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

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Complexes [{WBr$_2$(CO)(RC≡CR′)$_2$}$_2$] react with NaS$_2$PMe$_2$, NaS$_2$CNMe$_2$, or Tl(2-SC$_5$H$_4$N) to give monoalkyne [W(LL′)$_2$(CO)(RC≡CR′)] (R = R′ = Me, LL′ = S$_2$CNMe$_2$ or 2-SC$_5$H$_4$N; R = Ph, R′ = Me, LL′ = S$_2$CNMe$_2$ or S$_2$PMe$_2$; R = R′ = Ph, LL′ = S$_2$PMe$_2$) or bis-alkyne derivatives [W(2-SC$_5$H$_4$N)$_2$-(PhC≡CPh)$_2$]. Dynamic n.m.r. studies of the monoalkyne complexes reveal fluxional behaviour due to propeller rotation of the co-ordinated alkyne (R = R′ = Me, LL′ = S$_2$CNMe$_2$ or 2-SC$_5$H$_4$N) whereas with R = Ph, R′ = Me or Ph, LL′ = S$_2$PMe$_2$ an alternative process attributed to dechelation of the chelate ligand is also observed. The S$_2$PMe$_2$ derivatives react with ligands L = CNBu^t, PMe$_2$Ph, or P(OMe)$_3$ to give 1 : 1 adducts [W(S$_2$PMe$_2$)$_2$(CO)(PhC≡CR)(L)] [R = Me, L = CNBu^t, PMe$_2$Ph, or P(OMe)$_3$; R = Ph, L = PMe$_2$Ph or P(OMe)$_3$] some of which, L = P(OMe)$_3$, dissociate in solution to give the equilibrium (i). ^{13}C N.m.r. studies of [W(S$_2$PMe$_2$)$_2$(CO)(PhC≡CMe){P(OMe)$_3$}] are

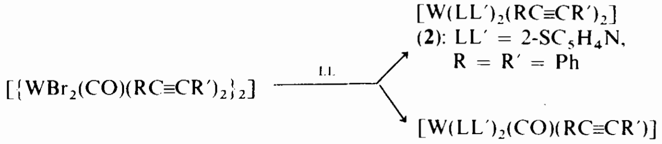
$$[\mathrm{W(S_2PMe_2)_2(CO)(PhC{\equiv}CR)(L)}] \rightleftharpoons [\mathrm{W(S_2PMe_2)_2(CO)(PhC{\equiv}CR)}] + \mathrm{L} \qquad \text{(i)}$$

interpreted in terms of a six-co-ordinate structure containing one monodentate and one bidentate S$_2$PMe$_2$ ligand, rather than a seven-co-ordinate bis-chelate structure.

An interesting feature of the organometallic chemistry of Mo^{II} and W^{II} is the existence of a range of six-co-ordinate complexes which formally have a 16-electron configuration and can therefore be described as co-ordinatively unsaturated.[1] This description is underlined by the fact that many of these derivatives can co-ordinate a two-electron donor to achieve an 18-electron configuration. Our interest in this area of chemistry concerns alkene and alkyne complexes, *e.g.* [WBr$_2$(CO)$_2$(L′)] ['diene' L′ = norbornadiene (nbd), cyclo-octa-1,5-diene (cod), or cyclo-octatetraene (cot)][2] and [WBr$_2$(CO)L(RC≡CR′)] [L = PPh$_3$, P(OMe)$_3$, or CNBu^t; R = R′ = Ph or Me; R = Ph, R′ = Me],[3] which exhibit marked differences in their reactivity towards two-electron donor ligands. The former react with ligands L to give seven-co-ordinate species [WBr$_2$(CO)$_2$L$_2$(L′)] [L′ = nbd; L = PMe$_2$Ph, P(OMe)$_3$, or CNBu^t], whereas the cod and cot derivatives form seven-co-ordinate diene-free complexes [WBr$_2$(CO)$_2$L$_3$]. In contrast, the alkyne derivatives do not react with two-electron donors L and show no tendency to achieve seven-co-ordination, a fact we attributed to the ability of the alkyne ligand to stabilise co-ordinative unsaturation by the involvement of both sets of filled C≡C π orbitals in bonding with the metal. This view is supported by a variety of chemical,[3,4] spectroscopic,[5] kinetic,[6] and theoretical studies[7] of related alkyne complexes of Mo^{II} and W^{II} including, for example, dithiocarbamate derivatives, which have been extensively studied by a number of workers.[8-10] Interestingly both mono- and bis-alkyne derivatives have been isolated from reactions of [M(S$_2$CNR$_2$)$_2$(CO)$_2$] (M = Mo or W, R = Me or Et) with a variety of alkynes, equation (1), but in several cases introduction of the second alkyne required more forcing conditions.[11]

$$[\mathrm{M(S_2CNR_2)_2(CO)_2}] \xrightarrow{\mathrm{R'C{\equiv}CR''}} [\mathrm{M(S_2CNR_2)_2(CO)(R'C{\equiv}CR'')}] \xrightarrow{\mathrm{R'C{\equiv}CR''}} [\mathrm{M(S_2CNR_2)(R'C{\equiv}CR'')_2}] \qquad (1)$$

Our previous report that [{WBr(CO)$_4$}$_2$] reacts with alkynes RC≡CR′ (R = R′ = Ph, Me, or Et; R = Ph, R′ = Me) to give good yields of dinuclear species [{WBr(μ-Br)(CO)-(RC≡CR′)$_2$}$_2$][3] provided an opportunity to investigate new routes to bis-chelate alkyne complexes. Apart from the dithiocarbamate derivatives already mentioned only bis-dithiophosphinate complexes [M(S$_2$PPr^i$_2$)$_2$(CO)(RC≡CR′)] (R = R′ = H, Ph, or O$_2$CMe; R = H, R′ = Ph or O$_2$CMe; R = Me, R′ = Ph)[12] and 2-mercaptopyridine and 2-mercaptopyridine *N*-oxide[13] derivatives have been briefly reported in the literature. Consequently attempts were made to extend the chemistry of these types of complex as will now be described.

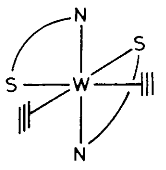


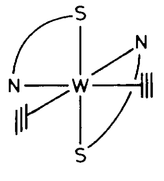
	LL′	R	R′
(1a)	S$_2$CNMe$_2$	Me	Me
(1b)	SC$_5$H$_4$N	Me	Me
(1c)	S$_2$CNMe$_2$	Ph	Me
(1d)	S$_2$PMe$_2$	Ph	Me
(1e)	S$_2$PMe$_2$	Ph	Ph

Scheme 1.

Results and Discussion

Reactions of [{WBr$_2$(CO)(RC≡CR′)$_2$}$_2$] with >2 mol equivalents of NaS$_2$CNMe$_2$, NaS$_2$PMe$_2$, or Tl(2-SC$_5$H$_4$N) are summarised in Scheme 1, which illustrates that monocarbonyl monoalkyne complexes [M(LL′)$_2$(CO)(RC≡CR′)] (**1**) are the favoured products although the bis-alkyne products [W(LL′)$_2$-(RC≡CR′)$_2$] were obtained in some cases, either as the sole product [W(SC$_5$H$_4$N)$_2$(PhC≡CPh)$_2$] (**2**) or as a mixture with the monocarbonyl product (**1**) (LL′ = S$_2$PMe$_2$, R = R′ = Ph; LL′ = SC$_5$H$_4$N, R = Ph, R′ = Me). In all cases the complexes are crystalline and moderately air-stable in the solid state but less so in solution. Complex (**2**) is formulated as a bis-alkyne derivative on the basis of elemental analysis whilst the ^{1}H n.m.r.


(2a)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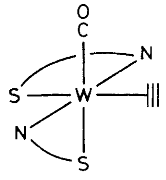
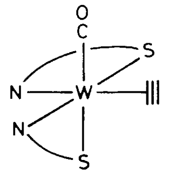

(I)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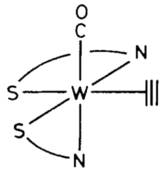
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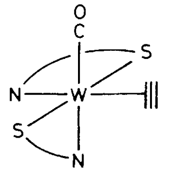
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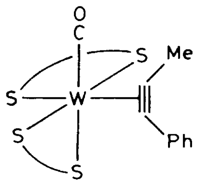
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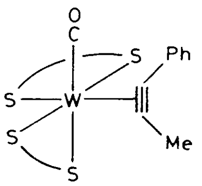

(VI)

spectrum exhibits signals due to the alkyne phenyl groups and three of the four well resolved multiplets expected for equivalent C_5H_4N groups. Assuming that the fourth is obscured by the diphenylacetylene resonances the integrated ratios are also consistent with the indicated stoicheiometry. Moreover no ν(CO) bands are present in the i.r. spectrum and consequently we propose that (**2**) has a similar structure to that of $[Mo(S_2CNEt_2)_2(PhC{\equiv}CPh)_2]$ as revealed by *X*-ray diffraction studies.[14] This has approximately octahedral co-ordination, the two *cis* alkyne ligands lying parallel to each other and to an S–Mo–S axis. With less symmetric pyridine-2-thiolate ligands co-ordinated to the metal several isomeric forms are possible based on such a structure. However the ^{1}H n.m.r. spectrum indicates that only one symmetrical form, (**2a**) or (**2b**) is present in solution, although the breadth of the aromatic phenyl resonances does not preclude the possibility that a minor isomer does exist.

The monocarbonyl complexes (**1**) are also formulated as six-co-ordinate derivatives, with two bidentate ligands LL′ in view of their similarity to alkyne complexes of this stoicheiometry isolated from the reactions of $[M(LL')_2(CO)_2]$ (M = Mo or W; LL′ = S_2CNMe_2, S_2CNEt_2, or $S_2PPr^i{}_2$)[8–10,12] with a variety of alkynes. In particular, complex (**1a**) has been synthesised previously[5] whilst the related derivative $[W(S_2CNEt_2)_2(CO)(HC{\equiv}CH)]$ has been structurally characterised by *X*-ray diffraction studies.[15] The latter has an essentially octahedral co-ordination geometry in which the alkyne lies parallel to the M–CO bond axis, a recurring feature of co-ordinatively unsaturated Mo^{II} and W^{II} alkyne carbonyl complexes[4,16] which can be explained by simple bonding arguments.[17]

In each case (**1**) exhibits an i.r. ν(CO) mode near 1 920 cm^{-1}, somewhat lower in frequency than those of the dibromo derivatives $[WBr_2(CO)L_2(RC{\equiv}CR')]$ [L = PPh_3, $P(OMe)_3$, or $CNBu^t$],[2] at 1 938—2 024 cm^{-1}. As with earlier studies of $[W(S_2CNEt_2)_2(CO)(MeC{\equiv}CMe)]$[5] the ^{1}H n.m.r. spectrum of the S_2CNMe_2 complex (**1a**) shows two Me signals at low temperature (−80 °C, $CD_3C_6D_5$) and as the temperature is raised these broaden and coalesce at *ca.* −47 °C to give a single sharp resonance at room temperature. As noted previously[5] this suggests that the alkyne adopts a fixed orientation at low temperature similar to that found in the solid state for $[W(S_2CNEt_2)_2(CO)(HC{\equiv}CH)]$ but at higher temperatures alkyne propeller rotation averages the two Me environments, a process for which a barrier to rotation of $\Delta G^{\ddagger} = 44.8 \pm 1$ kJ mol^{-1} was calculated. This compares with 46.4 ± 0.4 kJ mol^{-1} in $[W(S_2CNEt_2)_2(CO)(MeC{\equiv}CMe)]$.[5]

The pyridine-2-thiolato derivative (**1b**) exhibits similar dynamic effects in the proton n.m.r. spectrum but in this case two sets of n.m.r. signals are observed at −50 °C ($CDCl_3$) consistent with the presence of two isomeric forms. Although alkyne rotation results in only one broad Me resonance at room temperature two sets of C_5H_4N resonances persist, indicating that isomer equilibration does not occur. Isomerism presumably results from preferred dispositions of the chelate ring sulphur and nitrogen donor atoms with respect to the alkyne and carbonyl ligands as with complex (**2**). On this basis four isomeric forms are possible, (**I**), (**II**), (**III**), and (**IV**), but unfortunately, since each would be expected to exhibit similar n.m.r. spectroscopic features, we are unable structurally to identify the observed isomers.

Isomerism is also possible in the PhC≡CMe derivatives (**1c**) and (**1d**) but in these cases as a result of the availability of two preferred conformations for the asymmetric alkyne, (**V**) and (**VI**). However, as with $[W(S_2CNEt_2)_2(CO)(PhC{\equiv}CH)]$ only one isomer is present in solution according to variable-temperature n.m.r. studies. Heteronuclear nuclear Overhauser enhancement experiments have been interpreted in terms of the structural equivalent of (**V**) in the latter complex such that the bulkier phenyl group is distal to the CO ligand[5] and, by analogy, we tentatively assume that (**1c**) and (**1d**) have structure (**V**) at low temperatures.

The ^{1}H n.m.r. spectra of the dithiophosphinate complexes (**1d**) and (**1e**) are temperature dependent but, in contrast with (**1a**) and (**1b**), simple alkyne rotation is insufficient to explain the observed behaviour. Spectra were obtained over the temperature range −40 to 50 °C ($CDCl_3$) and 20 to 80 °C ($CD_3C_6D_5$). As the Figure shows, four methyl group doublets are observed in the spectrum of (**1d**) at −30 °C consistent with the proposed structure in which each S_2PMe_2 methyl group is in a unique environment. As the temperature is raised two of the four methyl group doublets broaden and coalesce at *ca.* 15 °C while the other two remain relatively sharp and distinct over this temperature range. However, above *ca.* 15 °C these also broaden, collapse, and eventually coalesce with the other methyl group signals to give one signal, a doublet, at *ca.* 80 °C. The spectra of (**1d**) and (**1e**) are quite similar, indicating that the phenomenon is not dependent on the nature of the alkyne, *i.e.* whether it is symmetrical [PhC≡CPh, (**1e**)] or not [PhC≡CMe, (**1d**)]. In any case alkyne rotation would not lead to methyl group exchange. However, it is apparent that the fluxional behaviour is a two-stage process, the first of which involves selective exchange of two methyl group environments (−30 to 15 °C) while at higher temperatures all four S_2PMe_2 methyl groups exchange.

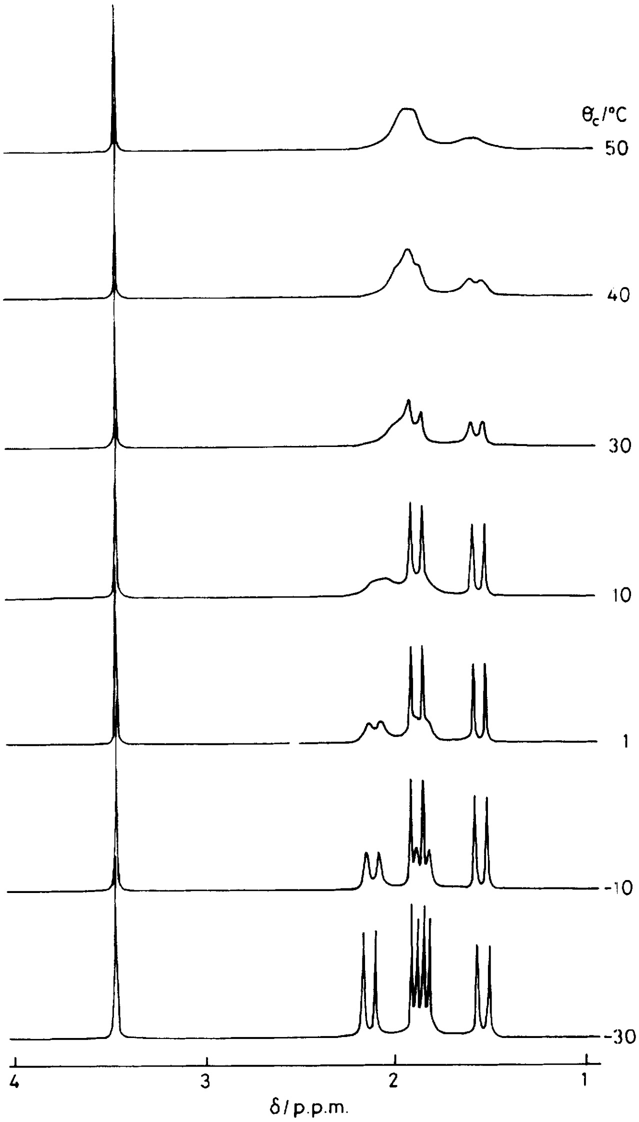
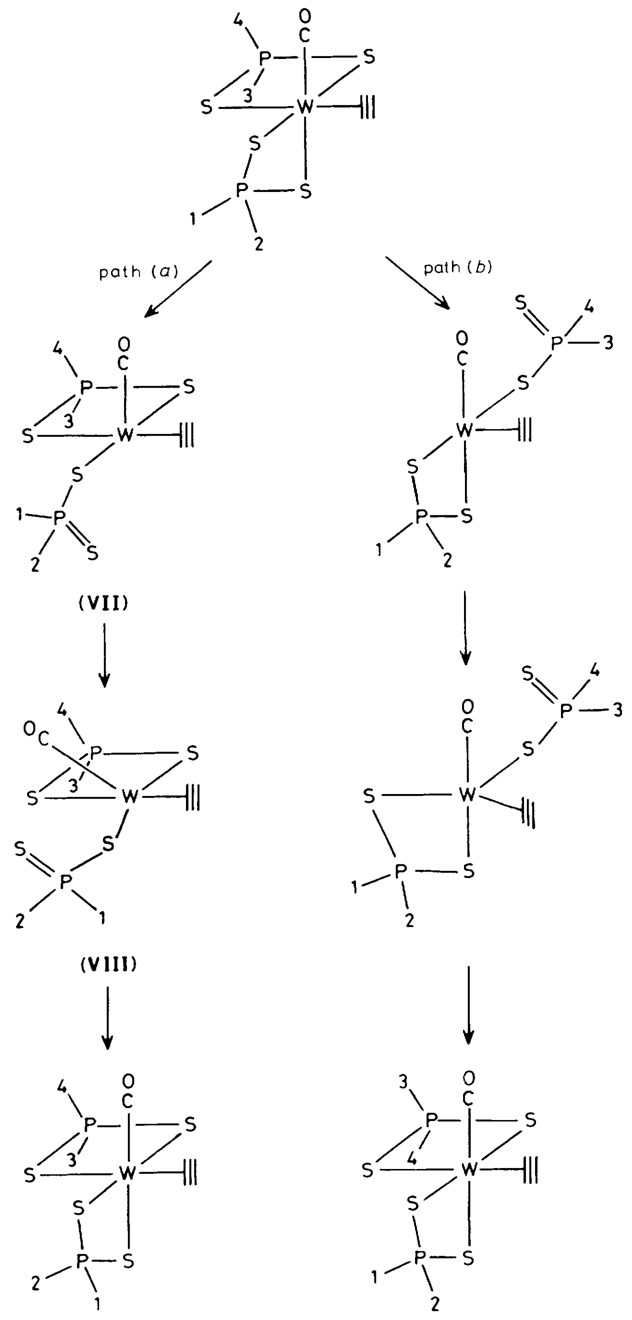


Figure. Variable-temperature ^1H n.m.r. spectra of $[W(S_2PMe_2)_2(CO)(PhC{\equiv}CMe)]$ (**1d**) (−30 to +50 °C) in $CDCl_3$ solution



Scheme 2.

If we consider the lower-energy process first it seems probable that exchange involves two methyl groups on the same chelate ligand. Although this could be achieved by a non-dissociative rotation of the chelate ligand a more plausible mechanism involves dechelation of a dithiophosphinate ligand to generate a five-co-ordinate intermediate (Scheme 2). Since only one chelate ligand is involved, selective bond fission must occur and this may be explained in terms of the different *trans* effects of the ligands present. Strong π acceptors usually exhibit high *trans* effects and on this basis it is reasonable to assume that the metal–sulphur bond *trans* to CO is selectively cleaved leading [path (*a*)] to the five-co-ordinate intermediate (**VII**). Since the metal centre in (**VII**) is asymmetric the two methyl groups Me(1) and Me(2) are diastereotopic and consequently rotation of the monodentate S_2PMe_2 ligand about the metal–sulphur bond is insufficient to exchange the two methyl environments. However, rearrangement to a trigonal-bipyramidal form (**VIII**) is possible, and subsequent re-co-ordination of the sulphur atom can result in the required exchange. We cannot exclude the alternative possibility of W–S bond fission *trans* to the alkyne, path (*b*), and this would lead to the selective exchange of Me(3) and Me(4) as the lower-energy process. However the lower *trans* effect of the alkyne relative to carbon monoxide may render this alternative less plausible.

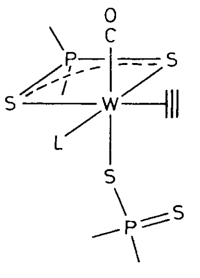
The intermediacy of a five co-ordinate trigonal-bipyramidal intermediate in the low-energy fluxional process is not surprising in view of the isolation of stable species $[Mo(SBu^t)_2(CNBu^t)_2(RC{\equiv}CR')]$ (R = R′ = H or Ph) from the reactions of $[Mo(SBu^t)_2(CNBu^t)_4]$ with alkynes.[18] Single-crystal *X*-ray diffraction studies of these derivatives revealed that the two thiolate ligands and an alkyne occupy the equatorial sites and the isocyanides the axial positions of a trigonal bipyramid. It is also pertinent to note that kinetic evidence has been obtained for a five-co-ordinate intermediate in the reactions of $[Mo(S_2CNMe_2)_2(CO)(RC{\equiv}CR')]$ (R = Ph, R′ = H, Me, or Ph; R = H, R′ = Bu^n; R = R′ = Et) with alkynes, which lead to the carbonyl-free bis-alkyne derivatives [$Mo(S_2CNMe_2)_2(RC{\equiv}CR')_2$].[6] However, CO dissociation rather than dechelation seems more probable in this case in view of the observed rate inhibition by free carbon monoxide. This is also in accord with the observation that the dithiocarbamate complexes only exhibit alkyne rotation with no evidence for fluxional behaviour involving the chelate ring.

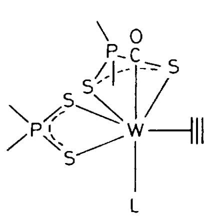
Interestingly, dechelation of one end of a dithiocarbamate ligand has been postulated to occur in the complexes [$W(S_2CNR_2)_2(O)(R'C{\equiv}CR'')$] (R = Me or Et; R' = R'' = H or Ph)[19] and [$W(S_2CNEt_2)_2(S)(PhC{\equiv}CPh)$][20] to explain the temperature dependence of the n.m.r. spectra. Selective fission of a W–S bond *trans* to the oxo or sulphido ligand was proposed to account for the fact that averaging of the four dithiocarbamate signals occurs with an identical energy barrier to that involving exchange of both ends of the alkyne. However, it is interesting to note that all four methyl group signals collapse at the same rate implying that once the five-co-ordinate intermediate is formed, exchange between the two dithiocarbamate ligands occurs readily. This is clearly not the case with (**1d**) and (**1e**) since complete methyl group exchange is observed as a distinct process only after selective exchange of two methyl groups has occurred. This higher-energy exchange process could obviously proceed *via* a number of different mechanistic pathways involving the five-co-ordinate structure (**VIII**), *e.g.* Berry pseudo-rotation *etc.*, and we do not speculate further. However, if the exchange processes observed with (**1d**) and (**1e**) and the dithiocarbamates [$W(S_2CNR_2)_2(X)(R'C{\equiv}CR')$] (X = O, R = Me or Et, R' = H or Ph; X = S, R = Et, R' = Ph) are similar, one or both of the following conclusions can be reached in view of the observed two-step exchange in the former. (*a*) Replacement of sulphur or oxygen, both π donors, by CO, a π acceptor, stabilises the five-co-ordinate intermediate to chelate exchange. (*b*) Dechelation to give the five-co-ordinate species occurs more readily in (**1d**) and (**1e**) as opposed to (**1a**) and (**1c**). Since the chelate donor ability of dithiophosphinates S_2PR_2 is thought to be somewhat lower than that of dithiocarbamates[21] the latter conclusion is clearly valid.

Interestingly, although the dithiocarbamate complexes [$M(S_2CNR_2)_2(CO)(RC{\equiv}CR)$] (M = Mo for W; R = H, alkyl, or aryl) show no evidence for fluxional behaviour attributable to dechelation of a chelate ligand,[8–10] as mentioned earlier kinetic evidence has been obtained for a five-co-ordinate intermediate resulting from CO dissociation in reactions of alkynes with [$Mo(S_2CNMe_2)_2(CO)(RC{\equiv}CR')$][6] (R = R' = Ph or Et; R = Ph, R' = H or Me; R = Bu^t, R' = H). In contrast nucleophiles L = CO, $P(OMe)_3$, or PEt_3, react to form alkyne-free products [$Mo(S_2CNMe_2)_2(CO)L_2$] possibly *via* seven-co-ordinate intermediates. It was therefore of interest to carry out reactions of dithiophosphinates (**1d**) and (**1e**) with nucleophiles with a view to trapping the five-co-ordinate species resulting from dechelation of the S_2PMe_2 ligand.

Reactions of (**1d**) with excess $CNBu^t$, PMe_2Ph, or $P(OMe)_3$ and of (**1e**) with PMe_2Ph or $P(OMe)_3$ in diethyl ether at room temperature readily afforded purple crystalline 1:1 adducts [$W(S_2PMe_2)_2(CO)(PhC{\equiv}CMe)(L)$] (**3a**)—(**3c**) and [$W(S_2PMe_2)_2(CO)(PhC{\equiv}CPh)(L)$] (**3d**) and (**3e**). The complexes are moderately stable in the solid state but the phosphite derivatives (**3c**) and (**3e**) are less stable in solution where n.m.r. studies indicate that ligand dissociation occurs reversibly to give complexes (**1d**) or (**1e**) and free $P(OMe)_3$. This accounts for the observation that solutions of the pure complex are deep blue in colour, characteristic of the precursor (**1d**) or (**1e**), but on addition of excess $P(OMe)_3$ this changes to the purple colour characteristic of the 1:1 adduct.

The i.r. spectra of complexes (**3**) in all cases exhibit a single ν(CO) band between 1 925 and 1 945 cm^{-1} which compares with 1 921 cm^{-1} for precursors (**1d**) or (**1e**). This tentatively suggests a six-co-ordinate structure (**IX**) with one mono and one bidentate S_2PMe_2 ligand, rather than a seven-co-ordinate species (**X**) with two bidentate ligands, on the basis that the latter might be expected to exhibit reduced C–O stretching frequencies due to increased electron density on the metal. The observed slight increase in ν(CO) is, however, explicable in terms of a six-co-ordinate structure resulting from displacement of a π-donor sulphur atom by a π-acceptor ligand L [L = $CNBu^t$, PMe_2Ph, or $P(OMe)_3$].


(**IX**)


(**X**)

More definitive evidence for a six-co-ordinate structure (**IX**) was obtained from the $^{13}C-\{^1H\}$ n.m.r. spectrum of (**3c**) which was recorded at −45 °C to minimise phosphite dissociation. Of particular interest are the chemical shifts of the alkyne C≡C carbons in view of their sensitivity to metal–alkyne bonding. Previous studies have shown that when an alkyne functions as a four-electron donor ligand, as with the six-co-ordinate structure (**IX**), pronounced low-field shifts are observed in the ^{13}C alkyne resonances.[4,5,22,23] Typically, C≡C chemical shift values for bis-dithiocarbamate complexes [$M(S_2CNR_2)_2(CO)(R'C{\equiv}CR'')$] are in the range 200—210 p.p.m.,[23] *e.g.* [$W(S_2CNEt_2)_2(CO)(HC{\equiv}CH)$] (δ 206.1 and 207.1). In the case of [$W(S_2PMe_2)_2(CO)\{P(OMe)_3\}_2(PhC{\equiv}CMe)$] two peaks are observed in the $^{13}C-\{^1H\}$ n.m.r. spectrum at δ 208.2 and 204.4 which, by analogy with the dithiocarbamate complexes, we assign to the alkyne carbons. Apart from aromatic C_6H_5 resonances no other peaks are observed in the range δ 100—200 p.p.m. and on this basis we conclude that the alkyne is acting as a four-electron donor. Consequently a six-co-ordinate structure (**IX**) is indicated for (**3c**) and by implication for the other 1:1 adducts (**3a**), (**3b**), (**3d**), and (**3e**).

The ^1H and $^{31}P-\{^1H\}$ n.m.r. spectra of complexes (**3**) do not distinguish between six- and seven-co-ordinate structures but in view of the ^{13}C n.m.r. data for (**3c**) they will be interpreted in terms of the former. Due to the existence of equilibria described earlier, the spectra were recorded at both 20 and −50 °C, and in the cases of the $P(OMe)_3$ and PMe_2Ph derivatives evidence for the existence of two isomeric forms was obtained. Since the spectra of (**3c**) are typical these will be described in detail. The ^1H n.m.r. spectrum of this derivative at −50 °C in $CDCl_3$ exhibits aromatic multiplets centred at δ 7.45 (5 H) and one methyl group doublet (J_{P-H} 1.5 Hz) at δ 3.35 due to the alkyne. Four distinct S_2PMe_2 doublets are also present in addition to a $P(OMe)_3$ doublet. Weak signals due to a second isomer are also present but are largely obscured by the major isomer peaks. However, two distinct sets of isomer resonances are present in the $^{31}P-\{^1H\}$ spectrum, of ratio 14:1. Three equal intensity resonances are observed for each isomer and in the case of the major species the low-field signal, δ 126.23, is assigned to the $P(OMe)_3$ ligand in view of significant coupling to tungsten ($^1J_{P-W}$ 407 Hz). This resonance is further coupled, J_{P-P} 8.5 Hz, to one of the S_2PMe_2 resonances, δ 63.47, which also shows weak coupling to tungsten ($^2J_{W-P}$ 7.0 Hz). A third resonance, δ 102.2, which shows no coupling to other nuclei, can be assigned to the second S_2PMe_2 ligand. Similar features are also observed with the minor isomer resonances except that due to signal–noise problems tungsten satellites could not be detected.

A number of isomeric forms are available to complexes (**3**) based upon displacement of a sulphur donor atom by a two-electron ligand L, but the spectra of (**3c**) and the other complexes do not uniquely define any one of them. Attempts were made to obtain crystals for *X*-ray diffraction studies but these were unsuccessful. Consequently we can only conclude that complexes (**3**) have structure (**IX**) or any variant of that in which the alkyne and carbonyl ligands occupy mutually *cis* positions about the octahedrally co-ordinated metal centre.

Finally, we note that as with previously reported mono- and bis-alkyne complexes of Mo^{II} and W^{II} [3,4] no evidence for seven-co-ordination was observed with the complexes described herein. The preference for six-co-ordination exhibited by d^4 configuration alkyne complexes contrasts with the ability of diene,[2] phosphine,[1] and carbonyl [1] derivatives to achieve seven-co-ordination and is particularly emphasised by the apparent inability of the monodentate S_2PMe_2 ligand in (**3**) to bond in a bidentate fashion without dissociation of another ligand. This clearly underlines the important role that the second (perpendicular) set of filled π orbitals on the alkyne have in stabilising co-ordinative unsaturation at the formally electron-deficient metal centre in complexes of this type.

Experimental

Reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over powdered calcium hydride (diethyl ether, hexane), sodium benzophenone (tetrahydrofuran), and P_2O_5 (dichloromethane) and distilled under nitrogen just before use. NaS_2PMe_2, Bu^tNC, and $Tl(2\text{-}SC_5H_4N)$ and complexes $[\{WBr_2(CO)(RC\equiv CR')_2\}_2]$ were prepared by literature methods, while $P(OMe)_3$, PMe_2Ph, and NaS_2CNMe_2 were obtained commercially. Proton, ^{13}C, and ^{31}P n.m.r. spectra were recorded on a Bruker WP-200 SY n.m.r. spectrometer operating at 200.13, 50.31, and 81.02 MHz respectively using $SiMe_4$ and 85% aqueous H_3PO_4 ($\delta = 0$ p.p.m.) as references.

Reaction of $[\{WBr_2(CO)(MeC\equiv CMe)_2\}_2]$ *with* NaS_2CNMe_2.—$[\{WBr_2(CO)(MeC\equiv CMe)_2\}_2]$ (28 mg, 0.06 mmol) and NaS_2CNMe_2 (36 mg, 0.12 mmol) were stirred at room temperature in diethyl ether (3 cm^3) for 18 h. The resulting mixture was centrifuged to give a pale green solution and a green solid. The solid was extracted with CH_2Cl_2 (3 cm^3), centrifuged to give a dark green solution, and after addition of hexane (*ca.* 5 cm^3), concentrated *in vacuo* to afford dark green crystals of $[W(S_2CNMe_2)_2(CO)(MeC\equiv CMe)]$ (**1a**) (17 mg, 54%) (Found: C, 25.6; H, 3.5; N, 5.35. $C_{11}H_{18}N_2OS_4W$ requires C, 26.1; H, 3.6; N, 5.5%). I.r. ($CHCl_3$): ν_{CO} at 1 903s cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, 3.35 (s, 3 H, NMe), 3.25 (s, 6 H, MeC≡CMe), 3.23 (s, 3 H, NMe), 3.22 (s, 3 H, NMe), 3.15 (s, 3 H, NMe).

Reaction of $[\{WBr_2(CO)(MeC\equiv CMe)_2\}_2]$ *with* $Tl(2\text{-}SC_5H_4N)$.—$[\{WBr_2(CO)(MeC\equiv CMe)_2\}_2]$ (25 mg, 0.056 mmol) and $Tl(2\text{-}SC_5H_4N)$ (65 mg, 0.21 mmol) were stirred at room temperature in diethyl ether (5 cm^3) for 18 h. A dark green solution obtained on centrifuging the mixture was treated with hexane (*ca.* 3 cm^3) and concentrated *in vacuo* to give green-brown lumps of $[W(SC_5H_4N)_2(CO)(MeC\equiv CMe)]$ (**1b**) (21 mg, 77%) (Found: C, 37.0; H, 3.0; N, 3.7. $C_{15}H_{14}N_2OS_2W$ requires C, 37.0; H, 2.9; N, 5.8%). I.r. (CCl_4): ν_{CO} at 1 921s cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 3.17 (s, 6 H, MeC≡CMe), 6.6—7.8 (overlapping multiplets, 6 H), 8.57 (dm, 1 H), 8.78 (dm, 1 H) (SC_5H_4N).

Reaction of $[\{WBr_2(CO)(PhC\equiv CMe)_2\}_2]$ *with* NaS_2CNMe_2.—$[\{WBr_2(CO)(PhC\equiv CMe)_2\}_2]$ (40 mg, 0.066 mmol) and NaS_2CNMe_2 (39 mg, 0.22 mmol) were stirred at room temperature in diethyl ether (3 cm^3) for 3 h. The mixture was centrifuged to give a green solution and a green solid. The solid was extracted with CH_2Cl_2 (5 cm^3), centrifuged to give a dark green solution and, after addition of hexane (*ca.* 5 cm^3), concentrated *in vacuo* to afford dark green crystals of $[W(S_2CNMe_2)_2(CO)(PhC\equiv CMe)]$ (**1c**) (19 mg, 51%) (Found: C, 33.7; H, 3.6; N, 4.8. $C_{16}H_{20}N_2OS_4W$ requires C, 33.8; H, 3.6; N, 4.9%). I.r. (CCl_4): ν_{CO} at 1 924s cm^{-1}. ^1H N.m.r. ($CDCl_3$, 20 °C): δ, 7.9—7.3 (m, 5 H, Ph), 3.42 (s, 3 H, Me), 3.30 (s, 3 H, Me), 3.18 (s, 3 H, Me), 3.17 (s, 6 H, Me).

Reaction of $[\{WBr_2(CO)(PhC\equiv CMe)_2\}_2]$ *with* NaS_2PMe_2.—$[\{WBr_2(CO)(PhC\equiv CMe)_2\}_2]$ (177 mg, 0.194 mmol) and NaS_2PMe_2 (100 mg, 0.67 mmol) were stirred at room temperature in diethyl ether (5 cm^3) for 1 h. The deep blue solution obtained on centrifuging the mixture was treated with hexane (*ca.* 3 cm^3) and concentrated *in vacuo* to give dark blue crystals of $[W(S_2PMe_2)_2(CO)(PhC\equiv CMe)]$ (**1d**) (48 mg, 43%) (Found: C, 29.0; H, 3.5; S, 22.2. $C_{14}H_{20}OP_2S_5W$ requires C, 29.1; H, 3.5; S, 22.2%). I.r. ($CHCl_3$): ν_{CO} at 1 912s cm^{-1}. ^1H N.m.r. ($CDCl_3$, −50 °C): δ, 8.0—7.3 (m, 5 H, Ph), 3.48 (s, 3 H, ≡CMe), 2.17 (d, J_{P-H} 12.9, 3 H, Me), 1.89 (d, J_{P-H} 12.6, 3 H, Me), 1.86 (d, J_{P-H} 12.8, 3 H, Me), 1.53 (d, J_{P-H} 12.6 Hz, 3 H, Me). $^{31}P\text{-}\{^1H\}$ N.m.r. ($CDCl_3$, 20 °C): δ, 101.47 (s, 1 P), 66.35 (s, 1 P).

Reaction of $[\{WBr_2(CO)(PhC\equiv CPh)_2\}_2]$ *with* NaS_2PMe_2.—$[\{WBr_2(CO)(PhC\equiv CPh)_2\}_2]$ (80 mg, 0.11 mmol) and NaS_2PMe_2 (62 mg, 0.42 mmol) were stirred at room temperature in CH_2Cl_2 (3 cm^3) for 20 min. A dark green solution obtained on centrifuging the reaction mixture was treated with hexane (*ca.* 3 cm^3) and concentrated to give green crystals of $[W(S_2PMe_2)_2(CO)(PhC\equiv CPh)]$ (**1e**) (29 mg, 41%) (Found: C, 36.1; H, 3.9. $C_{19}H_{22}OP_2S_4W$ requires C, 35.6; H, 3.5%). I.r. ($CHCl_3$): ν_{CO} at 1 921s cm^{-1}. ^1H N.m.r. ($CDCl_3$, −24 °C): δ, 7.8—7.3 (m, 10 H, Ph), 2.10 (d, J_{P-H} 12.9, 3 H, Me), 1.90 (d, J_{P-H} 12.7, 6 H, Me), 1.50 (d, J_{P-H} 12.7 Hz, 3 H, Me). $^{31}P\text{-}\{^1H\}$ N.m.r. ($CDCl_3$, 20 °C): δ, 103.34 (br s, 1 P), 67.82 (br s, 1 P).

Reaction of $[\{WBr_2(CO)(PhC\equiv CPh)_2\}]$ *with* $Tl(2\text{-}SC_5H_4N)$.—$[\{WBr_2(CO)(PhC\equiv CPh)_2\}]$ (73 mg, 0.1 mmol) and $Tl(2\text{-}SC_5H_4N)$ (100 mg, 0.22 mmol) were stirred at room temperature in CH_2Cl_2 (3 cm^3) for 18 h. A yellow-green solution obtained on centrifuging the mixture was treated with hexane (*ca.* 3 cm^3) and on concentrating *in vacuo* yellow crystals of $[W(2\text{-}SC_5H_4N)_2(PhC\equiv CPh)_2]$ (**2**) (35 mg, 46%) were obtained (Found: C, 59.3; H, 3.7; N, 3.8. $C_{38}H_{28}N_2S_2W$ requires C, 60.0; H, 3.7; N, 3.7%). ^1H N.m.r. ($CDCl_3$, 20 °C): δ, 8.51 (d, *J* 5.1, 2 H), 7.40 (m, 22 H), 6.8 (d, *J* 8.1, 2 H), 6.65 (t, *J* 6.1 Hz, 2 H).

Reaction of $[W(S_2PMe_2)_2(CO)(PhC\equiv CMe)]$ (**1d**) *with* Bu^tNC.—A solution of (**1d**) (18 mg, 0.031 mmol) in CH_2Cl_2 (1 cm^3) was treated with Bu^tNC (4 mg, 0.05 mmol) at room temperature when an immediate colour change from blue to purple was observed. On adding hexane (*ca.* 1 cm^3) and concentrating the solution *in vacuo* purple crystals of $[W(S_2PMe_2)_2(CO)(PhC\equiv CMe)(CNBu^t)]$ (**3a**) were obtained (18 mg, 90%) (Found: C, 33.9; H, 4.3; N, 2.1. $C_{19}H_{29}NOP_2S_4W$ requires C, 34.5; H, 4.3; N, 2.1%). I.r. ($CHCl_3$): $\nu_{C\equiv N}$ at 2 174s, ν_{CO} at 1 942vs cm^{-1}. ^1H N.m.r. ($CDCl_3$, 20 °C): δ, 7.58—7.34 (m, 5 H, Ph), 3.42 (s, 3 H, ≡CMe), 2.25 (d, J_{P-H} 13.1, 3 H, Me), 2.18 (d, J_{P-H} 12.2, 3 H, Me), 2.08 (d, J_{P-H} 12.4, 3 H, Me), 1.86 (d, J_{P-H} 12.9 Hz, 3 H, Me), 1.38 (s, 9 H, Bu^t).

Reaction of $[W(S_2PMe_2)_2(CO)(PhC\equiv CMe)]$ (**1d**) *with* PMe_2Ph.—A solution of (**1d**) (21 mg, 0.036 mmol) in CH_2Cl_2 (1 cm^3)

was treated with PMe$_2$Ph (10 mg, 0.07 mmol) when an immediate colour change from blue to purple was observed. On adding hexane (*ca.* 1 cm^3) and concentrating the solution *in vacuo* purple crystals were obtained which after recrystallisation from CH$_2$Cl$_2$–hexane gave [W(S$_2$PMe$_2$)$_2$(CO)(PhC$\equiv$CMe)(PMe$_2$Ph)] (**3b**) (18 mg, 65%) (Found: C, 36.8; H, 4.3; P, 13.3. $C_{22}H_{31}OP_3S_4W$ requires C, 36.9; H, 4.4; P, 13.0%). I.r. (CHCl$_3$): ν_{CO} at 1 928s cm^{-1}. ^{1}H N.m.r. (CDCl$_3$, 20 °C): δ, 7.6—7.1 (m, 10 H, Ph), 3.12 (d, J_{P-H} 1.3, 3 H, $\equiv$CMe), 2.33 (d, J_{P-H} 13.1, 3 H, Me), 2.12 (d, J_{P-H} 12.5, 3 H, Me), 2.05 (d, J_{P-H} 12.4, 3 H, Me), 1.79 (d, J_{P-H} 8.6, 3 H, PMe), 1.46 (d, J_{P-H} 8.4, 3 H, PMe), 1.36 (d, J_{P-H} 12.7 Hz, 3 H, Me). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$, 20 °C): δ, 94.32 (s, 1 P, S$_2$PMe$_2$), 64.93 (d, J_{P-P} 9.7, 1 P, S$_2$PMe$_2$), -17.83 (d, J_{P-P} 8.8 with two doublet satellites J_{P-W} 255 Hz, 1 P, PMe$_2$Ph).

Reaction of [W(S$_2$PMe$_2$)$_2$(CO)(PhC$\equiv$CMe)] (**1d**) *with* P(OMe)$_3$.—A solution of (**1d**) (25 mg, 0.043 mmol) in CH$_2$Cl$_2$ (1 cm^3) was treated with P(OMe)$_3$ (10 mg, 0.08 mmol) when a colour change from blue to purple was observed. On adding hexane (*ca.* 1 cm^3) and concentrating the solution *in vacuo* purple crystals were obtained which were recrystallised from CH$_2$Cl$_2$–hexane to give [W(S$_2$PMe$_2$)$_2$(CO)(PhC$\equiv$CMe){P(OMe)$_3$}] (**3c**) (15 mg, 50%) (Found: C, 28.9; H, 4.1. $C_{17}H_{29}O_4P_2S_4W$ requires C, 29.1; H, 4.2%). I.r. (CHCl$_3$): ν_{CO} at 1 940s cm^{-1}. ^{1}H N.m.r. (CDCl$_3$, -50 °C): δ, 7.45 (m, 5 H, Ph), 3.46 (d, J_{P-H} 10.9, 9 H, OMe), 3.35 (d, J_{P-H} 1.5, 3 H, $\equiv$CMe), 2.24 (d, J_{P-H} 11.2, 3 H, Me), 2.18 (d, J_{P-H} 12.1, 3 H, Me), 2.05 (d, J_{P-H} 12.5, 3 H, Me), 1.89 (d, J_{P-H} 13.0 Hz, 3 H, Me). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$, -50 °C): major isomer δ, 126.23 [d, J_{P-P} 8.5, J_{P-W} 407, P(OMe)$_3$], 102.2 (s, S$_2$PMe$_2$), 63.47 (d, J_{P-P} 8.5, J_{P-W} 7.0 Hz, S$_2$PMe$_2$); minor isomer δ, 123.1 [d, J_{P-P} 8.0, P(OMe)$_3$], 89.3 (s, S$_2$PMe$_2$), 62.75 (d, J_{P-P} 8.0, S$_2$PMe$_2$). ^{13}C-{^{1}H} N.m.r. (CD$_2$Cl$_2$, -45 °C): δ, 21.47 (s, $\equiv$C*Me*), 25.22 (dd, J_{P-C} 53, J_{P-C} 3.5, S$_2$PMe), 31.1 (d, J_{P-C} 44.5, S$_2$PMe), 128.70 (s, Ph), 129.06 (s, Ph) 129.16 (s, Ph), 137.38 (s, Ph), 204.4 (s, *C*$\equiv$C), 208.2 (s, C$\equiv$*C*), 226.0 (CO) [**N.B.:** P(OMe)$_3$ signal obscured by solvent peak].

Reaction of [W(S$_2$PMe$_2$)$_2$(CO)(PhC$\equiv$CPh)] (**1e**) *with* PMe$_2$Ph.—A solution of (**1e**) (14 mg, 0.022 mmol) in CH$_2$Cl$_2$ (1 cm^3) was treated with P(OMe)$_3$ (4 mg, 0.03 mmol) at room temperature when an immediate colour change from green to violet was observed. On adding hexane (*ca.* 1 cm^3) and concentrating the solution violet crystals were obtained which were recrystallised from CH$_2$Cl$_2$–hexane to give [W(S$_2$PMe$_2$)$_2$(CO)(PhC$\equiv$CPh)(PMe$_2$Ph)] (**3d**) (16 mg, 95%) (Found: C, 40.9; H, 4.2; P, 11.7. $C_{27}H_{33}OP_3S_4W$ requires C, 41.65; H, 4.3; P, 11.9%). I.r. (CHCl$_3$): ν_{CO} at 1 939s cm^{-1}. ^{1}H N.m.r. (CDCl$_3$, 20 °C): δ, 7.60—7.24 (m, 15 H, Ph), 2.35 (d, J_{P-H} 13.1, 3 H, Me), 1.95 (d, J_{P-H} 12.2, 3 H, Me), 1.94 (d, J_{P-H} 8.4, 3 H, PMe), 1.89 (d, J_{P-H} 10.9, 3 H, Me), 1.42 (d, J_{P-H} 8.1, 3 H, PMe), 1.11 (d, J_{P-H} 12.7, 3 H, Me). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$, 20 °C): δ, 93.92 (s, 1 P, S$_2$PMe$_2$), 65.19 (d, J_{P-P} 7.7, 1 P, S$_2$PMe$_2$), -19.48 (d, J_{P-P} 7.6 with two doublet satellites J_{P-W} 258 Hz, 1 P, PMe$_2$Ph).

Reaction of [W(S$_2$PMe$_2$)$_2$(CO)(PhC$\equiv$CPh)] (**1e**) *with* P(OMe)$_3$.—A solution of (**1e**) (15 mg, 0.023 mmol) in CH$_2$Cl$_2$ (1 cm^3) was treated with P(OMe)$_3$ (4 mg, 0.03 mmol) at room temperature when an immediate colour change from green to purple was observed. Hexane (*ca.* 1 cm^3) was added and the solution concentrated to give purple crystals of [W(S$_2$PMe$_2$)$_2$(CO)(PhC$\equiv$CPh){P(OMe)$_3$}] (**3e**) (12 mg, 70%) (Found: C, 35.1; H, 4.1. $C_{22}H_{31}O_4P_3S_4W$ requires C, 34.6; H, 4.1%). I.r. (Nujol): ν_{CO} at 1 952s cm^{-1}. ^{1}H N.m.r. (CDCl$_3$, -50 °C): δ, 7.40 (m, 10 H, Ph), 3.50 (d, J_{P-H} 11.0, 9 H, OMe), 2.26 (d, J_{P-H} 13.0, 3 H, Me), 1.95(d, J_{P-H} 13.0, 3 H, Me), 1.87 (d, J_{P-H} 12.5, 6 H, Me). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$, -50 °C): δ 123.68 [d, J_{P-P} 8.3, with two doublet satellites J_{P-W} 410, 1 P, P(OMe)$_3$], 101.87 (s, 1 P, S$_2$PMe$_2$), 63.47 (d, J_{P-P} 8.1, 1 P, S$_2$PMe$_2$).

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