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Synthesis, structural characterisation and reactivity of molybdenum half-sandwich complexes containing keto- and amido-phosphines

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Abstract

The keto-functionalised *N*-pyrrolyl phosphine ligand $PPh_2NC_4H_3\{C(O)CH_3\text{-}2\}$ $\mathbf{L^1}$ reacts with $[MoCl(CO)_3(\eta^5\text{-}C_5R_5)]$ (R = H, Me) to give $[MoCl(CO)_2(\mathbf{L^1}\text{-}\kappa^1P)(\eta^5\text{-}C_5R_5)]$ (R = H **1a**; Me **1b**). The phosphine ligands $PPh_2CH_2C(O)Ph$ ($\mathbf{L^2}$) and $PPh_2CH_2C(O)NPh_2$ ($\mathbf{L^3}$) react with $[MoCl(CO)_3(\eta^5\text{-}C_5R_5)]$ in an analogous manner to give the compounds $[MoCl(CO)_2(L\text{-}\kappa^1P)(\eta^5\text{-}C_5R_5)]$ (L = $\mathbf{L^2}$, R = H **2a**, Me **2b**; L = $\mathbf{L^3}$, R = H **3a**, Me **3b**). Compounds **1**–**3** react with $AgBF_4$ to give $[Mo(CO)_2(L\text{-}\kappa^2P,O)(\eta^5\text{-}C_5R_5)]BF_4$ (L = $\mathbf{L^1}$, R = H **4a**, Me **4b**; L = $\mathbf{L^2}$, R = H **5a**, Me **5b**; L = $\mathbf{L^3}$, R = H **6a**, Me **6b**) following displacement of chloride. The X-ray crystal structure of **4a** revealed a lengthening of both Mo–P and C=O bonds on co-ordination of the keto group. The lability of the co-ordinated keto or amido group has been assessed by addition of a range of phosphines to compounds **4**–**6**. Compound **4a** reacts with PMe_3, PMe_2Ph and $PMePh_2$ to give $[Mo(CO)_2(\mathbf{L^1}\text{-}\kappa^1P)(L)(\eta^5\text{-}C_5H_5)]BF_4$ (L = PMe_3 **7a**; PMe_2Ph **7b**; $PMePh_2$ **7c**) but does not react with PPh_3, **5a** reacts with PMe_2Ph, $PMePh_2$ and PPh_3 to give $[Mo(CO)_2(\mathbf{L^2}\text{-}\kappa^1P)(L)(\eta^5\text{-}C_5H_5)]BF_4$ (L = PMe_2Ph **8b**; $PMePh_2$ **8c**; PPh_3 **8d**), and **6a** reacts with PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3 to give $[Mo(CO)_2(\mathbf{L^3}\text{-}\kappa^1P)(L)(\eta^5\text{-}C_5H_5)]BF_4$ (L = PMe_3 **10a**; PMe_2Ph **10b**; $PMePh_2$ **10c**; PPh_3 **10d**). No reaction was observed for the pentamethylcyclopentadienyl compounds **4b**–**6b** with PMe_3, PMe_2Ph, $PMePh_2$ or PPh_3. These results are consistent with the displacement of the co-ordinated oxygen atom being influenced by the steric properties of the *P*,*O*-ligand, with PPh_3 displacing the keto group from $\mathbf{L^2}$ but not from the bulkier $\mathbf{L^1}$. In the reaction of $[Mo(CO)_2(\mathbf{L^2}\text{-}\kappa^2P,O)(\eta^5\text{-}C_5H_5)]BF_4$ (**5a**) with PMe_3 the phosphine does not displace the keto group, instead it acts as a base, with the only observed molybdenum-containing product being the enolate compound $[Mo(CO)_2\{PPh_2CH{=}C(O)Ph\text{-}\kappa^2P,O\}(\eta^5\text{-}C_5H_5)]$ **9**. Compound **9** can also be formed from the reaction of **2a** with BuLi or NEt_3, and a single crystal X-ray analysis has confirmed the enolate structure.

Keywords: Keto-phosphines; Amido-phosphines; Molybdenum; Half-sandwich compounds

1. Introduction

Bifunctional ligands containing both hard and soft donor atoms are of interest catalytically, in part through their potential for hemilability [1]. Ketophosphines such as $PPh_2CH_2C(O)Ph$ have attracted considerable interest for their ability to act as uni- or bidentate ligands and for the facile and reversible transformations between the co-ordination modes [2]. Although the chemistry of keto- and amido-phosphines with late transition metal centres has been well developed [3], the reactivity of these ligands with earlier transition metals has received far less attention. Recently, we reported the synthesis of the keto-functionalised *N*-pyrrolyl phosphine ligand $PPh_2NC_4H_3\{C(O)CH_3\text{-}2\}$ ($\mathbf{L^1}$) and the reaction of this ligand with $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ to form $[MoCl(CO)_2(\mathbf{L^1}\text{-}\kappa^1P)(\eta^5\text{-}C_5H_5)]$ (**1a**) [4]. Prior to this, the only previously reported crystal structure of a group 6 metal ketophosphine complex was of $[W(CO)_4(PPh_2OH)(\mathbf{L^2})]$ [$\mathbf{L^2}$ = $PPh_2CH_2C(O)Ph$], in which the β-ketophosphine has been formed in situ [5]. Accounts of molybdenum η^6-arene complexes with $\mathbf{L^2}$ and amide-derived ligands $PPh_2NRC(O)CH_3$ (R = H, Me) have also recently appeared [6], as has a report on molybdenum(III), -(IV) and -(V) half-sandwich complexes of the amidophosphine $Ph_2PCH_2C(O)NPh_2$, $\mathbf{L^3}$ [7].

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In this paper the molybdenum(II) chemistry of **1a** and related compounds incorporating $\mathbf{L^2}$ and $\mathbf{L^3}$ is developed, and the displacement of the co-ordinated keto or amido groups on reaction with phosphines investigated.

2. Results and discussion

On heating $[MoCl(CO)_3(\eta^5\text{-}C_5R_5)]$ (R = H or Me) at reflux for 6 h with one equivalent of $\mathbf{L^1}$, $\mathbf{L^2}$ or $\mathbf{L^3}$, the complexes $[MoCl(CO)_2(L)(\eta^5\text{-}C_5R_5)]$ (L = $\mathbf{L^1}$, R = H **1a**, Me **1b**; L = $\mathbf{L^2}$, R = H **2a**, Me **2b**; L = $\mathbf{L^3}$, R = H **3a**, Me **3b**) were formed in good yield (79–93%) as dark red or orange powders. Co-ordination of the phosphorus atom was generally accompanied by a significant downfield shift in $\delta(^{31}P)$ relative to the free ligands [$\Delta\delta = 56.4$–69.5 ppm], though for **1b** the shift is very small [$\Delta\delta = 2.4$ ppm]. Non-co-ordination of the oxygen donor was reflected in the small changes in ν(C=O) relative to the free ligands [$\Delta\nu$(C=O) = +15 to −14 cm^{-1}]. The value of $\Delta\delta(^{31}P)$ is usually a reliable indicator of coordination mode, so the chemical shift observed for **1b** is surprising and difficult to rationalise. However, the ^1H- and $^{13}C\{^1H\}$-NMR spectra, together with the IR spectrum, microanalysis and reactivity all suggest that the proposed structure is correct.

The crystal structure of complex **1a** demonstrated the *cis* (or *lat*) arrangement of ligands around the molybdenum centre [4], and spectroscopic evidence revealed that this orientation was also present in the other complexes **1**–**3**. Hence, two metal carbonyl resonances were observed in the $^{13}C\{^1H\}$-NMR spectra as doublets, with one having a $^2J_{CP}$ coupling constant significantly larger (18.2–31.4 Hz) than the other (≤ 8.2 Hz), while in the ^1H-NMR spectra for complexes **2-3**, the methylene protons were seen as a pair of mutually coupled doublet of doublets, indicating their inequivalence. The reaction of $\mathbf{L^3}$ with $[MoCl(CO)_3(\eta^5\text{-}C_5Me_5)]$ to give a *P*-co-ordinated complex contrasts with the observation that $[Mo(\mu\text{-}Cl)_2(\eta^5\text{-}C_5Me_5)]_2$ does not react with $\mathbf{L^3}$ [7].

Addition of one equivalent of $AgBF_4$ to dichloromethane solutions of complexes **1**–**3** resulted in the precipitation of AgCl and the formation of the complexes $[Mo(CO)_2(L\text{-}\kappa^2P,O)(\eta^5\text{-}C_5R_5)]BF_4$ (L = $\mathbf{L^1}$, R = H **4a**, Me **4b**; L = $\mathbf{L^2}$, R = H **5a**, Me **5b**; L = $\mathbf{L^3}$, R = H **6a**, Me **6b**) in good yield (83–97%) and these reactions are summarised in Scheme 1. Co-ordination of the carbonyl group of the phosphines was indicated by the large decrease in ν(C=O) from that of the κ^1P-co-ordinated ligands ($\Delta\nu$(C=O) = −97 to −122 cm^{-1}). The coupling patterns observed for the metal carbonyl peaks in the $^{13}C\{^1H\}$-NMR spectra for complexes **4**–**6** were similar to those observed for complexes **1**–**3**, suggesting the retention of the *cis*-conformation. In contrast, the reaction of $[Mo(\mu\text{-}Cl)_2(\eta^5\text{-}C_5H_5)]_2$ with $\mathbf{L^3}$ leads to both the *cis* and *trans* isomers of $[MoCl_2(\mathbf{L^3}\text{-}\kappa^2P,O)(\eta^5\text{-}C_5H_5)]$ [7].

The identity of **4a** was confirmed by X-ray crystallography analysis, and the structure of the cation is shown in Fig. 1 with selected bond distances and angles given in Table 1. The complex cation adopts a *pseudo*-square pyramidal metal geometry, with the *cis* carbonyls, oxygen and phosphorus atoms forming the base of the pyramid, and the cyclopentadienyl ring the apex. The keto C=O bond length of 1.251(3) Å is longer than that observed in both the free ligand $\mathbf{L^1}$ and in complex

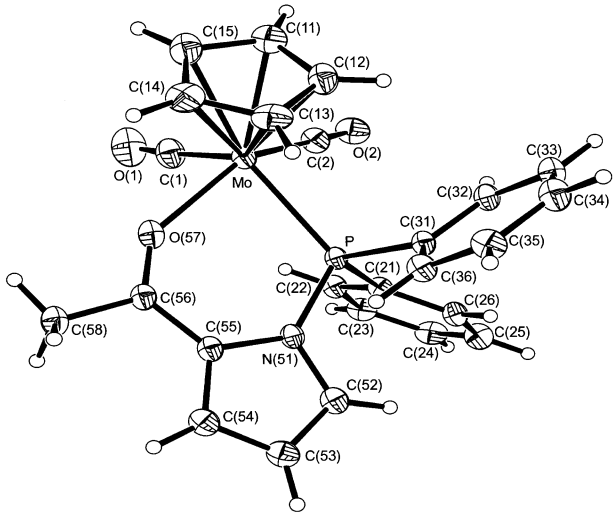
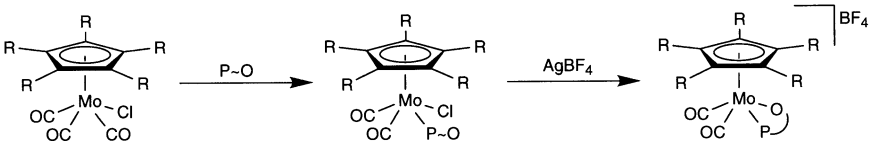


Fig. 1. Structure of the cation present in $[Mo(CO)_2(\mathbf{L^1}\text{-}\kappa^2P,O)(\eta^5\text{-}C_5H_5)]BF_4$ (**4a**) with thermal ellipsoids shown at the 30% probability level.



1a P~O = $\mathbf{L^1}$, R = H
1b P~O = $\mathbf{L^1}$, R = Me
2a P~O = $\mathbf{L^2}$, R = H
2b P~O = $\mathbf{L^2}$, R = Me
3a P~O = $\mathbf{L^3}$, R = H
3b P~O = $\mathbf{L^3}$, R = Me

4a P~O = $\mathbf{L^1}$, R = H
4b P~O = $\mathbf{L^1}$, R = Me
5a P~O = $\mathbf{L^2}$, R = H
5b P~O = $\mathbf{L^2}$, R = Me
6a P~O = $\mathbf{L^3}$, R = H
6b P~O = $\mathbf{L^3}$, R = Me

Scheme 1.

Table 1
Selected bond lengths (Å) and bond angles (°) for $[Mo(CO)_2(\mathbf{L}^1\text{-}\kappa^2P,O)(\eta^5\text{-}C_5H_5)]BF_4$ (**4a**) and the equivalent parameters for **1a** where relevant [4]

	4a	1a
Bond lengths		
Mo–C(1)	1.993(3)	1.961(5)
Mo–C(2)	1.978(3)	1.969(6)
Mo–P	2.4399(6)	2.5176(16)
Mo–O(57)	2.1619(17)	
P–N(51)	1.733(2)	1.748(4)
N(51)–C(52)	1.383(3)	1.383(7)
N(51)–C(55)	1.406(3)	1.407(6)
C(52)–C(53)	1.369(4)	1.355(8)
C(53)–C(54)	1.395(4)	1.395(8)
C(54)–C(55)	1.387(4)	1.366(8)
C(55)–C(56)	1.427(3)	1.451(7)
C(56)–O(57)	1.251(3)	1.222(7)
C(56)–C(58)	1.505(3)	1.495(7)
Bond angles		
P–Mo–O(57)	83.61(5)	
P–Mo–C(1)	117.29(9)	111.62(16)
P–Mo–C(2)	78.06(7)	77.86(16)
C(1)–Mo–C(2)	77.55(11)	76.0(2)
C(1)–Mo–O(57)	79.57(10)	
C(2)–Mo–O(57)	139.64(9)	

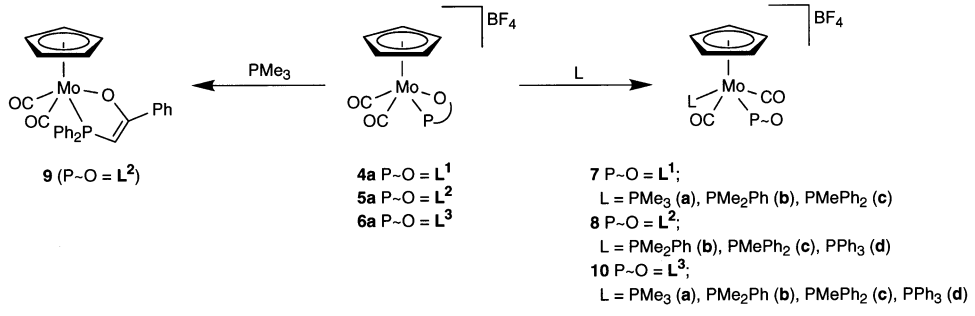
1a [1.216(2) and 1.222(6) Å, respectively [4]], consistent with a reduction in bond order upon co-ordination. The P–N bond length of 1.733(2) Å is similar to that observed in **1a** within experimental error [1.748(4) Å], but shorter than in the free phosphine $\mathbf{L}^1$ [1.7637(14) Å]. The sum of angles around the nitrogen atom in **4a** is 360° as in both $\mathbf{L}^1$ and **1a**. The bite angle in **4a** is 83.61(5)°, which is close to that observed for the phosphine–phosphine oxide ligand $PEt_2CH_2CH_2P(O)Et_2$ which also forms a six-membered chelate ring around molybdenum [83.0(2)°] [8].

Complexes **4a** and **5a** were also prepared by addition of $HBF_4{\cdot}OEt_2$ and the appropriate phosphine to $[Mo(CH_3)(CO)_3(\eta^5\text{-}C_5H_5)]$. Reaction of complexes **4**–**6** with NEt_3BzCl led to re-formation of complexes **1**–**3**, hence the chloride anion is able to displace the co-ordinated keto or amido group.

The lability of the co-ordinated keto- or amido-groups in complexes **4**–**6** was also probed by the investigation of the reactions between these complexes and tertiary phosphines. Each of the complexes **4**–**6** was reacted with the phosphines from the series PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3 which span a range of steric and electronic properties, and the reactions are summarised in Scheme 2.

Complex **4a** was observed to react with PMe_3, PMe_2Ph and $PMePh_2$ to give the complexes $[Mo(CO)_2(L\text{-}\kappa^1P)(\mathbf{L}^1\text{-}\kappa^1P)(\eta^5\text{-}C_5H_5)]BF_4$ [L = PMe_3 **7a**, PMe_2Ph **7b**, $PMePh_2$ **7c**] as orange oils. The non-co-ordination of the keto group was indicated by the return of the ν(C=O) band to a frequency similar to that observed for the free ligand. The $^{13}C\{^1H\}$-NMR spectra showed one environment for the carbonyl ligands in all cases, in contrast to complexes **1**–**6**, which suggested that **7** exists in the *trans* (or *diag*) conformation. This resonance was observed as a pseudo-triplet, due to the similar magnitudes of the two $^2J_{CP}$ coupling constants. The *trans* orientation was also supported by the ^1H-NMR spectrum for **7b**, in which the two methyl groups on the PMe_2Ph ligand were observed to be equivalent. In contrast to these reactions, addition of PPh_3 to **4a** led to no reaction, even after 14 days.

Complex **5a** was observed to react with PMe_2Ph, $PMePh_2$ and PPh_3 to give the complexes $[Mo(CO)_2(L\text{-}\kappa^1P)(\mathbf{L}^2\text{-}\kappa^1P)(\eta^5\text{-}C_5H_5)]BF_4$ [L = PMe_2Ph **8b**, $PMePh_2$ **8c**, PPh_3 **8d**] as red oils. IR and NMR spectroscopic data are consistent with formation of the *trans* isomer. The reaction with PMe_3 did not give $[Mo(CO)_2(PMe_3)(\mathbf{L}^2\text{-}\kappa^1P)(\eta^5\text{-}C_5H_5)]BF_4$, as anticipated, but instead the neutral complex $[Mo(CO)_2\{PPh_2CH{=}C(O)Ph\text{-}\kappa^2P,O\}(\eta^5\text{-}C_5H_5)]$ **9**. The identity of **9** was confirmed spectroscopically and by a single crystal analysis, as detailed later. The amidophosphine complex **6a** reacted with PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3 to give the complexes $[Mo(CO)_2(L\text{-}\kappa^1P)(\mathbf{L}^3\text{-}\kappa^1P)(\eta^5\text{-}C_5H_5)]BF_4$ [L = PMe_3 **10a**, L = PMe_2Ph **10b**, $PMePh_2$ **10c**, PPh_3 **10d**] as red or orange oils, again with *trans* orientation of the phosphines. However, the reactions were all significantly slower than those observed for the $\mathbf{L}^2$ complexes, with the reactions to form **10a–c** taking 7



Scheme 2.

days to reach completion, compared with 18 h for **8b**–**c**. Both the reactions of **4a** and **5a** with PPh_3 were considerably slower than those with the other tertiary phosphines, taking 7 and 14 days to reach completion, to give complexes **8d** and **10d**, respectively.

In contrast to these observations on the reactivity of the cyclopentadienyl complexes **4a**, **5a** and **6a**, no reaction was observed on addition of any of the same range of tertiary phosphines to the pentamethylcyclopentadienyl complexes **4b**, **5b** and **6b**. After 14 days the only species observed in the $^{31}P\{^1H\}$- and ^1H-NMR spectra were starting materials.

The reaction of $[Mo(CO)_2(L\text{-}\kappa^2P,O)(\eta^5\text{-}C_5R_5)]^+$ with a 2-electron donor L′ to give $[Mo(CO)_2(L\text{-}\kappa^1P)(L')(\eta^5\text{-}C_5R_5)]^+$ is likely to occur via a 16-electron intermediate $[Mo(CO)_2(L\text{-}\kappa^1P)(\eta^5\text{-}C_5R_5)]^+$, present in solution as a minor component in equilibrium with $[Mo(CO)_2(L\text{-}\kappa^2P,O)(\eta^5\text{-}C_5R_5)]^+$. Although there is no direct evidence for this intermediate, ^{31}P magnetisation transfer experiments suggest that the phosphite exchange reaction of $[Mo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}PhC_2Ph\}(\eta^5\text{-}C_5H_5)]^+$ occurs via a 16-electron intermediate formed by a change in the bonding mode of the alkyne from $\eta^2(4e)$ to $\eta^2(2e)$ [9].

The observation of no reaction with the pentamethylcyclopentadienyl complexes **4b**, **5b** and **6b** suggests the reaction of this intermediate with L′ is sterically controlled, with the bulky pentamethylcyclopentadienyl group preventing attack when L′ is a phosphine, but allowing it when L′ is the smaller chloride. This is also supported by the longer reaction times required by PPh_3 in comparison with the other phosphines used, and by the faster reactions observed for the β-ketophosphine complex **5a** in comparison with the *N*-pyrrolyl ketophosphine complex **4a** and the β-amidophosphine complex **6a**, which is consistent with the smaller size of $\mathbf{L^2}$ versus $\mathbf{L^1}$ and $\mathbf{L^3}$. The observed *trans* orientation of the phosphine ligands in the products from these reactions also serves to reduce the steric interactions between the bulky ligands. The Cambridge Structural Database [10] reveals that of the six structures known for the cations $[M(CO)_2P^1P^2(\eta^5\text{-}C_5R_5)]^+$, where M is a Group 6 metal, P^1 and P^2 are phosphines or phosphites, and R = H or Me, five exist as the *trans* isomer. The only example of the *cis* orientation is for $[Cr(CO)_2\{P(OMe)_3\}_2(\eta^5\text{-}C_5Me_5)]BF_4$ [11] where both *cis* and *trans* structural isomers were formed together.

In contrast to the addition reactions observed with other tertiary phosphines, complex **5a** is deprotonated by PMe_3 to give $[Mo(CO)_2\{PPh_2CH{=}C(O)Ph\text{-}\kappa^2P,O\}(\eta^5\text{-}C_5H_5)]$ (**9**). Formation of the enolate group is indicated by the low value for the carbonyl stretching frequency [$\nu(C\cdots C{+}C\cdots O) = 1460\ cm^{-1}$, $\Delta\nu = -98\ cm^{-1}$ relative to **5a**]. The two inequivalent methylene protons observed for **5a** were no longer present in the ^1H-NMR spectrum, instead only a doublet ($^2J_{HP} = 1.2$ Hz) integrating to one proton was observed.

The structure of **9** was confirmed by a single crystal X-ray structural analysis. The molecular structure is shown in Fig. 2, with selected bond lengths and angles given in Table 2. The complex adopts a *pseudo*-square pyramidal metal geometry, with the *cis* carbonyls, oxygen and phosphorus atoms forming the base of the pyramid, and the cyclopentadienyl ring the apex. The single proton on the carbon atom C(9) was readily located during the refinement. Both the C–O and C=C bond distances [1.319(5) and 1.372(5) Å, respectively] support the description of **9** as an enolate, and are similar to those parameters observed in other compounds containing $[PPh_2CH{=}C(O)Ph]^-$ [3]. Formation of enolate compounds from the reaction of co-ordinated $\mathbf{L^2}$ with base are well-established in later transition metal chemistry, and the molybdenum(II) dimer $[Mo(\eta^3\text{-}C_3H_5)(\eta^6\text{-}C_6H_6)(\mu\text{-}Cl)]_2$ reacts with $\mathbf{L^2}$ in ethanol to

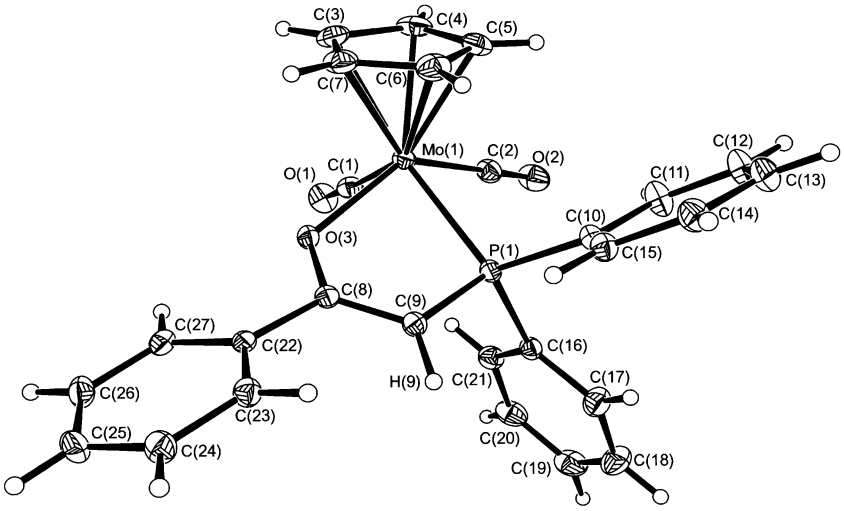


Fig. 2. Molecular structure of $[Mo(CO)_2\{PPh_2CH{=}C(O)Ph\text{-}\kappa^2P,O\}(\eta^5\text{-}C_5H_5)]$ (**9**) with thermal ellipsoids shown at the 30% probability level.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Mo(CO)_2\{PPh_2CH{=}C(O)Ph\text{-}\kappa^2P,O\}(\eta^5\text{-}C_5H_5)]$ (**9**)

Bond lengths	
Mo(1)–P(1)	2.4475(10)
Mo(1)–O(3)	2.151(2)
Mo(1)–C(1)	1.977(4)
Mo(1)–C(2)	1.974(4)
P(1)–C(9)	1.765(4)
C(8)–C(9)	1.372(5)
C(8)–O(3)	1.319(5)
Bond angles	
P(1)–Mo(1)–O(3)	76.54(7)
P(1)–Mo(1)–C(1)	114.62(12)
P(1)–Mo(1)–C(2)	78.77(12)
C(1)–Mo(1)–C(2)	75.43(17)
C(1)–Mo(1)–O(3)	84.22(13)
C(2)–Mo(1)–O(3)	137.53(17)

give enolate complexes [6a]. In addition to formation from the reaction of **5a** with PMe_3, compound **9** can also be formed using a more traditional base such as BuLi or NEt_3. The deprotonation reaction is reversible, and reaction of **9** with $HBF_4{\cdot}OEt_2$ leads to the re-formation of **5a**. Neither **4a** nor **6a** react with base to give analogous compounds to **9** — in these cases multiple intractable products resulted from the reactions.

3. Experimental

All experiments were performed in an atmosphere of dry, oxygen-free nitrogen using standard Schlenk line techniques. Solvents were dried by conventional methods and distilled under nitrogen prior to use. The complexes $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ [12] and $[MoCl(CO)_3(\eta^5\text{-}C_5Me_5)]$ [13], and the ligands $PPh_2NC_4H_3\{C(O)Me\text{-}2\}$ [4], $PPh_2CH_2C(O)Ph$ [3a] and $PPh_2CH_2C(O)NPh_2$ [14] were prepared by literature methods. Infrared spectra were recorded on a Nicolet Nexus FT-IR spectrometer using NaCl solvent cells. NMR spectra were recorded using JEOL JNM-EX 270 (270 MHz) or Varian Mercury (400 MHz) spectrometers, and were referenced internally to the solvent (^{13}C and ^{1}H), or externally to 85% H_3PO_4 (^{31}P). Microanalyses were performed by the University of Bath service. A number of the compounds could only be isolated as oils, for which satisfactory microanalyses could not be obtained. ^{13}C and ^{31}P resonances were observed as singlets unless otherwise stated.

3.1. Preparation of $[MoCl(CO)_2(L\text{-}\kappa^1P)(\eta^5\text{-}C_5R_5)]$ ($L = \boldsymbol{L^1}$, $R = H$ **1a**, *Me* **1b**; $L = \boldsymbol{L^2}$, $R = H$ **2a**, *Me* **2b**; $L = \boldsymbol{L^3}$, $R = H$ **3a**, *Me* **3b**)

$[MoCl(CO)_3(\eta^5\text{-}C_5R_5)]$ (200 mg) and one equivalent of L were dissolved in hexane (20 ml). The solution was brought to reflux for 6 h resulting in the formation of a red precipitate. This was separated by filtration, the volatiles were removed in vacuo and the residue recrystallised from dichloromethane–toluene to give the product as a dark red powder.

1a: Yield 89%. Anal. Found (Calc. for $C_{25}H_{21}ClMoNO_3P$): C 54.9 (55.0), H 3.94 (3.88), N 2.64 (2.57)%. ^{1}H-NMR ($CDCl_3$): δ 7.72–7.38 [m, 10H, Ph], 7.20 [m, 1H, pyr], 6.46 [m, 1H, pyr], 6.21 [m, 1H, pyr], 5.61 [s, 5H, C_5H_5], 2.31 [s, 3H, Me]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 254.2 [d, M-CO, $^2J_{PC} = 31.4$ Hz], 242.9 [d, M–CO, $^2J_{PC} < 1$ Hz], 185.5 [C=O], 135.2–128.0 [m, Ph/pyr], 96.1 [C_5H_5], 26.0 [Me]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 112.2. ν_{max} (CH_2Cl_2): ν(CO) 1970, 1888; ν(C=O) 1654 cm^{-1}.

1b: Yield 79%. Anal. Found (Calc. for $C_{30}H_{31}ClMoNO_3P{\cdot}1/4CH_2Cl_2$): C 57.5 (57.0), H 4.92 (4.98), N 2.39 (2.20)%. ^{1}H-NMR ($CDCl_3$): δ 7.39–7.22 [m, 10H, Ph], 7.12 [m, 1H, pyr], 6.39 [m, 1H, pyr], 6.22 [m, 1H, pyr], 2.41 [s, 3H, Me], 1.94 [s, 15H, C_5Me_5]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 246.3 [d, M–CO, $^2J_{PC} = 30.5$ Hz], 227.4 [d, M–CO, $^2J_{PC} < 5$ Hz], 188.1 [C=O], 132.8–124.8 [m, Ph/pyr], 108.8 [C_5Me_5], 25.7 [Me], 10.7 [$C_5\mathit{Me}_5$]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 58.6. ν_{max} (CH_2Cl_2): ν(CO) 1964, 1880; ν(C=O) 1658 cm^{-1}.

2a: Yield 91%. Anal. Found (Calc. for $C_{27}H_{22}ClMoO_3P$): C 57.8 (58.2), H 3.98 (3.98)%. ^{1}H-NMR ($CDCl_3$): δ 7.78–7.28 [m, 10H, Ph], 5.37 [s, 5H, C_5H_5], 4.41 [dd, 1H, CH_2, $^2J_{HH} = 15.6$, $^2J_{HP} = 9.9$ Hz], 4.14 [dd, 1H, CH_2, $^2J_{HH} = 15.6$, $^2J_{HP} = 7.9$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 256.8 [d, M–CO, $^2J_{PC} = 29.5$ Hz], 243.6 [d, M–CO, $^2J_{PC} = 8.2$ Hz], 195.2 [d, C=O, $^1J_{PC} = 5.7$ Hz], 137.1–128.2 [m, Ph], 95.2 [C_5H_5], 36.4 [d, CH_2, $^1J_{PC} = 20.4$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 48.2. ν_{max} (CH_2Cl_2): ν(CO) 1970, 1888; ν(C=O) 1656 cm^{-1}.

2b: Yield 85%. ^{1}H-NMR ($CDCl_3$): δ 7.67–7.18 [m, 15H, Ph], 4.64 [dd, 1H, CH_2, $^2J_{HH} = 14.9$, $^2J_{HP} = 8.1$ Hz], 3.73 [dd, 1H, CH_2, $^2J_{HH} = 14.9$, $^2J_{HP} = 7.0$ Hz], 1.70 [s, 15H, C_5Me_5]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 259.0 [d, M–CO, $^2J_{PC} = 27.1$ Hz], 246.2 [d, M–CO, $^2J_{PC} = 5.4$ Hz], 195.2 [d, C=O, $^2J_{PC} = 8.1$ Hz], 137.0–127.6 [m, Ph], 106.3 [C_5Me_5], 34.1 [d, CH_2, $^1J_{PC} = 13.6$ Hz], 10.0 [$C_5\mathit{Me}_5$]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 45.4. ν_{max} (CH_2Cl_2): ν(CO) 1960, 1879; ν(C=O) 1656 cm^{-1}.

3a: Yield 93%. Anal. Found (Calc. for $C_{33}H_{27}ClMoNO_3P{\cdot}1/3CH_2Cl_2$): C 59.1 (59.2) H 4.07 (4.12), N 2.02 (2.07)%. ^{1}H-NMR ($CDCl_3$): δ 7.74–7.18 [m, 15H, Ph], 5.37 [s, 5H, C_5H_5], 3.51 [dd, 1H, CH_2, $^2J_{HH} = 16.0$, $^2J_{HP} = 11.7$ Hz], 3.33 [dd, 1H, CH_2, $^2J_{HH} = 16.0$, $^2J_{HP} = 6.9$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 257.5 [d, M–CO, $^2J_{PC} = 19.5$ Hz], 243.7 [d, M–CO, $^2J_{PC} = 6.7$ Hz], 167.3 [C=O], 142.4–126.5 [m, Ph], 95.6 [C_5H_5], 35.7 [d, CH_2, $^1J_{PC} = 25.7$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 52.1. ν_{max} (CH_2Cl_2): ν(CO) 1964, 1872; ν(C=O) 1666 cm^{-1}.

3b: Yield 79%. Anal. Found (Calc. for $C_{38}H_{37}ClMoNO_3P{\cdot}1/4CH_2Cl_2$): C 62.2 (62.1) H 5.23 (5.11), N 1.90 (1.89)%. ^{1}H-NMR ($CDCl_3$): δ 7.73–7.09

[m, 15H, Ph], 3.84 [dd, 1H, CH_2, $^2J_{HH} = 16.0$, $^2J_{HP} = 8.0$ Hz], 3.29 [dd, 1H, CH_2, $^2J_{HH} = 16.0$, $^2J_{HP} = 6.5$ Hz], 1.77 [s, 15H, C_5Me_5]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 258.6 [d, M–CO, $^2J_{PC} = 18.2$ Hz], 245.8 [d, M–CO, $^2J_{PC} = 4.8$ Hz], 167.4 [C=O], 121.3–110.6 [m, Ph], 96.9 [C_5Me_5] 31.9 [d, CH_2, $^1J_{PC} = 26.0$ Hz], 9.8 [Me]. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 52.1. ν_{max} (CH_2Cl_2): ν(CO) 1944, 1860; ν(C=O) 1669 cm^{-1}.

3.2. Preparation of [Mo(CO)$_2$(L-κ^2P,O)(η^5-C$_5$R$_5$)] (L = **L**^{1}, R = H **4a**, Me **4b**; L = **L**^{2}, R = H **5a**, Me **5b**; L = **L**^{3}, R = H **6a**, Me **6b**)

One equivalent of $AgBF_4$ was added to a solution of $[MoCl(CO)_2(L\text{-}P)(\eta^5\text{-}C_5R_5)]$ in dichloromethane (20 mL). The mixture was stirred with the exclusion of light for 30 min–2 h, resulting in the formation of AgCl. The solution was filtered through Celite, the solvent removed in vacuo and the residue recrystallised from dichloromethane–toluene to give a dark red powder.

4a: Yield 97%. Anal. Found (Calc. for $C_{25}H_{21}BF_4MoNO_3P \cdot 1/4CH_2Cl_2$): C 49.2 (49.0), H 3.73 (3.50), N 2.17 (2.26)%. ^{1}H-NMR ($CDCl_3$): δ 7.67–7.45 [m, 11H, Ph/pyr], 7.29 [m, 1H, pyr], 6.56 [m, 1H, pyr], 5.55 [s, 5H, C_5H_5], 2.59 [s, 3H, Me]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 248.0 [d, M–CO, $^2J_{PC} = 30.0$ Hz], 240.0 [d, M–CO, $^2J_{PC} = 3.2$ Hz], 199.3 [d, C=O, $^3J_{PC} = 6.8$ Hz], 135.9–129.7 [m, Ph/pyr], 116.3, [pyr], 97.7 [C_5H_5], 27.8 [Me]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 114.6. ν_{max} (CH_2Cl_2): ν(CO) 1997, 1928; ν(C=O) 1553 cm^{-1}.

4b: Yield 83%. ^{1}H-NMR ($CDCl_3$): δ 7.85–7.56 [m, 10H, Ph], 7.20 [m, 1H, pyr], 7.16 [m, 1H, pyr] 6.59 [m, 1H, pyr], 2.79 [s, 3H, Me], 1.66 [s, 15H, C_5Me_5]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 244.4 [d, M–CO, $^2J_{PC} = 28.0$ Hz], 225.9 [d, M–CO, $^2J_{PC} < 2$ Hz], 202.7 [d, C=O, $^2J_{PC} = 8.1$ Hz], 135.1–123.8 [m, Ph/pyr], 109.4 [C_5Me_5], 27.3 [Me], 10.6 [C_5Me_5]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 108.9. ν_{max} (CH_2Cl_2): ν(CO) 1990, 1916; ν(C=O) 1558 cm^{-1}.

5a: Yield 83%. ^{1}H-NMR ($CDCl_3$): δ 7.98–7.33 [m, 15H, Ph], 5.53 [s, 5H, C_5H_5] 5.00 [dd, 1H, CH_2, $^2J_{HH} = 18.3$, $^2J_{HP} = 9.0$ Hz], 3.73 [dd, 1H, CH_2, $^2J_{HH} = 18.3$, $^2J_{HP} = 12.3$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 247.0 [d, M–CO, $^2J_{PC} = 29.7$ Hz], 241.9 [d, M–CO, $^2J_{PC} < 2$ Hz], 216.1 [d, C=O, $^2J_{PC} = 10.4$ Hz], 137.2–128.9 [m, Ph], 96.1 [d, C_5H_5, $^2J_{PC} = 8.3$ Hz], 44.7 [d, CH_2, $^1J_{PC} = 28.3$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 72.5. ν_{max} (CH_2Cl_2): ν(CO) 1987, 1912; ν(C=O) 1556 cm^{-1}.

5b: Yield 95%. ^{1}H-NMR ($CDCl_3$): δ 8.15–7.41 [m, 15H, Ph], 5.00 [dd, 1H, CH_2, $^2J_{HH} = 19.0$, $^2J_{HP} = 8.2$ Hz], 4.29 [dd, 1H, CH_2, $^2J_{HH} = 19.0$, $^2J_{HP} = 11.2$ Hz], 1.70 [s, 15H, C_5Me_5]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 251.3 [d, M–CO, $^2J_{PC} = 27.2$ Hz], 245.8 [d, M–CO, $^2J_{PC} < 2$ Hz], 214.8 [d, C=O, $^2J_{PC} = 12.5$ Hz], 133.6–128.0 [m, Ph], 108.9 [C_5Me_5], 44.5 [d, CH_2, $^1J_{PC} = 26.5$ Hz], 10.2 [C_5Me_5]. $^{31}P\{^1H\}$ ($CDCl_3$); δ 65.6. ν_{max} (CH_2Cl_2): ν(CO) 1980, 1905; ν(C=O) 1559 cm^{-1}.

6a: Yield 88%. Anal. Found (Calc. for $C_{33}H_{26}BF_4MoNO_3P \cdot CH_2Cl_2$): C 51.7 (52.1), H 3.98 (3.60), N 1.74 (1.79)%. ^{1}H-NMR ($CDCl_3$): δ 7.61–7.10 [m, 20H, Ph], 5.51 [s, 5H, C_5H_5], 4.42 [dd, 1H, CH_2, $^2J_{HH} = 16.0$, $^2J_{HP} = 8.6$ Hz], 3.04 [dd, 1H, CH_2, $^2J_{HH} = 16.0$, $^2J_{HP} = 12.5$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 250.2 [d, M–CO, $^2J_{CP} = 19.8$ Hz], 242.4 [d, M–CO, $^2J_{CP} < 2$ Hz], 179.6 [d, C=O, $^2J_{CP} = 8.8$ Hz], 141.8–125.4 [m, Ph], 95.8 [C_5H_5], 31.7 [d, CH_2, $^2J_{CP} = 16.2$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 65.7. ν_{max} (CH_2Cl_2): ν(CO) 1980, 1902; ν(C=O) 1542 cm^{-1}.

6b: Yield 93%. ^{1}H-NMR ($CDCl_3$): δ 7.59–7.23 [m, 20H, Ph], 4.23 [dd, 1H, CH_2, $^2J_{HH} = 15.1$, $^2J_{HP} = 8.6$ Hz], 2.94 [dd, 1H, CH_2, $^2J_{HH} = 15.1$, $^2J_{HP} = 12.3$ Hz], 1.60 [s, 15H, C_5Me_5]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 251.1 [d, M–CO, $^2J_{PC} = 18.6$ Hz], 244.3 [d, M–CO, $^2J_{PC} < 2$Hz], 178.8 [d, C=O, $^2J_{PC} = 10.6$ Hz], 120.4–109.9 [m, Ph], 98.2 [C_5Me_5], 31.5 [d, CH_2, $^1J_{PC} = 15.9$ Hz], 10.5 [C_5Me_5]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 57.1. ν_{max} (CH_2Cl_2): ν(CO) 1963, 1888; ν(C=O) 1547 cm^{-1}.

3.3. Preparation of [Mo(CO)$_2$(L)(**L**^{1}-κ^1P)(η^5-C$_5$H$_5$)][BF$_4$] (L = PMe$_3$ **7a**, PMe$_2$Ph **7b**, PMePh$_2$ **7c**)

Typical preparation (**7c**): $PMePh_2$ (21 μl, 0.110 mmol) was added to a solution of **4a** (61 mg, 0.102 mmol) in CH_2Cl_2 (15ml) and the solution stirred at room temperature (r.t.) for 48 h. The product was isolated as an orange oil by addition of hexane to a dichloromethane solution.

7a: Yield 85%. ^{1}H-NMR ($CDCl_3$): δ 7.65–7.20 [m, 20H, Ph], 7.30 [m, 1H, pyr], 7.04 [m, 1H, pyr], 6.44 [m, 1H, pyr], 5.22 [s, 5H, C_5H_5], 2.16 [s, 3H, Me], 1.66 [d, 9H, PMe_3, $^2J_{HP} = 10.3$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): 231.1 [t, M–CO, $^2J_{CP} = 29.6$ Hz], 184.4 [C=O], 135.7–127.3 [m, Ph/pyr], 124.8 [pyr], 111.0 [d, pyr, $J_{CP} = 7.6$ Hz], 93.5 [C_5H_5], 25.5 [Me], 18.1 [d, PMe_3, $^1J_{CP} = 35.2$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 125.1 [d, $PPh_2NC_4H_3C(O)Me$, $^2J_{PP} = 24$ Hz], 20.3 [d, PMe_3, $^2J_{PP} = 24$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1972, 1896; ν(C=O) 1664 cm^{-1}.

7b: Yield 86%. ^{1}H-NMR ($CDCl_3$): δ 7.68–7.28 [m, 25H, Ph], 7.15 [m, 1H, pyr], 6.96 [m, 1H, pyr], 6.42 [m, 1H, pyr], 5.14 [s, 5H, C_5H_5], 2.16 [s, 3H, Me], 1.96 [d, 6H, PMe_2Ph, $^2J_{HP} = 9.9$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 231.2 [t, $^2J_{CP} = 29.2$ Hz], 184.7 [C=O], 136.5–125.9 [m, Ph/pyr], 112.3 [d, pyr, $J_{CP} = 9.6$ Hz], 96.3 [C_5H_5], 25.8 [Me], 18.8 [d, Me, $^1J_{CP} = 34.3$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 127.7 [d, $PPh_2NC_4H_3C(O)Me$, $^2J_{PP} = 21$ Hz], 26.2 [d, PMe_2Ph, $^2J_{PP} = 21$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1974, 1898; ν(C=O) 1669 cm^{-1}.

7c: Yield 90%. ^{1}H-NMR ($CDCl_3$): δ 7.75–7.22 [m, 20H, Ph], 6.60 [m, 1H, pyr], 5.21 [s, 5H, C_5H_5], 2.21 [d, 3H, PCH_3, $^2J_{HP} = 9.4$ Hz], 2.05 [s, 3H, CH_3]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 230.8 [t, $^2J_{CP} = 29.2$ Hz] 185.1 [C=O], 137.9 [d, pyr, $J_{CP} = 12.4$ Hz], 133.9–128.2 [m, Ph/pyr], 126.6 [pyr], 112.6 [d, pyr, $J_{CP} = 9.5$ Hz], 96.1 [C_5H_5], 25.7

[Me], 19.8 [d, Me, $^1J_{CP} = 34.8$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 122.5 [d, $Ph_2PNC_4H_3C(O)Me$, $^2J_{PP} = 21$ Hz], 40.6 [d, PPh_2Me, $^2J_{PP} = 21$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1978, 1900; ν(C=O) 1669 cm^{-1}.

3.4. Preparation of [Mo(CO)$_2$(L)(**L**^{2}-κ^1P)(η^5-C$_5$H$_5$)][BF$_4$] (L = PMe$_2$Ph **8b**, PMePh$_2$ **8c**, PPh$_3$ **8d**)

Typical preparation (**8c**): $PMePh_2$ (23 μl, 0.114 mmol) was added to a solution of **5a** (68 mg, 0.112 mmol) in dichloromethane (15 ml) and the solution stirred at r.t. for 18 h. The product was isolated as an red oil by addition of hexane to a dichloromethane solution.

8b: Yield 88%. ^{1}H-NMR ($CDCl_3$): δ 7.79–7.35 [m, 25H, Ph], 5.28 [s, 5H, C_5H_5] 4.33 [d, 2H, CH_2, $^2J_{HP} = 8.6$ Hz], 2.06 [d, 6H, Me, $^2J_{HP} = 9.0$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 234.3 [t, M–CO, $^2J_{CP} = 27.6$ Hz], 193.0 [d, C=O, $^1J_{CP} = 3.7$ Hz], 144.8–128.0 [m, Ph], 94.7 [C_5H_5], 40.7 [d, CH_2, $^1J_{CP} = 28.5$ Hz], 18.8 [d, P*Me*$_2$Ph, $^1J_{CP} = 34.2$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 52.1 [d, $PPh_2CH_2C(O)Ph$, $^2J_{PP} = 21$ Hz], 25.6 [d, PMe_2Ph, $^2J_{PP} = 21$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1972, 1890; ν(C=O) 1663 cm^{-1}.

8c: Yield 90%. ^{1}H-NMR ($CDCl_3$): δ 7.73–7.27 [m, 30H, Ph], 5.21 [s, 5H, C_5H_5] 4.42 [d, 2H, CH_2, $^2J_{HP} = 8.6$ Hz], 2.23 [d, 3H, Me, $^2J_{HP} = 9.0$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 234.1 [t, M–CO, $^2J_{CP} = 27.1$ Hz], 193.3 [d, C=O, $^1J_{CP} = 4.7$ Hz], 134.3–128.3 [m, Ph], 95.1 [C_5H_5], 40.6 [d, CH_2, $^1J_{CP} = 27.1$ Hz], 19.9 [d, PPh_2Me, $^1J_{CP} = 35.6$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 48.8 [d, $PPh_2CH_2C(O)Ph$, $^2J_{PP} = 20$ Hz], 41.2 [d, $PMePh_2$, $^2J_{PP} = 20$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1973, 1892; ν(C=O) 1665 cm^{-1}.

8d: Reaction time 7 days, yield 94%. ^{1}H-NMR ($CDCl_3$): δ 7.81–7.33 [m, 30H, Ph], 5.17 [s, 5H, C_5H_5] 4.62 [d, 2H, CH_2, $^2J_{HP} = 8.3$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 233.9 [t, M–CO, $^2J_{PC} = 27.1$ Hz], 193.3 [d, C=O, $^2J_{PC} = 5.7$ Hz], 136.3–128.0 [m, Ph], 95.4 [C_5H_5], 40.9 [d, CH_2, $^1J_{PC} = 28.5$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 57.7 [d, PPh_3, $^2J_{PP} = 19$ Hz], 47.3 [d, $PPh_2CH_2C(O)Ph$, $^2J_{PP} = 19$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1974, 1895; ν(C=O) 1684 cm^{-1}.

3.5. Preparation of [Mo(CO)$_2${PPh$_2$CH=C(O)Ph-P,O}(η^5-C$_5$H$_5$)] (**9**)

Triethylamine (19 μl, 0.135 mmol) was added to a solution of **2a** (74 mg, 0.133 mmol) in CH_2Cl_2 (10 ml). The solution was stirred for 2 h, the solvent removed in vacuo and the crude product recrystallised from CH_2Cl_2–hexane to give orange crystals of **9**. Yield 65 mg (94%). Anal. Found (Calc for $C_{27}H_{21}MoO_3P \cdot 1/4CH_2Cl_2$): C 60.6 (60.4), H 4.21 (4.00)%. ^{1}H-NMR ($CDCl_3$): δ 7.74–7.20 [m, 15H, Ph], 5.19 [d, 1H, PCH, $^2J_{HP} = 1.2$ Hz], 5.04 [s, 5H, C_5H_5]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 253.2 [d, M–CO, $^2J_{CP} = 29.7$ Hz], 242.7 [d, M–CO, $^2J_{CP} = 4.1$ Hz], 181.1 [d, C = ***C***O, $^2J_{CP} = 30.1$ Hz], 132.2–125.7 [m, Ph], 94.0 [C_5H_5], 45.6 [d, P***C***H=C, $^1J_{CP} = 69.7$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 68.4. ν_{max} (CH_2Cl_2): ν(CO) 1990, 1913; ν(C$\cdot\cdot$C+C$\cdot\cdot$O) 1460 cm^{-1}. Compound **9** was also prepared from the reaction of **2a** with *n*-butyl lithium and of **5a** with PMe_3.

3.6. Preparation of [Mo(CO)$_2$(L)(**L**^{3}-κ^1P)(η^5-C$_5$H$_5$)][BF$_4$] (L = PMe$_3$ **10a**, PMe$_2$Ph **10b**, PMePh$_2$ **10c**, PPh$_3$ **10d**)

Typical preparation (**10c**): $PMePh_2$ (12 μl, 0.063 mmol) was added to a solution of **6a** (44 mg, 0.063 mmol) in CH_2Cl_2 (15 ml) and the solution stirred at r.t. for 7 days. The product was isolated as a red oil by addition of hexane to a dichloromethane solution.

10a: Orange oil, yield 88%. ^{1}H-NMR ($CDCl_3$): δ 7.88-6.97 [m, 10H, Ph], 5.36 [s, 5H, C_5H_5], 3.85 [d, 2H, CH_2, $^2J_{HP} = 8.2$ Hz], 1.70 [d, 9H, Me, $^2J_{HP} = 10.2$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 235.7 [t, M–CO, $^2J_{CP} = 17.6$ Hz], 165.1 [C=O], 134.0–127.1 [m, Ph], 94.8 [C_5H_5], 27.4 [d, CH_2, $^1J_{CP} = 16.9$ Hz], 18.2 [d, P*Me*$_3$, $^1J_{CP} = 34.9$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 55.6 [d, $PPh_2CH_2C(O)NPh_2$, $^2J_{PP} = 21$ Hz], 22.5 [d, PMe_3, $^2J_{PP} = 21$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1968, 1888; ν(C=O) 1663 cm^{-1}.

10b: Orange oil, yield 85%. ^{1}H-NMR ($CDCl_3$): δ 7.61–6.86 [m, 25H, Ph], 5.07 [s, 5H, C_5H_5], 3.67 [d, 2H, CH_2, $^2J_{HP} = 8.2$ Hz], 2.04 [d, 6H, Me, $^2J_{HP} = 9.9$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 235.3 [t, M–CO, $^2J_{CP} = 17.6$ Hz], 164.9 [C=O], 134.6–126.5 [m, Ph], 94.7 [C_5H_5], 27.5 [d, CH_2, $^1J_{CP} = 17.1$ Hz], 18.7 [d, P*Me*$_2$Ph, $^1J_{CP} = 33.9$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 55.8 [d, $PPh_2CH_2C(O)NPh_2$, $^2J_{PP} = 21$ Hz], 26.5 [d, PMe_2Ph, $^2J_{PP} = 21$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1968, 1888; ν(C=O) 1663 cm^{-1}.

10c: Yield 86%. ^{1}H-NMR ($CDCl_3$) δ 7.73–6.86 [m, 30H, Ph], 5.20 [s, 5H, C_5H_5], 3.72 [d, 2H, CH_2, $^2J_{HP} = 7.8$ Hz], 2.16 [d, 3H, Me, $^2J_{HP} = 9.4$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 235.2 [t, M–CO, $^2J_{CP} = 17.5$ Hz], 165.1 [C=O], 134.1–126.1 [m, Ph], 94.9 [C_5H_5], 27.6 [d, CH_2, $^1J_{CP} = 16.9$ Hz], 20.1 [d, Me, $^1J_{CP} = 33.3$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$); δ 55.6 [d, $PPh_2CH_2C(O)NPh_2$, $^2J_{PP} = 18$ Hz], 41.3 [d, $PMePh_2$, $^2J_{PP} = 18$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1972, 1892; ν(C=O) 1663 cm^{-1}.

10d: Reaction time 14 days, yield 90%. ^{1}H-NMR ($CDCl_3$): δ 7.79–7.27 [m, 35H, Ph], 5.20 [s, 5H, C_5H_5], 3.65 [d, 2H, CH_2, $^2J_{HP} = 7.8$ Hz]. $^{13}C\{^1H\}$ ($CDCl_3$): δ 234.8 [t, M–CO, $^2J_{CP} = 17.4$ Hz], 165.0 [C=O], 136.7–126.8 [m, Ph], 95.2 [C_5H_5], 27.8 [d, CH_2, $^1J_{CP} = 16.8$ Hz]. $^{31}P\{^1H\}$ ($CDCl_3$): δ 60.1 [d, PPh_3, $^2J_{PP} = 18$ Hz], 54.6 [d, $PPh_2CH_2C(O)NPh_2$, $^2J_{PP} = 18$ Hz]. ν_{max} (CH_2Cl_2): ν(CO) 1974, 1896; ν(C=O) 1663 cm^{-1}.

3.7. Crystallography

4a: crystals suitable for an X-ray structural analysis were grown from the slow diffusion of toluene into a dichloromethane solution of **4a**. $C_{25}H_{21}BF_4MoNO_3P$, $M = 597.15$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, triclinic, space group $P-1$, $a = 10.2215(7)$, $b = 10.9379(7)$, $c =$

11.0922(8) Å, $\alpha = 89.078(1)$, $\beta = 84.012(1)$, $\gamma = 79.200(1)^\circ$, $U = 1211.51(14)$ Å^3, $Z = 2$, $\rho_{calc} = 1.637$ gcm^{-3}, $\mu = 0.667$ mm^{-1}, crystal size $2.0 \times 0.2 \times 0.2$ mm, $1.85 \leq \theta \leq 27.51^\circ$. 12695 reflections collected of which 5507 were independent [$R_{int} = 0.0271$] and 4310 observed ($\geq 2\sigma$). Final R indices $R_1 = 0.0313$, $wR_2 = 0.0702$ [$I \geq 2\sigma(I)$].

9: crystals suitable for an X-ray structural analysis were grown from the slow evaporation of a chloroform-*d* solution of **9**. $C_{27}H_{21}MoO_3P$, $M = 520.35$, $T = 170(2)$ K, $\lambda = 0.71073$ Å, orthorhombic, space group $P2_12_12_1$, $a = 8.2520(1)$, $b = 14.3430(3)$, $c = 19.0700(2)$ Å, $U = 2257.10(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.531$ g cm^{-3}, $\mu = 0.679$ mm^{-1}, crystal size $0.15 \times 0.15 \times 0.15$ mm, $1.78 \leq \theta \leq 27.48^\circ$. A total of 34 621 reflections collected of which 5171 were independent [$R_{int} = 0.0436$] and 4913 observed ($\geq 2\sigma$). Final R indices $R_1 = 0.0340$, $wR_2 = 0.0868$ [$I \geq 2\sigma(I)$].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 189988 and 189989 for compounds **4a** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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