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Addition of diphenylphosphine to molybdenum alkynyl complexes

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Abstract

The reaction of $[CpMo(CO)_3(C{\equiv}CR)]$ ($Cp = \eta\text{-}C_5H_5$) with PPh_2H in the presence of Me_3NO gives the expected substituted complex $[CpMo(CO)_2(PPh_2H)(C{\equiv}CPh)]$ as the major product when R = Ph. The phosphine ligand in this compound can be subjected to a deprotonation–alkylation sequence to afford $[CpMo(CO)_2(PPh_2Me)(C{\equiv}CPh)]$. In contrast, when $R = CO_2Me$, treatment of $[CpMo(CO)_3(C{\equiv}CR)]$ with PPh_2H and Me_3NO leads directly to $[CpMo(CO)_2(PPh_2C{=}CHCO_2Me)]$ by addition of the P–H bond across the alkynyl triple bond; this compound has been structurally characterised and contains a three-membered (MoPC) ring with an exocyclic $=CHCO_2Me$ group. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Alkyne; Phosphide; Crystal structures

1. Introduction

Phosphine ligands are ubiquitous in homogeneous transition metal catalyst systems. The ability to confer a variety of properties on the resulting complexes by changing the electronic, steric and stereochemical properties of the ligand through its substituents allows almost unlimited variation on the theme: recent areas of development include water-soluble phosphines, polymer-bound phosphines, and chiral bidentate phosphines for asymmetric synthesis. Under the relatively harsh conditions of many catalytic reactions, however, slow deactivation of catalysts occurs, often involving P–C bond cleavage in the phosphine ligand to form phosphido groups which then either lead to formation of inactive polynuclear compounds or undergo undesirable side-reactions with coordinated organic species. Examples of this are particularly prevalent in hydroformylation catalysis [1].

For some years we have been investigating the interaction of phosphido ligands with coordinated organic fragments at molybdenum and iron centres, utilising the nucleophilic properties of the ligand to form new P–C bonds. For example, we have shown that migration of acyl ligands from molybdenum to phosphorus can be induced by deprotonation of $[CpMo(CO)_2(PPh_2H)(COMe)]$, a process which we proposed to occur via an intermediate containing a three-membered MoPC ring formed by nucleophilic attack of the phosphido group on the acyl carbonyl [2]. We have also demonstrated that both anionic and neutral phosphido ligands are sufficiently nucleophilic to attack electron-deficient alkynes to form vinylphosphine ligands or in some cases metallacycles [3]. A logical further step was therefore to investigate the attack of phosphido groups on coordinated alkyne or acetylide ligands. In this paper we show that by varying the electronic character of the acetylide ligand, addition of a P–H functionality to its triple bond can be readily induced.

2. Results and discussion

The acetylide complex $[CpMo(CO)_3(C{\equiv}CPh)]$ (**1a**) is readily prepared by the reaction of $[CpMo(CO)_3Cl]$ with phenylacetylene in diethylamine solvent in the presence of CuI catalyst [4]. No change was observed when a solution of **1a** in MeCN was stirred overnight at room temperature with one equivalent of PPh_2H, but on addition of Me_3NO, a rapid reaction ensued to afford two products which were separated by column

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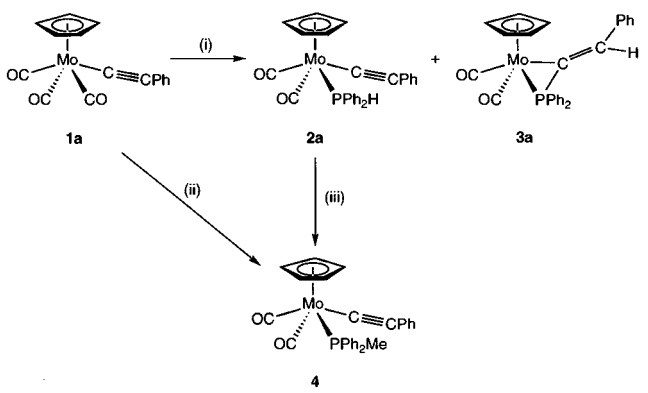
chromatography (Scheme 1). The major complex formed (42% yield) was the expected substitution product [$CpMo(CO)_2(PPh_2H)(C{\equiv}CPh)$] (**2a**). This compound displayed two absorptions (1960 and 1878 cm^{-1}) in its IR spectrum in an intensity ratio characteristic of a *cis*-dicarbonyl structure, and also a weaker absorption due to $\nu(C{\equiv}C)$ at 2085 cm^{-1}. The ^{1}H-NMR spectrum showed the presence of only one isomer; the expected doublet due to the P–H proton was discernible even though one of its components was partially masked by the phenyl protons. The $^{31}P\{^1H\}$-NMR spectrum comprised a single peak in a position typical of terminal phosphine ligands.

The minor product of this reaction also displayed a *cis*-dicarbonyl pattern in its IR spectrum, but the C≡C absorption was absent. Moreover the ^{1}H-NMR spectrum contained an unexpected doublet at δ 8.67 (J = 12.5 Hz) and the ^{31}P chemical shift of −87.7 ppm was also distinctly unusual; such a figure is characteristic of the presence of a three-membered ring. By comparison with the compound crystallographically characterised below, we can identify this complex as [$CpMo(CO)_2(PPh_2C{=}CHPh)$] (**3a**) in which addition of the P–H bond across the C≡C bond of the acetylide ligand has occurred to produce an α-phosphinovinyl moiety. The compound consists of a single isomer (the *Z*-isomer, in which the PPh_2 and H are situated *cis* to each other) as shown by the magnitude of the P–H coupling in the ^{1}H-NMR spectrum (12.5 Hz) as discussed below.

The reaction of **1a** with PPh_2H was also investigated under thermal conditions; although the yields of **2a** and **3a** were virtually unchanged, other products were also formed which made separation more difficult. Use of freshly sublimed Me_3NO as opposed to the commercial dihydrate also did not improve the yield of **2a**.

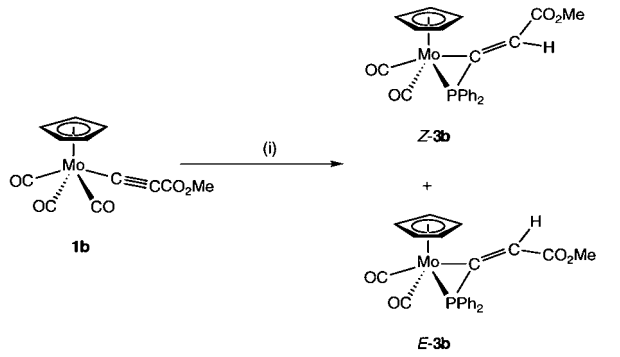
We then investigated the behaviour of **2a** on deprotonation to ascertain whether an anionic phosphido group could attack the phenylacetylide ligand. Deprotonation of the phosphine ligand of **2a** with the organic base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) under similar conditions to those used previously for [$CpMo(CO)_2(PPh_2H)(COMe)$], followed by treatment with MeI afforded a 77% yield of [$CpMo(CO)_2(PPh_2Me)(C{\equiv}CPh)$] (**4**) arising from simple deprotonation and alkylation at the phosphorus atom [5]. However, a small amount of **3a** was also produced, demonstrating that there is some degree of attack on the acetylide ligand; presumably the resulting anion is reprotonated by $DBUH^+$ in the solution, abstracts a proton from further **2a**, or is reprotonated during the work-up procedure. Complex **4** displayed very similar spectroscopic characteristics to **2a** (see Section 3) and its identity was also confirmed by independent synthesis from **1a** and PPh_2Me in 68% yield.



Scheme 1. Synthesis of complexes derived from [$CpMo(CO)_3(CCPh)$] (**1a**). Reagents and conditions: (i) PPh_2H, Me_3NO, MeCN; (ii) PPh_2Me, Me_3NO, MeCN; (iii) DBU, then MeI.

In previous work we have observed that phosphido ligands are sufficiently nucleophilic to attack activated alkynes such as dmad ($MeO_2CC{\equiv}CCO_2Me$) or methyl propiolate, but react poorly with simple alkynes such as acetylene itself [3]. We therefore decided to introduce an electron-withdrawing substituent into the acetylide ligand in the hope of inducing P–C bond formation with the phosphido group. Unfortunately the preparation of the acetylide complex [$CpMo(CO)_3(C{\equiv}CCO_2Me)$] (**1b**) cannot be achieved in the same way as that of **1a** because the activated alkyne methyl propiolate itself reacts rapidly with the diethylamine solvent. Therefore we used a route involving deprotonation of the alkyne with BuLi in THF followed by reaction with [$CpMo(CO)_3Cl$], which gave the desired product as a yellow solid, typically in 30% yield. In its IR spectrum the compound showed two strong carbonyl absorptions (2048 and 1972 cm^{-1}), a peak at 2108 cm^{-1} due to the acetylide functionality, and a weaker peak due to the ester carbonyl at 1687 cm^{-1}; the NMR spectra were as expected. After we had prepared this complex, an alternative synthesis was published which involves reaction of $[CpMo(CO)_3]^-$ with $ClC{\equiv}CCO_2Me$, giving **1b** in 64% yield [6]; although the yield of our procedure is lower, it does avoid the preparation of the potentially explosive chloroalkyne.

The reaction of **1b** with PPh_2H in MeCN again did not proceed until the addition of Me_3NO to the mixture. In this case only one identifiable product, [$CpMo(CO)_2(PPh_2C{=}CHCO_2Me)$] (**3b**) was formed (Scheme 2), though a small amount of a minor product was observed which may be the analogue of **2a**, i.e. [$CpMo(CO)_2(PPh_2H)(C{\equiv}CCO_2Me)$]. The fact that no reaction occurs without Me_3NO shows that substitution of the carbonyl ligand occurs before addition of the P–H bond across the alkynyl functionality. Complex **3b** again shows two CO bands in its IR spectrum, but no acetylide peak. Inspection of the ^{1}H-NMR spectrum revealed the presence of two isomers: the major one (*Z*) has the phosphorus atom situated *cis* to the H on the exocyclic double bond, and gives rise to a doublet at δ



Scheme 2. Synthesis of complexes derived from $[CpMo(CO)_3(CCCO_2Me)]$ (**1b**). Reagents and conditions: (i) PPh_2H, Me_3NO, MeCN.

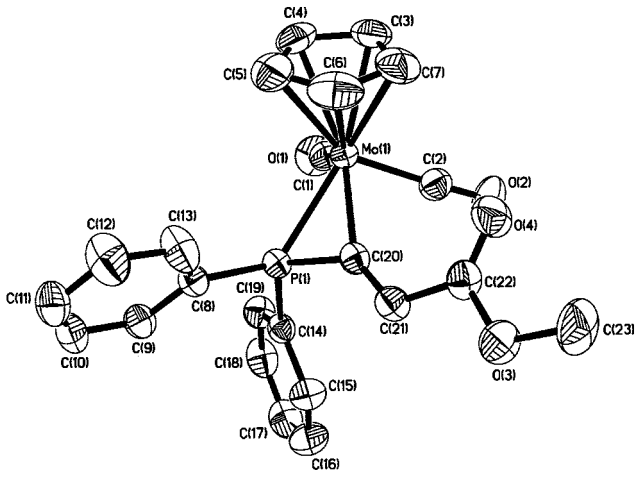


Fig. 1. Molecular structure of complex **3b** in the crystal showing the atomic numbering scheme.

7.70 with $J(PH) = 11.3$ Hz due to the CH group, whereas the minor one (*E*) has the PPh_2 and H *trans* to each other as revealed by the larger coupling constant, $J(PH) = 32.3$ Hz, for a doublet at δ 6.68. The $^{31}P\{^1H\}$-NMR spectrum contains peaks at -71.5 and -90.0 ppm for the *E* and *Z* isomers, respectively. The mass spectrum and $^{13}C\{^1H\}$-NMR spectrum of **3b** confirmed the above findings, though the $CHCO_2Me$ carbon signals of both isomers were obscured by the phenyl region.

The two isomers of **3b** interconvert slowly in solution. A ^{1}H-NMR spectrum of the sample from which the crystal used for the structure determination was selected (see below) showed that the isomer ratio was 4.2:1 in favour of the *Z*-isomer. After standing in solution for 24 h, the ratio had changed to 0.7:1. The interconversion may take place through opening of the three-membered ring, but another possibility is that protonation by traces of acid could occur at the exocyclic methylene group to give a cationic species in which there could be free rotation about the $C–CH_2CO_2Me$ single bond, followed by loss of the proton.

A closely related complex, $[CpW(CO)_2(PPh_2C{=}CH_2)]$, has been prepared by Kreißl and co-workers by deprotonation of $[CpW(CO)_2(PPh_2CMe)]^+$ [7]. For comparison the ^{1}H-NMR spectrum of this complex in CD_2Cl_2 contained peaks for the methylene group at δ 7.12 with $J(PH) = 13.7$ Hz and δ 6.05 with $J(PH) = 37.6$ due to the protons *cis* and *trans* to phosphorus, respectively; a small $J(HH)$ of 1.2 Hz was also observed. The ^{31}P-NMR shift was -124.1 ppm. Very recently, Ipaktschi and co-workers have reported the addition of PPh_2Cl to the vinylidene complexes $[CpW(CO)(NO)(=C=CHR)]$ (R = H, Me, Ph) to afford $[CpW(NO)(Cl)(PPh_2C{=}CHR)]$, which also display very similar spectroscopic properties; in the cases where R is not H, two interconverting isomers are again observed, with the *E*:*Z* ratios being 3:1 and 1:1.2 for R = Me and Ph, respectively [8]. The similarity of these data to those obtained for the two isomers of **3b** reinforces our view that the isomers differ in the stereochemistry about the exocyclic double bond.

Crystallisation of **3b** by diffusion of diethyl ether into a dichloromethane solution provided large rectangular blocks suitable for structure determination. The result is shown in Fig. 1, with selected bond lengths and angles collected in Table 1. Only the *Z* isomer is present in the crystal selected for study. The molecule consists of a standard four-legged piano stool arrangement in which the basal positions are occupied by two *cis* carbonyl groups and the α-phosphinovinyl ligand. The latter forms a three-membered ring involving Mo(1), P(1) and C(20) in which the P(1)–C(20) bond is rather short, 1.748(3) Å, a phenomenon previously noted in other phosphinovinyl complexes and suggestive of the possible contribution of a phospha-allene canonical form ($Ph_2P{=}C{=}CHCO_2Me$) [9]. In fact the bond lengths

Table 1
Selected bond lengths (Å) and angles (°) for complex **3b**

Bond lengths			
Mo(1)–C(2)	1.954(3)	Mo(1)–C(1)	1.977(3)
Mo(1)–C(20)	2.143(3)	Mo(1)–P(1)	2.4131(8)
P(1)–C(20)	1.748(3)	O(1)–C(1)	1.153(3)
O(2)–C(2)	1.146(4)	C(20)–C(21)	1.346(4)
C(21)–C(22)	1.467(4)		
Bond angles			
C(2)–Mo(1)–C(1)	82.80(12)	C(2)–Mo(1)–C(20)	79.04(11)
C(1)–Mo(1)–C(20)	117.74(10)	C(2)–Mo(1)–P(1)	103.94(8)
C(1)–Mo(1)–P(1)	84.83(8)	C(20)–Mo(1)–P(1)	44.62(7)
C(20)–P(1)–Mo(1)	59.47(9)	O(1)–C(1)–Mo(1)	178.3(2)
O(2)–C(2)–Mo(1)	176.8(3)	C(21)–C(20)–P(1)	136.4(2)
C(21)–C(20)–Mo(1)	147.5(2)	P(1)–C(20)–Mo(1)	75.91(10)
C(20)–C(21)–C(22)	122.4(2)		

and angles within this ring are almost identical to those found in the dinuclear complex $[Mo_2Cl_2(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PC{=}CHMe)Cp_2]$ which contains a similar arrangement. The C(20)–C(21) distance of 1.346 Å is within the range expected for a double bond, but there is also some shortening of the C(21)–C(22) bond to 1.467(4) Å. A canonical form in which a negative charge was localised on the carbonyl oxygen and a positive charge on the MoPC ring could account for this. Additional weight is given to this idea by the fact that the CO_2Me group is coplanar with the MoPC ring in the solid state.

In conclusion, we have shown that addition of the P–H bond of a coordinated phosphine ligand to an alkynyl ligand can be induced simply by changing the substituent on the latter from Ph to CO_2Me. The mechanism of formation of **3** from **1** presumably involves CO substitution as its first step (as shown by the requirement for Me_3NO and the isolation of **2**) followed by transfer of the hydrogen from the phosphine to the β-carbon of the acetylide and attack of the nucleophilic phosphido group on the α-carbon. It is possible that the presence of NMe_3 in the reaction mixture (arising from the decarbonylation reaction) has a bearing on the outcome; for example it is conceivable that the presence of the electron-withdrawing CO_2Me substituent in **1b** renders the phosphine ligand in the putative substituted complex **2b** more prone to deprotonation by this weak base, resulting in direct and complete conversion to **3b** by attack of the phosphido group on the more activated acetylide ligand.

3. Experimental

General experimental techniques were as detailed in recent papers from this laboratory [10]. Infra-red spectra were recorded in CH_2Cl_2 solution on a Perkin–Elmer 1600 FTIR machine using 0.5 mm NaCl cells. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or on an AM250 spectrometer. Chemical shifts are given on the δ scale relative to $SiMe_4 = 0.0$ ppm. The ^{13}C{^{1}H}-NMR spectra were recorded using an attached proton test technique (JMOD pulse sequence). The ^{31}P{^{1}H}-NMR spectra were referenced to 85% $H_3PO_4 = 0.0$ ppm with downfield shifts reported as positive. Mass spectra were recorded on a Kratos MS 80 instrument operating in fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

Literature methods were used to prepare $[CpMo(CO)_3Cl]$ [11] and $[CpMo(CO)_3(C{\equiv}CPh)]$ [4]. The alkynes, phosphine ligands, trimethylamine-*N*-oxide, methyl iodide and DBU were all obtained from Aldrich and used without further purification. Anhydrous Me_3NO was prepared by sublimation or by azeotropic distillation from toluene. Light petroleum refers to the fraction boiling in the range 60–80 °C.

3.1. Reaction of $[CpMo(CO)_3(C{\equiv}CPh)]$ with PPh_2H

The complex $[CpMo(CO)_3(C{\equiv}CPh)]$ (0.203 g, 0.587 mmol) was dissolved in MeCN (25 ml) and treated with $Me_3NO{\cdot}2H_2O$ (65.2 mg, 0.587 mmol) followed by diphenylphosphine (0.17 ml, 0.853 mmol). After stirring for 30 min, the solvent was removed in vacuo and the residue adsorbed onto a small amount of silica, which was then loaded onto a silica column. Elution with CH_2Cl_2–light petroleum (1:3) afforded a small yellow band due to $[CpMo(CO)_2(PPh_2C{=}CHPh)]$ (**3a**) (44.1 mg, 15%). Continued elution with a 1:1 mixture of the same solvents gave $[CpMo(CO)_2(PPh_2H)(C{\equiv}CPh)]$ (**2a**) as a bright yellow powder (124.0 mg, 42%).

2a: M.p. 133–136 °C. IR ν(C≡C) 2085w; ν(CO) 1960s, 1878s cm^{-1}. ^{1}H-NMR: δ 7.65–6.79 (m, 15H, Ph), 6.87 (d, J(PH) = 382 Hz, 1H, PH), 5.30 (s, 5H, Cp). ^{13}C{^{1}H}-NMR: δ 250.9 (d, $J = 31$ Hz, CO), 236.9 (d, $J = 2$ Hz, CO), 136.4 (d, $J = 37$ Hz, C_{ipso}), 134.0–125.1 (m, Ph), 105.8, 105.3 (both s, C≡C), 92.5 (s, Cp). ^{31}P{^{1}H}-NMR: δ 37.5 (s). Anal. Found: C, 63.89; H, 4.27. Calc. for $C_{27}H_{21}MoO_2P$: C, 64.28; H, 4.17%. Mass spectrum: m/z 507 $[M + H^+]$, 450 $[M - 2CO]^+$.

3a: M.p. 185–188 °C. IR ν(CO) 1951s, 1876s cm^{-1}. ^{1}H-NMR: δ 8.67 (d, $J = 12.5$ Hz, 1H, CH), 7.80–7.13 (m, 15H, Ph), 5.26 (s, 5H, Cp). ^{31}P{^{1}H}-NMR: δ −87.7 (s, PPh_2). Anal. Found: C, 64.00; H, 4.14. Calc. for $C_{27}H_{21}MoO_2P$: C, 64.28; H, 4.17%. Mass spectrum m/z 506 $[M^+]$, 450 $[M - 2CO]^+$.

3.2. Preparation of $[CpMo(CO)_2(PPh_2Me)(C{\equiv}CPh)]$ (**4**) from **2a**

Complex **2a** (101.9 mg, 0.20 mmol) was dissolved in THF (15 ml) and treated with 1.1 equivalent of DBU (0.033 ml, 2.23 mmol) After stirring at room temperature (r.t.) for 15 min, methyl iodide (0.0126 ml, 0.20 mmol) was added and stirring continued for a further 3 h. After removal of the solvent in vacuo the residue was chromatographed to afford three yellow bands which were eluted with a 1:1 mixture of CH_2Cl_2 and light petroleum. The first consisted of a small amount of complex **3a** and the second of unreacted starting material, while the third contained $[CpMo(CO)_2(PPh_2Me)(C{\equiv}CPh)]$ (**4**). Yield = 81.0 mg, 77%.

3.3. Preparation of $[CpMo(CO)_2(PPh_2Me)(C{\equiv}CPh)]$ (**4**) from **1a**

The complex $[CpMo(CO)_3(C{\equiv}CPh)]$ (441.6 mg, 1.28 mmol) was dissolved in MeCN (50 ml) and treated with

PPh_2Me (0.26 ml, 1.40 mmol) and anhydrous trimethylamine-*N*-oxide (126.7 mg, 1.69 mmol). The solution changed colour from orange to deep red and gas evolution was observed. The reaction was stirred for 1.5 h. After removal of the solvent under vacuum and absorption of the residue onto silica, the product was chromatographed to afford **4** as a bright yellow powder (447.9 mg, 68.4%) which was eluted with a 1:1 mixture of CH_2Cl_2 and light petroleum.

4: M.p.176–179 °C. IR ν(C≡C) 2085w, ν(CO) 1958s, 1875s cm^{-1}. ^{1}H-NMR δ 7.62–6.83 (m, 15H, Ph), 5.29 (s, 5H, Cp), 2.22 (d, J(PH) = 8.2 Hz, 3H, Me). $^{13}C\{^1H\}$-NMR: δ 251.7 (d, J = 29 Hz, CO), 238.6 (s, CO), 139.0 (d, J = 42 Hz, C_{ipso}), 136.2 (d, J = 47 Hz, C_{ipso}), 132.8–124.9 (m, Ph), 107.9, 107.5 (both s, C≡C), 92.5 (s, Cp), 19.5 (d, J = 34 Hz, Me). $^{31}P\{^1H\}$-NMR: δ 40.7. Anal. Found: C, 64.56; H, 4.34. Calc. for $C_{28}H_{23}MoO_2P$: C, 64.86; H, 4.44%. Mass spectrum m/z 521 $[M + H^+]$, 492, 464 $[M - nCO]^+$ (n = 1–2).

3.4. Preparation of [CpMo(CO)$_3$(C≡CCO$_2$Me)] (1b)

The alkyne methyl propiolate (0.68 ml, 7.65 mmol) was dissolved in THF (20 ml) and cooled to −78 °C. Butyl lithium (5.3 ml of a 1.6 M solution in hexanes, 8.48 mmol) was added and the solution was allowed to stir for 10 min. The complex $[CpMo(CO)_3Cl]$ (2.1277 g, 7.6 mmol) was added as a solid, and the solution was allowed to warm to r.t. The solvent was evaporated to dryness and the residue chromatographed. The product, $[CpMo(CO)_3(C{\equiv}CCO_2Me)]$, was recovered as a yellow band by elution with CH_2Cl_2. Yield 31%. M.p. 98–102 °C. IR: ν(C≡C) 2108w, ν(CO) 2048s, 1972s cm^{-1}. ^{1}H-NMR: δ 5.57 (s, 5H, Cp), 3.67 (s, 3H, Me). These data correspond with those recently published [6].

3.5. Reaction of [CpMo(CO)$_3$(C≡CCO$_2$Me)] with PPh$_2$H

The complex $[CpMo(CO)_3(C{\equiv}CCO_2Me)]$ (0.75 g, 2.3 mmol) was dissolved in MeCN (20 ml) and treated with 1.1 equivalent of $Me_3NO{\cdot}2H_2O$ (0.28 g, 2.52 mmol). After stirring for 10 min, diphenylphosphine (0.45 ml, 2.59 mmol) was added. After removal of the solvent in vacuo and absorption of the residue onto silica the product was separated by chromatography. A minor product, tentatively identified as $[CpMo(CO)_2(PPh_2H)(C{\equiv}CCO_2Me)]$ (**2b**) by comparison with **2a**, was eluted as a small yellow band with a 2:3 mixture of CH_2Cl_2 and light petroleum [ν(C≡C) 2083w, ν(C≡O) 1969s, 1896s cm^{-1}]. Unfortunately, contamination of this complex by oily phosphine-containing material prevented the acquisition of further data. Elution with CH_2Cl_2 gave a further yellow band of $[CpMo(CO)_2(PPh_2C{=}CHCO_2Me)]$ (**3b**) (581 mg, 52%).

3b: IR: ν(CO) 1967s, 1895s cm^{-1}. ^{1}H-NMR: *Z*-isomer: 7.70 (d, J(PH) = 11.3 Hz, 1H, CH), 5.36 (s, 5H, Cp), 3.77 (s, 3H, Me); *E*-isomer: 6.68 (d, J(PH) = 32.3, 1H, CH), 5.28 (s, 5H, Cp), 3.55 (s, 3H, Me). $^{13}C\{^1H\}$-NMR: *Z*-isomer: δ 232.3 (d, J(PC) = 17 Hz, CO), 178.9 (d, J(PC) = 32 Hz, P*C*C), 169.3 (d, J(PC) = 21 Hz, CO_2Me), 133.2–127.4 (m, Ph), 90.0 (s, Cp), 50.9 (s, Me); *E*-isomer: δ 232.3 (d, J(PC) = 17 Hz, CO), 177.0 (d, J(PC) = 23 Hz, P*C*C), 161.1 (d, J(PC) = 6 Hz, CO_2Me), 133.2–127.4 (m, Ph), 91.4 (s, Cp), 50.8 (s, Me). $^{31}P\{^1H\}$-NMR: *E*-isomer δ −71.5, *Z*-isomer δ −90.0 (s, PPh_2). Anal. Found: C, 56.87; H, 3.99; Calc. for $C_{23}H_{19}MoO_4P$: C, 56.76; H, 3.91%. Mass spectrum m/z 488, 460, 432 $[M - nCO]+$ (n = 0–2).

3.6. Crystal structure determination

Crystal data for $[CpMo(CO)_2(PPh_2C{=}CHCO_2Me)]$ (**3b**) are collected in Table 2. Three-dimensional, r.t. X-ray data were collected in the θ range shown on a Siemens P4 diffractometer by the ω-scan method. Of

Table 2
Summary of crystallographic data for complex **3b**

Identification code	ma062
Empirical formula	$C_{23}H_{19}MoO_4P$
Formula weight	486.29
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.012(2)
b (Å)	9.728(2)
c (Å)	13.951(2)
α (°)	79.68(2)
β (°)	86.21(2)
γ (°)	78.130(10)
V (Å^3)	1046.4(4)
Z	2
D_{calc} (Mg m^{-3})	1.543
Absorption coefficient (mm^{-1})	0.729
F(000)	492
Crystal size (mm)	0.73 × 0.43 × 0.32
Theta range for data collection (°)	2.17–25.00
Index ranges	$-1 \le h \le 9$, $-11 \le k \le 11$, $-16 \le l \le 16$
Reflections collected	4554
Independent reflections	3695 [R_{int} = 0.0452]
Absorption correction	Psi scans
Max/min transmission	0.9467 and 0.3977
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3695/0/262
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0292, wR_2 = 0.0785
R indices (all data)	R_1 = 0.0331, wR_2 = 0.0818
Largest difference peak and hole (e Å^{-3})	0.483 and −0.615

the reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by the analysis of 10 azimuthal scans, those independent reflections which exceeded the significance level $|F|/\sigma(|F|) > 4.0$ were used in refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at the final R values shown with allowance for the thermal anisotropy of all non-hydrogen atoms. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.2894P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the programme package SHELXL93 [12] as implemented on the Viglen 486dx computer.

4. Supplementary material

Crystallographic data for the structure determination of complex **3b** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 161950. 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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