Synthesis and Nuclear Magnetic Resonance Studies of Co-ordinatively Unsaturated Alkyne Complexes of Tungsten(II)

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$[\{WBr_2(CO)_4\}_2]$ reacts with alkynes RC≡CR′ (R = R′ = Me, Et, or Ph) and PhC≡CMe to give dimeric complexes $[\{WBr_2(CO)(RC{\equiv}CR')_2\}_2]$. These react with nucleophiles (L) to give monoalkyne complexes $[WBr_2(CO)L_2(RC{\equiv}CR')]$ [L = $CNBu^t$, $P(OMe)_3$, or PPh_3; R = R′ = Me or Ph; R = Me, R′ = Ph) which exist in *cis* and/or *trans* isomeric forms and which exhibit alkyne 'propeller rotation' according to ^1H and ^{31}P n.m.r. studies. The isolation of $[WBr_2(CO)(CNBu^t)(MeC{\equiv}CMe)_2]$ indicates that the reactions proceed *via* monomeric bis-alkyne intermediates.

For many years the bonding between a metal and an alkyne in mononuclear alkyne complexes was thought to involve only two interactions: (*a*) π donation, alkyne→metal; (*b*) π back-donation, metal→alkyne, as found in simple alkene complexes.[1] Following King's suggestion[2] that the second, perpendicular ($\pi_\perp$) set of π orbitals on the alkyne could conceivably participate in bonding with a metal the ability of alkynes to formally function as three- or four-electron donor ligands seems to be firmly established on both an experimental[3] and a theoretical basis.[4] Moreover in certain circumstances π donation *via* the perpendicular alkyne orbitals is thought to contribute as much to the metal–alkyne bond as the more familiar π back-donation.[4c]

Experimentally this type of bonding produces observable effects on the M–C distances which exhibit a distinct shortening[5] and on ^{13}C n.m.r. resonances which exhibit pronounced high-frequency shifts.[3d,6] Previously we have noted that three- and four-electron donation by alkynes also produces observable effects on the chemistry of the co-ordinated triple bond and significantly enhanced reactivity towards nucleophiles is found.[7] This effect is particularly pronounced with alkynes bearing electron-withdrawing CF_3 groups and a variety of novel complexes have been obtained ostensibly as a result of initial attack at a C≡C triple bond in complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$[7](M = Mo or W). Similar effects are also observed with complexes $[Mo\{P(OMe)_3\}_2(RC{\equiv}CR')(\eta^5\text{-}C_nH_m)]^+$(R = Me, R′ = Me, Et, or Pr^i; C_nH_m = C_5H_5 or C_9H_7)[8] although it seems probable that in this case the reactivity is also enhanced by the positive charge on the complexes. With a view to examining the generality of this phenomenon we have extended our studies to alkyne complexes derived from $[\{WBr_2(CO)_4\}_2]$ the preliminary results of which have been published previously.[9] During the course of this work related studies were reported by Templeton and co-workers[10] and Umland and Vahrenkamp,[11] which prompts us now to published full details of our initial investigation.

Results and Discussion

The reaction of alkynes RC≡CR′ (R = R′ = Me, Et, or Ph; R = Me, R′ = Ph) with $[\{WBr_2(CO)_4\}_2]$ in hexane at *ca.* 20 °C gives moderate to good yields of yellow complexes $[\{WBr_2(CO)(RC{\equiv}CR')_2\}_2]$ (**1**). Molecular weight studies established the dimeric nature of the complexes in solution whereas the dominant ions in the mass spectra are derived from mononuclear species $[WBr_2(RC{\equiv}CR')_2]^+$. In some cases very weak dinuclear ions were observed due to $[\{WBr_2(RC{\equiv}CR')\}_2]^+$ but none due to a molecular ion. A number of structural isomers are possible for (**1**) based on bridging halide or alkyne ligands. However monomeric bis(alkyne) d^4 metal complexes appear to exhibit a preference for *cis* alkynes and simple bonding arguments suggest that these will also lie *cis* to and coplanar with a carbonyl ligand.[4] Accordingly structure (**1**) is proposed consistent with the presence of two sets of CH_3 resonances in the ^1H n.m.r. spectra of (**1a**) and (**1b**). Interestingly the spectrum of (**1b**) contains four rather than two multiplets reflecting the diasterotopic nature of the hydrogens of the CH_2 groups attached to the alkyne carbon atoms. These features cannot be reconciled with a structure containing two bridging and two terminal alkynes but are consistent with the bromide bridged structures. The n.m.r. data do not distinguish between the *cis* and *trans* isomers (**1**) and (**1′**) but since the i.r. spectra in the ν(CO) region show two closely spaced peaks of similar intensity the *cis* structure is indicated with a small interaction between the two carbonyls.

Complexes (**1**) or (**1′**) can conceivably attain the favoured 18-electron configuration in two different ways. In the absence of a metal–metal double bond the $\pi_\perp$ orbitals of the alkyne could participate in bonding such that each C≡C bond formally donates three electrons to the metal. Alternatively if each alkyne functions as a simple two-electron donor a metal–metal double bond is required. On the basis of ^{13}C n.m.r. studies to be discussed later in this paper the former explanation appears to be more plausible.

In order to assess the reactivity of the alkyne complexes towards nucleophiles reactions of (**1a**), (**1c**), and (**1d**) with $CNBu^t$, $P(OMe)_3$, and PPh_3 respectively were carried out. Addition of two molar excess of ligand at 20 °C in diethyl ether–hexane led to facile bridge cleavage and substitution of one alkyne ligand giving deeply coloured crystalline adducts $[WBr_2(CO)L_2(RC{\equiv}CR')]$ (**3**)—(**5**). The 1:1 reaction of $CNBu^t$ with $[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}_2]$ gave moderate quantities of a pale yellow bis(alkyne) complex $[WBr_2(CO)(CNBu^t)(MeC{\equiv}CMe)_2]$ (**2**) illustrating that alkyne displacement is preceded by cleavage of tungsten–bromine bonds. The spectroscopic features of (**2**) are consistent with the illustrated structure involving two *cis* alkynes and a *cis* CO ligand as suggested for the precursor (**1**). The presence of weak CH_3–CH_3 coupling (J_{HH} = 0.8 Hz) in the ^1H n.m.r. spectrum in particular indicates inequivalence of the methyl groups at either end of equivalent alkynes rather than two symmetrically situated alkynes in inequivalent sites. Although other isomers are clearly possible only a single form was detected spectroscopically in solution. Interestingly the structure assigned is analogous to that predicted spectroscopically and confirmed by *X*-ray diffraction studies[12] for the norbornadiene (bicyclo[2.2.1]hexa-2,5-diene, nbd) complex $[WBr_2(CO)_2(nbd)]$ which also exists in a single isomeric form with *cis* bromide ligands (see preceding paper). Related bis(alkyne) complexes of Mo^{II} and W^{II}, $[M(L\text{–}L)_2(RC{\equiv}CR')_2]$ (R = R′ = Ph; R = H or Me, R′ = Ph)

Table 1. Physical and analytical data for the complexes[a]

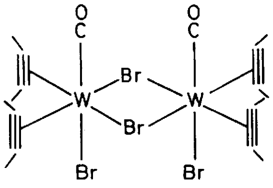
				Analysis (%)		
	Complex	Colour	Yield (%)	C	H	P‡ or N*
(1a)[b]	$[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}_2]$	Yellow	42	22.6 (22.50)	2.6 (2.50)	
(1b)[c]	$[\{WBr_2(CO)(EtC{\equiv}CEt)_2\}_2]$	Yellow	15	28.9 (29.10)	3.7 (3.75)	
(1c)	$[\{WBr_2(CO)(PhC{\equiv}CMe)_2\}_2]$	Yellow	48	37.0 (37.80)	2.6 (2.65)	
(1d)	$[\{WBr_2(CO)(PhC{\equiv}CPh)_2\}_2]$	Yellow	66	47.6 (47.80)	3.0 (2.75)	
(2)	$[WBr_2(CO)(CNBu^t)(MeC{\equiv}CMe)_2]$	Pale yellow	46	29.9 (29.85)	3.7 (3.75)	2.5 *(2.50)
(3a)	$[WBr_2(CO)(CNBu^t)_2(MeC{\equiv}CMe)]$	Purple	75	30.6 (30.40)	4.1 (4.05)	4.8 *(4.75)
(3b)	$[WBr_2(CO)(CNBu^t)_2(PhC{\equiv}CMe)]$	Blue	71	37.3 (36.70)	4.1 (3.95)	4.1 *(4.30)
(3c)	$[WBr_2(CO)(CNBu^t)_2(PhC{\equiv}CPh)]$	Blue	20	38.9 (41.90)	3.9 (3.90)	3.7 *(3.90)
(4a)	$[WBr_2(CO)(PPh_3)_2(MeC{\equiv}CMe)]$	Grey-purple	65	53.6 (51.80)	4.0 (3.80)	6.5 ‡(6.55)
(4b)	$[WBr_2(CO)(PPh_3)_2(PhC{\equiv}CMe)]$	Blue-green	72	54.0 (54.55)	3.9 (3.75)	5.8 ‡(6.15)
(4c)	$[WBr_2(CO)(PPh_3)_2(PhC{\equiv}CPh)]$	Blue-green	68	55.0 (56.00)	3.8 (3.70)	
(5a)	$[WBr_2(CO)\{P(OMe)_3\}_2(MeC{\equiv}CMe)]$	Purple	58	20.0 (19.95)	3.5 (3.60)	9.1 ‡(9.35)
(5b)	$[WBr_2(CO)\{P(OMe)_3\}_2(PhC{\equiv}CMe)]$	Purple	54	26.0 (26.55)	3.6 (3.60)	
(5c)	$[WBr_2(CO)\{P(OMe)_3\}_2(PhC{\equiv}CPh)]$	Blue-green	22	31.9 (32.05)	3.6 (3.60)	

[a] Calculated values are given in parentheses. [b] Br, 32.5 (33.30); O, 3.2 (3.35%). [c] Br, 29.7 (29.85%).

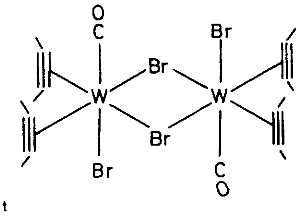
containing two bidentate ligands L–L = $S_2CNR''_2$ (R″ = Me or Et) are also known[13,14] although interestingly it has been found that formation of such species from *e.g.* $[Mo(S_2CNMe_2)_2(CO)_2]$ which proceeds *via* a monoalkyne derivative requires more drastic conditions to introduce the second alkyne,[13] equation (1).

$$[Mo(S_2CNMe_2)_2(CO)_2] \xrightarrow{RC\equiv CR'} [Mo(S_2CNMe_2)_2(CO)(RC\equiv CR')] \xrightarrow[110\,^{\circ}C]{RC\equiv CR'} [Mo(S_2CNMe_2)_2(RC\equiv CR')_2] \quad (1)$$

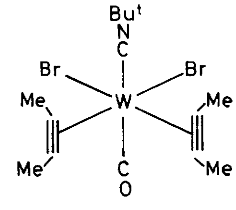
Reaction of $[MoBr_2(CO)_2(PEt_3)_2]$ with alkynes MeC≡CMe and PhC≡CH at 40 °C in CH_2Cl_2 has been reported to give only monoalkyne derivatives $[MoBr_2(CO)(PEt_3)_2(RC{\equiv}CR')]$ even in the presence of up to a ten-fold excess of alkyne[10] and it is perhaps not surprising that in the presence of excess ligand, complexes $[\{WBr_2(CO)(RC{\equiv}CR')_2\}_2]$ give 2:1 adducts **(3)**, **(4)**, and **(5)**. Complexes **(3)**, **(4)**, and **(5)** are deep blue, green, or purple crystalline derivatives moderately air sensitive in the solid state, but significantly more so in solution. In several cases the complexes react with chlorinated solvents CCl_4 and $CHCl_3$ but are relatively stable in dichloromethane and diethyl ether. Sensitivity to chloroform did not preclude the use of this solvent for recording of i.r. or n.m.r. spectra provided deoxygenation was carried out rigorously and spectra were recorded rapidly or, in the case of n.m.r., at low temperatures (Tables 2 and 3).



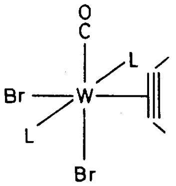
(1)



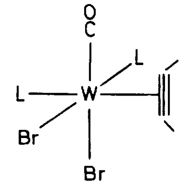
(1′)



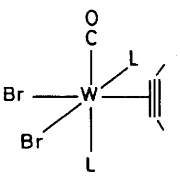
(2)



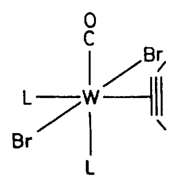
(I) *trans*



(II) *cis*



(III) *cis*



(IV) *cis*

The structures are presumed to be based on a distorted octahedron as revealed for the analogous molybdenum complex $[MoBr_2(CO)(PEt_3)_2(PhC{\equiv}CH)]$ by single-crystal *X*-ray diffraction studies.[10] Previously simple bonding arguments have been proposed which suggest that the most stable arrangement of CO and alkyne ligands in d^4 metal complexes of this type is *cis* with the alkyne C≡C axis lying parallel to the M–CO axis.[4] In this situation metal–carbonyl and metal–alkyne π back-donation from the two filled π orbitals on the metal to ligand π^* orbitals is maximised. Moreover this arrangement allows the second filled $\pi_\perp$ orbital on the alkyne to interact in a bonding manner with the remaining empty metal $d\pi$ orbital. This arrangement, which was first revealed in $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[4a,15] has been confirmed in later structural studies of $[Mo(CO)(PEt_3)(MeC{\equiv}CMe)(\eta^5\text{-}C_9H_7)]^+$,[3d] $[W(S_2CNMe_2)_2(CO)(HC{\equiv}CH)]$,[5] and of particular interest $[MoBr_2(CO)(PEt_3)_2(PhC{\equiv}CH)]$.[10] The last complex and its but-2-yne analogue were isolated from the reactions of $[MoBr_2(CO)_2(PEt_3)_2]$ with alkynes PhC≡CH and MeC≡CMe but only one geometric isomer (*trans*) was detected in each case. In contrast, Umland and Vahrenkamp[11] recently reported that related complexes $[WI_2(CO)_2L(PhC{\equiv}CH)]$ (L = PMe_3, $AsMe_3$, or $CNBu^t$) could be isolated in two isomeric forms with either *cis* or *trans* carbonyl ligands although only the *cis* form of $[WI_2(CO)_2L(HC{\equiv}CH)]$ (L = PMe_3 or $AsMe_3$) was obtained. Comprehensive ^1H, $^{31}P\text{-}\{^1H\}$, and ^{13}C n.m.r. studies of **(3)**, **(4)**,

Table 2. Hydrogen-1 n.m.r. data for the complexes[a]

Complex	Isomer	Solvent	δ(RC≡CR')		δ(L)
(**1a**)		C_6D_6	2.95 (s, 6 H), 2.35 (s, 6 H)		
(**1b**)		$C_6D_5CD_3$	3.95 (m, 2 H), 3.30 (m, 2 H),	0.95 (t, J = 7.45, 6 H)	
			3.05 (m, 2 H), 2.75 (m, 2 H)	0.85 (t, J = 7.40, 6 H)	
(**1c**)		$CDCl_3$	7.20 (m, 10 H)	3.20 (s, 3 H), 3.15 (s, 3 H)	
(**1d**)		$CDCl_3$	7.35 (m)		
(**2**)		$CDCl_3$	2.93 (q, J = 0.80, 6 H)	2.89 (q, J = 0.80, 6 H)	1.80 (s, 9 H)
(**3a**)	*cis*	$CDCl_3$	3.16 (s, 6 H)		1.74 (s, 9 H), 1.36 (s, 9 H)
(**3b**)	*cis*	$CDCl_3$	3.35 (s, 3 H), 7.48 (m, 5 H)		1.59 (s, 9 H), 1.36 (s, 9 H)
(**3c**)	*cis*	$CDCl_3$	7.48 (s, 10 H)		1.52 (s, 9 H), 1.38 (s, 9 H)
(**4a**)	*trans*	CD_2Cl_2	2.35 (t, J_{PH} = 1.40, 6 H)		7.55 (m), 7.30 (m) (30 H)
(**4b**)	*trans*	$CDCl_3$	2.45 (s, 3 H)		7.46 (m), 7.23 (m) (35 H)
(**4c**)	*trans*	$CDCl_3$	7.46 (m), 7.18 (m)		
(**5a**)	*trans*	CD_2Cl_2	3.16 (t, J_{PH} = 1.70, 6 H)		3.63 (apparent t, 18 H)
	cis	CD_2Cl_2	3.06 (d, J_{PH} = 2.0, 6 H)		3.94 (d, J_{PH} = 9.80, 9 H)
					3.47 (d, J_{PH} = 10.50, 9 H)
(**5b**)	*trans*	CD_2Cl_2	3.41 (t, J_{PH} = 1.0, 3 H), 7.4—8.0 (m)		3.57 (apparent t, 18 H)
	cis	CD_2Cl_2[b]	3.16 (br s, 3 H), 7.4—8.0 (m)		3.92 (d, J_{PH} = 9.9, 9 H)
					3.40 (d, J_{PH} = 10.5, 9 H)
(**5c**)	*trans*	$CDCl_3$	7.4—7.8 (m, 10 H)		3.61 (apparent t, 18 H)

[a] At 20 °C unless stated otherwise; J values are in Hz. [b] At −72 °C.

Table 3. Phosphorus-31 n.m.r.[a] and i.r. data for the complexes

Complex	Isomer	Solvent	^{31}P N.m.r. δ(L)	I.r. ($CHCl_3$) ν(CO)/cm^{-1}	ν(C≡N)/cm^{-1}
(**1a**)				2 098wm, 2 060vs	
(**1b**)				2 078s, 2 060vs	
(**1c**)				2 140wm, 2 004vs	
(**1d**)				2 144wm, 2 120vs	
(**2**)				2 092vs	2 218s
(**3a**)	*cis*			2 002vs	2 194s, 2 160s
(**3b**)	*cis*			2 010vs	2 200m, 2 163s
(**3c**)	*cis*			2 024vs	2 202s, 2 165s
(**4a**)	*trans*	$CDCl_3$	3.50 (s, J_{WP} = 272)	1 938s	
(**4b**)	*trans*	$CDCl_3$	3.80 (s, J_{WP} = 268)	1 946s	
(**4c**)	*trans*	$CDCl_3$	5.06 (s, J_{WP} = 270)	1 960s (Nujol)	
(**5a**)	*trans*	CD_2Cl_2	120.57 (s, J_{WP} = 399)	1 965s	
	cis	CD_2Cl_2[b]	124.20 (d, J_{PP} = 29.8) 121.06 (d, J_{PP} = 29.8, J_{WP} = 285)	1 994s	
(**5b**)	*trans*	CD_2Cl_2	118.80 (s, J_{WP} = 419)	1 962s	
	cis	CD_2Cl_2[c]	119.17 (AB quartet, J_{WP} = 448)	2 005s	
(**5c**)	*trans*	$CDCl_3$	118.0 (s, J_{WP} = 422)	1 972s	

[a] J Values are in Hz. [b] At −72 °C. [c] At −70 °C.

and (**5**) have revealed that in some cases two isomeric forms are possible and that isomer preferences appear to be dictated by the ligand L as well as the alkyne.

*Hydrogen-*1 *and* ^{31}P-{^{1}H} *N.M.R. Spectra.*—The isocyanide complexes (**3a**)—(**3c**) exhibit two equal intensity ν(C≡N) bands near 2 200 cm^{-1} suggesting *cis* isocyanide ligands and this is supported by the ^{1}H n.m.r. spectra which contain two CNBu^t resonances. In contrast, the triphenylphosphine ligands in (**4a**)—(**4c**) appear to adopt a *trans* arrangement on the basis of the singlet in the ^{31}P-{^{1}H} n.m.r. spectra which also exhibit ^{183}W satellites. A *trans* arrangement of $P(OMe)_3$ ligands in $[WBr_2(CO)\{P(OMe)_3\}_2(PhC{\equiv}CPh)]$ is also indicated by the ^{31}P-{^{1}H} n.m.r. singlet and is further supported by the methyl group triplet in the ^{1}H n.m.r. which presumably results from the phenomenon of virtual coupling, a feature of *trans*-bisphosphine and -phosphite complexes.[16] However, the but-2-yne and 1-phenylpropyne analogues (**5a**) and (**5b**) can exist in both *cis* and *trans* isomeric forms although the latter appears to be thermodynamically more stable in solution.

If n.m.r. samples of these complexes are prepared and the spectra recorded immediately at low temperatures (< −30 °C) only the *cis* isomer is observed. This exhibits two equal intensity $P(OMe)_3$ methyl group doublets in the ^{1}H n.m.r. and two phosphorus doublets in the ^{31}P-{H} n.m.r. spectra. On warming to ambient temperature isomerisation to a *trans* isomer exhibiting similar spectroscopic features to (**5c**) is observed, the 1-phenylpropyne adduct undergoing the more rapid transformation of the two. This is also reflected in the i.r. spectra where the ν(CO) peak of the *cis* isomer at *ca.* 2 000 cm^{-1} is replaced by the lower frequency band due to the *trans* isomer at *ca.* 1 960 cm^{-1}. Clearly metal–carbonyl back-donation is more effective in the *trans* isomer.

Only one *trans* isomer, (I), is possible with *cis* CO and alkyne

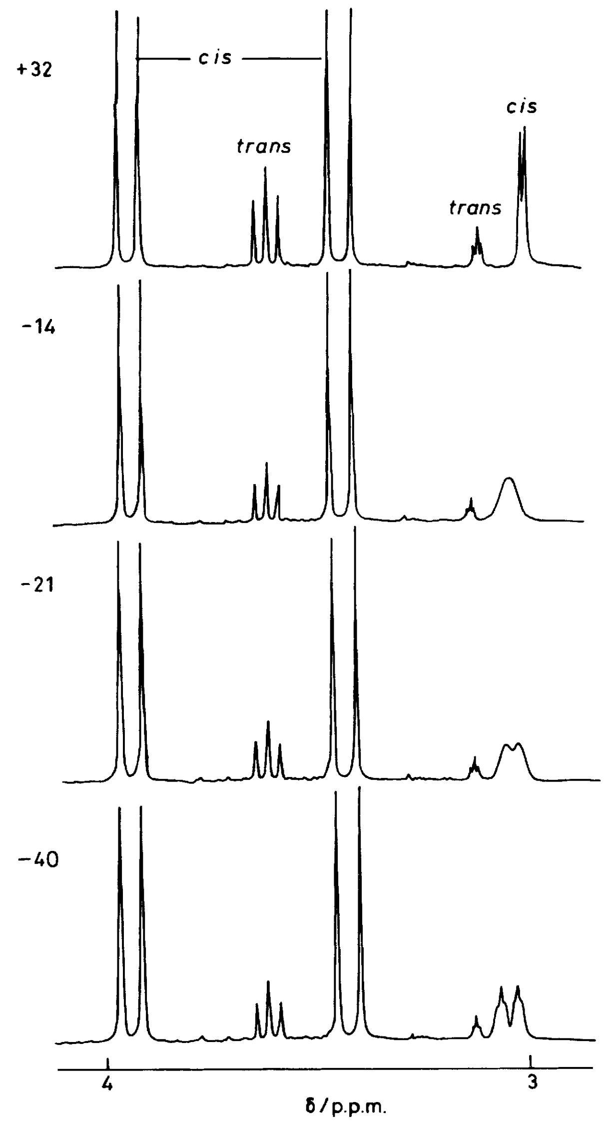


Figure. Variable-temperature (°C) ^{1}H n.m.r. spectrum of [$WBr_2(CO)\{P(OMe)_3\}(MeC{\equiv}CMe)$] (**5a**)

ligands and this is found with [$MoBr_2(CO)(PEt_3)_2(PhC{\equiv}CH)$]. However, three *cis* isomers are possible, one with a bromine *trans* to CO, (**II**), the others, (**III**) and (**IV**), with ligand L[= $CNBu^t$, PPh_3, or $P(OMe)_3$] *trans* to CO. Since the *cis* and *trans* isomers of (**5a**) and (**5b**) exhibit significantly different ν(CO) frequencies it seems unlikely that the *cis* isomer has the *trans* Br–W–CO arrangement found in the *trans* isomer, (**I**), and we therefore exclude structure (**II**). The alternatives, (**III**) and (**IV**), with a π-acceptor L *trans* to CO, are more likely to result in decreased M–CO π back-donation and hence in the higher observed ν(CO) frequency as a result of greater competition for electron density. Moreover in (**III**) and (**IV**), π donation from both bromines to the empty *d*π orbital on the metal is also possible whereas only one bromine in (**II**) can participate in π donation. It is more difficult on the basis of available evidence to distinguish between (**III**) and (**IV**) but as will now be described, variable-temperature n.m.r. studies allow tentative conclusions to be reached in favour of (**IV**).

A consequence of the directional nature of the metal–alkyne bonding in (**3**), (**4**), and (**5**) and many other alkyne complexes is the presence of a distinct barrier to alkyne 'propeller' rotation about the metal–alkyne bond axis. Dynamic n.m.r. studies of a wide range of molybdenum(II) and tungsten(II) alkyne derivatives reveal barriers in the range 35—80 kJ mol^{-1}.[3d,10,17,18] The ^{1}H n.m.r. spectra of (**1**) and (**2**) are clearly consistent with stereochemically rigid structures at ambient temperature on the n.m.r. time-scale, *i.e.* alkyne rotation does not occur. In contrast, variable-temperature ^{1}H and where appropriate ^{31}P-{^{1}H} n.m.r. studies of complexes (**3**), (**4**), and (**5**) reveal fluxional behaviour in several cases.

Hydrogen-1 n.m.r. spectra of (**3a**) and (**4a**) at *ca.* −80 °C reveal two distinct methyl group environments in accord with a specific alkyne orientation. On raising the temperature the peaks broaden and coalesce [−50 °C, (**3a**), −63 °C, (**4a**)] to give a singlet for (**3a**) and a triplet (J_{PH} = 1.40 Hz) for (**4a**), presumably as a result of the onset of alkyne rotation. Analysis of the spectra gave barriers to rotation $\Delta G^\ddagger = 49.5 \pm 2$ for (**3a**) and 42.4 ±2 kJ mol^{-1} for (**4a**). Variable-temperature ^{1}H and ^{31}P-{^{1}H} n.m.r. studies of *cis*-[$WBr_2(CO)\{P(OMe)_3\}_2(MeC{\equiv}CMe)$] (**5a**) similarly reveal fluxional behaviour. As illustrated in the Figure, two MeC≡CMe multiplets are observed in the ^{1}H n.m.r. spectrum at −40 °C which collapse to a doublet (T_c = −14 °C) at higher temperatures due to the onset of alkyne rotation. The presence of a doublet splitting indicates selective coupling to only one phosphorus (J_{PH} = 2.0 Hz) whereas *trans*-(**5a**) exhibits a triplet (J_{PH} = 1.7 Hz) due to coupling to the two equivalent phosphorus nuclei. The differential coupling in *cis*-(**5a**) is more easily explained in terms of structure (**IV**) [L = $P(OMe)_3$] where one $P(OMe)_3$ is *cis* to the alkyne whereas the other is *trans*. The similarity of the doublet and triplet couplings in the *cis* and *trans* forms suggests that the coupling in the former arises from $P(OMe)_3$ *cis* to the alkyne. The alternative *cis* structure (**III**), with two $P(OMe)_3$ ligands *cis* to a rotating alkyne, seems less plausible although this is not an unequivocal conclusion. However, further support for structure (**IV**) for (**5a**) was obtained from the variable-temperature ^{31}P-{^{1}H} n.m.r. spectra. At −72 °C in CD_2Cl_2 two doublets are observed with intensity distortions resulting from second-order effects. As the temperature is raised the high-frequency doublet broadens significantly, an effect which reaches a maximum at *ca.* −30 °C, but above this temperature peak sharpening occurs. No such effect is observed in the other phosphorus doublet. This is clearly explicable in terms of structure (**IV**) where the onset of alkyne rotation is expected to affect the *cis* phosphite to a much greater extent than the more distant *trans* ligand as a result of a proximity effect.

The ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra of *cis*-(**5b**) at low temperatures (*ca.* −80 °C) are comparable with those of *cis*-(**5a**) but more drastic changes are observed as the temperature is raised. One of the two $P(OMe)_3$ doublets in the ^{1}H spectrum collapses completely to a broad hump at 20 °C while the lower frequency signal gradually changes into a multiplet consisting of a broad central resonance lying between a 1:1 doublet. Such resonances are frequently found in *cis* complexes when P–P coupling is of intermediate magnitude[16] and since simple doublets were obtained at low temperatures it appears that alkyne rotation also leads to changes in P–P coupling. The ^{31}P-{^{1}H} n.m.r. spectrum of *cis*-(**5b**) is almost identical to that of *cis*-(**5a**) at −70 °C and again as the temperature is raised the high-frequency doublet broadens. However, this is accompanied by a gradual decrease in the separation of the two doublets which eventually emerge to give a singlet at −20 °C which subsequently broadens considerably above this temperature. Presumably alkyne rotation leads to accidental degeneracy of the two $P(OMe)_3$ resonances.

Unlike the *cis* isomers, *trans*-(**5a**) and -(**5b**) do not exhibit significant changes in ^{1}H and ^{31}P-{^{1}H} spectra over the temperature range −80 to +20 °C which either suggests stereochemical rigidity with, in the case of (**5a**), accidental degeneracy of $MeC\equiv CMe$ methyl groups ^1H n.m.r. resonances or alternatively significantly lower barriers to alkyne rotation. The latter explanation seems more probable in view of the fact that *trans*-(**4a**) is fluxional as is the *trans* isomer of $[MoBr_2(CO)(PEt_3)_2(MeC\equiv CMe)]$ which has been reported to exhibit propeller rotation with a barrier $\Delta G^\ddagger = 54.6$ kJ mol^{-1}.[10] These data, in conjunction with the fact that *cis*-$[WI_2(CO)_2L(HC\equiv CH)]$ (L = PMe_3 or $AsMe_3$) appears to be stereochemically rigid,[11] indicate that barriers to alkyne rotation in this type of complex are clearly influenced by the nature of the auxiliary ligands co-ordinated to the metal and also by their geometrical disposition with respect to the alkyne. Previously we have reported that alkyne rotation in bis(hexafluorobut-2-yne)(*N*-oxopyridine-2-thiolato)(pyridine-2-thiolato)tungsten(II) appears to be influenced significantly by the nature of the donor atom *trans* to the alkyne ligand[7a] a conclusion which also must apply to monoalkyne complexes of the type reported herein.

Assuming that the alkyne can adopt a preferred orientation parallel to the W–CO in both *cis* and *trans* isomers of (**3b**), (**4b**), and (**5b**), two conformational isomers are possible in each case as a result of the asymmetry of the 1-phenylpropyne ligand. However, only one set of signals was observed in both ^1H and $^{31}P-\{^1H\}$ n.m.r. spectra even at −80 °C in the case of (**5b**). It appears that only one conformer exists, or alternatively both are possible but interconvert rapidly, even at −80 °C. Interestingly only one set of resonances is observed for $[MoBr_2(CO)(PEt_3)_2(PhC\equiv CH)]$[10] and related monoalkyne derivatives $[MX(CO)(PhC\equiv CMe)(\eta^5-C_5H_5)]$ (M = Mo or W; X = Cl, Br, I, or SC_6F_5),[19,20] whereas the maximum number of conformational isomers of $[MoX(PhC\equiv CMe)_2(\eta^5-C_5H_5)]$ (X = Cl, Br or I),[19b,20] $[Mo(S_2CNMe_2)_2(RC\equiv CH)_2]$ (R = Ph or Bu^n),[13] $[WX(CF_3C\equiv CCF_3)(PhC\equiv CMe)(\eta^5-C_5H_5)]$ (X = Cl, Br, or I),[19b,20] and $[Mo(CO)(PPh_3)(Pr^iC\equiv CH)(\eta^5-C_5H_5)]^+$ [3d] have been detected at moderately low temperatures. The observation that barriers to rotation in these complexes vary widely suggests that the second explanation, *viz.* rapid alkyne rotation, may be responsible for the appearance of one set of signals particularly since we were unable to slow down rotation of the but-2-yne ligand in *trans*-(**5a**) even at −80 °C.

Carbon-13 *N.M.R. Spectra.*—Templeton and Ward[6] and others[3d] have shown that involvement of both sets of π orbitals on the alkyne in bonding with a metal leads to pronounced high-frequency shifts of the ^{13}C n.m.r. resonances of the alkyne carbons (see Table 4). Thus four-electron donation, as in $[W(S_2CNEt_2)_2(CO)(RC\equiv CR')]$, leads to δ values > 200 p.p.m., three-electron donation in $[Mo(S_2CNEt_2)_2(RC\equiv CR')_2]$ produces shifts in the region 167—190 p.p.m., while two-electron donation results in values close to 120 p.p.m. Otsuka and co-workers[4d] subsequently pointed out that a correlation between δ and the number of electrons formally donated by the alkyne should only hold for complexes involving auxiliary ligands capable of efficient back-bonding such as CO. Significantly, complexes $[Mo(SBu^t)_2(CNBu^t)_2(RC\equiv CR')]$ (R = R′ = H, Ph, or Et), which can only achieve a 16-electron configuration if the alkyne functions as a full four-electron donor but which have no efficient π-acceptor ligands, exhibit reduced δ values in the range 171—184 p.p.m.[4d] The alkyne ligands in the complexes described in the present work can clearly function as three- and four-electron donors and consequently ^{13}C n.m.r. spectra of a limited range of derivatives were examined. The results are given in Table 4 along with selected examples from the literature for comparison.

The bis(alkyne) complex (**2**) with formal three-electron donor alkynes exhibits two equal intensity resonances near δ 160 p.p.m. clearly in the region intermediate between two- and four-electron donor alkynes and close to that of other three-electron donors, *e.g.* $[Mo(S_2CNEt_2)_2(HC\equiv CPh)_2]$ (δ 177.1 and 183.2). Significantly (**1a**) also exhibits two resonances in this region and on this basis we conclude that the dinuclear complexes (**1**) achieve the 18-electron configuration as a result of alkyne π donation rather than as a result of metal–metal bond formation as discussed earlier. The monoalkyne derivatives (**3a**) and (**3b**), where four-electron donation is expected, exhibit two and three resonances respectively in the region δ 200—210, one of which must be due to the ^{13}CO group. In the case of (**3a**) the peak at δ 210.6 is approximately half the intensity of the lower frequency peak at δ 203.4 and we therefore assign the latter to the two C≡C carbons of the rotating alkyne. The situation is less well defined with (**3b**) but since the chemical shift of the highest frequency peak (δ 210.1) is almost identical to that of the ^{13}CO resonance of (**3a**) we assign the lower frequency resonances at δ 206.7 and 202.2 to the alkyne carbons. Comparison of these shifts with those of other four-electron donor alkynes clearly indicates that for this type of complex a distinct correlation exists between $\delta(^{13}C\equiv C)$ and the number of electrons donated by the alkyne to the metal centre.

Table 4. Carbon-13 chemical shifts of alkyne carbons bound to molybdenum(II) and tungsten(II)

Complex	δ(C≡C)	N^a	Ref.
$[W(S_2CNEt_2)_2(CO)(HC\equiv CH)]$	206.1, 207.1	4	6
$[Mo(SBu^t)_2(CNBu^t)_2(HC\equiv CH)]$	171.7	4	4*d*
$[WBr_2(CO)(CNBu^t)_2(MeC\equiv CMe)]$	203.4	4	*b*
$[WBr_2(CO)(CNBu^t)_2(PhC\equiv CMe)]$	206.7, 202.2	4	*b*
$[Mo(S_2CNEt_2)_2(HC\equiv CPh)_2]$	183.2, 177.1	3	6
$[WBr_2(CO)(CNBu^t)(MeC\equiv CMe)_2]$	161.4, 156.7	3	*b*
$[\{WBr_2(CO)(MeC\equiv CMe)_2\}_2]$	179.8, 162.6	3	*b*
$[Mo(HC\equiv CH)_2(\eta^5-C_5H_5)_2]$	117.7	2	6

[a] *N* = Number of electrons formally donated by each alkyne to the metal. [b] This work.

An interesting correlation also exists between the number of electrons donated by the alkyne(s) in complexes (**1**)—(**5**) and the colour of the complex. Bis(alkyne) derivatives (**1**) and (**2**) with three-electron donor alkynes are consistently pale yellow whereas monoalkyne derivatives (**3**), (**4**), and (**5**) with four-electron donor alkynes are invariably deep-purple, -blue, or -green. A similar correlation is found with related cyclopentadienyl complexes $[MCl(RC\equiv CR')_2(\eta^5-C_5H_5)]$ (M = Mo or W; R = R′ = Me, Ph, or CF_3) and $[MCl(CO)(RC\equiv CR')(\eta^5-C_5H_5)]$ (M = Mo or W; R = R′ = Me or Ph) which are respectively yellow or orange and deep-green or -blue in colour.[19,20] Studies of the electronic absorption spectra of formal 16-electron complexes, *e.g.* $[MoX_2(CO)_2(PPh_3)_2]$ (X = Cl, Br, or I) and $[Mo(S_2CNEt_2)_2(CO)(RC\equiv CR')]$ (R = R′ = H or Ph), where deep-blue, -purple, and -green colours are also found reveal a low-energy visible transition with an absorption coefficient *ca.* 10^2 dm^3 mol^{-1} cm^{-1} assigned as a *d*π–*d*π transition.[10,21] Since in alkyne complexes the transition is to the lowest unoccupied molecular orbital which is destabilised by π-donation from the alkyne it is to be expected that changes in the donor properties of the alkyne(s) will affect the energy of the transition. Thus a significant change in transition energy on going from mono- to bis-alkyne complexes is to be expected and hence the observed change in colour.

It is of interest to compare the alkyne adducts reported herein with related d^4 complexes of divalent molybdenum and tungsten. Thus dinuclear alkyne complexes (**1**) contrast with mononuclear diene derivatives $[WBr_2(CO)_2L']$ (L′ = cycloocta-1,5-diene, cyclo-octatetraene, or norbornadiene) obtained under similar conditions from $[\{WBr_2(CO)_4\}_2]$ (see previous paper). It is conceivable that formation of (**1**) proceeds *via* intermediate mononuclear dicarbonyls $[WBr_2(CO)_2(RC\equiv CR')_2]$ which subsequently dimerise as a result of CO expulsion and halogen-bridge formation. Interestingly the diene complexes are observed to dimerise in the chamber of a mass spectrometer giving ions derived from $[\{WBr_2(CO)L'\}_2]$ in support of this suggestion. Moreover, reaction of $CF_3C\equiv CCF_3$ with $[\{WBr_2(CO)_4\}_2]$ gives a mononuclear bis(alkyne) complex $[WBr_2(CO)(CF_3C\equiv CCF_3)_2]$[7b] indicating that loss of a carbonyl ligand from $[WBr_2(CO)_2(RC\equiv CR')_2]$ is probably quite facile. Co-ordinative unsaturation in the diene complexes and comparable phosphine derivatives, *e.g.* $[MoX_2(CO)_2(PR_3)_2]$ (X = halide, R = alkyl or aryl)[22] may or may not be stabilised by π donation from the halogen ligands (see previous paper) whereas π donation from the alkyne $\pi_\perp$ orbitals is also possible in the alkyne derivatives. This may in some part be responsible for the ease with which CO loss occurs to give dimeric derivatives (**1**). This may also be responsible for the fact that six-co-ordinate alkyne derivatives (**3**) do not appear to react further with excess nucleophile L to give seven-co-ordinate species $[WBr_2(CO)L_3(RC\equiv CR')]$ whereas seven-co-ordinate diene and phosphine complexes, *e.g.* $[WBr_2(CO)_2LL']$ $[WBr_2(CO)L_2L']$, or $[WBr_2(CO)_2L_3]$ [L = CNBu^t, PMe$_2$Ph or P(OMe)$_3$] are readily obtained on reaction of $[WBr_2(CO)_2L]$ with nucleophiles (see previous paper).

Conceivably reactions of the alkyne complexes with nucleophiles proceed *via* seven-co-ordinate intermediates but the π-donor abilities of the alkynes are sufficient to render these too unstable to be detected. Similarly substitution of carbon monoxide and/or an alkyne ligand in $[Mo(CO)(MeC\equiv CMe)_2(\eta^5\text{-}C_5H_5)]^+$ by phosphines and phosphites may proceed *via* an associative mechanism but again intermediates were not detected.[4d] Kinetic studies of alkyne substitution in $[Mo(S_2CNMe_2)_2(CO)(RC\equiv CR')]$ by two two-electron donors CO, PEt$_3$, or P(OMe)$_3$ or by another alkyne, *i.e.* alkyne exchange, provide evidence for associative mechanisms proceeding *via* seven-co-ordinate intermediates.[18] In contrast CO substitution by an alkyne to give a bis(alkyne) complex $[Mo(S_2CNMe_2)_2(RC\equiv CR')_2]$ proceeds by a much slower carbonyl dissociation to give a five-co-ordinate intermediate $[Mo(S_2CNMe_2)_2(RC\equiv CR')]$,[18] reminescent of stable isocyanide derivatives $[Mo(SBu^t)_2(CNBu^t)_2(RC\equiv CR')]$,[4d] and the bis(alkyne) derivative $[WBr_2(CO)(CF_3C\equiv CCF_3)_2]$.[7b]

A third substitution mechanism has been observed in the reactions of $[M(SC_6F_5)(CO)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with phosphines which proceed *via* initial attack on the co-ordinated alkyne to give unstable η^2-vinyl intermediates.[7c,20] Subsequent CO expulsion and transfer of the phosphine to the metal gives the final product $[M(SC_6F_5)(PR_3)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; PR$_3$ = PEt$_3$, PMe$_2$Ph, or PMePh$_2$).[20] Formation of η^2-vinyl complexes by addition of nucleophiles to co-ordinatively unsaturated mono- and bis-alkyne complexes is now well documented but so far has only been observed when the alkynes possess electronegative substituents as in $[MCl(CF_3C\equiv CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W)[7] or when the complex bears a positive charge, *e.g.* $[Mo\{P(OMe)_3\}_2(RC\equiv CR')(\eta^5\text{-}C_5H_5)]^+$.[8] At the present stage of our studies of dihalogen–alkyne complexes evidence pointing to a particular mechanism for CO and alkyne substitution has not been obtained and we are unable to reach any conclusions. Studies currently in progress will hopefully resolve this situation.

Experimental

I.r. spectra were recorded as solutions on a Perkin-Elmer 580 spectrophotometer and mass spectra on a Vacuum Generators updated AEI MS9 mass spectrometer. Hydrogen-1, ^{13}C, and ^{31}P n.m.r. spectra were obtained at 200.13, 50.31, and 81.02 MHz respectively on a Bruker WP 200 SY spectrometer. Solvents were refluxed over calcium hydride (hexane, diethyl ether) or P_2O_5 (CH_2Cl_2) under nitrogen and distilled just before use.

All manipulations were carried out under nitrogen using standard Schlenk techniques. $[\{WBr_2(CO)_4\}_2]$ was prepared by the published method.[23]

Reactions of $[\{WBr_2(CO)_4\}_2]$ *with Alkynes.*—In a typical reaction freshly prepared $[\{WBr_2(CO)_4\}_2]$ (1 g) was suspended in hexane (50 cm^3) under nitrogen and a 10% molar excess of alkyne added. The reaction mixture was stirred at ambient temperature for 15 h. Volatiles were removed and the crude product $[\{WBr_2(CO)(RC\equiv CR')_2\}_2]$ recrystallised from CH_2Cl_2–hexane at −15 °C. Yields of products (Table 2) were found to be variable and seemed to depend significantly on the purity of the precursor $[\{WBr_2(CO)_4\}_2]$ which is sensitive to air and moisture.

Reaction of $[\{WBr_2(CO)(MeC\equiv CMe)_2\}_2]$ *with* CNBu^t (*Molar Ratio* 1:1).—The complex (200 mg) was suspended in 20 cm^3 of a 1:1 mixture of diethyl ether and hexane and CNBu^t (35 mg) added dropwise. The mixture was stirred for 30 min and then reduced in volume to *ca.* 10 cm^3. The crude product was filtered off and recrystallised from CH_2Cl_2–hexane twice at −15 °C to give pale yellow crystals of (**2**) in 62% yield.

Reactions of $[\{WBr_2(CO)(RC\equiv CR')_2\}_2]$ (R = R′ = Me *or* Ph; R = Me, R′ = Ph) *with* L [= CNBu^t, PPh$_3$, *or* P(OMe)$_3$] (*Molar Ratio* 1:2).—In a typical reaction $[\{WBr_2(CO)(RC\equiv CR')_2\}_2]$ (250 mg) was suspended in 30 cm^3 of a 1:1 mixture of diethyl ether–hexane and a 2 molar excess of ligand L added. The reaction mixture was stirred for *ca.* 5 h and the volume of liquid reduced to *ca.* 15 cm^3. The crude product was filtered off and recrystallised from dichloromethane–hexane at −15 °C twice to give pure crystals of $[WBr_2(CO)L_2(RC\equiv CR')]$. Yields are reported in Table 1 along with physical and analytical data.

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