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Insertion of alkynes into molybdenum–phosphine and –carbon bonds. Crystal structures of the alkyne–ylide complex $[\mathrm{MoO(SC_6H_2Pr^i_3}\text{-}2,4,6)_2\{\eta^2\text{-}\mathrm{CHC(tol)}\}\{\mathrm{C(tol)CHPMePh_2}\}]$ (tol = $\mathrm{C_6H_4Me}$-4) and the phosphonium–alkylidene complex $[\mathrm{MoO(SC_6H_2Pr^i_3}\text{-}2,4,6)_3\{=\mathrm{C(Ph)CH{=}C(Ph)CH_2PMe_2Ph}\}]$

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Treatment of $[\mathrm{MoH(SC_6H_2R_3}\text{-}2,4,6)_3(\mathrm{PMePh_2})]$ **1a** (R = Me or Pr^i) with HC≡CR′ (R′=Ph or $\mathrm{C_6H_4Me}$-4) in tetrahydrofuran (thf)–MeOH gave the diamagnetic ylide complexes $[\mathrm{MoO(SC_6H_2R_3}\text{-}2,4,6)_2\{\eta^2\text{-}\mathrm{CHC(R')}\}\{\mathrm{C(R')CHPMePh_2}\}]$ **2**, the source of the oxide ligand most probably being adventitious water. The crystal structure of one example, **2a** (R′ = $\mathrm{C_6H_4Me}$-4, R = Pr^i), confirms their structure [Mo–O 1.69(2), Mo–C$_{\mathrm{ylide}}$ 2.12(3), Mo–C$_{\mathrm{alkyne}}$ 2.07(3) and 2.21(3) Mo–S 2.410(9) and 2.475(9), Ph$_2$MeP–C 1.77(3)Å]. Treatment of $[\mathrm{MoH(SC_6H_2Pr^i_3}\text{-}2,4,6)_3(\mathrm{PMe_2Ph})_2]$ **1b** with HC≡CPh under similar conditions gave the phosphonium–alkylidene complex $[\mathrm{MoO(SC_6H_2Pr^i_3}\text{-}2,4,6)_3\{=\mathrm{C(Ph)CH{=}C(Ph)CH_2PMe_2Ph}\}]$ **3**, whose crystal structure has been determined [Mo–O 1.691(3), Mo–C 1.990(5), Mo–S 2.424(1), 2.434(1) and 2.432(1), PhMe$_2$P–C 1.808(6) Å]. Spectroscopic data for these complexes are discussed. Neither PhC≡CPh nor PhC≡CMe reacted with **1b**.

We have explored the reactions of the electron-deficient complexes[1] $[\mathrm{MoH(SC_6H_2R_3}\text{-}2,4,6)_3(\mathrm{PMePh_2})]$ **1a** (R = Me or Pr^i) and $[\mathrm{MoH(SC_6H_2Pr^i_3}\text{-}2,4,6)_3(\mathrm{PMe_2Ph})_2]$ **1b** with, for example, $\mathrm{C_5H_5N}$ to give[2] $[\mathrm{MoH(SR)_3(C_5H_5N)(PMePh_2)}]$, CO to give[3] $[\mathrm{Mo(SC_6H_2Pr^i_3}\text{-}2,4,6)_2(\mathrm{CO})_3(\mathrm{PMePh_2})]$, RNC to give[4] $[\mathrm{Mo(SR)_2(RNC)_4}]$ and thermally to give[5] S–C cleavage reactions. Here we report an extension of these studies to reactions with HC≡CR (R = Ph or $\mathrm{C_6H_4Me}$-4) in thf–methanol, where addition of oxide to the metal occurs, together with the formal insertion of alkyne into an Mo–P bond to give ylide complexes (from **1a**, R = Ph or $\mathrm{C_6H_4Me}$-4) and into Mo–P and Mo–C bonds to give a novel phosphonium–alkylidene complex (from **1b**, R = Ph), as is described below. The preparation of the phosphonium–alkylidene complex has been the subject of a preliminary report.[6]

Results and Discussion

Preparation and structure of ylide complexes

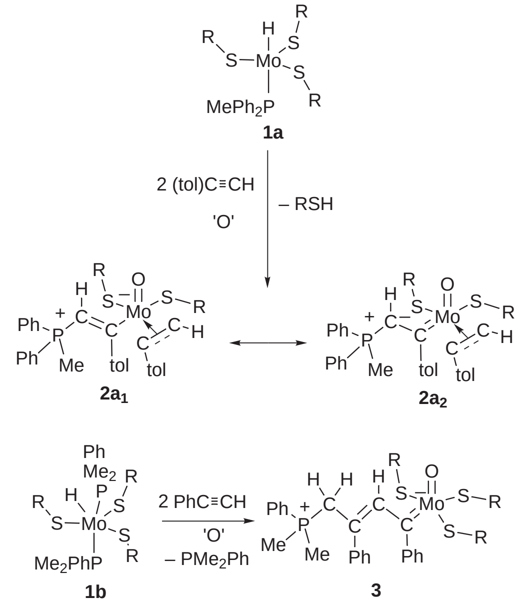
Reaction of $[\mathrm{MoH(SC_6H_2Pr^i_3}\text{-}2,4,6)_3(\mathrm{PMePh_2})]$ **1a** with $\mathrm{HC{\equiv}CC_6H_4Me}$-4 in thf under dinitrogen at room temperature gave a red solution which gave a red-brown powder after treatment with MeOH at −70 °C. Recrystallisation of this powder from $\mathrm{CH_2Cl_2}$ and hexane gave pink-red crystals which have been characterised spectroscopically (see below) and by crystal structure determination, which shows them to be of the ylide complex $[\mathrm{MoO(tipt)_2}\{\eta^2\text{-}\mathrm{CHC(tol)}\}\{\mathrm{C(tol)CHPMePh_2}\}]$ **2a** (tipt = $\mathrm{SC_6H_2Pr^i_3}$-2,4,6; tol = $\mathrm{C_6H_4Me}$-4) [Fig. 1, reaction (1)].

$$[\mathrm{MoH(tipt)_3(PMePh_2)}] + 2\mathrm{HC{\equiv}CC_6H_4Me\text{-}4} + \text{‘O’} \longrightarrow$$

$$[\mathrm{MoO(tipt)_2}\{\eta^2\text{-}\mathrm{CHC(tol)}\}\{\mathrm{C(tol)CHPMePh_2}\}] + \mathrm{Htipt} \quad (1)$$

$$\mathbf{2a}, \text{ (‘O’ = source of oxide)}$$

Analogues of **2a**, $[\mathrm{MoO(SC_6H_2R_3}\text{-}2,4,6)_2\{\eta^2\text{-}\mathrm{CHC(R')}\}\{\mathrm{C(R')CHPMePh_2}\}]$ **2b**–**2d** (R = Me or Pr^i, R′ = Ph or $\mathrm{C_6H_4Me}$-4) have been obtained by a similar route (below and Experimental section). On the basis of their spectroscopic properties and the crystal structure of **2a**, these insertion products are best described as analogues of resonance-stabilised ylides in which the resonance stabilisation involves the organometallic fragment, as is discussed below and shown in Scheme 1. The IR spectra of the complexes **2** contain a band at 920–960 cm^{-1} assigned to Mo=O stretching and a weak band at around 1900 cm^{-1} which is assigned to the C≡C stretch of the co-ordinated alkyne.



Scheme 1 Formation of compounds **2** and **3**. R = $\mathrm{C_6H_2Pr^i_3}$-2,4,6 or $\mathrm{C_6H_2Me_3}$-2,4,6; ‘O’ = source of oxide, see text

An immediate question concerning the obviously complicated nature of the formation of complexes **2** is how does the metal–oxygen bond form? The possible sources of the oxide ligand in compounds **2** are thf, MeOH or adventitious moisture or dioxygen of air. Although thf cannot be excluded as the source, we have not been able to isolate compounds **2** from

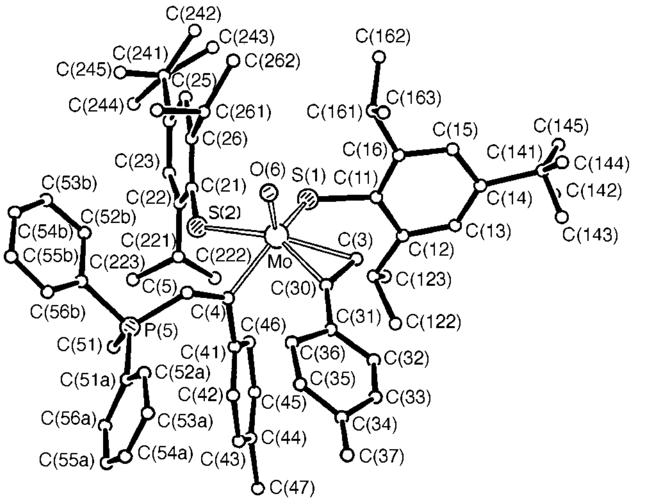


Fig. 1 View of the complex [MoO(tipt)$_2${η^2-CHC(tol)}{C(tol)CHP-MePh$_2$}]·0.5C$_4$H$_8$O·0.5MeOH **2a**. The atom numbering scheme and the alternative sites in the disordered isopropyl groups are indicated

Table 1 Selected molecular dimensions in [MoO(tipt)$_2${η^2-CHC(tol)}-{C(tol)CHPMePh$_2$}] **2a**. Bond lengths in Å, angles in °. Estimated standard deviations (e.s.d.s) are in parentheses

(a) About the Mo atom			
Mo–S(1)	2.410(9)	Mo–C(30)	2.07(3)
Mo–S(2)	2.475(9)	Mo–C(4)	2.12(3)
Mo–C(3)	2.21(3)	Mo–O(6)	1.694(21)
S(1)–Mo–S(2)	79.4(3)	C(3)–Mo–C(4)	111.4(13)
S(1)–Mo–C(3)	79.7(9)	C(30)–Mo–C(4)	80.5(12)
S(2)–Mo–C(3)	150.1(9)	S(1)–Mo–O(6)	112.5(7)
S(1)–Mo–C(30)	114.4(10)	S(2)–Mo–O(6)	102.3(7)
S(2)–Mo–C(30)	146.3(9)	C(3)–Mo–O(6)	105.3(10)
C(3)–Mo–C(30)	36.4(9)	C(30)–Mo–O(6)	100.0(10)
S(1)–Mo–C(4)	130.3(9)	C(4)–Mo–O(6)	110.5(12)
S(2)–Mo–C(4)	68.3(8)		
(b) In the tipt ligands			
S(1)–C(11)	1.82(4)	S(2)–C(21)	1.67(4)
Mo–S(1)–C(11)	113.3(11)	Mo–S(2)–C(21)	122.9(13)
(c) In the acetylene ligand			
C(3)–C(30)	1.34(4)	C(30)–C(31)	1.48(4)
Mo–C(3)–C(30)	66.5(23)	C(3)–C(30)–C(31)	137(4)
Mo–C(30)–C(3)	77.2(24)	C(30)–C(31)–C(32)	129(4)
Mo–C(30)–C(31)	145.4(29)	C(30)–C(31)–C(36)	122(4)
(d) In the phosphonium ylide ligand			
C(4)–C(41)	1.49(4)	P(5)–C(51a)	1.77(3)
C(4)–C(5)	1.37(3)	P(5)–C(51b)	1.82(4)
C(5)–P(5)	1.766(29)	P(5)–C(51c)	1.764(23)
Mo–C(4)–C(41)	121.5(27)	C(5)–P(5)–C(51a)	115.7(14)
Mo–C(4)–C(5)	118.8(26)	C(5)–P(5)–C(51b)	104.8(18)
C(41)–C(4)–C(5)	120(3)	C(5)–P(5)–C(51c)	112.5(15)
C(4)–C(41)–C(42)	127(4)	C(51a)–P(5)–C(51c)	108.8(16)
C(4)–C(41)–C(46)	116(4)	C(51a)–P(5)–C(51b)	109.5(20)
C(4)–C(5)–P(5)	127.2(25)	C(51b)–P(5)–C(51c)	105.1(14)

reactions carried out in thf alone; intractable oils result. The starting complexes **1a** and **1b** are very sensitive to moisture and this seems to be the most likely source of the oxide ligand, since we have not been able to detect significant amounts of methane, which would be generated were a methoxide intermediate involved in the reaction and dioxygen is more easily excluded from the system used than water.[7,8] Water as a source of Mo=O species is well documented and a number has been prepared by this and other means, including the anions [MoO(SR)$_4$]$^-$ (R = alkyl or aryl) which have been discussed in the context of oxomolybdenum enzymes.[2,9]

The ^{1}H NMR spectrum of complex **2a** showed the expected downfield shift of the methine proton signals, as well as a slight downfield shift of the methyl proton signals, relative to those from free Htipt. The C*H* signals for free Htipt appear as two septets at δ 3.54 and 2.75 and are shifted to 1.91 and 2.05 on co-ordination. Also the C*H*$_3$ signals for free Htipt appear as two doublets at 1.18 and 1.22 which are shifted to δ 0.92 and 0.91 in the complex. The methyl group of PMePh$_2$ appears as a doublet at δ 1.73 and the methyl group of the HC≡CC$_6$H$_4$Me-4 ligand appears as a singlet at δ 1.78. Complex **2a** showed a singlet in its ^{31}P NMR spectrum at δ −114.9. Its ^{13}C NMR spectrum shows the Mo*C* resonance at δ 230.1.

The molecular structure of [MoO(tipt)$_2${η^2-CHC(tol)}-{C(tol)CHPMePh$_2$}] **2a**, is shown in Fig. 1 and the molecular dimensions are in Table 1. It is a monooxomolybdenum complex with one HC≡CC$_6$H$_4$Me-4 molecule bound side-on to the molybdenum, whereas the other HC≡CC$_6$H$_4$Me-4 unit has formally inserted into the Mo–P bond to give a phosphonium ylide ligand. The co-ordination about the molybdenum atom is approximately square pyramidal with an apical oxo group and the η^2-alkyne occupying a single site and lying in the basal plane, *cis* to the ylide ligand.

In this structure the Mo–O bond distance [1.69(2) Å] is similar to the Re–O bond distance [1.700(6) Å] in the related compound [ReOR$_3$(CHCHPMe$_3$)] (R = CH$_2$SiMe$_3$).[10] The Mo–C (ylide) distance in **2a** [2.12(3) Å] is slightly longer than the Mn–C distance in the phosphonium ylide complex [Mn(η^5-C$_5$H$_5$)(CO)$_2${C(CO$_2$Me)CHPPh$_3$}] [1.985(3) Å][11] and also longer than the Re–C distance [1.996(9) Å] in [ReO(CH$_2$SiMe$_3$)$_3${CHCH(PMe$_3$)}].[10] The metal–carbon bonds in the above complexes have distances which are at the long end of the observed range of M=C values (1.81–2.02 Å)[12,13] but shorter than M–C single bonds (2.01–2.29 Å),[13] indicating that they have some multiple bond character.

The C–C distances in the ylide ligands of the above complexes are close to olefin distances (1.34 Å for ethylene): 1.37(3) Å for **2a**; 1.345(13) Å for [ReO(CH$_2$SiMe$_3$)$_3${CHCH(PMe$_3$)}][10] and 1.361(4) Å for [Mn(η^5-C$_5$H$_5$)(CO)$_2${C(CO$_2$Me)CHPPh$_3$}].[11]

The P–C=C angle in **2a**, 127(3)°, is wider than the corresponding angle in the above rhenium complex [124.4(8)°].[10] Thus it is olefinic in nature [122.5(5)°][10] and very similar to the P–C=C angle in the related manganese complex above [126.9(2)°].[11]

The C(5)–P bond distance in **2a** [1.77(3) Å] is much longer than the P–C ylide bond distance of 1.661(8) Å reported for the unstabilised ylide Ph$_3$PCH$_2$.[14] Our value is also similar to those of [ReO(CH$_2$SiMe$_3$)$_3${CHCH(PMe$_3$)}][10] [1.75(5) Å] and of [Mn(η^5-C$_5$H$_5$)(CO)$_2${C(CO$_2$Me)CHPPh$_3$}][11] [1.76(3) Å], which are close to the P–C ylide distances reported for the resonance-stabilised ylides triphenylphosphonium cyclopentadienide [1.72(2) Å][15] and triphenylphosphonium dicyanomethanide [1.75(8) Å].[16]

Thus the above structural data indicate that compound **2a** can be regarded as an ylide complex and its bonding can be represented essentially by two resonance forms, *viz.* a σ-vinyl form, [(tipt)$_2${CHC(tol)}OMo–C(tol)=CHP$^+$MePh$_2$] **2a$_1$**, and a 'carbene ylide' form, [(tipt)$_2${CHC(tol)}OMo=C(tol)HC–P$^+$-MePh$_2$] **2a$_2$** (see Scheme 1), with **2a$_1$** the dominant component.

Compound **2a** is diamagnetic, but occasionally is contaminated with a paramagnetic impurity whose EPR spectrum in solution shows a *g* factor and ^{95}Mo hyperfine splitting ($g = 1.990$, $A_{iso} = 2.93$ mT) similar to those reported for the molybdenum(v) anion [MoO(SC$_6$H$_4$NH$_2$-2)$_4$]$^-$.[17] Magnetic moment measurements of **2a** in the solid state at 20 °C confirmed that it is diamagnetic ($\mu_{eff} < 0.2\ \mu_B$; $\mu_B \approx 9.27 \times 10^{-24}$

J T^{-1}); quantitative EPR measurements in the solid state showed only 1% paramagnetism.

In a similar way to **2a**, the analogue [MoO(tmt)$_2${η^2-CHC(tol)}{C(tol)CHPMePh$_2$}] **2b** (tmt = SC$_6$H$_2$Me$_3$-2,4,6) was prepared from [MoH(tmt)$_3$(PMePh$_2$)] and HC≡CC$_6$H$_4$Me-4 in thf. Its IR spectrum shows a band at 920 cm^{-1} (Mo=O stretch) and also a weak broad band at 1890 cm^{-1} (C≡C stretch of the co-ordinated alkyne). The ^{31}P NMR spectrum shows a singlet at δ −112.7 for co-ordinated phosphine and a weak singlet at δ −168.1 due to some free phosphine, presumably formed from slight decomposition in solution. The ^{1}H NMR spectrum shows two singlets in a 1 : 2 ratio at δ 2.23 and 2.30 distinguishing the *ortho*- and *para*-methyl groups of the tmt ligand which are slightly shifted from those of the free thiolate. The methyl groups of the phosphine ligand and of HC≡CC$_6$H$_4$Me-4 appear as a broad resonance at δ 1.27. The aromatic protons from tmt and HC≡CC$_6$H$_4$Me-4 give a broad resonance from δ 6.8 to 7.4. The ^{13}C NMR does not show an assignable Mo=C resonance. Carbons of the methyl groups of tmt (*para* and *ortho*) and PMePh$_2$ appear in the appropriate region, δ 21.2, 22.1 and 30.0 respectively. These spectra, together with microanalysis, lead to the conclusion that compound **2b** is an analogue of **2a**, *i.e.* a phosphonium ylide complex.

The reactions of complex **1a** with an excess of HC≡CPh in thf solution at reduced temperature produce brown-red crystals formulated as [MoO(SC$_6$H$_2$R$_3$-2,4,6)$_2$(η^2-CHCPh)-{C(Ph)CHPMePh$_2$}] (R = Pr^i **2c** or Me **2d**). Compound **2c** was recrystallised from toluene–MeOH as dark red prisms. The presence of the oxo-ligand was revealed by a pronounced (Mo=O) stretching absorption at 960 cm^{-1}. The ^{31}P NMR spectrum showed a singlet at δ −99.2. The ^{1}H NMR spectrum shows the two *ortho*-isopropyl group resonances as septets at δ 2.9 and 3.5 with a total integration twice that of the *para*-isopropyl group. The aryl region is complicated as expected; protons of the two phenyl rings in the HC≡CPh derived ligands, the phenyl rings of the phosphine and the thiolate rings appear as a multiplet in the range δ 6.8–7.4. The methyl group of the PMePh$_2$ ligand appears as a doublet at δ 1.35; also the methyl groups of the tipt ligands give two doublets at δ 1.15 and 1.20.

Compound **2d** was prepared and characterised as for **2c** (Experimental section).

Preparation and structure of [MoO(tipt)$_3${=C(Ph)CH=C(Ph)-CH$_2$PMe$_2$Ph}] 3

Reaction of [MoH(tipt)$_3$(PMe$_2$Ph)$_2$] **1b** with an excess of HC≡CPh in thf for 18 h at room temperature produces a red solution which, after removal of the solvent and addition of cool MeOH at −20 °C, gave red crystals which were recrystallised from thf–MeOH to give a good yield of red plates of the novel diamagnetic phosphonium–alkylidene complex [MoO-(tipt)$_3${=C(Ph)CH=C(Ph)CH$_2$PMe$_2$Ph}] **3**, reaction (2).[6]

$$\text{[MoH(tipt)}_3\text{(PMe}_2\text{Ph)}_2\text{]} + 2\text{PhC≡CH} + \text{‘O’} \longrightarrow$$
$$\text{[MoO(tipt)}_3\text{\{=C(Ph)CH=C(Ph)CH}_2\text{PMe}_2\text{Ph\}]} + \text{PMe}_2\text{Ph} \quad (2)$$

Microanalysis of various preparations of complex **3** were inconsistent and could not easily be reconciled with the structure eventually determined by X-ray analysis (see below). This may be due to the occlusion of varying quantities of solvent molecules in the crystals, a common feature of this class of complex (see Experimental section), or possibly an artefact of the combustion microanalytical technique employed. A combination of X-ray crystallography and spectroscopy (NMR, IR) has been used to determine the structure, the crystal structure being shown in Fig. 2. Molecular dimensions are presented in Table 2.

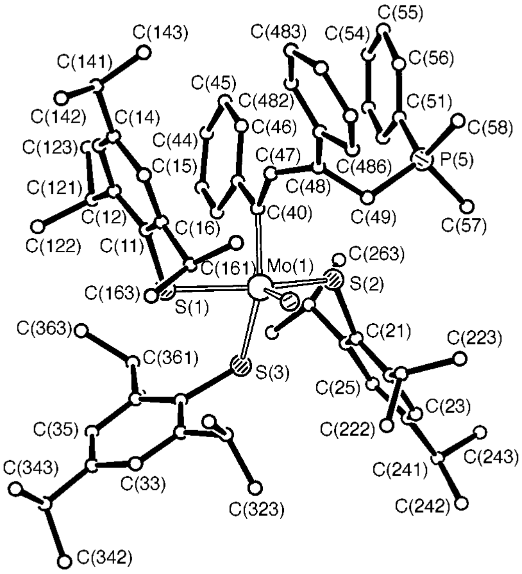


Fig. 2 View of the complex [MoO(tipt)$_3${=C(Ph)CH=C(Ph)CH$_2$-PMe$_2$Ph}]·2MeOH·C$_6$H$_5$Me **3**, indicating the atom numbering scheme. The disorder (involving the Mo atom) is not shown

The molybdenum in complex **3** has essentially square pyramidal geometry with an apical oxide ligand, as found also in **2a**. The apical Mo=O distance [1.691(3) Å] is within the normal range (1.68–1.72 Å)[18,19] and is similar to that [1.69(2) Å] in **2a**. The Mo–C distance [1.990(5) Å] is shorter than the Mo–C (ylide) distance in **2a** [2.12(3) Å] and is closer to the Mo–C distance in [Mo(CHBu^t)(NC$_6$H$_3$Pr$^i_2$-2,6)(OSO$_2$CF$_3$)$_2$-(MeOCH$_2$CH$_2$OMe)], 1.93(1) Å,[20] which is in the region typical of molybdenum(VI) alkylidene complexes. Therefore the Mo–C(40) bond in **3** has essentially alkylidene character.

The C(49)–C(48) distance in the C(Ph)CH$_2$PMe$_2$Ph group in complex **3** [1.493(8) Å] is significantly longer than the C(47)–C(48) distance [1.384(7) Å] and the P–CH$_2$C(Ph) bond distance [1.808(6) Å] is much longer than the generally observed P–C ylide distance of around 1.68–1.78 Å[10,11] and is also longer than the P–CHC(tol) distance in **2a** [1.77(3) Å].

Compound **3** can therefore be regarded as a phosphonium alkylidene complex of Mo^{VI} (Scheme 1), whereas **2a** and its analogues are ylide complexes whose bonding can be represented by resonance forms, as indicated above and in Scheme 1. The IR spectrum of **3** shows a band at 920 cm^{-1} (Mo=O stretching) but no assignable C≡C band. Its ^{1}H NMR spectrum shows the expected features for the co-ordinated tipt, with these resonances shifted downfield relative to the free thiol. The methyl groups of the tipt ligands give two doublet signals, at δ 1.0 and 1.1 and the methine groups appear as two septets at δ 2.6 and 3.0. The methyl groups of the PMe$_2$Ph ligand give a broad doublet at δ 1.6. The phenyl protons of the tipt and alkylidene ligands appear as broad signals in the aromatic region. The (Me$_2$Ph)PC*H*$_2$ resonance is a singlet at δ 3.4. The ^{31}P NMR spectrum shows a singlet at δ −108.24. To confirm the conclusions obtained from the X-ray analysis, namely the existence of a CH$_2$ group in the structure, distortionless enhancement by polarisation transfer (DEPT) (^{13}C) NMR was used. DEPT-135 allows methylene carbons to be unambiguously distinguished from methyl and methine carbons. However, no quaternary carbon resonances are measured by this technique. The NMR assignments thus obtained are shown in Table 3. No proton-decoupled ^{13}C spectrum was recorded because of the low concentration and relative instability of the complex in solution. This analysis shows the CH$_2$ resonance to be at δ 31.

As for compounds **2**, the process by which **3** is produced is complex. It involves generation of an Mo=O bond, together with formal insertion of the alkyne into an molybdenum–phosphine bond, followed by a second formal insertion of

Table 2 Selected molecular dimensions in $[MoO(tipt)_3\{=C(Ph)CH=C(Ph)CH_2PMe_2Ph\}]$ **3**. Details as in Table 1.

(a) About the disordered Mo atoms (see Experimental section)

Mo(1)···Mo(2)	1.243(7)		
Mo(1)–S(1)	2.424(1)	Mo(2)–S(1)	2.409(7)
Mo(1)–S(2)	2.434(1)	Mo(2)–S(2)	2.462(7)
Mo(1)–S(3)	2.432(1)	Mo(2)–S(3)	2.442(7)
Mo(1)–C(40)	1.990(5)	Mo(2)–C(40)	1.796(8)
Mo(1)–O(6)	1.691(3)		
S(1)–Mo(1)–S(2)	149.79(5)	S(1)–Mo(2)–S(2)	148.7(3)
S(1)–Mo(1)–S(3)	83.95(4)	S(1)–Mo(2)–S(3)	84.1(2)
S(2)–Mo(1)–S(3)	81.06(4)	S(2)–Mo(2)–S(3)	80.3(2)
S(1)–Mo(1)–C(40)	90.8(1)	S(1)–Mo(2)–C(40)	96.2(3)
S(2)–Mo(1)–C(40)	83.1(1)	S(2)–Mo(2)–C(40)	86.3(3)
S(3)–Mo(1)–C(40)	137.7(2)	S(3)–Mo(2)–C(40)	153.4(4)
S(1)–Mo(1)–O(6)	104.7(1)		
S(2)–Mo(1)–O(6)	105.3(1)		
S(3)–Mo(1)–O(6)	114.3(1)		
C(40)–Mo(1)–O(6)	107.6(2)		

(b) In the tipt ligands

S(1)–C(11)	1.785(5)	S(3)–C(31)	1.807(5)
S(2)–C(21)	1.792(5)		
Mo(1)–S(1)–C(11)	109.2(2)	Mo(2)–S(2)–C(21)	120.6(2)
Mo(2)–S(1)–C(11)	108.3(2)	Mo(1)–S(3)–C(31)	113.5(2)
Mo(1)–S(2)–C(21)	118.9(2)	Mo(2)–S(3)–C(31)	114.5(2)

(c) In the phosphonium–alkylidene ligand

C(40)–C(41)	1.479(8)	C(49)–P(5)	1.808(6)
C(40)–C(47)	1.451(7)	P(5)–C(51)	1.746(9)
C(47)–C(48)	1.384(7)	P(5)–C(57)	1.771(7)
C(48)–C(49)	1.493(8)	P(5)–C(58)	1.761(8)
Mo(1)–C(40)–C(41)	122.5(4)	C(49)–P(5)–C(51)	111.3(3)
Mo(1)–C(40)–C(47)	121.2(4)	C(49)–P(5)–C(57)	106.1(3)
C(41)–C(40)–C(47)	116.1(4)	C(51)–P(5)–C(57)	107.7(4)
C(40)–C(47)–C(48)	130.3(5)	C(49)–P(5)–C(58)	114.4(4)
C(47)–C(48)–C(49)	120.9(5)	C(51)–P(5)–C(58)	108.8(5)
C(48)–C(49)–P(5)	116.2(4)	C(57)–P(5)–C(58)	108.3(5)

(d) Torsion angles

O(6)–Mo(1)–S(1)–C(11)	76.0(2)
O(6)–Mo(1)–S(2)–C(21)	88.4(2)
O(6)–Mo(1)–S(3)–C(31)	80.2(2)
O(6)–Mo(1)–C(40)–C(41)	175.7(4)
O(6)–Mo(1)–C(40)–C(47)	−10.3(4)
Mo(1)–C(40)–C(47)–C(48)	64.1(7)
C(40)–C(47)–C(48)–C(49)	0.7(9)
C(40)–C(47)–C(48)–C(481)	−173.9(6)
C(47)–C(48)–C(49)–P(5)	112.1(5)

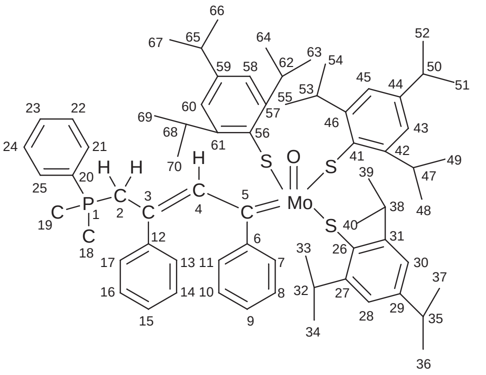
alkyne into the resulting Mo–C bond to produce complex **3** as a phosphonium alkylidene of Mo^{VI}.

Despite considerable effort, we have not yet been able to isolate a PMe_2Ph analogue of **2a**–**2d** by variation of the conditions of the reaction used to obtain **3**, nor have we been able to convert **2a**–**2d** (which have a different phosphine coligand from **3**) into analogues of **3**. It appears therefore that the altered steric/basicity properties of the PMe_2Ph ligand in **1b** compared to $PMePh_2$ in **1a** allow a different mechanistic pathway to operate, giving **3** rather than an analogue of **2**.

Experimental

All reactions were carried out under a dinitrogen or argon atmosphere using standard Schlenk techniques unless otherwise stated. Microanalysis was undertaken by Surrey University or by Butterworth Analytical Laboratories Ltd. Infrared spectra were obtained as Nujol mulls using a Perkin-Elmer 883 spectrometer, ^{1}H, ^{31}P and ^{13}C NMR spectra on a JEOL GSX270 instrument and EPR spectra for solids or solutions using a Bruker ER200D spectrometer. The GLC measurements were made with a Philips PU 4400 gas chromatograph and mass spectra were obtained on a VG Masstorr instrument.

Table 3 DEPT-^{13}C NMR assignments for $[MoO(tipt)_3\{=C(Ph)CH=C(Ph)CH_2PMe_2Ph\}]$ **3**



Atoms	δ (assignment)
33, 34, 39, 40, 48, 49, 54, 55, 63, 64, 69, 70	25 (CH_3)
36, 37, 51, 52, 66, 67	26 (CH_3)
18, 19	16 (CH_3)
2	31 (CH_2)
32, 38, 47, 53, 62, 68	33 (CH)
35, 50, 65	36 (CH)
4	125 (CH)
7–11, 13–17, 21–25, 28, 30, 43, 45, 58, 60	129–136 (CH)

The thiols Htmt and Htipt[22] and the molybdenum phosphine starting materials[23] were prepared as described in the literature. Solvents were dried and freshly distilled before use. All other chemicals were either from Aldrich or BDH Chemicals and used without further purification.

Preparations

$[MoO(tipt)_2\{\eta^2\text{-}CHC(tol)\}\{C(tol)CHPMePh_2\}]$ 2a. To a solution of $[MoH(tipt)_3(PMePh_2)]$ (0.19 g, 0.18 mmol) in thf (30 cm^3) under dinitrogen was added an excess of $HC\equiv CC_6H_4Me$-4 (1.5 cm^3) and the mixture was stirred at 0 °C for 3.5 h. The solvent was evaporated till dryness under vacuum and the resulting red-brown oil was dissolved in CH_2Cl_2 (5 cm^3). Methanol (10 cm^3) was added at −70 °C and the product extracted as a red-brown powder. After recrystallisation from CH_2Cl_2 and hexane, pink-red crystals were obtained which were subjected to X-ray analysis. Yield 0.35 g (41%) (Found: C, 71.4; H, 7.9. $C_{61}H_{75}MoOPS_2\cdot 0.5C_4H_8O\cdot 0.5CH_3OH$ requires C, 71.2; H, 7.9%). IR: 940s (br) [ν(Mo=O)], 1900w (br) cm^{-1} [ν(C≡C)]. NMR (CD_2Cl_2): ^{1}H, δ 7.8–6.8 (m, aromatic), 2.05 [spt, 4 H, J_{HH} = 7.4, $(CH_3)_2CH$], 1.91 [spt, 2 H, J_{HH} = 7.4], 1.73 (d, 3 H, J_{PH} = 23.0, PCH_3), 0.92 [d, 24 H, J_{HH} = 6, $(CH_3)_2CH$] and 0.91 [d, 12 H, J_{HH} = 6 Hz, $(CH_3)_2CH$]; ^{31}P, δ −114.9 ($PMePh_2$); ^{13}C, δ 230.1 (MoC).

In a repeated experiment in a vessel closed with a septum, gas samples removed by a syringe and subjected to GLC and mass spectroscopic analyses did not show detectable amounts of methane or H_2.

$[MoO(tmt)_2\{\eta^2\text{-}CHC(tol)\}\{C(tol)CHPMePh_2\}]$ 2b. Using the same technique as for complex **2a** above, **1a** (R = Me) and an excess of $HC\equiv CC_6H_4Me$-4 were allowed to react to produce **2b** as a red-brown solid. Yield 0.35 g (79%) (Found: C, 70.0; H, 6.6; S, 7.3. $C_{49}H_{53}MoOPS_2$ requires C, 69.3; H, 6.3; S, 7.6%). IR: 920s (br) [ν(Mo=O)], 1890w (br) cm^{-1} [ν(C≡C)]. NMR (CD_2Cl_2): ^{1}H, δ 7.4–6.8 (m, aromatic), 2.3 (s, 12 H, CH_3), 2.2 (s, 6 H, CH_3) and 1.75 (d, 3 H, J_{PH} = 27.0 Hz, PCH_3); ^{31}P, δ −112.7 ($PMePh_2$); ^{13}C, δ 21.2, 22.1 (CH_3), 30.0 (PCH_3).

$[MoO(tipt)_2\{\eta^2\text{-CHCPh}\}\{C(Ph)CHPMePh_2\}]$ 2c. To a stirred solution of $[MoH(tipt)_3(PMePh_2)]$ (0.6 mmol) in thf (20 cm^3) at 0 °C was added HC≡CPh (1 cm^3, excess). The colour changed from green to red-brown immediately. The solution was stirred for 2 h at 0 °C and then 1 h at room temperature. The red-brown solid was filtered off, washed with MeOH, dried *in vacuo*, then recrystallised from MeOH–toluene. Yield 0.37 g (47%) of red crystals of complex **2c** (Found: C, 78.8; H, 7.1. $C_{59}H_{71}MoOPS_2\cdot 4CH_3C_6H_5$ requires C, 78.9; H, 7.8%). IR: 960s (br) [ν(Mo=O)], 1890w (br) cm^{-1} [ν(C≡C)]. NMR (CD_2Cl_2): ^{1}H, δ 7.4–6.8 (m, aromatic), 3.51 [spt, 4 H, J_{HH} = 7.4, $(CH_3)_2CH$], 2.90 [spt, 2 H, J_{HH} = 7.4, $(CH_3)_2CH$], 1.75 (d, 3 H, J_{PH} = 29.2, PCH_3), 1.20 [d, 24 H, J_{HH} = 5.8, $(CH_3)_2CH$] and 1.15 [d, 12 H, J_{HH} = 5.8 Hz, $(CH_3)_2CH$]; ^{31}P, δ −99.2 ($PMePh_2$).

$[MoO(tmt)_2(\eta^2\text{-CHCPh})\{C(Ph)CHPMePh_2\}]$ 2d. To a stirred solution of $[MoH(tmt)_3(PMePh_2)]$ (0.7 mmol) in thf (50 cm^3) at 0 °C was added HC≡CPh (1 cm^3, excess). The colour changed immediately from green to red. The mixture was stirred for 1 h. The volume was reduced to a minimum (2 cm^3) and the product precipitated as a red-brown solid by addition of cold MeOH. It was filtered off and dried under vacuum, then recrystallised from toluene–methanol to give **2d** as red-brown crystals. Yield 0.39 g (47%) (Found: C, 75.6; H, 6.3. $C_{47}H_{47}MoOPS_2\cdot 4CH_3C_6H_5$ requires C, 75.9; H, 6.7%). IR: 960s (br) [ν(Mo=O)], 1900w (br) cm^{-1} [ν(C≡C)]. NMR (CD_2Cl_2): ^{1}H, δ 7.4–6.8 (m, aromatic), 2.2 (s, 12 H, CH_3), 2.1 (s, 6 H, CH_3) and 1.75 (d, 3 H, J_{PH} = 27.0 Hz, PCH_3); ^{31}P, δ −97.2 ($PMePh_2$).

$[MoO(tipt)_3\{{=}C(Ph)CH{=}C(Ph)CH_2PMe_2Ph\}]$ 3. To a stirred solution of $[MoH(tipt)_3(PMe_2Ph)_2]$ **1b** (0.12 g, 0.11 mmol) in thf (30 cm^3) was added HC≡CPh (1.5 cm^3, excess). The colour changed from green to red over 3 h. The red solution was stirred for 15 h at room temperature. The thf was evaporated under vacuum till dryness and MeOH (10 cm^3) was added at −20 °C, affording fine red crystals which were collected by filtration and washed with MeOH (10 cm^3). The compound was recrystallised from toluene–MeOH to give deep red, diamond-shaped plate, single crystals of complex **3** which were suitable for X-ray crystallography. Yield 0.12 g (83%). IR: 920s (br) cm^{-1} [ν(Mo=O)]. NMR (CD_2Cl_2): ^{1}H, δ 7.8–6.8 (m, aromatic), 3.4 (s, 2 H, PCH_2), 3.0 [spt, 6 H, J_{HH} = 7.4, $(CH_3)_2CH$], 2.6 [spt, 3 H, J_{HH} = 7.4, $(CH_3)_2CH$], 1.6 (d, 3 H, J_{PH} = 24.7, PCH_3), 1.1 [d, 36 H, J_{HH} = 7.3, $(CH_3)_2CH$] and 1.0 [d, 18 H, J_{HH} = 7.3 Hz, $(CH_3)_2CH$]; ^{31}P, δ −108.2 ($PMePh_2$). The assignment of ^{13}C resonances is shown in Table 3.

Attempted reaction of $[MoH(tipt)_3(PMe_2Ph)_2]$ with PhC≡CPh and PhC≡CMe. To a stirred solution of $[MoH(tipt)_3(PMe_2Ph)_2]$ (1.19 g, 1.75 mmol) in thf at room temperature was added PhC≡CPh (0.3 g, 10-fold excess). The mixture was stirred for 18 h at 20 °C and then refluxed for 5 h. The solution changed during reflux from green to brown-green. The solvent was reduced to a minimum (2 cm^3) under vacuum and methanol (10 cm^3) was added at −20 °C. The only material that could be isolated from the reaction was starting material. Using the same technique, $[MoH(tipt)_3(PMe_2Ph)_2]$ was treated with PhC≡CMe but the solid that was collected was only starting material.

Crystallography

$[MoO(tipt)_2\{\eta^2\text{-CHC(tol)}\}\{C(tol)CHPMePh_2\}]\cdot 0.5C_4H_8O\cdot 0.5MeOH$ 2a. *Crystal data.* $C_{61}H_{75}MoOPS_2\cdot 0.5C_4H_8O\cdot 0.5CH_4O$, M = 1067.4, monoclinic, space group $I2/c$ (equivalent to no. 15), a = 22.747(5), b = 23.616(3), c = 24.304(4) Å, β = 90.880(14)°, U = 13 055(4) Å^3, Z = 8, D_c = 1.086 g cm^{-3}, $F(000)$ = 4536, T = 293 K, μ(Mo-Kα) = 3.2 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Crystals were mostly very small and deep red: some were lighter and larger. One pink crystal, *ca.* 0.24 × 0.24 × 0.55 mm, was mounted on a glass fibre and coated in epoxy resin; at this stage it had already turned orange-red and by the end of the analysis it had turned deep red. However this change clearly did not affect the structure determination and appears to be a surface effect since the crystal integrity was not affected. Moreover, the NMR and other spectroscopic parameters of the bulk crystals were the same whether they were small and red or larger and lighter coloured.

After photographic examination this crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the centred settings of 25 reflections, θ *ca.* 8.5°) and for measurement of diffraction intensities (to θ_{max} 18°; there were few observable intensities beyond this level). During processing the intensities were corrected for Lorentz-polarisation effects, crystal deterioration (by 26.7% overall), absorption (by semi-empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). Of 4487 unique reflection entered into the SHELX system,[24] only 1447 had $I > 2\sigma_I$. The structure was determined by the heavy atom method and refined, on F, by full-matrix least-squares methods in SHELXN.[24]

Only the Mo, S and P atoms were allowed anisotropic thermal parameters. All lighter atoms were refined isotropically. Hydrogen atoms were included, where possible, in calculated positions; those in the *ortho*-Pr^i groups in the tipt ligands were calculated with staggered conformations, but those in the *para*-Pr^i groups (where some disorder was identified) and those in the methyl groups of tolyl groups were not included. The thermal parameters of all the hydrogen atoms were set to ride on those of the parent carbon atoms.

The atoms of the disordered solvent molecules were not fully resolved; seven part atoms in two distinct molecules (each molecule lying about a two-fold symmetry axis) were included in the refinement, but the refined individual atoms do not form chemically recognisable molecules. For the crystal data calculations above, one molecule is assumed to be of MeOH, the other of thf (although this site might sometimes be occupied by a toluene molecule).

The refinement was concluded with the R and R_g indices[24] at 0.107 and 0.085 respectively for the 1736 reflections with $I > 1.5\sigma_I$ weighted $w = \sigma^{-2}(F)$. There were no peaks significantly above the background noise (*ca.* 0.35 e Å^{-3}) in a final difference map.

Scattering factor curves for neutral atoms were taken from ref. 25. Computer programs used in this analysis have been noted above and in Table 4 of ref. 26 and were run on the Micro VAX 3600 machine in the Nitrogen Fixation Laboratory.

$[MoO(tipt)_3\{{=}C(Ph)CH{=}C(Ph)CH_2PMe_2Ph\}]\cdot 2MeOH\cdot C_6H_5Me$ 3. *Crystal data.* $C_{69}H_{93}MoOPS_3\cdot 2CH_4O\cdot C_7H_8$, M = 1317.8, monoclinic, space group $P2_1/n$ (equivalent to no. 14), a = 17.205(1), b = 21.814(2), c = 19.860(2) Å, β = 92.121(8)°, U = 7448.3(13) Å^3, Z = 4, D_c = 1.175 g cm^{-3}, $F(000)$ = 2824, T = 293 K, μ(Mo-Kα) = 3.2 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Crystals were deep red, diamond-shaped plates. One, *ca.* 0.17 × 0.43 × 0.60 mm, was mounted on a glass fibre and subjected to photographic and diffractometer procedures similar to those described above. For the determination of accurate cell parameters, 25 reflections, with θ *ca.* 10.3° were selected; intensity data were measured to θ_{max} = 23°. In the processing of the data similar corrections were applied; there was a *ca.* 15% reduction in the intensities during the data collection. 10 240 Unique reflections (6528 with $I > 2\sigma_I$) were entered into the SHELX program system[24] for structure determination (by the heavy atom method) and refined, on F, by large-block-matrix least-squares methods.

During the refinement process a persistent difference peak was noted near the centre of the complex molecule; this was then included as an alternative site for the Mo atom, refining to

6.37(12)% occupancy. No other alternative sites, *e.g.* for the oxo ligand O(6), or the phosphonium–alkylidene, were observed; the tipt ligands would, we believe, occupy the same sites in either orientation. Some atoms for the solvent molecules (MeOH and toluene) were identified and included, but these molecules were not fully resolved. In the complex all non-hydrogen atoms (except for the lower-occupancy Mo atom) were refined anisotropically, all other atoms isotropically. Hydrogen atoms were included in calculated positions but with freely refined isotropic thermal parameters. Refinement was terminated with $R = 0.090$ and $R_g = 0.069$[24] for all 10 240 reflections, weighted $w = (\sigma_{F^2} + 0.000\,27F^2)^{-1}$. In a final difference map the only peak of significance was *ca.* 0.6 e Å^{-3} and close to the Mo atom.

Scattering curves, computer programs and facilities used in this analysis were as for complex **2a** above.

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