Reactivity of the 30-electron dimolybdenum anion [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-PCy$_2$)(μ-CO)$_2$]$^-$ towards β,γ-unsaturated organic halides: Alkenyl, allenyl and alkoxycarbyne derivatives

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ARTICLE INFO

ABSTRACT

The 30-electron dimolybdenum anion [Mo$_2$Cp$_2$(μ-PCy$_2$)(μ-CO)$_2$]$^-$ reacts at room temperature with allyl chloride to give the unsaturated σ:π-bonded alkenyl derivative *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCH$_2$)-(μ-PCy$_2$)(CO)$_2$], this requiring a 2,1-hydrogen shift in the allyl moiety probably induced by the unsaturated nature of the dimetal center. In a similar way, the dimolybdenum anion reacts with *trans*-1-chloro-2-butene (crotyl chloride) to give a mixture of the alkenyl complexes *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CEtCH$_2$)(μ-PCy$_2$)(CO)$_2$] and *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCHMe)(μ-PCy$_2$)(CO)$_2$] in a 3:2 ratio, which could not be separated by column chromatography. All these alkenyl species exhibit a dynamic behavior in solution (fast on the NMR timescale even at low temperatures) involving alternative π-bonding of the alkenyl ligand to each metal center. In contrast, the title anion reacts with propargyl chloride (ClCH$_2$–C≡CH) without further rearrangement of the propargyl moiety, to afford the allenyl derivative *trans*-[Mo$_2$Cp$_2${μ-η^2:η^3-CH$_2$CCH}(μ-PCy$_2$)(CO)$_2$] as the major species. Acryloyl chloride (ClC(O)–CH=CH$_2$) also reacts with the title anion to give a mixture of two products, the carbyne complex [Mo$_2$Cp$_2${μ-COC(O)CHCH$_2$}(μ-PCy$_2$)(μ-CO)] and the vinyl *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CHCH$_2$)(μ-PCy$_2$)(CO)$_2$], in a 1:1 ratio. This reaction is a unique case in which a single electrophile can attack both nucleophilic positions in the dimolybdenum anion, these being located at the O(carbonyl) and metal sites, respectively. The formation of the vinyl derivative requires the decarbonylation of a metal-bound acryloyl group, which proved to be an irreversible reaction, since the addition of CO to the above alkenyl complex gave instead the tricarbonyl vinyl derivative *cis*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CHCH$_2$)(μ-PCy$_2$)(CO)$_3$]. The structure of this electron-precise complex was confirmed through a single-crystal X-ray diffraction analysis (Mo−Mo = 3.0858(7) Å).

1. Introduction

The chemistry of metal carbonyl anions is of paramount importance in organometallic synthesis mainly due to their high nucleophilicity, which allows these molecules to react with a great variety of electrophiles to form new M−E bonds (E = H, C, *p*- or *d*-block elements) [1]. Although the number of mono- and polynuclear metal carbonyl anions reported in the literature is considerable, dinuclear anions bearing a metal–metal bond are comparatively scarce. Among these ones, there are only a few compounds bearing a multiple metal–metal bond according to the Effective Atomic Number (EAN) formalism, and in most of these cases no reactivity studies have been carried out, due to their instability or synthetic difficulties [2]. A few years ago, we discovered an efficient synthetic route leading to the triply bonded dimolybde-

num anions [Mo$_2$Cp$_2$(μ-PA$_2$)(μ-CO)$_2$]$^-$ (A = Cy, Ph, Et) via the corresponding chloro complexes [Mo$_2$Cp$_2$(μ-Cl)(μ-PA$_2$)(CO)$_2$] [3]. In that preliminary report, the synthetic potential of these unsaturated species was already evident for the most stable member of that group, the dicyclohexylphosphide-bridged anion [Mo$_2$Cp$_2$-(μ-PA$_2$)(μ-CO)$_2$]$^-$ (**1**), which showed two different nucleophilic sites located at the metal atoms and the O atoms of the CO ligands, respectively. It was also noticed then that, due to the unsaturated nature of the anion, some rearrangements in the incoming electrophile could be induced, as shown by the reaction with allyl chloride to give the alkenyl derivative *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCH$_2$)(μ-PCy$_2$)(CO)$_2$], this requiring an unprecedented 2,1-hydrogen shift in the hydrocarbon fragment [3].

We have reported recently a detailed study on the reactivity of the anion **1** towards simple hydrocarbon halides RX revealing that, depending on the electrophile being used, three main type of products might be formed: (a) agostic alkyl complexes [Mo$_2$Cp$_2$(μ-R)(μ-PCy$_2$)(CO)$_2$], (b) alkoxycarbyne complexes

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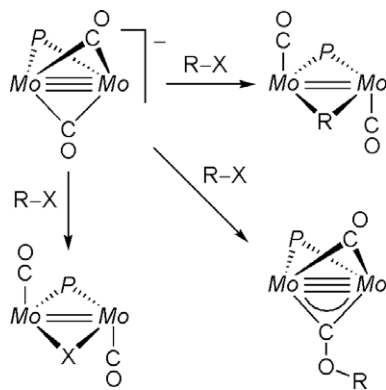
Scheme 1. Pathways in the reactions of the anion **1** with simple hydrocarbon halides. (*Mo* = MoCp; *P* = PCy$_2$).

$[Mo_2Cp_2(\mu\text{-COR})(\mu\text{-PCy}_2)(\mu\text{-CO})]$ and (c) the halide derivatives $[Mo_2Cp_2(\mu\text{-PCy}_2)(\mu\text{-X})(CO)_2]$ (Scheme 1). The formation of these products can be rationalized by assuming that three different elemental processes might be involved in these reactions: (1) nucleophilic attack of the anion through the metal center to give the alkyl-bridged derivatives, (2) nucleophilic attack of the anion through the oxygen atom of the carbonyl ligand to give the carbyne-bridged derivatives, and (3) electron transfer, mainly to give the halide-bridged derivatives [2].

In this paper we report our results on the reactions of the unsaturated anion **1** with several β,γ-unsaturated organic halides, including allyl chloride. These substrates were of special interest as potential candidates to observe unusual rearrangements after coordination to the metal centers, as found in our preliminary study of the reaction with allyl chloride mentioned above [3]. At the same time, the unsaturated nature of the dimetal center might also induce the coordination of the multiple C–C bonds present in the added electrophile. As it will be discussed below, unusual 2,1-H shift processes indeed prevail in the reactions with allyl chlorides of the formula ClCH$_2$–CR=CR'H (R = H; R' = H, Me) to afford unsaturated σ:π-bound alkenyl derivatives, but no rearrangement occurs in the reaction with propargyl chloride (ClCH$_2$–C≡CH), this giving an electron-precise allenyl compound. Finally, the reaction with acryloyl chloride (ClC(O)–CH=CH$_2$) provides a unique case in which a single electrophile can attack to both nucleophilic positions in the dimolybdenum anion. When compared to the results obtained in the reactions of **1** with simple hydrocarbon halides, the results here reported reveal at least two substantial differences in the behavior of the β,γ-unsaturated organic halides: (a) the electron-transfer processes essentially are no longer under operation and (b) agostic interactions (C–H···Mo) are not observed. The latter was to be expected due to the presence of multiple C–C bonds in the incoming electrophile, which are electron-donors more efficient than single C–H bonds.

2. Results and discussion

2.1. Reactions of the anion **1** with allyl, propargyl and acryloyl chlorides

The reaction of the lithium salt of **1** with allyl chloride (ClCH$_2$–CH=CH$_2$) takes place readily at room temperature to give the 32-electron alkenyl complex *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCH$_2$)-(μ-PCy$_2$)(CO)$_2$] (**2a**), this requiring a rare 2,1-H shift in the allyl ligand, as discussed below. In a similar way, the room temperature reaction of **1** with the *trans* isomer of crotyl chloride [ClCH$_2$–CH=CHMe] gives a mixture of two alkenyl compounds derived

from comparable H-shifts, these being identified as *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CEtCH$_2$)(μ-PCy$_2$)(CO)$_2$] (**2b**) and *trans*-[Mo$_2$Cp$_2$-(μ-η^1:η^2-CMeCHMe)(μ-PCy$_2$)(CO)$_2$] (**2c**), which are obtained in a 3:2 ratio (Chart 1). Unfortunately, this mixture could not be separated using chromatographic techniques. To check the relevance of the observed H-shifts in the above reactions the anion **1** was treated with ClCH$_2$–CMe=CH$_2$, a molecule in which an H-shift from the C^2 atom was not possible, but this gave only a complex reaction mixture under similar conditions. Although we could not isolate nor characterize the corresponding products being formed, the spectroscopic data of the crude reaction mixture clearly denote that no alkenyl derivatives are there present in significant amounts.

In contrast to the above reactions, no H-shifts were observed in the reactions of the lithium salt of **1** with the propargyl halides XCH$_2$–C≡CH (X = Br, Cl), which instead lead to the formation of the corresponding allenyl derivative *trans*-[Mo$_2$Cp$_2${μ-η^2:η^3-CH$_2$CCH}](μ-PCy$_2$)(CO)$_2$] (**4**) as the major product in both cases, the reaction being completed after 5 min (X = Br) or 2 h (X = Cl) at room temperature. Some *trans*-[Mo$_2$Cp$_2$(μ-Br)(μ-PCy$_2$)(CO)$_2$] [2] and another uncharacterized product were respectively formed as minor products in these reactions, depending on the halide used. Although the reaction was much faster when using allyl bromide, it turned out to be less reproducible, and quite variable amounts of the bromoderivative were actually obtained. Therefore, propargyl chloride was preferred as a precursor in the formation of the allenyl complex **4**.

The result of the reaction of **1** with acryloyl chloride was hardly predictable. Previously, we had found that the reaction of **1** with a related electrophile as benzoyl chloride led to the quantitative formation of the corresponding carbyne complex [Mo$_2$Cp$_2$(μ-PCy$_2$){μ-COC(O)Ph}(μ-CO)] [2]. In contrast, acryloyl chloride reacts with **1** to give a 1:1 mixture of the corresponding alkoxycarbyne derivative [Mo$_2$Cp$_2$(μ-PCy$_2$){μ-COC(O)CH=CH$_2$}(μ-CO)] (**5**) and the vinyl complex *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CHCH$_2$)(μ-PCy$_2$)(CO)$_2$] (**2d**) (Chart 1). To account for this difference in reactivity, we propose that the higher steric demand of the phenyl *vs.* the vinyl group prevents the
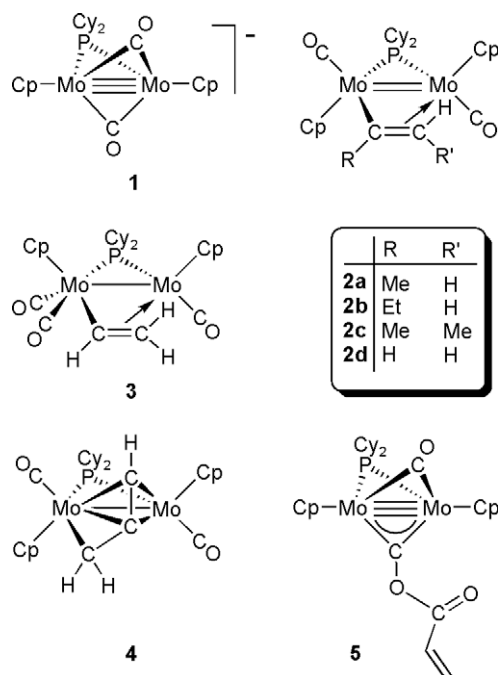

Chart 1.

benzoyl fragment from accessing to the intermetallic region, thus suppressing the formation of any acyl or related metal derivative.

The formation of the vinyl complex **2d** requires the spontaneous liberation of a CO at some intermediate stage of the reaction, a matter to be discussed below. In any case, such a decarbonylation process is irreversible, since the reaction of **2a** with CO (1 atm) takes place readily to yield the corresponding electron-precise tri-carbonyl derivative cis-$[Mo_2Cp_2(\mu$-η^1:η^2-$CHCH_2)(\mu$-$PCy_2)(CO)_3]$ (**3**), the reaction being completed in $ca.$ 1 h at room temperature. We note that the carbonylation reaction of the related complex $trans$-$[Mo_2Cp_2\{\mu$-η^1:η^2-$CHCH(ptol)\}(\mu$-$PCy_2)(CO)_2]$ to give an analogous tricarbonyl derivative requires 24 h for completion [4], a difference possibly reflecting the higher protection of the unsaturated center provided by the ptol substituent.

2.2. Solution structure of the dicarbonyl alkenyl complexes 2a–d

The spectroscopic data for compounds **2a–d** are comparable to those of the alkenyl complexes $trans$-$[Mo_2Cp_2(\mu$-η^1:η^2-$CRCHR')(\mu$-$PCy_2)(CO)_2]$ (R, R' = H, ptol, CO_2Me), recently prepared by us through the reaction of the unsaturated hydride $[Mo_2Cp_2(\mu$-H)$(\mu$-$PCy_2)(CO)_2]$ with the pertinent 1-alkynes [4]. The solution structure of the latter compounds has been discussed at length already, and therefore only the relevant details for compounds **2a–d** will be discussed here. First, we note that compounds **2a–d** also exhibit three or even four C–O stretching bands in the IR spectra, when recorded in petroleum ether (Table 1). This can be explained analogously by assuming the presence in solution of two different and interconverting $trans$-dicarbonyl isomers (**A** and **B** in Scheme 2). Isomer **A** would exhibit an almost antiparallel arrangement of the CO ligands, with a relative angle close to 180°, whereas in the isomer **B** this angle would be close to 90°. Note that in both isomers the R' group is proposed to point away from the dimetal center, which should be sterically favoured over the alternative possibility (R' pointing towards the dimetal center) when R' = Me. In any case, the different arrangement of the carbonyl ligands in both isomers would then account for the pattern observed in the IR spectra of **2a–d**, so that we can assign the strong band at
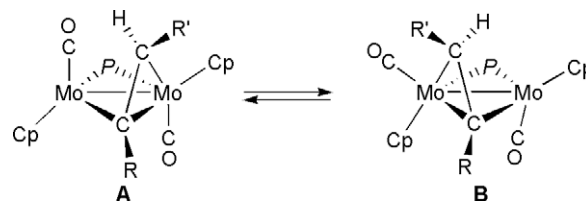
Scheme 2. Isomerization process proposed for compounds **2** in solution (P = PCy_2).

$ca.$ 1840 cm^{-1}, and the shoulder (not detected for **2a**) at $ca.$ 1870 cm^{-1} to the C–O stretching bands of the isomers of type **A**, whereas the more separated bands and having similar relative intensities, at $ca.$ 1890 (vs) and 1810 (vs) cm^{-1} can be safely assigned to the isomers of type **B**. Both isomers would be interconverting through a dynamic process well established for bridging alkenyl compounds, known as the windshield wiper movement [5]. In our case, this dynamic process is an isomerization process, since as a result of it the CHR group gets close to either a CO ligand (isomer **A**) or to a Cp ring (isomer **B**). This process is fast on the NMR timescale for compounds **2**, since the corresponding NMR spectra suggest the presence of a single species in each case and are not significantly modified even when recorded at $ca.$ 213 K.

The ^{31}P NMR spectra of compounds **2a–d** exhibit a single and relatively shielded resonance in the range 128–135 ppm. These values are analogous to those found for the related alkenyl compounds mentioned above [4] and are also consistent with the formulation of a metal–metal double bond for these compounds. The ^1H and ^{13}C NMR spectra are also in good agreement with the presence in each case of a single species in solution having no symmetry elements. Thus, compounds **2a–d** all exhibit separate resonances for the inequivalent Cp (^1H, ^{13}C), CO (^{13}C) and Cy groups (twelve different signals in the ^{13}C NMR spectra). The chemical shifts and coupling constants of these resonances (Table 1 and experimental section) are comparable to those measured for the above mentioned alkenyl complexes $trans$-$[Mo_2Cp_2(\mu$-η^1:η^2-$CRCHR')(\mu$-$PCy_2)(CO)_2]$ (R, R' = H, ptol, CO_2Me) [4], and therefore deserve no further comments.

Table 1
Selected IR[a] and NMR[b] spectroscopic data for new compounds.

Compound	ν_{CO} (cm^{-1})	δ_P	δ_H/H_α [J_{HH}] $H_{\beta,\gamma}$ [J_{HH}]	δ_C/C_α $C_{\beta,\gamma}$
$[Mo_2Cp_2(\mu$-η^1:η^2-$CMeCH_2)(\mu$-$PCy_2)(CO)_2]$ (**2a**)	1888 (vs), 1838 (s) 1808 (vs)[c]	131.2	5.07 [2.6], 4.68 [2.6]	174.6 79.6[d]
$[Mo_2Cp_2(\mu$-η^1:η^2-$CEtCH_2)(\mu$-$PCy_2)(CO)_2]$ (**2b**)	1883 (vs), 1873 (m, sh) 1841 (s), 1806 (vs)[c]	128.4	5.03 [2], 4.76 [2]	
$[Mo_2Cp_2(\mu$-η^1:η^2-$CMeCHMe)(\mu$-$PCy_2)(CO)_2]$ (**2c**)	1883 (vs), 1873 (m, sh) 1841 (s), 1806 (vs)[c]	130.5	6.17	–
$[Mo_2Cp_2(\mu$-η^1:η^2-$CHCH_2)(\mu$-$PCy_2)(CO)_2]$ (**2d**)	1886 (m), 1871 (m, sh) 1843 (vs), 1821 (m, sh)[c]	135.0	8.56 [12,9] 5.28 [12,3], 4.91 [9,3]	153.2 84.2[e]
$[Mo_2Cp_2(\mu$-η^1:η^2-$CHCH_2)(\mu$-$PCy_2)(CO)_3]$ (**3**)	1937 (vs), 1864 (m) 1834 (m)	250.5[e]	8.93 [9,9] 3.34 [9], 1.07 [9][f]	148.2 32.7[f]
$[Mo_2Cp_2\{\mu$-η^2:η^3-$CH_2CCH\}(\mu$-$PCy_2)(CO)_2]$ (**4**)	1867 (m, sh), 1844 (vs)	163.3	4.17 [1.5], 4.00 [1.1] 4.72 [1.5, 1.1]	68.9, 112.5 61.0
$[Mo_2Cp_2\{\mu$-$COC(O)CHCH_2\}(\mu$-$PCy_2)(\mu$-$CO)]$ (**5**)	1743 (w, C=O) 1684 (vs, μ-CO)	229.6	6.12 [17, 10][g] 6.44 [17, 1.5][h], 5.93 [10, 1.5][h]	159.7[i] 128.5[j] 132.4[k]

[a] Recorded in dichloromethane solution, unless otherwise stated.
[b] Recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$) or 75.47 MHz ($^{13}C\{^1H\}$) at 290 K in CD_2Cl_2 solutions unless otherwise stated, δ in ppm relative to TMS (^1H, $^{13}C\{^1H\}$) or external 85% aqueous H_3PO_4 ($^{31}P\{^1H\}$), J in Hz; the bridgehead carbon atoms of the alkenyl or allenyl ligands are referred to as C_α.
[c] In petroleum ether.
[d] At 100.63 MHz and 213 K.
[e] In C_6D_6.
[f] In $CDCl_3$.
[g] –C(O)–CH=CH_2.
[h] –C(O)–CH=CH_2.
[i] –C(O)–CH=CH_2.
[j] –C(O)–CH=CH_2.
[k] –C(O)–CH=CH_2.

2.3. Structure of the tricarbonyl complex 3

An X-ray diffraction analysis was performed on compound 3 (Fig. 1 and Table 2). The molecule of 3 is built from MoCp(CO) and MoCp(CO)$_2$ moieties arranged in a cisoid conformation and bridged by PCy$_2$ and vinyl ligands. The latter one is σ-bound to the dicarbonyl fragment and π-bound to the monocarbonyl fragment. The intermetallic separation, 3.0858(7) Å, is very similar to the corresponding distance measured for the isostructural and isoelectronic compound [Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCHMe)(μ-PMe$_2$)-(CO)$_3$] (3.056(1) Å) [6], and consistent with the presence of a single Mo–Mo bond, as it should be proposed for this 34-electron molecule under the EAN formalism. As expected, this intermetallic separation is much longer (by *ca.* 0.4 Å) than that measured for the 32-electron dicarbonyl compound *trans*-[Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCHMe)(μ-SPh)(CO)$_2$] [7], the latter being isoelectronic with compounds 2a–d and bearing a double Mo=Mo bond according to the same formalism. The σ-bond of the vinyl group in 3 [Mo(1)–C(5), 2.240(2) Å] is more than 0.1 Å longer than the corresponding values in the mentioned alkenyl compounds [6,7]. In contrast, the Mo(2)–C(5) and Mo(2)–C(4) distances of 2.107(2) and 2.298(2) Å, respectively, are in all cases shorter than the corresponding values in the mentioned compounds. This is suggestive of a particularly strong η^2-bonding interaction of the vinyl ligand with the Mo(2) atom. As for the C–C distance within the vinyl ligand, 1.413(3) Å, it is similar to those measured in other alkenyl compounds and is *ca.* 0.07 Å longer than that found for ethylene, as expected. The coordination of the dicyclohexylphosphide ligand is very asymmetric, it being placed much closer to the monocarbonyl center (P–Mo(1) = 2.3292(6) Å) than to the dicarbonyl center (P–Mo(1) = 2.5702(6) Å), thus counterbalancing the difference in the coordination numbers of both metal centers. Thus we could formally consider the phosphide ligand to act as a two-electron donor to the Mo(1), and as a one-electron donor to the dicarbonyl center Mo(2). Under this view, the formal oxidation states of the metal centers would be III and I, respectively. The same effect has been observed for other dinuclear alkenyl complexes having different coordination numbers at each metal center, such as [Mn$_2$(μ-η^1:η^2-CHCH$_2$)(μ-PPh$_2$)(CO)$_7$] [8], (Mn–P: 2.255(2) and 2.367(1) Å) and the mentioned [Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCHMe)(μ-PMe$_2$)(CO)$_3$] [6], (Mo–P: 2.300(3) and 2.515(3) Å).

The spectroscopic data for compound 3 (Table 1) are in good agreement with the solid-state structure discussed above and are comparable to those of the related tricarbonyl [Mo$_2$Cp$_2${μ-η^1:η^2-CHCH(*p*tol)}(μ-PCy$_2$)(CO)$_3$] previously reported by us [4]. Compound 3 exhibits three bands in the IR spectrum with the expected pattern for tricarbonyl derivatives of type [M$_2$Cp$_2$(μ-X)(μ-Y)(CO)$_3$] (X, Y = 3-electron donor group) having a cisoid arrangement of the CpM(CO)$_2$ and CpM(CO) fragments [9], thus indicating the reten-

tion in solution of the solid-state conformation. Compound 3 exhibits a characteristically deshielded resonance in the ^{31}P NMR spectrum at 250.5 ppm, some 115 ppm downfield from that of its precursor 2d and consistent with the presence of a single metal–metal bond in this 34-electron molecule. Its ^{1}H NMR exhibits strongly shielded H$_β$ vinyl resonances at 3.34 and 1.07 ppm, several ppm below those of the dicarbonyl precursor 2d. This can be explained by recalling the high strength of the vinyl-Mo(2) π-interaction apparent in the crystal structure, perhaps approaching the description of the Mo(2)–C$_α$–C$_β$ triangle as a metallacyclopropane ring. A similar shielding effect is observed in the ^{13}C NMR resonances, with the one corresponding to C$_β$ appearing at 32.7 ppm, some 50 ppm upfield of the corresponding resonance in the dicarbonyl 2d.

2.4. Solution structure of the allenyl complex 4

Crystals suitable for an X-ray diffraction analysis could not be obtained for this compound. Regardless of this fact, the spectroscopic data collected in solution for 4, when combined with the data available for a significant number of allenyl-bridged complexes described in the literature, are enough to support the proposed structure (Chart 1). Its IR spectrum exhibits two bands with the typical pattern of a *trans*-dicarbonyl complex, at 1867 (m, sh) and 1844 (vs) cm^{-1}. The NMR spectra are in good agreement with the asymmetric structure of 4, this implying the appearance of separate resonances for the pairs of CO and Cp ligands, and also for all C atoms in the Cy rings (see experimental section). The allenyl ligand gives rise to three distinct ^{1}H NMR resonances in the range 4.72–4.00 ppm, all of them exhibiting very small H–H couplings. These chemical shifts are somewhat lower than those measured previously for the related cations of formula [Mo$_2$L$_2$(μ-η^2:η^3-RC≡C–CR′R″)(CO)$_4$]$^+$ (R, R′, R″=H, alkyl or aryl group; L = Cp or related ligand) [10], a fact that can be attributed to the differences in the overall charges in these complexes. The allenyl ligand also gives rise to three resonances in the ^{13}C spectrum, easily assigned through a standard DEPT experiment, at 61.0 (CH), 112.5 (C) and 68.9 (CH$_2$) ppm, close to those found for [Mo$_2$Cp′$_2$(μ-η^2:η^3-HC≡C–CH$_2$)(CO)$_4$][BF$_4$] (Cp′ = η^5-C$_5$H$_4$Me) [10f], a complex isoelectronic with 4 and characterized through an X-ray diffraction study. Finally, the ^{31}P NMR spectrum exhibits a resonance at 163.3 ppm, a chemical shift some 30–35 ppm higher than those measured for the 32-electron alkenyl compounds 2a–d (Table 1), but much lower than that found for the electron-precise 3 (see above). We note, however, that there are other examples of related electron-precise compounds displaying similar ^{31}P chemical shifts, such as the structurally characterized formimidoyl derivative [Mo$_2$Cp$_2$(μ-η, κ:η, κ-CHN^{t}Bu)(μ-PCy$_2$)(CO)$_2$] [11]. Unfortunately, in the absence of diffraction data for compound 4

Table 2
Selected bond lengths (Å) and angles (deg) for compound 3.

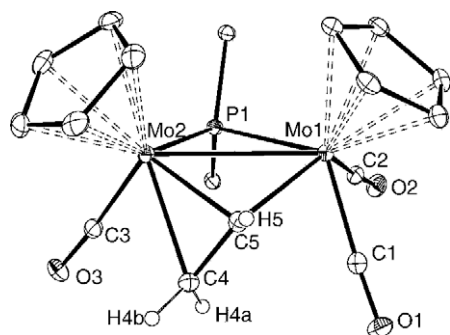|			
Mo(1)–Mo(2)	3.0858(7)	Mo(2)–P(1)–Mo(1)	77.90(2)
Mo(1)–C(5)	2.240(2)	C(2)–Mo(1)–C(1)	79.0 (1)
Mo(2)–C(5)	2.107(2)	C(2)–Mo(1)–Mo(2)	115.5(1)
Mo(2)–C(4)	2.298(2)	C(1)–Mo(1)–Mo(2)	104.5(1)
Mo(1)–P(1)	2.5702(6)	C(3)–Mo(2)–Mo(1)	117.2(1)
Mo(2)–P(1)	2.3292(6)	C(4)–C(5)–Mo(2)	78.8(1)
C(4)–C(5)	1.413(3)	C(4)–C(5)–Mo(1)	125.0(2)
Mo(1)–C(1)	1.956(2)	C(4)–Mo(2)–Mo(1)	72.9(1)
Mo(1)–C(2)	1.952(2)	C(5)–C(4)–Mo(2)	64.1(1)
Mo(2)–C(3)	1.927(2)	Mo(2)–C(5)–Mo(1)	90.4(1)
		C(1)–Mo(1)–P(1)	116.5(1)
		C(2)–Mo(1)–P(1)	72.8(1)
		C(3)–Mo(2)–P(1)	86.0(1)
		C(4)–Mo(2)–P(1)	100.8(1)
		C(5)–Mo(2)–P(1)	95.9(1)

Fig. 1. ORTEP diagram (30% probability) of compound 3, with H atoms (except those of the vinyl group) and Cy rings (except the C^1 atoms) omitted for clarity.

we cannot define with precision the exact coordination mode of its allenyl ligand since, due to the high unsaturation of the dimetal center, this ligand might be acting as a five- (I in Fig. 2) or three- (II in Fig. 2) electron-donor ligand or, most likely, somehow between these extreme coordination modes.

2.5. Solution structure of the alkoxycarbyne complex 5

The spectroscopic data for **5** are completely analogous to those of other 30-electron alkoxycarbyne compounds previously characterized by our group [2,3]. These unsaturated molecules can be properly described as having a triple intermetallic bond, according to the EAN formalism and to DFT calculations on the methoxycarbyne complex $[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\mu\text{-CO})]$ [12]. Therefore, a detailed structural discussion is not needed for compound **5**. We note, however, that its IR spectrum exhibits, in addition to the strong band characteristic of the C–O stretch of the bridging carbonyl ligand (1684 cm^{-1}), a weak band due to the C–O stretch of the acryloyl moiety (1743 cm^{-1}), these positions being comparable to those measured for the benzoyl derivative $[Mo_2Cp_2\{\mu\text{-COC(O)Ph}\}(\mu\text{-PCy}_2)(\mu\text{-CO})]$ [2]. We also note that compound **5** exhibits the same fluxional behavior observed for the alkoxycarbyne complexes mentioned above, this involving the rotation of the alkoxy group around the O–C(carbyne) bond, thus creating an apparent symmetry plane relating both metal centers. The most relevant NMR resonances are those arising from the bridging C atoms, which appear at 342.5 (carbyne) and 300.7 ppm (carbonyl), in positions comparable to those of the mentioned alkoxycarbyne dimolybdenum complexes, whereas the ^{1}H and ^{13}C NMR resonances arising from the acryloyl moiety fall in the regions expected for organic acryloyl derivatives.

2.6. Proposed mechanism for the reaction of complex 1 with allyl chloride

The mechanism we propose for the formation of the alkenyl derivatives **2a–c** involves the coordination of the allyl group at the dimetal center to form an intermediate allylic species **C** which could not be detected (Scheme 3). We note, however, that a related allyl-bridged product could be obtained and fully characterized from the reaction of allyl chloride with the electron-precise binuclear anion $[Fe_2(\mu\text{-SEt})(\mu\text{-CO})(CO)_6]^{-}$ [13]. Moreover, from our previous studies on the reactions of **1** with MeI and PhCH$_2$Cl to give the corresponding agostic alkyl-bridged derivatives [14], we can safely assume that such an intermediate is likely to have a transoid arrangement of its CpMo(CO) fragments. This intermediate then would undergo a 2,1-hydrogen shift giving rise to the alkenyl ligand present in the final products. Under this scheme, the reaction with crotyl chloride should yield exclusively the dimethyl-substituted vinyl derivative **2c**. As stated above, however, this reaction gives a mixture of complexes **2c** and **2b**. To account for the formation of the isomer having an ethyl-substituted vinyl ligand (**2b**) in this reaction we suggest that an isomerization in the allylic intermediate (**C** to **D**) is taking place at some extent prior to the 2,1-shift of the hydrogen atom.
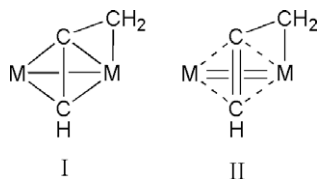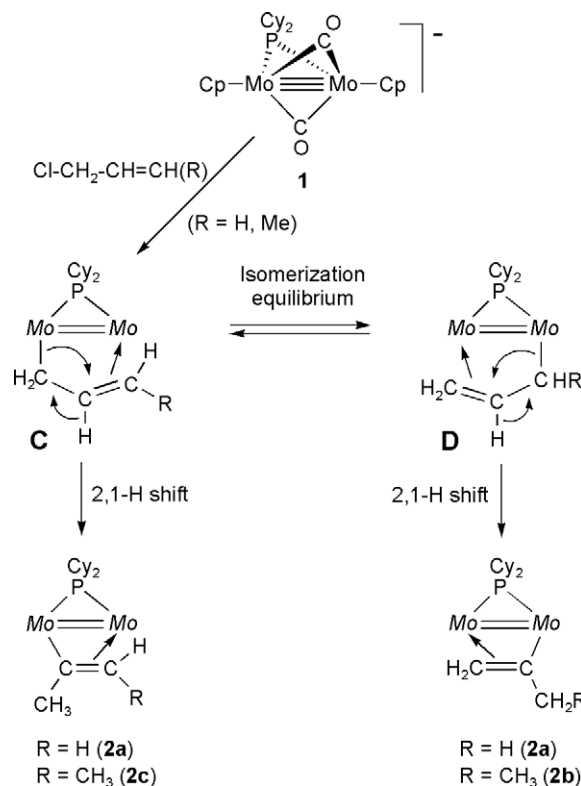

Fig. 2. Extreme views of the binding of a $\mu\text{-}\eta^{2}\text{:}\eta^{3}$-allenyl ligand to a dimetal center.


Scheme 3. Proposed pathways for the formation of the alkenyl complexes **2** (*Mo* = MoCp).

To our knowledge, the transformation of an allyl complex into its alkenyl isomer through a 2,1-H shift has no precedent in the literature. Instead, the reverse process, that is, the isomerization of an alkenyl complex to render the corresponding allyl isomer, is well documented for mononuclear species [15], and there are also a few examples involving dinuclear compounds. Thus, the photochemical reactions of the hydrides $[Mn_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_8]$ and $[MnMoCp(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_6]$ in the presence of 1-propyne have been shown to yield the allyl compounds $[Mn_2(\eta^3\text{-C}_3H_5)(\mu\text{-PPh}_2)(CO)_7]$ and $[MnMoCp(\eta^3\text{-C}_3H_5)(\mu\text{-PPh}_2)(CO)_5]$, respectively [16]. Although no vinyl precursor could be detected in the latter reactions, the authors propose the occurrence of a 1,2-H shift in a vinyl intermediate, ruling out the possibility of a 1,3-shift on the basis of additional experiments using deuterated alkynes. Finally, we can quote an example in which an allyl group eventually transforms into an alkenyl ligand, but possibly through an 1,3-shift, this occurring in the reaction of $[Fe_2(\mu\text{-CO})(CO)_6(\mu\text{-Ph}_2PCH_2PPh_2)]$ with $Ph_2PCH_2CH{=}CH_2$ to give $[Fe_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-CHCHMe})(CO)_6(\mu\text{-Ph}_2PCH_2PPh_2)]$ [17].

2.7. Proposed mechanism for the reaction of compound 1 with acryloyl chloride

As stated above, this is the only instance in which the anion **1** gives simultaneously products resulting in the attachment of a C-based electrophile to either the metal center or to the oxygen atom of the carbonyl ligand. As a result of this, a mixture of the vinyl complex **2d** and the carbyne complex **5** is obtained in the reaction of **1** with acryloyl chloride (Scheme 4). The formation of the vinyl complex requires the binding of the acryloyl fragment to the molybdenum atoms, likely to give an α,β-unsaturated acyl-bridged intermediate **E**, followed by decarbonylation to give a terminally-bound vinyl intermediate **F**, which would finally rearrange into
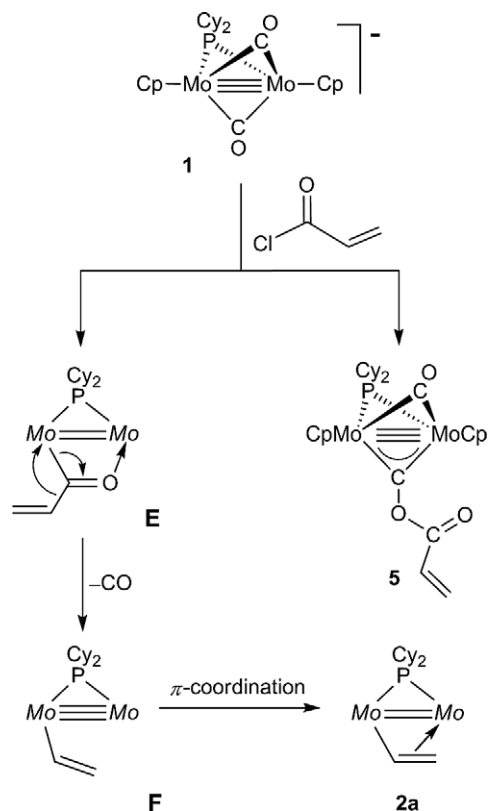
Scheme 4. Reaction pathways of the anion **1** with acryloyl chloride (*Mo* = MoCp).

the more stable vinyl-bridged geometry. In the second case, the S_N reaction would take place at the hardest nucleophilic site of the anion, located at the oxygen atom of the bridging CO ligands. There are some reports in the literature where decarbonylation have been observed or proposed to occur in α,β-unsaturated acyl-bridged complexes. For instance, the thermolysis of the diiron acyl complexes [Fe$_2$(CO)$_4${μ-C(O)CR=CHR'}(μ-PPh$_2$)(μ-dppm)] has been shown to give the corresponding alkenyl derivatives [Fe$_2$(CO)$_4$(μ-CR=CHR')(μ-dppm)] (R, R' = H, Ph) [18]. A similar process is proposed to occur spontaneously in the reaction of the anionic compounds [Mo$_2$Cp$_2$(μ-PPhR)(CO)$_4$]$^-$ (R = H, Ph) with acryloyl chloride. In this case, a vinyl intermediate might be also involved but was not detected, and the products obtained are the phosphaalkene complex [Mo$_2$Cp$_2$(μ-κ^1:η^2-PhP=CHMe)(CO)$_4$] and the alkenylphosphine complex [Mo$_2$Cp$_2$(μ-κ^1:η^2-Ph$_2$PCH=CH$_2$)(CO)$_4$], respectively [19].

In summary, we have shown that the unsaturated anion **1** reacts with β,γ-unsaturated organic chlorides to give products of nucleophilic substitution mainly involving the dimetal site, while the electron-transfer processes are almost absent in these reactions. The high unsaturation of the dimetal center in **1** allows and induces different rearrangements in the incoming electrophile: In the reaction with allyl halides, a rare 2,1-H shift to give the corresponding alkenyl derivatives is observed. In the reaction with acryloyl chloride, decarbonylation takes place to give a vinyl derivative. The latter reaction is a unique case in which both nucleophilic sites of the anion (Mo and O atoms) are involved to bind the incoming electrophile.

3. Experimental

All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Sol-

vents were purified according to literature procedures, and distilled prior to their use [20]. Tetrahydrofuran (THF) solutions of the lithium salt of the anion [Mo$_2$Cp$_2$(μ-PCy$_2$)(μ-CO)$_2$]$^-$ (**1**) were prepared "in situ" as described previously [2,3], and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338–345 K. Filtrations were carried out through diatomaceous earth. Low-temperature chromatographic separations were carried out using jacketed columns refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat, or by tap water. Commercial aluminum oxide (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 desired. IR stretching frequencies of CO ligands were measured in solution (using CaF$_2$ windows) and are referred to as ν(CO). 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$_2$Cl$_2$ solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H$_3$PO$_4$ solutions (^{31}P). Coupling constants (J) are given in Hertz. The metal-bound carbon atoms of the alkenyl ligands are referred to as C$_\alpha$ and C$_\beta$, with C$_\alpha$ corresponding to the bridgehead carbon atom, and the corresponding H atoms are labeled analogously.

3.1. Preparation of trans-[Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCH$_2$)(μ-PCy$_2$)(CO)$_2$] (2a)

An excess of allyl chloride (0.1 mL, 1.2 mmol) was added to a solution of **1** (Li$^+$ salt, ca. 0.1 mmol) in THF (10 mL) and the mixture was stirred for 30 min at room temperature to yield a red solution. After removal of the solvent under vacuum, the residue was extracted with toluene and the extract was filtered through diatomaceous earth. The solvent was removed again under vacuum, the residue was then extracted with CH$_2$Cl$_2$–petroleum ether (1:4) and the extracts were chromatographed through an alumina column (activity IV) at 253 K. Elution with the same solvent mixture gave a red fraction (yellow-greenish in the column) which yielded, after removal of solvents under vacuum, compound **2a** as an orange-yellow air-sensitive solid (0.028 g, 45%). Anal. Calc. for C$_{27}$H$_{37}$Mo$_2$O$_2$P: C, 52.60; H, 6.05. Found: C, 52.36; H, 6.29%. ^{1}H NMR: δ 5.36, 5.31 (2 × s, Cp, 2 × 5H), 5.07, 4.68 (2 × d, J_{HH} = 2.6, CH$_2$, 2 × 1H), 2.27 (s, CH$_3$, 3H), 2.10–1.00 (m, Cy, 22H). ^{13}C{^{1}H} NMR (213 K): δ 250.0 (d, J_{CP} = 14, CO), 237.9 (d, J_{CP} = 13, CO), 174.6 (s, C$_\alpha$), 90.0, 89.0 (2 × s, Cp), 79.3 (s, C$_\beta$), 44.8 (d, J_{CP} = 21, C^1–Cy), 42.5 (d, J_{CP} = 17, C^1–Cy), 38.7 (s, CH$_3$), 34.4, 33.9, 32.5, 31.7 (4 × s, C^2–Cy), 28.2 (d, J_{CP} = 12, C^3–Cy), 28.1 (d, J_{CP} = 13, C^3–Cy), 27.9 (d, J_{CP} = 12, C^3–Cy), 27.7 (d, J_{CP} = 11, C^3–Cy), 26.3 (s, 2 × C^4–Cy).

3.2. Reaction of compound 1 with crotyl chloride

An excess of crotyl chloride (0.1 mL, 0.98 mmol) was added to a solution of **1** (Li$^+$ salt, ca. 0.1 mmol) in THF (10 mL) and the mixture was stirred for 10 min at room temperature to yield a red solution containing a 3:2 mixture of the compounds trans-[Mo$_2$Cp$_2$(μ-η^1:η^2-CEtCH$_2$)μ-PCy$_2$)(CO)$_2$] (**2b**) and trans-[Mo$_2$Cp$_2$(μ-η^1:η^2-CMeCHMe)(μ-PCy$_2$)(CO)$_2$] (**2c**). After removal of the solvent under vacuum, the residue was extracted with toluene (2 × 7 mL) and filtered through diatomaceous earth. Workup as described for **2a** gave a 3:2 mixture of compounds **2b** and **2c** as an orange-yellowish air-sensitive solid (0.035 g, 54%). Anal. Calc. for C$_{28}$H$_{39}$Mo$_2$O$_2$P: C, 53.34; H, 6.24. Found: C, 52.95; H, 5.98%. ^{1}H NMR data for **2b**: δ 5.35, 5.31 (2 × s, Cp, 2 × 5H), 5.03, 4.76 (2 × d, J_{HH} = 2, EtC = CH$_2$, 2 × 1H), 2.68, 2.04 (2 × dq, J_{HH} = 14, 7, CH$_3$CH$_2$C=CH$_2$, 2 × 1H), 1.15 (t, J_{HH} = 7, CH$_3$CH$_2$C=CH$_2$, 3H). The resonances due to the H

atoms of the Cy group are overlapping with those of the isomer **2c** (2.40–1.10 ppm). ^{1}H NMR data for **2c**: δ 6.17 (q, J_{HH} = 5.5, CHMe, 1H), 5.29, 5.20 (2 × s, Cp, 2 × 5H), 2.10 (s, CH$_3$C, 3H), 1.91 [d, J_{HH} = 5.5, CH(CH$_3$), 3H]. The resonances due to the H atoms of the Cy group are overlapping with those of the isomer **2b** (2.40–1.10 ppm).

3.3. Reaction of compound **1** with acryloyl chloride

Neat acryloyl chloride (20 µL, 0.25 mmol) was added to a solution of **1** (Li$^+$ salt, *ca.* 0.1 mmol) in THF (10 mL) and the mixture was stirred for 5 min at room temperature to give a deep red solution containing a 1:1 mixture of the complexes *trans*-[Mo$_2$Cp$_2$(µ-η^1:η^2-CHCH$_2$)(µ-PCy$_2$)(CO)$_2$] (**2d**) and [Mo$_2$Cp$_2$(µ-PCy$_2$){µ-CO-C(O)CH=CH$_2$}(µ-CO)] (**5**). After removal of the solvent under vacuum, the residue was extracted with CH$_2$Cl$_2$–petroleum ether (1:4) and the extracts were chromatographed through alumina (activity IV) at 285 K. Elution with the same solvent mixture gave a green fraction, and further elution with neat dichloromethane gave a red fraction. Removal of solvents from the first fraction yielded compound **2d** as a yellow-greenish solid (0.027 g, 45%), and compound **5** was analogously obtained as a red solid from the second fraction (0.025 mg, 40%). *Selected data for compound* **2d**: Anal. Calc. for C$_{26}$H$_{35}$Mo$_2$O$_2$P: C, 51.84; H, 5.86. Found: C, 51.96; H, 6.09%. ^{1}H NMR: δ 8.56 (ddd, J_{PH} = 1, J_{HH} = 12, 9, H$_\alpha$, 1H), 5.39, 5.33 (2 × s, Cp, 2 × 5H), 5.28 (dd, J_{HH} = 12, 3, H$_\beta$, 1H), 4.91 (dd, J_{HH} = 9, 3, H$_\beta$, 1H), 2.80–0.90 (m, Cy, 22H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 252.2 (d, J_{CP} = 13, CO), 236.3 (d, J_{CP} = 13, CO), 153.2 (s, C$_\alpha$), 89.5, 89.2 (2 × s, Cp), 84.2 (s, C$_\beta$), 45.4 (d, J_{CP} = 20, C^1–Cy), 45.3 (d, J_{CP} = 18, C^1–Cy), 34.7, 34.2 (2 × d, J_{CP} = 3, 2 × C^2–Cy), 33.0, 32.9 (2 × s, 2 × C^2–Cy), 28.4 (d, J_{CP} = 13, 2 × C^3–Cy), 28.3 (d, J_{CP} = 10, C^3–Cy), 28.1 (d, J_{CP} = 11, C^3–Cy), 26.5, 26.4 (2 × s, C^4–Cy). *Selected data for compound* **5**: Anal. Calc. for C$_{27}$H$_{35}$Mo$_2$O$_3$P: C, 51.44; H, 5.60. Found: C, 51.26; H, 5.85%. ^{1}H NMR: δ 6.44 (dd, J_{HH} = 17, 1.5, H$_\beta$, 1H), 6.12 (dd, J_{HH} = 17, 10, H$_\alpha$, 1H), 5.93 (dd, J_{HH} = 10, 1.5, H$_\beta$, 1H), 5.82 (s, Cp, 10H), 2.80–0.40 (m, Cy, 22H). ^{13}C{^{1}H} NMR: δ 342.5 (d, J_{CP} = 17, µ-COR), 300.7 (d, J_{CP} = 9, CO), 159.7 [s, C(O)R], 132.4 (s, C$_\beta$), 128.5 (s, C$_\alpha$), 95.7 (s, Cp), 41.8 (d, J_{CP} = 18, C^1–Cy), 41.5 (d, J_{CP} = 19, C^1–Cy), 33.6, 33.2 (2 × d, J_{CP} = 3, 2 × C^2–Cy), 27.6 (d, J_{CP} = 13, C^3–Cy), 27.5 (d, J_{CP} = 12, C^3–Cy), 26.4, 26.3 (2 × s, C^4–Cy).

3.4. Preparation of cis-[Mo$_2$Cp$_2$(µ-η^1:η^2-CHCH$_2$)(µ-PCy$_2$)(CO)$_3$] (**3**)

A Schlenk flask containing compound **2d** (0.027 g 0.045 mmol) was filled with CO. Dichloromethane (8 mL) was then added, and the mixture was stirred at room temperature for 1 h to give an orange solution. After removal of the solvent under vacuum, the residue was extracted with CH$_2$Cl$_2$–petroleum ether (1:4) and the extracts were chromatographed through alumina (activity IV) at 285 K. Elution with the same solvent mixture gave an orange fraction which yielded, after removal of solvents, compound **3** as an orange solid (0.022 g, 78%). The crystals of **3** used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated solution of the compound in toluene at 253 K. Anal. Calc. for C$_{27}$H$_{35}$Mo$_2$O$_3$P: C, 51.44; H, 5.60. Found: C, 51.17; H, 5.92%. ^{1}H NMR (CDCl$_3$): δ 8.93 (td, J_{HH} = 9, J_{PH} = 1, H$_\alpha$, 1H), 5.16, 5.15 (2 × s, Cp, 2 × 5H), 3.34 (d, J_{HH} = 9, H$_\beta$, 1H), 2.70–0.20 (m, Cy, 22H), 1.07 (d, J_{HH} = 9, H$_\beta$, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 242.3 (d, J_{CP} = 23, CO), 239.6 (d, J_{CP} = 20, CO), 237.3 (d, J_{CP} = 1, CO), 148.2 (d, J_{CP} = 9, C$_\alpha$), 92.9, 91.0 (2 × s, Cp), 59.1 (d, J_{CP} = 11, C^1–Cy), 46.6 (s, C^2–Cy), 42.2 (d, J_{CP} = 17, C^1–Cy), 36.8 (d, J_{CP} = 2, C^2–Cy), 32.8 (s, C^2–Cy), 32.7 (d, J_{CP} = 6, C$_\beta$), 29.1 (d, J_{CP} = 11, C^3–Cy), 28.3 (d, J_{CP} = 8, C^3–Cy), 28.2 (s, C^2–Cy), 27.9 (d, J_{CP} = 11, C^3–Cy), 27.3 (d, J_{CP} = 13, C^3–Cy), 26.5, 26.0 (2 × s, C^4–Cy).

3.5. Preparation of trans-[Mo$_2$Cp$_2${µ-η^2:η^3-CH$_2$CCH}](µ-PCy$_2$)(CO)$_2$] (**4**)

Propargyl chloride (50 µL, 70% w/w in toluene, 0.45 mmol) was added to a solution of **1** (Li$^+$ salt, *ca.* 0.07 mmol) in THF (10 mL), and the mixture was stirred for 2 h at room temperature to give an orange solution containing compound **4** as the major product, along with minor amounts of another compound that could not be isolated or purified. After removal of the solvent, the residue was extracted with CH$_2$Cl$_2$–petroleum ether (1:4) and the extracts were chromatographed through alumina (activity IV) at 253 K. Elution with the same solvent mixture gave an orange fraction which yielded, after removal of solvents, compound **4** as an orange solid (0.030 g, 70%). Anal. Calc. for C$_{27}$H$_{35}$Mo$_2$O$_2$P: C, 52.78; H, 5.74. Found: C, 52.56; H, 5.82%. ^{1}H NMR: δ 5.06, 4.98 (2 × s, Cp, 2 × 5H), 4.72 (ddd, J_{PH} = 3.5, J_{HH} = 1.5, 1.1, CH, 1H), 4.17 (t, J_{PH} = J_{HH} = 1.5, CH$_2$, 1H), 4.00 (t, J_{PH} = J_{HH} = 1.1, CH$_2$, 1H), 2.20–1.10 (m, Cy, 22H). ^{13}C{^{1}H} NMR: δ 244.4 (d, J_{CP} = 11, CO), 236.0 (d, J_{CP} = 8, CO), 112.5 (s, CH$_2$CCH), 91.0, 87.2 (2 × s, Cp), 68.9 (s, CH$_2$CCH), 61.0 (d, J_{CP} = 21, CH$_2$CCH), 51.2 (d, J_{CP} = 15, C^1–Cy), 47.3 (d, J_{CP} = 10, C^1–Cy), 35.4 (d, J_{CP} = 5, C^2–Cy), 35.3 (d, J_{CP} = 4, C^2–Cy), 34.9 (d, J_{CP} = 1, C^2–Cy), 34.8 (d, J_{CP} = 1, C^2–Cy), 28.8 (d, J_{CP} = 10, C^3–Cy), 28.7 (d, J_{CP} = 12, C^3–Cy), 28.6, 28.5 (2 × d, J_{CP} = 10, 2 × C^3–Cy), 26.8, 26.7 (2 × d, J_{CP} = 1, 2 × C^4–Cy).

3.6. X-ray structure determination of compound **3**

The X-ray intensity data for compound **3** were collected on a Smart-CCD-1000 BRUKER diffractometer using graphite-monochromated Mo Kα radiation at 120 K. Cell dimensions and orientation matrixes were initially determined from least-squares refinements of reflections measured in three sets of 30 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART [21] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT [21], and a multi-scan absorption

Table 3
Crystal data for compound **3**.

Molecular formula	C$_{27}$H$_{35}$Mo$_2$O$_3$P
Molecular weight	630.40
Crystal System	monoclinic
Space group	P2$_1$/c
Radiation (λ, Å)	0.71073
a (Å)	10.820(2)
b (Å)	12.901(2)
c (Å)	18.133(4)
α (°)	90
β (°)	91.810(3)
γ (°)	90
V (Å^3)	2529.9(8)
Z	4
D$_{Calc}$ (g cm^{-3})	1.655
Absorption coefficient (mm^{-1})	1.081
T (K)	120
θ range (°)	1.88–26.41
Index ranges (h, k, l)	−13, 13; 0, 16; 0, 22
Reflections collected	21417
Independent reflection	5181 [R_{int} = 0.0264]
Reflection with $I > 2\sigma(I)$	4595
R indexes ($I > 2\sigma(I)$)[a]	R_1 = 0.0192, wR_2 = 0.0472[b]
R indexes (all data)[a]	R_1 = 0.0238, wR_2 = 0.0490[b]
Goodness-of-fit (GOF)	1.074
Restraints/parameters	0/438
$\Delta\rho$ (max., min.) (e Å^{-3})	0.382, −0.407

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.
[b] $a = 0.0224$, $b = 1.4423$.

correction was applied with SADABS [22]. Using the program suite WINGX [23], the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least squares on F^2 with SHELXL97 [24]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the Fourier map and were given an overall isotropic thermal parameter. Crystallographic data and structure refinement details for compound **3** are collected in Table 3.

Acknowledgments

Appendix A. Supplementary material

CCDC 740498 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.003.

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