P–C Coupling Reactions of Pyramidal Phosphinidene-Bridged Dimolybdenum Complexes with Alkynes†

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Abstract

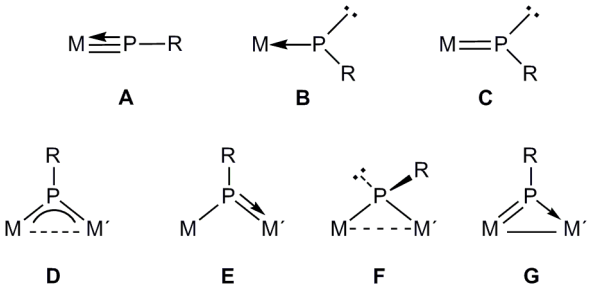
The new pyramidal phosphinidene-bridged complex [$Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2\{P(OMe)_3\}$] (**2b**) was prepared in situ upon reaction of the trigonal phosphinidene complex [$Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2$] (**1**) with $P(OMe)_3$. This complex underwent an unexpected Michaelis-Arbuzov-like rearrangement when dissolved in tetrahydrofuran, to give the phosphanyl-phosphonate isomer [$Mo_2Cp\{\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}P(Me)C_5H_4\}(\eta^6\text{-}HMes^*)(CO)_2\{P(O)(OMe)_2\}$] in a quantitative way. The reactions of complex **2b**, and also its PMe_3 analogue [$Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2(PMe_3)$] (**2a**), with different internal alkynes (EtC≡CC(O)Me and MeC≡CCO_2Me) and terminal alkynes (HC≡CR; R = 4-C_6H_4Me, C(O)Me, CO_2Me) were then investigated. These reactions proceeded in all cases rapidly at room temperature (less than 1 min) with very high regioselectivity, to give the corresponding metallacyclic products [$Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CR^1CR^2C(O)\}(\eta^6\text{-}HMes^*)(CO)(PX_3)$] in high yield (X = Me, OMe; R^1 = Et, Me, H; R^2 = C(O)Me, CO_2Me, 4-C_6H_4Me). Spectroscopic data for these complexes indicate that they all share the same structure, further confirmed through an X-ray single crystal study on the EtC≡CC(O)Me derivative of compound **2b**.

Keywords: Molybdenum; Phosphorus ligands; Carbonyl complexes; Phosphinidene complexes; Metallacycles. P–C coupling reactions.

1. Introduction

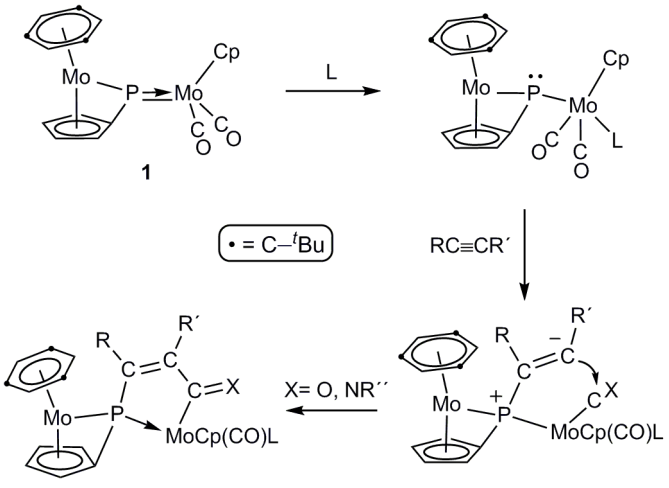
Transition metal complexes bearing phosphinidene ligands (PR) bound to one [1] or two [2] metal atoms are species particularly reactive, thanks to the combination at the P site of a low coordination environment with M–P multiple bonding and/or the presence of a lone electron pair, as it can be recognized in the diverse coordination modes of PR ligands reported to date (Chart 1) [3]. As a result, many of these complexes react readily with all sorts of saturated and unsaturated organic molecules, whereby a great variety of organophosphorus compounds and ligands can be built [1,2,4].

Chart 1



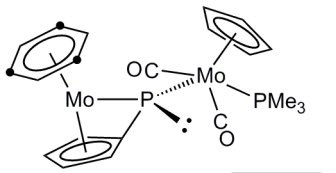
In the context of our continued work on the chemistry of PR-bridged binuclear complexes (types **D** to **G**), we found some time ago that the type **E** dimolybdenum complex $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ (**1**) underwent interesting multicomponent reactions with alkynes and olefins in the presence of CO, CNR and PR_3 ligands, to give different derivatives displaying 4- and 5-membered phosphametallacycles [5]. It was proposed at the time that these reactions proceeded through intermediate pyramidal PR complexes (type **F**) derived from initial addition of the added ligand L at the $MoCp(CO)_2$ site, which then would attack a molecule of the olefin/alkyne, thus triggering the formation of $MoPC_3$ metallacycles that might further evolve depending on the particular case (Scheme 1).

Scheme 1. Multicomponent reactions of compound 1



Shortly after that, we were able to characterize one of these presumed intermediate species, the pyramidal phosphinidene complex [$Mo_2Cp(\mu$-κ^1:κ^1,η^5-PC_5H_4)(η^6-HMes*)$(CO)_2(PMe_3)$] (**2a**) (Chart 2), which can be prepared in situ upon addition of stoichiometric amounts of PMe_3 on toluene solutions of **1** [6]. Compound **2a** proved to display a high nucleophilicity enabling it to react with different C- and N-based electrophilic organic compounds, such as alkyl halides [7], S-containing heterocumulenes [8], diazoalkanes and organic azides [9]. In this paper we analyse the reactions of complex **2a**, as well as those of its $P(OMe)_3$ analogue [$Mo_2Cp(\mu$-κ^1:κ^1,η^5-PC_5H_4)(η^6-HMes*)$(CO)_2${$P(OMe)_3$}] (**2b**), with different internal and terminal alkynes. This study was made with the aim of: (a) supporting the mechanistic proposal of the multicomponent reactions of **1** mentioned above; (b) gaining additional information concerning the selectivity of the P–C couplings involved; and (c) checking whether any H-shift processes might take place (in the case of terminal alkynes), as observed in the multicomponent reactions of **1** with olefins [5b]. As it will be shown below, the reactions of compounds **2a,b** with alkynes support the mechanistic proposal mentioned above and have a pronounced regioselectivity which can be rationalized on simple electronic grounds. However, no H-shift processes have been detected in the reactions studied.

Chart 2



2a • = C–^{t}Bu

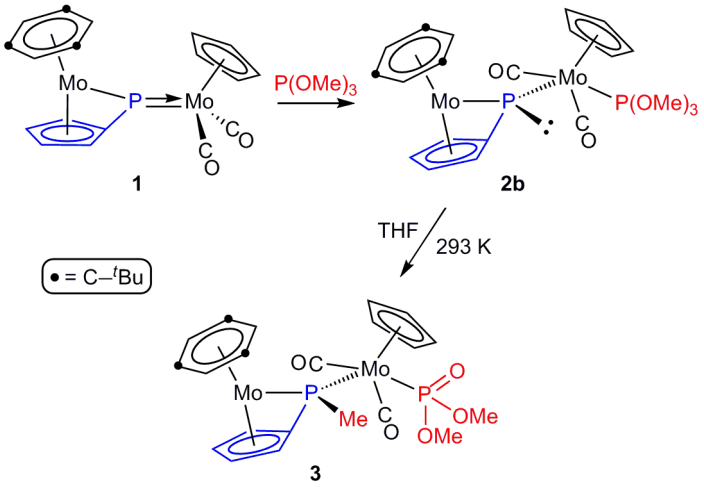
2. Results and Discussion

*2.1. Reaction of compound **1** with $P(OMe)_3$*

As noted above, previous work revealed that compound **1** reacts rapidly with stoichiometric amounts of PMe_3 to give quantitatively the pyramidal phosphinidene complex **2a**. In a similar way, addition of stoichiometric amounts of $P(OMe)_3$ on toluene solutions of **1** yields the corresponding derivative [$Mo_2Cp(\mu$-κ^1:κ^1,η^5-PC_5H_4)(η^6-HMes*)$(CO)_2${$P(OMe)_3$}] (**2b**) in a quantitative way (Scheme 2). As it was the case of **2a**, the phosphite complex **2b** proved to be quite reactive, and decomposed rapidly upon manipulation, so it could not be isolated as a solid material in the conventional way. Even so, it can be used for further reactivity studies when prepared in situ (see the Experimental section). More precisely, this product can be safely handled in toluene, benzene or petroleum ether solutions, provided that air is rigorously

excluded from the medium. However, when dissolved in tetrahydrofuran, **2b** undergoes an unexpected rearrangement to be discussed below.

Scheme 2. $P(OMe)_3$ derivatives of compound 1



Spectroscopic data for **2b** in solution are comparable to those of **2a** (Table 1 and Experimental section), with the expected differences derived from the replacement of the PMe_3 ligand (a strong donor) with $P(OMe)_3$, a better acceptor ligand. Thus, the IR spectrum of **2b** displays two C–O stretches at frequencies some 15-20 cm^{-1} above those of **2a** and with the same relative intensities (medium and strong, in order of decreasing frequencies), which are characteristic of transoid $M(CO)_2$ oscillators [10]. The pyramidal phosphinidene ligand in **2b** gives rise to a poorly deshielded ^{31}P NMR resonance at 124.6 ppm, as found for **2a** (δ_P 122.0 ppm), while the $P(OMe)_3$ ligand produces a more deshielded resonance (δ_P 197.9 ppm), some 50 ppm above the chemical shift of the free ligand. The two-bond coupling between these resonances in **2b** is higher than in **2a** (34 vs 26 Hz), an effect that can be attributed to the presence of very electronegative O atoms bound to P in the case of the phosphite complex [11].

Table 1. Selected IR and $^{31}P\{^{1}H\}$ NMR Data for New Isolated Compounds.[a]

Compound	ν(CO)	$\delta(PC_5H_4)$	$\delta(PX_3)$	J_{PP}
$[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-HMes*})(CO)_2(PMe_3)]$ (**2a**)[b]	1910 (m), 1842 (vs)	122.0	27.3	26
$[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-HMes*})(CO)_2\{P(OMe)_3\}]$ (**2b**)	1926 (m), 1863 (vs)[c]	124.6[c]	197.9[c]	34[c]
$[Mo_2Cp\{\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}P(Me)C_5H_4\}(\eta^6\text{-HMes*})(CO)_2\{P(O)(OMe)_2\}]$ (**3**)	1953 (m), 1872 (vs)	35.0[d]	114.7[d]	38[d]
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)C(Et)C\{C(O)Me\}C(O)\}(\eta^6\text{-HMes*})(CO)(PMe_3)]$ (**4a**)	1814 (s), 1677 (m), 1532 (m)[e]	106.1 (br)[e]	30.8 (br)[e]	
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)C(Et)C\{C(O)Me\}C(O)\}(\eta^6\text{-HMes*})(CO)\{P(OMe)_3\}]$ (**4b**)	1832 (s), 1682 (m), 1538 (m)	101.0	194.4	8
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)C(Me)C(CO_2Me)C(O)\}(\eta^6\text{-HMes*})(CO)(PMe_3)]$ (**5a**)	1813 (s), 1721 (m), 1531 (m)[e]	110.3[d]	30.7[d]	6[d]
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)C(Me)C(CO_2Me)C(O)\}(\eta^6\text{-HMes*})(CO)\{P(OMe)_3\}]$ (**5b**)	1830 (s), 1721 (m), 1544 (m)	101.7	192.9	10
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC(4\text{-}C_6H_4Me)C(O)\}(\eta^6\text{-HMes*})(CO)(PMe_3)]$ (**6a**)	1812 (s), 1543 (m)[e]	99.3[d]	29.8[d]	6[d]
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC(4\text{-}C_6H_4Me)C(O)\}(\eta^6\text{-HMes*})(CO)\{P(OMe)_3\}]$ (**6b**)	1834 (s), 1550 (m)	90.4	195.0	9
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC\{C(O)Me\}C(O)\}(\eta^6\text{-HMes*})(CO)(PMe_3)]$ (**7a**)	1817 (s), 1675 (m), 1532 (m)[e]	94.3[d]	28.7[d]	8[d]
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC\{C(O)Me\}C(O)\}(\eta^6\text{-HMes*})(CO)\{P(OMe)_3\}]$ (**7b**)	1834 (s), 1676 (m) 1544 (w)	85.3	194.3	9
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC(CO_2Me)C(O)\}(\eta^6\text{-HMes*})(CO)(PMe_3)]$ (**8a**)	1817 (s), 1721 (m), 1531 (m)[e]	95.0[d]	26.8[d]	7[d]
$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC(CO_2Me)C(O)\}(\eta^6\text{-HMes*})(CO)\{P(OMe)_3\}]$ (**8b**)	1838 (s), 1720 (m), 1544 (w)	93.3	192.9	9

[a] IR data recorded in dichloromethane solution, with C–O stretching bands [ν(CO)] in cm^{-1}; NMR data recorded in CD_2Cl_2 solution at 121.48 MHz and 293 K unless otherwise stated, with chemical shifts (δ) in ppm relative to external 85% aqueous H_3PO_4, and P-P couplings (J_{PP}) in hertz. [b] Data taken from reference 6; IR data in toluene solution; NMR data in C_6D_6 solution. [c] In toluene solution. [d] In C_6D_6 solution. [e] In tetrahydrofuran solution.

*2.2. Michaelis-Arbuzov-like rearrangement of compound **2b**.*

Although compound **2b** is relatively stable in poorly donor solvents such as toluene or petroleum ether, it undergoes a very fast isomerization at room temperature when dissolved in tetrahydrofuran, to give the phosphanyl-phosphonate complex $[Mo_2Cp\{\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}P(Me)C_5H_4\}(\eta^6\text{-HMes*})(CO)_2\{P(O)(OMe)_2\}]$ (**3**) in almost quantitative yield (Scheme 2). This isomer of **2b** can be isolated as a green microcrystalline solid upon chromatographic workup.

Unfortunately, we were not able to grow X-ray-quality crystals of **3**. Yet, its structure can be unambiguously stablished on the basis of the spectroscopic data available. First we note that **3** displays two C–O stretches with the same pattern as its precursor, thus denoting the retention of the transoid arrangement of the CO ligands (therefore also of the P-donor ones) around the MoCp fragment. Conclusive evidence for the Me transfer (from O to P atoms) occurred in the formation of **3** is provided by its ^{1}H NMR spectrum, which displays an OMe resonance at 3.92 ppm (J_{HP} = 11) with intensity corresponding to just two methyl groups, while the resonance for a third methyl group appears much more shielded, and also coupled to phosphorus (δ_H 1.62 ppm, J_{HP} = 8

Hz). For comparison, the cationic methylated derivative of **2a** [$Mo_2Cp\{\mu$-κ^1:κ^1,η^5-$P(Me)C_5H_4\}(\eta^6$-HMes*)$(CO)_2(PMe_3)](BAr'_4)$ displays a very similar ^{1}H NMR resonance for its PMe group (δ_H 1.82 ppm, J_{HP} = 8 Hz; Ar' = 3,5-$C_6H_3(CF_3)_2$) [7]. The latter complex also displayed a relatively shielded ^{31}P NMR resonance for its bridging phosphanyl group (δ_P 12.6 ppm), which is a characteristic signature of bridging PR_2 groups in the absence of metal-metal bonds [12]. This is also the case of compound **3**, which gives rise to a phosphanyl resonance at just 35.0 ppm. As for the ^{31}P chemical shift of the phosphonate ligand in **3** (δ_P 114.7 ppm), we note that we are not aware of a related molybdenum complex to be used for comparative purposes. Yet similar shifts have been previously found by us for *P*:*O*-bridging phosphonate ligands in dimolybdenum complexes of type $[Mo_2Cp_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_x]$ (x = 1, 2; δ_P 125-140 ppm) [13].

Compound **3** follows from a (likely intermolecular) Me-transfer from the coordinated $P(OMe)_3$ ligand (thus transformed into a phosphonate ligand) to the phosphinidene ligand (then converted into a bridging phosphanyl ligand). Although we are not aware of any precedent for this rearrangement involving phosphinidene complexes, we note that it bears some relationship with the extensively studied Michaelis-Arbuzov reaction, whereby phosphites are converted into phosphonates through reaction with alkyl halides (eq. 1) [14].

$$P(OR^1)_3 + R^2{-}X \rightarrow R^2{-}P(O)(OR^1)_2 + R^1{-}X \qquad \text{(eq. 1)}$$

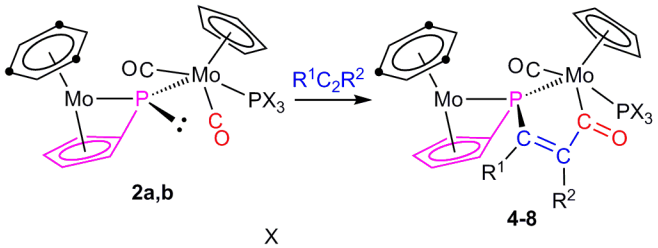
We note, however, that dealkylation of metal-bound $P(OR)_3$ ligands to give the corresponding phosphonate derivatives is not a rare process itself, as it can be induced in a number of ways, for instance upon heating [15], reaction with radicals [16], or reaction with anions (in the case of cationic complexes) [17]. What is unusual in the transformation of **2b** into **3** is that it takes place at room temperature, and that the alkyl group detached from the O atom remains in the complex, then achieving an effective isomerization of the original molecule. Seemingly, this is facilitated by the high basicity of the pyramidal phosphinidene ligand in **2b**. Thus, the mechanism and scope of such a rearrangement might deserve a more detailed study in the future.

*2.3. Reactions of compounds **2a,b** with alkynes.*

We studied the reactions of compounds **2a** and **2b** with some internal alkynes (EtC≡CC(O)Me and MeC≡CCO_2Me) and also terminal alkynes (HC≡CR; R = 4-C_6H_4Me, C(O)Me, CO_2Me). In all cases these reactions proceeded rapidly at room temperature (less than 1 min) with very high regioselectivity, to give a single metallacyclic product $[Mo_2Cp\{\mu$-$\kappa^2_{P,C}$:κ^1_P,η^5-$P(C_5H_4)CR^1CR^2C(O)\}(\eta^6$-HMes*)$(CO)(PX_3)]$ (**4**-**8**) in each case (X = Me, OMe; R^1 = Et, Me, H; R^2 = C(O)Me, CO_2Me, 4-C_6H_4Me; see Scheme 3). These complexes follow from the specific binding of the phosphinidene P atom to the less electrophilic carbon atom of the alkyne (CR^1),

while the alkyne carbon bearing the more electron-withdrawing group (CR^2) binds to one carbonyl of the $Mo(CO)_2$ fragment, then closing a phosphametallacycle. This gives further support to our mechanistic proposal for the multicomponent reactions of compound **1** with alkynes mentioned above, since such a regioselectivity is the one providing a more efficient stabilization of the negative charge in the zwitterionic intermediate formed upon initial nucleophilic attack of the phosphinidene ligand to the alkyne molecule (Scheme 1). We note that the same regioselectivity was actually observed in the reaction of the pyramidal phosphinidene complex $[Fe_2Cp_2(\mu\text{-}PCy)(\mu\text{-}CO)(CO)_2]$ with HC≡CR at 348 K (R = 4-C_6H_4Me), which yielded a comparable phosphametallacylic derivative $[Fe_2Cp_2\{\mu\text{-}\kappa^1_P\text{:}\kappa^2_{P,C}\text{-}CyPCHCRC(O)\}(\mu\text{-}CO)(CO)]$ [18], and also in the multicomponent reactions of **1** with alkynes in the presence of CO or CNR ligands (Scheme 1). In the latter reactions of **1**, however, two conformers differing in the relative position of the C_5 rings with respect to the average plane of the $MoPC_3$ metallacycle were obtained in many cases (both rings on the same side of this plane -*syn*- or on opposite sides -*anti*-). This is not the case of compounds **4** to **8**, which were obtained as *anti* isomers in all cases (see below), surely favoured by the increased steric demands imposed by the PX_3 ligands present in these molecules. In agreement with this interpretation, we note that only *anti* isomers were either obtained in the multicomponent reactions of compound **1** with dimethyl acetylenedicarboxylate (DMAD) in the presence of the same PX_3 ligands [5a].

Scheme 3. Alkyne Derivatives of Compounds 2a,b



• = C–^{t}Bu

X			
Me	OMe	R^1	R^2
4a	**4b**	Et	C(O)Me
5a	**5b**	Me	CO_2Me
6a	**6b**	H	4-C_6H_4Me
7a	**7b**	H	C(O)Me
8a	**8b**	H	CO_2Me

*2.4. Solid-state structure of compound **4b**.*

The structure of **4b** was determined through an X-ray diffraction study. Although the quality of the diffraction data was not very high, a clear definition of the molecular structure of this complex was still possible (Figure 1 and Table 2). The structure turned to be very similar to that one previously determined by us for the related dicarbonyl complex *anti*-$[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)C(CO_2Me)C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)_2]$, which is the major isomer obtained in the reaction of **1** with DMAD in the presence of CO [5]. Therefore, only a few comments are necessary here. Indeed the

molecule of **4b** can be viewed as derived from replacement in the mentioned dicarbonyl complex of a CO ligand with a $P(OMe)_3$ ligand, *trans* to the bridging P atom (P–Mo–P = 119.38(5)°). This has little consequences on the geometry of the $MoPC_3$ ring of the molecule, which exhibits a puckered cyclopentene-like conformation, with the P and C atoms almost in the same plane. The endocyclic C2–C3 and C3–C4 lengths of 1.511(7) and 1.349(6) Å approach the respective reference figures for single and double bonds between $C(sp^2)$ atoms (1.46 and 1.34 Å, respectively) [19,20], indicating no significant delocalization of the π bonding interaction with the exocyclic C=O bond (1.252(5) Å). We also note that the C_5 rings of the molecule are located on different sides of the average plane defined by the $MoPC_3$ ring (*anti* conformation).

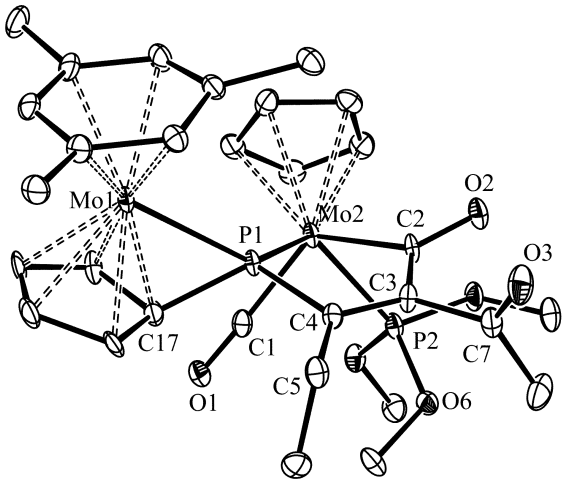


Figure 1. ORTEP diagram (30% probability) of compound **4b** with H atoms and ^{t}Bu groups (except their C^1 atoms) omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (°) for Compound **4b.**

Mo1–P1	2.599(1)	Mo1–P1–Mo2	134.74(6)
Mo2–P1	2.452(1)	Mo1–P1–C4	114.4(1)
Mo2–P2	2.347(1)	Mo2–P1–C4	107.6(1)
Mo2–C1	1.948(5)	Mo1–P1–C17	56.4(2)
Mo2–C2	2.185(4)	P1–Mo2–P2	119.38(5)
P1–C17	1.796(4)	C1–Mo2–C2	119.5(2)
P1–C4	1.834(5)	C1–Mo2–P1	76.7(1)
C4–C3	1.349(6)	C1–Mo2–P2	77.6(1)
C3–C2	1.511(7)	C2–Mo2–P1	72.4(1)
C2–O2	1.252(5)	C2–Mo2–P2	74.6(1)
C3–C7	1.510(6)	P1–C4–C3	109.0(4)
C4–C5	1.503(7)	C4–C3–C2	120.3(4)
C7–O3	1.217(6)	C3–C2–Mo2	122.8(3)

On the basis of a conventional electron count, the Mo(1)–P(1) and Mo(2)–P(1) bonds should be formulated respectively as single and single dative bonds, which is in agreement with their significantly different lengths of 2.599(1) and 2.452(1) Å, respectively (cf. 2.557(1) and 2.474(1) Å for the mentioned dicarbonyl complex). We finally note that the phosphite P–Mo length in **4b** (2.347(1) Å) is even shorter, as

expected (cf. 2.352(3) Å for the W–P length in $[W_2Cp_2\{\mu\text{-}(OEt)_2POP(OEt)_2\}(CO)_4]$ [13].

*2.5. Solution structure of complexes **4** to **8**.*

Spectroscopic data for complexes **4a,b** to **8a,b** (Tables 1 and 2, and Experimental section) are similar to each other and fully consistent with the structure found in the crystal for **4b**. Their IR spectra display two C–O stretches in each case (excluding bands arising from substituents in the alkyne), with the most energetic one corresponding to the unique carbonyl ligand (1812-1838 cm^{-1}), while the less energetic one corresponds to the acyl group (1532-1550 cm^{-1}). Stretching frequencies for phosphite complexes **4b** to **8b** were systematically higher than those of PMe_3 complexes **4a** to **8a**, as expected from the better acceptor properties of the $P(OMe)_3$ ligand. Besides, the carbonyl ligand for PMe_3 complexes gave ^{13}C NMR resonances displaying relatively high two-bond P-C couplings of 31 Hz to both P atoms of the molecule, in agreement with the *cis* positioning of these atoms around Mo (angles C–Mo–P ca. 77º in the crystal of **4a**) [21]. The coupling to the $P(OMe)_3$ ligand in compounds **4b** to **8b**, however, was expectedly higher (ca. 42 Hz).

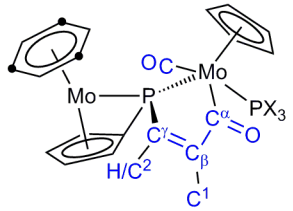
The ^{31}P NMR spectra of these compounds display in each case two resonances, corresponding to the bridging P atom (δ_P 90-110 ppm), and to the PX_3 ligand respectively (δ_P ca. 30 ppm for PMe_3 complexes and ca. 193 ppm for $P(OMe)_3$ complexes). These two resonances display a low P-P coupling of 6-10 Hz in all cases, consistent with the transoid positioning of the P ligands around Mo (P–Mo–P ca. 119º in the crystal for **4a**) [21].

The ^{13}C NMR spectra for compounds **4** to **8** revealed well defined patterns of chemical shifts and P-C couplings supporting the presence in all cases of $MoPC_3$ cycles analogous to the one present in complex **4b** (Table 2 and Experimental section). The acyl carbon (C^α) gives rise in all cases to a strongly deshielded resonance (δ_C 276-290 ppm) which displays two very different couplings, with the large one corresponding to the coupling to the PX_3 ligand. The latter is of a magnitude comparable to the coupling displayed by the carbonyl ligands (ca. 30 Hz for PMe_3 complexes, 37 Hz for $P(OMe)_3$ complexes), as expected from the *cis* positioning of the corresponding C and P atoms around Mo [21]. In contrast, the coupling to the bridging P atom is very low in all cases (10-12 Hz). This can be explained as resulting from partial cancellation of a large two-bond *cis*-coupling (C–Mo–P ca 72º in **4b**) with a similar three-bond (C–C–C–P) contribution (often opposite in sign [11]) that the five-membered cycle enables in these molecules. This balance changes substantially for the next carbon of the cycle (C^β), which displays a large coupling to the bridging P in all cases (33-49 Hz). This can be explained by recalling that, in that case, the two-bond contribution to the overall coupling is now expected to be small, due to the higher angle involved (C^β–C^γ–P ca.

109º in **4b**), while the three-bond contribution can remain high, due to a favourable torsion angle close to 0º (P–Mo–C^{α}–C^{β} ca. 24.8º in **4b**) [11]. The exocyclic carbon attached to that position (C^{1}) also displayed a quite large three-bond coupling of 20-30 Hz, favoured by a large torsion angle in this case (C–C–C–P ca. 171º in **4b**). Besides this, the last C atom of the phosphametallacycle (C^{γ}) could be unambiguously identified on the basis of its significantly higher intensity in the case of compounds **6** to **8** (it being bound to H) and standard DEPT experiments. We finally note that all derivatives of terminal alkynes (compounds **6** to **8**) gave rise to quite deshielded ^{1}H NMR resonances for the former alkyne proton, in the range ca. 6.9-7.5 ppm, these displaying a modest two-bond P-C coupling of 8-10 Hz with the bridging P atom.

Table 2. Selected ^{1}H and ^{13}C{^{1}H} NMR Data for Compounds **4-8**.[a]

Compd	$\delta_C(C^{\alpha})$	$\delta_C(C^{\beta})$	$\delta_C(C^{\gamma})$	$\delta_C(C^{1})$	$\delta_C(C^{2})/\delta_H(H)$	δ_C(CO)
4a	289.5 (30, 11)	170.6 (42)	162.4 (8)	207.8 (23)	24.7 (s)	257.2 (31, 31)
4b	282.7 (37, 11)	169.3 (42)	162.7 (9)	206.8 (21)	23.9 (s)	257.5 (42, 27)
5a	283.9 (30, 12)	163.4 (49)	157.3 (3)	170.0 (30)	18.0 (s)	257.5 (31, 31)
5b	283.9 (37, 11)	162.6 (48)	158.5 (4)	169.3 (30)	17.9 (s)	257.7 (42, 27)
6a	288.8 (31, 11)	166.8 (36)	148.7 (9)	134.7 (21)	7.18 (m)	258.4 (m)
6b					6.91 (10, 2)	
7a	290.0 (30, 11)	167.9 (33)	155.7 (s)	200.9 (21)	7.48 (9, 2)	258.1 (31, 31)
7b					7.39 (9, 2)	
8a	285.2 (m)	160.7 (41)	153.9 (s)	167.5 (28)	7.42 (8)	258.0 (31, 31)
8b	276.2 (38, 10)	160.8 (39)	154.8 (s)	166.8 (27)	7.49 (8, 2)	256.6 (41, 28)



[a] Chemical shifts (δ) in ppm relative to tetramethylsilane, with P-C coupling constants (in Hz) given between brackets; see the Experimental section for further details. Labelling according to the figure shown above.

3. Conclusions

The new pyramidal phosphinidene complex [$Mo_2Cp(\mu$-κ^1:κ^1,η^5-$PC_5H_4)(\eta^6$-HMes*)$(CO)_2${$P(OMe)_3$}] (**2b**) can be readily prepared in situ upon reaction of the trigonal phosphinidene complex [$Mo_2Cp(\mu$-κ^1:κ^1,η^5-$PC_5H_4)(\eta^6$-HMes*)$(CO)_2$] (**1**) with $P(OMe)_3$. This product, however, undergoes full rearrangement when dissolved in tetrahydrofuran, to give the phosphanyl-phosphonite isomer [Mo_2Cp{μ-κ^1:κ^1,η^5-$P(Me)C_5H_4$}$(\eta^6$-HMes*)$(CO)_2${$P(O)(OMe)_2$}], as a result of Me-transfer from O to P atoms. Since such a rearrangement does not take place in poorly coordinating solvents

such as petroleum ether or toluene, the mentioned Me-transfer likely is of intermolecular nature and somehow assisted by the solvent, while the high basicity of the pyramidal phosphinidene ligand in **2b** likely plays a critical role in the process. Reactions of **2b**, as well as those of its PMe_3 analogue **2a**, with different internal and terminal alkynes (R^1CCR^2; R^1 = H, Me, Et; R^2 = C(O)Me, CO_2Me, 4-C_6H_4Me), proceed rapidly at room temperature with very high regioselectivity, to give single metallacyclic products of type $[Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CR^1CR^2C(O)\}(\eta^6\text{-HMes*})(CO)(PX_3)]$, where R^2 always is an electron-withdrawing group. Such a regioselectivity is the one providing a more efficient stabilization of the negative charge in the zwitterionic intermediate formed upon initial nucleophilic attack of the phosphinidene ligand to the alkyne molecule. Moreover, this selectivity is the same as the one observed in the multicomponent reactions of compound **1** in the presence of different ligands, thus supporting the participation of pyramidal phosphinidene-bridged intermediates in the latter reactions.

4. Experimental

All manipulations and reactions were carried out under an argon (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use [22]. Compound $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-HMes*})(CO)_2(PMe_3)]$ (**2a**) was prepared in situ as described previously [6], typically upon addition of stoichiometric amounts of PMe_3 on toluene solutions of $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-HMes*})(CO)_2]$ (**1**) [7], in a Schlenk tube equipped with a Young´s valve. All other reagents were obtained from commercial suppliers and used as received. Petroleum ether refers to that fraction distilling in the range 338-343 K. Filtrations were carried out through diatomaceous earth unless otherwise stated. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Commercial aluminium oxide (activity I, 70-290 mesh) was degassed under vacuum prior to use. The latter was mixed under argon with the appropriate amount of water to reach activity IV. IR stretching frequencies of CO ligands were measured in solution (using CaF_2 windows), are referred to as ν(CO), and are given in wave numbers (cm^{-1}). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 295 K unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^1H, ^{13}C), or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in hertz.

*4.1. Preparation of $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-HMes*})(CO)_2\{P(OMe)_3\}]$ (**2b**).*

Neat $P(OMe)_3$ (5 μL, 0.042 mmol) was added at room temperature to a red solution of complex **1** (0.020 g, 0.031 mmol) in toluene (2 mL), contained in a Schlenk tube

equipped with a Young´s valve, whereupon the solution turned green immediately. Removal of volatiles under vacuum gave a solid residue shown (by IR and NMR) to contain almost pure phosphinidene complex **2b**. This material, however, was quite air-sensitive, and could not be isolated as a crystalline solid, but could be used for further reactivity studies (yield assumed to be ca. 100%).

4.2. Preparation of [$Mo_2Cp\{\mu$-κ^1:κ^1,η^5-$P(Me)C_5H_4\}(\eta^6$-HMes)$(CO)_2\{P(O)(OMe)_2\}$] (**3**).*

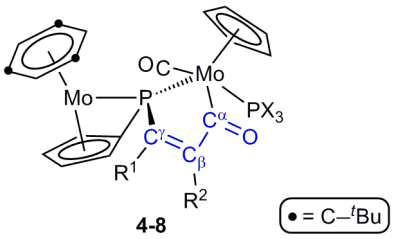
The crude compound **2b**, prepared in situ as described above (ca. 0.031 mmol), was dissolved in tetrahydrofuran (3 mL), and the solution was stirred for 3 min at room temperature. After removal of solvent under vacuum, the residue was extracted with a minimum dichloromethane and the extract was chromatographed on alumina at 263 K. Elution with dichloromethane/tetrahydrofuran (9:1) gave a green fraction yielding, upon removal of solvents, compound **3** as a green microcrystalline solid (0.020 g, 83%). Anal. Calc. for $C_{33}H_{48}Mo_2O_5P_2$: C, 50.91; H, 6.21. Found: C, 50.75; H, 6.43. ^{1}H NMR (300.13 MHz, C_6D_6): δ 5.17 (s, 5H, Cp), 4.74 (m, 1H, C_5H_4), 4.57 (d, J_{HP} = 4, 3H, C_6H_3), 4.57, 4.52, 4.30 (3m, 3 x 1H, C_5H_4), 3.92 (d, J_{HP} = 11, 6H, POMe), 1.62 (d, J_{HP} = 8, 3H, PMe), 1.06 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2): δ 237.5 (m, br, 2MoCO), 113.5 [s, C(C_6H_3)], 98.2 [d, J_{CP} = 16, C^1(C_5H_4)], 93.3 (s, br, Cp), 90.7 [d, J_{CP} = 9, CH(C_5H_4)], 87.7 [d, J_{CP} = 4, CH(C_5H_4)], 85.0 [s, br, CH(C_5H_4)], 84.4 [d, J_{CP} = 15, CH(C_5H_4)], 71.3 [s, CH(C_6H_3)], 51.4, 51.3 (2d, J_{CP} = 7, POMe), 35.1 [s, C^1(^{t}Bu)], 31.4 [s, C^2(^{t}Bu)], 21.9 (s, PMe).

4.3. Preparation of [$Mo_2Cp\{\mu$-$\kappa^2_{P,C}$:κ^1_P,η^5-$P(C_5H_4)C(Et)C\{C(O)Me\}C(O)\}(\eta^6$-HMes)$(CO)(PMe_3)$] (**4a**).*

Neat 3-hexyn-2-one (6 μL, 0.062 mmol) was added to a tetrahydrofuran solution (0.5 mL) of compound **2a** (0.031 mmol), prepared in situ as described above, and the mixture was stirred at room temperature for 1 min to give a dark green solution. After removal of volatiles under vacuum, the residue was dissolved in tetrahydrofuran (2 mL) and the solution was filtered. Removal of the solvent from the filtrate and washing of the residue with petroleum ether yielded compound **4a** as a green microcrystalline solid (0.022 g, 85%). Anal. Calc. for $C_{39}H_{56}Mo_2O_3P_2$: C, 56.66; H, 6.83. Found: C, 56.87; H, 6.91. ^{1}H NMR (400.13 MHz, THF-d_8): δ 5.34, 5.17, 5.15 (3m, 3 x 1H, C_5H_4), 4.99 (s, 5H, Cp), 4.77 (d, J_{HP} = 2, 3H, C_6H_3), 4.63 (m, 1H, C_5H_4), 2.51, 2.22 (2ddq, 2 x 1H, J_{HH} = 13, 8, J_{HP} = 7, CH_2), 2.06 [s, 3H, C(O)Me], 1.28 (d, J_{HP} = 9, 9H, PMe), 1.20 (s, 27H, ^{t}Bu), 1.09 (t, 3H, J_{HH} = 8, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, THF-d_8): δ 289.5 (dd, J_{CP} = 30, 11, C^α), 257.2 (t, J_{CP} = 31, MoCO), 207.8 [d, J_{CP} = 23, *C*(O)Me], 170.6 (d, J_{CP} = 42, C^β), 162.4 (d, J_{CP} = 8, C^γ), 110.2 [s, br, C(C_6H_3)], 93.6 (s, Cp), 92.8 [d, J_{CP} = 12, C^1(C_5H_4)], 90.8 [d, J_{CP} = 4, CH(C_5H_4)], 87.9 [d, J_{CP} = 10, CH(C_5H_4)], 86.2 [s,

CH(C_5H_4)], 86.1 [d, J_{CP} = 15, CH(C_5H_4)], 70.5 [s, CH(C_6H_3)], 35.3 [s, C^1(^{t}Bu)], 31.9 [s, C(O)*Me*], 31.5 [s, C^2(^{t}Bu)], 24.7 (s, CH_2), 20.1 (d, J_{CP} = 30, PMe), 16.9 (s, CH_3). Labels for carbon atoms in the $MoPC_3$ ring according to the drawing shown in Chart 3.

Chart 3



4.4. Preparation of [$Mo_2Cp\{\mu$-$\kappa^2_{P,C}$:κ^1_P,η^5-$P(C_5H_4)C(Et)C\{C(O)Me\}C(O)\}$($\eta^6$-HMes)(CO){$P(OMe)_3$}] (**4b**).*

Neat 3-hexyn-2-one (6 μL, 0.062 mmol) was added to a toluene solution (2 mL) of compound **2b** (0.031 mmol), prepared in situ as described above, and the mixture was stirred at room temperature for 1 min to give a dark green solution. After removal of volatiles under vacuum, the residue was dissolved in a minimum dichloromethane and the solution was chromatographed on alumina at 253 K. Elution with dichloromethane/tetrahydrofuran (9:1) gave a green fraction yielding, upon removal of solvents, compound **4b** as a green microcrystalline solid (0.021 g, 77%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calc. for $C_{39}H_{56}Mo_2O_6P_2$: C, 53.55; H, 6.45. Found: C, 53.68; H, 6.39. ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ 5.29, 5.15 (2m, 2 x 1H, C_5H_4), 5.14 (s, 5H, Cp), 5.10 (m, 1H, C_5H_4), 4.76 (s, br, 3H, C_6H_3), 4.57 (m, 1H, C_5H_4), 3.45 (d, J_{HP} = 11, 9H, POMe), 2.54, 2.45 (2ddq, J_{HH} = 13, 8, J_{HP} = 7, 2 x 1H, CH_2), 2.08 (s, 3H, C(O)Me), 1.16 (s, 27H, ^{t}Bu), 1.06 (t, 3H, J_{HH} = 8, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): δ 282.7 (dd, J_{CP} = 37, 11, C^α), 257.5 (dd, J_{CP} = 42, 27, MoCO), 206.8 (d, J_{CP} = 21, *C*(O)Me), 169.3 (d, J_{CP} = 42, C^β), 162.7 (d, J_{CP} = 9, C^γ), 119.8 [s, C(C_6H_3)], 93.9 (s, Cp), 91.7 [d, J_{CP} = 16, C^1(C_5H_4)], 90.2 [d, J_{CP} = 4, CH(C_5H_4)], 87.0 [d, J_{CP} = 10, CH(C_5H_4)], 86.1 [s, CH(C_5H_4)], 84.5 [d, J_{CP} = 17, CH(C_5H_4)], 71.0 [s, br, CH(C_6H_3)], 52.2 (d, J_{CP} = 6, POMe), 35.0 [s, C^1(^{t}Bu)], 31.7 [s, C(O)*Me*], 31.3 [s, C^2(^{t}Bu)], 23.9 (s, CH_2), 16.6 (s, CH_3).

4.5. Preparation of [$Mo_2Cp\{\mu$-$\kappa^2_{P,C}$:κ^1_P,η^5-$P(C_5H_4)C(Me)C(CO_2Me)C(O)\}$($\eta^6$-HMes)(CO)($PMe_3$)] (**5a**).*

The procedure is analogous to the one described for **4a**, but now using methyl 2-butynoate (7 mL, 0.062 mmol), to give compound **5a** as a brown-green microcrystalline solid (0.022 g, 85%). Anal. Calc. for $C_{38}H_{54}Mo_2O_4P_2$: C, 55.08; H, 6.57. Found: C,

54.87; H, 6.21. ^{1}H NMR (400.13 MHz, C_6D_6): δ 5.10 (s, 5H, Cp), 4.84, 4.81, 4.79, 4.68 (4m, 4 x 1H, C_5H_4), 4.55 (s, br, 3H, C_6H_3), 3.51 (s, 3H, OMe), 2.28 (d, J_{HP} = 7, C*Me*), 1.43 (d, J_{HP} = 9, 9H, PMe), 1.01 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): δ 283.9 (dd, J_{CP} = 30, 12, C^{α}), 257.5 (t, J_{CP} = 31, MoCO), 170.0 (d, J_{CP} = 30, *C*O_2Me), 163.4 (d, J_{CP} = 49, C^{β}), 157.3 (d, J_{CP} = 3, C^{γ}), 119.7 [s, C(C_6H_3)], 93.1 (s, Cp), 92.9 [d, J_{CP} = 11, C^{1}(C_5H_4)], 89.9 [d, J_{CP} = 4, CH(C_5H_4)], 86.9 [d, J_{CP} = 10, CH(C_5H_4)], 86.7 [s, CH(C_5H_4)], 85.3 [d, J_{CP} = 18, CH(C_5H_4)], 69.8 [s, br, CH(C_6H_3)], 51.1 (s, OMe), 34.6 [s, C^{1}(^{t}Bu)], 31.3 [s, C^{2}(^{t}Bu)], 20.2 (d, J_{CP} = 30, PMe), 18.0 (s, C^{γ}*Me*).

4.6. Preparation of [$Mo_2Cp\{\mu$-$\kappa^{2}_{P,C}$:κ^{1}_{P},η^{5}-$P(C_5H_4)C(Me)C(CO_2Me)C(O)\}(\eta^{6}$-HMes)(CO){$P(OMe)_3$}] (**5b**).*

The procedure is analogous to the one described for **4b**, but now using methyl 2-butynoate (7 mL, 0.062 mmol), to give compound **5b** as a brown-green microcrystalline solid (0.021 g, 77%). Anal. Calc. for $C_{38}H_{54}Mo_2O_7P_2$: C, 52.06; H, 6.21. Found: C, 52.25; H, 6.42. ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ 5.28, 5.26 (2m, 2 x 1H, C_5H_4), 5.12 (s, 5H, Cp), 5.08 (m, 1H, C_5H_4), 4.77 (s, br, 3H, C_6H_3), 4.58 (m, 1H, C_5H_4), 3.63 (s, 3H, OMe), 3.45 (d, J_{HP} = 11, 9H, POMe), 2.15 (d, J_{HP} = 7, CMe), 1.16 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): δ 278.2 (dd, J_{CP} = 37, 11, C^{α}), 257.7 (dd, J_{CP} = 42, 27, MoCO), 169.3 (d, J_{CP} = 30, *C*O_2Me), 162.6 (d, J_{CP} = 48, C^{β}), 158.5 (d, J_{CP} = 4, C^{γ}), 111.2 [s, br, C(C_6H_3)], 93.6 (s, Cp), 91.6 [d, J_{CP} = 13, C^{1}(C_5H_4)], 90.2 [d, J_{CP} = 3, CH(C_5H_4)], 86.8 [d, J_{CP} = 10, CH(C_5H_4)], 86.5 [s, CH(C_5H_4)], 83.9 [d, J_{CP} = 17, CH(C_5H_4)], 71.1 [s, br, CH(C_6H_3)], 52.3 (d, J_{CP} = 6, POMe), 51.5 (s, OMe), 35.0 [s, C^{1}(*^{t}*Bu)], 31.3 [s, C^{2}(*^{t}*Bu)], 17.9 (s, C^{γ}*Me*).

4.7. Preparation of [$Mo_2Cp\{\mu$-$\kappa^{2}_{P,C}$:κ^{1}_{P},η^{5}-$P(C_5H_4)CHC(4$-$C_6H_4Me)C(O)\}(\eta^{6}$-HMes)(CO)(PMe_3)] (**6a**).*

The procedure is analogous to the one described for **4a**, but now using (*p*-tolyl)acetylene (8 μL, 0.062 mmol), to give compound **6a** as a green microcrystalline solid (0.020 g, 76%). Anal. Calc. for $C_{42}H_{56}Mo_2O_2P_2$: C, 59.57; H, 6.67. Found: C, 59.43; H, 6.39. ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.68, 7.09 (2d, J_{HH} = 8, 2 x 2H, C_6H_4), 7.18 (m, 1H, HC^{γ}), 5.23 (s, 5H, Cp), 4.95 (m, 2H, C_5H_4), 4.88 (m, 1H, C_5H_4), 4.61 (d, J_{HP} = 4, 3H, C_6H_3), 4.59 (m, 1H, C_5H_4), 2.13 (s, 3H, Me), 1.24 (d, J_{HP} = 9, 9H, PMe), 1.00 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): δ 288.8 (dd, J_{CP} = 31, 11, C^{α}), 258.4 (m, MoCO), 166.8 (d, J_{CP} = 36, C^{β}), 148.7 (d, J_{CP} = 9, C^{γ}), 136.5 [s, C^{4}(C_6H_4)], 134.7 [d, J_{CP} = 21, C^{1}(C_6H_4)], 129.0, 128.7 [2s, CH(C_6H_4)], 108.2 [s, C(C_6H_3)], 93.0 (s, Cp), 92.1 [d, J_{CP} = 2, C^{1}(C_5H_4)], 89.6 [d, J_{CP} = 4, CH(C_5H_4)], 85.3 [d, J_{CP} = 9, CH(C_5H_4)], 84.0 [s, CH(C_5H_4)], 82.5 [d, J_{CP} = 15, CH(C_5H_4)], 70.1 [s, CH(C_6H_3)], 34.3 [s, C^{1}(*^{t}*Bu)], 31.3 [s, C^{2}(*^{t}*Bu)], 21.2 (s, Me), 20.4 (d, J_{CP} = 30, PMe).

*4.8. Preparation of [$Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC(4\text{-}C_6H_4Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)\{P(OMe)_3\}$] (**6b**).*

The procedure is analogous to the one described for **4b**, but now using (*p*-tolyl)acetylene (8 μL, 0.062 mmol). In the chromatography, a green fraction was eluted with dichloromethane/petroleum ether (3:1) to give, upon removal of solvents, compound **6b** as a green microcrystalline solid (0.018 g, 65%). Anal. Calc. for $C_{42}H_{56}Mo_2O_5P_2$: C, 56.38; H, 6.31. Found: C, 56.55; H, 6.29. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 7.15, 7.05 (2d, J_{HH} = 8, 2 x 2H, C_6H_4), 6.91 (dd, J_{HP} = 10, 2, 1H, HC^γ), 5.31 (m, 1H, C_5H_4), 5.22 (s, 5H, Cp), 5.06, 5.03 (2m, 2 x 1H, C_5H_4), 4.84 (d, J_{HP} = 4, 3H, C_6H_3), 4.80 (m, 1H, C_5H_4), 3.43 (d, J_{HP} = 11, 9H, POMe), 2.30 (s, 3H, Me), 1.17 (s, 27H, ^{t}Bu).

*4.9. Preparation of [$Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC\{C(O)Me\}C(O)\}(\eta^6\text{-}HMes^*)(CO)(PMe_3)$] (**7a**).*

The procedure is analogous to the one described for **4a**, but now using 3-butyn-2-one (5 μL, 0.062 mmol), to give compound **7a** as a green microcrystalline solid (0.022 g, 88%). Anal. Calc. for $C_{37}H_{52}Mo_2O_3P_2$: C, 55.64; H, 6.56. Found: C, 55.29; H, 6.74. ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.48 (dd, J_{HP} = 9, 2, 1H, HC^γ), 5.13 (s, 5H, Cp), 4.91, 4.79, 4.67 (3m, 3 x 1H, C_5H_4), 4.59 (d, J_{HP} = 4, 3H, C_6H_3), 4.50 (m, 1H, C_5H_4), 2.46 [s, 3H, C(O)Me], 1.25 (d, J_{HP} = 9, 9H, PMe), 0.96 (s, 27H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6): δ 290.0 (dd, J_{CP} = 30, 11, C^α), 258.1 (t, J_{CP} = 31, MoCO), 200.9 [d, J_{CP} = 21, *C*(O)Me], 167.9 (d, J_{CP} = 33, C^β), 155.7 (s, C^γ), 108.5 [s, $C(C_6H_3)$], 92.7 (s, Cp), 89.8 [d, J_{CP} = 4, $CH(C_5H_4)$], 85.1 [d, J_{CP} = 9, $CH(C_5H_4)$], 84.3 [s, $CH(C_5H_4)$], 83.9 [d, J_{CP} = 15, $C^1(C_5H_4)$], 82.7 [d, J_{CP} = 15, $CH(C_5H_4)$], 70.5 [s, $CH(C_6H_3)$], 34.3 [s, $C^1(^t$Bu)], 31.8 (s, Me), 31.3 [s, $C^2(^t$Bu)], 20.3 (d, J_{CP} = 30, PMe).

*4.10. Preparation of [$Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC\{C(O)Me\}C(O)\}(\eta^6\text{-}HMes^*)(CO)\{P(OMe)_3\}$] (**7b**).*

The procedure is analogous to the one described for **4b**, but now using 3-butyn-2-one (5 μL, 0.062 mmol), to give compound **7b** as a green microcrystalline solid (0.019 g, 72%). Anal. Calc. for $C_{37}H_{52}Mo_2O_6P_2$: C, 52.49; H, 6.19. Found: C, 52.28; H, 6.41. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 7.39 (dd, J_{HP} = 9, 2, 1H, HC^γ), 5.32 (m, 1H, C_5H_4), 5.19 (s, 5H, Cp), 4.99 (m, 2H, C_5H_4), 4.85 (d, J_{HP} = 4, 3H, C_6H_3), 4.82 (m, 1H, C_5H_4), 3.42 (d, J_{HP} = 11, 9H, POMe), 2.11 (s, 3H, Me), 1.14 (s, 27H, ^{t}Bu).

*4.11. Preparation of [$Mo_2Cp\{\mu\text{-}\kappa^2_{P,C}\text{:}\kappa^1_P,\eta^5\text{-}P(C_5H_4)CHC(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)(PMe_3)$] (**8a**).*

The procedure is analogous to the one described for **4a**, but now using methyl propiolate (6 μL, 0.062 mmol), to give compound **8a** as a green microcrystalline solid

(0.021 g, 83%). Anal. Calc. for $C_{37}H_{52}Mo_2O_4P_2$: C, 54.55; H, 6.43. Found: C, 54.27; H, 6.51. ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.42 (d, J_{HP} = 8, 1H, HC$^\gamma$), 5.14 (s, 5H, Cp), 4.92, 4.81, 4.67 (3m, 3 x 1H, C_5H_4), 4.62 (d, J_{HP} = 5, 3H, C_6H_3), 4.51 (m, 1H, C_5H_4), 3.49 (s, 3H, OMe), 1.39 (d, J_{HP} = 9, 9H, PMe), 1.00 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): δ 285.2 (m, C$^\alpha$), 258.0 (t, J_{CP} = 31, MoCO), 167.5 (d, J_{CP} = 28, *C*O$_2$Me), 160.7 (d, J_{CP} = 41, C$^\beta$), 153.9 (s, C$^\gamma$), 108.7 [s, C(C_6H_3)], 92.7 (s, Cp), 92.4 [d, J_{CP} = 3, C^1(C_5H_4)], 89.7 [d, J_{CP} = 4, CH(C_5H_4)], 85.1 [d, J_{CP} = 9, CH(C_5H_4)], 84.2 [s, CH(C_5H_4)], 82.5 [d, J_{CP} = 16, CH(C_5H_4)], 70.6 [s, br, CH(C_6H_3)], 51.1 (s, OMe), 34.3 [s, C^1(^{t}Bu)], 31.3 [s, C^2(^{t}Bu)], 20.3 (d, J_{CP} = 30, PMe).

4.12. Preparation of [Mo$_2$Cp{μ-$\kappa^2_{P,C}$:κ^1_P,η^5-P(C_5H_4)CHC(CO$_2$Me)C(O)}(η^6-HMes)(CO){P(OMe)$_3$}] (**8b**).*

The procedure is analogous to the one described for **4b**, but now using methyl propiolate (6 μL, 0.062 mmol), to give compound **8b** as a green microcrystalline solid (0.020 g, 75%). Anal. Calc. for $C_{37}H_{52}Mo_2O_7P_2$: C, 51.52; H, 6.08. Found: C, 51.37; H, 6.11. ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.49 (dd, J_{HP} = 8, 2, 1H, HC$^\gamma$), 5.40 (s, 5H, Cp), 5.00, 4.83, 4.64 (3m, 3 x 1H, C_5H_4), 4.61 (d, J_{HP} = 4, 3H, C_6H_3), 4.47 (m, 1H, C_5H_4), 3.57 (d, J_{HP} = 11, 9H, POMe), 3.51 (s, 3H, OMe), 0.98 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6): δ 276.2 (dd, J_{CP} = 38, 10, C$^\alpha$), 256.6 (dd, J_{CP} = 41, 28, MoCO), 166.8 (d, J_{CP} = 27, *C*O$_2$Me), 160.8 (d, J_{CP} = 39, C$^\beta$), 154.8 (s, C$^\gamma$), 109.0 [s, C(C_6H_3)], 93.4 (s, Cp), 92.1 [d, J_{CP} = 6, C^1(C_5H_4)], 89.7 [d, J_{CP} = 4, CH(C_5H_4)], 85.0 [d, J_{CP} = 9, CH(C_5H_4)], 84.2 [s, CH(C_5H_4)], 82.5 [d, J_{CP} = 15, CH(C_5H_4)], 71.1 [s, br, CH(C_6H_3)], 52.5 (d, J_{CP} = 6, POMe), 51.1 (s, OMe), 34.3 [s, C^1(^{t}Bu)], 31.3 [s, C^2(^{t}Bu)].

*4.12. X-ray Data Collection, Structure Determination and Refinements for **4b**.*

Data collection for this compound was performed at 130 K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu Kα radiation. Images for a small needle-shaped crystal were collected at a 63 mm fixed crystal-detector distance using the oscillation method, with 1º oscillation and variable exposure time per image (1.1-6.0 s). Data collection strategy was calculated with the program *CrysAlis Pro CCD* [23], and data reduction and cell refinement was performed with the program *CrysAlis Pro RED* [23]. An empirical absorption correction was applied using the *SCALE3 ABSPACK* algorithm as implemented in the program *CrysAlis Pro RED*. Using the program suite *WinGX* [24], the structure was solved by Patterson interpretation and phase expansion using *SHELXL2016* [25], and refined with full-matrix least squares on F^2 using *SHELXL2016*. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically placed and refined using a riding model. A disordered solvent molecule (possibly n-hexane) could not be uniquely identified in the asymmetric unit, and its contribution to the diffraction patter was removed via

SQUEEZE [26], as implemented in *PLATON* [27]. Upon squeeze application and convergence, the strongest residual peak (1.06 eA^{-3}) was placed near the Mo(1) atom. Further details of this crystallographic study are given in Table 3.

Table 3. Crystal Data for Compound **4b**

parameter	**4b**
mol formula	$C_{39}H_{56}Mo_2O_6P_2$
mol wt	874.66
cryst syst	monoclinic
space group	$P2_1/c$
radiation (λ, Å)	1.54184
a, Å	20.1938(16)
b, Å	10.5455(3)
c, Å	21.7531(9)
α, deg	90
β, deg	109.386(6)
γ, deg	90
V, Å^3	4369.8(4)
Z	4
calcd density, g cm^{-3}	1.329
absorp coeff, mm^{-1}	5.705
temperature, K	130.4(8)
θ range (deg)	4.16-69.07
index ranges (h, k, l)	–17, 22; –12, 11: –26, 14
no. of reflns collected	18934
no. of indep reflns (R_{int})	5956 (0.0453)
reflns with $I > 2\sigma(I)$	5024
R indexes [data with $I > 2\sigma(I)$][a]	R_1 = 0.0482; wR_2 = 0.1367[b]
R indexes (all data)[a]	R_1 = 0.0566; wR_2 = 0.1506[b]
GOF	0.811
no. of restraints / params	0 / 456
$\Delta\rho$(max., min.), eÅ^{-3}	1.063 / –0.900
CCDC deposition no	2015575

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] a = 0.1389, b = 3.7558.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Data

A CIF file containing full crystallographic data for compound **4b** (CCDC 2015575) and a PDF file containing ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra for all new compounds. Supplementary data to this article can be found online at…

References

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