

The reactions of the anions $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PRR}')^-]$ ($\text{R}, \text{R}' = \text{H}, \text{Ph}$) towards chloroarsines and chlorophosphines; synthesis of complexes containing both bridging phosphido and arsenido groups

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Deprotonation of the complexes $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)(\mu\text{-H})]$ (R^1 and $\text{R}^2 = \text{H}$ or Ph ; Cp = cyclopentadienyl) in THF yields the related anions $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)]^-$. The reactivity of these anions towards Ph_2PCl , $(\text{EtO})_2\text{PCl}$, Ph_2AsCl and Me_2AsCl has been investigated. The outcome of the reactions with chlorophosphines depends on the nature of the substituents on the bridging phosphido ligand. Thus reaction of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PH}_2)]^-$ with Ph_2PCl yields $[\text{Cp}_2(\text{CO})_4\text{Mo}_2\{\mu\text{-P}(\text{H})\text{PPh}_2\}(\mu\text{-H})]$, whereas the analogous reaction with $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhR})]^-$ yields $[\text{Cp}_2(\text{CO})_x\text{Mo}_2(\mu\text{-PPH}_2)(\mu\text{-PPhR})]$ ($\text{R} = \text{H}$, $x = 4$; $\text{R} = \text{Ph}$, $x = 2$). Thermolysis of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPH}_2)]$ in toluene yields $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPH}_2)]$ and $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPH}_2)]$. In contrast, the reaction of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)]^-$ with chloroarsines is not dependent on the nature of the R groups either on the phosphorus or arsenic atoms, yielding $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)(\mu\text{-AsR}^3_2)]$ in all cases. These complexes are the first example of transition metal compounds containing both a bridging phosphido and a bridging arsenido group. The crystal structures of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2\{\mu\text{-P}(\text{H})\text{PPh}_2\}(\mu\text{-H})]$, $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})\{\mu\text{-P}(\text{OEt})_2\}]$, and $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PH}_2)(\mu\text{-AsMe}_2)]$ are reported.

Introduction

The chemistry of dinuclear complexes containing bridging phosphido groups has been the subject of much study.^{1,2} The reactions of anionic complexes of this type, which should be more nucleophilic than related uncharged species, have, however, received less attention.³⁻⁵

Herein we report the results of the nucleophilic reactions of a series of dinuclear anionic complexes $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)]^-$ ($\text{R}^1, \text{R}^2 = \text{H}, \text{Ph}$) with Ph_2PCl , $(\text{EtO})_2\text{PCl}$, Ph_2AsCl and Me_2AsCl . It has been found that the nature of the R substituents on the μ -phosphido group in the anions has a strong effect on the product distribution obtained from reaction with Ph_2PCl , but that there is no such effect on reaction with R_2AsCl ($\text{R} = \text{Me}$ or Ph). We also report on attempts to decarbonylate the series of complexes $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)(\mu\text{-AsR}^3_2)]$ (R^1 and $\text{R}^2 = \text{H}$ or Ph ; $\text{R}^3 = \text{Me}$ or Ph); here again the product distribution appears to be dependent on the nature of the R substituents on the μ -phosphido group.

Results and discussion

(a) Reaction of deprotonated $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)(\mu\text{-H})]$ ($\text{R}^1 = \text{R}^2 = \text{H}$ **1**; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}$ **2**; $\text{R}^1 = \text{R}^2 = \text{Ph}$ **3**) with Ph_2PCl

Deprotonation of a solution of **1** or **2** in THF using a slight excess of $^n\text{BuLi}$ proceeds rapidly at -78°C to yield a purple solution of the corresponding anions $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhR})]^-$ ($\text{R} = \text{H}$ **4** or Ph **5**). In contrast, deprotonation of **3** is somewhat slower, requiring stirring of a THF solution of **3** with $^n\text{BuLi}$ at room temperature for 1 h to yield green $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPH}_2)]^-$ **6**.

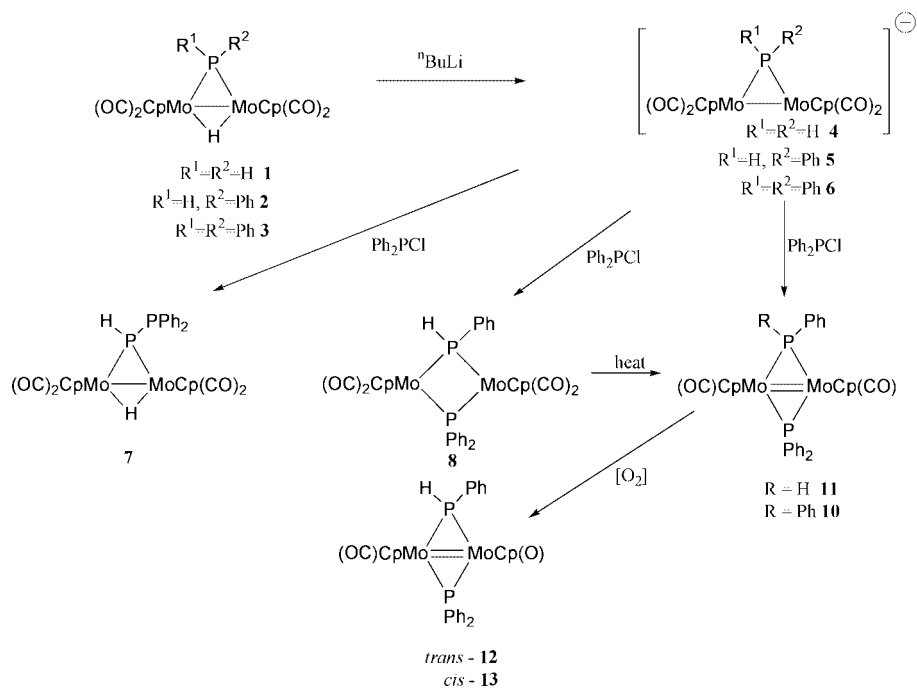
Complex **4** reacts rapidly with Ph_2PCl at -78°C giving $[\text{Cp}_2(\text{CO})_4\text{Mo}_2\{\mu\text{-P}(\text{H})\text{PPh}_2\}(\mu\text{-H})]$ **7** in low (10–20%) yield in addition to unreacted starting material and decomposition products. The analogous reaction of **5** with Ph_2PCl at room

temperature proceeds somewhat more slowly, giving $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPH}_2)]$ **8** in high (70–80%) yield. The reaction with **6** at room temperature again proceeds differently, giving $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPH}_2)_2]$ **10** in moderate (50–60%) yield (Scheme 1).

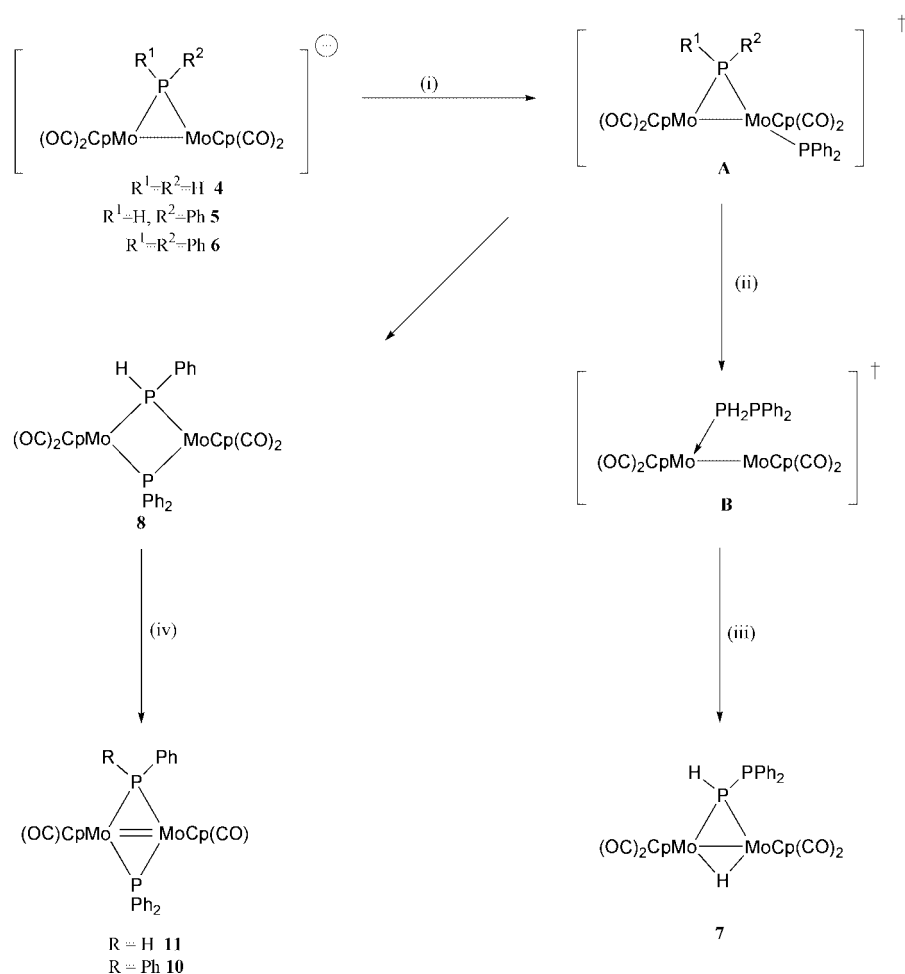
A possible set of reaction pathways leading to the formation of the observed products is shown in Scheme 2. It is proposed that in each case the first step in the reaction is attack of the anionic metal centre present in **4–6** on the electrophilic phosphorus atom to give the neutral intermediate **A** in which the PPh_2 unit is terminally bonded to one of the metal centres. Reaction from then on can follow one of two pathways. When the anion is $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PH}_2)]^-$ **4** reductive elimination with the formation of a P–P bond presumably occurs to give the 34-electron intermediate **B**. Subsequent oxidative addition of a P–H bond in a manner similar to that reported by Hartung *et al.*⁶ would then regenerate a bridging hydride and phosphido group to give **7**.

In the reactions involving **5** and **6** the reductive elimination step leading to P–P bond formation does not occur, perhaps for steric reasons. It may be that the transition state required for reductive elimination is unattainable due to steric clashes of the bulky phenyl groups on each phosphorus atom. Instead, the terminally-bonded phosphido phosphorus atom in intermediate **A** (Scheme 2) donates its lone pair to the second metal centre, causing metal–metal bond cleavage, to yield $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhR})(\mu\text{-PPH}_2)]$.

In the case of **5** ($\text{R} = \text{Ph}$) reaction stops at this point and $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPH}_2)]$ **8** is obtained. The spectroscopic characterisation of **8** did not define the structure unambiguously; the NMR data do not distinguish between the two possible structural isomers $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPH}_2)]$ and $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\eta^1:\eta^1\text{-PPhHPPH}_2)]$. In order to characterise the new complex unambiguously a single crystal X-ray analysis was clearly needed, but no crystals suitable for such an analysis could be grown. Hence **5** was also reacted with



Scheme 1 Reactivity of 1–3 towards $nBuLi$ and Ph_2PCL .



Scheme 2 Proposed reaction pathway for the formation of 7–11 from 4–6 and Ph_2PCL . (i) Ph_2PCL ; (ii) reductive elimination; (iii) oxidative addition; (iv) decarbonylation.

$(EtO)_2PCL$ to yield $[Cp_2(CO)_4Mo_2(\mu-PPhH)\{\mu-P(OEt)_2\}]$ **9** the structure of which was elucidated by a single crystal X-ray diffraction study (see below).

In the reaction of **6** with Ph_2PCL , which gives the known compound $[Cp_2(CO)_2Mo_2(\mu-PPh_2)]$ **10**, it is assumed that

$[Cp_2(CO)_4Mo_2(\mu-PPh_2)]$ is first formed as an intermediate and that decarbonylation then occurs. Complex **10**, which is the sole product of the reaction, was identified by comparison of its 1H , ^{31}P NMR and IR spectroscopic data with the literature values.^{7,8} In a previous study it was found that thermolysis of

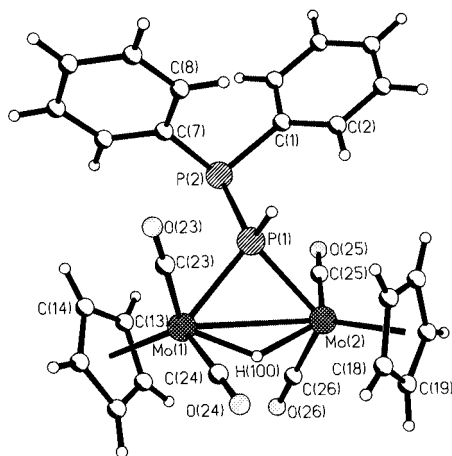


Fig. 1 Molecular structure of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2\{\mu\text{-P(H)PPh}_2\}(\mu\text{-H})]$ **7**.

$[\text{Cp}(\text{CO})_3\text{Mo}(\text{PPh}_2)]$ also led directly to the formation of **10**, suggesting that decarbonylation of the assumed intermediate $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPh}_2)_2]$ is facile.⁸

These observations prompted us to investigate whether **8** could be converted to an analogue of **10**. Overnight thermolysis of a solution of **8** in toluene did indeed yield $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPh}_2)]$ **11** as the sole product in near quantitative yield. During the conversion of **8** to **11** a faint red band was sometimes noticed on the TLC plate, especially when the solvent was removed on a rotary evaporator rather than on a vacuum line prior to separation. It seemed likely that this red complex was an oxo complex derived from replacement of a carbonyl ligand in **11** by an oxygen atom since such reactions are well documented.^{8,9} Accordingly, a small portion of **11** in dichloromethane was stirred in an open vessel for several hours leading to a colour change from green to blue. A small amount each of two new red complexes was then obtained after TLC, in addition to several ionic products which were inseparable and not fully characterised. It was found that the yield of the two red complexes was considerably increased by carrying out the reaction in a sealed, air-filled vessel rather than in the open air. The new red complexes were assigned on the basis of spectroscopic data (see below) as *trans*- and *cis*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPh}_2)]$ **12** (*trans*) and **13** (*cis*).

(b) Characterisation of complexes 7–13

Complexes **7–13** have been characterised by ^1H , ^{31}P NMR, IR spectroscopy and FAB MS. In addition **7** and **9** have each been the subject of a single crystal X-ray diffraction study.

The ^{31}P NMR spectrum of **7** exhibits two doublets at δ 105.49 and -9.23 which are assigned respectively to the bridging phosphorus atom ($\mu\text{-PHPPH}_2$) and to the uncoordinated phosphorus atom ($\mu\text{-PHPPH}_2$). The observed $^1J_{\text{P-P}}$ coupling of 314.3 Hz is typical of a one-bond interaction.¹⁰ The presence of a bridging hydride was confirmed by a doublet resonance at δ -12.61 ($^2J_{\text{P-H}} = 36$ Hz) in the ^1H NMR spectrum.

The molecular structure of **7** is shown in Fig. 1, with selected bond lengths and angles being listed in Table 1. The Mo(1)–P(1)–Mo(2) angle of $85.56(5)^\circ$ is typical of metal–phosphorus–metal systems in which a metal–metal single bond is present between the two metal centres.¹¹ Additionally, this small M–P–M bond angle is as expected in the light of ^{31}P NMR data for related three-membered phosphacycles: the smaller the M–P–M bond angle, the more downfield is the phosphorus resonance in the ^{31}P NMR spectrum.¹² The two MoPH planes lie at an angle of 171.5° to each other, indicating a slight deviation from planarity of the Mo_2PH core. The recorded P(1)–P(2) bond length of $2.188(2)$ Å falls within the range of documented phosphorus–phosphorus single bond lengths.¹³

The ^{31}P NMR spectrum of **8** exhibits two doublets at δ -91.33 and -142.17 with $^2J_{\text{P-P}}$ of 309 Hz. This P–P coupling

Table 1 Selected bond lengths (Å) and angles ($^\circ$) for complexes **7** and **9**

7		9	
Mo(1)–P(1)	2.419(2)	Mo(1)–P(1)	2.5290(9)
Mo(1)–H(100)	1.76(6)	Mo(1)–P(2)	2.4801(9)
Mo(1)–Mo(2)	3.278(1)	Mo(2)–P(1)	2.5047(9)
Mo(2)–H(100)	1.82(6)	Mo(2)–P(2)	2.4967(8)
Mo(2)–P(1)	2.407(2)	P(1)–C(15)	1.825(3)
P(1)–H(1)	1.299	P(1)–H(100)	1.29(3)
P(1)–P(2)	2.188(2)	P(2)–O(10)	1.637(2)
P(2)–C(1)	1.853(6)	P(2)–O(11)	1.635(2)
P(2)–C(7)	1.848(7)		
Mo(1)–Mo(2)–H(100)	23(2)	Mo(1)–P(1)–Mo(2)	107.32(3)
Mo(1)–Mo(2)–P(1)	47.38(4)	Mo(1)–P(2)–Mo(2)	109.12(3)
Mo(1)–P(1)–H(1)	108.9		
Mo(1)–P(1)–P(2)	119.96(8)	Mo(1)–P(1)–H(100)	105.9(1)
Mo(1)–P(1)–Mo(2)	85.56(5)	Mo(1)–P(1)–C(15)	117.62(1)
Mo(2)–P(1)–H(1)	108.9	Mo(1)–P(2)–O(10)	119.18(9)
Mo(2)–P(1)–P(2)	122.47(9)	Mo(1)–P(2)–O(11)	106.77(8)
Mo(2)–Mo(1)–P(1)	47.06(4)		
P(1)–H(100)–Mo(1)	70(2)	Mo(2)–P(1)–H(100)	117.4(1)
P(1)–H(100)–Mo(2)	70(2)	Mo(2)–P(1)–C(15)	115.71(1)
P(1)–P(2)–C(1)	103.3(2)	Mo(2)–P(2)–O(10)	102.39(8)
P(1)–P(2)–C(7)	98.7(2)	Mo(2)–P(2)–O(11)	118.24(9)

constant is more typical of a one-bond interaction than a two-bond one,¹⁰ and initially led us to speculate that **8** had the formula $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\eta^1:\eta^1\text{-PPhHPPH}_2)]$, but the presence of such a P–P bond was not compatible with the observed ^1H NMR spectrum, which suggests a $^1J_{\text{P-H}}$ and a $^3J_{\text{P-H}}$ interaction.¹⁴ Additionally, the observed resonances in the ^{31}P NMR spectrum have very different ^{31}P chemical shifts from that of the diphosphane ligand in the known complex $[(\text{CO})_4\text{Co}_2\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-P}_2\text{Ph}_4)]$.¹⁵ The observed shifts are more typical of phosphido groups bridging two non-bonded metal centres;¹⁶ thus the upfield shift of the two resonances as compared to those of **7** and **1–3** reflects the opening of the Mo–P–Mo angle caused by the absence of a metal–metal bond.¹² Although bis-phosphido bridged complexes are common there are few examples of complexes which contain two inequivalent phosphido bridges and therefore there is little information on the P–P coupling in such systems.¹⁷ The range of quoted $^2J_{\text{P-P}}$ coupling constants varies from 5 to 160 Hz, but it should be noted that in all these reported cases a metal–metal bond is present which will affect the geometry at the phosphorus atom and therefore the coupling constant. Additionally, Grim has shown that the most important term in determining the magnitude of the geminal phosphorus coupling for the complexes $[(\text{CO})_4\text{Mo}(\text{DPPM})]$ is the through-metal term,¹⁸ and clearly the presence of a metal–metal bond will alter the degree of through-metal coupling.

In the ^1H NMR spectrum of **8** a doublet of doublets at δ 5.31 integrating to 1 proton is assigned to the P–H proton. Both the $^1J_{\text{P-H}}$ coupling constant of 322.6 Hz and the $^3J_{\text{P-H}}$ constant of 7.9 Hz are in the expected range.¹⁴ Two resonances at δ 5.40 and 4.89, each integrating to 5 protons, are assigned to the non-equivalent cyclopentadienyl groups.

The ^{31}P NMR spectrum of **9** shows two doublets at δ 195.79 and -142.43 with a $^2J_{\text{P-P}}$ of 413.9 Hz, again this coupling is unusually high. The ^1H NMR spectrum shows that the two OEt groups are in different environments, as confirmed by the single crystal X-ray analysis (see below).

The molecular structure of **9** is shown in Fig. 2 and selected bond lengths and angles are listed in Table 1. The Mo(1)–P(1)–Mo(2) and Mo(1)–P(2)–Mo(2) bond angles of $107.32(3)$ and $109.12(3)^\circ$ respectively are typical for phosphido-bridged metal complexes in which there is no metal–metal bond.^{16,17} The two MoP_2 planes lie at an angle of 31.6° to each other, indicating a highly folded butterfly structure. The two phosphorus atoms bridge the metal atoms unsymmetrically, with P(1) approaching

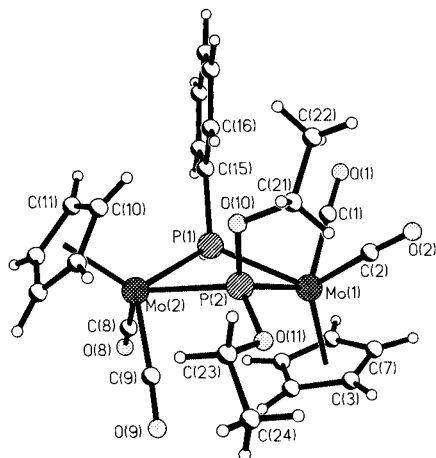


Fig. 2 Molecular structure of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})\{\mu\text{-P}(\text{OEt})_2\}]$ **9**.

Mo(2) more closely, whereas P(2) approaches Mo(1). Additionally, the molybdenum–phosphorus bond lengths to the bridging $(\text{EtO})_2\text{P}$ ligand [$\text{Mo}(1)\text{-P}(2)$ 2.4801(9) Å; $\text{Mo}(2)\text{-P}(2)$ 2.4967(8) Å] are significantly shorter than the corresponding bond lengths to the phenylphosphido ligand [$\text{Mo}(1)\text{-P}(1)$ 2.5290(9) Å; $\text{Mo}(2)\text{-P}(1)$ 2.5047(9) Å], reflecting the fact that the $(\text{EtO})_2\text{P}$ group is a better σ -donor and π -acid than the phenylphosphido group.

The ^{31}P NMR spectrum of **11** shows two double resonances at δ 96.78 and 34.84; these are assigned as $\mu\text{-PPh}_2$ and $\mu\text{-PPhH}$ respectively and are significantly downfield from those of the parent complex **8**. Furthermore the $^2J_{\text{P-P}}$ of 8.9 Hz is greatly reduced from the corresponding P–P coupling of 309 Hz recorded for **8**. The M–P–M angle of 69° in **10** may be compared with the average angle of 108° in **9** and it is plausible to assume that such a decrease in angle also occurs on conversion of **8** to **11**, thus accounting for the downfield shift in the phosphorus resonances. Surprisingly there is little precedent in the literature for the observed decrease in the P–P coupling constant which accompanies the formation of the multiple metal–metal bond in **11**. To the authors' knowledge there exists only one other case in which metal–metal bonds of differing order are supported by inequivalent phosphido bridging ligands. The complexes $[(\text{CO})_6\text{Fe}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-PPh}_2)]$ and $[(\text{CO})_5\text{Fe}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-PPh}_2)]$, which contain a single and double metal–metal bond respectively, show very similar $^2J_{\text{P-P}}$ coupling constants of 29.5 and 56.9 Hz.¹⁹ However, it should be noted that these two complexes contain a similar Fe_2P_2 core geometry: both are essentially planar with the P_2Fe planes lying respectively at an angle of 178 and 169° to each other, whereas in the present case **8** and **9** are butterfly type complexes and **10** and **11** possess planar Mo_2P_2 cores. This flattening of the core is presumably necessary to allow the large degree of metal–metal interaction present in **10** and **11**.

The ^1H NMR spectrum of **11** exhibits a multiplet at δ 7.69–7.18 which is assigned to phenyl protons, as well as to half of the double doublet due to the P–H proton; the observable part of this double doublet resonates at δ 5.87 ($^3J_{\text{P-H}} = 2.1$ Hz). In order to be sure that the P–H proton was correctly assigned a ^{31}P NMR spectrum with proton coupling was recorded. This clearly shows a $^1J_{\text{P-H}}$ coupling of 369.3 Hz for the phosphorus atom resonating at δ 34.84. Two Cp signals are observed in the ^1H NMR spectrum at δ 5.36 and 5.33. There are two possible isomers for **11** in which the Cp rings either lie mutually *cis* or *trans*, but only two Cp signals were observed in solution. The geometry of **11** is therefore assumed to be identical to that of **10** in which the Cp rings are located *trans* to each other.⁸ The infrared spectrum of **11** shows one carbonyl stretch at 1871 cm^{-1} , indicating a large amount of electron density at the metal centres, and an associated high degree of metal–ligand back-bonding.

The NMR spectroscopic data do not allow any formal differentiation between the *trans* and *cis* isomers **12** and **13**. However assignment is made by comparison of the spectroscopic data with those of the known complexes *trans*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPh}_2)]$ and *cis*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPh}_2)]$. In these known complexes it was found that the *trans* isomer had the higher ^{31}P NMR shift, and additionally the higher carbonyl stretching frequency.⁸ In the present case it was found that the ^{31}P NMR spectra showed two doublets for each isomer, which had moved downfield by *ca.* 60 ppm compared to the parent complex **11**; a similar shift on formation of such oxo species has been previously reported.^{8,9} In the ^1H NMR spectra it is again only possible to locate one half of the double doublet corresponding to the P–H proton. A ^1H coupled ^{31}P NMR spectrum again confirmed the presence of the P–H proton. It is interesting to note that the *trans* isomer **12** has a slightly higher $^1J_{\text{P-H}}$ coupling constant of 367.8 Hz, as compared to 337.6 Hz for the *cis* isomer **13**. The carbonyl stretching frequencies of 1845 and 1822 cm^{-1} for **12** and **13** respectively are very low for terminal carbonyl groups. This drop reflects the increased electron density at the Mo centres caused by loss of a carbonyl group.

(c) Reaction of 4–6 with chloroarsines

Reaction of **4–6** with the chloroarsine Me_2AsCl proceeds rapidly at -78°C to yield $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)(\mu\text{-AsMe}_2)]$ ($\text{R}^1 = \text{R}^2 = \text{H}$ **14**; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}$ **15**; $\text{R}^1 = \text{R}^2 = \text{Ph}$ **16**) as the sole isolable product in high (65–80%) yield. The outcome of these reactions showed no dependence on the substituents on the μ -phosphido group. In order to determine whether or not the lack of other products analogous to those obtained in the reaction with Ph_2PCl was associated with the lower steric demands of the less bulky methyl groups the series of reactions was repeated using Ph_2AsCl . Again only one product was obtained in each case, affording the complexes $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)(\mu\text{-AsPh}_2)]$ **17–19** ($\text{R}^1 = \text{R}^2 = \text{H}$ **17**; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}$ **18**; $\text{R}^1 = \text{R}^2 = \text{Ph}$ **19**).

It is assumed that the initial reaction of **4–6** with R_2AsCl yields one intermediate $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PR}^1\text{R}^2)(\sigma\text{-AsR}_2)]$, similar to intermediate **A** in Scheme 1. In contrast to the course of the reaction with Ph_2PCl , reductive elimination at one of the metal centres to form a phosphorus–arsenic bond does not occur, even with the less sterically bulky Me_2AsCl . This is presumably because arsenic–phosphorus bonds of the type which would be formed are relatively weak. Instead the terminally bound arsenic atom donates its lone pair to the second metal centre, forming a bridging arsenido group with concomitant metal–metal bond scission.

To the authors' knowledge complexes **14–19** represent the first known examples of complexes in which two metal centres are bridged by both a phosphido and arsenido group. One related complex containing a phosphinidene ligand and an arsenido group, $[\text{Cp}(\text{CO})_8\text{MoCo}_2(\mu_3\text{-P}^t\text{Bu})(\mu\text{-AsMe}_2)]$ has previously been obtained by Vahrenkamp from the reaction of $[(\text{CO})_9\text{Co}_3(\mu_3\text{-P}^t\text{Bu})]$ with $[\text{Cp}(\text{CO})_3\text{Mo}(\text{AsMe}_2)]$.²⁰ The Co_2Mo triangle in this complex is capped by a P^tBu group, and a Co–Mo edge is bridged by the arsenido group.

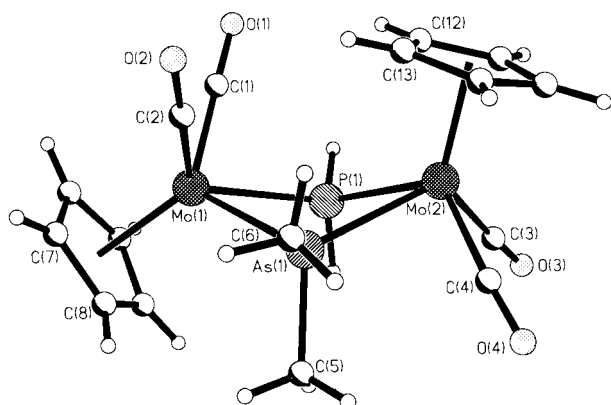
(d) Characterisation of complexes 14–19

Complexes **14–19** have been characterised by ^1H NMR, ^{31}P NMR, IR spectroscopy, by FAB MS spectrometry and by C,H microanalysis. The presence of a large amount of arsenic in the sample precluded microanalytical results for phosphorus being obtained.

Complex **14** has been the subject of a single crystal X-ray diffraction study and the molecular structure of **14** is shown in Fig. 3 with bond lengths and angles being listed in Table 2. The Mo_2AsP core is best described as a butterfly structure with no hinge As–P bond; the two MoPAs planes lie at an angle of 145° to each other. The $\text{Mo}\cdots\text{Mo}$ separation of 4.12 Å clearly

Table 2 Selected bond lengths (Å) and angles (°) for **14**

Mo(1)–As(1)	2.610(3)	Mo(2)–As(1)	2.597(3)
Mo(1)–P(1)	2.497(7)	As(1)–C(5)	1.94(2)
Mo(2)–P(1)	2.512(7)	As(1)–C(6)	1.97(2)
Mo(1)–As(1)–Mo(2)	104.60(1)	Mo(1)–As(1)–C(6)	117.6(7)
Mo(1)–P(1)–Mo(2)	110.7(3)	Mo(2)–As(1)–C(6)	112.0(7)
Mo(1)–As(1)–C(5)	109.0(8)	As(1)–Mo(1)–P(1)	64.3(2)
Mo(2)–As(1)–C(5)	115.4(8)	As(1)–Mo(2)–P(1)	64.3(2)
C(5)–As(1)–C(6)	98.8(1)		

**Fig. 3** Molecular structure of $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PH}_2)(\mu\text{-AsMe}_2)]$ **14**.

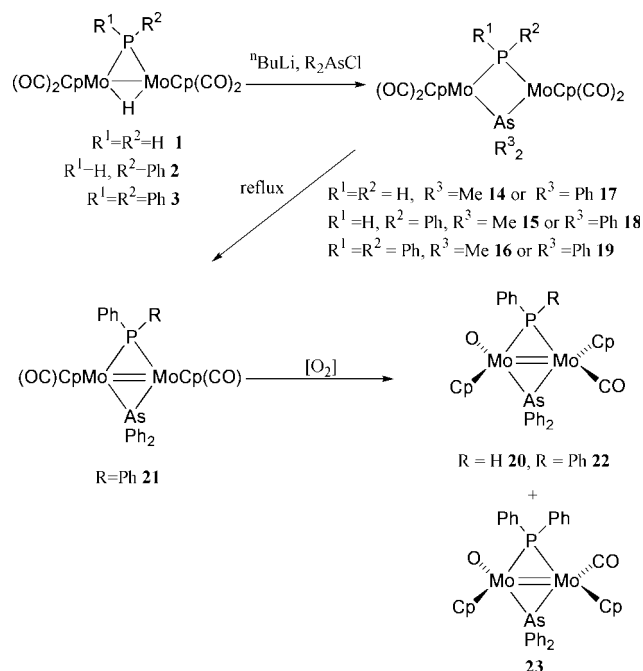
represents a non-bonding interaction, and the two Cp groups are arranged *trans* to the Mo–Mo vector. The Mo–As–Mo and Mo–P–Mo bond angles of 104.6(1) and 110.7(3)° are typical for ligand-bridged complexes in which there is no metal–metal bond between the two metal centres.^{21,16} The two Mo–As separations (Mo(1)–As(1) 2.610(3); Mo(2)–As(1) 2.597(3) Å) are almost identical within experimental error as are the two P–Mo separations (Mo(1)–P(1) 2.497(7); Mo(2)–P(1) 2.512(7) Å).

The ¹H NMR spectrum of **14** shows one resonance at δ 5.30 integrating to 10 protons which is assigned to the Cp groups. A doublet at δ 2.22 (¹J_{P-H} 299.8 Hz) is assigned to the P–H protons and a singlet resonance at δ 1.52 integrating to 6 protons is assigned to the AsMe₂ protons. Likewise, the ¹H NMR spectrum of **16** exhibits only one methyl resonance at δ 1.58 thus indicating that these complexes are fluxional. A wing flapping mechanism, similar to that proposed by Keller and Vahrenkamp,²¹ would result in the two methyl groups of AsMe₂ becoming equivalent in both **14** and **16**, likewise the R groups of the PR₂ moiety would also become equivalent on the NMR timescale. In the ¹H NMR spectrum of **15** two methyl resonances are observed at δ 1.58 and 1.57 reflecting the fact that even with wing flapping fluxionality the two methyl groups are always in different environments due to the two different substituents on the μ-phosphido group. Complexes **15** and **18** both exhibit two Cp signals, which indicates that the Cp groups lie *trans* to each other in solution. It is reasonable to assume that this holds true for **14**, **16**, **17** and **19**, and indicates that the solution structure of **14** is the same as its solid state structure.

The ³¹P NMR spectra of **14**–**19** all show a very upfield singlet resonance, which reflects the large M–P–M bond angle in these butterfly complexes, and also suggests an increased electron density at the phosphorus atom as compared to the related bis-phosphido-bridged species which show similar M–P–M bond angles but whose phosphorus resonances have a less upfield chemical shift.

(e) Attempted decarbonylation of **14**–**19**

Complexes **14**–**19** were thermolysed to determine whether or not they would undergo decarbonylation in a similar way to the analogous bis-phosphido-bridged complexes (Scheme 3). Thermolysis of solutions of **14**–**18** for several days caused a

**Scheme 3** Reactivity of **1**–**3** towards ⁿBuLi and R₂AsCl (R = Me or Ph).

gradual colour change from orange to dark green after which spot TLC revealed the presence of three new products. However, attempts to separate these products by preparative TLC using either silica or alumina plates led to substantial decomposition and to the reformation of starting material. In the case of reaction with **18** it was possible to isolate a trace amount of a new red complex. The infrared spectrum of this new complex revealed only one absorption in the carbonyl region at 1832 cm⁻¹, and on this basis the complex is tentatively formulated as $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-AsPh}_2)]$ **20** although a full spectroscopic analysis could not be undertaken due to the low yield.

By contrast thermolysis of a toluene solution of **19** led to the formation of a green solution after several hours and chromatographic separation of the products was possible. Three new complexes $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsPh}_2)]$ **21** (60–70% yield), *trans*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsPh}_2)]$ **22** (2–3% yield) and *cis*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsPh}_2)]$ **23** (2–3% yield) were obtained.

It has been previously shown that decarbonylation of bis-phosphido-bridged molybdenum complexes is dependent on the steric properties of the R groups on the bridging ligand. Thus Hayter's compound $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PMe}_2)_2]$ was not reported to decarbonylate^{7,8} and Heck has shown that $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_4)(\text{CO})_4\text{Mo}_2(\mu\text{-PMe}_2)]$ loses only one carbonyl ligand on heating to yield $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_4)(\text{CO})_3\text{Mo}_2(\mu\text{-PMe}_2)]$.²² Furthermore Böttcher *et al.* reported that the bis-phosphido-bridged di-iron clusters $[(\text{CO})_6\text{Fe}_2(\mu\text{-PR}^1_2)(\mu\text{-PR}^2_2)]$ would decarbonylate to give $[(\text{CO})_5\text{Fe}_2(\mu\text{-PR}^1_2)(\mu\text{-PR}^2_2)]$, complexes which contain a formal iron–iron double bond, only when both R¹ and R² were bulky groups such as ^tBu and Ph.¹⁹ These observations go some way towards explaining why no new products were obtained in the thermolysis reactions of **14**–**17**. However, as previously shown, complex **8** decarbonylates on reflux to give **11**. Accordingly if steric influences were the sole determining factor it might be expected that **18** would also decarbonylate to yield stable products.

Decarbonylation of bis-arsenido-bridged complexes has been less well explored than decarbonylation of phosphido-bridged analogues. The complex $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-AsMe}_2)_2]$ was not reported to decarbonylate,⁷ nor were the complexes $[(\text{CO})_8\text{Re}_2(\mu\text{-AsPh}_2)_2]$ or $[(\text{CO})_4\text{Ir}_2(\mu\text{-As}^t\text{Bu}_2)_2]$,²³ all having been formed under conditions which might have been expected to

Table 3 Crystallographic data for the complexes **7**, **9** and **14**^a

Compound	7	9	14
Formula	C ₂₆ H ₂₂ Mo ₂ O ₄ P ₂	C ₂₄ H ₂₆ Mo ₂ O ₆ P ₂	C ₁₆ H ₁₈ AsMo ₂ O ₄ P
<i>M</i>	652.26	664.27	572.07
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	14.222(6)	9.7396(5)	10.9454(4)
<i>b</i> /Å	10.378(4)	17.1917(7)	21.547(6)
<i>c</i> /Å	17.861(6)	15.346(1)	8.022(5)
β /°	104.16(3)	97.401(3)	
<i>V</i> /Å ³	2556.1(16)	2548.1(2)	1891.8(15)
<i>Z</i>	4	4	4
μ /mm ⁻¹	1.137	1.147	3.162
Reflections collected	4674	7464	3954
Independent reflections	4484	4492	3002
	<i>R</i> _{int} = 0.0407	<i>R</i> _{int} = 0.0265	<i>R</i> _{int} = 0.1010
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0438	<i>R</i> ₁ = 0.0307	<i>R</i> ₁ = 0.0814
	<i>wR</i> ₂ = 0.1008	<i>wR</i> ₂ = 0.0637	<i>wR</i> ₂ = 0.1652
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0660	<i>R</i> ₁ = 0.0496	<i>R</i> ₁ = 0.1662
	<i>wR</i> ₂ = 0.1109	<i>wR</i> ₂ = 0.0705	<i>wR</i> ₂ = 0.2083

^a Data in common: graphite-monochromated Mo-*K*α radiation, λ = 0.71073 Å; *T* = 180(2) K.

lead to decarbonylation. A series of complexes [(CO)_xMM'-(μ-AsMe₂)₂] (*M*, *M*' = Fe, *x* = 6; *M*, *M*' = Cr, Mo, *x* = 8; *M* = Fe, *M*' = Cr, Mo, *x* = 7) which already formally contain one metal–metal bond were likewise not reported to decarbonylate.²⁴ It is concluded that decarbonylation of bis-arsenido-bridged complexes is difficult to achieve even when the *R* substituents at the bridging arsenido ligands are very bulky groups. It may be that decarbonylation is more difficult for complexes containing a μ-AsR₂ group than a μ-PR₂ group because of the fact that the former is a poor π-acid ligand.

The decarbonylation of **19** leads to a large increase in the amount of electron density present at the metal centres, this being reflected in the unusually low stretching frequency of the remaining terminal carbonyl ligands which occurs between 1847 and 1821 cm⁻¹.

We therefore propose that decarbonylation will only occur, and lead to stable products, in mixed arsenido and phosphido bridged complexes if both the bridging phosphido and arsenido groups are good π-acids, as is the case in **19**. The nature of the substituents at the bridging phosphido group is especially important in any event since bridging arsenides are significantly poorer π-acids than bridging phosphides. Thus in the present series of reactions decarbonylation only leads to stable products when sufficient electron density can be removed from the metal centres by the co-ligands.

The ³¹P NMR spectra of **20–23** all show a considerable downfield shift compared to the starting complex **19**, which indicates that the M–P–M bond angle has been decreased considerably in **20–23**, this being necessary to allow the metals to approach within bonding distance. The ¹H NMR spectra of **21**, **22** contain multiplet peaks due to the phenyl protons as well as two resonances due to the inequivalent Cp rings.

Experimental

Unless otherwise stated all experiments were carried out under an atmosphere of dry, oxygen-free nitrogen, using conventional Schlenk line techniques, and solvents freshly distilled from the appropriate drying agent. NMR spectra were, unless otherwise stated, recorded using a Bruker DRX 250 spectrometer, with SiMe₄ as an external standard for ¹H spectra, and H₃PO₄ for ³¹P spectra; all spectra were recorded in CDCl₃. Infrared spectra were, unless otherwise stated, recorded in hexane solution in 0.5 mm NaCl solution cells, using a Perkin-Elmer 1710 Fourier-Transform spectrometer. FAB mass spectra were obtained using a Kratos Concept instrument, with 3-nitrobenzyl alcohol as a matrix.

Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh).

Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. **1–3**,^{1,3} Me₂AsCl^{25,26} and Ph₂AsCl²⁷ were prepared by the literature method.

Crystal structure determinations

Data for **7** and **14** were collected by the ω/2θ scan method on a Rigaku AFC7R four-circle diffractometer. Data for the complex **9** were collected on a Nonius Kappa CCD diffractometer. All data were collected at 180(2) K using an Oxford Cryostream cooling apparatus.

For **7** the P–H hydrogen atom was initially placed in a calculated position (P–H 1.29 Å) and allowed to ride on the phosphorus atom with an isotropic displacement parameter fixed at *U* = 0.10 Å².

For **14** the crystals were of poor quality and the data are poor (*R*_{int} = 0.10). For this structure the light atoms (C,O) were refined with isotropic temperature factors. The P–H protons were not located in the final difference map: coordinates for these two atoms are not included in the table of atomic coordinates.

Table 3 shows crystallographic data for complexes **7**, **9** and **14**.

CCDC reference number 186/1930.

See <http://www.rsc.org/suppdata/dt/b0/b001193m/> for crystallographic files in .cif format.

(i) Reaction of [Cp₂(CO)₄Mo₂(μ-PHR)(μ-H)] with ⁿBuLi

A solution of [Cp₂(CO)₄Mo₂(μ-PHR)(μ-H)] (*R* = H **1**, *R* = Ph **2**) (300 mg, 0.64 mmol **1**, 300 mg, 0.57 mmol **2**) in THF (60 ml) was cooled to –78 °C and 1.1 equiv. of 1.6 M ⁿBuLi in hexane (0.45 ml **1**; 0.4 ml **2**) was added dropwise over 5 minutes during which time the solution turned a deep purple to give [Cp₂(CO)₄Mo₂(μ-PHR)][–] (*R* = H **4**, *R* = Ph **5**). In each case *in situ* ¹H NMR spectroscopy revealed that no bridging hydride was present. The solutions were used with no further purification or spectroscopic analysis.

(ii) Reaction of [Cp₂(CO)₄Mo₂(μ-PPh₂)(μ-H)] with ⁿBuLi

To a solution of [Cp₂(CO)₄Mo₂(μ-PPh₂)(μ-H)] **3** (300 mg, 0.5 mmol) in THF (60 ml) was added 1.1 equiv. of 1.6 M ⁿBuLi in hexane (0.35 ml) over 5 minutes. The solution was stirred at room temperature for 1 h during which time the solution turned

a deep green to give $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPh}_2)]^-$ **6** as the sole product. The solution was used with no further purification or spectroscopic analysis.

(iii) Reaction of 4–6 with Ph_2PCl

A solution of the metal anion (300 mg, 0.64 mmol **4**; 300 mg, 0.57 mmol **5**; 300 mg, 0.5 mmol **6**) in THF (60 ml) was cooled to -78°C and Ph_2PCl (1.1 equiv.) was added dropwise over 5 minutes.

For 4. The solution was then stirred for 30 minutes, during which time the solution turned a dark brown. The solvent was removed *in vacuo*, and the residue was dissolved in the minimum CH_2Cl_2 and applied to the base of TLC plates. Elution with 1:1 CH_2Cl_2 :hexane yielded a trace of starting material **1** and $[\text{Cp}_2(\text{CO})_4\text{Mo}_2\{\mu\text{-P}(\text{H})\text{PPh}_2\}(\mu\text{-H})]$ **7** (83 mg, 20%). Suitable crystals for single X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 :hexane solution of **7** at -20°C . $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1933(vs), 1872(s); NMR: ^1H , δ 7.88–7.07 [m, 10H, Ph], 5.54 [dd, $^1J(\text{PH})$ 320, $^2J(\text{PH})$ 10.2, 1H, $\mu\text{-PH}$], 5.11 [s, 5H, Cp], 4.69 [d, $^3J(\text{PH})$ 1.38, 5H, Cp], -12.61 [dd, $^2J(\text{PH})$ 36, $^3J(\text{PH})$ 1 Hz, 1H, $\mu\text{-H}$]; ^{31}P , δ 105.49 [d, $^1J(\text{PP})$ 314.3, $\mu\text{-PHPPH}_2$], -9.23 [d, $^1J(\text{PP})$ 314.3 Hz, $\mu\text{-PHPPH}_2$]; *m/z* 664 (M^+), 578 ($\text{M}^+ - 3\text{CO}$) (Found: C 46.75, H 3.31, P 9.19; $\text{C}_{26}\text{H}_{22}\text{Mo}_2\text{O}_4\text{P}_2$ requires C 47.57, H 3.38, P 9.44%).

For 5. The solution was allowed to warm to RT and stirred overnight. The solvent was removed *in vacuo*, the residue was dissolved in the minimum CH_2Cl_2 and applied to the base of TLC plates. Elution with 1:1 CH_2Cl_2 :hexane yielded $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPh}_2)]$ **8** (330 mg, 80%) as the sole isolable product. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 1954(m), 1942(vs), 1879(s), 1867(m); NMR: ^1H , δ 7.6–7.2 [m, 15H, Ph], 5.31 [dd, $^1J(\text{PH})$ 322.6, $^3J(\text{PH})$ 7.9 Hz, 1H, PH], 5.40 [s, 5H, Cp], 4.89 [s, 5H, Cp]; ^{31}P , δ -91.33 [d, $^2J(\text{PP})$ 309, $\mu\text{-PPh}_2$], -142.17 [d, $^2J(\text{PP})$ 309 Hz, $\mu\text{-PPhH}$]; *m/z* 730 (M^+), 673 ($\text{M}^+ - 2\text{CO}$) (Found: C 52.06, H 3.79, P 7.54; $\text{C}_{32}\text{H}_{26}\text{Mo}_2\text{O}_4\text{P}_2$ requires C 52.46, H 3.58, P 8.46%).

For 6. A similar procedure was followed as for **5** to yield $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPh}_2)_2]$ **10** (224 mg, 60%). Spectroscopic data were in accordance with literature values.⁸

(iv) Reaction of 5 with $(\text{EtO})_2\text{PCl}$

Using an identical procedure to that for the reaction of **5** with Ph_2PCl reaction of **5** with 1.1 equiv. of $(\text{EtO})_2\text{PCl}$ gave $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-PPhH})\{\mu\text{-P}(\text{OEt})_2\}]$ **9** (242 mg, 64%) as the sole isolable product. Suitable crystals for single X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 :hexane solution of **9** at -20°C . $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 1962(s), 1941(vs), 1890(s), 1871(s); NMR: ^1H (400 MHz), δ 7.71–7.3 [m, 5H, Ph], 5.37 [s, 5H, Cp], 5.06 [s, 5H, Cp], 3.92 [dd, $^1J(\text{PH})$ 312.7, $^3J(\text{PH})$ 19.5, 1H, PH], 4.09 [qd, $^3J(\text{HH})$ 6.9, $^3J(\text{PH})$ 3.3, 2H, POCH_2], 3.79 [qd, $^3J(\text{HH})$ 7, $^3J(\text{PH})$ 2.7, 2H, POCH_2], 1.42 [t, $^3J(\text{HH})$ 7, 3H, POCH_2CH_3], 1.35 [t, $^3J(\text{HH})$ 6.9 Hz, 3H, POCH_2CH_3]; ^{31}P , δ 195.79 [d, $^2J(\text{PP})$ 413.9, $\mu\text{-P}(\text{OEt})_2$], -142.43 [d, $^2J(\text{PP})$ 413.9 Hz, $\mu\text{-PPhH}$]; *m/z* 668 (M^+), 640 ($\text{M}^+ - \text{CO}$), 612 ($\text{M}^+ - 2\text{CO}$) (Found: C 43.10, H 3.92, P 9.06; $\text{C}_{24}\text{H}_{26}\text{Mo}_2\text{O}_6\text{P}_2$ requires C 43.12, H 3.92, P 9.27%).

(v) Thermolysis of 8

A solution of **8** (200 mg, 0.27 mmol) in toluene (60 ml) was refluxed for 16 h during which time the solution colour changed from orange to green. The solvent was removed *in vacuo*, the residue was dissolved in the minimum CH_2Cl_2 and applied to the base of TLC plates. Elution with 3:2 CH_2Cl_2 :hexane yielded $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPh}_2)]$ **11** (155 mg, 90%) as the sole product. $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1871. NMR: ^1H ,

δ 7.69–7.18 [m, 15H, Ph], 6.60 [dd, $^1J(\text{PH})$ 369.3, $^3J(\text{PH})$ 2.1 Hz, 1H, PH], 5.36 [s, 5H, Cp], 5.33 [s, 5H, Cp]; ^{31}P , δ 96.78 [d, $^2J(\text{PP})$ 8.9, $\mu\text{-PPh}_2$], 34.84 [d, $^2J(\text{PP})$ 8.9 Hz, $\mu\text{-PPhH}$]; *m/z* 673 (M^+), 644 ($\text{M}^+ - \text{CO}$), 615 ($\text{M}^+ - 2\text{CO}$) (Found: C 53.05, H 4.12, P 8.73; $\text{C}_{30}\text{H}_{26}\text{Mo}_2\text{O}_2\text{P}_2$ requires C 53.26, H 3.88, P 9.16%).

(vi) Oxidation of 11

A solution of **11** (100 mg, 0.15 mmol) in CH_2Cl_2 was stirred in a sealed, air filled flask for 4 h, during which time the solution turned brown. The solvent was removed, the residue was dissolved in the minimum CH_2Cl_2 and applied to the base of TLC plates. Elution with 3:2 CH_2Cl_2 :hexane yielded *trans*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPh}_2)]$ (**12**, 29 mg, 32%) and *cis*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-PPh}_2)]$ (**13**, 10 mg, 10%).

For 12. $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1845; NMR: ^1H , δ 8.36–7.11 [m, 15H, Ph], 6.83 [dd, $^1J(\text{PH})$ 367.8, $^3J(\text{PH})$ 1.9 Hz, 1H, PH], 5.24 [s, 5H, Cp], 4.82 [s, 5H, Cp]; ^{31}P , δ 173.55 [d, $^2J(\text{PP})$ 6.54, $\mu\text{-PPh}_2$], 102.54 [d, $^2J(\text{PP})$ 6.54 Hz, $\mu\text{-PPhH}$]; *m/z* 661 (M^+) (Found: C 52.46, H 4.03, P 8.81; $\text{C}_{29}\text{H}_{26}\text{Mo}_2\text{O}_2\text{P}_2$ requires C 51.5, H 3.87, P 9.16%).

For 13. $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1822; NMR: ^1H , δ 8.32–7.15 [m, 15H, Ph], 6.41 [dd, $^1J(\text{PH})$ 337.6, $^2J(\text{PH})$ 1.2 Hz, 1H, PH], 5.02 [s, 5H, Cp], 4.91 [s, 5H, Cp]; ^{31}P , δ 172.19 [d, $^2J(\text{PP})$ 5.47, $\mu\text{-PPh}_2$], 95.95 [d, $^2J(\text{PP})$ 5.47 Hz, $\mu\text{-PPhH}$]; *m/z* 661 (M^+); microanalysis for **13** was not recorded.

(vii) Reaction of 4–6 with R_2AsCl

A solution of the metal anion (300 mg, 0.64 mmol **4**; 300 mg, 0.57 mmol **5**; 300 mg, 0.5 mmol **6**) in THF (60 ml) was cooled to -78°C and R_2AsCl (R = Me or Ph 0.9 equiv.) was added dropwise over 5 minutes. The resulting mixture was stirred for a further 1/2 h at -78°C during which time the solution colour changed from purple to a clear orange. The solution was then filtered through a silica pad and washed with a small amount of hexane. After removal of solvent *in vacuo* the residue was dissolved in the minimum CH_2Cl_2 and applied to the base of TLC plates.

For 4. Elution with 1:1 CH_2Cl_2 :hexane yielded a trace of starting material **1** and $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PH}_2)(\mu\text{-AsMe}_2)]$ **14** (249 mg, 68%) or $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PH}_2)(\mu\text{-AsPh}_2)]$ **17** (329 mg, 74%). Slow evaporation of a CH_2Cl_2 :hexane solution of **14** at 0°C yielded crystals suitable for an X-ray diffraction analysis.

14: $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1929(vs), 1857(s); NMR: ^1H , δ 5.30 [s, 10H, Cp], 2.22 [d, $^1J(\text{PH})$ 299.8 Hz, 2H, $\mu\text{-PH}_2$], 1.52 [s, 6H, AsCH_3]; ^{31}P , δ -249.44 [s, $\mu\text{-PH}_2$]; *m/z* 572 (M^+), 544 ($\text{M}^+ - \text{CO}$) (Found: C 33.38, H 3.05; $\text{AsC}_{16}\text{H}_{18}\text{Mo}_2\text{O}_4\text{P}$ requires C 33.34, H 3.15%).

17: $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 1956(m), 1945(vs), 1887(s), 1872(s); NMR: ^1H , δ 7.83–7.28 [m, 10H, Ph], 5.15 [s, 10H, Cp], 3.85 [d, $^1J(\text{PH})$ 355.6 Hz, 1H, PH]; ^{31}P , δ -240.04 [s, $\mu\text{-PH}_2$]; *m/z* 806 (M^+), 750 ($\text{M}^+ - 2\text{CO}$) (Found: C 45.64, H 3.29; $\text{AsC}_{26}\text{H}_{22}\text{Mo}_2\text{O}_4\text{P}$ requires C 44.58, H 3.17%).

For 5. Elution with 3:2 CH_2Cl_2 :hexane yielded a trace of starting material **2** and $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-AsMe}_2)]$ **15** (284 mg, 77%) or $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-AsPh}_2)]$ **18** (352 mg, 80%).

15. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 1952(m), 1938(vs), 1882(s), 1866(m); ^1H , δ 7.56–7.22 [m, 5H, Ph], 5.28 [s, 5H, Cp], 5.24 [s, 5H, Cp], 4.61 [d, $^1J(\text{PH})$ 309 Hz, 1H, PH], 1.58 [s, AsCH_3], 1.57 [s, AsCH_3]; ^{31}P , δ -199.53 [s, $\mu\text{-PPhH}$]; *m/z* 652 (M^+), 591 ($\text{M}^+ - 2\text{CO}$) (Found: C 39.21, H 3.34; $\text{AsC}_{22}\text{H}_{22}\text{Mo}_2\text{O}_4\text{P}_2$ requires C 40.5, H 3.40%).

18: $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 1957(s), 1942(vs), 1886(vs), 1867(s); NMR: ^1H , δ 7.8–7.2 [m, 15H, Ph], 5.47 [s, 5H, Cp], 5.42 [d,

$^1J(\text{PH})$ 316.4 Hz, 1H, PH], 4.96 [s, 5H, Cp]; ^{31}P , δ -157.5 [s, μ -PPhH]; m/z 775 (M^+), 719 ($\text{M}^+ - 2\text{CO}$) (Found: C 49.71, H 3.63; $\text{AsC}_{32}\text{H}_{26}\text{Mo}_2\text{O}_4\text{P}$ requires C 49.49, H 3.38%).

For 6. Elution with 3:2 CH_2Cl_2 :hexane yielded starting material **3** (18 mg, 6%) and $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsMe}_2)]$ **16** (257 mg, 71%) or a trace of starting material and $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsPh}_2)]$ **19** (313 mg, 74%).

16: $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 1946(m), 1936(vs), 1873(s), 1864(m); NMR: ^1H , δ 7.57–7.22 [m, 10H, Ph], 5.07 [s, 10H, Cp], 1.58 [s, 6H, AsCH_3]; ^{31}P , δ -120.64 [s, $\mu\text{-PPh}_2$]; m/z 724 (M^+), 696 ($\text{M}^+ - \text{CO}$), 670 ($\text{M}^+ - 2\text{CO}$) (Found: C 45.45, H 3.53; $\text{AsC}_{28}\text{H}_{26}\text{Mo}_2\text{O}_4\text{P}$ requires C 46.16, H 3.6%).

19: $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 1964(m), 1949(vs), 1881(s), 1867(m); NMR: ^1H , δ 7.72–7.10 [m, 20H, Ph], 4.95 [s, 10H, Cp]; ^{31}P , δ -120.37 [s, $\mu\text{-PPh}_2$]; m/z 820 ($\text{M}^+ - \text{CO}$), 795 ($\text{M}^+ - 2\text{CO}$), 767 ($\text{M}^+ - 3\text{CO}$) (Found: C 53.96, H 3.70; $\text{AsC}_{38}\text{H}_{30}\text{Mo}_2\text{O}_4\text{P}$ requires C 53.53, H 3.55%).

(viii) Thermolysis of 18 and 19

A solution of **18** or **19** (200 mg, 0.27 mmol **18**; 200 mg, 0.23 mmol **19**) in toluene (60 ml) was refluxed for 16 h during which time the solution colour turned from orange to a dark green. The solvent was removed *in vacuo* and the residue dissolved in the minimum CH_2Cl_2 and applied to the base of TLC plates.

For 18. Substantial decomposition occurred on the TLC plates and only one red product was obtained in trace yield. This is tentatively formulated by comparison of its colour and carbonyl stretching frequency as $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPhH})(\mu\text{-AsPh}_2)]$ **20**. $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1832.

For 19. Elution with 3:2 CH_2Cl_2 :hexane led to the isolation of 3 new complexes with decreasing R_f : $[\text{Cp}_2(\text{CO})_2\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsPh}_2)]$ **21**, *trans*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsPh}_2)]$ **22**, *cis*- $[\text{Cp}_2(\text{CO})(\text{O})\text{Mo}_2(\mu\text{-PPh}_2)(\mu\text{-AsPh}_2)]$ **23**.

21: $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1847(br, s); NMR: ^1H , δ 7.68–7.19 [m, 20H, Ph], 5.37 [s, 10H, Cp]; ^{31}P , δ 92.25 [s, $\mu\text{-PPh}_2$]; m/z 796 (M^+), 768 ($\text{M}^+ - \text{CO}$) (Found: C 53.87, H 3.67; $\text{AsC}_{36}\text{H}_{30}\text{Mo}_2\text{O}_2\text{P}$ requires C 54.28, H 3.8%).

22: $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1821(br, s); NMR: ^1H , δ 8.05–7.15 [m, 20H, Ph], 5.05 [d, $J(\text{PH})$ 1.47, 5H, Cp], 4.91 [d, $J(\text{PH})$ 1.13 Hz, 5H, Cp]; ^{31}P , δ 172.58 [s, $\mu\text{-PPh}_2$]; m/z 784 (M^+), 756 ($\text{M}^+ - \text{CO}$) (Found: C 53.48, H 3.83; $\text{AsC}_{35}\text{H}_{30}\text{Mo}_2\text{O}_2\text{P}$ requires C 53.58, H 3.86%).

23: $\tilde{\nu}_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ (CO) 1842(s); NMR: ^1H , δ 8.05–7.15 [m, 20H, Ph], 5.20 [d, $J(\text{PH})$ 0.2 Hz, 5H, Cp], 4.90 [s, 5H, Cp]; ^{31}P , δ 168.71; m/z 784 (M^+), 756 ($\text{M}^+ - \text{CO}$) (Found: C 53.61, H 3.91; $\text{AsC}_{35}\text{H}_{30}\text{Mo}_2\text{O}_2\text{P}$ requires C 53.58, H 3.86%).

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