Synthesis and Reactions of the Co-ordinatively Unsaturated Hexafluorobut-2-yne Complex $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$. The Crystal and Molecular Structure of $[\{W[C(CF_3){=}C(CF_3)P(OEt)_2O](\mu\text{-}Br)(CO)(CF_3C{\equiv}CCF_3)\}_2]$†

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Reaction of $[\{WBr_2(CO)_4\}_2]$ with $CF_3C{\equiv}CCF_3$ in pentane affords the bis(alkyne) complex $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$ (**1**) in which the carbonyl ligand appears to function as a σ-donor ligand only, according to i.r. data. Complex (**1**) reacts with $P(OMe)_3$ and $P(OEt)_3$ to give dimeric complexes $[\{W[C(CF_3){=}C(CF_3)P(OR)_2O](\mu\text{-}Br)(CO)(CF_3C{\equiv}CCF_3)\}_2]$ containing a novel vinylphosphonate ligand resulting from a Michaelis–Arbuzov type elimination of alkyl bromide. The structure of the complex with R = Et has been determined by *X*-ray analysis. Four centrosymmetric molecules occupy a monoclinic cell with $a = 24.068(2)$, $b = 8.440(2)$, $c = 25.197(2)$ Å, $\beta = 121.50(1)°$, space group $I2/a$ (no. 15, C^6_{2h}), and $R = 0.036$ for 2 872 reflections. The tungsten co-ordination is octahedral with mutually *cis* carbonyl and σ-alkenyl carbon atoms both *trans* to μ-Br groups, and with phosphate O *trans* to a four-electron donor η^2-$CF_3C{\equiv}CCF_3$. The bonding in the novel vinylphosphonate $W[C(CF_3){=}C(CF_3)P(OEt)_2O]$ chelate ring is discussed.

The co-ordination chemistry of alkynes and the early transition metals has attracted much attention in recent years.[1–7] This is in part a consequence of the unusual ability of such metals to co-ordinate up to three C≡C bonds without promoting alkyne cyclisation or oligomerisation reactions, a phenomenon which may reflect the participation of both sets of filled alkyne π orbitals in bonding with the metal.[8–11] Our interest in this area has primarily centred around cyclopentadienyl molybdenum(II) and tungsten(II) complexes synthesized *via* the reactions in equation (1).[12]

$$\begin{array}{ccccc} [MX(CO)_3(\eta^5\text{-}C_5H_5)] & \xrightarrow{RC\equiv CR} & [MX(CO)(RC{\equiv}CR)(\eta^5\text{-}C_5H_5)] & \xrightarrow{RC\equiv CR} & [MX(RC{\equiv}CR)_2(\eta^5\text{-}C_5H_5)] \\ M = Mo \text{ or } W & & X = Cl, Br, I, \text{ or } SR'; R = Ph & & X = Cl, R = CF_3 \text{ or } Ph \end{array} \qquad (1)$$

Recently we extended these studies to reactions of alkynes with $[\{WBr_2(CO)_4\}_2]$ which gave dinuclear bis(alkyne) products $[\{WBr_2(CO)(RC{\equiv}CR')_2\}_2]$ (R = R' = Ph, Et, or Me; R = Ph, R' = Me).[13] The extensive chemistry which we have developed from bis(hexafluorobut-2-yne) complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W)[14] therefore prompted us to extend our initial work on $[\{WBr_2(CO)_4\}_2]$ to reactions with $CF_3C{\equiv}CCF_3$, the results of which are now reported. Some of this work has been published previously as a communication.[14a]

Results and Discussion

The reaction of $CF_3C{\equiv}CCF_3$ with $[\{WBr_2(CO)_4\}_2]$ in pentane gives deep blue-green solutions which according to i.r. and ^{19}F n.m.r. studies contain a mixture of products. One of these, $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$ (**1**), proved to be sufficiently volatile to enable isolation and purification by vacuum techniques, but attempted crystallisation of the remaining involatile residue did not yield pure products, due in part to the instability of the species present. The volatile species (**1**) is an air-sensitive yellow crystalline solid which sublimes readily *in vacuo* at ambient temperature. Analytical data are in accord with the formulation $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$‡ although the highest peak in the mass spectrum $m/z = 668$ corresponds to $[M - CO]^+$ and is accompanied by peaks due to $[M - (CO + F)]^+$ and $[M - (CO + Br)]^+$. The i.r. spectrum contains two ν(C≡C) modes near 1 810 cm^{-1} some 40 cm^{-1} to high frequency of those observed for the bis(hexafluorobutyne) complex $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$.[12] Interestingly the ν(CO) mode for complex (**1**) appears at the exceptionally high frequency of 2 172 cm^{-1} which is comparable with that of $BH_3(CO)$, 2 165 cm^{-1}, and significantly higher than that of free carbon monoxide, 2 143 cm^{-1}.[15] It is commonly accepted that the bonding between CO and a low-valent transition metal involves a synergic combination of σ donation, OC⟶M, and π back donation, M⟶CO, whereas CO adducts with main-group elements, as in $BH_3(CO)$, only involve σ donation. The π back donation populates the CO antibonding orbitals and normally leads to a substantial decrease in the CO stretching frequency whereas σ donation from the weakly antibonding 5σ level leads to a slight increase. Since a net increase in ν(CO) from the free-ligand value is observed with complex (**1**) it must be concluded that the CO ligand is acting almost exclusively as a σ donor towards the tungsten and that metal–ligand π bonding is virtually absent.[15] We attribute this highly unusual situation to the ability of hexafluorobut-2-yne to function as a good π-acceptor ligand, in this case a more effective one than carbon monoxide.

On the basis of the spectroscopic data discussed so far a monomeric formulation for complex (**1**) seems probable, particularly in view of the high volatility of the complex. The ^{19}F n.m.r. spectrum (Table 1) consists of a single sharp resonance consistent with structure (**1**^{i}) in which the two

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† Di-μ-bromo-bis{carbonyl[3-(diethoxyphosphoryl)hexafluorobut-2-en-2-yl-C^2O](η-hexafluorobut-2-yne)tungsten}.

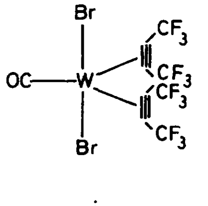
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ *Note added in proof:* an alternative formula $[WBr_2(CO)_2(CF_3C{\equiv}CCF_3)_2]$ should also be considered in view of a recent *X*-ray diffraction study of $[WI_2(CO)_2(MeC{\equiv}CMe)_2]$ (P. K. Baker, personal communication).

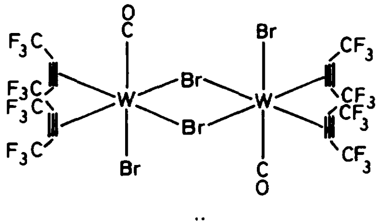
Table 1. N.m.r. data for the complexes[a]

Complex	^1H	^{19}F
(1)		-57.45(s)
(2a)	3.98 (d, $J_{P-H} = 11.6$, 3 H)	δ_1 -53.86 [dq, $J_{P-F} = 10.3$, $J(F^1F^3) = 14.3$, 3 F]
	3.94 (d, $J_{P-H} = 11.7$, 3 H)	δ_2 -57.08 [qq, $J(F^2F^3) = 2.8$, $J(F^2F^4) = 2.8$, 3 F]
		δ_3 -57.42 [qqq, $J(F^3F^1) = 14.4$, $J(F^3F^2) = 2.8$, $J(F^3F^4) = 2.6$, 3 F]
		δ_4 -59.03 [qq, $J(F^4F^2) = 2.8$, $J(F^4F^3) = 2.6$, 3 F]
(2b)	4.05 (d, $J_{P-H} = 10.7$, 3 H)	δ_1 -56.22 [dq, $J_{P-F} = 8.8$, $J(F^1F^3) = 13.6$, 3 F]
	4.0 (d, $J_{P-H} = 10.6$, 3 H)	δ_2 -58.02 (m, 6 F)
		δ_3 -58.83 [br q, $J(F^3F^1) = 13.8$, 3 F]
(3a)[b]	4.45 (m, 4 H)	δ_1 -53.01 (dq, $J_{P-F} = 10.3$, $J_{F-F} = 14.2$, 3 F)
	1.45 (m, 6 H)	$\left.\begin{matrix}\delta_2\\\delta_3\end{matrix}\right\}$ -56.2 (2 overlapping multiplets, 6 F)
		δ_4 -57.69 (m, 3 F)
(3b)[b]	4.42 (m, 4 H)	δ_1 -52.74 [dq, $J_{P-F} = 10.1$, $J(F^1F^2) = 14.4$, 3 F]
	1.40 (m, 6 H)	δ_2 -55.55 [qqq, $J(F^2F^1) = 14.3$, $J(F^2F^3) = 2.7$, $J(F^2F^4) = 2.4$, 3 F]
		δ_3 -56.44 [qq, $J(F^3F^2) = 2.7$, $J(F^3F^4) = 3.2$, 3 F]
		δ_4 -58.19 [qq, $J(F^4F^2) = 2.4$, $J(F^4F^3) = 3.2$, 3 F]
(3c)[b]	4.45 (m, 2 H)	δ_1 -53.65 [dq, $J_{P-F} = 10.3$, $J(F^1F^3) = 14.4$, 3 F]
	3.91 (m, 2 H)	δ_2 -55.87 (spt, 3 F)
	1.54 (t, 3 H)	δ_3 -58.10 [br q, $J(F^3F^1) = 14.4$, 3 F]
	1.22 (t, 3 H)	δ_4 -58.75 (m, 3 F)
(3d)[b]		δ_1 -53.60 [dq, $J_{P-F} = 10.2$, $J(F^1F^3) = 14.2$, 3 F]
		δ_2 -56.87 (spt, 3 F)
		δ_3 -57.0 [qm, $J(F^3F^1) = 14.2$, 3 F]
		δ_4 -58.96 (spt, 3 F)

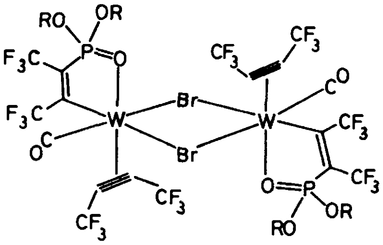
[a] $\delta(SiMe_4) = 0$, $\delta(CCl_3F) = 0$. [b] In $(CD_3)_2CO$.



(1^i)



(1^{ii})



(2) R = Me

(3) R = Et

bromide ligands occupy the two axial sites of a trigonal bipyramid and the two equatorial alkynes adopt orientations parallel to the W–Br axis. Less symmetric isomeric structures are also possible in which alkyne propeller rotation and/or alkyne site exchange could result in a single CF_3 n.m.r. resonance although no evidence for this was found in the ^{19}F n.m.r. spectrum at −90 °C ($CD_3C_6D_5$ solution). However, we cannot completely exclude a dimeric structure (1^{ii}) similar to that proposed for complexes $[\{WBr_2(CO)(RC{\equiv}CR')_2\}_2]$ obtained from the reactions of $[\{WBr_2(CO)_4\}_2]$ with PhC≡CPh, PhC≡CMe, MeC≡CMe, and EtC≡CEt.[13] Unfortunately, complex (1) was too unstable for molecular-weight studies in solution. The dimeric structure (1^{ii}) is formally derived from that established for the tetracarbonyl dimer in the solid state[16] by replacement of three terminal carbonyls on each metal by two alkynes so as to generate a six-co-ordinate octahedral geometry at each metal centre. Such a structure would also require facile alkyne propeller rotation to explain the ^{19}F n.m.r. data, whereas it may be significant that $[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}_2]$ is stereochemically rigid on the ^1H and ^{13}C n.m.r. time-scale at 20 °C.

Although structure (1^i) is more compatible with the data available we note that both (1^i) and (1^{ii}) share a common feature, namely co-ordinative unsaturation. The ability of both sets of filled alkyne π orbitals to participate in bonding with a single metal centre is reasonably well established[8–10] and in the case of (1^i) it is necessary to consider that each alkyne functions as a four-electron donor in order that the metal achieves an 18-electron configuration. In the case of (1^{ii}) the alkynes would be considered as three-electron donors. The structure (1^i) can be compared with that established for five-co-ordinate molybdenum(II) complexes $[Mo(SBu^t)_2(CNBu^t)_2(RC{\equiv}CR)]$ (R = H or Ph)[3] which at best can achieve only a 16-electron configuration with a four-electron donor alkyne, or six-co-ordinate $[WBr_2(CO)(CNBu^t)(MeC{\equiv}CMe)_2]$ with three-electron donor alkynes.[13] The latter was obtained from the reaction of the dimer $[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}_2]$ with 1 molar equivalent of $CNBu^t$ and spectroscopic data clearly indicate that the isocyanide has attacked the metal centre. This contrasts with our previous observations that bis(hexafluorobut-2-yne) complexes, $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, CF_3, SC_6F_5, or SC_6H_4Me-4), give η^2-vinyl complexes $[MX\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (L = $CNBu^t$, tertiary phosphine, or phosphite) resulting from attack of ligand L at an alkyne carbon.[14] In view of this difference limited studies of the chemistry of complex (1) were carried out.

The reaction of complex (1) with triphenylphosphine gave an intractable material from which pure products could not be isolated. However, reactions of trimethyl and triethyl phosphite in diethyl ether at room temperature gave murky green solutions from which dark green crystals of complexes (2) and (3) were obtained by multiple recrystallisation. On the basis of carbon, hydrogen, and phosphorus analysis complex (2) was originally[14a] assigned the stoicheiometry $[WBr_2(CO)(CF_3C{\equiv}C\text{-}CF_3)\{P(OMe)_3\}]$. However, subsequent analysis for bromine

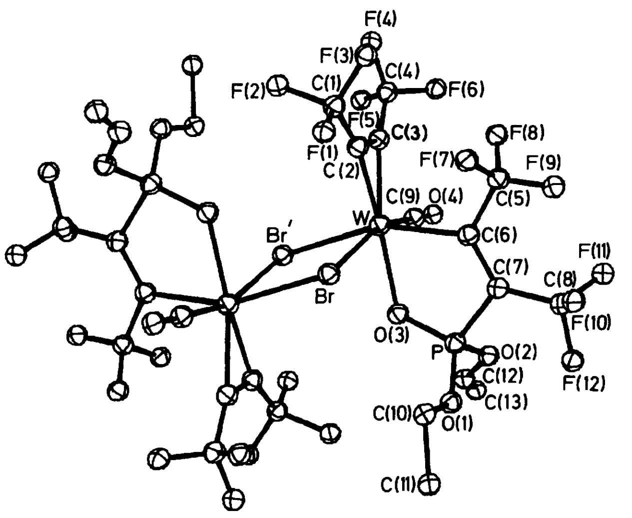


Figure 1. A perspective view of the centrosymmetric molecule $[\{W[C(CF_3)=C(CF_3)P(OEt)_2O](\mu\text{-}Br)(CO)(CF_3C\equiv CCF_3)\}_2]$ (3), showing the atom-numbering scheme. Atoms are represented by spheres of arbitrary size and hydrogen atoms are omitted

combined with data for complex (3) is more consistent with the presence of only one bromide ligand. This conflicting situation could not be resolved by mass spectrometry due to decomposition in the ionisation chamber and consequently single-crystal *X*-ray diffraction studies of complex (3) were carried out. These confirmed that loss of bromine had occurred and indicated that the overall reaction is that given in equation (2). Although the precise reaction mechanism is unclear the

$$2[WBr_2(CO)(CF_3C\equiv CCF_3)_2] + 2\,P(OEt)_3 \longrightarrow [\{W[C(CF_3)=C(CF_3)P(OEt)_2O](\mu\text{-}Br)(CO)(CF_3C\equiv CCF_3)\}_2] + 2\,EtBr \quad (2)$$

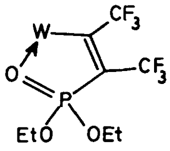
structural results (Figure and Table 2) suggest that nucleophilic attack by $P(OEt)_3$ at a co-ordinated hexafluorobut-2-yne is followed by a Michaelis–Arbuzov type elimination of EtBr[17] and dimerisation to give the $W_2(\mu\text{-}Br)_2$ ring system.

In the solid each molecule of complex (3) lies on a crystallographic inversion centre. The tungsten atoms display octahedral co-ordination, with O(3) *trans* to the centroid of the alkyne C(2)–C(3) bond, and carbonyl C(9) and σ alkenyl C(6) *trans* to Br and Br′ respectively. There are substantial deviations of the bond angles at W from the idealised octahedral values of 90 and 180°. These can be explained only in part by the constraints imposed by chelate ring formation. A more important factor appears to be the bending away from the η^2-bonded alkyne molecule by the ligands *cis* to it, revealed by O(3)–W–Br, -Br′, -C(6), and -C(9) angles 8—13° less than 90°. This distortion is also apparent in the mononuclear complex $[MoBr_2(CO)(PEt_3)_2(PhC\equiv CH)]$ which has several structural features in common with complex (3), including the *fac* arrangement of CO, alkyne, and Br[18] ligands within the distorted octahedron. Substantial deformations from octahedral geometry have been observed in a number of d^4 complexes of molybdenum(II) and tungsten(II) containing a variety of ligand types.[19] Extended-Hückel calculations indicate that electronic rather than steric factors are responsible for such distortions,[19] a conclusion which may also apply in the case of complex (3).

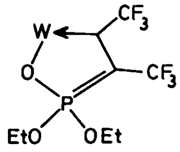
Table 2. Selected distances (Å) and angles (°) in complex (3)

W–Br	2.681(1)	W–Br′	2.605(1)[a]
W–O(3)	2.096(6)	W–C(2)	1.998(11)
W–C(3)	2.014(10)	W–C(6)	2.171(9)
W–C(9)	2.002(10)	P–O(1)	1.510(10)
P–O(2)	1.556(9)	P–O(3)	1.493(7)
P–C(7)	1.711(11)	O(1)–C(10)	1.419(19)
O(2)–C(12)	1.422(27)	O(4)–C(9)	1.121(12)
C(1)–C(2)	1.453(19)	C(2)–C(3)	1.341(14)
C(3)–C(4)	1.459(15)	C(5)–C(6)	1.535(17)
C(6)–C(7)	1.334(13)	C(7)–C(8)	1.494(20)
C(10)–C(11)	1.517(26)	C(12)–C(13)	1.05(4)[b]
Br–W–Br′	82.5(1)	Br–W–O(3)	80.2(2)
Br–W–C(2)	84.2(3)	Br–W–C(3)	123.0(3)
Br–W–C(6)	90.0(3)	Br–W–C(9)	161.9(3)
Br′–W–O(3)	81.4(2)	Br′–W–C(2)	101.4(3)
Br′–W–C(3)	100.4(3)	Br′–W–C(6)	158.4(3)
Br′–W–C(9)	91.2(3)	O(3)–W–C(2)	163.7(4)
O(3)–W–C(3)	156.8(4)	O(3)–W–C(6)	77.3(3)
O(3)–W–C(9)	82.0(4)	C(2)–W–C(3)	39.0(5)
C(2)–W–C(6)	97.9(4)	C(2)–W–C(9)	113.8(4)
C(3)–W–C(6)	100.7(4)	C(3)–W–C(9)	74.8(4)
C(6)–W–C(9)	89.7(4)	O(1)–P–O(2)	105.0(6)
O(1)–P–O(3)	114.4(5)	O(1)–P–C(7)	114.0(6)
O(2)–P–O(3)	112.1(5)	O(2)–P–C(7)	106.9(6)
O(3)–P–C(7)	104.3(5)	P–O(1)–C(10)	125.3(10)
P–O(2)–C(12)	125.8(12)	W–O(3)–P	123.4(4)
W–C(2)–C(1)	153.3(9)	W–C(2)–C(3)	71.1(6)
C(1)–C(2)–C(3)	135.6(10)	W–C(3)–C(2)	69.8(6)
W–C(3)–C(4)	152.6(10)	C(2)–C(3)–C(4)	137.5(11)
W–C(6)–C(5)	117.5(8)	W–C(6)–C(7)	121.9(7)
C(5)–C(6)–C(7)	120.6(10)	P–C(7)–C(6)	112.7(8)
P–C(7)–C(8)	118.6(10)	C(6)–C(7)–C(8)	128.6(12)
W–C(9)–O(4)	179.2(9)	O(1)–C(10)–C(11)	108.3(13)
O(2)–C(12)–C(13)	140.3(26)[b]		

[a] Co-ordinates of primed atoms are derived from those of the corresponding unprimed atoms in Table 3 by the operation $\bar{x}, \bar{y}, \bar{z}$.
[b] Subject to systematic error because of disorder of C(13).



(I)



(II)

The W_2Br_2 ring in complex (3) is exactly planar. The two independent WBr bonds differ in length by 0.08 Å, the longer bond being *trans* to the carbonyl. The intramolecular W ··· W distance of 3.973(1) Å precludes direct bonding between the metal atoms; it is *ca.* 1 Å longer than the W–W bond in $[(OC)_3W(\mu\text{-}Br)(\mu\text{-}Me_2C_2)(\mu\text{-}Ph_2AsCH_2AsPh_2)WBr(CO)_2]$, for example.[20]

The most novel feature of the structure of complex (3) is the presence of a chelating diethyl vinylphosphonate ligand. The $WOPC_2$ ring is planar to within ±0.03 Å. The lengths of the W–O(3), W–C(6), and P–C(7) bonds suggest orders close to unity [*cf.* W^{II}–O, 2.10—2.13,[21] W^{II}–C(alkenyl), 2.19,[22] and $=C-P^V$, 1.79 Å[23]], whereas the C(6)–C(7) distance is consistent with a fixed double bond. Conclusions regarding the P–O bond lengths must be made with caution in the case of P–O(1) and P–O(2) since the OEt groups undergo substantial thermal motion and C(13) is disordered. However, typical P^V=O and P^V–O bond lengths are 1.46 and 1.59 Å[24] and we therefore consider that all the P–O linkages in (3) possess some multiple-bond character, with P–O(3) [1.493(7) Å] being closest to a double bond. The tungsten–vinylphosphonate bonding in complex (**3**) is therefore best described by (**I**) with some contributions from similar canonical forms involving P=O–Et groups. Invocation of the ylide–carbene form (**II**) does not appear necessary to explain the observed geometry of complex (**3**) which contrasts with the $P(OEt)_3$ adduct of $[Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)]$ which is believed to involve a significant contribution from an ylide–carbene similar to (**II**).[25]

The tungsten atoms in complex (**3**) can attain an 18-electron configuration only if the η^2-$CF_3C{\equiv}CCF_3$ donates both its π-electron pairs as a four-electron donor ligand.[8–11] As is expected under these circumstances[8,10,18,26–28] the W–CO and alkyne C≡C bonds are parallel [C(3)–C(2)–W–C(9) 4.0(6)°] so that both filled t_{2g} metal orbitals can π donate to the carbonyl and the third and empty t_{2g} orbital is correctly oriented for π donation of a second electron pair from $CF_3C{\equiv}CCF_3$. In $[(OC)_5W(SMe)W(CO)(CF_3C{\equiv}CCF_3)(\eta^5$-$C_5H_5)]$, the only other structural example of a four-electron donor $CF_3C{\equiv}CCF_3$–W system, the W–C(alkyne) bonds [2.033(11) and 2.062(11) Å] are longer and the η^2-bonded C≡C distance [1.299(16) Å] is slightly shorter than in (**3**).[29] Evidently the tungsten–alkyne interaction is stronger in complex (**3**), a feature we attribute to the inability of the other ligands to function as effective π donors to the metal atoms.

The spectroscopic properties of complexes (**2**) and (**3**) are similar and can be explained in terms of the solid-state structure of (**3**). For example, a single ν(CO) mode is observed in the i.r. spectrum at *ca.* 2 000 cm^{-1} consistent with the *trans* disposition of the two CO ligands while a ν(C≡C) band is observed at *ca.* 1 700 cm^{-1} some 100 cm^{-1} to lower frequency relative to that of the precursor (**1**). A band of similar intensity but lower frequency, *ca.* 1 500 cm^{-1}, we attribute to the ν(C=C) mode of the vinylphosphonate ligand.

The ^1H and, in particular, the ^{19}F n.m.r. data (Table 1) reveal the presence of several isomeric forms of complexes (**2**) and (**3**) in solution, two in the case of the $PO(OMe)_2$ derivative [(**2a**) and (**2b**)] and four in the case of (**3**) [(**3a**)—(**3d**)]. Apart from (**2b**) each isomer exhibits four distinct CF_3 resonances, a doublet of quartets and a quartet of quartets for the vinyl CF_3 group and two quartets of quartets for the alkyne CF_3 substituents. Fluorine-19 homodecoupling experiments were carried out on (**2a**) and (**3b**) (see Table 1) and in the case of the latter are summarised in Figure 2. The only notable feature is intra-ligand coupling between the two alkyne CF_3 substituents and the CF_3 on the metal-bonded carbon of the vinyl ligand. Since a through-bond interaction would involve coupling over six bonds we attribute this to a through-space coupling mechanism[30] as observed in related complexes.

Isomerism in complexes (**2**) and (**3**) presumably results from different arrangements of the ligands about the metal centres in the two complexes. In each case a centre or plane symmetry must exist since each isomer only gives rise to four CF_3 n.m.r. resonances. Since only one ν(CO) mode was observed in all cases, a centre rather than a plane of symmetry is indicated with *trans* CO ligands. On this basis it is possible to generate four distinct geometric isomers (**III**)—(**VI**) taking into account the requirement for a *cis* arrangement of the $CF_3C{\equiv}CCF_3$ and CO ligands in which the alkyne C≡C bond lies parallel to the M–CO axis. Isomers (**III**) and (**IV**) are based upon a *trans* arrangement of the CO with respect to a bridging bromide whereas isomers (**V**) and (**VI**) have the alkyne *trans* to a bromide ligand. It is not possible to assign specific peaks in the n.m.r. spectra to particular isomers except that complex (**3**) was obtained as a mixture of two isomers (**3a**) and (**3b**) in the first batch of crystals isolated and this provided the *X*-ray sample. It was also observed that in solution (**3a**) isomerises slowly to (**3b**) at room temperature. The second batch of crystals isolated contained only one isomeric form (**3c**) which on heating at 50 °C in $CDCl_3$ slowly isomerised to (**3d**). We note that six-co-ordinate monoalkyne complexes $[WBr_2(CO)(MeC{\equiv}CR)\{P(OMe)_3\}_2]$ (R = Me or Ph) are obtained from the reaction of $[\{WBr_2(CO)(MeC{\equiv}CR)_2\}_2]$ with $P(OMe)_3$ with a *cis* arrangement of $P(OMe)_3$ ligands, but rearrangement occurs readily in solution to a more stable isomeric form with *trans* $P(OMe)_3$ and *trans* alkyne and bromine ligands.[13]

The structure of complex (**3**) clearly implicates a mechanism of formation involving attack by the phosphite at an alkyne carbon possibly giving an η^2-vinyl intermediate (**4**) (see Scheme). This is supported by the isolation of such species from reactions of bis(hexafluorobut-2-yne) complexes $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5$-$C_5H_5)]$ with $P(OMe)_3$, $P(OEt)_3$, and other nucleophiles and their characterisation by *X*-ray diffraction studies.[14] Phosphite adducts $[MoCl\{\eta^2$-$C(CF_3)C(CF_3)P(OR)_3\}(CF_3C{\equiv}CCF_3)(\eta^5$-$C_5H_5)]$ (R = Me, Et, or Ph) and $[W(SC_6H_4Me$-$4)\{\eta^2$-$C(CF_3)C(CF_3)P(OR)_3\}(CF_3C{\equiv}CCF_3)(\eta^5$-$C_5H_5)]$ (R = Me or Et) are relatively stable, whereas in the present situation this is not the case and facile elimination of alkyl bromide apparently results in the formation of the vinylphosphonate product. This constitutes an interesting extension of the well known Michaelis–Arbuzov reaction, in which an alkyl halide and an alkyl phosphite react to form a phosphonate with alkyl transfer to phosphorus.[17] An increasing number of analogous reactions has also been reported in organometallic chemistry where a metal halide, *e.g.* $[CoX_2(CO)(\eta^5$-$C_5H_5)]$, $[FeX(CO)_2(\eta^5$-$C_5H_5)]$, and $[ReBr_2(CO)_2(\eta^5$-$C_5H_5)]$, replaces the alkyl halide and consequently leads to a metal phosphonate.[31] In the present case there is added novelty, in that

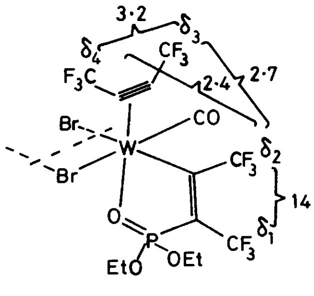
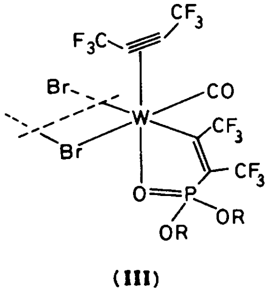
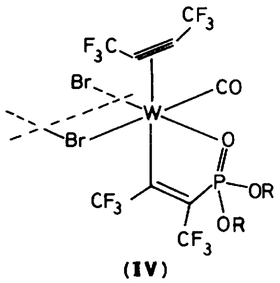


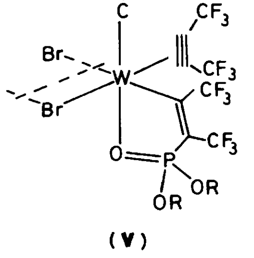
Figure 2. ^{19}F N.m.r. coupling connectivities in $[\{W[C(CF_3){=}C(CF_3)P(OEt)_2O](\mu$-$Br)(CO)(CF_3C{\equiv}CCF_3)\}_2]$, isomer (**3b**)



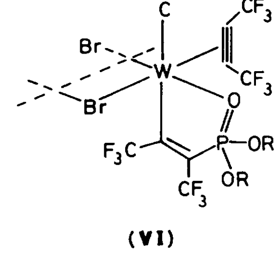
(III)



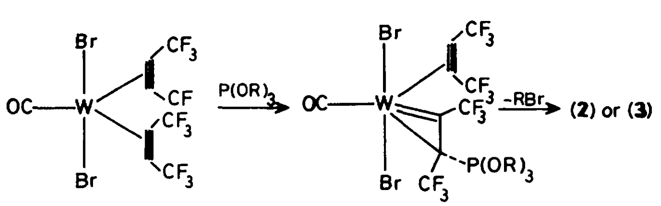
(IV)



(V)



(VI)



(1) (4)

Scheme. R = Me or Et

initial attack at the co-ordinated alkyne leads to a vinyl rather than a metal phosphonate. Consequently the formation of complexes (**2**) and (**3**) has features in common with both the organic and organometallic versions of the reaction in that phosphorus–carbon bond formation is accompanied by metal–halogen bond cleavage.

Studies designed to extend this reaction to a wider variety of unsaturated organic ligands are curently in progress.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer and mass spectra on a Vacuum Generators updated A.E.I. MS9. Hydrogen-1 and ^{19}F n.m.r. spectra were recorded in $CDCl_3$ (unless stated otherwise) at 200.1 and 188.2 MHz respectively on a Bruker WP200 SY spectrometer. Coupling constants are in Hz. All reactions and manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried by refluxing under nitrogen over powdered calcium hydride and distilled just before use. The complex $[\{WBr_2(CO)_4\}_2]$ was prepared by the published method.[16]

Reaction of $[\{WBr_2(CO)_4\}_2]$ *with* $CF_3C{\equiv}CCF_3$.—In a typical reaction the complex (*ca.* 1 g) and pentane (40 cm^3) were transferred to a thick glass tube fitted with a Westef stopcock. The solution was degassed thoroughly by the freeze–thaw method following which $CF_3C{\equiv}CCF_3$ (2 g) was condensed in at -196 °C. The tube was sealed and held at 40 °C for 72 h when a deep blue-green solution was obtained. Carbon monoxide and excess of $CF_3C{\equiv}CCF_3$ were removed *in vacuo* following which the solvent and remaining volatiles were condensed into a Schlenk tube at -196 °C. The resulting yellow solution was concentrated *in vacuo* and subsequently cooled to -20 °C whereupon pale yellow crystals formed. The remaining yellow solution was removed and the crystals dried under a stream of nitrogen. Sublimation onto a cold finger at 30 °C, 10^{-3} Torr (0.133 Pa) gave $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$ (**1**) (65 mg, 4%) (Found: C, 15.9; F, 31.9. Calc. for $C_9Br_2F_{12}OW$: C, 15.5; F, 32.75%). I.r. (CCl_4): ν(CO) 2 172s, ν(C≡C) 1 834wm and 1 818wm cm^{-1}.

Reactions of $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$.—*With* $P(OMe)_3$. A 10% solution of $P(OMe)_3$ in diethyl ether was added slowly to a stirred solution of $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$ (35 mg) in diethyl ether (10 cm^3) until the pale yellow colour just disappeared. The resultant murky brown solution slowly turned deep green and hexane (10 cm^3) was added. The solution was centrifuged to remove solids and following concentration and cooling to -20 °C an oily green solid was obtained. This was recrystallised several times from diethyl ether–hexane to give dark green crystals of $[\{W[C(CF_3)C{=}(CF_3)P(OMe)_2O](\mu\text{-}Br)(CO)(CF_3C{\equiv}CCF_3)\}_2]$ (**2**) (8 mg, 22%) (Found: C, 18.5; H, 0.9; Br, 11.6; P, 4.5. Calc. for $C_{22}H_{12}Br_2F_{24}O_8P_2W_2$: C, 18.20; H, 0.85; Br, 11.05; P, 4.30%). I.r. (CCl_4): ν(CO) 2 010s, ν(C≡C) 1 702wm, and ν(C=C) 1 596wm cm^{-1}.

Table 3. Fractional co-ordinates of non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	0.093 69(1)	0.047 26(4)	0.058 73(2)
Br	−0.019 69(4)	0.200 93(10)	−0.009 81(4)
P	0.076 09(14)	0.143 63(34)	0.170 84(12)
O(1)	0.019 0(5)	0.210 5(10)	0.172 9(4)
O(2)	0.120 0(5)	0.064 0(11)	0.235 5(4)
O(3)	0.057 7(3)	0.031 2(7)	0.118 4(3)
O(4)	0.204 8(3)	−0.160 2(9)	0.162 5(3)
F(1)	0.044 6(5)	0.296 9(14)	−0.085 9(5)
F(2)	0.070 5(5)	0.089 8(15)	−0.113 9(4)
F(3)	0.140 9(4)	0.264 1(11)	−0.064 2(4)
F(4)	0.223 1(6)	−0.025 5(18)	−0.008 7(7)
F(5)	0.213 7(5)	−0.205 5(13)	0.037 1(7)
F(6)	0.265 0(4)	−0.024 9(16)	0.085 0(7)
F(7)	0.139 5(6)	0.429 6(13)	0.046 9(7)
F(8)	0.220 0(4)	0.299 7(12)	0.100 4(5)
F(9)	0.200 4(7)	0.481 3(14)	0.139 9(7)
F(10)	0.129 4(5)	0.562 9(10)	0.182 5(5)
F(11)	0.211 9(6)	0.430 5(16)	0.243 4(5)
F(12)	0.127 7(7)	0.414 3(11)	0.245 1(5)
C(1)	0.092 2(6)	0.194 8(19)	−0.065 8(7)
C(2)	0.109 0(4)	0.111 2(12)	−0.009 0(5)
C(3)	0.157 2(4)	0.014 6(12)	0.030 5(5)
C(4)	0.214 9(5)	−0.058 1(18)	0.035 8(8)
C(5)	0.176 2(7)	0.366 8(17)	0.103 1(8)
C(6)	0.135 4(4)	0.255 0(10)	0.117 4(4)
C(7)	0.124 3(5)	0.288 8(12)	0.162 8(4)
C(8)	0.148 9(10)	0.425 7(19)	0.206 8(8)
C(9)	0.165 1(4)	−0.085 7(11)	0.125 0(5)
C(10)	−0.032 4(8)	0.301 1(20)	0.125 0(6)
C(11)	−0.079 6(10)	0.343 7(25)	0.145 5(9)
C(12)	0.109 5(15)	−0.087 4(30)	0.253 5(10)
C(13)	0.130 2(13)	−0.163 8(28)	0.293 3(11)

With $P(OEt)_3$. Complex (**1**) (30 mg) was treated similarly with triethyl phosphite to give dark green crystals of $[\{W[C(CF_3){=}C(CF_3)P(OEt)_2O](\mu\text{-}Br)(CO)(CF_3C{\equiv}CCF_3)\}_2]$ (**3**) in 18% yield (Found: C, 19.9; H, 1.1; Br, 10.1. Calc. for $C_{26}H_{20}Br_2F_{24}O_8P_2W_2$: C, 20.7; H, 1.35; Br, 10.6%). I.r. (CCl_4): ν(CO) 2 015s, ν(C≡C) 1 700wm, and ν(C=C) 1 506wm cm^{-1}.

X-Ray Analysis of Complex (**3**).—The crystal was a needle of dimensions 0.36 × 0.22 × 0.18 mm.

Crystal data. $C_{26}H_{20}Br_2F_{24}O_8P_2W_2$, $M = 1\,505.9$, monoclinic, $a = 24.068(2)$, $b = 8.440(2)$, $c = 25.197(2)$ Å, $\beta = 121.50(1)°$, $U = 4\,364$ Å^3, $Z = 4$, molecular symmetry $C_i - \bar{1}$, $D_c = 2.292$ g cm^{-3}, $F(000) = 2\,816$, space group $I2/a$ (no. 15, C_{2h}^6), equivalent positions $\pm(x, y, z)$ $\pm(x, \bar{y}, \frac{1}{2} + z)$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 74.1$ cm^{-1}.

Measurements. An Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator was used in conjunction with Mo-K_α radiation. The cell dimensions were obtained by a least-squares fit to the setting angles of 25 automatically centred reflections. Integrated intensities of reflections in the range $2 \leqslant \theta \leqslant 27°$ were estimated from continuous θ—2θ scans of 1.12° in θ, the scan speed being adjusted to give $\sigma(I)/I \leqslant 0.02$, subject to a maximum counting time of 120 s. Correction for background, Lorentz polarisation effects, crystal decomposition, *X*-ray absorption (Gaussian quadrature), and merging of symmetrically equivalent intensities gave $|F_o|$ values for 2 872 independent reflections with $I \geqslant 3\sigma(I)$. Merging 1 505 duplicate $|F_o|$ gave *R*(internal) 0.038.

Structure analysis. The structure was solved and refined using conventional Patterson, difference Fourier, and full-matrix least-squares techniques. Hydrogen atoms were not included in the structure-factor calculations. In the later stages of the analysis anisotropic displacement parameters were refined for all non-hydrogen atoms. Adjustment of 289 parameters converged to R 0.036, R' 0.045 ($w^{-1} = \sigma^2 + 0.0004F_o^2$ where σ is the standard deviation of $|F_o|$ from counting statistics). The final difference synthesis showed random fluctuations of $|\Delta\rho| < 1.6$ e Å^{-3}. The analysis was hampered by the large and anisotropic thermal displacements of the CF_3 and OEt groups. Disorder is however probable only in the case of C(13), which is involved in bond lengths and angles obviously subject to systematic error (see Table 1). Neutral atom scattering factors and complex anomalous dispersion corrections were taken from ref. 32. All calculations were performed on a GOULD SEL 3227 computer using the GX program system.[33] Final atomic coordinates are given in Table 3.

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