Co-ordinatively Unsaturated Alkyne Complexes of Tungsten: Synthesis and Dynamic Nuclear Magnetic Resonance Studies of some But-2-yne Derivatives

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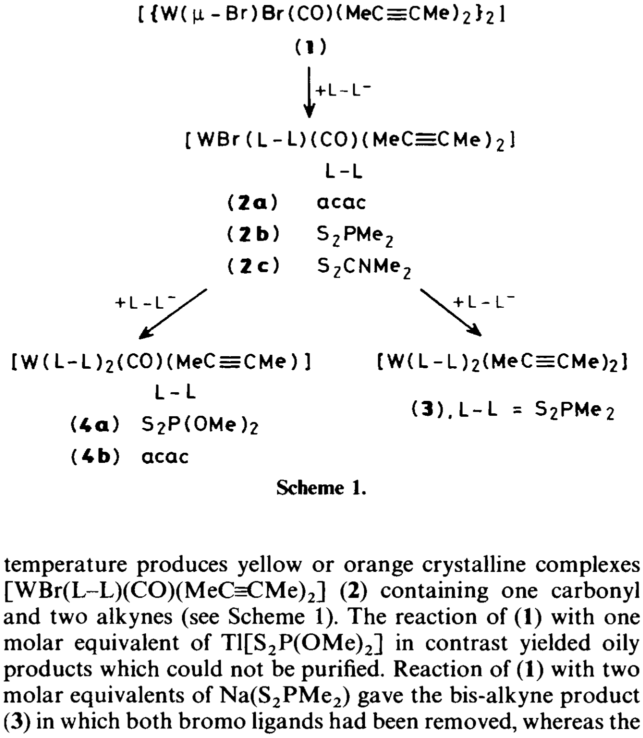
Reactions of [{W(μ-Br)Br(CO)(MeC≡CMe)$_2$}$_2$] (**1**) with one molar equivalent of Na(S$_2$CNMe$_2$), Na(S$_2$PMe$_2$), or Tl(acac) (acac = acetylacetonate) give mononuclear derivatives [WBr(L–L)(CO)(MeC≡CMe)$_2$] (**2**) (L–L = S$_2$CNMe$_2$, S$_2$PMe$_2$, or acac). The ^{1}H and ^{13}C n.m.r. spectra of the acac complex are temperature independent whereas dynamic ^{1}H n.m.r. studies of the S$_2$CNMe$_2$ and S$_2$PMe$_2$ derivatives have been interpreted in terms of a molecular rearrangement involving dechelation of the bidentate ligand which exchanges the alkyne environments and the ends of the dithiolate ligand. The reaction of (**1**) with two molar equivalents of Na(S$_2$PMe$_2$) gives the bis-alkyne complex [W(S$_2$PMe$_2$)$_2$(MeC≡CMe)$_2$] (**3**) whereas Na[S$_2$P(OMe)$_2$] and Tl(acac) give mono-alkyne derivatives [W(L–L)$_2$(CO)(MeC≡CMe)] (**4**) [L–L = S$_2$P(OMe)$_2$ or acac]. ^{1}H N.m.r. studies of (**3**) suggest fluxional behaviour involving dechelation of S$_2$PMe$_2$ which exchanges both the S$_2$PMe$_2$ methyls and the alkyne methyls without necessarily requiring alkyne propeller rotation. In contrast, fluxional behaviour in (**4**) [L–L = S$_2$P(OMe)$_2$] clearly involves alkyne propeller rotation in addition to two other processes, one of which exchanges the methyl groups of one S$_2$P(OMe)$_2$ group. However, the only dynamic process observed with (**4**) (L–L = acac) appears to involve alkyne propeller rotation.

A current topic of interest in organometallic chemistry is the ability of alkynes to stabilise co-ordinative unsaturation at metal centres, in particular Mo$^{\mathrm{II}}$ and W$^{\mathrm{II}}$, by involvement of both sets of filled π orbitals in bonding with the metal.[1,2] Two particular types of complex of interest in this area are bis-chelate derivatives [M(L–L)$_2$L(RC≡CR′)] and [M(L–L)$_2$(RC≡CR′)$_2$] (M = Mo or W; R = H, alkyl, or aryl; L–L = S$_2$CNMe$_2$, S$_2$CNEt$_2$, or S$_2$PPr$^i_2$; L = O, S, CO, or alkyne) which have been studied extensively by Templeton[3–12] and others.[13–19] Halogen complexes, *e.g.* [{M(μ-X)X(CO)(RC≡CR)$_2$}$_2$] (M = Mo, X = I; M = W, X = Br) and their derivatives have also been synthesized[20–24] and recently we have demonstrated that the tungsten dimers afford an efficient route to the chelate complexes on reaction with Na(S$_2$CNMe$_2$), Na(S$_2$PMe$_2$), or Tl(SC$_5$H$_4$N) in diethyl ether or tetrahydrofuran.[25] Significantly, dynamic n.m.r. studies of the monocarbonyl complexes [W(L–L)$_2$(CO)(RC≡CR′)] have shown that with L–L = S$_2$CNMe$_2$ and R = R′ = Me, alkyne propeller rotation is observed as the only form of fluxional behaviour. However, with L–L = S$_2$PMe$_2$, R = Ph, R′ = Ph or Me, an additional process, apparently involving selective dechelation of one of the dithiophosphinate sulphur atoms is observed, a difference we ascribed to the weaker donor abilities of the S$_2$PMe$_2$ ligand. In an effort to substantiate this conclusion and also to extend the chemistry of these alkyne complexes we have now synthesized a wider range of chelate compounds derived from the but-2-yne complex [{W(μ-Br)Br(CO)(MeC≡CMe)$_2$}$_2$] (**1**).[20]

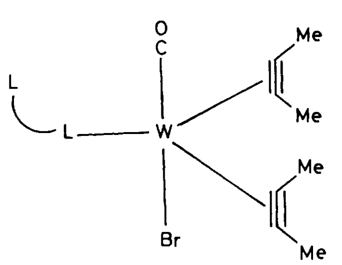
Results and Discussion

Previously we observed that [{W(μ-Br)Br(CO)(RC≡CR′)$_2$}$_2$] reacts with two molar equivalents of Na(S$_2$CNMe$_2$), Na(S$_2$PMe$_2$), or Tl(SC$_5$H$_4$N) to give primarily mono-alkyne complexes [W(L–L)$_2$(CO)(RC≡CR′)$_2$], although bis-alkyne derivatives were sometimes detected as side products and in one case [W(SC$_5$H$_4$N)$_2$(PhC≡CPh)$_2$] obtained as the main product of the reaction.[25] We have now observed that reaction of (**1**) with one molar equivalent of Na(S$_2$CNMe$_2$), Na(S$_2$PMe$_2$), or Tl(acac) (acac = acetylacetonate) in diethyl ether at room temperature produces yellow or orange crystalline complexes [WBr(L–L)(CO)(MeC≡CMe)$_2$] (**2**) containing one carbonyl and two alkynes (see Scheme 1). The reaction of (**1**) with one molar equivalent of Tl[S$_2$P(OMe)$_2$] in contrast yielded oily products which could not be purified. Reaction of (**1**) with two molar equivalents of Na(S$_2$PMe$_2$) gave the bis-alkyne product (**3**) in which both bromo ligands had been removed, whereas the corresponding reactions with Tl(acac) and Tl[S$_2$P(OMe)$_2$] gave mono-alkyne derivatives (**4**) of a type observed previously.[25]

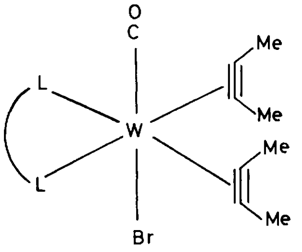


Scheme 1.

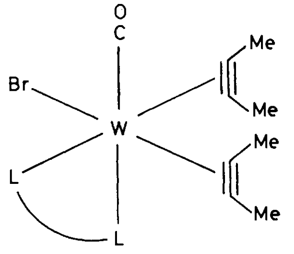
Complexes (**2**) are yellow or yellow-brown crystalline derivatives, slightly air sensitive in the solid state but more so in solution. They are formulated as mono-chelate derivatives on the basis of elemental analyses and spectroscopic data. In all cases the highest peak in the mass spectrum corresponds to [M – CO]$^+$ indicating facile loss of carbon monoxide on ionization of the parent. The i.r. spectrum in each case exhibits a single ν(CO) peak near 2 020 cm^{-1} somewhat lower in frequency than the two bands of the parent complex (**1**) at 2 098 and



(I)



(II)



(III)

2 060 cm^{-1}. However, each of the three complexes exhibits quite distinctive variable-temperature ^1H n.m.r. spectra indicating that each has unique structural and/or dynamic features. Previous studies of mono- and bis-alkyne complexes of Mo^{II} and W^{II} indicate that two basic structures are possible for (**2**), a five-co-ordinate trigonal bipyramid (**I**) as found in $[Mo(SBu^t)_2(CNBu^t)_2(RC{\equiv}CR)]$ (R = H or Ph)[26] or a six-co-ordinate form with a bidentate ligand $L{-}L^-$, similar to that of *e.g.* $[Mo(S_2CNEt_2)_2(PhC{\equiv}CPh)_2]$.[27] Moreover two isomeric forms of the latter are possible, the symmetric isomer (**II**) and the asymmetric structure (**III**). Both five- and six-co-ordinate structures have other isomeric forms available but in a variety of structural studies it has been established that alkyne carbonyl complexes of Mo^{II} and W^{II} invariably adopt a structure in which the alkyne (or alkynes) occupy a *cis* position with respect to CO and with the C≡C axis parallel to the M–CO bond.[15,23,28–30] Simple bonding arguments readily account for this in terms of optimised π forward donation (alkyne→metal) and π back donation (metal→alkyne).[12]

In both (**II**) and (**III**) the alkyne is required to involve both sets of C≡C π orbitals in bonding with the metal if the latter is to achieve a formal 18-electron configuration. However, in (**I**) the two alkynes must function as four-electron donors and consequently donate a total of eight electrons whereas in (**II**) and (**III**) six electrons are required such that each alkyne is formally a three-electron donor. Previously it has been established that ^{13}C n.m.r. chemical shifts of alkyne carbons are sensitive to metal–alkyne bonding; the greater the electron donation the higher the value.[31] On this basis we exclude the five-co-ordinate structure (**I**) in favour of a six-co-ordinate form since in all three cases (**2a**), (**2b**), and (**2c**) the ^{13}C n.m.r. spectrum exhibits δ(C≡C) values in the range 140—185 p.p.m., which is consistent with three-electron donation. Four-electron donation generally leads to higher δ values of *ca.* 210—250 p.p.m. (see below). More detailed, structural information is also revealed by ^{13}C n.m.r. studies in conjunction with dynamic ^1H n.m.r. spectra which will now be described for each individual complex.

The simplest $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum is exhibited by (**2a**) where two alkyne MeC≡ environments are indicated at −10 °C whereas only one acac methyl signal is observed. Similarly the ^1H n.m.r. spectrum exhibits two alkyne Me quartets (J_{H-H} = 1.0 Hz) and one acac methyl resonance. The alkyne methyl group coupling is significant since it indicates that two equivalent alkynes are present but that the ends of each alkyne are in different environments. A structure containing two inequivalent alkynes each of which undergoes alkyne rotation so as to exchange the methyl groups on each is therefore excluded. Superficially the data are consistent with a stereochemically rigid symmetric structure (**II**) whereas the less symmetric form (**III**) contains four alkyne MeC≡ and two acac methyl group environments. However, a fluxional process is conceivable which could equilibrate the two alkynes and the two acac methyls although this would have to exhibit a very low-energy barrier in view of the fact that little change is observed in the ^1H n.m.r. spectrum down to −80 °C (CD_2Cl_2). Nonetheless evidence for fluxional behaviour was obtained in the case of the other two complexes in the series as will now be described.

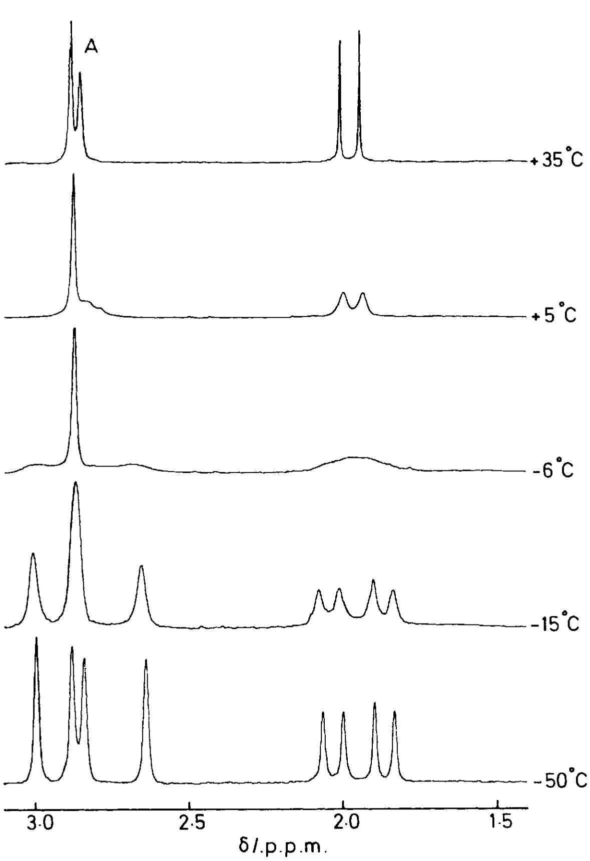


Figure 1. Variable-temperature ^1H n.m.r. spectra of $[WBr(S_2PMe_2)(CO)(MeC{\equiv}CMe)_2]$ (**2b**) in CD_2Cl_2: A = MeC≡CMe resonances

The ^1H n.m.r. spectrum of (**2b**) at +35 °C, as for (**2a**), exhibits two alkyne methyl group signals. One of these is a quartet, J_{H-H} = 1.0 Hz [*cf.* (**2a**)], whereas the other peak is broadened indicating fluxional behaviour. This is confirmed by the presence of only one S_2PMe_2 doublet since both symmetric, (**II**), and asymmetric, (**III**), isomers should give rise to two doublets. Consequently variable-temperature ^1H n.m.r. spectra were recorded between +35 and −50 °C (Figure 1). At −50 °C a frozen spectrum is obtained in which four alkyne quartets and two S_2PMe_2 doublets are observed. This indicates that the preferred structure at this temperature is the asymmetric form (**III**) and this is confirmed by the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at −30 °C which exhibits four sets of alkyne MeC≡ resonances and two S_2PMe_2 doublets. At higher temperatures fluxional behaviour exchanges the two S_2PMe_2 methyl groups and the two alkyne ligands (Figure 1).

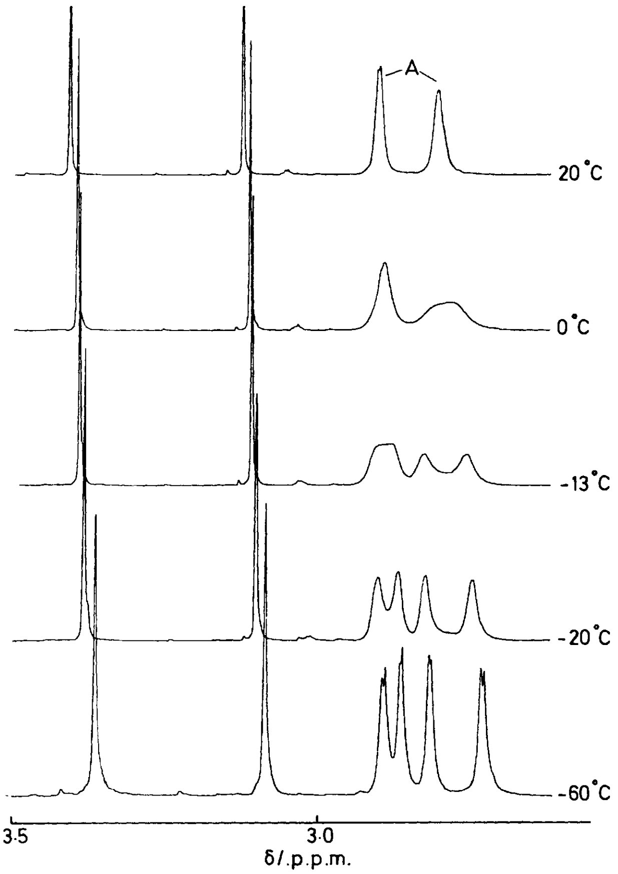
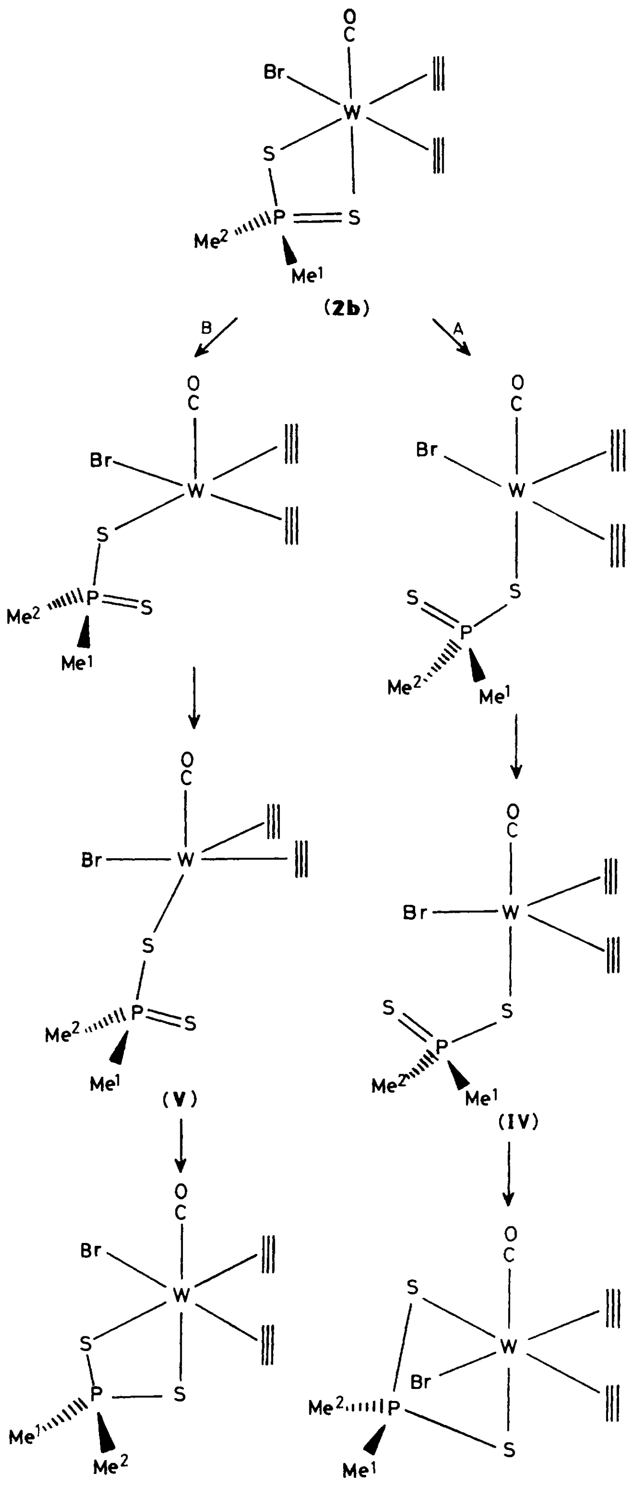


Figure 2. Variable-temperature ^1H n.m.r. spectra of $[WBr(S_2CNMe_2)(CO)(MeC{\equiv}CMe)_2]$ (**2c**) in CD_2Cl_2: A = $MeC{\equiv}CMe$ resonances

In contrast the dynamic ^1H n.m.r. spectra of the dithiocarbamate complex (**2c**) are somewhat simpler (Figure 2). At low temperatures (−60 °C) the asymmetric form (**III**) is again indicated with two $SCNMe_2$ methyl signals and four alkyne quartets being observed. However as the temperature is raised only the alkyne signals broaden and coalesce suggesting that only alkyne exchange is occurring. The presence of CH_3–CH_3 coupling in the two alkyne resonances at 20 °C again confirms that alkyne exchange rather than rotation is occurring.

Superficially the difference in dynamic behaviour between (**2b**) and (**2c**) would appear to indicate different structural and/or dynamic properties. However a detailed consideration of possible exchange mechanisms reveals that this is not necessarily the case. Previously two mechanisms have been considered to explain intramolecular rearrangements in six-co-ordinate octahedral complexes containing chelate ligands, namely twist and bond rupture processes.[32] Although the available n.m.r. data do not uniquely define one particular dynamic process it is clear that a simple localised twisting motion of the chelate ligand is insufficient to account for the n.m.r. data since this would (*a*) exchange the methyl groups of the S_2CNMe_2 and S_2PMe_2 ligands, (*b*) *not* exchange the alkyne ligands. Moreover, a more realistic trigonal twist mechanism would result in a *trans* disposition of alkyne and CO ligands although a combination of two sequential twists could overcome this objection.

Previously we have accounted for fluxional behaviour in $[W(S_2PMe_2)_2(CO)(PhC{\equiv}CR)]$ (R = Me or Ph) in terms of a dissociative mechanism in which dechelation of one of the dithiophosphinate ligands leads to a five-co-ordinate intermediate.[25] Trapping of the intermediate proved possible by addition of $P(OMe)_3$, PMe_2Ph, or $CNBu^t$ which gave six-co-ordinate derivatives containing one mono- and one bi-dentate S_2PMe_2 ligand. A related mechanism can similarly be applied to explain the dynamic behaviour of (**2b**) (Scheme 2) and (**2c**).



Scheme 2.

As illustrated dechelation can occur in two ways, path A involving sulphur dissociation *trans* to an alkyne ligand and path B, *trans* to CO. If we consider the former, subsequent rearrangement to a trigonal-bipyramidal intermediate (**IV**) allows reco-ordination in two ways, one of which results in exchange of the alkyne groups. In the case of the S_2PMe_2 complex this also equilibrates the chelate ligand methyl groups. However this is not the case with the S_2CNMe_2 derivatives as a consequence of the planar geometry of the dithiocarbamate ligand. It is also apparent that rotation of the NMe_2 moiety about the N–C bond does not occur since this would accomplish methyl group exchange and this is not observed in practice. The alternative process (path B) involving dechelation of sulphur *trans* to the carbonyl ligand leads to a trigonal bipyramid (**V**) in which alkynes occupy both equatorial and axial sites. However, reco-ordination of sulphur, although exchanging methyl groups of the S_2PMe_2 ligand, in (**2b**) does not exchange alkyne sites and is clearly at variance with experimental facts. Moreover this would also exchange the S_2CNMe_2 methyls in (**2c**) which is not observed in practice. Not surprisingly *X*-ray diffraction studies of $[Mo(SBu^t)_2(CNBu^t)_2(RC\equiv CR)]$ (R = H or Ph) have illustrated that alkynes prefer equatorial sites in d^4 trigonal-bipyramidal metal complexes.[26] We therefore suggest that the dynamic ^1H n.m.r. data for (**2b**) and (**2c**) are most readily interpreted in terms of the structure which undergoes exchange *via* path A in Scheme 2. The key feature of this process is selective fission of the tungsten–sulphur bond *trans* to an alkyne rather than the bond *trans* to carbon monoxide.

Returning to the spectroscopic features of the acac complex (**2a**), it is clear that structurally the planar acac ligand resembles an S_2CNMe_2 group rather than S_2PMe_2. On this basis the process in Scheme 2 which accounts for the behaviour of (**2c**), *i.e.* rearrangements *via* path A, is insufficient to account for the n.m.r. spectra of (**2a**) in which the acac methyl groups remain equivalent down to −80 °C. We are left with two possibilities. In the first of these (**2a**) has the asymmetric structure (**III**) but undergoes rearrangement with a very low energy barrier so as to exchange the two acac methyl groups as well as the alkyne ligands but not the ends of the alkynes. This could be accomplished by, for example, a combination of paths A and B in Scheme 2 assuming that alkyne propeller rotation does not occur at any stage. Alternatively (**2a**) could simply have the symmetric form (**I**) as a consequence of the larger chelate ring bite relative to that of (**2b**) and (**2c**).

As illustrated in Scheme 1 the stoicheiometry of complexes obtained by replacement of both bromo ligands in $[\{WBr_2(CO)(MeC\equiv CMe)_2\}_2]$ with the anionic ligand L–L$^-$ depends on the nature of the ligand. The S_2PMe_2 derivative (**3**) analyses as a bis-alkyne derivative $[W(S_2PMe_2)_2(MeC\equiv CMe)_2]$ although the highest peak in the mass spectrum at *m*/*z* 486 corresponds to $[M - MeC\equiv CMe]^+$. Related bis-dithiocarbamate complexes of this type have been isolated previously from reactions of $[Mo(S_2CNR_2)_2(CO)_2]$ with excess alkyne[9,14] whereas $[Mo(S_2PPr^i{}_2)_2(CO)_2]$ only gives mono-alkyne derivatives $[Mo(S_2PPr^i)_2(CO)(RC\equiv CR')]$.[13] Previously we isolated complexes $[W(L\text{–}L)_2(CO)(RC\equiv CR')]$ (L–L = S_2CNMe_2 or SC_5H_4N, $RC\equiv CR'$ = $MeC\equiv CMe$; L–L = S_2CNMe_2 or S_2PMe_2, $RC\equiv CR'$ = $PhC\equiv CMe$; L–L = S_2PMe_2, $RC\equiv CR'$ = $PhC\equiv CPh$) from the reactions of $[\{WBr_2(CO)(alkyne)_2\}_2]$ with sodium and thallium salts of L–L$^-$.[25] In contrast, $Tl(SC_5H_4N)$ and $[\{WBr_2(CO)(PhC\equiv CPh)_2\}_2]$ gave the bis-alkyne complex $[W(SC_5H_4N)_2(PhC\equiv CPh)_2]$ comparable with (**3**). This illustrates that, depending on the nature of the alkyne and the bidentate ligand L–L, CO loss is an alternative to alkyne displacement.

The structure of $[Mo(S_2CNEt_2)_2(PhC\equiv CPh)_2]$ has been shown by *X*-ray diffraction studies to consist of an octahedrally co-ordinated metal with the two *cis* alkynes lying approximately parallel to each other and to two *trans* molybdenum–sulphur bonds.[27] Accordingly we propose such a structure for (**3**) since it is compatible with the ^1H and ^{13}C n.m.r. spectra as will now be described. The ^1H n.m.r. spectrum at −80 °C (see Figure 3) exhibits two broad S_2PMe_2 doublets and two alkyne methyl group signals as expected for structure (**3**). As the temperature is raised the S_2PMe_2 peaks collapse to one doublet above *ca.* −32 °C whereas the alkyne signals coalesce to the single resonance above −18 °C. The $^{13}C\text{-}\{^1H\}$ spectrum at −60 °C also confirms a rigid structure, the two alkyne $Me\mathit{C}\equiv$ resonances occurring at δ 188.22 and 180.38 which is in the region expected for alkynes which act as formal three-electron donors. It is clear from the ^1H n.m.r. spectra that fluxional behaviour equilibrates both alkyne and S_2PMe_2 methyl environments and again a detailed assessment of the mechanism is required.

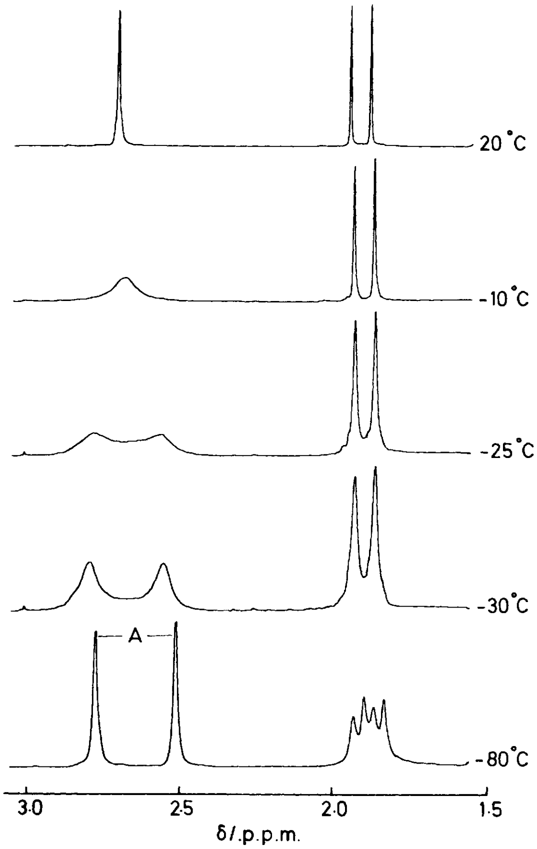
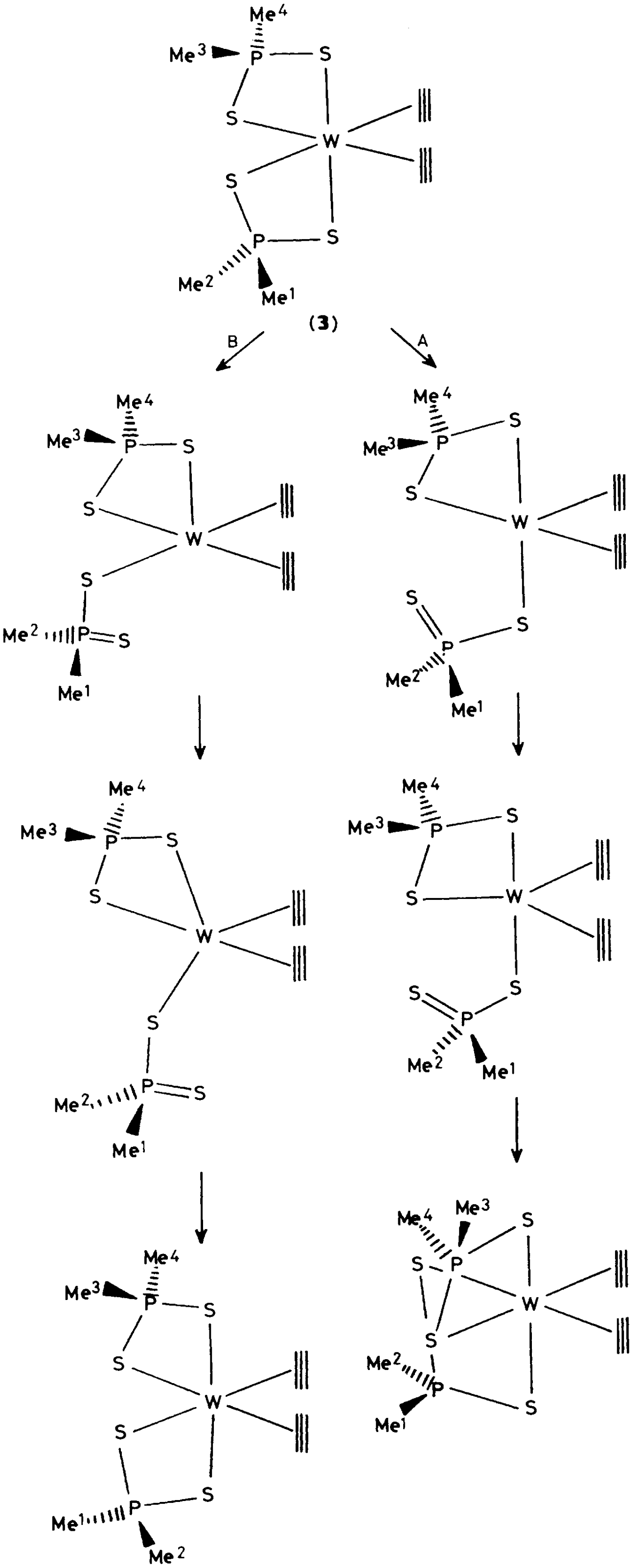


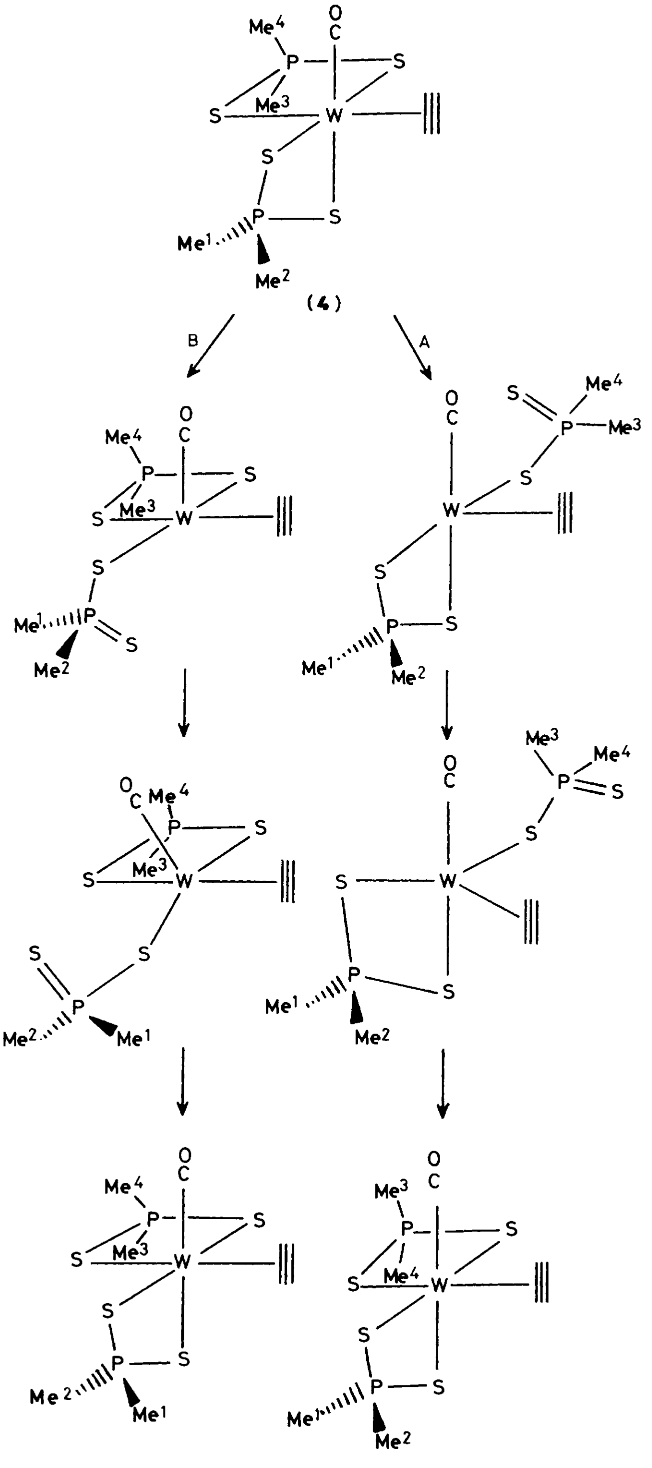
Figure 3. Variable-temperature ^1H n.m.r. spectra of $[W(S_2PMe_2)_2(MeC\equiv CMe)_2]$ (**3**) in CD_2Cl_2: A = $MeC\equiv CMe$ resonances

Although alkyne rotation must exchange the alkyne methyl groups it cannot equilibrate the S_2PMe_2 methyls. However this can be accomplished by dechelation of one S_2PMe_2 ligand as shown in Scheme 3, path A, which also illustrates that such a process simultaneously leads to alkyne methyl group exchange. The alternative, dechelation of sulphur *trans* to another sulphur (Scheme 3, path B) only achieves localised methyl group exchange on the dechelating S_2PMe_2 ligand and to accomplish exchange of all four S_2PMe_2 methyl and all four alkyne methyls requires two sequential dechelation processes involving different S_2PMe_2 ligands in addition to alkyne propeller rotation. We favour path A in Scheme 3 for reasons given in the discussion of fluxional behaviour of (**2b**) and because it parallels path A in Scheme 2.

In principle it is possible to distinguish between the two alternatives path A and path B in Scheme 3 since in the latter the two independent exchanges would probably proceed with different energy barriers. In the former, alkyne exchange and S_2PMe_2 exchange would have the same barrier unless alkyne rotation occurs *prior* to sulphur dechelation, *i.e.* for path A,



Scheme 3.



Scheme 4.

$\Delta G^\ddagger$(MeC≡CMe) $\leqslant$ $\Delta G^\ddagger$(S_2PMe_2) whereas for path B, $\Delta G^\ddagger$(MeC≡CMe) can also be greater than $\Delta G^\ddagger$(S_2PMe_2). However, although it was possible to determine the barrier for alkyne methyl group exchange ($\Delta G_{255}^\ddagger = 52.0 \pm 2$ kJ mol^{-1}),[33] this was not feasible in the case of dithiophosphinate methyl group scrambling since the low-temperature limiting spectrum was not reached at *ca.* −90 °C. Interestingly we note that different barriers have previously been reported for [$Mo(S_2CNMe_2)_2(EtC{\equiv}CEt)_2$]. In this case exchange of the alkyne carbons in the ^{13}C n.m.r. spectrum occurs with $\Delta G^\ddagger = 70 \pm 0.8$ kJ mol^{-1}, whereas S_2CNMe_2 methyl group exchange has an activation energy of 77.3 kJ mol^{-1}. It was concluded that the lower energy barrier was consistent with rotation of the NMe_2 group about

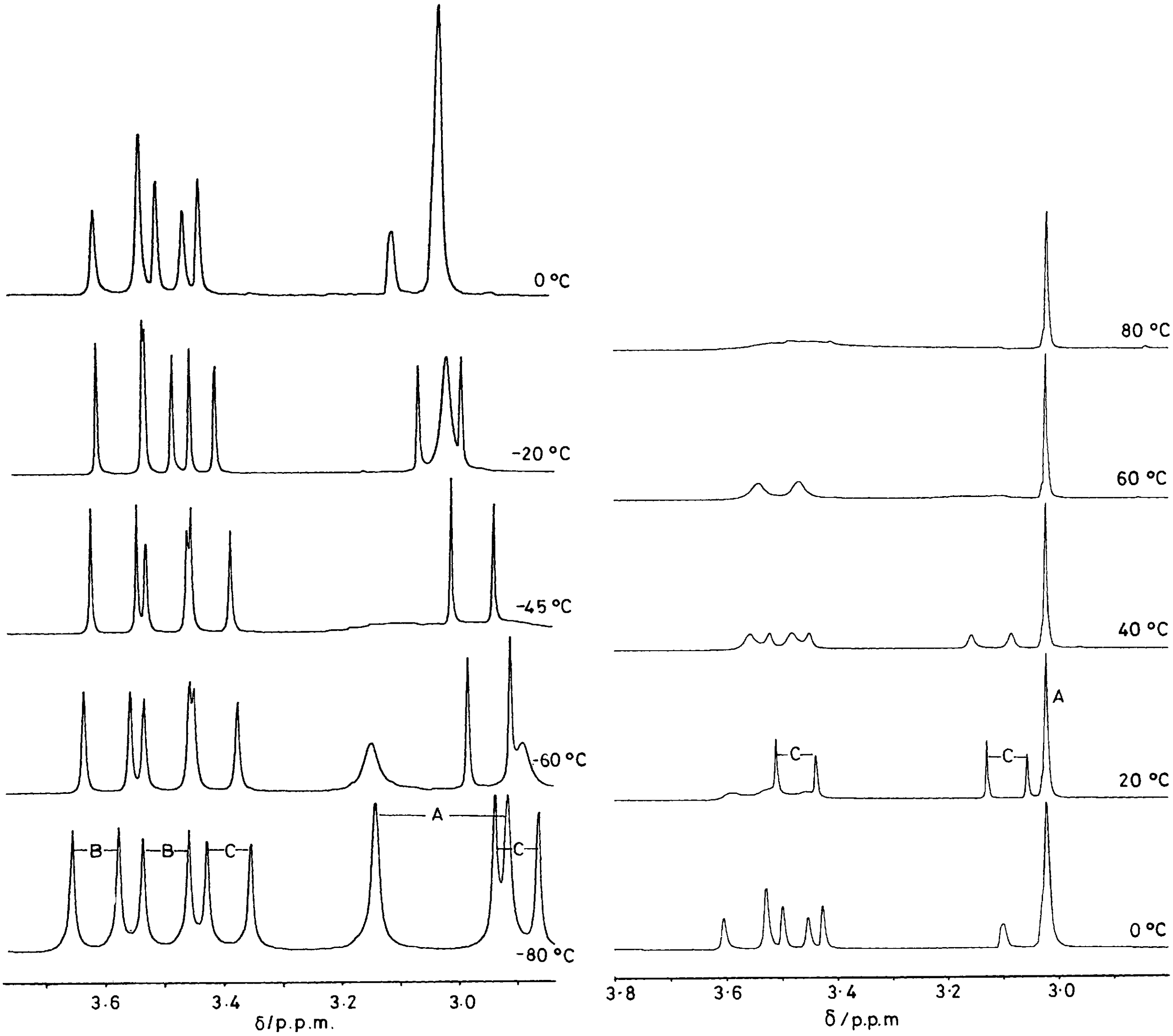


Figure 4. Variable-temperature ^1H n.m.r. spectra of $[W\{S_2P(OMe)_2\}_2(CO)(MeC{\equiv}CMe)]$ (**4a**): A = $MeC{\equiv}CMe$ resonances, B = first $S_2P(OMe)_2$ ligand, C = second $S_2P(OMe)_2$ ligand. Different vertical scales are employed for the low- (−80 to 0 °C) and high-temperature spectra (0 to 80 °C)

the C–N bond rather than dechelation of the S_2CNMe_2 ligands. It is however pertinent to note that the process in Scheme 3, path A, would also exchange the ends of the alkynes but not lead to S_2CNMe_2 methyl group exchange. This clearly provides an alternative explanation for the n.m.r. data reported previously for $[Mo(S_2CNMe_2)_2(EtC{\equiv}CEt)_2]$, *i.e.* exchange of the ends of the alkyne may occurs as a result of S_2CNMe_2 dechelation rather than alkyne propeller rotation. In support of this alternative proposal we draw attention to the parallel with alkyne complexes (**2b**) and (**2c**) where it is clear that alkyne rotation is not observed. In these two complexes dechelation of a bidentate ligand can be detected by the S_2PMe_2 ligand but not by S_2CNMe_2. Although this also applies to complexes of type (**3**), *i.e.* $[M(L\text{–}L)_2(RC{\equiv}CR)_2]$, we note that dechelation of S_2CNMe_2 may be a higher energy process than for S_2PMe_2, as discussed previously,[25] and later in this paper, in view of the stronger chelating ability of the former.[34] We conclude that with (**3**) exchange affects both types of ligand and dechelation of an S_2PMe_2 group is highly probable. We are not able to reach definite conclusions concerning alkyne rotation.

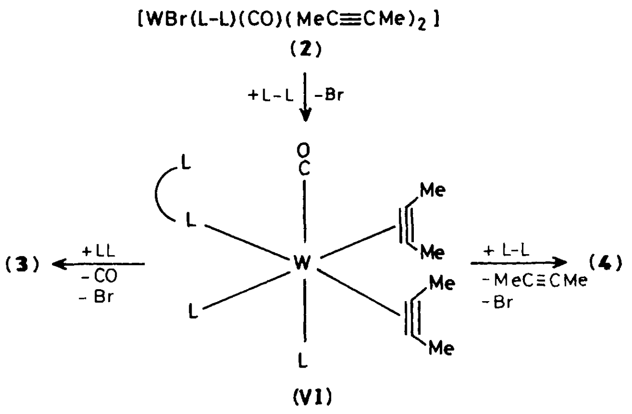
The formulation of $S_2P(OMe)_2$ and acac derivatives (**4a**) and (**4b**) as mono-alkyne derivatives $[W(L\text{–}L)_2(CO)(MeC{\equiv}CMe)]$ is based on elemental analyses and spectroscopic data. Moreover, similar complexes have been isolated previously from the reactions of $[\{WBr_2(CO)(RC{\equiv}CR')_2\}_2]$ with $Na(S_2CNMe_2)$ ($RC{\equiv}CR'$ = $MeC{\equiv}CMe$ or $PhC{\equiv}CMe$), $Tl(SC_5H_4N)$ ($RC{\equiv}CR'$ = $MeC{\equiv}CMe$), and $Na(S_2PMe_2)$ ($RC{\equiv}CR'$ = $PhC{\equiv}CMe$ or $PhC{\equiv}CPh$). Dynamic ^1H n.m.r. studies of (**4a**) established a 'frozen' structure for the complex at −80 °C ($CD_3C_6D_5$) which gives rise to two alkyne methyl resonances and four doublets due to the two $S_2P(OMe)_2$ ligands (see Figure 4). This is directly comparable with the spectra of $[W(S_2PMe_2)_2(CO)(PhC{\equiv}CR)_2]$ (R = Me or Ph) and a similar structure (**4**) is therefore proposed in which the alkyne lies parallel to the *cis* CO ligand as found in $[W(S_2CNEt_2)_2(CO)(HC{\equiv}CH)]$.[15] In this situation the alkyne formally functions as a four-electron donor and accordingly three peaks are observed above δ 200 in the ^{13}C n.m.r. spectrum at −60 °C, one at δ 231.27 which we tentatively assign to the metal-bound carbonyl and the other two at δ 217.36 and 210.25 to the alkyne

C≡C carbons. These chemical shift values contrast with those of the alkynes in (**2**) (*ca.* δ 144—185) and (**3**) (δ 188.22 and 180.38) which reflect three-electron donation to the metal. Interestingly we note that the carbonyl peak in the spectrum of (**4a**) is a doublet, presumably as a result of coupling to one phosphorus, whilst the peak of one of the alkyne carbons is broadened, possibly for the same reason. This selective coupling is readily explained in terms of structure (**4**) if a through-space coupling mechanism is invoked.[35]

The ^1H n.m.r. spectrum of (**4a**) was recorded between −80 and +80 °C. Above −80 °C the two alkyne methyl resonances broaden and collapse to a singlet at −43 °C consistent with the onset of alkyne propeller rotation. A barrier to rotation $G_{230}^{\ddagger} = 47.20 \pm 2$ kJ mol^{-1} was determined by established methods.[33] At higher temperatures two of the $S_2P(OMe)_2$ doublets begin to broaden and eventually coalesce ($T_c = 23$ °C) to give one doublet. On close examination the second $S_2P(OMe)_2$ signals (Figure 4) are observed to broaden slightly, from −20 to 0 °C (at the same time as the B signals), but sharpen again, from 0 to +20 °C, before broadening a second time and ultimately coalescing with the other $S_2P(OMe)_2$ signals at *ca.* 80 °C. The main features of the spectra are similar to those of $[W(S_2PMe_2)_2(CO)(PhC{\equiv}CR)]$ (R = Me or Ph)[25] except that in the latter case the nature of the alkyne resonance precluded dynamic behaviour involving the alkynes being observed. Taking into account our previous conclusions for the S_2PMe_2 derivatives,[25] the three main phases of dynamic behaviour in complex (**4a**) can be ascribed in terms of increasing coalescence temperature to (*a*) alkyne propeller rotation, (*b*) selective exchange of OMe groups on *one* $S_2P(OMe)_2$ ligand *via* dechelation and a five-co-ordinate trigonal-bipyramidal intermediate (Scheme 4), and (*c*) exchange of all four OMe environments by some indeterminate polytopal rearrangement. However, it is not readily apparent why the $S_2P(OMe)_2$ signals (Figure 4) should exhibit reversible broadening between −20 °C and +20 °C.

It is pertinent to note that in the case of (**4a**) dechelation and rearrangement *via* a trigonal-bipyramidal intermediate only accomplishes localised methyl group exchange on the monodentate $S_2P(OMe)_2$ ligand, *i.e.* two consecutive dechelations are required to exchange all four OMe groups. Moreover, alkyne methyl group exchange is not accomplished in Scheme 4. This and the fact that it proceeds at temperatures well below that of total $S_2P(OMe)_2$ methyl group scrambling provides strong evidence for alkyne propeller rotation. We also note that dechelation as in Scheme 4 would also accomplish methyl group exchange in planar ligands such as S_2CNMe_2 and more particularly the acac ligands in (**4b**). However no such exchange is observed with $[W(S_2CNMe_2)_2(CO)(MeC{\equiv}CR)]$ (R = Me or Ph),[25] a situation which pertains in the case of the acac complex.

The ^{13}C and ^1H n.m.r. spectra of (**4b**) at low temperatures are comparable to those of (**4a**). For example, at −50 °C the ^{13}C spectrum shows six peaks between 180 and 210 p.p.m. consistent with four acac carbonyl and two alkyne MeC≡ environments and this is confirmed by the four acac and two alkyne methyl peaks at 15—30 p.p.m. The ^1H n.m.r. spectrum at −50 °C (CD_2Cl_2) similarly exhibits two alkyne methyl resonances at δ 3.16 and 3.11 in addition to two acac C–H and four acac methyl group peaks. This is indicative of a frozen structure similar to that of (**4a**). As with the latter the alkyne resonances broaden and collapse ($T_c = 8$ °C) to a sharp singlet at higher temperature again indicating alkyne propeller rotation for which a barrier $\Delta G_{281}^{\ddagger} = 60.90 \pm 2$ kJ mol^{-1} was determined. However, unlike (**4a**) no change in the chelate ligand resonances was observed over this temperature range implying that dechelation and exchange of the acac ligands does not occur. As mentioned previously this result was also obtained with $[W(S_2CNMe_2)_2(CO)(MeC{\equiv}CMe)]$ and attributed to the stronger chelating abilities of the dithiocarbamate ligand which inhibits tungsten–sulphur bond fission in complexes of this type. If the conclusion is correct our observation of S_2CNMe_2 methyl group exchange in (**2c**) suggests that the ease with which dechelation occurs varies significantly and depends markedly on the other ligands co-ordinated to the metal.



Scheme 5.

Conclusions

The reactions of bidentate anions L–L$^-$ with $[\{W(\mu\text{-}Br)Br(CO)(MeC{\equiv}CMe)_2\}_2]$ proceed *via* sequential displacement of Br$^-$ giving monomeric bis-alkyne complexes $[WBr(L\text{–}L)(CO)(MeC{\equiv}CMe)_2]$ as the initial products. Replacement of the second bromo ligand is more complex and can be rationalised in terms of the mechanism in Scheme 5 in which we propose the intermediacy of a bis-alkyne species (**VI**) containing one mono- and one bi-dentate ligand L–L. Support for a six-co-ordinate intermediate of this type is obtained from the fact that complexes of type (**4**) undergo reaction with two-electron donors L to give six-co-ordinate complexes $[W(\eta^2\text{-}L\text{–}L)(\sigma\text{-}L\text{–}L)(CO)(L)(RC{\equiv}CR)]$ as mentioned previously.[25] Subsequent co-ordination of the free donor atom in the σ-L–L ligand then proceeds *via* CO loss to give the bis-alkyne product (**3**), or alkyne dissociation to give mono-alkyne derivatives (**4**). Relatively subtle factors seem to influence the preferred reaction pathway since with L–L = S_2PMe_2 the bis-alkyne product (**3**) is obtained when the alkyne is MeC≡CMe whereas with PhC≡CMe or PhC≡CPh a mono-alkyne complex of type (**4**) is the sole product.[25] This could infer that steric factors are important, *i.e.* bulky phenyl groups on the alkyne promote alkyne dissociation. However the fact that $[\{W(\mu\text{-}Br)Br(CO)(PhC{\equiv}CPh)_2\}_2]$ and $Tl(SC_5H_4N)$ react *via* CO dissociation to give the bis-alkyne product $[W(SC_5H_4N)_2(PhC{\equiv}CPh)_2]$ indicates that electronic factors are at least as important.

As discussed earlier the dynamic n.m.r. data do not unequivocally distinguish between non-dissociative (twist) and bond rupture (dechelation) mechanisms for the fluxional behaviour observed in complexes (**2**), (**3**), and (**4**) which leads to exchange involving the chelate and/or alkyne ligands. A trigonal twist is usually considered to be a high-energy process in view of the particular stability associated with the octahedron[36] and the low coalescence temperatures observed with exchange processes involving (**2**), (**3**), and (**4**) would therefore argue in favour of a dissociative mechanism. However, we note that although Mo^{II} and W^{II} alkyne complexes are generally octahedral or near to octahedral in shape, the d^4 configuration can induce distortions,[37] in some instances towards a trigonal prism as observed with $[Mo(S_2CNPr^i_2)_2(CO)_2]$.[38] It may be that the energy difference between an octahedron and a trigonal prism is less pronounced in this class of compound and so facilitates fluxional behaviour.

Despite the above arguments, support exists for the bond rupture mechanisms depicted in Schemes 2—4. For example, Scheme 2 adequately accounts for alkyne exchange in (**2b**) and (**2c**) in terms of a process which effects the S_2PMe_2 methyl group n.m.r. resonances but not those of the dithiocarbamate ligand. In complexes of type (**4**), *i.e.* $[W(L–L)_2(CO)(RC{\equiv}CR)]$, exchange of chelate ligand methyls is observed with L–L = S_2PMe_2 or $S_2P(OMe)_2$ but not with more strongly bound chelates such as S_2CNMe_2[25] where dissociation is less probable. Moreover, trapping of a species containing a monodentate S_2PMe_2 ligand was previously achieved by addition of L = $CNBu^t$, $P(OMe)_3$, or PMe_2Ph which gave $[W(S_2PMe_2)_2(CO)(L)(PhC{\equiv}CR)]$ (R = Me or Ph). In contrast, addition of Lewis bases to $[Mo(S_2CNMe_2)_2(CO)(RC{\equiv}CR)]$ (R = H or Et) has been reported to yield alkyne-substitution products $[Mo(S_2CNMe_2)_2(CO)L_2]$ [L = CO, $P(OMe)_3$, or PEt_3][7] which emphasises differences in the chelating abilities of the two types of ligand.

We also note that dissociation to give a five-co-ordinate intermediate may be facilitated by the variable electron-donor ability of both the alkyne and sulphur donors such as S_2CNMe_2 and S_2PMe_2. Formation of a five-co-ordinate intermediate would normally be a high-energy process but the presence of a π-donor ligand may reduce the energy barrier by stabilisation *via* π donation. We note that with complexes (**2**) or (**3**) the process (**III**) ⟶ (**IV**) merely requires the alkynes to change from three- to four-electron donation. The comparable process with mono-alkyne derivatives (**4**), *i.e.* (**4**) ⟶ (**VII**) involves complexes in which the alkyne is already a four-electron donor and extra π-donation in (**VII**) must involve the sulphur-donor ligands. This may help to explain why only S_2PMe_2 and $S_2P(OMe)_2$ derivatives of type (**4**) exhibit fluxional behaviour involving the chelate ligands.

Experimental

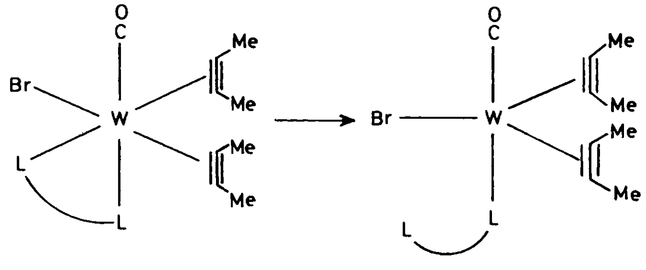
N.m.r. spectra were recorded on a Bruker WP 200 SY spectrometer at 200.13 (^1H) and 50.32 MHz (^{13}C). Coupling constants (*J*) are in Hz and chemical shifts are referenced to $SiMe_4$ (δ = 0). I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer with polystyrene as reference and mass spectra on a Vacuum Generator updated A.E.I. M.S. 11. Reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents (Et_2O and hexane) were dried by refluxing over powdered calcium hydride under nitrogen and distilled just before use. $[\{W(\mu\text{-}Br)Br(CO)(MeC{\equiv}CMe)_2\}_2]$,[20] $Na(S_2PMe_2)$,[39] and Tl(acac)[40] were prepared by literature methods; $Na(S_2CNMe_2)$ was obtained commercially (Aldrich). $Tl[S_2P(OMe)_2]$ was obtained from the reaction of $[NH_4][S_2P(OMe)_2]$ (Aldrich) and $Tl(O_2CMe)$ in methanol.

Reaction of $[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}_2]$ *with* Tl(acac), 1:1 *Molar Ratio.*—Complex (**1**) (50 mg) and Tl(acac) (60 mg) were stirred in diethyl ether (10 cm^3) for 15 h. The mixture was filtered, concentrated *in vacuo*, hexane (2 cm^3) added and on cooling to −15 °C yellow crystals of $[WBr(acac)(CO)(MeC{\equiv}CMe)_2]$ (**2a**) were obtained; yield 20 mg (38%) (Found: C, 31.5; H, 3.5. $C_{13}H_{19}BrO_3W$ requires C, 31.25; H, 3.80%). *M*/*z* = 468 $[M - CO]^+$. I.r. (Nujol): ν(CO) 2 030s cm^{-1}. ^1H N.m.r. ($CDCl_3$, 20 °C); δ 5.38 (s, 1 H, >CH), 3.12 (q, *J* 1.0, 6 H, MeC≡), 2.92 (q, *J* 1.0, 6 H, MeC≡), 1.87 (s, 6 H, OCMe). ^{13}C N.m.r. (CD_2Cl_2, −10 °C); δ 207.71 (CO), 188.07 (>C=O), 171.58, 157.187 (s, Me*C*≡), 101.26 (s, >CH), 26.76 (s, *Me*C=O), 18.84, 18.34 (s, *Me*C≡).

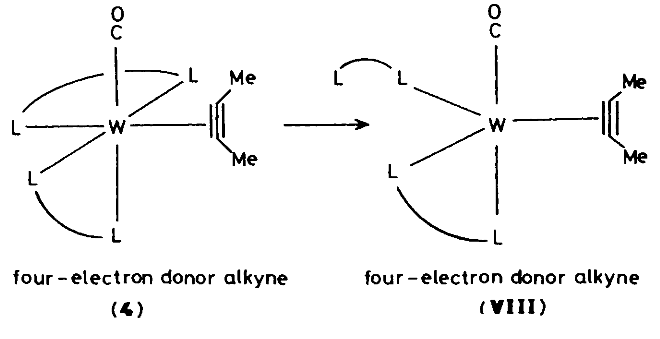
Reaction of $[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}_2]$ *with* $Na(S_2PMe_2)$, 1:1 *Molar Ratio.*—Complex (**1**) (50 mg) and $Na(S_2PMe_2)$ (16 mg) were stirred in diethyl ether (10 cm^3) for 2 h. After filtration the yellow-brown solution was concentrated *in vacuo*, hexane (2 cm^3) added and on cooling to 15 °C yellow-green crystals of $[WBr(S_2PMe_2)(CO)(MeC{\equiv}CMe)_2]$ (**2b**) were obtained; yield 37 mg (68%) (Found: C, 25.4; H, 3.4. $C_{11}H_{18}BrOPS_2W$ requires C, 25.15; H, 3.45%). *M*/*z* = 494 $[M - CO]^+$. I.r. (Nujol): ν(CO) 2 040s cm^{-1}. ^1H N.m.r. (CD_2Cl_2, 15 °C); δ 2.89 (q, *J* 1.0, 6 H, MeC≡), 2.85 (s br, 6 H, MeC≡), 1.97 (d, *J* 13.0, 6 H, PMe_2). ^{13}C N.m.r. (CD_2Cl_2, −30 °C); δ 208.90 (d, J_{P-C} 4.0, J_{W-C} 99.0), 185.28, 165.15, 156.77, 149.41 (s, Me*C*≡), 33.14 (d, J_{P-C} 46.0, PMe), 19.64, 18.47, 17.81, 15.14 (s, *Me*C≡).

Reaction of $[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}_2]$ *with* $Na(S_2CNMe_2)$, 1:1 *Molar Ratio.*—Complex (**1**) (50 mg) and $Na(S_2CNMe_2)$ (15 mg) were stirred in diethyl ether (10 cm^3) for 2 h. The mixture was filtered, concentrated *in vacuo*, hexane (2 cm^3) added and on cooling to −15 °C yellow-brown crystals of $[WBr(S_2CNMe_2)(CO)(MeC{\equiv}CMe)_2]$ (**2c**) were obtained; yield 31 mg (57%) (Found: C, 27.9; H, 3.7; N, 2.4. $C_{12}H_{18}BrNOS_2W$ requires C, 27.7; H, 3.45; N, 2.70%). *M*/*z* = 489 $[M - CO]^+$. I.r. (Nujol): ν(CO) 2 025s cm^{-1}. ^1H N.m.r. (CD_2Cl_2, 20 °C); δ, 3.41 (s, 3 H, NMe), 3.12 (s, 3 H, NMe) 2.90 (s, br, 6 H, MeC≡), 2.81 (s, br, 6 H, MeC≡). ^{13}C N.m.r. (CD_2Cl_2, −60 °C); δ 209.91, 206.33 (CO and S_2*C*NMe_2, unassigned), 184.30, 169.13, 149.25, 144.59 (s, Me*C*≡), 39.13, 38.88 (s, S_2CN*Me*$_2$), 19.49, 17.37, 16.94, 15.74 (s, *Me*C≡).

Reaction of $[\{WBr_2(CO)(MeC{\equiv}CMe)_2\}]$ *with* $Na(S_2PMe_2)$, 1:2 *Molar Ratio.*—Complex (**1**) (50 mg) and $Na(S_2PMe_2)$ (30 mg) were stirred in diethyl ether (10 cm^3) for 15 h. After filtration the yellow solution was concentrated *in vacuo*, hexane (2 cm^3) added and on cooling to −15 °C yellow crystals of $[W(S_2PMe_2)_2(MeC{\equiv}CMe)_2]$ (**3**) were obtained; yield 30 mg (53%) (Found: C, 26.2; H, 4.0. $C_{12}H_{24}P_2S_4W$ requires C, 26.55; H, 4.45%). *M*/*z* = 486 $[M - C_4H_6]^+$. ^1H N.m.r. ($CDCl_3$, 18 °C); δ 2.73 (s, 12 H, MeC≡), 1.93 (d, *J* 13.0, 12 H, PMe). ^{13}C N.m.r. (CD_2Cl_2, −60 °C); δ 188.22 (d, J_{P-C} 6.2, Me*C*≡), 180.38 (d, J_{P-C} 12.0 Me*C*≡), 31.24 (d, J_{P-C} 45.5, PMe), 27.42 (d, J_{P-C} 48.0, PMe), 19.04 (s, *Me*C≡), 18.05 (s, *Me*C≡).



three-electron donor alkyne (**III**) four-electron donor alkyne (**IV**)



four-electron donor alkyne (**4**) four-electron donor alkyne (**VIII**)

Reaction of [{WBr$_2$(CO)(MeC≡CMe)$_2$}$_2$] *with* Tl[S$_2$P(OMe)$_2$], 1:2 *Molar Ratio*.—Complex (**1**) (50 mg) and Tl[S$_2$P(OMe)$_2$] (76 mg) were stirred in diethyl ether (8 cm^3) for 14 h. The resulting mixture was centrifuged to give a blue solution which was concentrated *in vacuo*. Slow addition of hexane (*ca.* 3 cm^3) and cooling to −15 °C gave purple crystals of [W{S$_2$P(OMe)$_2$}$_2$(CO)(MeC≡CMe)] (**4a**); yield 29 mg (48%) (Found: C, 18.8; H, 2.8. $C_9H_{18}O_5P_2S_4W$ requires C, 18.6; H, 3.10%). *M/z* = 578 [*M*]$^+$. I.r. (CHCl$_3$); ν(CO) 1 920s cm^{-1}. ^{1}H N.m.r. (CDCl$_3$, 20 °C); δ 3.84 (d, *J* 14.5, 3 H, OMe), 3.80 (d, *J* 15.0, 6 H, OMe), 3.63 (d, *J* 14.5, 3 H, OMe), 3.26 (s, 6 H, MeC≡). ^{13}C N.m.r. (CD$_2$Cl$_2$, −60 °C); δ 231.27 (d, J_{P-C} 3.3, CO), 217.36 (s, br, Me*C*≡), 210.25 (s, Me*C*≡), 21.93, 19.80 (s, *Me*C≡) [**N.B.** P(OMe)$_2$ methyl signals obscured by solvent resonance].

Reaction of [{WBr$_2$(CO)(MeC≡CMe)$_2$}] *with* Tl(acac), 1:3 *Molar Ratio*.—Complex (**1**) (50 mg) and Tl(acac) (90 mg) were stirred in diethyl ether (10 cm^3) for 15 h. The mixture was filtered, concentrated *in vacuo* and hexane (*ca.* 2 cm^3) added. On cooling to −15 °C red brown crystals of [W(acac)$_2$(CO)(MeC≡CMe)] (**4b**) were obtained; yield 30 mg (62%) (Found: C, 38.4; H, 4.2. $C_{15}H_{20}O_5W$ requires C, 38.8; H, 4.30%). *M/z* = 462 [*M*]$^+$. I.r. (Nujol); ν(CO) 1 862s cm^{-1}. ^{1}H N.m.r. (CD$_2$Cl$_2$, 40 °C); δ 5.52 (s, 1 H, >CH), 5.48 (s, 1 H, >CH), 3.20 (s, 6 H, MeC≡), 2.18 (s, 3 H, OCMe), 2.16 (s, 3 H, OCMe), 2.10 (s, 3 H, OCMe), 1.87 (s, 3 H, OCMe). ^{13}C N.m.r. (CD$_2$Cl$_2$, −50 °C); δ 242.47 (s, CO), 209.37, 194.24, 188.70, 187.91, 187.21, 185.25 (s, C=O or Me*C*≡, unassigned), 101.70, 100.21 (s, H–C), 28.15, 26.58, 26.39, 25.89 (s, *Me*C=O), 20.27, 16.28 (s, *Me*C≡).

Acknowledgements

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