{FF} 8.0) and −56.69 (q, J_{FF} 8.0 Hz).

With CO. A solution of complex (**4a**) (0.012 g, 0.021 mmol) in Et_2O (20 cm^3) at room temperature was treated with CO (4 atm) and stirred for 7 d. The resulting yellow solution was evaporated to dryness and the residue crystallised from CH_2Cl_2–hexane to give complex (**9h**) as a yellow powder (0.005 g, 40%); M^+ at *m/z* 596. I.r. ($CHCl_3$): ν(CO) 2 062s, 2 010s, ν(C=O) 1 771s cm^{-1}. N.m.r.: ^1H, δ 1.28 (d, 3 H, *J* 7.0, Pr^i methyl), 1.43 (d, 3 H, *J* 7.0, Pr^i methyl), 3.36 (spt, 1 H, *J* 7.0, Pr^i methine), and 5.75 (s, 5 H, C_5H_5); ^{19}F, −53.66 (q, J_{FF} 7.5) and −57.14 (q, J_{FF} 7.5 Hz).

A solution of complex (**4d**) (0.25 g) in diethyl ether (20 cm^3) was treated similarly and gave (**9d**) identified by mass spectroscopy, M^+ at *m/z* 554, and comparison of i.r. and n.m.r. spectral parameters with published data.[7a]

With PMe_2Ph. A suspension of complex (**4a**) (0.047 g, 0.082 mmol), in hexane (10 cm^3) was treated with PMe_2Ph (*ca.* 0.4 mmol) and stirred for 3 h at room temperature to give yellow crystals of complex (**9e**) (0.030 g, 51%) (Found: C, 38.7; H, 3.0; P, 4.7. $C_{25}H_{23}F_6O_3PSW$ requires C, 39.0; H, 3.3; P, 4.4%). I.r. ($CHCl_3$): ν(CO) 1 964s, ν(C=O) 1 740 (sh), 1 730s cm^{-1}. N.m.r.: ^1H, δ 1.21 (d, 3 H, *J* 7.0, Pr^i methyl), 1.34 (d, 3 H, *J* 6.5, Pr^i methyl), 1.96 (d, 3 H, J_{PH} 9.0, PMe_2Ph methyl), 1.97 (d, 3 H, J_{PH} 9.0, PMe_2Ph methyl), 3.24 (q, 1 H, *J* 6.5, Pr^i methine), 4.92 (d, J_{PH} 1.5, 5 H, C_5H_5), and 7.44 (m, 5 H, Ph); ^{19}F, −52.82 (q, J_{FF} 8.0) and −57.01 (q, J_{FF} 8.0 Hz).

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References

1 J. L. Davidson, in 'Reactions of Coordinated Ligands,' ed. P. S. Braterman, Plenum, London, 1985; J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, 1980; R. F. Heck, 'Organotransition Metal Chemistry: A Mechanistic Approach,' Academic Press, San Francisco, 1974.

2 See, for example, (*a*) C. McDade and J. E. Bercaw, *J. Organomet. Chem.*, 1985, **279**, 281; (*b*) R. M. Laine and P. C. Ford, *ibid.*, 1977, **124**, 29; (*c*) A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, 1972, **94**, 1886; (*d*) H. Scordia, R. Kergout, M. Kubicki, J. Guerhais, and P. L' Haridon, *Organometallics*, 1983, **2**, 1681; (*e*) T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* 1974, 106; (*f*) H. C. Clark, P. L. Fiess, and C. S. Wong, *Can. J. Chem.*, 1977, **55**, 177; (*g*) P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 511.

3 J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1976, 2044; H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1971, **10**, 18; H. G. Alt, *J. Organomet. Chem.*, 1977, **127**, 349; T. G. Appleton, M. H. Chisholm, H. C. Clark, and K. Yasafuku, *J. Am. Chem. Soc.*, 1974, **96**, 6600; B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, 1970, 308; J. M. Huggins and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 3002.

4 (*a*) J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 1975, 2283; (*b*) F. Y. Petillon, F. Le Floch-Perennou, J. C. Guerchais, and D. W. Sharp, *J. Organomet. Chem.*, 1979, **173**, 89; (*c*) E. Lindner, C-P. Krieg, W. Hiller, and R. Fawzi, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 523 and refs. therein; (*d*) C. Bianchini and A. Meli, *J. Organomet. Chem.*, 1982, **236**, C75; (*e*) A. J. Carty, P. H. Dixneuf, A. Gorgues, F. Hartstock, H. Le Bozec, and N. J. Taylor, *Inorg. Chem.*, 1981, **20**, 3929; (*f*) P. Robert, H. Le Bozee, P. Dixneuf, F. Hartstock, N. J. Taylor, and A. J. Carty, *Organometallics*, 1982, **1**, 1148.

5 J. L. Davidson, M. Shiralian, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1984, 2167.

6 P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 1976, 241.

7 (*a*) F. Y. Petillon, F. Le Floch-Perennou, J. E. Guerchais, D. W. A. Sharp, Lj. Manojlović-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1980, **202**, 23; (*b*) J. E. Guerchais, F. Le Floch-Perennou, F. Y. Petillon, A. N. Keith, Lj. Manojlović-Muir, K. W. Muir, and D. W. A. Sharp, *J. Chem. Soc., Chem. Commun.*, 1979, 410.

8 J. L. Davidson and L. Carlton, *J. Chem. Soc., Chem. Commun.*, 1984, 964.

9 R. Fields, *Annu. Rep. NMR Spectrosc.*, 1977, **7**, 1.

10 J. A. K. Howard, R. Stanfield, and P. W. Woodward, *J. Chem. Soc., Dalton Trans.*, 1976, 246.

11 B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585 and refs. therein; S. R. Allen, P. K. Baker, S. G. Barnes, M. Green, L. Trollope, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1981, 873.

12 Lj. Manojlović-Muir and K. W. Muir, *J. Organomet. Chem.*, 1979, **168**, 403.

13 R. B. King and L. W. Houk, *Can. J. Chem.*, 1969, **47**, 2959.

14 E. D. Schermer and W. H. Baddley, *J. Organomet. Chem.*, 1971, **27**, 83.

15 L. V. Rybin, N. A. Stelzer, I. A. Garbusova, B. V. Loskin, and M. I. Rybinskya, *J. Organomet. Chem.*, 1984, **265**, 295.

16 F. Y. Petillon, J. L. Le Quere, F. Le Floch-Perennou, J. E. Guerchais, M. B. Gomes de Lima, Lj. Manojlović-Muir, K. W. Muir, and D. W. A. Sharp, *J. Organomet. Chem.*, 1984, **255**, 231.

17 H. Brix and W. Beck, *J. Organomet. Chem.*, 1982, **234**, 151.

18 J. L. Davidson, I. E. P. Murray, P. N. Preston, M. V. Russo, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1981, 1059.

19 J. L. Davidson, G. Vasapollo, Lj. Manojlović-Muir, *J. Chem. Soc., Chem. Commun.*, 1982, 1025.

20 M. Green, N. C. Norman, and A. G. Orpen, *J. Am. Chem. Soc.*, 1981, **103**, 1267; S. R. Allen, R. G. Beevor, M. Green, N. C. Norman, A. G. Orpen, and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1985, 435.

21 J. L. Davidson, W. F. Wilson, Lj. Manojlović-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1983, **254**, C6.

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

23 H. Brunner and H. Vogt, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 405.

24 W. Uedelhov, K. Ebert, and F. R. Kreissl, *Chem. Ber.*, 1979, **112**, 3376.

25 M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 1067.

26 M. Bottrill and M. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 820; S. R. Allen, M. Green, N. C. Norman, K. E. Paddick, and A. G. Orpen, *ibid.*, 1983, 1625.

27 E. W. Tilley, E. D. Schermer, and W. H. Baddley, *Inorg. Chem.*, 1968, **7**, 1925.

28 W. Malisch and M. Kuhn, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 84.

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