Stabilisation of Vinylic Intermediates in the Addition, Cyclisation, and Oligomerisation Reactions of Alkynes by Co-ordination to Molybdenum and Tungsten. The Crystal and Molecular Structure of [W(SC₆H₄Me-p){η²-C(CF₃)·C(CF₃)PEt₃} (η²-CF₃C≡CCF₃)(η-C₅H₅)] and [WCl{η²-C(CF₃)·C(CF₃)CNBuᵗ}(η²-CF₃C≡CCF₃)(η-C₅H₅)]

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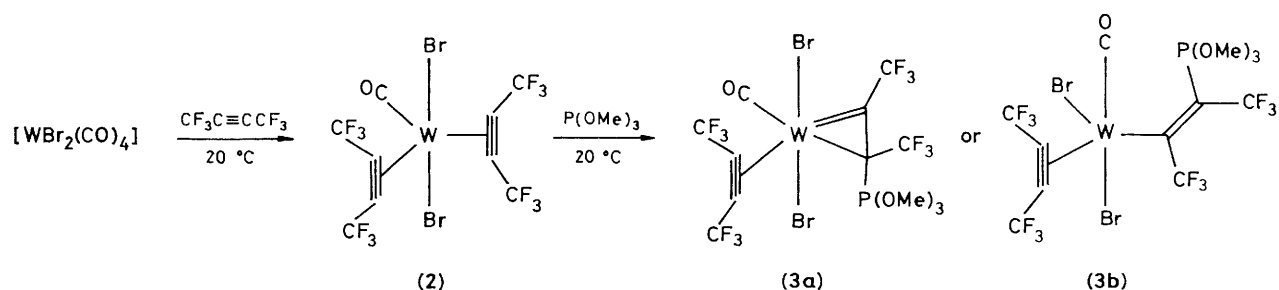ᵃ Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS, U.K.
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Nucleophilic attack of phosphines, phosphites, and t-butyl isocyanide (L) on the bis-hexafluorobut-2-yne complexes [WBr₂CO(CF₃C≡CCF₃)₂] and [MX(CF₃C≡CCF₃)₂(η-C₅H₅)] (M = Mo, W; X = Cl, SC₆F₅ : M = W; X = SC₆H₄Me-p) occurs at an acetylenic carbon atom to give 1 : 1 adducts shown by X-ray

diffraction studies to contain a metal-stabilised 1–3 dipolar vinyl ligand $\overset{+}{L}C(CF_3)\cdot\overset{-}{C}(CF_3)$ co-ordinated in an η² manner to the metal centre.

Recently we reported that co-ordinatively unsaturated alkyne complexes (1) react with anionic sulphur–nitrogen ligands to give novel η²-vinyl complexes resulting from sulphur co-ordination to the metal and nitrogen addition to an alkyne carbon atom, while hydride addition to the cationic alkyne complex [Mo {P(OMe)₃}₂(PhC≡CPh)(η-C₅H₅)]⁺ has also been reported to give an η²-vinyl complex [Mo {η²-C(Ph)·C(Ph)H }-

{P(OMe)₃ }₂(η-C₅H₅)].² The latter result was interpreted in terms of initial hydride attack at the metal followed by alkyne insertion into the resulting metal–hydride bond to give an η¹-vinyl complex which subsequently rearranges to the η²-form. We now report that η²-vinyl complexes can be obtained from the reactions of simple nucleophiles with complexes (1) apparently via direct attack at an acetylenic carbon.


Scheme 1

Scheme 2

(1)

a; M = Mo
b; M = W

(4)

a; M = W, X = SC_6H_4Me -p, L = PEt_3
b; M = W, X = Cl, L = $CNBu^t$
c; M = Mo, X = CF_3, L = $CNBu^t$ (ref. 5a)
d; M = Mo, W; X = Cl, SC_6F_5;

L = PEt_3, PMe_2Ph, PPh_3, $P(OMe)_3$

(5)

a; M = Mo; X = Cl, Br, I; Y = O
b; M = W; X = Cl, SC_6H_4Me; Y = NBu^t
c; M = Mo, X = CF_3, Y = NBu^t (ref. 5a)
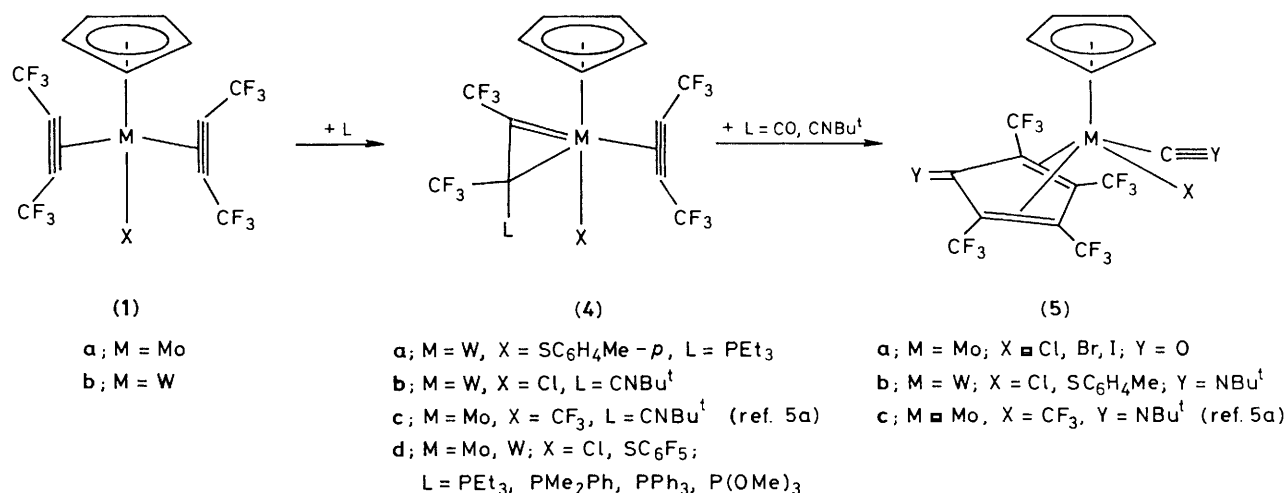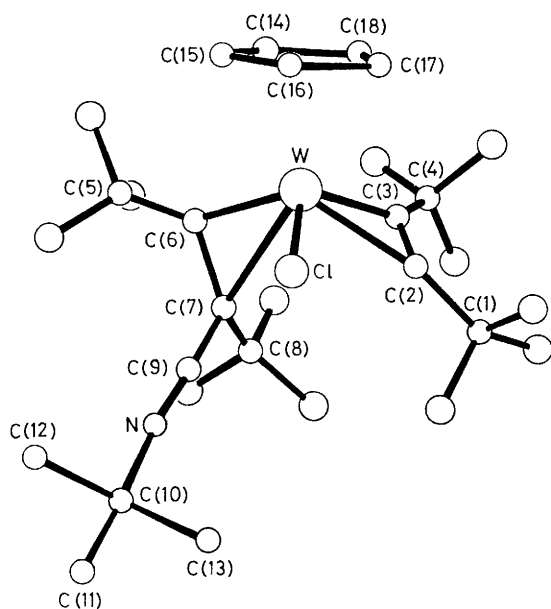
Figure 1. The molecular structure of [(η-C_5H_5)WCl($F_3CC_2CF_3$)-{$F_3CCC(CF_3)CNBu^t$}] (**4b**). Selected dimensions (Å and °) are: W–Cl 2.416(3), W–C(2) 2.108(9), W–C(3) 2.097(8), C(2)–C(3) 1.293(12), W–C(6) 1.894(8), W–C(7) 2.304(10), C(6)–C(7) 1.410(12), C(7)–C(9) 1.415(12), N–C(9) 1.128(12), N–C(10) 1.466(13); ∠C(7)–C(9)–N 176(1), C(9)–N–C(10) 173(1). Here and in Figure 2 F atoms are unnumbered.
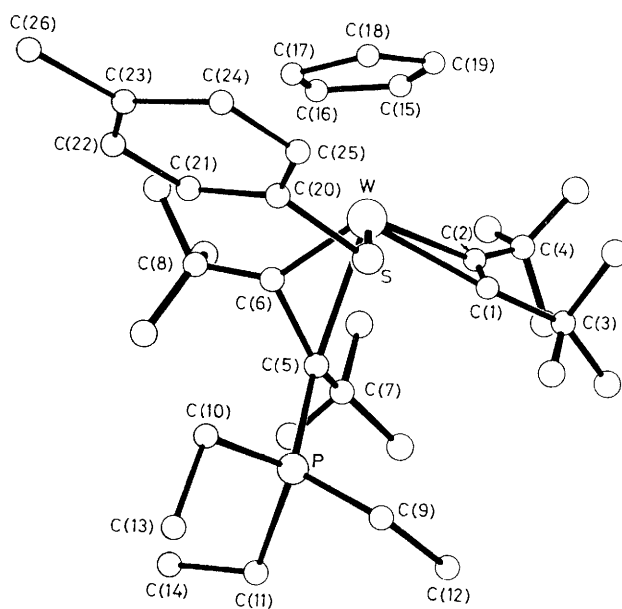
Figure 2. The molecular structure of [(η-C_5H_5)W(SC_6H_4-Me-p)($F_3CC_2CF_3$) {$F_3CCC(CF_3)PEt_3$}] (**4a**). Selected distances (Å) are: W–S 2.425(2), W–C(1) 2.167(5), W–C(2) 2.128(6), C(1)–C(2) 1.288(7), W–C(5) 2.330(5), W–C(6) 1.910(5), C(5)–C(6) 1.448(6), P–C(5) 1.810(5), P–C(9) 1.808(5), P–C(10) 1.796(6), P–C(11) 1.814(6).

Reaction of $CF_3C{\equiv}CCF_3$ with [$WBr_2(CO)_4$] (hexane; 20 °C) gives a novel co-ordinatively unsaturated complex (**2**) related to the five-co-ordinate monoalkyne complex [$Mo(SBu^t)_2(CNBu^t)_2(HC{\equiv}CH)$].[3] A notable feature of (**2**) is the exceptionally high ν_{CO} i.r. frequency (2172 cm^{-1}), comparable with that of H_3BCO (2165 cm^{-1}), and significantly higher than that of free CO (2143 cm^{-1}).[4] This implies that $CF_3C{\equiv}CCF_3$ is capable of acting as a more effective π-acceptor than carbon monoxide and as a result there is little, if any, M–CO back donation in (**2**), i.e., CO is acting as a σ-donor ligand only. Complex (**2**) and related hexafluorobut-2-yne complexes (**1a,b**) react (Et_2O; 20 °C) with nucleophiles (Schemes 1 and 2) to give the 1 : 1 adducts (**3**) and (**4**) respectively. ^{19}F and ^{31}P N.m.r. studies suggested that nucleophilic attack had occurred at an acetylenic carbon atom rather than at the metal[5] and this has been confirmed by X-ray diffraction

studies of [W(SC_6H_4Me-p) {η^2-C(CF_3)·C(CF_3)PEt_3 }(η^2-CF_3-C{\equiv}CCF_3)(η-C_5H_5)] (**4a**) and [WCl {η^2-C(CF_3)·C(CF_3)$CNBu^t$ }-(η^2-CF_3C{\equiv}CCF_3)(η-C_5H_5)] (**4b**) which reveal the presence of novel η^2-vinyl ligands (Figures 1 and 2).†

Attachment of η^5-C_5H_5, a 2 e donor η^2-alkyne, an anionic ligand X (4a, X = SC_6H_4Me-p, M = W; 4b, X = Cl), and the η^2-vinyl to W completes an 18 e configuration at each metal atom. The W–C bond lengths involved in the W–η^2-vinyl inter-action suggest a metallated cyclopropene ring $\overline{W=C(CF_3)-C}$-$(CF_3)L$, the W=C bonds being *ca* 0.4 Å shorter than the W–C bonds. In both molecules the η^2-alkyne C≡C bond is parallel (to within 2°) to the W–X bond and both these bonds are roughly normal to the η^2-vinyl WC_2 ring. In contrast both C≡C bonds in $[WCl(CF_3C≡CCF_3)_2(\eta$-$C_5H_5)]$ lie approximately parallel to each other and to the W–Cl bond,[6] *i.e.* co-ordination of the nucleophile to the acetylenic carbon results in rotation of the fluorocarbon moiety by *ca.* 90°. With respect to the WC_2 ring the C–L (L = $CNBu^t$ or PEt_3) and W–X bonds are *cis*, the X–W–C–L torsion angles being respectively 9(1) and $-3(1)$°. The relative orientations of the ligands in these complexes may be determined by electronic factors and further structural studies are in hand to investigate this point. The existence of η^2-vinyl ligands $C(CF_3)\cdot C(CF_3)L$ in complexes (4) supports the contention that a similar species (3a) is formed in the reaction of (2) with $P(OMe)_3$. However we do not at this stage rule out the possibility of an isomeric η^1-vinyl structure (3b) in view of the large J_{FF} value (14.42 Hz) observed for the CF_3 groups on the $C(CF_3)\cdot C(CF_3)P(OMe)_3$ moiety since this value is characteristic of *cis*-CF_3 groups in fluoro-olefin derivatives.[7a]

The formation of η^2-vinyl complexes (4) by direct nucleophilic attack at a co-ordinated alkyne has mechanistic implications for several reactions. The carbonylation of (1a) to give (5a) (CO; 3 atm; 90 °C) parallels the formation of (5b, c) from the reaction of (1) with two molar equivalents of Bu^tNC.[5a] The isolation of intermediates (4b, c) in the latter reactions suggests that η^2-vinyl complexes may also be involved in the carbonylation reactions and in other cyclisations of co-ordinated alkynes. It is also conceivable that the η^2-vinyl complex $[M\{\eta^2$-$C(Ph)\cdot C(Ph)H\}\{P(OMe)_3\}_2(\eta$-$C_5H_5)]$ referred to earlier[2] could result from direct attack of hydride ion at the co-ordinated alkyne rather than at the metal.

Previously it has been postulated that nucleophilic addition of alcohols, thiols, phosphines, and isocyanides (L) to electrophilic acetylenes proceeds *via* zwitterionic intermediates $\overset{+}{L}CR\overset{-}{=}CR$.[7] The stabilisation of such a species by co-ordina-tion to a metal as in (3) and (4) lends credence to this suggestion. We also note that the previously observed activation of C≡C bonds in dinuclear metal acetylides towards attack by phosphines and amines has been attributed to the σ–π-co-ordination of the triple bond.[8] The formation of 1 : 1 adducts (3) and (4) clearly indicates that C≡C triple bonds can also be activated by co-ordination to a single metal centre, a fact which possibly may be attributed to the involvement of both acetylenic π-orbitals in bonding with the metal.[1,3]

Added in proof. Recently published X-ray diffraction studies of $[Cr\{\eta^1$-$C(OSiMe_3):C(H)PMe_3\}(CO)_5]$ reveal the presence of an η^1-vinyl ligand similar to that in (3b).[9]

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