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Reactivity of the Phosphinidene-Bridged Complexes $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^tBu_3)(CO)_2]$ and $[Mo_2Cp_2(\mu\text{-}PH)(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^tBu_3)(CO)_2]$ toward Alkynes: Multicomponent Reactions in the Presence of Ligands

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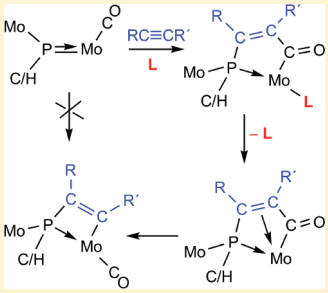
Supporting Information

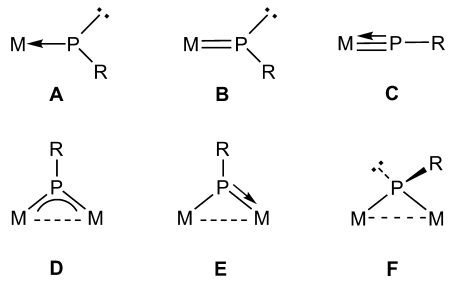
ABSTRACT: The cyclopentadienylidene-phosphinidene complex $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ (**1**) (Cp = η^5-C_5H_5; Mes* = 2,4,6-$C_6H_2{}^tBu_3$) reacted with RC≡CR′ in refluxing toluene solutions to give the corresponding phosphide derivatives $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PCR{=}CR'\}(\eta^6\text{-}HMes^*)(CO)_2]$ (R = R′ = CO_2Me; R = H, R′ = CO_2Me, *p*-tol), displaying a phosphametallacyclobutene ring. In contrast, the phosphinidene complex $[Mo_2Cp_2(\mu\text{-}PH)(\eta^6\text{-}HMes^*)(CO)_2]$ (**2**) reacted with $MeO_2CC{\equiv}CCO_2Me$ at room temperature to give first the monocarbonyl phosphide-acyl complex $[Mo_2Cp_2\{\mu\text{-}\kappa^1{:}\kappa^1,\eta^3\text{-}PHC(CO_2Me){=}C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)]$, the latter evolving progressively to the isomeric dicarbonyl $[Mo_2Cp_2(\mu\text{-}\kappa^1{:}\kappa^1,\eta^1\text{-}PHC(CO_2Me){=}C(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (Mo−P ca. 2.57 Å). When different ligands such as CO, PMe_3, $P(OMe)_3$, or CNXyl were added at room temperature to toluene solutions containing compound **1** and different alkynes, relatively fast multicomponent reactions took place to give with good yields the corresponding phosphide-acyl complexes $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PCR{=}CR'C(O)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (R = R′ = CO_2Me; R = H, R′ = CO_2Me, *p*-tol), and $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PC(CO_2Me){=}C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)(L)]$ (L = PMe_3, $P(OMe)_3$) or the related phosphide-iminoacyl derivatives $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PCR{=}CR'C(NXyl)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (Xyl = 2,6-$C_6H_3Me_2$; R = R′ = CO_2Me; R = H, R′ = CO_2Me, C(O)Me), respectively, all of them displaying five-membered phosphametallacyclopentenone or phosphametallacyclopentenimine rings. Separate experiments revealed that the latter complexes (R = R′ = CO_2Me) could be decarbonylated photochemically to yield the corresponding monocarbonyls $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^3\text{-}(C_5H_4)PC(CO_2Me){=}C(CO_2Me)C(X)\}(\eta^6\text{-}HMes^*)(CO)]$ (X = O, NXyl), the latter rearranging at room temperature to give the corresponding phosphametallacyclobutene isomers $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PC(CO_2Me){=}C(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)(CX)]$. A side product was also formed during the photochemical treatment of the dicarbonyl substrate, it being finally isolated after chromatographic workup as the alkenylphosphide-chloride complex $[Mo_2CpCl\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^2\text{-}(C_5H_4)PC(CO_2Me){=}CH(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)]$ (Mo−P = 2.553(2) and 2.436(2) Å).



INTRODUCTION

Phosphinidene ligands (PR) are the phosphorus analogues of carbenes,[1] and their metal complexes are particularly attractive synthons for the design of phosphaorganic molecules on the coordination sphere of metal centers.[2] As is the case of their carbene counterparts, mononuclear complexes having bent phosphinidene ligands can be roughly divided into electrophilic ones (Fischer type), displaying a reactivity comparable to that of singlet carbenes, and nucleophilic ones (Schrock type), displaying a phospha-Wittig reactivity.[1,2] This can be rationalized by considering that, in a simplified way, the metal−phosphorus bonding in these complexes approaches the extreme descriptions of single-dative and double bonds, respectively (**A** and **B** in Chart 1), while the high reactivity of these molecules arises from the presence of both the multiple M−P bonds and the lone electron pair at phosphorus, coupled to the availability in both cases of a low-energy, P-centered LUMO. This chemistry has developed as an exciting area of

Chart 1



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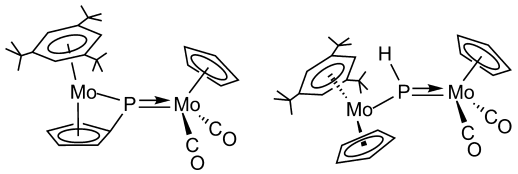
research since the early observations of [2+1] cycloaddition reactions of transient electrophilic phosphinidene complexes with alkenes and alkynes to form coordinated phosphiranes and phosphirenes.[2,3] In contrast with the latter behavior, the nucleophilic complexes have been shown instead to undergo [2+2] cycloaddition reactions with alkynes, and even with alkenes in a few instances, to give phosphametallacycles.[2,4] Compared to this state of facts, the chemistry of phosphinidene-bridged binuclear complexes has been comparatively little explored until recently,[5−8] in spite of the diverse behavior that might be anticipated for the different coordination modes of the PR ligands in binuclear environments (**D** to **F** in Chart 1).

In our early studies on the behavior of the metal−metal bonded complex $[Mo_2Cp_2(\mu\text{-PMes*})(CO)_4]$ (Cp = η^5-C_5H_5; Mes* = 2,4,6-$C_6H_2{}^tBu_3$; type **D**), we found that HC≡C(*p*-tol) would insert into the Mo−P bond of the complex under photochemical activation, to give a rare phosphaallyl derivative $[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2,\kappa^1\text{-C(}p\text{-tol)CHPMes*)(CO)}_4]$.[6a] This result was somewhat reminiscent of the only other related reaction involving binuclear phosphinidene complexes, that of the transient complex of type **D** $[Fe_2(\mu\text{-P}^t\text{Bu})(CO)_6]$ with RC≡CR′ to give the corresponding derivatives $[Fe_2(\mu\text{-}\kappa^1,\eta^1{:}\kappa^1,\eta^2\text{-CRCR′P}^t\text{Bu})(CO)_6]$.[9] In the case of our dimolybdenum substrate, however, a photoexcited state involving a pyramidal phosphinidene ligand (type **F** in Chart 1) was proposed to be involved in this and related reactions.[6a,c] Interestingly, the diiron complex $[Fe_2Cp_2(\mu\text{-PCy})(\mu\text{-CO})(CO)_2]$, having a quite nucleophilic pyramidal PR ligand of type **F**, was later shown to react readily with alkynes, although in a more complex way, with the incoming molecule being eventually bound not only to P but also to the Cp or carbonyl ligands, depending on the particular alkyne used.[7b] Neither of the above reactions are strictly comparable to those observed between mononuclear phosphinidene complexes and alkynes.

In contrast to the above behavior, a preliminary study on the reactivity of an asymmetric complex of type **E** as the cyclopentadienylidene-phosphinidene complex $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-PC}_5H_4)(\eta^6\text{-HMes*})(CO)_2]$ (**1**) (Chart 2) revealed

Chart 2



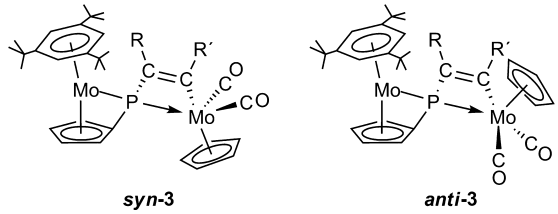
1 **2**

that this compound failed to react with alkenes and alkynes at room temperature, but reacted with alkynes in refluxing toluene solutions to give products apparently resulting from a [2+2] cycloaddition of the alkyne to its multiple Mo−P bond.[8b] This is reminiscent of the behavior of nucleophilic mononuclear phosphinidene complexes[2,4] and also of some mononuclear phosphide complexes.[10] Interestingly, however, we found recently that the reactivity of **1** could be dramatically increased in the presence of CO or CNXyl ligands (Xyl = 2,6-$C_6H_3Me_2$), with **1** then being able to react rapidly at room temperature with several electron-poor alkynes and alkenes to give novel five-membered phosphametallacycles resulting from a highly selective coupling between the alkyne/alkene, the added ligand, and the Mo−P multiple bond.[8e] This resulted in a multicomponent reaction (MCR), perhaps involving a pyramidal intermediate of type **F**, that is largely unprecedented in the chemistry of isolable phosphinidene complexes, although a few related MCRs involving transient phosphinidene-derived mononuclear complexes have been reported,[11] and thus deserved a more detailed analysis. In this paper we report our full studies on the reactivity of **1** toward different alkynes, both in the absence and in the presence of two-electron donor ligands such as CO, isocyanides, or phosphines. For comparative purposes, we have also studied some of these reactions using the isoelectronic phosphinidene complex $[Mo_2Cp_2(\mu\text{-PH})(\eta^6\text{-HMes*})(CO)_2]$ (**2**) as the starting substrate (Chart 2). According to recent density functional theory (DFT) calculations, the PH complex **2** displays a π(Mo−P) bonding interaction essentially located at the P−MoCp(CO)$_2$ bond,[8d] whereas that interaction in **1** is largely delocalized over the Mo−P−Mo skeleton (not represented in Chart 2), and this difference should lead to an increased reactivity for **2** (compared to **1**) concerning the [2+2] cycloadditions. As it will be discussed below, our results suggest unexpectedly that, rather than two different reaction pathways ([2+2] cycloaddition vs MCR processes, depending on the presence of ligands), the reactions of compounds **1** and **2** toward alkynes might be rationalized through a single reaction pathway involving initially the formation of intermediates having pyramidal phosphinidene ligands of type **F**.

RESULTS AND DISCUSSION

Reactions of Complexes 1 and 2 with Alkynes. The cyclopentadienylidene-phosphinidene complex **1** reacts readily with several alkynes in refluxing toluene to give the corresponding derivatives $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-(C}_5H_4)PCR{=}CR'\}(\eta^6\text{-HMes*})(CO)_2]$ (**3a**: R = R′ = CO_2Me; **3b**: R = H, R′ = CO_2Me; **3c**: R = H, R′ = *p*-tol). Compounds **3a−c** exist in solution as an equilibrium mixture of *syn* and *anti* isomers in each case, with the *syn*/*anti* ratio being dependent on the solvent (Chart 3). These isomers differ in the

Chart 3



***syn*-3** ***anti*-3**

relative orientation of the cyclopentadienyl rings with respect to the average plane of the phosphametallacyclobutene ring of the molecule, as discussed later on. We also note that the reaction with methyl propiolate is not selective, since it actually gives a mixture of **3b** and the corresponding phosphide-acyl complex $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-(C}_5H_4)PCH{=}C(CO_2Me)C(O)\}(\eta^6\text{-HMes*})(CO)_2]$ (**6b**), a product more conveniently prepared in the presence of CO, as discussed later on (Chart 4).

As predicted on the basis of its better-suited electronic structure, the phosphinidene complex **2** is more reactive than **1**, and it is able to react with the activated alkynes DMAD (dimethyl acetylenedicarboxylate) and methyl propiolate at room temperature. Unfortunately the latter reaction gave a mixture of products that could not be characterized. In contrast, the reaction of **2** with DMAD takes place at room temperature

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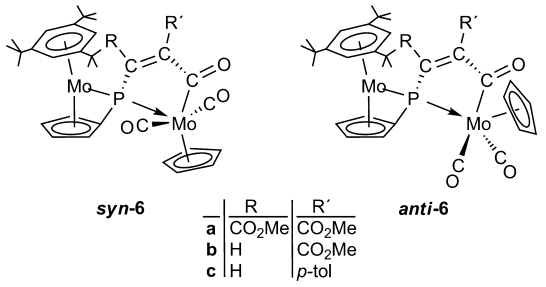
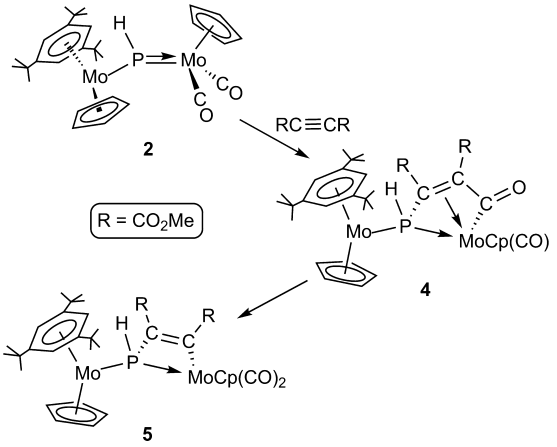
Chart 4



almost instantaneously and with high selectivity, but gives unexpectedly the monocarbonyl phosphide-acyl complex $[Mo_2Cp_2\{\mu\text{-}\kappa^1{:}\kappa^1,\eta^3\text{-}PHC(CO_2Me){=}C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)]$ (**4**), the latter evolving progressively to the isomeric dicarbonyl $[Mo_2Cp_2(\mu\text{-}\kappa^1{:}\kappa^1,\eta^1\text{-}PHC(CO_2Me){=}C(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**5**). Compound **5** displays a phosphametallacyclobutene ring comparable to those of compounds **3a**–**c**, while compound **4** displays a sort of phosphametallacyclopentenone ring. But more importantly, the fact that **5** is formed from **4** has critical mechanistic implications concerning the hypothetical [2+2] cycloadditions supposed initially to be responsible for the formation of compounds such as **3** and **5**, a matter to be discussed later on. We finally note that the isomerization **4**/**5** is completed in ca. 24 h in toluene solution at room temperature, whereas it becomes faster when adding some tetrahydrofuran to these toluene solutions, then

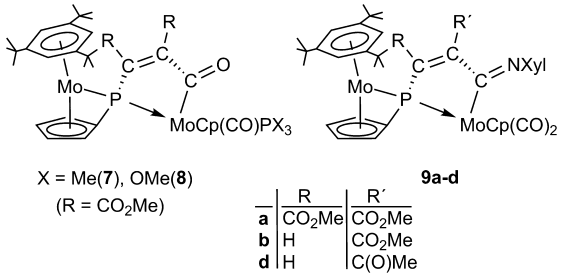
Scheme 1



being completed in ca. 1 h, an observation with no obvious explanation.

Reactions in the Presence of Other Ligands. When different ligands such as CO, PMe_3, $P(OMe)_3$, or CNXyl are added at room temperature to toluene solutions containing compound **1** and different alkynes, relatively fast MCR reactions take place to give with good yields the corresponding phosphide-acyl complexes $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PCR{=}CR'C(O)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**6a**: R = R′ = CO_2Me; **6b**: R = H, R′ = CO_2Me; **6c**: R = H, R′ = *p*-tol), and $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PC(CO_2Me){=}C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)(L)]$ (**7**: L = PMe_3; **8**: L = $P(OMe)_3$) or the related phosphide-iminoacyl derivatives $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^1\text{-}(C_5H_4)PC(R){=}C(R')C(NXyl)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**9a**: R = R′ = CO_2Me; **9b**: R = H, R′ = CO_2Me; **9d**: R = H, R′ = C(O)Me), respectively (Charts 4 and 5). All these complexes are derived from the regioselective coupling of the

Chart 5



entering alkyne with the P atom of the phosphinidene ligand and either carbonyl or isocyanide ligands bound to molybdenum. Moreover, as found for compounds **3**, most of these compounds (except for the more congested molecules **7**, **8**, and **9a**) exist in solution as solvent-dependent equilibrium mixtures of the corresponding *syn* and *anti* isomers, these also differing in the relative orientation of the cyclopentadienyl rings with respect to the average plane defined by the five-membered phosphametallacycle (only shown for compounds **6** in Chart 4). We finally note that the reaction with (*p*-tolyl)acetylene in the presence of CO gave also significant amounts of the diphosphanediyl complex $[Mo_2\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^5\text{-}(C_5H_4)PP(C_5H_4)\}(\eta^6\text{-}HMes^*)_2]$, a singular molecule derived from the reaction of **1** with CO, as shown by independent experiments.[12]

Photochemical Transformations Relating Different Phosphametallacycles. Since the phosphide-acyl complexes **6** have one more CO group than the corresponding compounds of type **3**, we examined possible interconversion routes between these two types of compounds using the DMAD derivatives **3a** and **6a**. First we noticed that **3a** did not react with CO (3 atm) even in refluxing toluene. This indicates the presence of a significant kinetic barrier to the insertion of CO into the Mo–C bonds of compounds of type **3**. The same applies to the reverse reaction, since compound **6a** does not experience any significant transformation in refluxing toluene after a few hours. However, a CO molecule indeed can be removed out of **6a** upon irradiation with visible–UV light, although that reaction does not yield **3a**, but the monocarbonyl $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^3\text{-}(C_5H_4)PC(CO_2Me){=}C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)]$ (**10**), an isomer of **3a** still retaining a five-membered phosphametallacyclopentenone ring (Scheme 2), along with small and variable amounts of a second complex identified by a ^{31}P NMR resonance at 45.8 ppm. Upon chromatographic workup, this minor product is transformed into the chloro complex $[Mo_2CpCl\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^2\text{-}(C_5H_4)PC(CO_2Me){=}CH(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)]$ (**11**), with an alkenylphosphide ligand (Chart 6). Thus, this minor side product is tentatively formulated as the corresponding hydroxo complex $[Mo_2Cp(OH)\{\mu\text{-}\kappa^1,\eta^5{:}\kappa^1,\eta^2\text{-}(C_5H_4)PC(CO_2Me){=}CH(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)]$, possibly arising from the reaction with trace amounts of water present in the photolytic experiment.

Compound **10** is structurally related to **4**, but thermally more robust, and it can be isolated in a conventional way. Yet, the solutions of **10** also rearrange progressively (rapidly upon heating) to yield its dicarbonyl isomer **3a**, having the four-membered phosphametallacycle, with the transformation being completed in ca. 3 d at room temperature. Interestingly, this

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Scheme 2

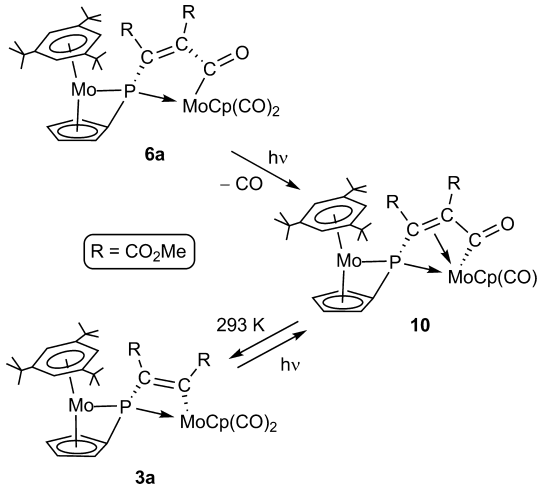
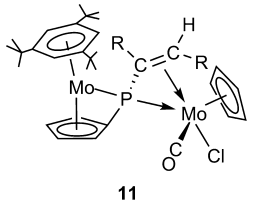


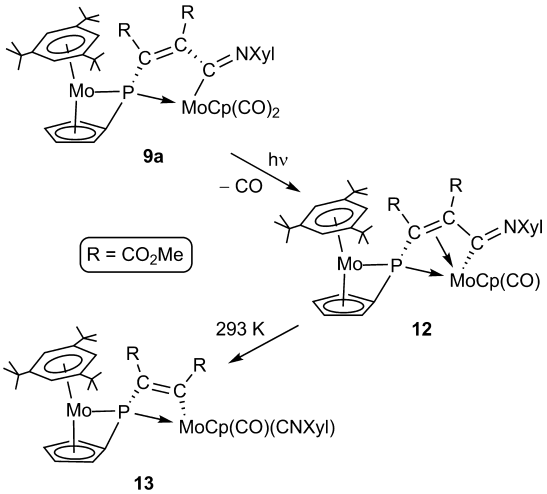
Chart 6



transformation can be reversed photochemically. Thus, irradiation of toluene solutions of **3a** with visible–UV light for 1 h at room temperature cleanly yields its isomer **10**, along with a small amount of the hydroxo complex mentioned above. As it was the case of **3a**, compound **10** does not react with CO (3 atm) at room temperature so as to give **6a**.

Similar transformations were also observed for the phosphide-iminoacyl complex **9a** (Scheme 3). Thus, the

Scheme 3



irradiation of the latter complex with visible–UV light in toluene solutions gave as the major product the monocarbonyl derivative $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5\text{:}\kappa^1,\eta^3\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(NXyl)\}(\eta^6\text{-HMes*})(CO)]$ (**12**), structurally related to compounds **4** and **10**, along with smaller amounts of the isomer $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5\text{:}\kappa^1,\eta^1\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)\}(\eta^6\text{-HMes*})(CNXyl)(CO)]$ (**13**), an isocyanide complex structurally related to compounds **3** and **5**. Upon standing at room temperature (more rapidly in the presence of added tetrahydrofuran), compound **12** transforms progressively into **13**, the latter being the product that could be finally isolated in the conventional way.

Solid-State Structure of Compounds 3a and 5. The structure of the cyclopentadienylidene-phosphinidene complex **3a** (Figure 1 and Table 1) was confirmed during our

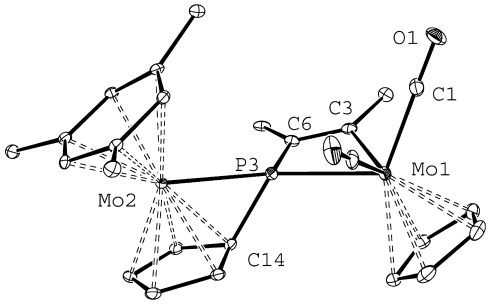


Figure 1. ORTEP diagram (30% probability) of compound ***syn*-3a**,[8b] with H atoms and ^{t}Bu and CO_2Me groups (except the C^1 atoms) omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for *syn*-3a[8b]

parameter	3a
Mo1–P	2.4810(8)
Mo2–P	2.5136(9)
Mo1–CC	2.198(3)
C=C	1.352(4)
CC–P	1.799(3)
P–CMo	1.779(3)
OC–Mo1–CO	77.7(1)
Mo1–P–Mo2	144.61(3)
Mo1–P–CC	87.0(1)
Mo2–P–CC	126.7(1)

preliminary study on this chemistry,[8b] and that of the phosphinidene complex **5** has been now examined also through an X-ray analysis. Although the poor quality of the diffraction data prevents a detailed analysis of the metric parameters for **5**, the connectivity and overall conformation of the molecule is thus firmly established.

The molecule of **3a** corresponds to the *syn* isomer, with the cyclopentadienylic rings placed on the same side of the average plane defined by the atoms of the almost flat phosphametallacyclobutene ring (average torsion angle ca. 10°, C(3)–C(6) = 1.352(4) Å). The latter is derived from a formal [2+2] cycloaddition of an alkyne molecule to the short P–Mo bond of compound **1**, almost perpendicularly to the Mo_2P plane, as expected by considering the orbital interactions involved. As a result, however, *both* Mo–P distances are elongated. In particular, the long Mo–P length of 2.5153(7) Å now approaches the reference values of single-bond lengths (e.g., 2.555(3) Å for the corresponding distance in the asymmetrically bridged $[W_2Cp_2(\mu\text{-PMes})(CO)_4(PH_2Mes)]$, with Mes = 2,4,6-$C_6H_2Me_3$,[13] or 2.608(1) Å in $[Mo_2\{\mu\text{-}\kappa^1,\eta^5\text{:}\kappa^1,\eta^5\text{-}(C_5H_4)PP(C_5H_4)\}(\eta^6\text{-HMes*})_2]$),[12] while the Mo(1)–P length of 2.4810(8) Å within the ring has a value closer to those of single-dative P→Mo bonds (ca. 2.45 Å for $MoPR_3$ complexes).

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Table 2. Selected IR and ^{31}P NMR Data for New Compounds

compound	ν(MoC≡O)[a]	ν(C═O)[a]	ν(MoC═X)[a]	δ(P)[b]/ppm
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**3a**)	1944 (vs), 1864 (s)	1696 (m)		−21.5 (*syn*) −12.7 (*anti*)
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PCH=C(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**3b**)	1933 (vs), 1848 (m)	1728 (s)		−25.4 (*syn*) −12.4 (*anti*)
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PCH=C(p\text{-tol})\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**3c**)	1923 (vs), 1836 (s)			−23.9 (*syn*) −10.5 (*anti*)
$[Mo_2Cp_2\{\mu\text{-}PHC(CO_2Me)=C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)]$ (**4**)	1913 (vs)[c]	1699 (s)[c]	1699 (s)[c]	−6.0 (d, 317)[d]
$[Mo_2Cp_2\{\mu\text{-}PHC(CO_2Me)=C(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**5**)	1941 (vs), 1860 (s)[c]	1698 (m)[c]		−137.8 (d, 258)[d]
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**6a**)	1949 (vs), 1877 (s)	1730 (m)	1589 (m, sh), 1566 (m)	82.3 (*syn*) 83.8 (*anti*)
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PCH=C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**6b**)	1942 (vs), 1866 (s)	1724 (m)	1580 (m, sh), 1565 (m)	79.7 (*syn*) 76.1 (*anti*)
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PCH=C(p\text{-tol})C(O)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**6c**)	1936 (vs), 1857 (s)		1580 (m)	86.3 (*syn*)[d] 84.0 (*anti*)[d]
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)(PMe_3)]$ (**7**)	1807 (s)	1735 (s)	1652 (m)	102.7 [d, 7, μ-P], 29.7 [d, 7][d]
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)\{P(OMe)_3\}]$ (**8**)	1839 (s)	1731 (s)	1632 (m)	191.9 [d, 11] 93.5 [d, 11, μ-P]
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(NXyl)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**9a**)	1942 (vs), 1869 (s)	1730 (m)	1540 (w)	81.5
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PCH=C(CO_2Me)C(NXyl)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**9b**)	1939 (vs), 1863 (s)	1718 (m)	1542 (w)	75.4 (*syn*) 68.2 (*anti*)
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PCH=C\{C(O)Me\}C(NXyl)\}(\eta^6\text{-}HMes^*)(CO)_2]$ (**9d**)	1937 (vs), 1860 (s)	1691 (m)	1531 (w)	76.4 (*syn*) 67.1 (*anti*)
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(O)\}(\eta^6\text{-}HMes^*)(CO)]$ (**10**)	1946 (vs)[e]	1687 (s, br)[e]	1687 (s, br)[e]	57.5
$[Mo_2CpCl\{\mu\text{-}(C_5H_4)PC(CO_2Me)=CH(CO_2Me)\}(\eta^6\text{-}HMes^*)(CO)]$ (**11**)	1982 (vs)	1691 (m)		45.5
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(NXyl)\}(\eta^6\text{-}HMes^*)(CO)]$ (**12**)	1928 (vs)	1683 (vs)	1587 (w)	49.8
$[Mo_2Cp\{\mu\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)\}(\eta^6\text{-}HMes^*)(CNXyl)(CO)]$ (**13**)	2047 (vs, C≡N), 2007 (m, C≡N), 1848 (vs)	1689 (s)		−8.5 (*syn*)[d] 8.9 (*anti*)[d]

[a]Recorded in CH_2Cl_2 solution, unless otherwise stated; data in cm^{-1}; X = O, NXyl. [b]Recorded in CD_2Cl_2 solutions at 290 K and 121.50 MHz unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; J(PH) given in brackets, J(PP) given in square brackets, both in hertz. [c]In petroleum ether solution. [d]In C_6D_6 solution. [e]ν(CO) 1946 (vs), 1758 (m), 1694 (m) cm^{-1} in petroleum ether solution.

The coordination environment around the P atom is not tetrahedral, but rather of a distorted pyramidal-trigonal type, with the Mo(1), Mo(2), P, and C(6) atoms almost in the same plane (sum of angles around P ca. 358°) and the cyclopentadienylidene C(14) atom occupying the apical position. Although initially we considered this perhaps as resulting from a residual π(Mo−P) interaction in the molecule (cf. the bonding in $[\{Cp(CO)_2Mo\}_2PMn(CO)_4]$, a complex displaying a phosphide ligand with a T-shaped environment),[14] our recent work on the heterometallic derivatives of **1** indicates that this unusual geometry around P rather emerges from the geometrical constraints imposed by the bifunctional PC_5H_4 ligand and steric effects.[8d]

The molecule of **5** has two significant differences when compared to that of **3a**. First, it corresponds to an *anti* isomer, with the cyclopentadienylic rings placed at opposite sides of the average plane of the phosphametallacyclobutene ring, which is also quite flat. Second, it displays a relatively normal tetrahedral environment around phosphorus, in agreement with the comments made above on the origin of the structural anomalies displayed by different derivatives of **1**.

Solution Structure of Compounds 3a−c, 5, and 13. The spectroscopic data available for these compounds (Table 2 and Experimental Section) indicate that all of them share the same basic structural features and are consistent with the solid-state structures discussed for **3a** and **5**. In addition, they clearly indicate that two isomers coexist in solution in each case, as mentioned before (*syn* and *anti* isomers, Chart 3) except for **5**, for which a single isomer is present in solution (presumably the *anti* isomer found in the crystal). The *syn* isomers appear to be favored in low-polarity solvents such as benzene or toluene, while more polar solvents such as dichloromethane seem to favor the *anti* isomers.

The IR spectrum of all these compounds (except for the monocarbonyl **13**) displays two C−O stretching bands corresponding to the terminal carbonyls, with relative intensities (very strong and strong, in order of decreasing frequency) as anticipated for $M(CO)_2$ oscillators having C−M−C angles less than 90° (ca. 78° in the crystal of **3a**),[15] with their wavenumbers expectedly increasing with the number of CO_2Me groups present in the original alkyne [1904 cm^{-1} (**3a**) > 1891 cm^{-1} (**3b**) > 1880 cm^{-1} (**3c**)]. At the same time, they display strongly shielded ^{31}P NMR resonances, in the range +10 to −20 ppm (ca. −140 ppm for the PH complex **5**), which is consistent with the presence of a ligand of type PR_2 bridging two metal atoms *without* a metal−metal bond.[16] These shifts are not very different from those measured for the relatively scarce number of mononuclear complexes reported to have

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comparable phosphametallacyclobutene rings (cf. 85.0 ppm for [Cp_2Zr{P(Mes*)C(H)=CPh}].[4e]

The major isomer for compound **3a** (almost the unique one in toluene solutions) gives rise to a ^{31}P NMR resonance more shielded than the minor isomer (Table 2) and thus is reasonably assigned to the isomer found in the crystal (*syn*). We have assumed that the same ordering of ^{31}P shifts between *syn* and *anti* isomers holds for the other compounds of this type, this being consistent with the NOESY spectra recorded for **3c**. Indeed, for that compound NOE enhancements were detected for the minor isomer in C_6D_6 solution between the Cp and ^{t}Bu groups, thus allowing its identification as the *anti* isomer. At the same time, significant NOE enhancements were also observed between the *ortho* protons of the C_6H_4 group and the Cp ligand and between the CH protons of the former alkyne and either the ^{t}Bu or C_5H_4 groups, thus confirming the regioselectivity of the reaction leading to these complexes, with the CH atom of the alkyne being specifically attached to the P atom of the starting substrate. This is also indicated by the fact that the PCH ^1H NMR resonances in both isomers of **3b** (ca. 7 ppm) display a relatively low $^2J_{PH}$ coupling of 11 Hz, consistent with a geminal arrangement of P and H atoms around a double C=C bond, a feature also present in the spectra of compounds of types **6** and **9** (see below). In contrast, *transoid* $^3J_{PH}$ couplings through a double C=C bond are expected to be significantly higher (ca. 30 Hz).[17]

The ^{13}C NMR spectra of compounds **3** and **5** are also consistent with the regioselective formation (for the terminal alkynes) of the phosphametallacycle ring, with the Mo-bound C atom of the alkyne giving rise to a quite deshielded resonance at ca. 200 ppm and displaying a relatively high P−C coupling (15−25 Hz), while the P-bound carbon atom gives rise to a more shielded resonance as expected (ca. 158 ppm in **3a** or **5**, ca. 140 ppm for the PCH resonance in **3c**) and displays a lower P−C coupling (<5 Hz), a feature also present in the spectra of compounds **6** to **9** (see below). We note that these chemical shifts are comparable to those measured for the mononuclear zirconium complexes [Cp_2Zr{P(Mes*)C(R)=CPh}] (R = Ph, Me, H), the latter displaying Zr−*C*Ph resonances also around 200 ppm.[4e] We finally note that the carbonyl ligands of the $Mo(CO)_2Cp$ fragments give rise to two distinct resonances in each case, with PC couplings of ca. 30 and 3 Hz in each case, as expected from their different positioning (*cis* and *trans*, respectively) relative to the P atom.[18]

Solid-State Structure of Compound 6a. The structure of the DMAD derivative **6a** (Figure 2 and Table 3) was confirmed

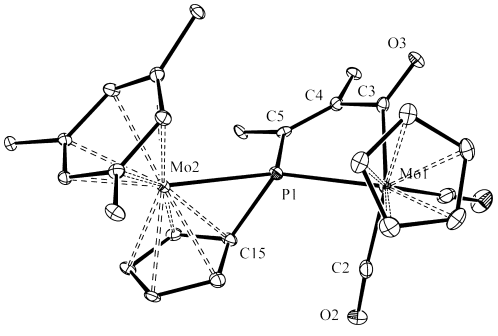

Figure 2. ORTEP diagram (30% probability) of compound ***anti*-6a**,[8e] with H atoms and ^{t}Bu and CO_2Me groups (except the C^1 atoms) omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *anti*-6a[8e]

Mo1−P	2.474(1)	Mo−P−Mo2	136.8(1)
Mo2−P	2.557(1)	Mo1−P−C5	105.0(2)
Mo1−C1	1.957(6)	Mo2−P−C5	117.0(2)
Mo1−C2	1.954(6)	Mo2−P−C155	57.3(2)
Mo1−C3	2.211(5)	Mo1−C3−C4	119.8(3)
C3−C4	1.518(7)	C3−C4−C5	118.7(4)
C4−C5	1.343(6)	C4−C5−P	112.8(4)
P−C5	1.820(5)	C1−Mo1−C2	77.5(2)
Mo2−C15	2.190(5)	C1−Mo1−P	116.2(2)
P−C15	1.787(5)	C2−Mo1−P	78.0(2)
C3−O3	1.221(6)	C3−Mo1−P	73.2(1)

during our preliminary study on the MCR reactions of compound **1**.[8e] The molecule in the crystal corresponds to an isomer of type *anti*, and it can be derived from that of **3a** after formal insertion of a CO molecule into the Mo−C bond of the phosphametallacyclobutene ring (a reaction not taking place actually, as noted above). This yields a more relaxed five-membered phosphametallacyclopentenone $MoPC_3$ ring (C=C = 1.343(6) Å), with the P and C atoms almost in a plane, but the Mo atom significantly deviated from it (by ca. 0.85 Å). Due to that unstrained geometry, the Mo−P lengths now approach better the expected values of single (Mo(2)−P = 2.557(1) Å) and single-dative (Mo(1)−P = 2.474(1) Å) bonds, as proposed on the basis of simple electron-count rules. Yet, the environment around the P atoms is of the unusual trigonal-pyramidal type characteristic of many derivatives of the cyclopentadienylidene-phosphinidene complex **1**, with the Mo(1), Mo(2), P, and C(5) atoms almost in the same plane (sum of angles around P ca. 359°) and the cyclopentadienylidene C(15) atom occupying the apical position.

The five-membered $MoPC_3$ ring in **6a** is comparable to that present in the diiron phosphide-acyl complex [Fe_2Cp_2{μ-κ^1:κ^1,η^1-CyPCHC(*p*-tol)C(O)}(μ-CO)(CO)], a related molecule derived from the reaction of the pyramidal-phosphinidene complex [Fe_2Cp_2(μ-PCy)(μ-CO)$(CO)_2$] with HC≡C(*p*-tol).[7b] The interatomic distances within the phosphametallacycles in these two compounds are comparable to each other, after allowing for the differences in the covalent radii for Mo and Fe,[19] with the main difference being of a conformational nature, since the $FePC_3$ ring in the diiron complex is almost planar, while the corresponding one in **6a** is not, as noted above.

Solution Structure of Compounds 6 to 9. The spectroscopic data available for these compounds (Table 2 and Experimental Section) indicate that all of them share the same basic structural features and are consistent with the solid-state structure discussed for **6a**. In addition, as was the case of compounds **3**, they clearly indicate that *syn* and *anti* isomers coexist in solution in most cases, as mentioned above (Chart 4) except for the DMAD derivatives **7**, **8**, and **9a**, for which a single isomer is present in solution. There is no clear trend concerning the influence of the solvent on the equilibrium ratio between these isomers.

The IR spectra of the dicarbonyl compounds **6** and **9** in the C−O stretching region display two strong bands at frequencies slightly higher than those of the corresponding complexes of type **3**, an effect ascribed to the influence of the acyl or iminoacyl groups now present in these molecules. The latter groups give rise to characteristic resonances at lower

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frequencies, at ca. 1580 and 1540 cm^{-1}, respectively, for compounds **6** and **9**. The monocarbonyl compounds **7** and **8** expectedly give rise to a single carbonyl stretch at lower frequencies (ca. 1820 cm^{-1}), whereas the C−O stretch of the corresponding acyl group (ca. 1640 cm^{-1}) now appears at frequencies higher than in the dicarbonyl compounds (Table 2).

All compounds **6** to **9** give rise to a ^{31}P NMR resonance in the range 65−85 ppm, a relatively low chemical shift still consistent with the presence of a phosphide-like bridging ligand in the absence of metal−metal bonds. Yet, these shifts are some 100 ppm higher than the corresponding values in compounds **3**, a difference that can be attributed to the higher ring strain in the four-membered cycles of the latter complexes, compared to the five-membered rings of complexes **6** to **9**. This shielding effect on P nuclei placed in strained rings is well documented for complexes having chelate diphosphine ligands.[20] We finally note that the ^{31}P chemical shifts in these compounds are rather insensitive to the *syn*/*anti* isomerism (Table 2).

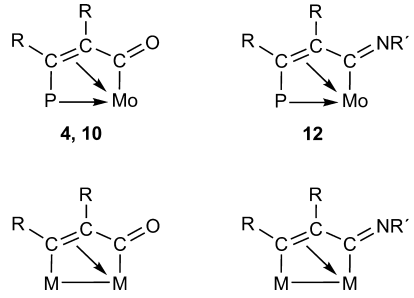
The identification of *syn* and *anti* isomers in the solutions of **6** and **9** was made on the basis of standard NOESY experiments, these allowing the identification of the relevant Cp/C_5H_4 (*syn*) and $Cp/^tBu$ (*anti*) enhancements and also confirming in the case of **6b** the spatial proximity of the former CH proton of the alkyne to the C_5H_4 ring. In addition, we note that all derivatives of terminal alkynes give rise to PCH ^1H NMR resonances at about 7 ppm and displaying low P−H couplings of ca. 8 Hz, as found for compounds **3b**,**c**, this indicating the same regioselectivity in the formation of the five-membered phosphametallacycles, with the terminal carbon of the alkyne being bound to the P atom. For further comparison, the mentioned diiron complex $[Fe_2Cp_2\{\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^1\text{-}CyPCHC(p\text{-}tol)C(O)\}(\mu\text{-}CO)(CO)]$ displays a comparable ^1H NMR resonance for its PCH atom (δ 7.90 ppm, J_{HP} = 13 Hz).[7b]

The ^{13}C NMR spectra of compounds **6** to **9** are also consistent with a regioselectivity (for terminal alkynes) identical to that of compounds **3**. Actually, the P-bound carbon atom of the former alkyne gives rise to a resonance comparable to the corresponding ones in compounds **3** (ca. 160 ppm and with unmeasurably small P−C couplings), while the other C atom of the alkyne, now bonded to an acyl or iminoacyl group, gives rise to a resonance at ca. 165−170 ppm displaying a relatively high P−C coupling (20−25 Hz). Finally, the acyl and iminoacyl groups give rise to diagnostic resonances much more deshielded (at ca. 270 and 210 ppm, respectively), as expected.

The monocarbonyl complexes **7** and **8** are obtained as single isomers in each case. Apart from the *syn*/*anti* isomerism, two possible arrangements of the $PMe_3/P(OMe)_3$ ligands (*trans* or *cis* relative to the other P atom) are possible. Fortunately, the ^{13}C spectrum of **8** allows the unambiguous identification of the complex as having a *trans* arrangement of its P ligands, since both the acyl (J_{PC} = 38 and 11 Hz) and the carbonyl resonances (J_{PC} = 42 and 28 Hz) display large P−C couplings to both P atoms, which is indicative of acute P−Mo−C angles.[18] This geometrical arrangement is likely to be the most favored on steric grounds. As for the isocyanide complex **13**, there are two isomers in solution. Since no splitting of the C−O stretching band of the carbonyl ligand is observed, we conclude that the observed isomerism must be of the *syn*/*anti* type. The isocyanide ligand is most likely placed *trans* to the P atom, since this expectedly leads to minimum steric repulsions, as found for the phosphine complexes **7** and **8**, and also corresponds to the initial position that this ligand must occupy after deinsertion from the $MoPC_3$ ring of **12** (kinetic product). Finally, the appearance of more than one C−N stretching band in the IR spectra of **13** cannot be taken as an indication of *cis*/*trans* isomerism around the MoCp(CO)(CNR) center. Actually, such splitting of C−N bands is a common feature of complexes having terminal isocyanide ligands and is due to the presence in solution of variable amounts of conformers with bent isocyanide ligands.[21]

Structural Characterization of Compounds 4, 10, and 12. Full characterization of these species was precluded because of their low thermal stability and easy transformation into the corresponding isomers having a four-membered phosphametallacyclobutene ring (**5**, **3a**, and **13**, respectively), although the available data allow unambiguous definition of the essential structural features of these molecules (Table 2 and Experimental Section). The IR spectra of these compounds display in each case two strong bands indicative respectively of the presence of a single carbonyl ligand (ca. 1930 cm^{-1}) and acyl (ca. 1690 cm^{-1} for **4** and **10**, masked with the bands from the CO_2Me groups) or iminoacyl ligands (1587 cm^{-1} for **12**). This could be corroborated through a ^{13}C NMR spectrum of compound **10**, this exhibiting two resonances at 254.0 and 237.0 ppm that can be assigned to the acyl and carbonyl ligands, respectively. The position of the former resonance actually is not very different from that in the phosphide-acyl precursor **6a** (ca. 265 ppm). This confirms that, upon decarbonylation of the precursor **6a** (and presumably also in the case of **9a**), the five-membered $MoPC_3$ rings are preserved, and we propose that they just rearrange to coordinate their C=C double bonds so as to fill the vacancy left by the carbonyl ligand (Schemes 2 and 3). This should be expectedly accompanied by a significant shielding of the corresponding carbon resonances. Unfortunately, these resonances could not be located in the spectrum of **10**, probably due to broadening effects. Although we are not aware of previous examples for a coordinated phosphide-acyl ligand analogous to that proposed here, we note the strong structural relationship with several alkenyl-acyl or alkenyl-iminoacyl and related ligands bridging dimetal centers (Chart 7).[22−25] Interestingly, some of these acyl complexes undergo decarbonylation and deinsertion reactions comparable to those relating our complexes, a matter to be discussed below.

Chart 7



Structural Characterization of Compound 11. The molecule of the chloro complex **11** (Figure 3 and Table 4) can be viewed as derived from that of **10** by removing the acyl group and replacing it with chlorine (at the metal) and hydrogen (at carbon) atoms, yielding an alkenyl-phosphide ligand π-bound to the MoCp(CO) fragment (Mo−C lengths ca. 2.25 Å, C−C = 1.43(1) Å) in an allyl-like fashion. Once

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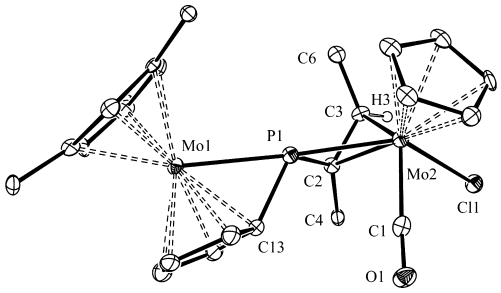


Figure 3. ORTEP diagram (30% probability) of compound **11**, with H atoms (except H3) and ^{t}Bu and CO_2Me groups (except the C^1 atoms) omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 11

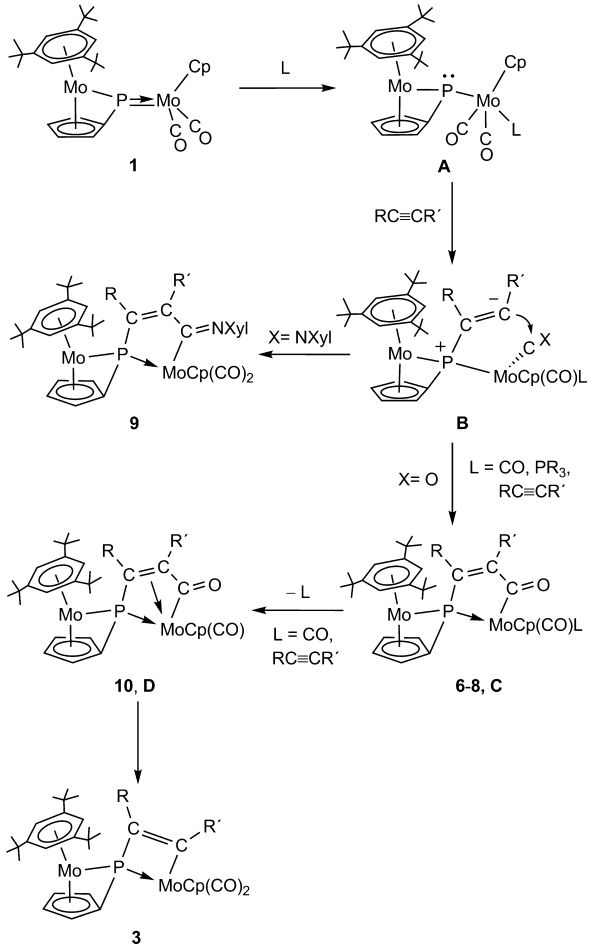
Mo1−P	2.553(2)	Mo1−P−Mo2	165.39(9)
Mo2−P	2.436(2)	Mo1−P−C2	132.7(2)
Mo2−Cl1	2.510(2)	Mo2−P−C2	61.8(2)
Mo2−C1	1.993(8)	Mo2−P−C135	121.5(2)
Mo2−C2	2.244(7)	C6−C3−C2	125.4(7)
Mo2−C3	2.258(8)	C3−C2−P	112.8(5)
P−C13	1.789(7)	C1−Mo2−C3	123.7(3)
P−C2	1.799(7)	C1−Mo2−P	82.4(2)
C2−C3	1.431(9)	C1−Mo2−Cl1	80.6(2)
C3−C6	1.468(10)	P−Mo2−Cl1	128.1(1)

more, the geometry around phosphorus is of the trigonal-pyramidal type, with the Mo(1), Mo(2), and C(2) atoms defining a plane containing the P atom, and the apical position being occupied by the cyclopentadienylidene C(13) atom. The Mo−P lengths of 2.553(2) Å (Mo1−P) and 2.436(2) Å (Mo2−P) are now very close to the reference values for single and single-dative Mo−P bond lengths,[8d] as proposed on the basis of simple electron-count formalism.

Spectroscopic data in solution for **11** are consistent with the structure found in the crystal. We note that the *E*-conformation of the alkenyl ligand found in the crystal is fully consistent with the large P−H coupling of the corresponding ^{1}H NMR resonance (31 Hz), while its relatively low chemical shift (4.84 ppm) is indicative of the retention of the π-coordination of the alkenyl group in solution.

Pathways in the Reactions of the Phosphinidene Complexes 1 and 2 with Alkynes. According to DFT calculations on compounds **1** and **2**, the π(Mo−P) bonding interactions in these molecules take place perpendicularly to the Mo−P−Mo plane, as the corresponding antibonding interactions do (incidentally, the LUMO in these molecules).[8d] Therefore, these orbitals would have the right shape to account for the formation of the phosphametallacyclobutene derivatives **3** and **5** via a concerted [2+2] cycloaddition pathway between the phosphinidene complex **1** or **2** and the corresponding alkyne, thus paralleling the behavior of the mononuclear nucleophilic phosphinidene complexes. However, there are several facts in support of an alternative reaction pathway: (a) the reactivity of **1** toward alkynes is dramatically increased in the presence of simple ligands (CO, PR_3, CNR, ...) to give derivatives having phosphametallacyclopentenone rings, (b) an intermediate (**4**) having the same phosphametallacyclopentenone ring is detected in the room-temperature reactions of **2** with DMAD, and (c) the latter type of molecules (**4**, **10**, and **12**) undergo fast thermal rearrangement into the corresponding phosphametallacyclobutene isomers **3**, **5**, and **13**. All of this gives support to an alternative and unified explanation to account for the formation of all alkyne derivatives of the phosphinidene complexes **1** and **2** (Scheme 4; only derivatives of **1** represented).

Scheme 4



All reactions would be initiated by the coordination of a ligand (L) to the $MoCp(CO)_2$ center of the phosphinidene complex. This ligand would be the added ligand in each case (CO, PR_3, CNR, ...) or, if no other ligand is added, a molecule of the alkyne itself, always used in excess. This would yield an intermediate species $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-HMes*})(CO)_2L]$ (**A**) having a pyramidal phosphinidene ligand. We have actually performed a DFT calculation of such an intermediate when L = CO (see the Experimental Section for details of the calculations). The optimized structure (Figure 4 and Table 5) expectedly features a four-legged piano-stool $Mo(CO)_3P$ fragment and a pyramidal environment around phosphorus (sum of angles 284.7°). The corresponding Mo−P length has been greatly increased, as anticipated from the bond order reduction to unity (2.835 Å, to be compared with 2.272 Å computed for **1**).[8d] The weakening of this bond is so large that an analysis of the topology of the electron density of the molecule, under the AIM theory,[26] failed to locate the corresponding bond critical point (cf. ρ = 0.311 e Å^{-3} for the short Mo(2)−P bond in **A**, while the short bond in **1** has a value of 0.627 e Å^{-3}).[8b] All of this actually justifies the fast homolytic cleavage of that Mo−P bond of **1** occurring under a CO atmosphere, to give the dimers $[Mo_2Cp_2(CO)_6]$ and

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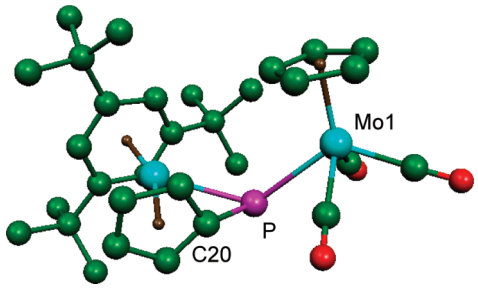

Figure 4. DFT-optimized structure of intermediate **A** (L = CO), with H atoms omitted for clarity.

Table 5. Selected Bond Lengths (A) and Angles (deg) for the DFT-Optimized Geometry of Intermediate A (L = CO)

Mo1−P	2.835	Mo1−P−Mo2	122.9
Mo2−P	2.701	Mo1−P−C20	107.3
P−C20	1.793	Mo2−P−C20	54.5
Mo1−CO(*cis*)	2.003	P−Mo1−CO(*cis*)	68.7
Mo1−CO(*cis*)	1.999	P−Mo1−CO(*cis*)	68.5
Mo1−CO(*trans*)	1.994	P−Mo1−CO(*trans*)	125.4

$[Mo_2\{\mu\text{-}\kappa^1,\eta^5\text{:}\kappa^1,\eta^5\text{-}(C_5H_4)PP(C_5H_4)\}(\eta^6\text{-HMes*})_2]$.[12] Of interest to the present discussion, however, is the fact that the electronic structure of this intermediate has been greatly modified, so that the P atom is now a much better donor site, as illustrated by the nature of the HOMO−2 orbital, corresponding to a nonbonding electron pair on the phosphorus atom quite high in energy (see the Supporting Information). As a result, it is expected that this pyramidal intermediate becomes a donor much stronger than the starting substrate **1**.

The intermediates of type **A**, therefore, would be nucleophilic enough to attack a molecule of alkyne to give a zwitterionic phosphide intermediate **B**, this resembling the alkylation and related reactions of stable complexes having pyramidal phosphinidene bridges.[7,27] The attack would occur specifically at the terminal carbon, in the case of terminal alkynes, both because of the smaller steric hindrance of that position and because in this way the negative charge generated in the resulting intermediate is better delocalized by the vicinal CO_2Me (or *p*-tol) groups. Incidentally, we note that the same type of regioselectivity has been found in the concerted [2+2] cycloadditions of mononuclear nucleophilic phosphinidene complexes with alkynes,[2j,4] or even in related reactions involving terminal trigonal PR_2 ligands.[10]

The zwitterionic intermediate **B** would then evolve differently depending on the nature of L: when L = alkyne, PR_3, or CO, an attack of the internal atom of the alkyne to a carbonyl in *cis* position would follow, yielding the phosphametallacyclopentenone derivatives of type **6**, **7**, and **8**. The overall result from **1** thus is parallel to that observed previously by us in the reactions of the stable pyramidal phosphinidene complex $[Fe_2Cp_2(\mu\text{-PCy})(\mu\text{-CO})(CO)_2]$ toward different alkynes. When L = alkyne (reactions in the absence of other ligands), the resulting complex **C** would not be stable, but would rearrange by ejection of L and coordination of the double bond of the $MoPC_3$ ring, to yield monocarbonyl intermediates **D** analogous to complexes **10** and **4**, which, due to the high temperature of the experiment (typically refluxing toluene), would rapidly rearrange into the isomers with the phosphametallacyclobutene ring (**3**), thus eluding detection. We should note that the observed transformations **6a** → **10** → **3a** discussed in the preceding sections actually are an exact representation of the sequence **C** → **D** → **3** here proposed. Moreover dimetal complexes having dimetallacyclopentenone rings also offer independent precedents of related transformations, not only of the coordination of the C═C double bond (analogous to the **C** → **D** step),[23a] but also of deinsertion of CO to give dimetallacyclobutene rings (analogous to the **D** → **3** step).[22,23b] Finally, when L = CNXyl, the nucleophilic attack of the carbanionic atom in the corresponding intermediate **B** would preferentially occur at the isocyanide, rather than at a carbonyl ligand. Although the origin of this chemoselectivity is not clear to us at the moment, we note that an analogous selectivity has been reported in the related reactions of the thiolate complexes [FeCp(SPh)(CNMe)(CX)] (X = O, S) with DMAD to give the thiametallacyclopentenimine derivatives $[FeCp\{\kappa^1,\eta^1\text{-SPhCR═CRC(NMe)}\}(CX)]$, derived from the specific binding of the alkyne to the isocyanide, rather than to the carbonyl or thiocarbonyl ligands.[28] We finally note that related phosphametallacyclopentenone rings have been also described as resulting from the reactions of mononuclear carbonyl complexes having pyramidal PR_2 ligands with activated alkynes.[29]

CONCLUDING REMARKS

Although the reactions of the phosphinidene complexes **1** and **2** with alkynes eventually lead to products containing either four-membered $MoPC_2$ rings (in the absence of other ligands) or five-membered $MoPC_3$ rings (in the presence of CO, CNR, or PR_3 ligands), they all seem to follow an analogous multicomponent reaction pathway involving an intermediate with a pyramidal phosphinidene ligand that reacts with the alkyne to give a five-membered $MoPC_3$ ring after cyclization involving a coordinated CO or CNR group. These reactions are regioselective, so that the terminal carbon of the alkyne is attached to the P atom, and chemoselective too, so that the ring is preferentially formed with the isocyanide (if added) rather than with the carbonyl ligands. These products can dissociate a CO (photochemically) or alkyne (thermally) ligand, then rearranging first through coordination of the double C═C bond of the phosphametallacyclopentenone ring and then through CO deinsertion from the latter ring, to finally yield the corresponding phosphametallacyclobutene isomer, with the latter step being reversed photochemically. The latter complexes, therefore, would not be formed through a [2+2] cycloaddition pathway, as might have been supposed on the basis of the known chemistry of mononuclear phosphinidene complexes.

EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. All reactions were carried out using Schlenk tubes equipped with J. Young valves. Solvents were purified according to literature procedures and distilled prior to use.[30] Petroleum ether refers to that fraction distilling in the range 338−343 K. The compounds $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-HMes*})(CO)_2]$ (**1**) and $[Mo_2Cp(\mu\text{-PH})(\eta^5\text{-}C_5H_5)(\eta^6\text{-HMes*})(CO)_2]$ (**2**) were prepared as described previously (Mes* = 2,4,6-$C_6H_2{}^tBu_3$).[6c,8d] Photochemical experiments were performed using jacketed Pyrex Schlenk tubes cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for the experiments with visible−UV light. Chromatographic separations were carried out using jacketed columns cooled by tap

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Table 6. Crystal Data for Compound 11

parameter	11·C_4H_8O
mol formula	$C_{39}H_{54}ClMo_2O_6P$
mol wt	877.12
cryst syst	monoclinic
space group	$P2_1/c$
radiation (λ, Å)	0.71073
a, Å	9.5448(4)
b, Å	16.4260(9)
c, Å	25.1954(13)
α, deg	90
β, deg	88.649(4)
γ, deg	90
V, Å^3	3949.1(3)
Z	4
calcd density, g cm^{-3}	1.475
absorpt coeff, mm^{-1}	0.787
temperature, K	100
θ range,deg	1.48 to 26.4
index ranges (h, k, l)	−11, 11; 0, 20; 0, 31
reflns collected	32 328
indep reflns (R_{int})	8053 (0.156)
reflns with $I > 2\sigma(I)$	4251
R indexes[a] [data with $I > 2\sigma(I)$]	R_1 = 0.0649
	wR_2 = 0.1242[b]
R indexes[a] (all data)	R_1 = 0.1488
	wR_2 = 0.1569[b]
GOF	0.984
restraints/params	0/454
$\Delta\rho$(max, min), e Å^{-3}	0.704, −0.821

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] a = 0.0533, b = 0.0000.

water or with a cryostat. Commercial aluminum oxide (Aldrich, activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity IV. All other reagents were obtained from the usual commercial suppliers and used as received. IR stretching frequencies were measured in solution and are referred to as ν (bond). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), or 75.47 MHz (^{13}C{^{1}H}) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz. ^{1}H and ^{13}C NMR assignments were usually carried out by combining the information from standard DEPT, HSQC, and NOESY experiments as appropriate. Compounds **3a**, **6a**,**b**, and **9a**,**b** were reported in separated communications.[8b,e] The synthesis and spectroscopic details of these compounds are reproduced here to facilitate comparison with the other compounds reported in this full paper.

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-$(C_5H_4)PC(CO_2Me)$=C-$(CO_2Me)\}(\eta^6$-HMes*)$(CO)_2$] (3a). Neat dimethyl acetylenedicarboxylate (DMAD) (9 μL, 0.073 mmol) was added to a solution, prepared in a glass bulb equipped with a J. Young valve, of compound **1** (0.023 g, 0.035 mmol) in toluene (2 mL). After closing the valve, the mixture was heated and stirred at 368 K for 2 h to give a brown solution. The solvent was then removed under vacuum, and the residue was chromatographed on an alumina column (activity IV) refrigerated with water. Elution with dichloromethane gave a green fraction, yielding, after removal of the solvent under vacuum, compound **3a** as a green microcrystalline solid (0.016 g, 57%). Unfortunately, no satisfactory elemental analysis could be obtained for this product due to its rapid decomposition upon manipulation in the air. In solution, this complex exists as an equilibrium mixture of *syn* and *anti* isomers, with their ratio being 8:1 in dichloromethane and 17:1 in toluene, as determined by ^{1}H NMR spectroscopy. *Spectroscopic data for* ***syn*-3a**: ^{1}H NMR: δ 5.36 (m, 1H, C_5H_4), 5.34 (s, 5H, Cp), 5.31, 5.03 (2 m, 2 × 1H, C_5H_4), 4.95 (d, J_{HP} = 4, 3H, C_6H_3), 4.06 (m, 1H, C_5H_4), 3.71, 3.53 (2s, 2 × 3H, OCH_3), 1.17 (s, 27H, ^{t}Bu). ^{1}H NMR (400.13 MHz, tol-d_8): δ 5.69 (m, 1H, C_5H_4), 5.16 (s, 5H, Cp), 4.97 (m, 1H, C_5H_4), 4.90 (d, J_{HP} = 4, 3H, C_6H_3), 4.65, 4.00 (2 m, 2 × 1H, C_5H_4), 3.68, 3.33 (2s, 2 × 3H, OCH_3), 1.13 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 253.7 (d, J_{CP} = 32, CO), 245.1 (d, J_{CP} = 3, CO), 199.2 (d, J_{CP} = 25, Mo−*C*=C), 176.4, 176.0 (2d, CO_2Me), 157.3 (d, J_{CP} = 4, P−*C*=C), 112.1 [s, C(C_6H_3)], 92.0 (s, Cp), 90.8 [d, J_{CP} = 4, CH(C_5H_4)], 88.6 [d, J_{CP} = 34, C(C_5H_4)], 88.0 [s, CH(C_5H_4)], 87.1 [d, J_{CP} = 8, CH(C_5H_4)], 80.5 [d, J_{CP} = 17, CH(C_5H_4)], 71.7 [s, CH(C_6H_3)], 51.3, 51.0 (2s, OCH_3), 35.1 [s, C(^{t}Bu)], 31.3 [s, CH_3(^{t}Bu)]. *Spectroscopic data for* ***anti*-3a**: ^{1}H NMR: δ 5.82 (m, 1H, C_5H_4), 5.38 (s, 5H, Cp), 4.88 (m, 1H, C_5H_4), 4.80 (d, J_{HP} = 5, 3H, C_6H_3), 4.75, 4.27 (2 m, 2 × 1H, C_5H_4), 3.70, 3.49 (2s, 2 × 3H, OCH_3), 1.18 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 112.1 [s, C(C_6H_3)], 92.9 (s, Cp), 73.8 [s, CH(C_6H_3)], 51.2, 51.1 (2s, 2 × OCH_3), 34.5 [s, C(^{t}Bu)], 31.5 [s, CH_3(^{t}Bu)]; other resonances of this isomer were masked by those of the major isomer and thus could not be identified in the spectra.

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-$(C_5H_4)PCH$=$C(CO_2Me)\}$-$(\eta^6$-HMes*)$(CO)_2$] (3b). The procedure is analogous to that described for **3a**, but using HC≡CCO_2Me (8 μL, 0.089 mmol) and a reaction time of 60 min at 383 K, to give a brown solution containing a mixture of the compounds **3b** and **6b**. The solvent was then removed under vacuum, the residue was extracted with petroleum ether (3 × 5 mL), and the extracts were filtered using a canula. Removal of the solvent from the filtrate gave compound **3b** as a brown powder (0.012 g, 40%). Unfortunately, no satisfactory elemental analysis could be obtained for **3b** due to its rapid decomposition upon manipulation in the air. In solution, this complex exists as an equilibrium mixture of *syn* and *anti* isomers, with their ratio being 5:6 in dichloromethane and 2:1 in toluene, as determined by ^{1}H NMR spectroscopy. The residue left after the extraction with petroleum ether was dissolved in CH_2Cl_2 and chromatographed at 288 K. Elution with dichloromethane gave a green fraction yielding, after removal of solvents, compound [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-$(C_5H_4)PCH$=$C(CO_2Me)C(O)\}(\eta^6$-HMes*)$(CO)_2$] (**6b**) as a greenish-brown powder (0.010 g, 32%). A more selective preparation of **6b** is described below. *Spectroscopic data for* ***syn*-3b**: ^{1}H NMR: δ 7.04 (d, J_{HP} = 11, 1H, PCH), 5.38 (s, 5H, Cp), 4.99 (d, J_{HP} = 4, 3H, C_6H_3), 5.22, 5.16, 4.84, 4.78 (4 m, 4 × 1H, C_5H_4), 3.90 (s, 3H, OMe), 1.17 (s, 27H, ^{t}Bu). *Spectroscopic data for* ***anti*-3b**: ^{1}H NMR: δ 6.97 (d, J_{HP} = 11, 1H, PCH), 5.32 (s, 5H, Cp), 5.11, 4.22 (2 m, 2 × 1H, C_5H_4), 4.90 (m, 2H, C_5H_4), 4.80 (d, J_{HP} = 4, 3H, C_6H_3), 3.62 (s, J_{HP} = 1, 3H, OCH_3), 1.19 (s, 27H, ^{t}Bu).

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-$(C_5H_4)PCH$=$C(p$-tol)$\}(\eta^6$-HMes*)$(CO)_2$] (3c). The procedure is analogous to that described for **3a**, but using HC≡C(*p*-tol) (20 μL, 0.158 mmol) and a reaction time of 3 h at 373 K to give a brown solution. The solvent was then removed under vacuum, the residue was extracted with CH_2Cl_2−petroleum ether (1:1), and the extracts were chromatographed at 288 K. Elution with dichloromethane/petroleum ether (1:2) gave a green fraction yielding, after removal of solvents, compound **3c** as a brown powder (0.018 g, 58%). In solution, this complex exists as an equilibrium mixture of *syn* and *anti* isomers, with their ratio being 5:6 in dichloromethane and 4:3 in toluene, as determined by ^{1}H NMR spectroscopy. Anal. Calcd for $C_{39}H_{47}Mo_2O_2P$: C, 60.78; H, 6.15. Found: C, 60.45; H, 5.98. *Spectroscopic data for* ***syn*-3c**: ^{1}H NMR (C_6D_6): δ 7.59, 7.09 (AA′XX′, J_{HH} +$J_{HH'}$ = 8, 2 × 2H, C_6H_4), 7.19 (d, J_{PH} = 11, 1H, PCH), 5.13 (s, 5H, Cp), 4.89, 4.83, 4.57, 4.16 (4 m, 4 × 1H, C_5H_4), 4.95 (d, J_{HP} = 4, 3H, C_6H_3), 2.18 (s, 3H, Me), 1.14 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6): δ 259.2 (d, J_{CP} = 30, MoCO), 247.5 (d, J_{CP} = 3, MoCO), 138.5 (d, J_{CP} = 4, PCH), 129.0 (s, *m*-C_6H_4), 126.7 (s, *o*-C_6H_4), 110.2 [s, C(C_6H_3)], 91.7 (s, Cp), 89.3 [s, CH(C_5H_4)], 86.0 [d, J_{CP} = 7, CH(C_5H_4)], 83.6 [s, CH(C_5H_4)], 80.1 [d, J_{CP} = 15, CH(C_5H_4)], 71.2 [s, CH(C_6H_3)], 34.7 [s, C(^{t}Bu)], 31.4 [s, CH_3(^{t}Bu)], 21.2 [s, CH_3(*p*-tol)]. Other resonances of this isomer could not be assigned unambiguously. *Spectroscopic data for* ***anti*-3c**:

^{1}H NMR: δ 7.63, 7.12 (AA′XX′, $J_{HH} + J_{HH'}$ = 8, 2 × 2H, C_6H_4), 6.85 (d, J_{PH} = 10, 1H, PCH), 5.19 (s, 5H, Cp), 5.17, 4.94, 4.64, 4.58 (4 m, 4 × 1H, C_5H_4), 4.57 (d, J_{HP} = 4, 3H, C_6H_3), 2.19 (s, 3H, Me), 1.05 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6): δ 138.6 (s, PCH), 129.6 (s, *m*-C_6H_4), 126.1 (s, *o*-C_6H_4), 105.9 [s, C(C_6H_3)], 92.5 (s, Cp), 89.6 [s, CH(C_5H_4)], 87.6 [d, J_{CP} = 8, CH(C_5H_4)], 83.9 [s, CH(C_5H_4)], 81.9 [d, J_{CP} = 11, CH(C_5H_4)], 74.1 [s, CH(C_6H_3)], 34.0 [s, C(^{t}Bu)], 31.6 [s, CH_3(^{t}Bu)], 21.1 [s, CH_3(*p*-tol)]. Other resonances of this isomer could not be assigned unambiguously.

Reaction of 2 with DMAD. Neat DMAD (8 μL, 0.065 mmol) was added to a solution of compound **2** (0.026 g, 0.040 mmol) in toluene (1 mL), and the mixture was stirred at room temperature for 20 min to give an orange-brown solution containing a mixture of compounds [$Mo_2Cp_2\{\mu$-κ^1:κ^1,η^3-PHC(CO_2Me)=C(CO_2Me)C(O)}(η^6-HMes*)(CO)] (**4**) and [$Mo_2Cp_2\{\mu$-κ^1:κ^1,η^1-PHC(CO_2Me)=C(CO_2Me)}(η^6-HMes*)$(CO)_2$] (**5**). Then tetrahydrofuran (0.5 mL) was added to the solution, and the mixture was further stirred for 1 h to yield an orange-brown solution containing compound **5** as the major species. The solvents were then removed under vacuum, the residue was extracted with toluene−petroleum ether (2:1), and the extracts were filtered using a canula. Removal of the solvents from the filtrate yielded compound **5** as a brown microcrystalline solid (0.029 g, 92%). The crystals used in the X-ray study of this complex were grown by slow diffusion at 253 K of layers of petroleum ether and toluene into a concentrated solution of the complex in dichloromethane. Anal. Calcd for $C_{36}H_{47}Mo_2O_6P$ (**5**): C, 54.14; H, 5.93. Found: C, 53.89; H, 5.79. *Spectroscopic data for compound* **4**: ^{1}H NMR (C_6D_6): δ 5.08 (d, J_{HP} = 1, 5H, Cp), 4.96 (d, J_{HP} = 6, 3H, C_6H_3), 4.55 (d, J_{HP} = 5, 5H, Cp), 4.05 (d, J_{HP} = 317, 1H, PH), 3.49, 3.28 (2s, 2 × 3H, OMe), 1.16 (s, 27H, ^{t}Bu). *Spectroscopic data for compound* **5**: ^{1}H NMR (C_6D_6): δ 5.14 (s, 5H, Cp), 4.54 (d, J_{HP} = 6, 3H, C_6H_3), 4.52 (d, J_{HP} = 5, 5H, Cp), 3.87 (d, J_{HP} = 258, 1H, PH), 3.75, 3.44 (2s, 2 × 3H, OMe), 1.13 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, toluene-d_8, 188 K): δ 258.6 (d, J_{CP} = 25, MoCO), 249.1 (s, MoCO), 200.5 (d, J_{CP} = 16, Mo*C*≡C), 177.1, 176.8 (2s, CO_2Me), 158.3 (d, J_{CP} = 5, PC≡C), 105.2 [s, C(C_6H_3)], 92.3, 84.8 (2s, Cp), 74.8 [s, CH(C_6H_3)], 51.3, 50.9 (2s, OMe), 34.9 [s, C(^{t}Bu)], 31.0 [s, CH_3(^{t}Bu)].

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(O)}(η^6-HMes*)$(CO)_2$] (6a). A toluene solution (4 mL) of compound **1** (0.030 g, 0.046 mmol) and DMAD (8 μL, 0.065 mmol) was placed in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, degassed under vacuum, and then refilled with CO. The solution was allowed to reach room temperature, the valve was then closed, and the mixture was further stirred at 313 K for 15 min to give a brown solution. The solvent was then removed under vacuum, and the residue was chromatographed at 253 K. Elution with dichloromethane gave a gray fraction yielding, after removal of the solvent under vacuum, compound **6a** as a brown microcrystalline solid (0.035 g, 92%). In solution, this complex exists as an equilibrium mixture of *syn* and *anti* isomers, with their ratio being 1:2 in dichloromethane and 1:4 in benzene, as determined by ^{1}H NMR spectroscopy. Anal. Calcd for $C_{37}H_{45}O_7Mo_2P$: C, 53.89; H, 5.50. Found: C, 53.94; H, 5.57. *Spectroscopic data for* ***syn*-6a**: ^{1}H NMR: δ 5.34 (s, 5H, Cp), 5.31, 5.07, 4.87, 4.52 (4 m, 4 × 1H, C_5H_4), 4.88 (d, J_{HP} = 3, 3H, C_6H_3), 3.72, 3.64 (2s, 2 × 3H, OMe), 1.18 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 268.0 [d, J_{CP} = 11, MoC(O)], 247.4 (d, J_{CP} = 30, MoCO), 239.8 (s, MoCO), 168.1, 167.0 (2s, CO_2Me), 164.2 (d, J_{CP} = 19, PC≡*C*), 157.5 (s, PC≡C), 114.2 [s, C(C_6H_3)], 95.6 (s, Cp), 90.9 [d, J_{CP} = 4, C(C_5H_4)], 89.0 [d, J_{CP} = 4, CH(C_5H_4)], 86.6 [d, J_{CP} = 10, CH(C_5H_4)], 85.3 [s, CH(C_5H_4)], 82.1 [d, J_{CP} = 18, CH(C_5H_4)], 73.0 [s, CH(C_6H_3)], 52.9, 52.5 (2s, OMe), 35.2 [s, C(^{t}Bu)], 31.3 [s, CH_3(^{t}Bu)]. *Spectroscopic data for* ***anti*-6a**: ^{1}H NMR: δ 5.15 (s, 5H, Cp), 5.18, 5.14, 5.07, 4.27 (4 m, 4 × 1H, C_5H_4), 4.95 (d, J_{HP} = 3, 3H, C_6H_3), 3.74, 3.68 (2s, 2 × 3H, OMe), 1.14 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 263.4 [d, J_{CP} = 11, MoC(O)], 249.6 (d, J_{CP} = 24, MoCO), 239.6 (s, MoCO), 168.7 (s, 2CO_2Me), 165.1 (d, J_{CP} = 20, PC≡*C*), 157.8 (s, PC≡C), 114.0 [s, C(C_6H_3)], 92.1 (s, Cp), 91.2 [d, J_{CP} = 20, C(C_5H_4)], 88.9 [d, J_{CP} = 10, CH(C_5H_4)], 87.9 [d, J_{CP} = 4, CH(C_5H_4)], 83.9 [d, J_{CP} = 18, CH(C_5H_4)], 83.6 [s, CH(C_5H_4)], 73.2 [s, CH(C_6H_3)], 52.7, 52.2 (2s, OMe), 35.6 [s, C(^{t}Bu)], [s, CH_3(^{t}Bu)].

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PCH=C(CO_2Me)C(O)}(η^6-HMes*)$(CO)_2$] (6b). The procedure is analogous to that described for **6a**, but using methyl propiolate (8 μL, 0.089 mmol) and a similar workup. This led to compound **6b** as a brown microcrystalline powder (0.032 g, 91%). In solution, this complex exists as an equilibrium mixture of *syn* and *anti* isomers, with their ratio being 1:2 in dichloromethane and 1:1 in benzene, as determined by ^{1}H NMR spectroscopy. Anal. Calcd for $C_{35}H_{43}Mo_2O_5P$: C, 54.84; H, 5.65. Found: C, 54.92; H, 5.66. *Spectroscopic data for* ***syn*-6b**: ^{1}H NMR: δ 7.53 (d, J_{HP} = 8H, 1H, PCH), 5.25, 5.15, 4.80, 4.47 (4 m, 4 × 1H, C_5H_4), 5.12 (s, 5H, Cp), 4.92 (d, J_{HP} = 4, 3H, C_6H_3), 3.71 (s, 3H, OMe), 1.13 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 271.3 [d, J_{CP} = 9, MoC(O)], 248.5 (d, J_{CP} = 20, MoCO), 239.6 (s, MoCO), 165.4 (s, CO_2Me), 160.3 (d, J_{CP} = 5, P*CH*=C), 112.5 [s, C(C_6H_3)], 91.6 (s, Cp), 90.5 [d, J_{CP} = 23, C(C_5H_4)], 88.6 [d, J_{CP} = 5, CH(C_5H_4)], 88.5 [d, J_{CP} = 8, CH(C_5H_4)], 83.9 [s, CH(C_5H_4)], 83.1 [d, J_{CP} = 16, CH(C_5H_4)], 72.0 [s, CH(C_6H_3)], 52.2 (s, OMe), 35.4 [s, C(^{t}Bu)], 31.2 [s, CH_3(^{t}Bu)].^{13}C NMR: δ 160.3 (dd, J_{CH} = 166, J_{CP} = 5, P*CH*=C). *Spectroscopic data for* ***anti*-6b**: ^{1}H NMR: δ 7.65 (d, J_{HP} = 8, 1H, PCH), 5.40, 5.04, 5.01, 4.79 (4 m, 4 × 1H, C_5H_4), 5.33 (s, 5H, Cp), 4.89 (d, J_{HP} = 4, 3H, C_6H_3), 3.67 (s, 3H, OMe), 1.15 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 268.2 [d, J_{CP} = 9, MoC(O)], 248.3 (d, J_{CP} = 27, MoCO), 239.9 (s, MoCO), 165.7 (s, CO_2Me), 162.9 (s, P*CH*=C), 111.0 [s, C(C_6H_3)], 94.8 (s, Cp), 90.7 [d, J_{CP} = 23, C(C_5H_4)], 90.5 [d, J_{CP} = 5, CH(C_5H_4)], 85.4 [d, J_{CP} = 8, CH(C_5H_4)], 84.6 [s, CH(C_5H_4)], 81.3 [d, J_{CP} = 16, CH(C_5H_4)], 73.1 [s, CH(C_6H_3)], 52.1 (s, OMe), 34.9 [s, C(^{t}Bu)], 31.3 [s, CH_3(^{t}Bu)]. ^{13}C NMR: δ 162.9 (d, J_{CH} = 166, P*CH*=C). The resonances for the internal carbon atoms of the alkyne in both isomers (PC=*C* resonances) could not be located in the spectrum.

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PCH=C(*p*-tol)C(O)}(η^6-HMes*)$(CO)_2$] (6c). The procedure is analogous to that described for **6a**, but using (*p*-tolyl)acetylene (20 μL, 0.158 mmol) and a reaction time of 40 min. After removal of the solvent from the reaction mixture, the residue was extracted with petroleum ether and the extracts were chromatographed at 288 K. Elution with dichloromethane−petroleum ether (1:9) gave a green fraction, yielding, after removal of the solvents, the known diphosphanediyl complex [$Mo_2\{\mu$-κ^1,η^5:κ^1,η^5-(C_5H_4)P−P(C_5H_4)}(η^6-HMes*)$_2$][12] (0.014 g, 69%). The residue left after petroleum ether extraction was dissolved in dichloromethane and chromatographed at 253 K. Elution with dichloromethane gave a red and then a green band, these yielding respectively the dimer [$Mo_2Cp_2(CO)_6$] (0.008 g, 72%) and compound **6c** as a green microcrystalline solid (0.007 g, 18%). In solution, the latter complex exists as an equilibrium mixture of *syn* and *anti* isomers, with their ratio being 1:2 in dichloromethane or benzene, as determined by ^{1}H NMR spectroscopy. *Spectroscopic data for* ***syn*-6c**: ^{1}H NMR (C_6D_6): δ 7.53, 7.09 (2 m, AA′BB′, J_{HH} = 8, 2 × 2H, C_6H_4), 7.41 (d, J_{HP} = 10, 1H, PCH), 4.96 (s, 5H, Cp), 4.80, 4.77, 4.73, 4.43 (4 m, 4 × 1H, C_5H_4), 4.78 (d, J_{HP} = 3, 3H, C_6H_3), 2.13 (s, 3H, C_6H_4*Me*), 1.04 (s, 27H, ^{t}Bu). *Spectroscopic data for* ***anti*-6c**: ^{1}H NMR (C_6D_6): δ 7.55, 7.02 (2 m, AA′BB′, J_{HH} = 8, 4H, C_6H_4), 7.07 (d, J_{HP} = 10, 1H, PCH), 5.31 (s, 5H, Cp), 4.80, 4.75, 4.70, 4.47 (4 m, 4 × CH, C_5H_4), 4.55 (d, J_{HP} = 4, 3H, C_6H_3), 2.08 (s, 3H, *p*-C_6H_4*Me*), 0.93 (s, 27H, ^{t}Bu).

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(O)}(η^6-HMes*)(CO)(PMe_3)] (7). Neat DMAD (8 μL, 0.065 mmol) and then PMe_3 (6 μL, 0.060 mmol) were added to a solution of compound **1** (0.030 g, 0.046 mmol) in toluene (4 mL), whereupon the mixture turned into a greenish-brown solution. After further stirring for 10 min, the solvent was removed under vacuum and the residue was chromatographed at 258 K. Elution with dichloromethane gave a green fraction yielding, after removal of the solvent, compound **7** as a green microcrystalline solid (0.026 g, 66%). Anal. Calcd for $C_{39}H_{54}Mo_2O_6P_2$: C, 53.68; H, 6.24. Found: C, 53.50; H, 6.08. ^{1}H NMR (C_6D_6): δ 5.11 (s, 5H, Cp), 5.01, 4.93, 4.80, 4.63 (4 m, 4 × 1H, C_5H_4), 4.73 (s, br, 3H, C_6H_3), 3.39, 3.35 (2s, 2 × 3H, OMe), 1.43 (d, J_{HP} = 9, 9H, PMe), 1.10 (s, 27H, ^{t}Bu).

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Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PC(CO_2Me)=C-(CO_2Me)C(O)}(η^6-HMes*)(CO){$P(OMe)_3$}] (8). The procedure is analogous to that described for **7**, but using $P(OMe)_3$ (6 μL, 0.051 mmol) and a reaction time of 20 min. After similar workup, compound **8** was isolated as a green microcrystalline solid (0.030 g, 70%). Anal. Calcd for $C_{39}H_{54}Mo_2O_9P_2$: C, 50.88; H, 5.91. Found: C, 50.73; H, 5.81. ^{1}H NMR: δ 5.25, 5.05, 4.86, 4.59 (4 m, 4 × 1H, C_5H_4), 5.16 (s, 5H, Cp), 4.83 (s, br, 3H, C_6H_3), 3.69, 3.60 (2s, 2 × 3H, OMe), 3.48 (d, J_{HP} = 11, 9H, POMe), 1.17 (s, 27H, ^{t}Bu). ^{1}H NMR (C_6D_6): δ 5.37 (s, 5H, Cp), 5.02, 4.87, 4.79, 4.58 (4 m, 4 × 1H, C_5H_4), 4.71 (s, br, 3H, C_6H_3), 3.66 (d, J_{HP} = 11, 9H, POMe), 3.43, 3.42 (2s, 2 × 3H, OCH_3), 1.06 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 278.4 [dd, J_{CP} = 38, 11, MoC(O)], 256.7 (dd, J_{CP} = 42, J_{CP} = 28, MoCO), 169.5, 169.3 (2s, 2 × CO_2Me), 165.6 (d, J_{CP} = 26, PC═*C*), 159.2 (s, PC═C), 112.2 [s, br, C(C_6H_3)], 94.2 (s, Cp), 90.2 [d, J_{CP} = 4, CH(C_5H_4)], 89.5 [d, J_{CP} = 12, C(C_5H_4)], 86.7 [d, J_{CP} = 9, CH(C_5H_4)], 84.8 [s, CH(C_5H_4)], 82.7 [d, J_{CP} = 18, CH(C_5H_4)], 72.0 [s, br, CH(C_6H_3)], 52.6, 51.8 (2s, 2 × OMe), 52.5 (d, J_{CP} = 6, POMe), 35.1 [s, C(^{t}Bu)], 31.3 [s, CH_3(^{t}Bu)].

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PC(CO_2Me)=C-(CO_2Me)C(NXyl)}(η^6-HMes*)($CO)_2$] (9a). Xylylisocyanide (185 μL of a 0.25 M solution in petroleum ether, 0.046 mmol) was added to a solution of compound **1** (0.030 g, 0.046 mmol) and DMAD (8 μL, 0.065 mmol) in toluene (2 mL), whereupon the mixture changed instantaneously from red to brown. The solvent was then removed under vacuum, and the residue was chromatographed at 253 K. Elution with dichloromethane gave a gray-purple fraction, yielding, after removal of the solvent under vacuum, compound **9a** as a brown microcrystalline solid (0.038 g, 89%). Anal. Calcd for $C_{45}H_{54}O_6Mo_2NP$: C, 58.26; H, 5.87; N, 1.51. Found: C, 58.16; H, 5.82; N, 1.34. ^{1}H NMR: δ 6.93, 6.84 [2d, J_{HH} = 7, 2 × 1H, *m*-H(Xyl)], 6.74 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 5.20 (s, 5H, Cp), 5.16, 5.09, 4.73, 4.28 (4 m, 4 × 1H, C_5H_4), 4.97 (s, br, 3H, C_6H_3), 3.65 (s, 3H, OMe), 3.30 (s, br, 3H, OMe), 2.13, 1.88 (2s, 2 × 3H, Me), 1.18 (s, 27H, ^{t}Bu). ^{1}H NMR (C_6D_6): δ 7.12−7.05 [m, 2H, *m*-H(Xyl)], 6.93 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 5.00 (s, 5H, Cp), 4.98 (s, br, 3H, C_6H_3), 4.89, 4.77, 4.74, 4.25 (4 m, 4 × 1H, C_5H_4), 3.77 (s, 3H, OMe), 3.20 (s, br, 3H, OMe), 2.36, 2.33 (2s, 2 × 3H, Me), 1.17 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.47 MHz): δ 253.5 (d, J_{CP} = 26, MoCO), 240.9 (s, MoCO), 206.6 [s, br, MoC(NXyl)], 168.9 (s, 2CO_2Me), 168.4 (d, J_{CP} = 22, PC═*C*), 151.8 (s, PC═C), 150.3 [s, br, C^1(Xyl)], 127.7, 127.4 [2s, $C^{3,5}$(Xyl)], 125.7, 125.0 [2s, br, $C^{2,6}$(Xyl)], 122.1 [s, C^4(Xyl)], 113.4 [s, br, C(C_6H_3)], 92.5 (s, Cp), 91.6 [d, J_{CP} = 20, C(C_5H_4)], 88.4 [d, J_{CP} = 4, CH(C_5H_4)], 88.3, 83.5 [2s, CH(C_5H_4)], 82.7 [d, J_{CP} = 17, CH(C_5H_4)], 72.9 [s, CH(C_6H_3)], 52.8, 51.8 (2s, OMe), 35.5 [s, C(^{t}Bu)], 31.3 [s, CH_3(^{t}Bu)], 19.7, 18.6 [2s, CH_3(Xyl)].

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PCH═C(CO_2Me)C-(NXyl)}(η^6-HMes*)($CO)_2$] (9b). The preparative and purification procedures are identical to those described for **9a**, but using methyl propiolate instead (8 μL, 0.089 mmol). Elution with dichloromethane gave a gray-brown band yielding compound **9b** as a greenish-brown microcrystalline solid (0.037 g, 92%). This compound was shown (by NMR) to exist in solution as an equilibrium mixture of *syn* and *anti* isomers, with the *syn*/*anti* ratio being 7:2 in C_6D_6 and 7:3 in CD_2Cl_2. Anal. Calcd for $C_{43}H_{52}O_4Mo_2NP$: C, 59.38; H, 6.03; N, 1.61. Found: C, 59.24; H, 5.95; N, 1.37. *Spectroscopic data for* ***syn*-9b**: ^{1}H NMR (400.13 MHz): δ 6.90, 6.84 [2d, J_{HH} = 7, 2H, *m*-H(Xyl)], 6.72 (d, J_{HP} = 7, 1H, PCH), 6.71 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 5.22, 5.13, 4.89, 4.43 (4 m, 4 × 1H, C_5H_4), 5.21 (s, 5H, Cp), 4.89 (d, J_{HP} = 3, 3H, C_6H_3), 3.17 (s, 3H, OMe), 2.13, 1.93 (2s, 2 × 3H, Me), 1.15 (s, 27H, ^{t}Bu). ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.12−7.05 [m, 2H, *m*-H(Xyl)], 6.90 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 6.86 [d, J_{HP} = 7, PCH], 5.04 (s, 5H, Cp), 4.80 (d, J_{HP} = 3, 3H, C_6H_3), 4.70 (m, 2H, C_5H_4), 4.61, 4.35 (2 m, 2 × 1H, C_5H_4), 3.16 (s, 3H, OMe), 2.41, 2.37 (2s, 2 × 3H, Me), 1.07 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz): δ 253.5 (d, J_{CP} = 28, MoCO), 241.1 (s, MoCO), 206.4 [s, br, MoC(NXyl)], 169.8 (d, J_{CP} = 22, PC=*C*), 158.4 [s, br, C^1(Xyl)], 151.7 (s, br, PCH), 127.7, 127.4 [2s, $C^{3,5}$(Xyl)], 126.1, 125.1 [2s, br, $C^{2,6}$(Xyl)], 121.7 [s, C^4(Xyl)], 111.9 [s, br, C(C_6H_3)], 92.8 [d, J_{CP} = 16, C(C_5H_4)], 92.1 (s, Cp), 88.5 [s, CH(C_5H_4)], 88.4 [d, J_{CP} = 4, CH(C_5H_4)], 83.4 [s, CH(C_5H_4)], 82.4 [d, J_{CP} = 15, CH(C_5H_4)], 71.8 [s, CH(C_6H_3)], 51.5 (s, OMe), 35.3 [s, C(^{t}Bu)], 31.3 [s, CH_3(^{t}Bu)], 19.4, 18.9 [2s, CH_3(Xyl)]. *Spectroscopic data for* ***anti*-9b**: ^{1}H NMR (400.13 MHz): δ 6.90, 6.84 [2d, J_{HH} = 7, 2H, *m*-H(Xyl)], 6.78 [d, J_{HP} = 7, 1H, PCH], 6.71 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 5.34, 5.01, 4.94, 4.78 (4 m, 4 × 1H, C_5H_4), 5.28 (s, 5H, Cp), 4.89 (d, J_{HP} = 3, 3H, C_6H_3), 3.05 (s, 3H, OMe), 2.19, 1.94 (2s, 2 × 3H, Me), 1.20 (s, 27H, ^{t}Bu). ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.12−7.05 [m, 2H, *m*-H(Xyl)], 6.90 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 6.79 (d, J_{HP} = 7, PCH), 5.23 (s, 5H, Cp), 5.02, 4.70, 4.43, 4.36 (4 m, 4 × 1H, C_5H_4), 4.58 (d, J_{HP} = 4, 3H, C_6H_3), 3.07 (s, 3H, OMe), 2.72, 2.18 (2s, 2 × 3H, Me), 0.98 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz): δ 251.7 (d, J_{CP} = 23, MoCO), 242.8 (s, MoCO), 208.1 [s, br, MoC(NXyl)], 168.6 (d, J_{CP} = 25, PC═*C*), 156.8 [s, br, C^1(Xyl)], 154.6 (s, br, PCH), 128.6, 123.9 [2s, br, $C^{2,6}$(Xyl)], 127.6, 127.3 [2s, br, $C^{3,5}$(Xyl)], 121.7 [s, C^4(Xyl)], 110.0 [s, C(C_6H_3)], 93.9 (s, Cp), 91.9 [d, J_{CP} = 8, C(C_5H_4)], 90.1 [d, J_{CP} = 5, CH(C_5H_4)], 85.2 [d, J_{CP} = 9, CH(C_5H_4)], 84.4 [s, CH(C_5H_4)], 80.8 [d, J_{CP} = 14, CH(C_5H_4)], 72.9 [s, CH(C_6H_3)], 51.3 (s, OMe), 34.8 [s, C(^{t}Bu)], 31.4 [s, CH_3(^{t}Bu)], 20.4, 19.0 [2s, CH_3(Xyl)].

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^1-(C_5H_4)PCH═C{C(O)Me}-C(NXyl)}(η^6-HMes*)($CO)_2$] (9d). The preparative and purification procedures are identical to those described for **9a**, but using 3-butyn-2-one instead (8 μL, 0.110 mmol). Elution with dichloromethane gave a gray-brown band yielding compound **9d** as a greenish-brown microcrystalline solid (0.037 g, 94%). This compound was shown (by NMR) to exist in solution as an equilibrium mixture of *syn* and *anti* isomers, with the *syn*/*anti* ratio being 9:4 in C_6D_6 or CD_2Cl_2. Anal. Calcd for $C_{43}H_{52}O_3Mo_2NP$: C, 60.49; H, 6.14; N, 1.64. Found: C, 60.37; H, 6.01; N, 1.49. *Spectroscopic data for* ***syn*-9d**: ^{1}H NMR (400.13 MHz): δ 6.95, 6.88 [2d, J_{HH} = 7, 2H, *m*-H(Xyl)], 6.79 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 6.50 (d, J_{HP} = 8, 1H, PCH), 5.09 (s, 5H, Cp), 5.22, 5.15, 4.93, 4.45, (4 m, 4 × 1H, C_5H_4), 4.88 (d, J_{HP} = 3, 3H, C_6H_3), 2.09, 2.00 (2s, 2 × 3H, Me), 2.06 [s, br, 3H, C(O)Me], 1.16 (s, 27H, ^{t}Bu). ^{1}H NMR (300.13 MHz, C_6D_6): δ 7.18, 7.11 [2d, J_{HH} = 7, 2H, *m*-H(Xyl)], 7.02 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 6.59 (d, J_{HP} = 8, 1H, PCH), 4.86 (s, 5H, Cp), 4.77 (d, J_{HP} = 4, 3H, C_6H_3), 4.75−4.66 (m, 3 × 1H, C_5H_4), 4.37 (m, 1H, C_5H_4), 2.41, 2.21 (2s, 2 × 3H, Me), 2.25 [s, 3H, C(O)Me], 1.06 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 252.7 (d, J_{CP} = 30, MoCO), 241.2 (s, MoCO), 214.4 [s, C(O)Me], 203.4 [s, br, MoC(NXyl)], 170.9 (d, J_{CP} = 20, PC═*C*), 152.5 [s, C^1(Xyl)], 144.5 (s, br, PCH), 127.9, 127.5 [2s, $C^{3,5}$(Xyl)], 126.0, 124.6 [2s, $C^{2,6}$(Xyl)], 122.1 [s, C^4(Xyl)], 111.8 [s, C(C_6H_3)], 91.9 (s, Cp), 92.6 [d, J_{CP} = 18, C(C_5H_4)], 89.0 [d, J_{CP} = 8, CH(C_5H_4)], 88.3 [d, J_{CP} = 4, CH(C_5H_4)], 83.6 [s, CH(C_5H_4)], 82.6 [d, J_{CP} = 15, CH(C_5H_4)], 71.6 [s, CH(C_6H_3)], 35.3 [s, C(^{t}Bu)], 31.3 [s, CH_3(^{t}Bu)], 29.8 [s, br, C(O)*Me*], 20.1, 18.8 [2s, Me(Xyl)]. *Spectroscopic data for* ***anti*-9d**: ^{1}H NMR (400.13 MHz): δ 6.95, 6.88 [2d, J_{HH} = 7, 2H, *m*-H(Xyl)], 6.81 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 6.59 (d, J_{HP} = 8, 1H, PCH), 5.10 (s, 5H, Cp), 5.07, 5.02, 4.99, 4.70, (4 m, 4 × 1H, C_5H_4), 4.86 (d, J_{HP} = 4, 3H, C_6H_3), 2.25, 1.96 (2s, 2 × 3H, Me), 2.02 [s, br, 3H, C(O)Me], 1.20 (s, 27H, ^{t}Bu). ^{1}H NMR (400.13 MHz, C_6D_6): δ 7.18, 7.11 [2d, J_{HH} = 7, 2H, *m*-H(Xyl)], 7.00 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 6.68 (d, J_{HP} = 8, 1H, PCH), 5.03 (s, 5H, Cp), 4.75−4.66 (m, 3 × 1H, C_5H_4), 4.56 (d, J_{HP} = 4, 3H, C_6H_3), 4.45 (m, 1H, C_5H_4), 2.67, 2.14 (2s, 2 × 3H, Me), 2.25 [s, 3H, C(O)Me], 0.97 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 253.8 (d, J_{CP} = 21, MoCO), 241.6 (s, MoCO), 212.9 [s, *C*(O)Me], 207.1 [s, br, MoC(NXyl)], 171.3 (d, J_{CP} = 20, PC═*C*), 152.9 [s, C^1(Xyl)], 148.3 (s, br, PCH), 128.1, 127.7 [2s, $C^{3,5}$(Xyl)], 125.8, 125.2 [2s, $C^{2,6}$(Xyl)], 122.3 [s, C^4(Xyl)], 110.0 [s, C(C_6H_3)], 92.6 (s, Cp), 90.0 [d, J_{CP} = 4, CH(C_5H_4)], 85.7 [d, J_{CP} = 8, CH(C_5H_4)], 84.3 [s, CH(C_5H_4)], 80.7 [d, J_{CP} = 15, CH(C_5H_4)], 72.7 [s, CH(C_6H_3)], 34.7 [s, C(^{t}Bu)], 31.5 [s, CH_3(^{t}Bu)], 30.3 [s, br, C(O)*Me*], 20.5, 19.2 [2s, Me(Xyl)]. The resonance for the C(C_5H_4) atom could not be identified in the spectrum of the mixture of isomers.

Preparation of [$Mo_2Cp\{\mu$-κ^1,η^5:κ^1,η^3-(C_5H_4)PC(CO_2Me)=C-(CO_2Me)C(O)}(η^6-HMes*)(CO)] (10). *Method A.* A solution of compound **3a** (0.032 g, 0.040 mmol) in toluene (5 mL) was irradiated with visible−UV light at 288 K for 1 h to give a green solution. The solvent was then removed under vacuum, and the residue was chromatographed at 253 K. Elution with dichloromethane gave a green

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fraction yielding, after removal of the solvent, compound **10** as a green powder (0.024 g, 75%). This complex progressively transforms back into **3a** at room temperature. Elution with dichloromethane–tetrahydrofuran (9:1) gave a second green fraction, yielding analogously small and variable amounts (<0.005 g) of the chloro complex $[Mo_2CpCl\{\mu\text{-}\kappa^1,\eta^5\text{:}\kappa^1,\eta^2\text{-}(C_5H_4)PC(CO_2Me)=CH\text{-}(CO_2Me)\}(\eta^6\text{-HMes*})(CO)]$ (**11**) as a green solid. The crystals used in the X-ray study of this complex were grown by slow diffusion at 273 K of a layer of petroleum ether into a concentrated solution of the complex in dichloromethane–tetrahydrofuran (5:1).

Method B. The procedure is analogous to that described in Method A, but using compound **6a** as starting material (0.033 g, 0.040 mmol) and a reaction time of 1.5 h. After similar workup of the resulting mixture, compounds **10** (0.022 g, 70%) and **11** (<0.005 g) were isolated analogously. *Spectroscopic data for* **10**: ^{1}H NMR (400.54 MHz, 233 K): δ 5.52, 5.32, 5.15, 4.26 (4 m, 4 × 1H, C_5H_4), 5.12 (s, 5H, Cp), 5.06, (s, br, 3H, C_6H_3), 3.56, 3.47 (2s, 2 × 3H, OMe), 1.21 (s, 27H, ^{t}Bu). ^{13}C{^{1}H} NMR (100.61 MHz, 233 K): δ 254.0 [s, MoC(O)], 237.0 (d, J_{CP} = 6, MoCO), 176.3, 175.7 (2s, CO_2Me), 107.9 [s, $C(C_6H_3)$], 93.6 (s, Cp), 88.3 [s, $CH(C_5H_4)$], 87.9 [d, J_{CP} = 8, $CH(C_5H_4)$], 86.3 [s, $CH(C_5H_4)$], 82.7 [d, J_{CP} = 23, $C(C_5H_4)$], 79.9 [d, J_{CP} = 18, $CH(C_5H_4)$], 78.0 [br, $CH(C_6H_3)$], 51.9, 51.6 (2s, OMe), 34.7 [s, $C(^tBu)$], 31.8 [s, $CH_3(^tBu)$]; the resonances of the other C atoms of the $MoPC_3$ ring could not be identified in the spectrum. *Spectroscopic data for* **11**: ^{1}H NMR (C_6D_6): δ 5.75, 4.77, 4.73, 4.14 (4 m, 4 × 1H, C_5H_4), 4.99 (d, J_{HP} = 3, 5H, Cp), 4.91 (d, J_{HP} = 5, 3H, C_6H_3), 4.84 (d, J_{HP} = 31, 1H, CH), 3.63, 3.30 (2s, 2 × 3H, OMe), 1.06 (s, 27H, ^{t}Bu).

Photolysis of Compound 9a. A solution of compound **9a** (0.037 g, 0.040 mmol) in toluene (5 mL) was irradiated with visible–UV light at 288 K for 1.5 h. Tetrahydrofuran (1 mL) was then added to the resulting solution, and the mixture was further stirred at room temperature for 1 h to give a brown solution. The solvent was then removed under vacuum, and the residue was chromatographed at 253 K. Elution with dichloromethane–petroleum ether (9:1) gave a brown fraction, yielding, after removal of the solvents, compound $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5\text{:}\kappa^1,\eta^1\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)\}(\eta^6\text{-HMes*})(CNXyl)\text{-}(CO)]$ (**13**) as a brown microcrystalline powder (0.026 g, 72%). This compound was shown (by NMR) to exist in solution as an equilibrium mixture of *syn* and *anti* isomers, with the *syn*/*anti* ratio being 5:1 in C_6D_6. If the addition of tetrahydrofuran and room temperature stirring steps are suppressed, then a mixture of compound **13** and its precursor $[Mo_2Cp\{\mu\text{-}\kappa^1,\eta^5\text{:}\kappa^1,\eta^3\text{-}(C_5H_4)PC(CO_2Me)=C(CO_2Me)C(NXyl)\}\text{-}(\eta^6\text{-HMes*})(CO)]$ (**12**) is obtained, the latter being isolated after chromatographic separation (elution with dichloromethane–tetrahydrofuran (4:1) at 253 K) as a greenish-brown powder (ca. 0.015 g, 40%). *Spectroscopic data for* **12**: ^{1}H NMR (400.13 MHz, CD_2Cl_2, 233 K): δ 7.07 [d, J_{HH} = 7, 1H, *m*-H(Xyl)], 6.97 [d, J_{HH} = 7, 1H, *m*-H(Xyl)], 6.91 [t, J_{HH} = 7, 1H, *p*-H(Xyl)], 5.46 (m, 1H, C_5H_4), 5.18–5.07 (m, 5H, C_6H_3 + C_5H_4), 4.85 (s, 5H, Cp), 4.25 (m, 1H, C_5H_4), 3.61, 3.51 (2s, 2 × 3H, OMe), 2.37, 2.01 (2s, 2 × 3H, Me), 1.23 (s, 27H, ^{t}Bu). *Spectroscopic data for* ***syn*-13**: ^{1}H NMR (C_6D_6): δ 6.90–6.70 (m, 3H, Xyl), 5.94, 4.63, 4.12 (3 m, 3 × 1H, C_5H_4), 5.33 (s, 5H, Cp), 5.02 (d, J_{HP} = 4, 4H, C_6H_3 + C_5H_4), 3.49, 3.34 (2s, 2 × 3H, OMe), 2.46 (s, 6H, Me), 1.20 (s, 27H, ^{t}Bu). *Spectroscopic data for* ***anti*-13**: ^{1}H NMR (C_6D_6): δ 6.89–6.78 (m, 3H, Xyl), 6.56, 4.79, 4.49, 4.13 (4 m, 4 × 1H, C_5H_4), 5.43 (s, 5H, Cp), 4.58 (d, J_{HP} = 5, 3H, C_6H_3), 3.74, 3.32 (2s, 2 × 3H, OMe), 2.36 (s, 6H, Me), 1.05 (s, 27H, ^{t}Bu).

X-ray Structure Determination of Compound 11. The X-ray intensity data were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated Mo Kα radiation at 100 K. The software APEX[31] was used for collecting frames with the ω/ϕ scan measurement method. The Bruker SAINT software was used for the data reduction,[32] and a multiscan absorption correction was applied with SADABS.[33] Using the program suite WinGX,[34] the structure was solved by Patterson interpretation and phase expansion using SHELXL97[35] and refined with full-matrix least-squares on F^2 using SHELXL97. All the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically, and all hydrogen atoms were geometrically placed and refined using a riding model. A molecule of tetrahydrofuran was present in the unit cell. Crystallographic data and structure refinement details are collected in Table 6.

Computational Details. Computations were carried out using the GAUSSIAN03 package,[36] in which the hybrid method B3LYP was applied with the Becke three-parameter exchange functional[37] and the Lee–Yang–Parr correlation functional.[38] Effective core potentials and their associated double-ζ LANL2DZ basis set were used for the metal atoms.[39] The light elements (P, O, C, and H) were described with the 6-31G* basis.[40] Geometry optimization was performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of compound **1**, and frequency analyses were performed to ensure that a minimum structure with no imaginary frequencies was achieved. For interpretation purposes, Mulliken charges were computed as usual,[41] and natural population analysis charges were derived from the natural bond order analysis of the data.[42] Molecular orbitals and vibrational modes were visualized using the Molekel program.[43] The topological analysis of ρ was carried out with the Xaim routine.[44]

■ ASSOCIATED CONTENT

Supporting Information

A pdf file containing tables of data from the DFT calculations of intermediate **A**, and a CIF file giving the crystallographic data for the structural analysis of compound **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

This work is dedicated to Prof. F. G. A. Stone in recognition of his outstanding contributions to modern inorganic chemistry, for his personal kindness, and for the good time we all had at Bristol in the eighties.

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