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Syntheses and NMR studies of mono alkyne complexes of molybdenum and tungsten

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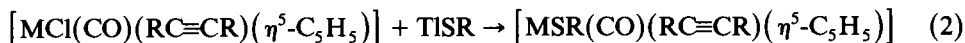
Abstract

Reactions of $[MCl(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ ($M = Mo, 1a; W, 1b$) with TISR ($R = Me, Et, ^nPr, ^iPr$ and tBu) give thiolate complexes $[MSR(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ which according to IR and NMR spectroscopy exist in two isomeric forms as a result of restricted rotation about the M–SR bond. Reactions of $[WCl(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ and metal salts $ML-L$, ($ML-L = TIS2-Ph, TIS4-Py, Tlacac, TIOAc, TIS_2P(OMe)_2$) ($acac = 2,4$ -pentanedionato, $Py = C_5H_4N$) give similar monoalkyne complexes $[WL-L(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ (**3**) in which the L–L species functions as a monodentate ligand. In contrast **1a** and **1b** react with $NaS_2CNMe_2 \cdot 2H_2O$ to give carbonyl-free derivatives $[M(S_2CNMe_2)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ containing a bidentate dithiocarbamate ligand. Oxidation of $[W\{S_2P(OMe)_2\}(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ in air gives the oxo complex $[W\{S_2P(OMe)_2\}(O)(PhC\equiv CPh)(\eta^5-C_5H_5)]$, thought to contain a monodentate $S_2P(OMe)_2$ ligand.

Introduction

A wide range of mono- and bisalkyne complexes of the general types $[M(X)(L)(RC\equiv CR)(\eta^5-C_5H_5)]$ ($M = Mo, W; X = Cl, Br, I, SR; L = CO, PR'_3$) and $[MX(RC\equiv CR)_2(\eta^5-C_5H_5)]$ ($M = Mo, W; X = Cl, Br, I, SC_6F_5$) have been isolated in recent years and form part of an expanding class of complexes in which both sets of filled π -orbitals on the alkyne are involved in bonding with the metal [1]. As a consequence the alkyne in the former can be regarded as a four-electron donor whereas in the latter both alkynes on average donate three electrons to the metal [2,3,4]. Previously we have observed fluxional behaviour and isomerism in monoalkyne complexes $[MSR(CO)(CF_3C\equiv CCF_3)(\eta^5-C_5H_5)]$ ($M = Mo, W; R = CF_3, C_6F_5$) which can be ascribed to the existence of two preferred orientations of the SR ligand about the M–S bond possibly resulting from sulphur \rightarrow metal π donation [4]. We therefore decided to expand the range of these complexes and also attempt synthesis of related complexes in which the thiolate ligand is replaced by a potentially chelating ligand. Two routes to monoalkyne complexes $[MSR(CO)(RC\equiv CR)(\eta^5-C_5H_5)]$ have been developed previously, eqs. 1 [4] and 2 [5]. The first is limited by the stability of the tricarbonyl thiolate complexes which dimerise readily

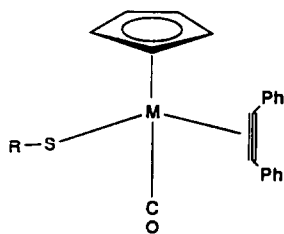
with $M = \text{Mo}$, particularly when R is not strongly electron withdrawing [6]. The second is limited by the range of alkyne ligands in complexes $[\text{MCl}(\text{CO})(\text{RC}\equiv\text{CR})-(\eta^5\text{-C}_5\text{H}_5)]$ to $\text{PhC}\equiv\text{CR}$, $R = \text{Ph}$ or Me only [7,8].



The latter route was employed in the present studies.

Results and discussion

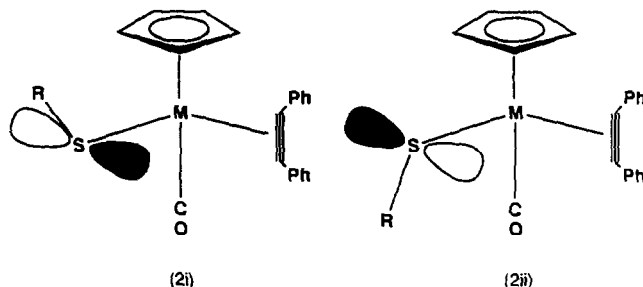
Reactions of $[\text{MCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ ($M = \text{Mo}$, **1a**; W , **1b**) with thallium(I) thiolates TISR ($R = \text{Me}$, Et , ${}^n\text{Pr}$, ${}^i\text{Pr}$ and ${}^t\text{Bu}$) were carried out in dichloromethane at room temperature. With $M = \text{W}$ the initial mixture changed from green to deep red within ca. 5 minutes whereas with $M = \text{Mo}$ the solution merely became deeper green in colour. The resulting solutions on work up gave deep purple ($M = \text{Mo}$) or dark red ($M = \text{W}$) crystals of $[\text{M}(\text{SR})(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**2a-j**) in yields of 64 to 75% depending on the metal and the thiolate ligand. The mass spectra of the complexes in each case show a peak corresponding to the molecular ion although the peak of highest intensity is that due to $\{M - \text{CO}\}^+$. This is similar to related complexes $[\text{MSR}(\text{CO})(\text{R}'\text{C}\equiv\text{CR}')(\eta^5\text{-C}_5\text{H}_5)]$ ($R = \text{CF}_3$, C_6F_5 ; $M = \text{Mo}$, $R' = \text{CF}_3$, CH_3 , Ph ; $M = \text{W}$, $R' = \text{CF}_3$, CH_3) where molecular ions are observed in every case [4,5]. Before describing the IR and NMR spectroscopic data for the complexes, it is appropriate to describe the structure of the SC_6F_5 derivative $[\text{MoSC}_6\text{F}_5(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ as revealed by X-ray diffraction studies [9]. This is based upon approximately octahedral coordination at the metal with the cyclopentadienyl ligand occupying a face and the other three ligands corners of the octahedron. Of significance here is the orientation of the alkyne which lies parallel to the $M\text{-CO}$ axis and hence perpendicular to the $M\text{-S}$ bond. The spectroscopic data for complexes **2** are consistent with such a structure and consequently this will be assumed in further structural and spectroscopic discussion



(2)

Two isomeric forms of complexes **2a-j** are indicated by the IR spectra which show two $\nu(\text{CO})$ modes in hexane solution. With the molybdenum derivatives these are observed at ca. 1935 and 1955 cm^{-1} whereas slightly lower values (ca. 1930 and 1945 cm^{-1}) are exhibited by the tungsten complexes. As mentioned previously the two isomers which give rise to two $\nu(\text{CO})$ modes are thought to result from two preferred orientations of the SR ligand with respect to the rest of the molecule, i.e.

2i and **2ii**. The former has been observed previously in X-ray diffraction studies of related compounds



$[\text{Mo}(\text{SC}_6\text{F}_5)(\text{L})(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{L} = \text{CO}$) [9] $[\text{Mo}(\alpha\text{C}_6\text{H}_4\text{NO}_2\text{-4})\text{-}(\text{L})(\text{MeC}\equiv\text{CMe})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{L} = \text{P}(\text{OMe})_3$) and $[\text{Mo}(\text{SC}_6\text{H}_4\text{SPh-2})(\text{L})(\text{MeC}\equiv\text{CMe})\text{-}(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{L} = \text{CO}$) [10] where the L-Mo-S-C (aryl) torsion angles are 175.5 , 178.6 and 179.5° , respectively. The alternative orientation **2ii** is that in which the SR ligand has rotated by ca. 180° about the M-S bond relative to the orientation **2i**. The origin of such orientational preferences appears to be electronic rather than steric and is a consequence of the electronic configuration of the metal. Formally the metal is divalent with a d^4 configuration, which means that two filled $d\pi$ orbitals are stabilised by interaction with the strong π -acceptor ligand CO . The third and empty $d\pi$ orbital is therefore orientated along the metal-sulphur and metal-alkyne bond axes. As such it is available for π interaction with both the alkyne π_\perp and sulphur $p\pi$ orbitals, each of which is filled. Sulphur to metal π bonding is therefore maximised at two particular orientations 180° apart as illustrated with **2i** and **2ii** [3b]. With this background in mind the NMR data for complexes **2a-j** will now be considered.

At room temperature the NMR spectra of the complexes show no sign of isomerism. Thus, the ^1H NMR spectrum in each case consists of a singlet at ca. δ 5.50 for the cyclopentadienyl group, a multiplet, at ca. δ 7.50 corresponding to two phenyl groups and other peaks below δ 3 corresponding to the alkyl groups attached to the sulphur atom. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra each exhibit a singlet for the cyclopentadienyl ligand at ca. δ 230 ($\text{M} = \text{W}$) or δ 235 ($\text{M} = \text{Mo}$), a series of aromatic resonances between ca. δ 127 and δ 140 and appropriate peaks below δ 50 corresponding to the carbons of the respective thiolate. Interestingly, two alkyne $\text{C}\equiv\text{C}$ resonances are observed in the $^{13}\text{C}\{^1\text{H}\}$ spectrum of every complex studied, indicating that the alkyne adopts a preferred orientation at ambient temperature rather than exhibiting propeller rotation. This is consistent with data for other carbonyl alkyne derivatives of this type, e.g. $[\text{MoSR}(\text{CO})(\text{MeC}\equiv\text{CMe})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Me}$, 2-SPh C_6H_4) [10], $[\text{WR}(\text{CO})(\text{HC}\equiv\text{CH})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Me}$, Et, Pr or ^tBu) [11,12,13] or $[\text{MSC}_6\text{F}_5(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$, W) [3b]. However, replacement of the carbonyl ligand in the SC_6F_5 derivatives by tertiary phosphines or phosphites results in a reduction in the barrier to alkyne rotation. Consequently a single alkyne CF_3 resonance is observed in the ^{19}F NMR spectra of complexes $[\text{MSC}_5\text{F}_5(\text{L})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$, W; $\text{L} = \text{PEt}_3$, PMe_2Ph or $\text{P}(\text{OMe})_3$) at or just above room temperature.

The ^{13}C NMR chemical shifts of the alkyne carbons of complexes **2** lie in the range ca. δ 175–181.5 when $\text{M} = \text{Mo}$ and δ 180–185 when $\text{M} = \text{W}$, the chemical

shift of the carbonyl ligand lying in the range δ 235–237.5, $M = Mo$, and δ 228–230, $M = W$. The $\delta(C\equiv C)$ values are similar to those reported for alkyl and acyl derivatives $[W(R)(CO)(R' C\equiv CH)(\eta^5-C_5H_5)]$ [12] ($R = Mo, Et, ^nPr, COMe, COEt$ or CO^nPr ; $R' = H$ or Ph) and are therefore consistent with the alkyne functioning as a 4-electron donor to the metal [14]. The values are somewhat lower than those of monoalkyne derivatives $[M(S_2CNMe_2)_2(CO)(RC\equiv CR')]$ ($R = H, Ph$; $R' = H$) [14] and $[WBr_2(CO)(CN^tBu)_2(RC\equiv CR')]$ [15] ($R = Me, Ph$; $R' = Me$), which are typically greater than 200 ppm. In fact the values of $\delta(C\equiv C)$ for **2** ($M = Mo$) are almost as low as those exhibited by bisalkyne derivatives $[MCl(PhC\equiv CPh)_2(\eta^5-C_5H_5)]$ ($M = Mo, \delta = 182.7$ and 173.7 ; $M = W, \delta = 185.8$ and 179.2 , in which the alkynes can formally be considered as three-electron donors [16]. The tungsten derivatives **2f–j** show a shift of ca. 13 ppm to lower δ values relative to $[WCl(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ (δ 197.1, 196.9) [16] suggesting that alkyne $\pi \perp \rightarrow$ metal π donation is more significant in the latter. This is consistent with the proposal that π donation from sulphur to metal should lead to reduced $\pi \perp$ donation from the alkyne (assuming that sulphur is a better π -donor than chlorine). We note that $\delta(C\equiv C)$ values in alkyne thiolate derivatives $[Mo(S^tBu)_2(CN^tBu)_2(RC\equiv CR')]$ ($R = R' = H$ or Ph ; $R = Ph, R = H$) appear in the region δ 171–184, a fact ascribed to the strong donor properties of the thiolate ligand [17].

Since the tungsten isotope ^{183}W (14% abundance) is magnetically active ($I = \frac{1}{2}$) coupling between the metal and some of the carbon nuclei, particularly those directly bonded to the metal, is to be expected in complexes **2**. In most cases this was not observed due to poor signal/noise ratio, but in the case of $[WMe(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ (**2f**) quite distinct coupling was observed ($^1J(W-CO) = 159.5$ Hz). Few tungsten carbonyl couplings have been published for this type of complex but this value compared closely with that observed for $[WPh(CO)(HC\equiv CH)(\eta^5-C_5H_5)]$ [12] ($^1J(W-CO) = 155.0$ Hz). The two metal-coordinated alkyne carbons resonances in **2f** also exhibit tungsten satellites and interestingly two quite different coupling constants were determined ($^1J(W-C) = 58.5$ Hz for the high field signal, $^1J(W-C) = 20.0$ Hz for the low field peak). However, since the two alkyne carbons are not symmetry related different $^1J(W-C)$ values are to be expected. Moreover, the two values are similar to those reported for alkyl and acyl derivatives $[W(R)(HC\equiv CH)(CO)(\eta^5-C_5H_5)]$ and $[W(COR)(HC\equiv CH)(CO)(\eta^5-C_5H_5)]$ ($R = Me, Et, ^nPr, ^tBu$) [12].

The final point of interest in the ^{13}C NMR spectra of complexes $[MSR(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)]$ concerns the appearance of the two alkyne $C\equiv C$ resonances. Thus at 26 °C one of the signals is relatively sharp whereas the other shows various degrees of broadening depending on the nature of the thiolate substituent. For example with **2f** the effect is small whereas with some complexes, e.g. the S^tBu derivatives **2e** and **2j** one of the peaks has broadened almost into the baseline. Consequently the $^{13}C\{^1H\}$ NMR spectra of **2e** and **2j** were also recorded at low temperatures, -60 °C for the latter and -70 °C in the case of the former. In both cases the broad peak sharpened significantly, becoming comparable in general appearance to the other alkyne resonance. Moreover in each case a new, low-intensity resonance was also observed, close to the C_5H_5 peak at ca. δ 95.

These data can be interpreted in terms of restricted rotation about the $M-SR$ bond which, due to a proximity effect, results in broadening of one alkyne carbon selectively at ambient temperature. At low temperatures exchange of the two

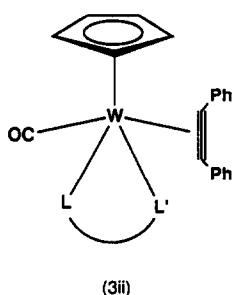
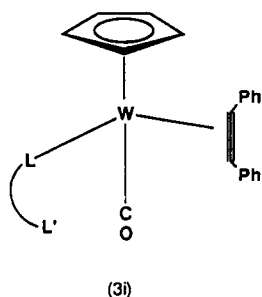
rotational isomers is frozen out but, due to the small quantity of minor isomer present, can only be detected in the ^{13}C NMR spectra by the most intense resonance, that of the cyclopentadienyl group. These conclusions are supported by variable temperature ^1H NMR spectra of **2e** and **2j** which were recorded in CD_2Cl_2 between 20°C and -90°C . One set of signals is observed at 20°C for **2j** but as the temperature is reduced broadening of both C_5H_5 and ^1Bu singlets occurs. Eventually at temperature below ca -60°C each singlet splits into two, consistent with the presence of two isomers **2i** and **2ii** ratio 1:10. Similarly two isomers of **2e** were detected at -80°C , ratio 1:15. Interestingly, however, no splitting of C_5H_5 and the Me resonances was detected in the ^1H NMR spectra of the SMe derivatives **2a** and **2f** down to -80°C . Superficially this would indicate the presence of only one isomer and the absence of rotational isomerism in these derivatives. However, this is negated by the observation of the two $\nu(\text{CO})$ modes in the IR spectra near 2000 cm^{-1} . It must therefore be concluded that two isomers exist but the barriers to rotation are significantly lower than those of the S^1Bu derivatives **2e** and **2j**. Alternatively, the chemical shift separation of the isomer peaks is very small, either explanation resulting in low coalescence temperatures. Interestingly both isomers of $[\text{M}(\text{SCF}_3)(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$) can readily be detected by ^{19}F NMR spectroscopy at ca. -50°C [3a]. This may partially reflect the larger chemical shifts which are a feature of ^{19}F NMR spectroscopy and the effect these have on coalescence temperatures. Alternatively, the barrier to rotation in $[\text{MSCF}_3(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$) may also be higher.

Assuming that $\text{S} \rightarrow \text{M}\pi$ donation occurs in monoalkyne complexes of type **2** this may be indicative of electron deficiency at the metal [18]. Although the alkyne is formally a four-electron donor, overlap of the $\pi \perp$ orbitals with the metal orbitals is not as efficient as that of the $\pi \parallel$ orbitals [2]. It was therefore of interest to induce coordination of another two electron donor to the metal so as to promote $4 \rightarrow 2$ electron donation by the alkyne. We attempted this previously by reacting $[\text{MSC}_6\text{F}_5(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$) with tertiary phosphines and phosphites but this resulted in carbonyl substitution rather than ligand addition [3b]. Accordingly a different approach was taken in which reactions of **1** with anionic bidentate ligands L-L^- were carried out.

Reactions between the complex $[\text{WCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ and metal salts ML-L ($\text{ML-L} = \text{TlS}_2\text{-Py}, \text{TlAcac}, \text{TlOAc}, \text{TlS}_2\text{P}(\text{OMe})_2$) proceed readily in dichloromethane at room temperature giving deep red to brown solutions from which red to brown crystals were isolated after several crystallisations from $\text{CH}_2\text{Cl}_2/\text{hexane}$. The products **3a-e**, which analysed as 1:1 complexes $[\text{W}(\text{LL})(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$, were obtained in yields ranging from 31 to 56% depending on the nature of the ligand, somewhat lower than those of the thiolate compounds **2**. Similar reactions between the molybdenum derivative $[\text{MoCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ and TlL-L ($\text{L-L} = \text{S}_2\text{-Py}, \text{acac}$ and OAc) were also carried out but all attempts to isolate crystalline products failed. In contrast reactions of $[\text{MCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$) with $\text{NaS}_2\text{CNMe}_2$ proceeded readily in dichloromethane at room temperature and dark brown crystalline complexes $[\text{M}(\text{S}_2\text{CNMe}_2)(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{4a}$; $\text{M} = \text{W}, \text{4b}$) were isolated on recrystallisation from $\text{CH}_2\text{Cl}_2/\text{hexane}$. Complexes **4a** and **4b** proved to be much more air sensitive than the relatively stable thiolate complexes studied.

Of the two most likely structures available to carbonyl derivatives $[\text{W}(\text{L-}$

$L(CO)(PhC\equiv CPh)(\eta^5-C_5H_5)$, **3i** and **3ii**, spectroscopic data favour the former, as will now be discussed. In contrast with thiolate complexes **2** the mass spectrum in each case (except for $L-L = S4-Py$) exhibits a peak at highest m/z value corresponding to $[M - CO]^+$ with no trace of the molecular ion $[M]^+$. Significantly, however, a molecular ion was observed with **3b** where the ligand $S4-Py$ is more akin to an alkylthiolate in that chelation is not possible. This may indicate that the driving force for loss of CO is chelation of the bidentate ligand. The IR spectra of complexes **3** show a single $\nu(CO)$ mode near 1940 cm^{-1} which is close to those of the alkylthiolates **2**. This argues in favour of a similar structure **3i** with a monodentate ligand $L-L$ on the basis that bidentate co-ordination as in **3ii** would be expected to increase $M-CO$ back donation and hence decrease the $\nu(CO)$ frequency. Despite this conclusion no splitting of the $\nu(CO)$ mode in the spectrum of **3a** was observed when the spectrum was recorded in petroleum ether. This may indicate either degeneracy of the two isomer bonds or alternatively that $S-M$ π donation does not occur to any extent and hence that rotational isomers do not exist. The $\nu(COO)$ region of the IR spectra of carboxylate complexes can in appropriate circumstances provide diagnostic data which distinguish between mono- and bidentate behaviour [19]. If the difference between $\nu(COO)_{asymm}$ and $\nu(COO)_{sym}$ stretching frequencies (denoted Δ) is similar to or smaller than that for $NaOOCR$ it is deemed to be characteristic of bidentate behaviour. For example $[MoBr(OAc)(CO)_2(PPh_3)_2]$ exhibits bands at 1530 and 1450 cm^{-1} , i.e. $\Delta = 80\text{ cm}^{-1}$, consistent with a bidentate acetate group. However, $[Mo(OAc)_2(CO)_2(PPh_3)_2]$ with both mono- and bidentate acetate ligands shows $\nu(COO)_{asymm}$ and $\nu(COO)_{sym}$ bands at 1530 and 1450 cm^{-1} ($\Delta = 80\text{ cm}^{-1}$ —bidentate) and 1618 and 1370 cm^{-1} ($\Delta = 248\text{ cm}^{-1}$ —monodentate). In the case of **3d** three strong bands are observed at 1667 cm^{-1} , 1577 cm^{-1} and 1362 cm^{-1} , which is somewhat ambiguous and the assignment of the third band is not easy. Tentatively, by comparison with $[Mo(OAc)_2(CO)_2(PPh_3)_2]$ we assign the 1667 cm^{-1} band as $\nu(COO)_{asymm}$ and that at 1362 cm^{-1} as $\nu(COO)_{sym}$ giving $\Delta = 305\text{ cm}^{-1}$. This suggests a monodentate ligand, a conclusion which is supported by ^{13}C NMR data, as will now be discussed.

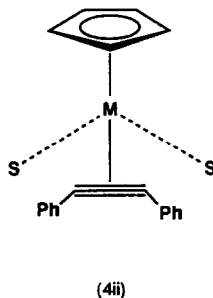
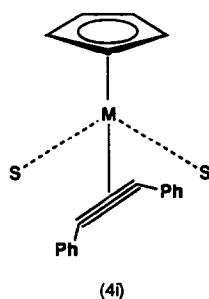


The 1H NMR data are unremarkable showing aromatic peaks (δ 7–8), a C_5H_5 singlet near δ 5.6 and appropriate resonances due to the ligand $L-L$. No structural information is provided by the spectra since, for example, the $acac$ and $S_2P(OMe)_2$ derivatives both show two methyl group environments consistent with either structure, **3i** or **3ii**. However, the ^{13}C NMR data are much more informative in view of

the fact that in **3i** the alkyne is formally a four-electron donor whereas in **3ii** it only requires to donate two electrons to the metal. The spectrum of **3** in each case exhibits two weak resonances in the region δ 180 to 195 which can be assigned to the alkyne carbons. Structure **3i** containing a monodentate ligand L-L is therefore suggested. Significantly, the $\delta(\text{C}\equiv\text{C})$ values exhibit a wider range than the thiolate complexes illustrating a sensitivity to the nature of the donor atom in the chelate ligand. The chemical shift of the carbonyl carbon is similarly also sensitive to the nature of L-L, which is not unexpected. In the case of the $\text{S}_2\text{P}(\text{OMe})_2$ complex **3a** the carbonyl peak appears as a doublet, $J(\text{P}-\text{C}) = 11.5$ Hz, presumably as a result of coupling to phosphorus.

As mentioned earlier the $\text{S}_2\text{CNMe}_2^-$ ligand is different from the other chelate anions L-L⁻ in that carbonyl products **3** are not obtained in reactions with $[\text{MCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$. Satisfactory analytical data were not obtained for the two complexes isolated, possibly due to their pronounced sensitivity to air, but spectroscopic data are consistent with the formula $[\text{M}(\text{S}_2\text{CNMe}_2)(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (M = Mo, **4a**; M = W, **4b**). The mass spectrum in each case contains a molecular ion and a peak $[\text{M} - \text{PhC}\equiv\text{CPh}]^+$ whilst a $\nu(\text{CO})$ mode is absent from the IR spectra. Three sets of resonances are present in the ^1H NMR spectra, viz. aromatic signals near δ 7.5, a C_5H_5 singlet at ca. δ 5.2 and an S_2CNMe_2 singlet around δ 3.2, ratio 10:5:6. Corresponding peaks are observed in the ^{13}C $\{^1\text{H}\}$ NMR spectra which were recorded at -25°C to minimise decomposition. Of particular interest are the alkyne δ C=C resonances which appear above 220 ppm. In each case two peaks are observed in this region, one of which is assigned to the S_2CNMe_2 carbon by analogy with those of $[\text{W}(\text{S}_2\text{CNEt}_2)_2(\text{PhC}\equiv\text{CH})(\text{MA})]$ (MA = maleic anhydride), δ 206.8, 206.4 [20] and $[\text{Mo}(\text{S}_2\text{CNEt}_2)(\eta^4\text{-C}_4\text{Ph}_4)(\eta^5\text{-C}_5\text{H}_5)]$, δ 220.8 [21]. In the case of **4b** the peak at δ 220.39 exhibits tungsten satellites ($J(\text{W}-\text{C}) = 59.8$ Hz) and is therefore assigned to the alkyne C=C carbons which are directly bonded to the metal. The lower field peak δ 235.44 with no tungsten coupling must therefore be due to the S_2CNMe_2 carbon. Unfortunately, the two corresponding peaks in the spectrum of **4a** exhibit similar chemical shifts (δ 222.51 and δ 220.60) and this, in conjunction with the absence of a magnetically active metal nucleus to couple to, renders assignment impossible.

The above spectroscopic data are consistent with two structures **4i** and **4ii**. Although only one C=C resonance is observed in the ^{13}C NMR spectra it is possible that alkyne rotation in an asymmetric structure **4i** is fast on the ^{13}C NMR timescale at -25°C leading to averaging of the two alkyne carbon environments. Alternatively the alkyne adopts the symmetrical conformation **4ii** with respect to the rest of the molecule which contains a plane of symmetry.

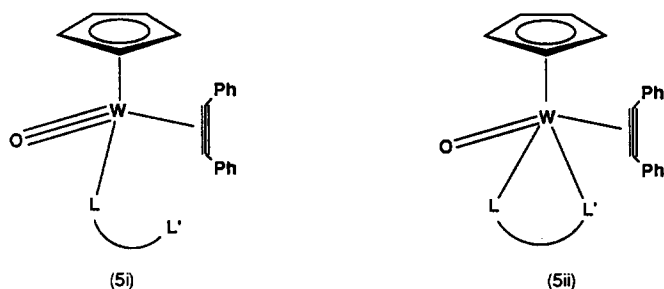


The data for complexes **4** can be compared with those for the related complex $[\text{MoS}_2\text{CNMe}_2(\text{MeC}\equiv\text{CMe})(\eta^5\text{-C}_5\text{H}_5)]$ [10] which also shows only one alkyne $\text{C}\equiv\text{C}$ resonance in the ^{13}C NMR spectrum. A symmetrical conformation (cf. **4ii**) is found in alkene complexes such as $[\text{Mn}(\text{alkene})(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ where restricted rotation has been studied by dynamic ^1H NMR spectroscopy [22]. Moreover, extended Hückel calculations of $[\text{Mo}(\text{HC}\equiv\text{CH})(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]^-$ suggest that the symmetrical orientation is the most favoured [23]. Although these observations provide support for structure **4ii** it must be pointed out that X-ray diffraction studies of the comparable bisphosphine cation $[\text{Mo}(\text{PMe}_3)_2(\text{MeC}\equiv\text{CMe})(\eta^5\text{-C}_9\text{H}_7)]^+$ revealed that in the solid state the alkyne lies approximately parallel to one of the Mo–P bonds of **4i** [3]. Consequently it is not possible to unambiguously distinguish between **4i** and **4ii** with the data available.

As mentioned earlier in this section complexes **3** and **4** are relatively air sensitive, particularly in solution. In this respect they resemble the precursors $[\text{MCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ which undergo oxidation in air to give oxo complexes $[\text{MCl}(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$) [16]. It is therefore not surprising that when a diethylether solution of $[\text{WS}_2\text{P}(\text{OMe})_2(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ was exposed to air a pale yellow complex $[\text{WS}_2\text{P}(\text{OMe})_2(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**5**) was isolated in 47% yield. The properties of this derivative are somewhat similar to those of the oxo complexes $[\text{MCl}(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$) although only ^1H and ^{13}C NMR spectra provide structural information. For example the former, in addition to aromatic peaks near δ 7.5, contains a C_5H_5 singlet at δ 6.36. This value is shifted to low field relative to the carbonyl complex **3e** by 0.5 ppm illustrating the effect of the higher oxidation state in the oxo complex, W^{IV} , as opposed to W^{II} in **3e**. The two $\text{S}_2\text{P}(\text{OMe})_2$ methyl group doublets experience a similar shift of ca 0.5 ppm to low field. This effect is also seen in the ^{13}C $\{^1\text{H}\}$ NMR spectrum where the C_5H_5 singlet appears at δ 106.40 some 12 ppm higher than in **3e**. The most significant effect however, is the shift of the alkyne $\text{C}\equiv\text{C}$ carbons to low δ where two doublets are observed at δ 147.94 and δ 146.57. The doublet splittings ($J = 5.9$ Hz and $J = 20.3$ Hz, respectively) presumably result from coupling to phosphorus. The low $\delta(\text{C}\equiv\text{C})$ values are comparable to those of $[\text{MoCl}(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$, $\delta(\text{C}\equiv\text{C}) = 146.55$ and 144.11 [16], and are significantly lower than those of complexes **3**. This can readily be explained by simple bonding arguments with particular reference to the related thiolate $[\text{MoSC}_6\text{F}_5(\text{O})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ [9] and the phenyl derivative $[\text{W}(\text{C}_6\text{H}_5)(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ [24]. X-ray diffraction studies of these two complexes reveal octahedral coordination at the metal with the cyclopentadienyl group occupying a face and the other three ligands corners of the octahedron. As such they are similar to carbonyls **2** except that the π -acceptor carbonyl has been replaced by a π -donor oxo ligand. The M–O distance in the oxo complexes is particularly short and approaches that expected for a formal $\text{M}\equiv\text{O}$ triple bond as a result of π donation from oxygen into two empty $d\pi$ orbitals. This leaves one filled $d\pi$ orbital to back donate into the alkyne π^* orbitals, which requires that the alkyne rotates by ca. 90° to lie perpendicular to the M–O bond as shown. Thus to a first approximation the alkyne functions as a two-electron donor and low $\delta(\text{C}\equiv\text{C})$ values are therefore to be expected.

When only a two-electron donor interaction is possible, as in $[\text{Mo}(\text{MeC}\equiv\text{CMe})(\eta^5\text{-C}_5\text{H}_5)_2]$, δ values in the region of 120 ppm are to be expected [14]. Hence

the larger values observed for $[\text{MCl}(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ and $[\text{WS}_2\text{P}(\text{OMe})_2(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ may reflect the fact that the alkyne $\pi \perp$ orbital is able to partially donate electron density into one of the two $d\pi$ orbitals which interact with the filled $p\pi$ orbitals on oxygen. The competition between two π donors for one empty metal $d\pi$ orbital is essentially the same situation as that described for $[\text{MSR}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ where the alkyne and thiolate are the π donors. Interactions of this type have been considered previously in oxo complexes of the type $[\text{MoS}_2\text{CNR}_2)_2(\text{O})(\text{R}^1\text{C}\equiv\text{CR})]$ which have been studied by Extended Hückel methods [2]. The $\delta(\text{C}\equiv\text{C})$ values for complex **5** are intermediate between those of $[\text{WCl}(\text{PhC}\equiv\text{CPh})_2(\eta^5\text{-C}_5\text{H}_5)]$, δ 185.53 and 179.15, where the alkynes are three-electron donors [16] and $[\text{Mo}(\text{MeC}\equiv\text{CMe})(\eta^5\text{-C}_5\text{H}_5)_2]$, δ 115.3, where only two-electron donation is possible [14]. Thus in **5** the alkyne can partially compete with the oxo ligand in π donation and as a result may be described approximately as a “two and a half” donor ligand on the basis of $\delta(\text{C}\equiv\text{C})$ values.



The preceding arguments are all based on the assignment of structure **5i** to $[\text{WS}_2\text{P}(\text{OMe})_2(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$. This seems reasonable on the basis that the ^1H and ^{13}C NMR data are very similar to those of $[\text{MoCl}(\text{O})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$. However it should be noted that as with carbonyls **2** an alternative structure **5ii**, containing a bidentate $\text{S}_2\text{P}(\text{OMe})_2$ ligand is also possible. The alkyne in **5ii** is strictly a two-electron donor and should possibly have $\delta(\text{C}\equiv\text{C})$ values similar to, e.g., $[\text{Mo}(\text{MeC}\equiv\text{CMe})(\eta^5\text{-C}_5\text{H}_5)_2]$, ca. δ 115 ppm [28]. Since the $\delta(\text{C}\equiv\text{C})$ values for **5** are more in accord with structure **5i** we exclude the alternative **5ii**.

Experimental

NMR spectra were recorded on a JEOL MH100 (^1H , 100 MHz) and a Bruker WP200 SY (^1H , 200.13 MHz, ^{13}C , 50.32 MHz); chemical shifts are referred to SiMe_4 ($\delta = 0$ ppm). IR spectra were recorded on a Perkin-Elmer 580 and mass spectra on a Vacuum Generator's updated AEI MS9. Reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried over powdered calcium hydride (Et_2O , hexane) or P_2O_5 (CH_2Cl_2) and distilled under nitrogen just before use. Complexes $[\text{MCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$) [7,8] and salts TISR , ($\text{R} = \text{Me}, \text{Et}, ^1\text{Pr}, ^n\text{Pr}, ^t\text{Bu}, \text{S}_2\text{P}(\text{OMe})_2, \text{S}_2\text{-C}_5\text{H}_4\text{N}$ and $\text{S}_4\text{-C}_5\text{H}_5\text{N}$) [25] were synthesised according to previously published procedures.

*Reaction of $[\text{MoCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**1a**) with TISMe .* A mixture of complex **1a** (200 mg, 0.5 mmol) and an excess of TISMe (190 mg, 0.75 mmol) were stirred in dichloromethane (25 cm^3) at room temperature for 1 h when the colour

changed from light green to dark green and a white precipitate formed. The mixture was filtered, the solution concentrated *in vacuo* and on addition of hexane (5 cm³) and cooling to -20 °C an impure solid was obtained. This was recrystallised from CH₂Cl₂/hexane to give deep purple crystals of [Mo(SMe)(CO)(PhC≡CPh)(η⁵-C₅H₅)] (2a) (142 mg, 69%). (Found C, 60.2; H, 4.0; calc. C, 60.7; H, 4.4%.) *M/z* 414 = [M]⁺. IR (hexane) ν(CO) 1959 (ms), 1935 (s) cm⁻¹. ¹H NMR (CDCl₃) δ 7.49 (m, 10H, Ph), 5.51 (s, 5H, C₅H₅), 2.66 (s, 3H, Me); ¹³C{¹H} NMR (CDCl₃, -10 °C) δ 235.7 (CO), 181.4, 180.6 (C≡C), 137.7–127.4 (Ph), 95.4 (C₅H₅), 30.3 (Me).

Reaction of [MoCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1a) with TlSEt. Complex 1a (200 mg, 0.5 mmol) and TlSEt (200 mg, 0.75 mmol) similarly gave, after 1.5 h, 146 mg (69%) of deep purple crystals of [Mo(SEt)(CO)(PhC≡CPh)(η⁵-C₅H₅)] (2b). (Found C, 60.9; H, 4.6; calc. C, 61.5; H, 4.7%.) *M/z* 428 = [M]⁺. IR (hexane) ν(CO) 1959 (s), 1938 (s) cm⁻¹. ¹H NMR (CDCl₃) δ 7.55 (m, 10H, Ph), 5.46 (s, 5H, C₅H₅), 3.0 (m, 2H, CH₂), 1.18 (t, 3H, Me). ¹³C{¹H} NMR (CDCl₃, 26 °C), δ 234.8 (CO) 180.8, 180.5 (C≡C), 137.9–127.3 (Ph), 95.4 (C₅H₅), 40.8 (CH₂), 19.1 (Me).

Reaction of [MoCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1a) with TlSⁿPr. Complex 1a (200 mg, 0.5 mmol) and TlSⁿPr (210 mg, 0.75 mmol) similarly gave, after 2 h, 149 mg (68%) of deep purple crystals of [Mo(SⁿPr)(CO)(PhC≡CPh)(η⁵-C₅H₅)] (2c). (Found C, 62.1; H, 4.9; calc. C, 62.4; H, 5.0%.) *M/z* 442 = [M]⁺. IR (hexane) ν(CO) 1955 (s), 1938 (s) cm⁻¹. ¹H NMR (CDCl₃) δ 7.46 (m, 10H, Ph), 5.50 (s, 5H, C₅H₅), 3.05 (m, 2H, CH₂), 1.55 (m, 2H, CH₂), 0.92 (t, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 26 °C) δ 234.9 (CO), 180.6, 180.3 (C≡C), 137.8–127.3 (Ph), 95.8 (C₅H₅), 48.9, 26.7 (CH₂), 13.4 (Me).

Reaction of [MoCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1a) with TlSⁱPr. Complex 1a (200 mg, 0.5 mmol) and TlSⁱPr (210 mg, 0.75 mmol) similarly gave, after 2 h, 140 mg (64%) of deep purple crystals of [Mo(SⁱPr)(CO)(PhC≡CPh)(η⁵-C₅H₅)] (2d). (Found C, 60.9; H, 4.7; calc. C, 62.4; H, 5.0%.) *M/z* 442 = [M]⁺. IR (hexane) ν(CO) 1958 (ms), 1939 (s) cm⁻¹. ¹H NMR (CDCl₃) δ 7.49 (m, 10H, Ph), 5.48 (s, 5H, C₅H₅), 3.24 (m, 1H, ⁱPr), 1.18 (d, 3H, Me), 1.14 (d, 3H, Me). ¹³C{¹H} NMR (CDCl₃, 26 °C) 235.2 (CO), 180.0, 173.1 (C≡C), 138–127.2 (Ph), 95.3 (C₅H₅), 49.0 (CHMe₂), 26.8, 23.0, (CHMe₂).

Reaction of [MoCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1a) with TlS^tBu. Complex 1a (200 mg, 0.5 mmol) and TlS^tBu (220 mg, 0.75 mmol) similarly gave, after 2.5 h, 148 mg (65%) of deep purple crystals of [Mo(S^tBu)(CO)(PhC≡CPh)(η⁵-C₅H₅)] (2e). (Found C, 63.1; H, 5.5; calc. C, 63.1; H, 5.3%.) *M/z* 456 = [M]⁺. IR (hexane) ν(CO) 1960 (w), 1930 (s) cm⁻¹. ¹H NMR (CDCl₃) δ 7.47 (m, 10H, Ph), 5.44 (s, 5H, C₅H₅), 1.29 (s, 9H, ^tBu). ¹³C{¹H} NMR (CD₂Cl₂, -70 °C) δ 237.5 (CO), 179.2, 175.6 (C≡C), 138.8–126.9 (Ph), 95.5, 94.2 (C₅H₅), 47.3 (CMe₃), 39.3 (CMe₃).

Reaction of [WCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1b) with TlSMe. Complex 1b (200 mg, 0.41 mmol) and an excess of TlSMe (155 mg, 0.615 mmol) were stirred in dichloromethane (20 cm³) at 20 °C for 1 h when a rapid change of colour from dark green to red occurred and a white precipitate formed. The mixture was filtered and the volume of the solution reduced to ca 5 cm³. Hexane (8 cm³) was added and on cooling to -15 °C dark red crystals were obtained. Several recrystallisations from CH₂Cl₂/hexane gave pure crystals of [WSMe(CO)(PhC≡CPh)(η⁵-C₅H₅)] (2f) (155 mg, 76%). (Found C, 50.3; H, 3.6; calc. C, 50.2; H, 3.6%.) *M/z* 502 = [M]⁺. IR (hexane) ν(CO) 1944 (s), 1936 (w) cm⁻¹. ¹H NMR (CDCl₃) δ 7.52 (m, 10H, Ph),

5.62 (s, 5H, C₅H₅), 2.66 (s, 3H, Me). ¹³C{¹H} NMR (CD₂Cl₂, 26 °C), 229.6 (*J*(W–C) 159.5, CO), 185.2 (*J*(W–C) 20.0, C≡C), 183.3 (*J*(W–CO) 58.5, C≡C), 139.6–127.7 (Ph), 94.1 (C₅H₅), 32.9 (Me).

Reaction of [WCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1b) with TlSEt. Complex **1b** (200 mg, 0.41 mmol) and TlSEt (163 mg, 0.615 mmol) similarly gave, after 1.5 h, 156 mg (74%) of dark red crystals of [WSEt(CO)(PhC≡CPh)(η⁵-C₅H₅)] (**2g**). (Found C, 51.6; H, 4.0; calc. C, 51.2; H, 3.9%.) *M/z* 516 = [*M*]⁺. IR (hexane) ν(CO) 1944 (s), 1930 (s). ¹H NMR (CDCl₃) δ 7.52 (m, 10H, Ph), 5.56 (s, 5H, C₅H₅), 2.90 (m, 2H, CH₂), 1.08 (t, 3H, Me). ¹³C{¹H} NMR (CDCl₃, 26 °C) δ 228.7 (CO) 184.8, 183.4 (C≡C), 139.0–127.4 (Ph), 93.9 (C₅H₅), 43.0 (CH₂), 18.9 (Me).

Reaction of [WCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1b) with TlSⁿPr. Complex **1b** (200 mg, 0.41 mmol) and TlSⁿPr (172 mg, 0.615 mmol) similarly gave, after 1 h, 160 mg (74%) of dark red crystals of [WSPⁿ(CO)(PhC≡CPh)(η⁵-C₅H₅)] (**2h**). (Found C, 52.6; H, 4.1; calc. C, 52.1; H, 4.1%.) *M/z* 530 = [*M*]⁺. IR (hexane) ν(CO) 1950 (s), 1933 (m) cm⁻¹. ¹H NMR (CDCl₃) δ 7.52 (m, 10H, Ph), 5.57 (s, 5H, C₅H₅), 2.98 (m, 2H, CH₄), 1.45 (m, 2H, CH₂), 0.86 (t, 3H, Me). ¹³C{¹H} NMR (CDCl₃, 26 °C) δ 228.4 (CO), 184.7, 183.4 (C≡C), 139.0–127.4 (Ph), 93.5 (C₅H₅), 51.4, 26.9 (CH₂), 13.3 (Me).

Reaction of [WCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1b) with TlSⁱPr. Complex **1b** (200 mg, 0.41 mmol) and TlSⁱPr (172 mg, 0.615 mmol) similarly gave, after 1.5 h, 162 mg (75%) of dark red crystals of [WSⁱPr(CO)(PhC≡CPh)(η⁵-C₅H₅)] (**2i**). (Found C, 52.5; H, 4.1; calc. C, 52.1; H, 4.1%.) *M/z* 530 = [*M*]⁺. IR (hexane) ν(CO) 1950 (s), 1935 (m) cm⁻¹. ¹H NMR (CDCl₃) 7.53 (m, 10H, Ph), 5.58 (s, 5H, C₅H₅), 3.08 (m, 1H, CH), 1.19 (d, 3H, Me), 1.04 (m, 3H, Me). ¹³C{¹H} NMR (CD₂Cl₂, 26 °C) 229.8 (CO), 183.5 (br), 182.3 (C≡C), 139.7–127.4 (Ph), 94.0 (C₅H₅), 52.2 (CHMe), 27.9, 27.3 (CHMe₂).

Reaction of [WCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1b) with TlS^tBu. Complex **1b** (200 mg, 0.41 mmol) and TlS^tBu (181 mg, 0.615 mmol) similarly gave, after 1.5 h, 161 mg (73%) of dark red crystals of [WS^tBu(CO)(PhC≡CPh)(η⁵-C₅H₅)] (**2j**). (Found C, 51.9; H, 4.3; calc. C, 53.0; H, 4.4%.) *M/z* 544 = [*M*]⁺. IR (hexane) ν(CO) 1953 (w), 1923 (s) cm⁻¹. ¹H NMR (CDCl₃) 7.52 (m, 10H, Ph), 5.57 (s, 5H, C₅H₅), 1.21 (s, 9H, ^tBu). ¹³C{¹H} NMR (CDCl₃, 26 °C) δ 230.9 (CO), 182.3, 180.2 (br) (C≡C), 139.3–126.8 (Ph), 93.86 (C₅H₅), 48.7, (CMe₃), 33.7 (CMe₃).

Reaction of [WCl(CO)(PhC≡CPh)(η⁵-C₅H₅)] (1b) with TlS₂P(OMe)₂. Complex **1b** (200 mg, 0.41 mmol) and TlS₂P(OMe)₂ (148 mg, 0.41 mmol) were stirred in CH₂Cl₂ (25 cm³) for 4 h at room temperature to give a red mixture. Solvent was removed *in vacuo*, and the residue chromatographed over a Florisil-packed column using diethyl ether as eluant. The resulting solution was concentrated *in vacuo* to ca. 5 cm³, hexane (10 cm³) added, and on cooling to –15 °C purple crystals were obtained. Recrystallisation from diethylether/hexane gave [W{S₂P(OMe)₂}(CO)(PhC≡CPh)(η⁵-C₅H₅)] (**3a**) (112 mg, 45%). (Found C, 43.1; H, 3.4; calc. C, 43.1; H, 3.4%.) *M/z* 485 = [*M* – CO]⁺. IR (KBr) ν(CO) 1952 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, –25 °C) δ 7.9–7.3 (m, 10H, Ph), 5.78 (s, 5H, C₅H₅), 3.36 (d, *J*(P–H), 14.4, 3H, Me), 3.21 (d, *J*(P–H), 14.3, 3H, Me). ¹³C{¹H} NMR (CD₂Cl₂, –25 °C) 224.9 (d, *J*(P–C), 11.5, CO), 195.9, 195.8 (C≡C), 138.9–127.2 (Ph), 94.9 (C₅H₅). OMe obscured by solvent peak.

Reaction of [WCl(CO)(Ph≡CPh)(η⁵-C₅H₅)] (1b) with TlS₂-Py. Complex **1b** (200 mg, 0.41 mmol) and TlS₂-Py (170 mg, 0.53 mmol) were treated as above to give red

crystals of $[\text{W}(\text{S}2\text{-Py})(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**3b**) (128 mg, 56%). (Found C, 52.6; H, 3.3; calc. C, 53.1; H, 3.4%.) M/z 537 = $[\text{M} - \text{CO}]^+$. IR (CHCl_3) $\nu(\text{CO})$ 1938 (s) cm^{-1} . ^1H NMR (CD_2Cl_2 , -25°C) δ 8.6 (br, d, 1H), 8.05 (br, d, 2H), 7.50 (m, 1H), 7.26 (m, 1H), 7.04 (m, 1H) ($\text{C}_5\text{H}_5\text{N} + \text{Ph}$), 5.60 (s, 5H, C_5H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -25°C) δ 228.6 (CO), 188.3, 186.6 ($\text{C}\equiv\text{C}$), 170.7, 148.4, 138.9–119.6 ($\text{C}_5\text{H}_5\text{N} + \text{Ph}$), 94.8 (C_5H_5).

*Reaction of $[\text{WCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**1b**) with TIS4-Py.* In a similar reaction, complex **1b** (200 mg, 0.41 mmol) and TIS4-Py (0.17 g, 0.53 mmol) were treated as above to give red crystals of $[\text{W}(\text{S}4\text{-Py})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**3c**) (120 mg, 52.1%). (Found C, 52.6; H, 3.4; calc. C, 53.1; H, 3.4%.) M/z 565 = $[\text{M}]^+$. IR (KBr) $\nu(\text{CO})$ 1930 (s) cm^{-1} . ^1H NMR (CD_2Cl_2 , -25°C) δ 8.31 (m, 2H), 7.89 (m, 2H), 7.50 (m, 8H), 7.13 (m, 2H) ($\text{C}_5\text{H}_4\text{N} + \text{Ph}$), 5.55 (s, 5H, C_5H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -25°C) 226.07 (CO), 192.3, 185.1 ($\text{C}\equiv\text{C}$), 163.5, 148.2, 139.3–126.9 ($\text{Ph} + \text{C}_5\text{H}_4\text{N}$), 94.8 (C_5H_5).

*Reaction of $[\text{WCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**1b**) with TIOAc.* Complex **1b** (200 mg, 0.41 mmol) and a small excess of TIOAc (120 mg, 0.45 mmol) were dissolved in CH_2Cl_2 and the solution stirred at room temperature for 1 h. The deep green solution which rapidly turned red was concentrated *in vacuo* to ca. 5 cm^3 and centrifuged. Hexane (10 cm^3) was added to the clear solution, and on cooling to -15°C deep red crystals were obtained. A second crystallisation from CH_2Cl_2 /hexane gave $[\text{W}(\text{OAc})(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**3d**) (107 mg, 51%). (Found C, 50.8; H, 3.5; calc. C, 51.4; H, 3.5%.) M/z 486 = $[\text{M} - \text{CO}]^+$. IR (KBr) $\nu(\text{CO})$ 1939 (s), 1931 (s) cm^{-1} . ^1H NMR (CD_2Cl_2 , -25°C) δ 7.9–7.3 (m, 10H, Ph), 5.78 (s, 5H, C_5H_5), 1.76 (s, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -25°C) δ 227.7 (CO), 193.5, 913.2 ($\text{C}\equiv\text{C}$), 179.2 (O_2CMe), 139.0–127.8 (Ph, 96.1 (C_5H_5), 21.8 (O_2CMe)).

*Reaction of $[\text{WCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**1b**) with Tlacac.* The acetylene complex **1b** (200 mg, 0.41 mmol) and Tlacac (140 mg, 0.46 mmol) (molar ratio 1:1:1) were treated as above to give dark red crystals of $[\text{W}(\text{acac})(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**3e**) (70 mg, 31%). (Found C, 53; H, 4.1; calc. C, 54.2; H, 4.0%.) IR (KBr) $\nu(\text{CO})$ 1920 (s) cm^{-1} . ^1H NMR (CD_2Cl_2 , -25°C) δ 7.6–7.1 (m, 10H, Ph), 5.48 (s, 5H, C_5H_5), 5.19 (s, 1H, acac, C–H), 1.90 (s, 3H, Me), 1.60 (s, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -25°C) δ 222.7 (CO), 189.9, 187.5 ($\text{C}\equiv\text{C}$), 164.7, 161.3 (acac, CO), 144.9–126.3 (Ph), 101.9 (acac, C–H), 93.7 (C_5H_5), 27.3 (acac, Me).

*Reaction of $[\text{MoCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**1b**) with $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$.* An equimolar amount of the molybdenum complex **1a** (200 mg, 0.5 mmol) and $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$ (90 mg, 0.5 mmol) was stirred in CH_2Cl_2 (25 cm^3) at room temperature for 2 h when the colour changed from light green to dark brown. The volume of the solution was reduced to ca. 5 cm^3 and then centrifuged. Hexane (5 cm^3) was added and on cooling to -15°C impure crystals obtained. A second crystallisation from CH_2Cl_2 /hexane gave black crystals of $[\text{Mo}(\text{S}_2\text{CNMe}_2)(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**4a**) (47 mg, 25%). (Found C, 44.5; H, 3.8; calc. C, 57.5; H, 4.6%.) ^1H NMR (CD_2Cl_2 , -25°C) δ 7.65–7.2 (m, 10H, Ph), 5.20 (s, 5H, C_5H_5), 3.19 (s, 6H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -25°C) δ 222.5, 220.1 (CNMe_2 and $\text{C}\equiv\text{C}$), 140.2–127.9 (Ph), 92.9 (C_5H_5), 39.1 (CNMe_2).

*Reaction of $[\text{WCl}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{H}_5)]$ (**1b**) with $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$.* Complex **1b** (200 mg, 0.41 mmol) and $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$ (73 mg, 0.41 mmol) were dissolved in CH_2Cl_2 (25 cm^3) and stirred at $+20^\circ\text{C}$ for 2 h. The colour changed

from dark green to brown and a white precipitate formed. The solution was concentrated *in vacuo* to ca. 8 cm³ and centrifuged. Hexane (10 cm³) was added and on cooling to -15°C dark brown crystals of [W(S₂CNMe₂)(PhC≡CPh)(η⁵-C₅H₅)] (**4b**) were obtained. These were recrystallised from CH₂Cl₂/hexane to give 48 mg, 21.5%. (Found C, 40.5; H, 3.41; calc. C, 48.3; H, 3.8%.) *M/z* 547 = [M]⁺. ¹H NMR (CD₂Cl₂, -25°C) δ 7.6–7.2 (m, 10H, Ph) 5.24 (s, 5H, C₅H₅), 3.08 (s, 6H, Me). ¹³C{¹H} NMR (CD₂Cl₂, -25°C) δ 235.4 (CNMe₂), 220.4 (*J*(W–C) 60.0, C≡C), 141.8–127.2 (Ph), 90.2 (C₅H₅), 38.4 (CNMe₂).

Oxidation of [W{S₂P(OMe)₂}(CO)(PhC≡CPh)(η⁵-C₅H₅)] (3a) by air. Complex **3a** (50 mg, 0.082 mmol) was dissolved in diethyl ether (10 cm³) in air and sealed in a tube until the red purple solution became yellow. The solution was then centrifuged and concentrated *in vacuo*, hexane added and on cooling to -15°C yellow crystals of [W{S₂P(OMe)₂}(O)(PhC≡CPh)(η⁵-C₅H₅)] (**5**) were obtained (23 mg, 47%). (Found C, 42.1; H, 3.5; calc. C, 42.0; H, 3.5%.) ¹H NMR (CDCl₃) δ 7.9–7.2 (m, 10H, Ph), 6.36 (s, 5H, C₅H₅), 3.87 (d, *J*(P–H), 14.5, 3H, Me), 3.80 (d, *J*(P–H) 14.5, 3H, Me). ¹³C{¹H} NMR (CDCl₃, 26°C) δ 147.9 (d, *J*(P–C), 6.0, C≡C), 146.6 (d, P–C), 19.5, C≡C), 136.1–128.2 (Ph), 54.0 (d, *J*(P–C) 8.0, OMe), 53.7 (d, *J*(P–C) 6.0, OMe).

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