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# Reactivity of the metallophosphines $[CpM(CO)_3PPh_2]$ ($Cp = \eta$-$C_5H_5$, M = Mo, W) towards alkynes. X-Ray crystal structure of $[CpMo(CO)_2\{Ph_2PCH{=}C(Ph)CO\}]$

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**Abstract**

The mononuclear phosphido complexes $[CpM(CO)_3PPh_2]$ ($Cp = \eta$-$C_5H_5$; M = Mo, W) react with the electron deficient alkynes methyl propiolate ($HC{\equiv}CCO_2Me$) and dimethyl acetylenedicarboxylate (DMAD, $MeO_2CC{\equiv}CCO_2Me$) to give the metallacyclic complexes $[CpM(CO)_2\{Ph_2PCR^1{=}C(R^2)CO\}]$ ($R^1$ = H, $CO_2Me$; $R^2 = CO_2Me$), which contain a five-membered chelate ring formed by the linking of the phosphido group, the alkyne, and one CO ligand. The molybdenum phosphido complex, though not the tungsten, also reacts with phenylacetylene to give the corresponding metallacycle $[CpMo(CO)_2\{Ph_2PCH{=}C(Ph)CO\}]$, which has been characterised by a single crystal X-ray structure determination. This complex can also be produced by the action of $PPh_2Cl$ on the dinuclear $\mu$-acetylide $Li[Cp_2Mo_2(\mu\text{-}C{\equiv}CPh)(CO)_4]$.

## Introduction

The chemistry of dinuclear complexes stabilised against fragmentation by bridging phosphido groups ($\mu$-$PR_2$) continues to attract considerable research attention. In a recent series of papers, we and our associates have described our studies of the chemistry of phosphido-bridged dimolybdenum complexes such as $[Cp_2Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ ($Cp = \eta$-$C_5H_5$) [1–4] and $[Cp_2Mo_2(\mu\text{-}PPh_2)_2(CO)_2]$ [5] in which the phosphido groups act as inert bridging ligands. However we have also discovered ways to induce the linking of phosphido groups to alkyne ligands to create new bridging ligands such as $\alpha$-phosphinovinyl $[\mu\text{-}C(PPh_2){=}CH_2]$, $\beta$-phosphinovinyl ($\mu$-$CH{=}CHPPh_2$), and vinylphosphine $[\mu\text{-}Ph_2PC(Me){=}CHMe]$ [6–8], and in a related study the formation of quaternised phosphole rings by the combination of alkynes with diphenylphosphido groups at dicobalt and dimanganese centres was reported [9].

As an extension of these studies, we decided to investigate the reaction of the anionic $\mu$-acetylide complex $[Cp_2Mo_2(\mu\text{-}C{\equiv}CPh)(CO)_4]^-$ with $PPh_2Cl$ in an attempt

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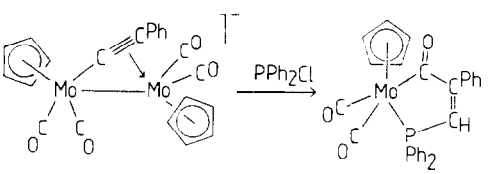
to prepare a dimolybdenum complex bridged by phosphido and acetylide ligands. An alternative possibility was that P–C bond formation would occur to give a phosphinoalkyne ligand. As described below, however, the reaction occurred with loss of one molybdenum to give the mononuclear metallacyclic complex $[CpMo(CO)_2\{Ph_2PCH{=}C(Ph)CO\}]$ as the major product. This result prompted us to study an alternative route to this and other analogous complexes using the metallophosphines $[CpM(CO)_3PPh_2]$ (M = Mo, W). The results of that study and the X-ray crystal structure of $[CpMo(CO)_2\{Ph_2PCH{=}C(Ph)CO\}]$ are presented in this paper.

## Results and discussion

*a) Synthesis and X-ray structure of $[CpMo(CO)_2\{Ph_2PCH{=}C(Ph)CO\}]$*

The $\mu$-acetylide anion $[Cp_2Mo_2(\mu\text{-}C{\equiv}CPh)(CO)_4]^-$ was first reported by Green and co-workers, who used it to prepare side-bound vinylidene complexes [10] and, more recently, acetylide-bridged trinuclear clusters [11]. It can be readily prepared as a THF solution by addition of one equivalent of LiC≡CPh to the triply-bonded complex $[Cp_2Mo_2(CO)_4]$ at −78°C. Addition of one equivalent of $PPh_2Cl$ to this solution followed by slow warming to room temperature gave a mixture of several products which could be separated by column chromatography on silica. Three of the minor products were identified as $[Cp_2Mo_2(CO)_6]$, the transverse alkyne complex $[Cp_2Mo_2(\mu\text{-}HC_2Ph)(CO)_4]$ (formed presumably by protonation of the anion [10]), and $[CpMo(CO)_3Cl]$, but the major product (13%) was a new complex having two strong absorptions in the IR spectrum (1953, 1880 $cm^{-1}$) indicative of a *cis*-dicarbonyl arrangement, together with a ketonic carbonyl peak at 1712 $cm^{-1}$. This red, air-stable compound was characterised as $[CpMo(CO)_2\{Ph_2PCH{=}C(Ph)CO\}]$ (**1a**) by its $^1H$, $^{13}C$, and $^{31}P$ NMR spectra, mass spectrum, and analysis, and subsequently by a single crystal X-ray diffraction study.




The $^1H$ NMR spectrum of **1a** showed a doublet at $\delta$ 7.78 with $J$(PH) of 7.4 Hz, corresponding to the CH group of the chelate ring, together with appropriate resonances for the Cp ligand and the phenyl groups. The two carbon atoms of the alkyne unit appear at 169.6 and 143.7 ppm in the $^{13}C$ NMR spectrum; while it was possible to assign them as CPh and CH respectively using a DEPT experiment, it was not possible to determine which of them was attached to the phosphorus atom, since the coupling constants $J$(CP) are virtually identical (37 and 38 Hz, respectively). Hence, while it was evident that only one isomer of **1a** was produced i.e., that the reaction is regiospecific, it was not possible to determine which one. However it seemed probable to us that the phosphido group was linked to the CH terminus of the alkyne, and this was indeed later confirmed by the structure determination. Two terminal carbonyl resonances were also observed in the $^{13}C$ NMR spectrum, one with a small $J$(CP) of 12 Hz and the other with a larger $J$(CP) of 27 Hz. These are thought to correspond to *trans* and *cis*-couplings respectively; it

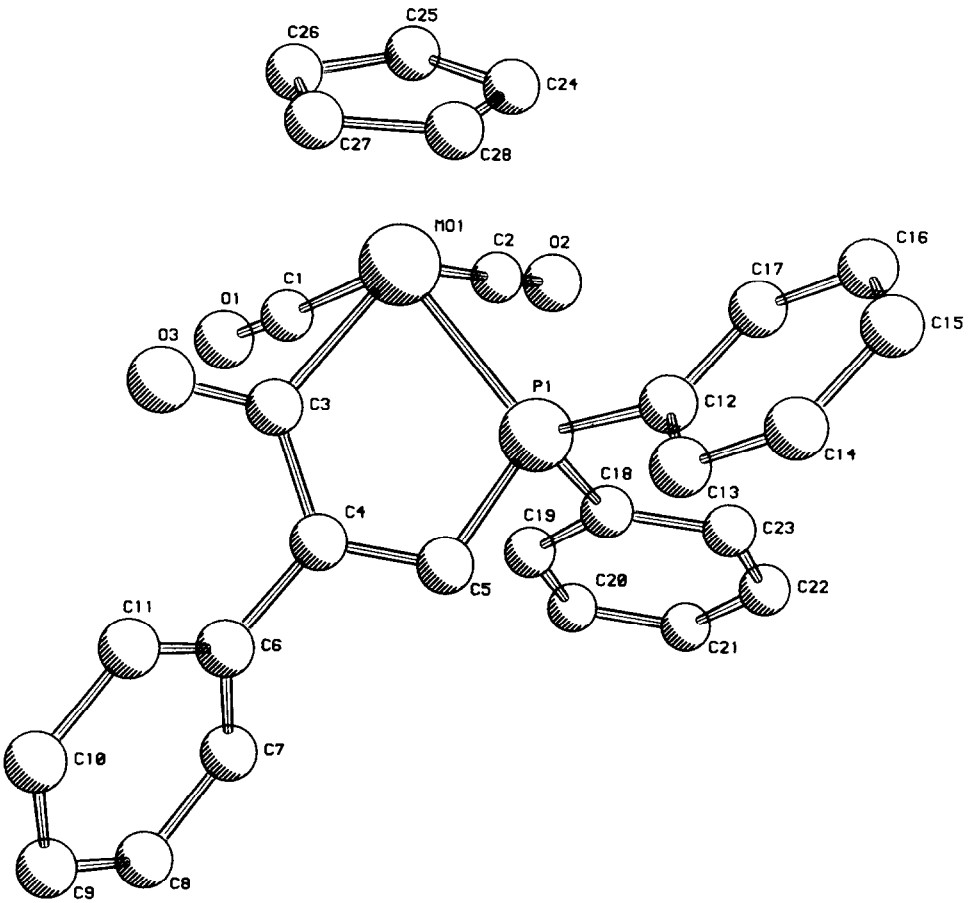



Fig. 1. Molecular structure of [CpMo(CO)$_2${Ph$_2$PCH=C(Ph)CO}] (**1a**) including the atom numbering scheme.

has been shown by Todd et al. that for similar complexes with a four-legged piano stool structure (e.g. *cis*-[CpMo(CO)$_2$(PPh$_3$)Cl] and *trans*-[CpMo(CO)(PPh$_3$)$_2$Cl]) the *cis* coupling is larger than the *trans* [12]. The acyl CO was observed as a singlet at 235.0 ppm. The $^{31}$P NMR spectrum of **1a** showed a single peak at 82.1 ppm.

In order to establish the structure of the complex unambiguously, an X-ray structure determination was carried out on a suitable single crystal. The result is shown in Fig. 1, with bond lengths and angles listed in Table 1 and atomic coordinates in Table 2. The molybdenum atom is in a square pyramidal environment with the four basal positions being occupied by two *cis*-carbonyl ligands, the diphenylphosphido group, and an acyl-like carbonyl group. The latter two form part of a five-membered metallacyclic ring, which is slightly puckered: atoms P(1), C(3), C(4), and C(5) form a plane (rms deviation 0.022 Å) which intersects with the Mo(1)–P(1)–C(3) plane at an angle of 6.3°. The bond lengths of the chelate ring are all normal, with the C(4)–C(5) bond of the alkene unit being 1.337(4) Å in length, though the Mo–C(3) bond [2.273(3) Å] is slightly longer than those found in other molybdenum acyl complexes [13].

Table 1

Bond lengths (Å) and angles (°) for complex **1a**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Mo(1)–P(1) | 2.433(2) | Mo(1)–C(1) | 1.963(3) |
| Mo(1)–C(2) | 1.974(4) | Mo(1)–C(3) | 2.273(3) |
| Mo(1)–C(24) | 2.323(4) | Mo(1)–C(25) | 2.318(4) |
| Mo(1)–C(26) | 2.360(4) | Mo(1)–C(27) | 2.388(4) |
| Mo(1)–C(28) | 2.353(4) | P(1)–C(5) | 1.803(3) |
| P(1)–C(12) | 1.829(3) | P(1)–C(18) | 1.848(3) |
| O(1)–C(1) | 1.160(4) | O(2)–C(2) | 1.169(5) |
| O(3)–C(3) | 1.220(4) | C(3)–C(4) | 1.539(3) |
| C(4)–C(5) | 1.337(4) | C(4)–C(6) | 1.492(4) |
| C(6)–C(7) | 1.397(4) | C(6)–C(11) | 1.390(4) |
| C(7)–C(8) | 1.397(5) | C(8)–C(9) | 1.372(6) |
| C(9)–C(10) | 1.377(5) | C(10)–C(11) | 1.389(5) |
| C(12)–C(13) | 1.395(4) | C(12)–C(17) | 1.402(4) |
| C(13)–C(14) | 1.393(4) | C(14)–C(15) | 1.371(5) |
| C(15)–C(16) | 1.387(5) | C(16)–C(17) | 1.384(4) |
| C(18)–C(19) | 1.393(4) | C(18)–C(23) | 1.397(4) |
| C(19)–C(20) | 1.386(4) | C(20)–C(21) | 1.385(5) |
| C(21)–C(22) | 1.368(5) | C(22)–C(23) | 1.391(5) |
| C(24)–C(25) | 1.408(5) | C(24)–C(28) | 1.381(6) |
| C(25)–C(26) | 1.404(6) | C(26)–C(27) | 1.416(5) |
| C(27)–C(28) | 1.411(6) | | |
| *Bond angles* | | | |
| P(1)–Mo(1)–C(1) | 109.6(1) | P(1)–Mo(1)–C(2) | 77.8(1) |
| C(1)–Mo(1)–C(2) | 78.7(1) | P(1)–Mo(1)–C(3) | 74.7(1) |
| C(1)–Mo(1)–C(3) | 74.5(1) | C(2)–Mo(1)–C(3) | 131.9(1) |
| Mo(1)–P(1)–C(5) | 108.4(1) | Mo(1)–P(1)–C(12) | 114.9(1) |
| C(5)–P(1)–C(12) | 105.8(1) | Mo(1)–P(1)–C(18) | 121.3(1) |
| C(5)–P(1)–C(18) | 99.4(1) | C(12)–P(1)–C(18) | 105.0(1) |
| Mo(1)–C(1)–O(1) | 176.8(3) | Mo(1)–C(2)–O(2) | 178.3(3) |
| Mo(1)–C(3)–O(3) | 120.5(2) | Mo(1)–C(3)–C(4) | 122.3(2) |
| O(3)–C(3)–C(4) | 117.2(2) | C(3)–C(4)–C(5) | 117.2(2) |
| C(3)–C(4)–C(6) | 120.9(2) | C(5)–C(4)–C(6) | 121.9(2) |
| P(1)–C(5)–C(4) | 116.5(2) | C(4)–C(6)–C(7) | 118.7(3) |
| C(4)–C(6)–C(11) | 123.4(2) | C(7)–C(6)–C(11) | 117.8(3) |
| C(6)–C(7)–C(8) | 120.2(3) | C(7)–C(8)–C(9) | 120.8(3) |
| C(8)–C(9)–C(10) | 119.8(3) | C(9)–C(10)–C(11) | 119.7(3) |
| C(6)–C(11)–C(10) | 121.7(3) | P(1)–C(12)–C(13) | 122.8(2) |
| P(1)–C(12)–C(17) | 118.0(2) | C(13)–C(12)–C(17) | 119.0(2) |
| C(12)–C(13)–C(14) | 119.6(3) | C(13)–C(14)–C(15) | 120.8(3) |
| C(14)–C(15)–C(16) | 120.2(3) | C(15)–C(16)–C(17) | 119.8(3) |
| C(12)–C(17)–C(16) | 120.6(3) | P(1)–C(18)–C(19) | 116.5(2) |
| P(1)–C(18)–C(23) | 124.7(2) | C(19)–C(18)–C(23) | 118.8(3) |
| C(18)–C(19)–C(20) | 120.7(3) | C(19)–C(20)–C(21) | 120.0(3) |
| C(20)–C(21)–C(22) | 119.7(3) | C(21)–C(22)–C(23) | 121.1(3) |
| C(18)–C(23)–C(22) | 119.6(3) | C(25)–C(24)–C(28) | 108.5(3) |
| C(24)–C(25)–C(26) | 108.0(3) | C(25)–C(26)–C(27) | 107.5(3) |
| C(26)–C(27)–C(28) | 107.5(3) | C(24)–C(28)–C(27) | 108.5(3) |

*b) Reactions of $[CpM(CO)_3PPh_2]$ (M = Mo, W) with alkynes*

Having prepared complex **1a**, we realised that a more convenient method for its synthesis could be envisaged, namely the reaction of the terminal phosphido

Table 2

Atom coordinates ($\times 10^4$) and temperature factors ($A^2 \times 10^3$) for complex **1a**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| Mo(1) | 2487(1) | 2406(1) | 998(1) | 37(1) |
| P(1) | 3885(1) | 3857(1) | 2664(1) | 35(1) |
| O(1) | 3738(3) | −213(2) | 822(3) | 88(1) |
| O(2) | 5337(3) | 2941(3) | 117(2) | 87(1) |
| O(3) | 1116(2) | 867(2) | 2511(2) | 59(1) |
| C(1) | 3295(4) | 769(3) | 921(3) | 52(1) |
| C(2) | 4290(4) | 2735(3) | 460(3) | 54(1) |
| C(3) | 2066(3) | 1686(2) | 2605(2) | 38(1) |
| C(4) | 2908(3) | 2232(2) | 3848(2) | 34(1) |
| C(5) | 3734(3) | 3289(2) | 3983(2) | 36(1) |
| C(6) | 2806(3) | 1595(2) | 4853(2) | 35(1) |
| C(7) | 4079(3) | 1303(3) | 5542(3) | 53(1) |
| C(8) | 4025(4) | 751(3) | 6516(3) | 66(1) |
| C(9) | 2729(4) | 487(3) | 6811(3) | 58(1) |
| C(10) | 1464(4) | 775(3) | 6146(3) | 57(1) |
| C(11) | 1509(3) | 1318(3) | 5173(3) | 48(1) |
| C(12) | 3273(3) | 5437(2) | 2850(2) | 37(1) |
| C(13) | 2648(3) | 5939(3) | 3786(2) | 40(1) |
| C(14) | 2100(3) | 7109(3) | 3821(3) | 52(1) |
| C(15) | 2171(3) | 7778(3) | 2949(3) | 53(1) |
| C(16) | 2792(3) | 7292(3) | 2015(3) | 52(1) |
| C(17) | 3334(3) | 6127(3) | 1962(3) | 47(1) |
| C(18) | 5873(3) | 4075(3) | 2892(2) | 42(1) |
| C(19) | 6627(3) | 3005(3) | 2937(3) | 50(1) |
| C(20) | 8124(3) | 3081(3) | 3151(3) | 62(1) |
| C(21) | 8886(4) | 4229(4) | 3325(3) | 66(1) |
| C(22) | 8154(4) | 5283(3) | 3269(3) | 64(1) |
| C(23) | 6652(3) | 5226(3) | 3050(3) | 51(1) |
| C(24) | 1262(4) | 3694(3) | −173(3) | 66(1) |
| C(25) | 1202(4) | 2498(3) | −860(3) | 70(1) |
| C(26) | 368(4) | 1681(3) | −412(3) | 73(1) |
| C(27) | −87(4) | 2384(4) | 558(3) | 74(1) |
| C(28) | 493(4) | 3623(3) | 696(3) | 68(1) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

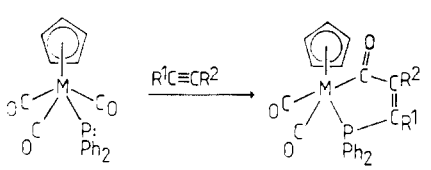
complex $[CpMo(CO)_3PPh_2]$ with phenylacetylene. Metallophosphines have also attracted considerable interest in recent years; since the lone pair of the phosphido group is not involved in bonding to the metal, it retains its nucleophilic character and can participate in reactions such as quaternisation [14], oxidation [15], and attack on other metal ligand fragments to give phosphido-bridged species [16]. To date only one report of the reactivity of a metallophosphine towards alkynes has appeared, that of Ashby and Enemark [17], who found that $[CpFe(CO)_2(PPh_2)]$ reacted with electrophilic alkynes to give metallacycles of the form $[CpFe(CO)\{Ph_2PC(R^1)=C(R^2)CO\}]$ ($R^1 = H$, $CO_2Me$; $R^2 = CO_2Me$). However similar reactions have been reported by Weber for Fe and Ru terminal diphosphene complexes [18], and such cycloadditions are also known for the reactions of electrophilic alkynes with species such as $[CpFe(CO)_2SR]$ [19], $[CpFe(CO)_2AsMe_2]$, and $[CpW(CO)_3AsMe_2]$ [20]. We therefore decided to undertake a short study of the reactivity of $[CpM(CO)_3PPh_2]$ towards alkynes.

The metallophosphine $[CpMo(CO)_3PPh_2]$ is readily prepared *in situ* as a toluene solution by addition of one equivalent of $PPh_2Cl$ to $Na[CpMo(CO)_3] \cdot 2DME$ (DME = 1,2-dimethoxyethane), followed by filtration to remove NaCl [21]. Treatment of this solution with phenylacetylene did indeed produce **1a** as the major product in 25% yield after 1 week. This represents the first incorporation of phenylacetylene into such a metallacycle. Several minor products were also observed; interestingly, the most abundant of these (11% yield) was the complex $[Cp_2Mo_2(\mu\text{-HCCPh})(\mu\text{-}PPh_2)(Cl)(CO)]$, which we have previously shown to be produced by the reaction of the $\mu$-alkyne complex $[Cp_2Mo_2(\mu\text{-HCCPh})(CO)_4]$ with $PPh_2Cl$ under relatively dilute conditions [6]. Its presence here is evidently a consequence of incomplete filtration of chloride from the reaction mixture, though its exact mode of formation remains obscure. Reaction of the analogous tungsten complex $[CpW(CO)_3PPh_2]$ with phenylacetylene under similar conditions gave several compounds in low yields, of which only $[Cp_2W_2(CO)_6]$ and $[CpW(CO)_3Cl]$ could be identified. No complex analogous to **1a** was obtained.

In contrast, reaction of $[CpM(CO)_3PPh_2]$ with the activated alkyne methyl propiolate ($HC{\equiv}CCO_2Me$) occurred smoothly for both Mo and W, affording the metallacycles **1b** and **1c** in yields of 75 and 64% respectively as orange air-stable crystalline solids. These complexes were readily identified by their spectroscopic characteristics, which are similar to those of **1a** and also to those of the analogous iron complexes prepared by Ashby and Enemark [17]; thus, both display a low-field doublet in the $^1H$ NMR spectrum which indicates that regioselective coupling with the CH terminus of the alkyne has occurred; moreover, in the $^{13}C$ NMR spectrum, the carboxylate carbon of the $CO_2Me$ group displays a coupling of around 30 Hz to phosphorus consistent with a *trans* disposition across the double bond.

In a similar manner, reaction of the phosphido complexes with DMAD ($MeO_2CC{\equiv}CCO_2Me$) provided **1d** (72%) and **1e** (54%) as brown crystalline solids which were characterised spectroscopically. In the $^{13}C$ NMR spectra of these compounds, only the carboxylate carbon *trans* to phosphorus displays a coupling to P (again of about 30 Hz), while the other, which is in a *gem* position, appears as a singlet.

As proposed by previous workers [17,20], the mechanism of the reaction is thought to involve initial nucleophilic attack on the alkyne by the phosphido group,



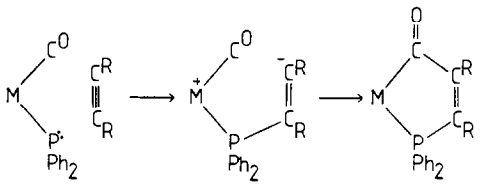

(1a) M = Mo, $R^1$ = H, $R^2$ = Ph

(1b) M = Mo, $R^1$ = H, $R^2$ = $CO_2Me$

(1c) M = W, $R^1$ = H, $R^2$ = $CO_2Me$

(1d) M = Mo, $R^1$ = $R^2$ = $CO_2Me$

(1e) M = W, $R^1$ = $R^2$ = $CO_2Me$



Scheme 1. Proposed mechanism for the reaction of the phosphido complexes with alkynes.

followed by attack on a carbonyl ligand to create the metallacyclic ring (Scheme 1). For the thiolate complexes [CpFe(CO)(L)SPh] (L = CS, CO, CNMe) a concerted cycloaddition mechanism was proposed as the preference for L to be incorporated into the metallacycle was in the order CNMe > CO > CS, while the susceptibility towards nucleophilic attack should be the reverse [19]. For both these mechanisms, however, activated electrophilic alkynes are expected to react more cleanly than alkynes with electron donating substituents. In keeping with this, the reactions of $[CpMo(CO)_3PPh_2]$ with MeC≡CMe or MeC≡CH gave only low yields of compounds such as $[Cp_2Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$, $[Cp_2Mo_2(\mu\text{-}PPh_2)_2(CO)_2]$, and $[Cp_2Mo_2(\mu\text{-}PPh_2)_2(O)(CO)]$, all of which we have previously shown to be derived from the decomposition of the mononuclear phosphido complex [5]. Reaction with PhC≡CPh gave a similar result, perhaps for steric reasons. The slightly higher yields of the molybdenum complexes **1b** and **1d** compared to the tungsten complexes **1c** and **1e**, and the unsuccessful synthesis of the tungsten analogue of **1a**, may possibly indicate that the $PPh_2$ group of the molybdenum phosphido species is somewhat more nucleophilic than that of the tungsten complex, as might be expected.

Further investigations into the reactivity of the metallacyclic complexes are currently under way in our Laboratory.

## Experimental

All reactions were carried out under dry argon or nitrogen by standard Schlenk techniques. Toluene and THF were dried by distillation from sodium. Chromatographic separations were performed under a slight positive pressure of inert gas on silica columns (Merck Kieselgel 60, 230–400 mesh); solvents for chromatography were used as received. All of the products described are relatively air-stable. IR spectra were recorded as $CH_2Cl_2$ solutions in NaCl cells on a Perkin–Elmer 1710 FT-IR instrument. NMR spectra were obtained in $CDCl_3$ solution on Bruker WP80 ($^1H$, $^{13}P$), Bruker AM-250 ($^1H$, $^{13}C$) or Varian XL 300 ($^{13}C$) spectrometers with chemical shifts measured on the $\delta$ scale relative to $SiMe_4$ = 0.0 ppm for $^1H$ and $^{13}C$ and to 85% $H_3PO_4$ = 0.0 ppm for $^{31}P$. Coupling constants are given in Hz. The $^{13}C$ NMR spectra were routinely recorded using an attached proton test technique [22]. Mass spectra were recorded on Kratos MS25 or MS80 instruments. Microanalyses were carried out by the Microanalytical Departments of the Universities of Manchester and Sheffield.

The salts $[Na][CpM(CO)_3] \cdot 2DME$ and the complex $[Cp_2Mo_2(CO)_6]$ were prepared by the literature methods [23,24]. All other chemicals were obtained from commercial sources and used as received: $PPh_2Cl$, PhC≡CH, HC≡$CCO_2$Me, DMAD, and PhC≡CPh from Aldrich, MeC≡CMe from Lancaster Synthesis, and MeC≡CH from Cambrian.

*Synthesis of [CpMo(CO)$_2${Ph$_2$PCH=C(Ph)CO}] (**1a**)*

*a) From Li[Cp$_2$Mo$_2$(μ-C≡CPh)(CO)$_4$].* A solution of [Cp$_2$Mo$_2$(CO)$_6$] (1.50 g, 3.06 mmol) in toluene (175 mL) was refluxed for 21 h with nitrogen purging the solution to produce [Cp$_2$Mo$_2$(CO)$_4$] (0.98 g, 2.26 mmol) which was evaporated to dryness and redissolved in THF (100 mL). This solution was cooled (−78°C) and treated with a solution of LiC≡CPh, freshly prepared by reacting PhC≡CH (0.25 mL, 2.28 mmol) with MeLi (1.53 mL of a 1.5 *M* solution in ether) in THF (30 mL). The reaction was monitored by IR spectroscopy. After adding a solution of PPh$_2$Cl (0.4 mL, 2.23 mmol) in THF (30 mL), the mixture was allowed to warm to room temperature and stirred for 17 h. There was no colour change, but the IR spectrum showed the presence of several species. After addition of silica (5 g) and removal of the solvent, the residue was loaded onto a silica chromatography column.

Elution with CH$_2$Cl$_2$/hexane (1 : 9 followed by 3 : 7) produced small amounts of [Cp$_2$Mo$_2$(CO)$_4$] and [Cp$_2$Mo$_2$(μ-HCCPh)(CO)$_4$], and a weak unidentified green band. Elution with CH$_2$Cl$_2$/hexane (1 : 1) produced a red band of [CpMo(CO)$_3$Cl] (72.8 mg, 11% based on PPh$_2$Cl), identified by its IR spectrum (2056 and 1978 cm$^{-1}$ in CH$_2$Cl$_2$). Further elution with the same solvent gave red [CpMo(CO)$_2${Ph$_2$PCH=C(Ph)CO}] (**1a**) (153.9 mg, 13%).

**1a**: M.p. 230°C (dec). IR: ν(CO) 1953, 1880, 1612 cm$^{-1}$. $^1$H NMR: δ 7.78 (d, *J*(HP) 7.4, 1H, CH); 7.66–7.29 (m, 15H, Ph); 5.01 (s, 5H, Cp). $^{13}$C NMR: δ 266.0 (d, *J*(CP) 12, CO); 245.4 (d, *J*(CP) 27, CO); 235.0 (s, acyl CO); 169.6 (d, *J*(CP) 37, CPh); 143.7 (d, *J*(CP) 38, CH); 136.2 (d, *J*(CP) 43, PC$_{ipso}$); 134.0 (d, *J*(CP) 28, PC$_{ipso}$); 133.5 (s, C$_{ipso}$); 131.5–127.6 (m, Ph); 92.8 (s, Cp). $^{31}$P NMR: δ 82.1. Anal. Found: C, 63.00; H, 4.20; P, 5.70. C$_{28}$H$_{21}$MoO$_3$P calc.: C, 63.16; H, 3.95; P, 5.83%. MS: *m/z* 504 (*M* − CO)$^+$.

Further elution of the chromatography column with CH$_2$Cl$_2$ and CH$_2$Cl$_2$/acetone (9 : 1) produced three minor bands which were not identified.

*b) From [CpMo(CO)$_3$PPh$_2$].* A solution of PPh$_2$Cl (0.67 mL, 3.73 mmol) in toluene (50 mL) was added dropwise to a suspension of Na[CpMo(CO)$_3$] · 2DME (1.6690 g, 3.72 mmol) in toluene (100 mL) at 0°C. The bright orange solution of [CpMo(CO)$_3$PPh$_2$] was warmed to room temperature and filtered to remove NaCl [21]. Phenylacetylene (0.53 mL, 4.80 mmol) was added and the solution was stirred for 7 days, then absorbed onto silica and chromatographed. Several minor yellow and orange bands were observed before elution of the major product as a red band with CH$_2$Cl$_2$/hexane (3 : 2). Comparison of the IR and $^1$H NMR spectra confirmed that it was **1a** (474.7 mg, 25%).

Further elution of the column with CH$_2$Cl$_2$/hexane (4 : 1) produced a darker red-purple band, which by comparison of its IR (1969 cm$^{-1}$ in CH$_2$Cl$_2$) and $^1$H NMR spectra with an authentic sample, was shown to be [Cp$_2$Mo$_2$(μ-HCCPh)(μ-PPh$_2$)(Cl)(CO)] (142.9 mg, 11%).

*Synthesis of [CpMo(CO)$_2${Ph$_2$PCH=C(CO$_2$Me)CO}] (**1b**)*

A toluene solution of [CpMo(CO)$_3$PPh$_2$] was prepared as above from Na[CpMo(CO)$_3$] · 2DME (1.6010 g, 3.57 mmol) and PPh$_2$Cl (0.65 mL, 3.62 mmol). To this was added methyl propiolate (0.4 mL, 4.50 mmol), causing a darkening of the solution. After stirring for 3 days the reaction mixture was dark red; a small amount of silica was added and the solvent was evaporated. Chromatography on a silica column produced a weak orange zone of [CpMo(CO)$_3$Cl] followed by a strong

red band of **1b**, which was eluted in $CH_2Cl_2$/acetone (19 : 1). Yield: 1.3721 g, 74.8%.

**1b**: M.p. 154–155 °C. IR: $\nu$(CO) 1960, 1888, 1734, 1595 $cm^{-1}$. $^1H$ NMR: $\delta$ 8.04 (d, $J$(HP) 6.0, 1H, CH); 7.62–7.21 (m, 10H, Ph); 4.98 (s, 5H, Cp); 3.80 (s, 3H, Me). $^{13}C$ NMR: $\delta$ 262.8 (d, $J$(CP) 12, CO); 244.9 (d, $J$(CP) 28, CO); 234.4 (s, acyl CO); 166.0 (d, $J$(CP) 30, $CO_2Me$); 161.8 (d, $J$(CP) 40, $CCO_2Me$); 148.5 (d, $J$(CP) 31, CH); 135.4 (d, $J$(CP) 44, $C_{ipso}$); 132.8 (d, $J$(CP) 47, $C_{ipso}$); 130.6–128.7 (m, Ph); 92.7 (s, Cp); 52.2 (s, Me). $^{31}P$ NMR: $\delta$ 89.3. Anal. Found: C, 56.18; H, 3.52. $C_{24}H_{19}MoO_5P$ calc.: C, 56.03; H, 3.70%. MS: $m/z$ 514 ($M^+$).

*Synthesis of [CpW(CO)$_2${Ph$_2$PCH=C(CO$_2$Me)CO] (**1c**)*

Methyl propiolate (0.35 mL, 3.93 mmol) was added to a toluene solution of [$CpW(CO)_3PPh_2$], prepared in an analogous way to the above from Na[$CpW(CO)_3$] · 2DME (1.6605 g, 3.10 mmol) and $PPh_2Cl$ (0.56 mL, 3.12 mmol). Again a slight darkening was observed, but after stirring for three days the solution was still orange. The IR spectrum, however, indicated that reaction was complete. After adding silica, the solvent was removed and the residue chromatographed to give a small orange band of [$CpW(CO)_3Cl$] (10 mg) and a large orange band of **1c** (1.1892 g, 63.7%) which was eluted using $CH_2Cl_2$/acetone (9 : 1).

**1c**: M.p. 180–181 °C. IR: $\nu$(CO) 1953, 1877, 1734, 1584 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.80 (d, $J$(HP) 7.3, 1H, CH); 7.61–7.22 (m, 10H, Ph); 5.06 (s, 5H, Cp); 3.80 (s, 3H, Me). $^{13}C$ NMR: $\delta$ 250.8 (d, $J$(CP) 9, $J$(CW) 68, CO); 235.3 (d, $J$(CP) 21, $J$(CW) 130, CO); 225.1 (s, $J$(CW) 166, acyl CO); 165.9 (d, $J$(CP) 29, $CO_2Me$); 165.2 (d, $J$(CP) 34, $CCO_2Me$); 147.3 (d, $J$(CP) 36, CH); 134.8 (d, $J$(CP) 50, $C_{ipso}$); 132.4 (d, $J$(CP) 53, $C_{ipso}$); 132.2–128.8 (m, Ph); 91.4 (s, Cp); 52.2 (s, Me). $^{31}P$ NMR: $\delta$ 62.7 ($J$(PW) 331). Anal. Found: C, 48.07; H, 3.24. $C_{24}H_{19}O_5PW$ calc.: C, 47.87; H, 3.18%. MS: $m/z$ 603 ($M^+$).

*Synthesis of [CpMo(CO)$_2${Ph$_2$PC(CO$_2$Me)=C(CO$_2$Me)CO}] (**1d**)*

A solution of [$CpMo(CO)_3PPh_2$] was prepared as above from Na[$CpMo(CO)_3$] · 2DME (2.10 g, 4.69 mmol) and $PPh_2Cl$ (0.84 mL, 4.68 mmol) in toluene (140 mL). To this was added an excess of DMAD (0.72 mL, 5.86 mmol) at room temperature, causing a colour change from orange to dark red. Although the reaction appeared complete, the solution was stirred for a further 60 h, after which the solution was absorbed onto a small amount of silica and chromatographed.

The column was eluted with $CH_2Cl_2$/hexane (1 : 3) to remove a small amount of [$Cp_2Mo_2(CO)_6$], and with a 1 : 1 mixture of the same solvents to give [$CpMo(CO)_3Cl$] (170.2 mg, 13%) as a red band. After removal of two further minor bands, the major product (**1d**) was eluted as a large red-purple zone firstly with $CH_2Cl_2$ and then $CH_2Cl_2$/acetone (9 : 1). Yield: 1.923 g, 72%. Analytically pure brown needles were obtained by diffusion of hexane into an ethyl acetate solution of the complex.

**1d**: M.p. 148–150 °C. IR: $\nu$(CO) 1966, 1896, 1737, 1723, 1584 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.58–7.39 (m, 10H, Ph); 4.85 (s, 5H, Cp); 3.84 (s, 3H, Me); 3.48 (s, 3H, Me). $^{13}C$ NMR: $\delta$ 264.2 (d, $J$(CP) 14, CO); 243.8 (d, $J$(CP) 27, CO); 234.0 (s, acyl CO); 166.4 (d, $J$(CP) 28, $CO_2Me$); 165.4 (d, $J$(CP) 44, $CCO_2Me$); 164.1 (s, $CO_2Me$); 146.7 (d, $J$(CP) 22, $CCO_2Me$); 135.2 (d, $J$(CP) 45, $C_{ipso}$); 132.8–128.3 (m, Ph); 93.3 (s, Cp); 52.5 (s, Me); 52.4 (s, Me). $^{31}P$ NMR: $\delta$ 53.4. Anal. Found: C, 54.25; H, 3.91. $C_{26}H_{21}MoO_7P$ calc.: C, 54.55; H, 3.67%. MS: $m/z$ 572 ($M^+$).

An unidentified turquoise band (248 mg) was also eluted using $CH_2Cl_2$/acetone (9 : 1). IR: $\nu$(CO) 1741, 1713, and 1660 $cm^{-1}$. $^1H$ NMR: $\delta$ 5.46 (d, $J$(HP) 1, 5H); 4.72 (d, $J$(HP) 14, 1H); 3.80 (s, 3H, Me); 3.70 (s, 3H, Me); 3.65 (s, 3H, Me); 3.13 (s, 3H, Me). MS: $m/z$ 470, no Mo isotope pattern. Further attempts to characterise this compound were rendered impossible by its decomposition overnight to a red material; however it may be a heterocycle formed by the incorporation of more than one DMAD molecule.

*Synthesis of [CpW(CO)$_2${Ph$_2$PC(CO$_2$Me)=C(CO$_2$Me)CO}] (**1e**)*

In a similar manner to the above, a solution of $[CpW(CO)_3PPh_2]$ in toluene (150 mL) was prepared using $Na[CpW(CO)_3] \cdot 2DME$ (2.40 g, 4.48 mmol) and $PPh_2Cl$ (0.8 mL, 4.46 mmol). An excess of DMAD (0.69 mL, 5.62 mmol) was added at room temperature, causing a colour change from orange to dark red. As above, the solution was stirred for 60 h then absorbed onto silica and chromatographed. Elution with $CH_2Cl_2$/hexane (1 : 3, followed by 1 : 1) produced a small pink band due to $[Cp_2W_2(CO)_6]$ and an unidentified yellow band. Elution with $CH_2Cl_2$ then gave **1e** (1.61 g, 54%) as a purple-brown zone, which was recrystallised from ethyl acetate/hexane.

**1e**: M.p. 79–80 °C. IR: $\nu$(CO) 1958, 1884, 1737, 1722 $cm^{-1}$. $^1H$ NMR: $\delta$ 7.58–7.40 (m, 10H, Ph); 4.94 (s, 5H, Cp); 3.84 (s, 3H, Me); 3.47 (s, 3H, Me). $^{13}C$ NMR: $\delta$ 251.7 (d, $J$(CP) 12, CO); 234.3 (d, $J$(CP) 20, CO); 224.6 (s, acyl CO); 169.1 (d, $J$(CP)38, $CCO_2Me$); 166.5 (d, $J$(CP)27, $CO_2Me$); 163.5 (s, $CO_2Me$); 145.6 (d, $J$(CP)28, $CCO_2Me$); 134.9 (d, $J$(CP) 50, $C_{ipso}$); 133.1–128.4 (m, Ph); 130.2 (d, $J$(CP) 54, $C_{ipso}$); 92.0 (s, Cp); 52.5 (s, Me); 52.4 (s, Me). $^{31}P$ NMR: $\delta$ 72.4 ($J$(PW) 328). Anal. Found: C, 47.50; H, 3.45. $C_{26}H_{21}O_7PW$ calc.: C, 47.27; H, 3.18%. MS: $m/z$ 660 ($M^+$).

*Crystal structure determination*

*Crystal data for **1a**:* $C_{28}H_{21}MoO_3P$, $M = 532.38$, crystallised by diffusion of hexane into a dichloromethane solution as orange-red blocks; crystal dimensions $0.45 \times 0.30 \times 0.40$ mm. Triclinic, $a = 9.460(8)$, $b = 10.909(10)$, $c = 11.836(8)$ Å, $\alpha = 99.78(6)$, $\beta = 101.17(6)$, $\gamma = 92.10(7)°$, $U = 1177.9(17)$ Å$^3$; $D_c = 1.501$ g cm$^{-3}$, $Z = 2$. Space group $P\bar{1}$ ($C_i^1$, No. 2), Mo-$K_\alpha$ radiation ($\bar{\lambda} = 0.71069$ Å), $\mu$(Mo-$K_\alpha$) = 6.36 $cm^{-1}$, $F(000) = 539.86$.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet $R3$ 4-circle diffractometer by the $\omega$ scan method. The 3720 independent reflections (of 4169 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.556 and 0.583). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.0315 (298 parameters, maximum shift/e.s.d. 0.016), with allowance for the thermal anisotropy for all non-hydrogen atoms. A final difference electron density synthesis showed peaks of $-0.76$ and $+0.28$ e Å$^{-3}$. Complex scattering factors were taken from the program package SHELXTL [25] as implemented on the Data General Nova 3 computer. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.00043(F)^2]$ was used in the latter

stages of the refinement. Table 2 lists atomic positional parameters with estimated standard deviations.

Tables of anisotropic thermal parameters, hydrogen atom position parameters, and observed and calculated structure factors are available from the authors.

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## References

1 K. Henrick, M. McPartlin, A.D. Horton and M.J. Mays, J. Chem. Soc., Dalton Trans., (1988) 1083.
2 G. Conole, K. Henrick, M. McPartlin, A.D. Horton and M.J. Mays, New J. Chem., 12 (1988) 559.
3 A.D. Horton and M.J. Mays, J. Chem. Soc., Dalton Trans., (1990) 155.
4 G. Conole, K. Henrick, M. McPartlin, A.D. Horton, M.J. Mays and E. Sappa, J. Chem. Soc. Dalton Trans., (1990) 2367.
5 T. Adatia, M.J. Mays, M. McPartlin, M.J. Morris and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1989) 1555.
6 G. Conole, K.A. Hill, M. McPartlin, M.J. Mays and M.J. Morris, J. Chem. Soc., Chem. Commun., (1989) 688.
7 M.J. Mays, M.J. Morris, P.F. Reinisch, M. McPartlin and H.R. Powell, Polyhedron, 8 (1989) 1807.
8 G. Conole, M. McPartlin, M.J. Mays and M.J. Morris, J. Chem. Soc., Dalton Trans., (1990) 2359.
9 D. Braga, A.J.M. Caffyn, M.C. Jennings, M.J. Mays, L. Manojlovic-Muir, P.R. Raithby, P. Sabatino and K.W. Woulfe, J. Chem. Soc., Chem. Commun., (1989) 1401.
10 R.J. Mercer, M. Green and A.G. Orpen, J. Chem. Soc., Chem. Commun., (1986) 567; S.F.T. Froom, M. Green, R.J. Mercer, K.R. Nagle, A.G. Orpen and S. Schwiegk, J. Chem. Soc., Chem. Commun., (1986) 1966.
11 A.W. Al-Saadoon, M. Green, R.J. Mercer and A.G. Orpen, J. Organomet. Chem., 384 (1990) C12.
12 L.J. Todd, J.R. Wilkinson, J.P. Hickey, D.L. Beach and K.W. Barnett, J. Organomet. Chem., 154 (1978) 151.
13 M.R. Churchill and J.P. Fennessey, Inorg. Chem., 7 (1968) 953; A.T. Liu, W. Beck, G. Huttner and H. Lorenz, J. Organomet. Chem., 129 (1977) 91; G.A. Jones and L.J. Guggenberger, Acta Crystallogr. Sect. B, 31 (1975) 900.
14 D.S. Bohle, T.C. Jones, C.E.F. Rickard and W.R. Roper, Organometallics, 5 (1986) 1612; R.C. Dobbie and P.R. Mason, J. Chem. Soc., Dalton Trans., (1974) 2439.
15 R.C. Dobbie and P.R. Mason, J. Chem. Soc., Dalton Trans., (1973) 1124.
16 P. Braunstein and E. de Jesus, J. Organomet. Chem., 365 (1989) C19; R.C. Dobbie and P.R. Mason, J. Chem. Soc., Dalton Trans., (1976) 189; R.J. Haines and C.R. Nolte, J. Organomet. Chem., 36 (1972) 163; R.J. Haines, A.L. du Preez and C.R. Nolte, ibid., 55 (1973) 199.
17 M.T. Ashby and J.H. Enemark, Organometallics, 6 (1987) 1323.
18 L. Weber, M. Frebel and R. Boese, Chem. Ber., 122 (1989) 2091; New J. Chem., 13 (1989) 303.
19 M.T. Ashby and J.H. Enemark, Organometallics, 6 (1987) 1318.
20 J.L. Davidson, M. Shiralian, L. Manojlovic-Muir and K.W. Muir, J. Chem. Soc., Dalton Trans., (1984) 2167; L. Carlton, J.L. Davidson and M. Shiralian, ibid., (1986) 1577; F.Y. Petillon, F. Le Floch-Perennou, J.E. Guerchais and D.W. Sharp, J. Organomet. Chem., 173 (1979) 89; F.Y. Petillon, F. Le Floch-Perennou, J.E. Guerchais, D.W.A. Sharp, L. Manojlovic-Muir and K.W. Muir, ibid., 202 (1980) 23; M.M. Kubicki, R. Kergoat, H. Scordia, L.C. Gomes de Lima, J.E. Guerchais and P. L'Haridon, ibid., 340 (1988) 41; R. Kergoat, M.M. Kubicki, L.C. Gomes de Lima, H. Scordia, J.E. Guerchais and P. L'Haridon, ibid., 367 (1989) 143.

21 W. Malisch, R. Maisch, I.J. Colquhoun and W. MacFarlane, J. Organomet. Chem., 220 (1981) C1.
22 R. Benn and H. Günther, Angew. Chem., Int. Ed. Engl., 22 (1983) 350.
23 R. Bender, P. Braunstein, J.-M. Jud and Y. Dusausoy, Inorg. Chem., 22 (1983) 3394.
24 R.B. King, Organometallic Syntheses, Vol. 1, Academic Press, New York, 1965, p. 109.
25 G.M. Sheldrick SHELXTL, An integrated system for solving refining and displaying crystal structures from diffraction data, 4th revision, University of Göttingen, 1983.