The Mechanistic Role of η^2-Vinyl Complexes in Metal-Promoted Alkyne Oligomerisations. The Crystal and Molecular Structures of $[W\{\eta^5\text{-}C(CF_3)=C(CF_3)C(CO_2Me)=C(CO_2Me)C(CF_3)=C(CF_3)SPr^i\}(\eta^5\text{-}C_5H_5)]$, $[WF\{\eta^5\text{-}C(=CF_2)C(CF_3)=C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)SPr^i\}(\eta^5\text{-}C_5H_5)]$, and $[W\{\eta^4\text{-}C(CF_3)C(CF_3)=C(Me)C(Me)SPr^i\}(\eta^2\text{-}CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$

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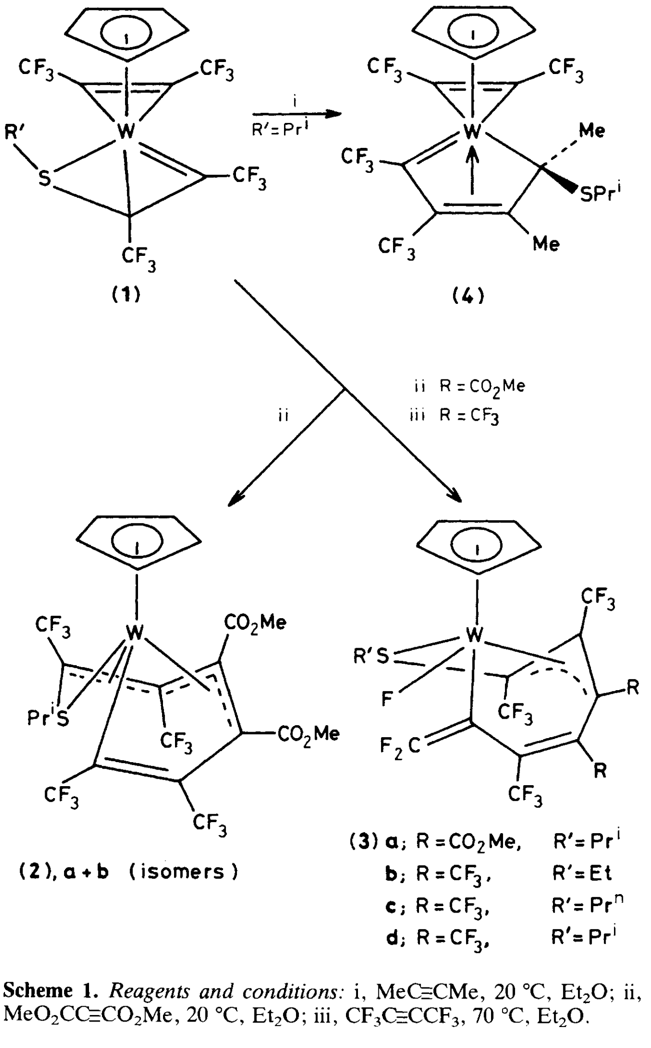
Reactions of alkynes RC≡CR (R = CF_3, CO_2Me, or Me) with η^2-vinyl complexes $[W\{\eta^2\text{-}C(CF_3)C(CF_3)SR'\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (R' = Et, Pr^n, or Pr^i) give isomeric products $[W(CF_3C_2CF_3)_2(RC_2R)SR'(\eta^5\text{-}C_5H_5)]$ resulting from insertion of the incoming alkyne into the M=C bond of the η^2-vinyl and thus illustrate that η^2-vinyls can act as intermediates in metal-promoted alkyne oligomerisation reactions.

Current interest in the physical properties of polyalkynes has focused attention on the mechanisms of metal-catalysed alkyne polymerisations for which η^1-vinyl,[1] η^1-carbene,[2] or μ_2-η^1-carbene[3] intermediates have been proposed. Recently we[4] and others[5] have drawn attention to the role of η^2-vinyl intermediates in metal–alkyne chemistry and we now illustrate that such species are also plausible intermediates in oligomerisation reactions.

η^2-Vinyl complexes (**1**)[4b] undergo reactions with alkynes RC≡CR (R = CF_3, CO_2Me, or Me) to give oligomerisation products (**2a**), (**2b**), (**3**), and (**4**) as illustrated in Scheme 1. Single crystal *X*-ray diffraction studies established that in (**2a**)† the incoming $MeO_2CC{\equiv}CCO_2Me$ has linked the hexafluorobut-2-yne and η^2-vinyl units in (**1**) to produce a hexatrienyl ligand $Pr^iSC(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)=C(CF_3)^-$ which is joined to the 18 e tungsten atom through a continuous η^5-SC(2)C(3)C(5)C(8) chain (Figure 1) and additionally through a σ-W–C(alkenyl) bond to C(13), leaving C(11) as the only hexatrienyl chain carbon atom not attached to the metal [W · · · C(11) 2.702(4) Å]. Although the carbon atoms of the hexatrienyl chain have nearly sp^2 hybridisation if W–C bonds are ignored, apart from that to C(13), significant π-overlap across chain C–C bonds is possible only for C(11)–C(13), the fixed double bond, and for C(5)–C(8): the R–C–C–R torsion angles, R = CF_3 or CO_2Me, are 54—96° except for values of 14 and 3° across C(5)–C(8) and C(11)–C(13) respectively. In (**2a**) the sulphur Pr^i substituent is *syn* with respect to the η^5-C_5H_5 ring, as indeed it also is in the solid-state structure of (**1**).[4b] Movement of the Pr^i substituent to the *anti* position produces (**2b**)† which in essential respects is otherwise structurally indistinguishable from (**2a**).



Scheme 1. *Reagents and conditions:* i, MeC≡CMe, 20 °C, Et_2O; ii, $MeO_2CC{\equiv}CO_2Me$, 20 °C, Et_2O; iii, $CF_3C{\equiv}CCF_3$, 70 °C, Et_2O.

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† The following applies to all four structure analyses. Enraf–Nonius CAD4F diffractometer. Mo-K_α radiation, $\lambda = 0.71069$ Å. Gaussian or empirical absorption correction. Fixed contributions for all H atoms. Full-matrix least-squares refinement [$w = 1/\sigma^2(F)$].

Crystal data for isomers (**2a**), (**2b**), and (**3a**): $C_{22}H_{18}F_{12}O_4SW$, $M = 790.3$, monoclinic, $Z = 4$, $F(000) = 1520$ electrons, 361 parameters. (**2a**): space group $P2_1/n$ (No. 14), $a = 14.737(3)$, $b = 11.015(4)$, $c = 16.651(5)$ Å, $\beta = 111.39(2)°$, $U = 2517(1)$ Å^3, $D_c = 2.086$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 48.8$ cm^{-1}, $R(R_w) = 0.022(0.028)$ for 3303 intensities $\geqslant 3\sigma(I)$ with $\theta(\text{Mo-}K_\alpha) \leqslant 25°$. (**2b**): space group $P2_1/a$ (No. 14), $a = 16.109(2)$, $b = 9.464(2)$, $c = 17.995(2)$ Å, $\beta = 109.42(1)°$, $U = 2587(1)$ Å^3, $D_c = 2.029$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 47.5$ cm^{-1}, $R(R_w) = 0.030(0.036)$ for 5674 intensities $\geqslant 3\sigma(I)$ with $\theta(\text{Mo-}K_\alpha) \leqslant 30°$. (**3a**): space group $P2_1/n$ (No. 14), $a = 8.974(1)$, $b = 30.188(2)$, $c = 9.976(1)$ Å, $\beta = 109.67(1)°$, $U = 2545(1)$ Å^3, $D_c = 2.072$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 48.3$ cm^{-1}, $R(R_w) = 0.021(0.026)$ for 3425 intensities $\geqslant 2\sigma(I)$ with $\theta(\text{Mo-}K_\alpha) \leqslant 25°$.

Crystal data for (**4**): $C_{20}H_{18}F_{12}SW$, $M = 702.3$, triclinic, space group $P\bar{1}$, $a = 8.856(2)$, $b = 8.916(3)$, $c = 15.242(1)$ Å, $\alpha = 76.23(2)$, $\beta = 85.82(1)$, $\gamma = 75.68(3)°$ (reduced cell), $U = 1132(1)$ Å^3, $Z = 2$, $D_c = 2.059$ g cm^{-3}, $F(000) = 672$ electrons, $\mu(\text{Mo-}K_\alpha) = 54.0$ cm^{-1}, 307 parameters, $R(R_w) = 0.029\ (0.037)$ for 5510 intensities $\geqslant 3\sigma(I)$ with $\theta(\text{Mo-}K_\alpha) \leqslant 30°$. Atomic co-ordinates for (**2a**), (**2b**), (**3a**), and (**4**) are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

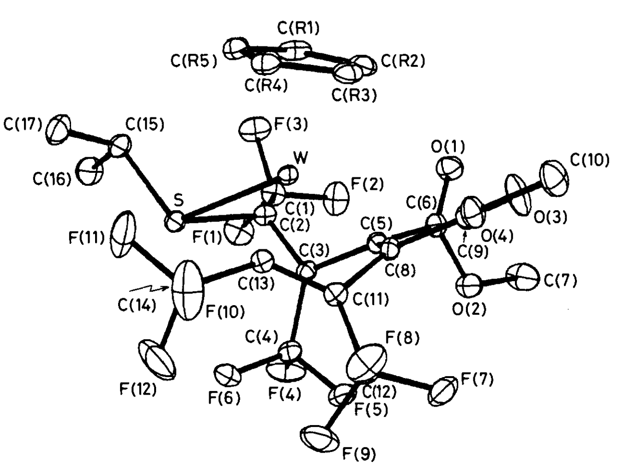


Figure 1. The molecular structure of $[(\eta^5\text{-}C_5H_5)\overline{WC(CF_3)=C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)SPr^i}]$ (**2a**). Hydrogen atoms and W–C bonds are omitted here and in Figures 2 and 3 for clarity. Selected bond lengths: W–S 2.522(2), W–C(2) 2.097(5), W–C(3) 2.113(5), W–C(5) 2.111(5), W–C(8) 2.284(5), and W–C(13) 2.150(5) Å. Apart from the position of the Pr^i group C(15)—C(17) the structure of isomer (**2b**) is essentially identical to that of (**2a**).

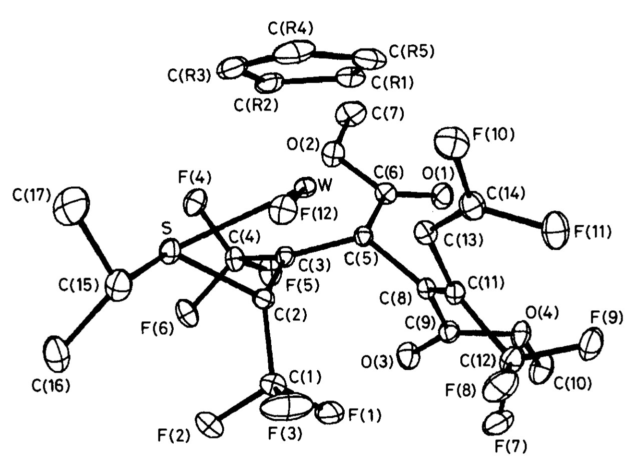


Figure 2. The molecular structure of $[(\eta^5\text{-}C_5H_5)\text{-}\overline{FWC(=CF_2)C(CF_3)=C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)SPr^i}]$ (**3a**). Selected bond lengths: W–S 2.494(2), W–F(12) 1.966(3), W–C(2) 2.111(4), W–C(3) 2.177(4), W–C(5) 2.312(4), and W–C(13) 2.195(4) Å.

The structure of (**3a**)† (Figure 2) involves, at least in a formal sense, an unusual transfer of a fluorine atom from C(14) to W and concomitant rupture of the long [2.303(4) Å] W–C(8) bond. Compound (**3a**) can be regarded as an 18 e tungsten(IV) piano-stool complex in which the hexatrienyl-metal attachment is via a *quasi* π-allylic interaction with the η^3-C(2)C(3)C(5) unit and through W–S and σ-alkenyl W–C(13) bonds. The W–C distances to C(2), C(3), and C(5) are rather variable (2.11—2.31 Å) and substantial twisting of the allylic unit is revealed by the C(1)–C(2)–C(3)–C(4) and C(4)–C(3)–C(5)–C(6) torsion angles of 81 and 23° respectively.

Unlike $MeO_2CC{\equiv}CCO_2Me$ the addition of $MeC{\equiv}CMe$ to (**1**) involves rupture of the W–S bond followed by the apparent insertion of the incoming alkyne into the Pr^iS–$C(CF_3)$ bond. Complex (**4**)† thus contains an η^4-butadienyl ligand (Figure 3). The short W–C(6) distance in (**4**) suggests that the W=C(carbene) bond also found in (**1**) is unaffected by the addition of $MeC{\equiv}CMe$. The coplanarity of the six-atom unit C(6)—C(11) and the extreme length of the W–C(7) and W–C(10) bonds are indicative of an η^2-alkene–W interaction (see ref. 6) whereas the valency angles around C(11) and the shorter W–C(11) distance are consistent with σ-W–C bonding. A closely related butadienyl ligand attached to ruthenium has recently been described.[7] However the three non-carbenoid Ru–C distances are nearly equal, consistent with a symmetrical π-allylic system rather than the irregular σ + π attachment to the metal found in (**4**).

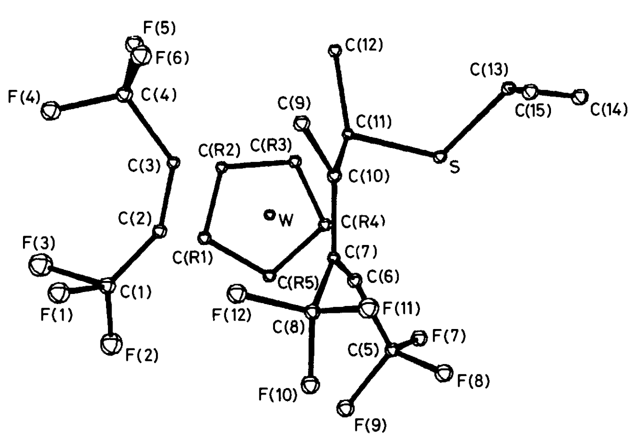
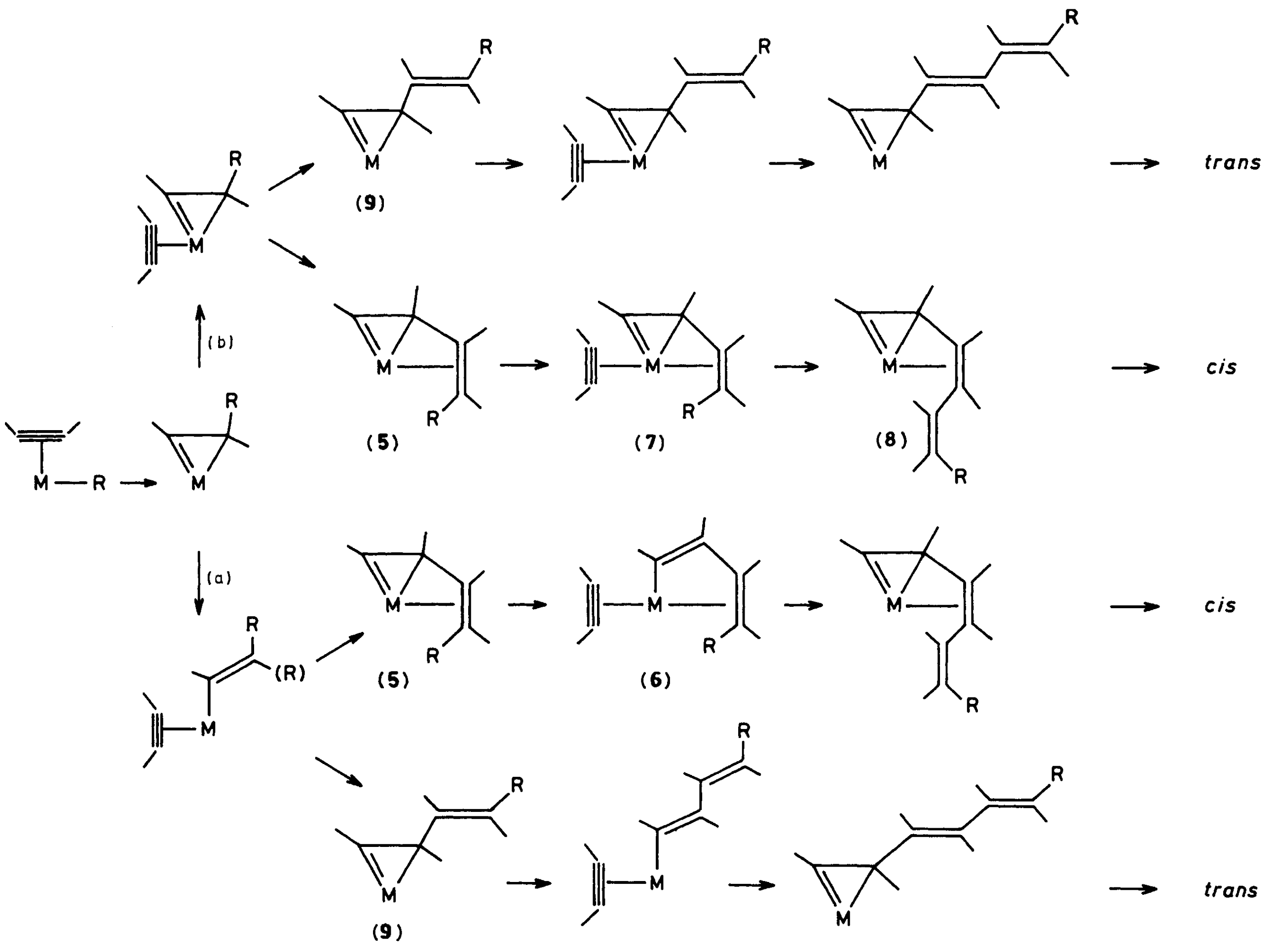


Figure 3. The molecular structure of $[(\eta^5\text{-}C_5H_5)W(\eta^2\text{-}F_3CC_2CF_3)\{\eta^4\text{-}C(CF_3)C(CF_3)CMeCMeSPr^i\}]$ (**4**). Selected bond lengths: W–C(2) 2.089(5), W–C(3) 2.161(5), W–C(6) 1.940(5), W–C(7) 2.347(5), W–C(10) 2.423(5), and W–C(11) 2.238(5) Å.

The structures of (**2**), (**3a**), and (**4**) are consistent with the preferential reaction of the incoming alkyne with the η^2-vinyl ligand *via* insertion into the W=C bond of (**1**). The structure of (**4**) provides a model for the initial outcome of this process although with $MeC{\equiv}CMe$ an additional feature involves migration of the SR group from the fluorocarbon to the hydrocarbon portion of the C_4 fragment. Subsequent insertion of the remaining co-ordinated alkyne does not occur at ambient temperature unlike the reaction of (**1**) with $MeO_2CC{\equiv}CCO_2Me$ which was observed by ^{19}F n.m.r. studies to give (**2a**), (**2b**), and (**3a**) at or below 0 °C *via* at least three unstable intermediates. It was also established that (**2**) and (**3a**) are both end products of the reaction, *i.e.* (**2**) is not the precursor of (**3a**) under the conditions of the experiment. Presumably one of the low-temperature intermediates fulfils this role in a process which may involve the fluorine equivalent of an agostic hydrogen.[8] Previously we have observed that fluorine abstraction from a CF_3 group occurs in the reaction of $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with octacarbonyldicobalt to generate a CF_2-containing fluorocarbon ligand.[9]

The transformation of (**1**) into (**2**), (**3**), and (**4**) provides a model for alkyne oligomerisation at a mononuclear metal centre and suggests new mechanisms for such processes involving η^2-vinyl intermediates (Scheme 2). Two basic mechanisms are possible which differ only with respect to the crucial insertion reaction; path (a) involves alkyne insertion into a metal–carbon single bond while path (b) involves insertion into a (formal) metal–carbon double bond. Conceivably either mechanism could operate depending upon the ease with which the metal can generate co-ordinative unsaturation by ligand dissociation. An important consequence of this concerns the stereochemistry of the oligomerisation product, *E* or *Z*. We note that in (**4**) where the two sp^2 carbons



Scheme 2

of the original η^2-vinyl remain co-ordinated to the metal *cis* addition has occurred. This may imply that co-ordination of the alkene function α to the η^2-vinyl as in (**5**) will favour *cis* addition by distorting the η^2-vinyl ligand prior to the crucial ring opening process (**5**) → (**6**) or (**5**) → (**7**) → (**8**). When more restrictive co-ordination prevents bonding of the α-alkene as in (**9**) either *cis* or *trans* addition can occur depending on the mode of ring opening of the η^2-vinyl. However the possibility of isomerisation occurring *e.g.* (**5**) → (**9**), prior to the step which controls stereochemistry means that we cannot exclude the possibility of *trans* products also being formed *via* (**5**).

Finally we note that with regard to Zeigler–Natta type alkyne polymerisation reactions, recent n.m.r. evidence has been shown to favour a four-centre η^1-vinyl mechanism rather than the recently proposed metallocycle route.[1] However the data available at present could also be interpreted in terms of either of the η^2-vinyl mechanisms proposed in Scheme 2.

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