



Reactivity of the unsaturated dimolybdenum anion $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$ towards electrophiles based on *p*- and *d*-block elements

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ABSTRACT

The 30-electron binuclear anion $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$ reacts with the chlorophosphite $\text{ClP}(\text{OEt})_2$ or the organotin chlorides Cl_2SnPh_2 or ClSnPh_3 to give compounds of the formula *trans*- $[\text{Mo}_2\text{Cp}_2(\mu\text{-E})(\mu\text{-PCy}_2)(\text{CO})_2]$, ($\text{E} = \text{P}(\text{OEt})_2, \text{SnPh}_3, \text{SnPh}_2\text{Cl}$). In contrast, this anion reacts with the organosilicon chlorides ClSiR_3 ($\text{R} = \text{Ph}, \text{Me}$) to give unstable silyloxy-carbyne-bridged complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-COSiR}_3)(\mu\text{-CO})]$, which rapidly hydrolyze to give the known hydride $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$. Two main types of products were also observed in the reactions of the title anion with different chlorocomplexes of the transition and post-transition metals. Thus, the reactions with $[\text{MCl}_2\text{Cp}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$) give moisture-sensitive isocarbonyl-bridged complexes of the type $[\text{Mo}_2\text{Cp}_2(\mu\text{-COM-ClCp}_2)(\mu\text{-PCy}_2)(\mu\text{-CO})]$. In contrast, softer metallic electrophiles such as $[\text{AuCl}(\text{PR}_3)]$ ($\text{R} = {}^i\text{Pr}, \text{ptol}$) react with the anion at the dimolybdenum site to form new trimetallic clusters of the formula $[\text{AuMo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)]$, also retaining a Mo–Mo triple bond. Subsequent reactions of the latter products with the solvate complexes $[\text{Au}(\text{PR}_3)(\text{THF})][\text{PF}_6]$ give the tetranuclear clusters $[\text{Au}_2\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)_2][\text{PF}_6]$ ($\text{Mo}\text{--}\text{Mo} = 2.5674(3) \text{ \AA}$ and $\text{Au}\text{--}\text{Au} = 2.7832(2) \text{ \AA}$ when $\text{R} = {}^i\text{Pr}$). Finally, the reaction of the title anion with HgI_2 gives the pentanuclear cluster $[\text{Hg}(\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2)_2]$ or the trinuclear cluster $[\text{Mo}_2\text{Cp}_2(\mu\text{-HgI})(\mu\text{-PCy}_2)(\text{CO})_2]$ depending on the stoichiometry being actually used for the reaction. The trinuclear species is only stable in tetrahydrofuran (THF), and decomposes to give a mixture of the dimeric species $[\text{Mo}_2\text{Cp}_2(\mu\text{-HgI})(\mu\text{-PCy}_2)(\text{CO})_2]_2$ along with variable amounts of the known iodide-bridged complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PCy}_2)(\text{CO})_2]$.

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1. Introduction

Metal carbonyl anions are very useful reagents in organometallic synthesis mainly due to their high nucleophilicity, which allows them to react with a great variety of electrophiles to form new M–E bonds ($\text{E} = \text{H}, \text{C}, p\text{- or } d\text{-block element}$) [1]. However, although the chemistry of mono- and polynuclear metal carbonyls has been widely explored, that of the binuclear anions having a metal–metal bond is comparatively less developed. This is specially so in the case of binuclear anions having multiple metal–metal bonds, of which only a few examples have been reported in the literature [2]. A few years ago we reported an efficient synthetic route to the dicyclohexylphosphide-bridged anion $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$ (**1**), for which a Mo–Mo triple bond must be formulated under the Effective Atomic Number (EAN) formalism (Chart 1) [3]. Subsequent DFT calculations on this anion allowed us to describe more precisely this multiple bond as being com-

posed of one σ and two δ components, with the latter ones also involving π -backbonding to the bridging carbonyls [4]. In our early report we found that this anion was reactive towards many different electrophiles, both based in *p*-block and in *d*-block elements, thus opening a new synthetic path to novel unsaturated derivatives that might be difficult or impossible to prepare from conventional (electron-precise) precursors [3]. Recently we have reported a detailed study of the reactivity of anion **1** towards C-based electrophiles RX revealing that, depending on the particular reagent being used, three different types of products can be formed: (a) alkyl-bridged complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-R})(\text{CO})_2]$, (b) alkoxycarbonyl-bridged complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-COR})(\mu\text{-PCy}_2)(\mu\text{-CO})]$, and (c) halide-bridged complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-X})(\text{CO})_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). These results suggest that there are three main pathways under operation in these reactions: (1) nucleophilic attack of the anion through its dimetal centre, (2) nucleophilic attack through the O atoms of the bridging carbonyls, and (3) electron transfer to the added reagent [2].

In this paper we complete our general study of the reactivity of the anion **1** by examining its reactions with electrophilic

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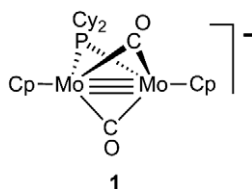


Chart 1.

molecules based on elements different from carbon, either *p*-block elements (S, P, Si, Sn) or *d*-block ones (Ti, Zr, Au, Hg). As it will be shown below, the multisite reactivity exhibited by **1** towards C-based electrophiles is also found when faced to these new electrophiles, these being incorporated either to the dimetal site, to give heterometallic clusters with Mo₂M (M = Sn, Au, Hg), Mo₂Au₂ and Mo₄Hg cores, or to the oxygen atom of the bridging carbonyl ligands, this leading to rather unstable silyloxy-carbyne and isocarbonyl-bridged Mo₂(μ₃-C:C:O-CO)M complexes (M = Ti, Zr). Some of these results were reported in our preliminary work on the reactivity of **1** [3].

2. Results and discussion

2.1. Reactions of the anion **1** with chlorophosphines

The anionic complex **1** (Li⁺ salt) reacts with ClP(OEt)₂ to give the mixed-phosphide derivative *trans*-[Mo₂Cp₂(μ-PCy₂){μ-P(OEt)₂}(CO)₂] (**2**) in moderate yield (Chart 2). This compound can be synthesized also by reacting **1** with the pyrophosphite (EtO)₂PO-P(OEt)₂, and also by the reaction of the anionic complex [Mo₂Cp₂{μ-P(OEt)₂}(μ-CO)₂]⁻ [1,2] with ClPCy₂, although the yields in the latter case are lower, due to the instability of the diethoxyphosphide-bridged anion.

Compound **2** was fully characterized by IR and NMR spectroscopy in solution. Its IR spectrum exhibits two C–O stretching bands at 1876 (m, sh) and 1848 (vs) cm⁻¹, with the pattern characteristic of *trans*-dicarbonyl complexes and with frequencies somewhat higher than those of the related complexes [Mo₂Cp₂(μ-PCy₂)(μ-PRR')₂(CO)₂] (R = R' = Ph, Cy; R = H, R' = Cy) [5], as expected from the lower basicity of the diethoxyphosphide ligand, when compared to diaryl or dialkylphosphide ligands. The ³¹P NMR spectrum exhibits two doubles at very different chemical shifts, 119.5 (PCy₂) and 352.1 [P(OEt)₂] ppm. The ³¹P shielding

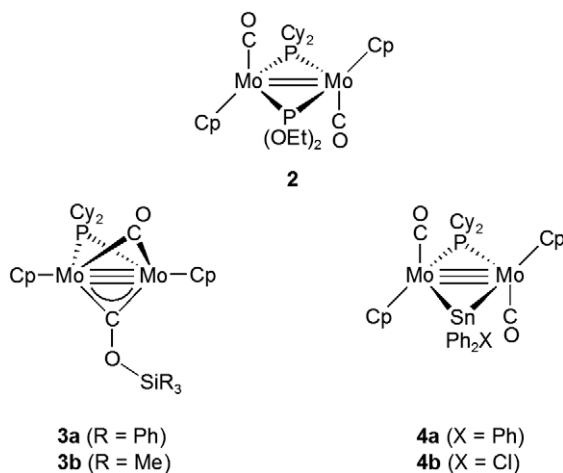
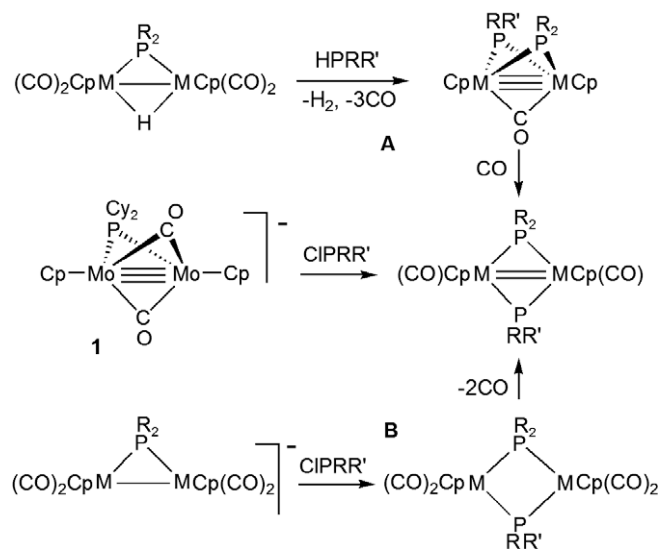


Chart 2.

of the PCy₂ group is consistent with the formulation of a double Mo–Mo bond for **2**, and is comparable to those found for other isoelectronic compounds bearing bridging PCy₂ ligands [5], whereas the shielding of the P(OEt)₂ group is comparable to that measured for the isoelectronic complex [Mo₂Cp₂{μ-OP(OEt)₂}-{μ-P(OEt)₂}(CO)₂] [6]. It should be kept in mind, however, that the ³¹P chemical shifts of diethoxyphosphide ligands are rather insensitive to the coordination environment and metal–metal bond order in this type of binuclear carbonyl complexes [2]. Besides this, the P–P coupling in **2** is quite low (19 Hz) as usually found for unsaturated phosphide complexes displaying almost flat M₂P₂ central rings, in contrast with the strong couplings (*ca.* 100 Hz) found for tetracarbonyl compounds of formula [Mo₂Cp₂(μ-PR₂)(μ-PR'₂)(CO)₄], these having puckered M₂P₂ central rings with no metal–metal bonds [7]. The ¹H NMR spectrum of **2** exhibits a single resonance for both Cp ligands at 5.40 ppm, but two different multiplets for the methylenic protons of the OEt groups, as expected for a *trans*-dicarbonyl structure, this implying that the metal centres are related by a C₂ operation, but not by a symmetry plane.

The synthetic route giving complex **2** can be also used to prepare other mixed-phosphide derivatives of the group 6 elements, by using the pertinent chlorophosphine (ClPCy₂, ClPPh₂, etc.), and it can be considered as a synthetic alternative to methods previously described for this sort of mixed-phosphide complexes. The main synthetic procedure previously developed to obtain these species is based on the photochemical treatment of the tetracarbonyl hydrides [Mo₂Cp₂(μ-H)(μ-PR₂)(CO)₄] with the pertinent primary or secondary phosphines HPRR' (**A** in Scheme 1) [5]. An alternative route to these species is the reaction of an electron-precise tetracarbonyl anion of the type [Mo₂Cp₂(μ-PR₂)(CO)₄]⁻ with the pertinent chlorophosphine, followed by decarbonylation (**B** in Scheme 1) [7]. A major drawback of the latter route is the decarbonylation step of the tetracarbonyl intermediate, only efficient in some of the cases. Our route is to be especially useful actually in those cases where decarbonylation is not possible (route **B**) or when the corresponding HPRR' reagent is not accessible (route **A**). Compound **2** is a good example of the limitations derived from latter circumstance, since the corresponding phosphonite HP(OEt)₂ is not a stable molecule.



Scheme 1. Synthetic routes to unsaturated mixed-phosphide bridged complexes of the group 6 elements.

2.2. Reactions of the anion **1** with organochlorides of the group 14 elements

The lithium salt of the anionic complex **1** reacts with the silicon chlorides ClSiR_3 ($\text{R} = \text{Ph}, \text{Me}$) to give solutions containing the new silyloxycarbyne-bridged complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-COSiR}_3)(\mu\text{-PCy}_2)(\mu\text{-CO})]$ [$\text{R} = \text{Ph}$ (**3a**), Me (**3b**)] as the major products (Chart 2). These compounds turned out to be extremely sensitive to air and moisture, and all attempts to isolate them as pure materials led to their progressive decomposition. In spite of this, the available IR and ^{31}P NMR data are very similar to those previously measured for the alkoxycarbyne complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-COR})(\mu\text{-PCy}_2)(\mu\text{-CO})]$ [$\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}, \text{Cy}, \text{C}(\text{O})\text{Ph}$] [2,3], then indicating a strong structural similarity. Thus, the IR spectra of compounds **3** exhibit a band in THF solution at *ca.* 1700 cm^{-1} , a typical frequency for the C–O stretch of the bridging carbonyl ligand in the mentioned carbyne complexes, whereas the chemical shifts for the P atoms in the ^{31}P NMR spectra, 230.8 (**3a**) and 220.7 (**3b**) ppm, compare well with the values of 223–229 ppm measured for these carbyne complexes. We should mention that, when recording the IR spectra of compounds **3a,b** in solution, a strong band at 1837 cm^{-1} is always observed, due to the formation of the hydride derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$ [2,8,9], presumably by fast hydrolysis of the silyloxycarbyne complexes within the IR plates.

In contrast to the reactions of **1** with silicon organochlorides, those with the tin organochlorides ClSnPh_3 and Cl_2SnPh_2 give the bridging stannyl complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-SnPh}_2\text{X})(\text{CO})_2]$ [$\text{X} = \text{Ph}$ (**4a**), Cl (**4b**)] after 20 h and 5 min, respectively (Chart 2). Compound **4a** was obtained only in moderate yield, since significant amounts of other by-products were also present in the crude reaction mixture, although they could not be properly characterized. We also note that this complex had been previously synthesized by us through the reaction of the unsaturated hydride $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$ with HSnPh_3 [8,10]. As for compound **4b**, it turned out to be much more unstable than **4a**, surely due to the presence of a reactive Sn–Cl bond left in the molecule, and it decomposes progressively upon workup, so it could not be isolated as a pure material. The available spectroscopic data for this complex, however, are very similar to those of the triphenylstannyl compound **4a** (previously characterized by X-ray diffraction methods [8,10]), and thus indicative of their structural analogy. The spectroscopic data in solution for **4a** have been discussed in detail previously, and therefore no further analysis of the data for compound **4b** is needed. We should note, however, that the coordination position of the SnR_3 groups in complexes **4**, bridging two metal atoms, is very unusual for triorganostannyl groups, which usually are found terminally-bound to transition metals. To our knowledge, there are only two other examples in the literature with the same coordination mode for a SnR_3 group, these being the tin-manganese complexes $[\text{Mn}_2\{\mu\text{-Sn:Sn,P-SnR}_2\text{OP}(\text{OEt})_2\}\{\mu\text{-P}(\text{OEt})_2\}(\text{CO})_6\text{L}]$ ($\text{R} = \text{Bu}, \text{Ph}$; $\text{L} = \text{CO}, \text{tertiary phosphine}$) [11], and the tin-germanium compound $[\text{K}(2,2,2\text{-crypt})][\text{Ge}_3(\mu_2\text{-SnPh}_3)]$ [12].

The anion **1** reacts with BrGePh_3 to give the bromide-bridged complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-Br})(\mu\text{-PCy}_2)(\text{CO})_2]$ [2] as the main product, thus implying the operation of an effective electron-transfer mechanism in this case. We recall here that a similar result (formation of the halide complex) was obtained in the reaction of **1** with ClCPh_3 [2]. In contrast, the reaction of **1** with ClPbPh_3 is thought to give first a Mo_2Pb compound analogous to compounds **4**, then extruding “ PbPh_2 ” to give the phenyl-bridged complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-Ph})(\mu\text{-PCy}_2)(\text{CO})_2]$ [9]. In summary, in the reactions with XEPh₃ electrophiles ($\text{E} = \text{group 14 element}$) we observe that the heavier elements of the group (Sn and Pb), which are softer electrophiles, tend to bind to the dimetal center of the anion, whereas the lighter

ones (harder electrophiles) either attack the O(carbonyl) atom of the anion (Si) or experience fast electron-transfer reactions giving eventually the corresponding halide-bridged complexes (C and Ge). From our previous work on the reactions of **1** with C-based electrophiles, however, we concluded that not only the nature of the electrophilic fragment to be added, but also that of the leaving group (halide) might be critical for directing the reaction of the anion **1** through one or another of the three main reaction pathways under operation [2].

2.3. Reactions of the anion **1** with group 4 metallocene dichlorides

We have also examined the reactions of the anion **1** with several transition metal-based electrophiles. When faced to several carbonyl halide complexes (i.e. reactions with $[\text{FeCp}(\text{CO})_2\text{Cl}]$, $[\text{ReBr}(\text{CO})_5]$, $[\text{MoClCp}(\text{CO})_3]$ or $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$) the anion **1** gives the corresponding halide-bridged derivative $[\text{Mo}_2\text{Cp}_2(\mu\text{-X})(\mu\text{-PCy}_2)(\text{CO})_2]$, this being indicative of the occurrence of dominant electron-transfer processes. In contrast, the reactions with the harder and oxophilic metallocene dichlorides $[\text{MCl}_2\text{Cp}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$) proceed very fast to give the heterometallic derivatives $[\text{Mo}_2\text{Cp}_2(\mu\text{-COMClCp}_2)(\mu\text{-PCy}_2)(\mu\text{-CO})]$ [$\text{M} = \text{Ti}$ (**5a**), Zr (**5b**)] (Chart 3). These compounds were easily hydrolyzed upon manipulation to give the unsaturated hydride $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$, and they could not be isolated as pure materials. However, the available IR and ^{31}P NMR data provide strong support for the proposed structure, strongly related to those of the silyloxy- or alkoxycarbyne compounds discussed above. Again, a characteristic single C–O stretching band at *ca.* 1690 cm^{-1} in THF denotes the presence of a single CO ligand in a bridging position. When compared to those of compounds **3**, the C–O stretches for compounds **5** are *ca.* 10 cm^{-1} less energetic. This difference must be taken as significant, since the frequencies of the bridging carbonyls in this sort of molecules are relatively insensitive to changes in the metal environment. It seems then that the metallic fragments MCp_2Cl have an electron-withdrawing influence on the dimolybdenum centre significantly weaker than the hard non-metal based electrophiles (C, Si). Finally, we note that the chemical shifts for the bridging P atoms in compounds **5** (*ca.* 220 ppm), are comparable to those in compounds **3** (Table 1) or to those in the alkoxycarbyne complexes mentioned above [2,3].

Complexes **5** have a $(\mu\text{-C,C,O-CO})$ ligand connecting the three metal atoms, which is an unusual coordination mode for a carbonyl ligand. There are only a few examples in the literature of

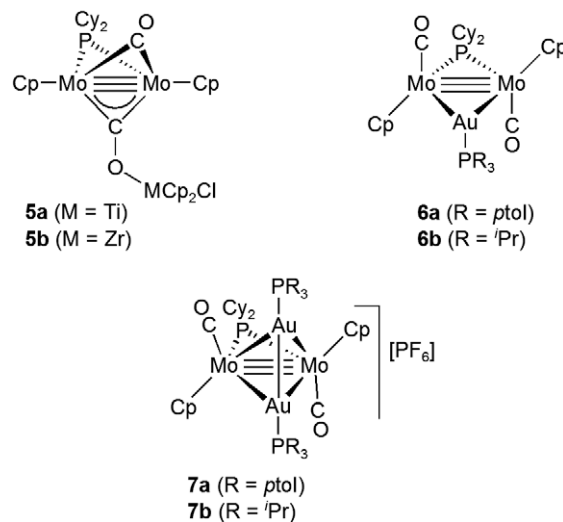


Chart 3.

Table 1
Selected IR^a and ³¹P{¹H} NMR^b data for new compounds.

Compound	$\nu(\text{CO})$	$\delta_{\text{P}}, [\text{J}]$
[Mo ₂ Cp ₂ (μ -PCy ₂){ μ -P(OEt) ₂ }(CO) ₂] (2)	1876 (m, sh), 1848 (vs)	352.1 [19] ^c 119.5 [19] ^c
[Mo ₂ Cp ₂ (μ -COSiPh ₃)(μ -PCy ₂)(μ -CO)] (3a)	1699 ^d	230.8 ^{e,f}
[Mo ₂ Cp ₂ (μ -COSiMe ₃)(μ -PCy ₂)(μ -CO)] (3b)	1700 ^d	220.7 ^e
[Mo ₂ Cp ₂ (μ -PCy ₂)(μ -SnPh ₃)(CO) ₂] (4a)	1865 (m), 1809 (vs)	248.5 [85] ^g
[Mo ₂ Cp ₂ (μ -PCy ₂)(μ -SnClPh ₂)(CO) ₂] (4b)	1887 (m, sh), 1837 (vs) ^d	235.7 [101] ^{g,h}
[Mo ₂ Cp ₂ (μ -COTiClCp ₂)(μ -PCy ₂)(μ -CO)] (5a)	1666	221.0 ^h
[Mo ₂ Cp ₂ (μ -COZrClCp ₂)(μ -PCy ₂)(μ -CO)] (5b)	1667	219.0 ^h
[AuMo ₂ Cp ₂ (μ -PCy ₂)(CO) ₂ {P(<i>ptol</i>) ₃ }] (6a)	1803 (m, sh), 1784 (vs) ^d	213.2, ⁱ 64.0 ⁱ
[AuMo ₂ Cp ₂ (μ -PCy ₂)(CO) ₂ (P ^{<i>i</i>} Pr ₃)] (6b)	1801 (m, sh), 1780 (vs) ^d	209.4 [10], ^{c,j,k} 90.4 [10] ^{c,j,k}
[Au ₂ Mo ₂ Cp ₂ (μ -PCy ₂)(CO) ₂ {P(<i>ptol</i>) ₃ } ₂][PF ₆] (7a)	1859 (m, sh), 1839 (vs)	244.5 [5], ^c 60.0 [5], ^c -144.2 [712] ^l
[Au ₂ Mo ₂ Cp ₂ (μ -PCy ₂)(CO) ₂ (P ^{<i>i</i>} Pr ₃) ₂][PF ₆] (7b)	1859 (m, sh), 1833 (vs)	239.2 [4], ^{c,m} 90.7 [4], ^{c,m} -144.4 [712] ^{l,m}
[HgMo ₄ Cp ₄ (μ -PCy ₂) ₂ (CO) ₄] (8)	1782	234.9 ^m
[Mo ₂ Cp ₂ (μ -HgI)(μ -PCy ₂)(CO) ₂] (9)	1831 (m, sh), 1798 (vs) ^d	223.5 [268] ^{h,n}
[Mo ₂ Cp ₂ (μ -HgI)(μ -PCy ₂)(CO) ₂] ₂ (10)	1869 (m, sh), 1830 (vs) ^d	251.4 [198] ^{h,n}

^a Recorded in dichloromethane solution, unless otherwise stated, ν in cm⁻¹.

^b Recorded in CD₂Cl₂ solutions at 290 K and 121.50 MHz, unless otherwise stated, δ in ppm relative to external 85% aqueous H₃PO₄, J in Hz.

^c $J(^{31}\text{P}-^{31}\text{P})$.

^d In tetrahydrofuran.

^e In CH₂Cl₂/D₂O.

^f At 81.04 MHz.

^g $J(^{31}\text{P}-^{117}\text{Sn}) \approx J(^{31}\text{P}-^{119}\text{Sn})$.

^h In tetrahydrofuran/D₂O.

ⁱ In C₆D₆.

^j In toluene-*d*₈.

^k At 162.04 MHz.

^l $J(^{31}\text{P}-^{19}\text{F})$.

^m In CDCl₃.

ⁿ $J(^{31}\text{P}-^{199}\text{Hg})$.

compounds displaying this type of coordination for carbon monoxide. In the unsaturated complex [Mo₂Ti₂Cp₂Cp*₂(μ -C,C,O-CO)₂(CO)₂] [13], the Mo–Mo separation of 2.647(1) Å suggests the presence of a double, rather than a triple intermetallic Mo–Mo bond, so that the Ti-bound carbonyl groups seem to be behaving (as concerning the dimolybdenum centre) as 3-electron donor bridging carbyne ligands, rather than 2-electron donor bridging carbonyls. Other related examples are the cobalt clusters [Co₃(μ -COMClCp₂)(CO)₉] (M = Ti [14], Zr [15]), for which we can assume the presence of a 3-electron donor carbyne according to the EAN formalism. In this context, we trust that the best way to view the Ti-bound CO ligands in compounds **5**, as concerning the dimolybdenum centres, is as 3-electron donor bridging carbynes, which is in good agreement with the corresponding spectroscopic data, closely related to those of the alkoxy-carbyne compounds [Mo₂Cp₂(μ -COR)(μ -PCy₂)(μ -CO)] [2].

2.4. Reactions of the anion **1** with gold–phosphine complexes

The isolobal relationship between the [AuPR₃]⁺ cations and the proton [16] gives support to the experimental finding that in many cases the reactions of organometallic complexes with gold cations proceed in a way similar to the corresponding protonation reactions. This principle has been exploited as a general procedure for the synthesis of heterometallic clusters of the transition metals containing group 11 fragments [17]. Thus we might anticipate that the anion **1** might react with the chlorocomplexes [AuCl(PR₃)] (R = *ptol*, *i*Pr) to give unsaturated Mo₂Au analogues of the hydride complex [Mo₂Cp₂(μ -H)(μ -PCy₂)(CO)₂]. Indeed this reaction takes place rapidly to give green-brownish solutions of the new heterometallic clusters [AuMo₂Cp₂(μ -PCy₂)(CO)₂(PR₃)] [R = *ptol* (**6a**), *i*Pr (**6b**)] (Chart 3). Since the above unsaturated hydride still retains some electron-donor ability for binding to other metal fragments [8] we also examined whether the isoelectronic complexes **6** could add further gold cations. Indeed, these trimetallic clusters react with tetrahydrofuran solutions of [Au(PR₃)(THF)][PF₆] (R = *ptol*, *i*Pr), prepared “in situ” from the corresponding chloride complexes

and Ti[PF₆], to give the tetranuclear clusters [Au₂Mo₂Cp₂(μ -PCy₂)(CO)₂(PR₃)₂][PF₆] (**7a,b**) (Chart 3), which were much more stable than their neutral precursors and could be fully characterized even through X-ray diffraction methods.

2.5. Solution structure of compounds **6a,b**

These unsaturated clusters turned out to be rather unstable, decomposing progressively upon the usual workup, so we could not isolate them as pure materials. Their IR spectra in THF solution exhibit C–O stretching bands at *ca.* 1800 (m, sh) and 1780 (vs) cm⁻¹, with the characteristic pattern of *trans*-dicarbonyl compounds of the type [M₂Cp₂(μ -X)(μ -Y)(CO)₂]. These frequencies, however, are some 50 cm⁻¹ lower than those of the related hydride complex, this being consistent with the lower electronegativity of the gold–phosphine fragment compared to the hydrogen atom. The chemical shifts for the bridging P atoms of the PCy₂ ligands (*ca.* 210 ppm) are lower than that in the related hydride (232.3 ppm) and comparable to the chemical shift in the anion **1** (208.5 ppm) [2], therefore consistent with the formulation of a Mo–Mo triple bond for these trinuclear clusters. As for the gold-bound phosphine, it gives rise to a resonance at 64.0 ppm (**6a**) and 90.4 ppm (**6b**), these being values comparable to those found in the literature for clusters with [AuP(*ptol*)₃] [18] or [AuP^{*i*}Pr₃] [19] groups bridging dimetal centres. The P–P coupling constant is negligible for **6a** and very low (10 Hz) for **6b**, as expected for a coupling through three bonds in this type of clusters [18,19]. The proton NMR spectra are essentially consistent with the structure proposed for **6a,b**, since they both exhibit a single resonance for the Cp ligands, related through a C₂ symmetry axis in the proposed structure. The absence of any symmetry plane relating both metal centres in this structure, however, should render inequivalent (diastereotopic) methyl groups for the isopropyl phosphine ligand in **6b**, but actually only a single resonance is observed for these groups in the room temperature ¹H NMR spectra. Either an accidental degeneracy or a concerted exchange of the carbonyl ligands, as proposed to occur for the related hydride complex [9], would account for this

spectroscopic observation, although we have not studied this matter in detail.

2.6. Structural characterization of compounds **7a,b**

Compound **7b** was characterized in the solid state through an X-ray diffraction analysis (Table 2 and Fig. 1). The cationic cluster exhibits an almost regular tetrahedral Mo_2Au_2 core. The coordination sphere around both Mo atoms is completed with one Cp and one CO ligand at each metal centre, placed in a transoid arrangement, and with a PCy_2 group symmetrically bridging both metals. The P and Mo atoms are almost in the same plane as the centroid of the Au–Au bond, which in turn is almost perpendicular to Mo–Mo bond. Finally, each of the gold atoms bear a phosphine ligand, with the P atom almost placed in the corresponding Mo_2Au plane in

Table 2
Selected bond lengths (Å) and angles (°) for compound **7b**.

Mo(1)–Mo(2)	2.5673(3)
Mo(1)–Au(1)	2.8216(2)
Mo(1)–Au(2)	2.9111(2)
Mo(2)–Au(1)	2.9142(2)
Mo(2)–Au(2)	2.8327(2)
Au(1)–Au(2)	2.7832(2)
Mo(1)–P(3)	2.403(1)
Mo(2)–P(3)	2.389(1)
Au(1)–P(1)	2.311(1)
Au(2)–P(2)	2.324(1)
Mo(1)–C(1)	1.941(3)
Mo(2)–C(2)	1.958(3)
Au(1)–C(1)	2.584(3)
Au(2)–C(2)	2.563(3)
Mo(2)–Mo(1)–Au(2)	61.89(1)
Mo(2)–Mo(1)–Au(1)	65.27(1)
Mo(2)–Au(1)–Mo(1)	53.15(1)
Mo(2)–Au(2)–Mo(1)	53.08(1)
Mo(1)–P(3)–Mo(2)	64.79(2)
C(1)–Mo(1)–Mo(2)	79.9(1)
C(2)–Mo(2)–Mo(1)	88.9(1)
Mo(1)–C(1)–O(1)	169.9(2)
Mo(2)–C(2)–O(2)	170.7(2)

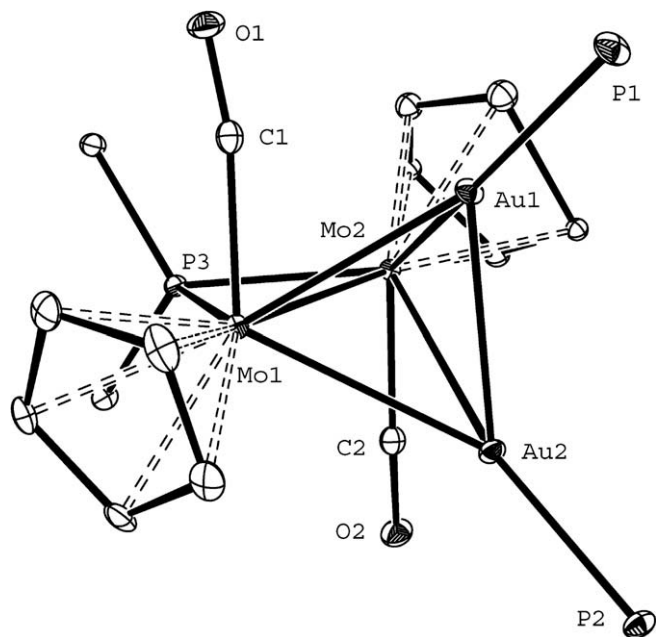


Fig. 1. ORTEP diagram (30% probability) of the cation in compound **7b**, with H atoms, Cy rings (except C^1 atoms) and ^iPr groups omitted for clarity.

both cases. This cationic cluster can also be viewed as two $\text{MoCp}(\text{CO})$ fragments bridged by a dicyclohexylphosphide and two $\text{Au}(\text{P}^i\text{Pr}_3)$ cations eventually coupled to each other. In any case, this structure strongly resembles that of the alkyne-bridged cation $[\text{Mo}_2\text{Cp}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2(\text{OME})_2\}(\mu\text{-PCy}_2)(\text{CN}^i\text{Bu})_2]\text{BF}_4$ [20], although the number of electrons available for intermetallic bonding is different. Incidentally, we note that the latter cation is also formed by the eventual coupling of two bridging (methoxycarbyne) ligands.

According to the EAN rule, a Mo–Mo triple bond can be formulated for **7b**, which is consistent with the experimental intermetallic distance of 2.5673(3) Å, a figure comparable to the values of 2.528(2) and 2.574(1) Å measured, respectively for the neutral 30-electron dimolybdenum compounds $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$ and $[\text{Mo}_2\text{Cp}_2(\mu\text{-SnPh}_3)(\mu\text{-PCy}_2)(\text{CO})_2]$ [8]. Thus it can be concluded that the intermetallic separations in all these electron-deficient molecules are largely determined by the orbital interactions, with only a modest influence of the size of the bridging atoms (H, Sn, Au). Moreover, we note that the Mo–Mo distance in **7b** is still ca. 0.1 Å shorter than that measured in the structurally related alkyne complex mentioned above (2.6550(5) Å), this being a 32-electron complex with a formal Mo–Mo double bond. As for the Mo–Au lengths we note that, because of the slight tilting of the Au–Au axis away from the perpendicular to the Mo–Mo axis, there are two different Mo–Au distances: $\text{Mo}(1)\text{–Au}(1)\approx\text{Mo}(2)\text{–Au}(2)\approx 2.83$ Å, and $\text{Mo}(1)\text{–Au}(2)\approx\text{Mo}(2)\text{–Au}(1)\approx 2.91$ Å. These intermetallic lengths are comparable to the average value found for the related electron-precise trinuclear cluster $[\text{AuMo}_2\text{Cp}_2(\mu\text{-PPh}_2)(\text{CO})_4(\text{PPh}_3)]$, although the asymmetry of the bridging AuPPh_3 moiety in that molecule is much higher, with the Mo–Au lengths differing by ca. 0.2 Å [21]. Finally, we note that the Au–Au distance of 2.7832(2) Å in **7b** falls in the short side of the range usually found in heterometallic clusters containing gold(I)–gold(I) bonding interactions (2.70–3.10 Å) [17]. This trend of gold atoms for binding to other gold atoms is known as “aurophilicity” and is a relevant element determining the structure and physical properties of many homo and heterometallic gold(I) compounds [22,23]. In the case of compound **7b**, by virtue of the isolobal relationship between H and the $\text{Au}(\text{PR}_3)$ fragments, we could consider this cation as a model of a dimolybdenum cation having a bridging dihydrogen ligand, a coordination mode yet to be experimentally determined for the hydrogen molecule.

A final feature to be noted in the structure of **7b** concerns the carbonyl ligands, which are slightly bent towards the Mo–Mo bond as usually found for related 30-electron dimolybdenum complexes [8–10], but also seem to be involved in weak semi-bridging interactions with the gold atoms, as denoted by the relatively short values of 2.584(3) and 2.563(3) Å for the C(1)–Au(1) and C(2)–Au(2) separations, respectively, and by the moderate deviation of the respective Mo–C–O angles (ca. 170°) from linearity. This feature is relatively common in heterometallic carbonyl clusters containing gold–phosphine moieties [17], although it is not clear if such interactions are of a truly bonding nature in all cases. For instance, even stronger C···Au interactions have been found in the heterometallic clusters $[\text{AuMo}_2\text{Cp}_2(\mu\text{-PPh}_2)(\text{CO})_4(\text{PPh}_3)]$ [2.405(5) Å] [21], and $[\text{Au}_3\text{Mn}_2\{\mu\text{-P}(\text{OEt})_2\}(\text{CO})_6(\text{PPh}_3)_3]$ [2.51(2) and 2.56(2) Å] [24]. In the case of compound **7b**, however, we trust that these Au···C contacts are genuinely bonding in origin, since the Au–Au bond is rotated by ca. 4° towards the carbonyl ligands. In contrast, the tilting of the C–C bond in the structurally related cation $[\text{Mo}_2\text{Cp}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2(\text{OME})_2\}(\mu\text{-PCy}_2)(\text{CN}^i\text{Bu})_2]^+$ is ca. 12° away from the terminal isocyanide ligands.

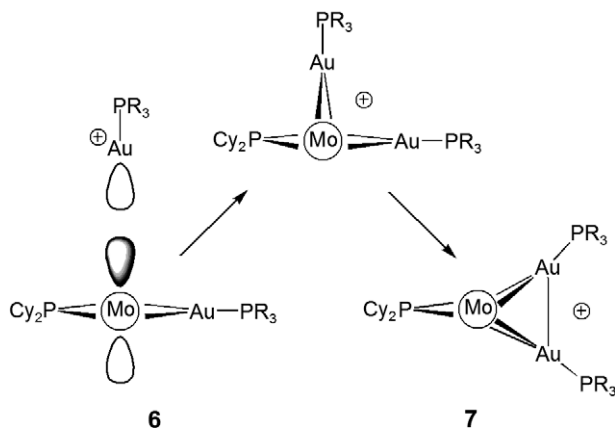
The IR and NMR spectra for compounds **7a,b** are also in good agreement with the solid-state structure just discussed for **7b**. Thus, the retention of the transoid arrangement of the CO ligands is denoted by the IR spectra, both showing two C–O stretching

bands with the characteristic pattern (of medium and strong intensities, in order of decreasing frequency) of such spatial arrangement. The ^{31}P NMR spectra exhibit in each case a single resonance for the gold-bound phosphine ligands, denoting the chemical equivalence of the AuPR_3 groups, while the resonance of the phosphide ligand appears as a strongly deshielded triplet (δ_{P} ca. 240 ppm), as invariably found for our 30-electron complexes. The P–P couplings in these compounds are relatively low (ca. 5 Hz) and comparable to those measured in the trinuclear clusters **6**. Finally, the ^1H NMR spectra exhibits in each case a single resonance for the Cp ligands, and for **7b** displays two distinct multiplets for the diastereotopic Me groups of the isopropyl substituents, as expected for the static structure of the cation.

As suggested above, the formation of the digold cations **7** from the neutral Mo_2Au clusters **6** might be considered as a model for the protonation of the isolobal hydride $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$. Actually, the reaction of the latter hydride with HBF_4 in dichloromethane takes place very rapidly at 233 K to give a mixture of several species containing hydride ligands. Unfortunately, all of them are thermally unstable and evolve at room temperature to give products containing no hydride ligands which could not be fully characterized, presumably arising from the elimination of dihydrogen in the low temperature intermediates. The formation of compounds **7**, in fact, can be rationalized by assuming for the neutral precursors **6** an electronic structure similar to that of the isoelectronic hydride $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$, previously determined using DFT methods [9]. According to the latter, compounds **6** should have an intermetallic π -bonding frontier orbital (HOMO-2 for the hydride complex) with the right shape and energy to bind an electrophile like the $[\text{Au}(\text{PR}_3)]^+$ cation approaching the dimetal centre from the normal to the Mo_2P plane (Scheme 2). A minimum rearrangement, no doubt driven by the aurophilic interaction thus established, would yield the final tetranuclear clusters **7**.

2.7. Reactions of the anion **1** with $\frac{1}{2}$ equivalent of HgI_2

The anion **1** reacts with half an equivalent of HgI_2 in THF to give brown solutions of the pentanuclear compound $[\text{HgMo}_4\text{Cp}_4(\mu\text{-PCy}_2)_2(\text{CO})_4]$ (**8**) (Chart 4). This compound, quite insoluble in most of the organic solvents, could be only characterized spectroscopically, since crystals suitable for an X-ray analysis could not be grown. The structure proposed for **8** is based on those of previously reported clusters having M_4Hg skeletons, such as $[\text{Fe}_2\{\mu\text{-C}=\text{CH}(\text{CH}_2\text{OCH}_3)\}(\mu\text{-S}^t\text{Bu})(\text{CO})_6]_2\text{Hg}$ [25] and $[\{\text{Ni}_2(\mu\text{-CNCH}_3)(\text{CNCH}_3)_4(\mu\text{-dppm})\}_2\text{Hg}][\text{NiCl}_4]$ [26], both of them characterized by X-ray



Scheme 2. View along the Mo–Mo axis of the interaction of the $[\text{Au}(\text{PR}_3)]^+$ cations ($\text{R} = \text{ptol}$, ^iPr) with compounds **6** to give **7** (terminal ligands omitted for clarity).

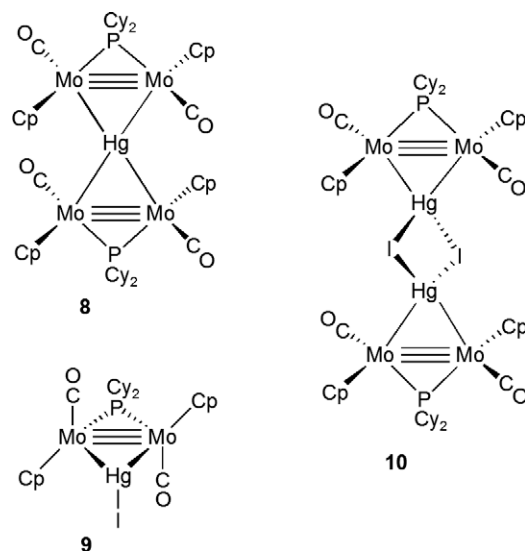


Chart 4.

diffraction methods, and that proposed for $[\text{Hg}\{\text{Mn}_2(\mu\text{-PPh}_2)(\text{CO})_8\}_2]$ [27], a cluster found to be also very insoluble in organic solvents. In all these compounds, the metal atoms around the Hg atom define a pseudotetrahedral geometry, although the angles formed by the two “ M_2Hg ” triangles can be quite different from 90° , depending on quite subtle factors. For instance, the Os_6Hg clusters $(\mu_4\text{-Hg})[\text{Os}_3(\mu\text{-PR}_2)(\mu\text{-CO})(\text{CO})_9]_2$ have been found to display quite different degrees of distortion from the ideal geometries depending on the substituents at the (remote to Hg) phosphide ligands, with the angle between Os_2Hg planes being $46.29(4)^\circ$ when $\text{R} = \text{Ph}$, and $84.93(3)^\circ$ when $\text{R} = ^i\text{Bu}$ [28].

The IR spectrum of **8** in dichloromethane solution displays a single band at 1782 cm^{-1} , this suggesting that both *trans*-dicarbonyl fragments of the cluster have similar metal environments. The ^1H NMR spectrum exhibits a single resonance for all the cyclopentadienyl ligands of the molecule, indicative of the presence of a symmetry element relating both dimolybdenum fragments. Unfortunately, a ^{13}C NMR spectrum could not be obtained for compound **8** due to its low solubility. Finally, its ^{31}P NMR spectrum exhibits a strongly deshielded resonance (234.9 ppm), as observed for all other molecules having 30-electron dimolybdenum centres reported in this work (Table 1). Because of its high electron deficiency, compound **8** would be a unique example among the reported clusters having a $\text{M}_4(\mu_4\text{-Hg})$ central core, and it could be viewed as an Hg atom coordinated by two Mo–Mo triple bonds.

2.8. Stoichiometric reactions of the anion **1** with HgI_2

When using one equivalent (instead of 0.5) of HgI_2 , the anion **1** reacts in THF to give the trinuclear cluster $[\text{Mo}_2\text{Cp}_2(\mu\text{-HgI})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**9**) which, upon removal of the solvent and addition of toluene, gives solutions containing variable amounts of the iodide-bridged complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PCy}_2)(\text{CO})_2]$ [2] and a new compound formulated as the hexanuclear complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-HgI})(\mu\text{-PCy}_2)(\text{CO})_2]_2$ (**10**), the latter being usually obtained in minor amounts. The characterization of compounds **9** and **10** was quite unsatisfactory, since none of them could be obtained as pure materials, and the structures proposed for these substances are somewhat speculative (Chart 4). In the first place, since compound **9** rapidly decomposes upon removal of the solvent (THF) we cannot rule out the possibility that **9** is actually forming an adduct with the solvent, perhaps by coordination of a THF molecule to the Hg atom, thus reducing the coordinative unsaturation of that metal

centre. In any case, the IR spectra for both compounds exhibit C–O stretching bands with the characteristic pattern of *trans*-dicarbonyl compounds. The ^{31}P NMR spectra of these compounds (Table 1) exhibit quite deshielded phosphide resonances (as invariably found for our triply-bonded dimolybdenum complexes) displaying ^{199}Hg couplings of 268 Hz (**9**) and 198 Hz (**10**), thus confirming the presence of Hg atoms bound to the dimolybdenum centres. For instance, the P–Hg coupling in the related (if electron-precise) heterometallic cluster $[\text{Mn}_2(\mu\text{-HgCl})(\mu\text{-PPh}_2)(\text{CO})_8]$ was found to be 258 Hz [27].

The dimerization of compound **9** to give **10** might just involve the formation of iodide bridges, thus achieving a pseudotetrahedral environment around the Hg atom. Precedents for this can be found in the structures of the clusters $[\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_2\text{Ph})(\mu_2\text{-Cl})(\text{HgCl})_2]$ [29] and $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_9)(\text{HgBr})_2]$ [30]. However, other alternative structures are possible.

The anion **1** also reacts easily with other binary metal halides such as CuCl, SnCl₂, and ZnCl₂, to yield in most cases solutions thought to contain the corresponding compounds of type $[\text{Mo}_2\text{Cp}_2(\mu\text{-M})(\mu\text{-PCy}_2)(\text{CO})_2]$ (M = Cu, SnCl, ZnCl) as major species, according to the available spectroscopic data. Unfortunately, these products also decomposed upon removal of the solvent (THF), to give the chloride-bridged complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-Cl})(\mu\text{-PCy}_2)(\text{CO})_2]$ [**2**] as the major organometallic species in solution.

3. Concluding remarks

In the preceding sections we have shown that the reactions of the unsaturated dimolybdenum anion **1** with electrophiles based on elements different from carbon follow analogous paths to those observed in the reactions of **1** with hydrocarbon halides, that is, binding of the electrophile at the dimetal site, binding at the O(carbonyl) atoms, and electron-transfer. Reactions with electrophiles based on soft metallic elements (Sn, Au, Hg) tend to incorporate the incoming fragment to the intermetallic region, whereas those reactions with electrophiles based on harder or more oxophilic elements (Si, Ti, Zr) lead to the incorporation of the electrophile at the O site of the bridging carbonyl ligands. At present, the factors favouring the electron-transfer processes responsible for the formation of the halide-bridged complexes $[\text{Mo}_2\text{Cp}_2(\mu\text{-X})(\mu\text{-PCy}_2)(\text{CO})_2]$, a dominant process in the reactions of **1** with several Mo, Re, Fe and Ir carbonyl halide complexes, are not clearly understood. Finally, the fact that the anion **1** reacts with chlorophosphines to give mixed-phosphide derivatives apparently does not fit into the above scheme, since this would lead us to rather predict for the phosphorus-based electrophiles a chemical behaviour comparable to that of the silicon halides.

4. Experimental

All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use [31]. Tetrahydrofuran solutions of the Li⁺ salt of the anion $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$ (**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 65–70 °C. Chromatographic separations were carried out using jacketed columns cooled by tap water at ca. 288 K or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial aluminium 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 CaF₂ windows and are referred to as $\nu(\text{CO})$. Nuclear Magnetic Resonance (NMR) spectra were routinely recorded at 300.13 (^1H), 121.50 ($^{31}\text{P}\{^1\text{H}\}$) or 75.47 MHz ($^{13}\text{C}\{^1\text{H}\}$), at 290 K in CD₂Cl₂ solutions unless otherwise stated. For some of the most sensitive products, ^{31}P NMR spectra were recorded directly using the crude reaction mixtures in non-deuterated solvents. In those cases, a coaxial tube containing D₂O was immersed into the solution and the data are then given as recorded in solvent/D₂O. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^1H , ^{13}C) or external 85% aqueous H₃PO₄ solutions (^{31}P). Coupling constants (*J*) are given in Hertz.

4.1. Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-P(OEt)}_2)(\text{CO})_2]$ (**2**)

Neat ClP(OEt)₂ (30 μL , 0.28 mmol) was added to a solution containing ca. 0.07 mmol of the lithium salt of the anion **1** in tetrahydrofuran (10 mL), and the mixture was stirred for 2 h to yield a brown solution. After removal of the solvents under vacuum, the residue was chromatographed through alumina (activity IV). A green fraction was eluted with dichloromethane–petroleum ether (1:4) which gave, after removal of solvents under vacuum, compound **2** as a green microcrystalline solid (25 mg, 46%). *Anal. Calc.* for C₂₉H₄₄Cl₂Mo₂O₃P (**2** · CH₂Cl₂): C, 44.58; H, 5.68. *Found*: C, 44.84; H, 5.39%. ^1H NMR δ 5.40 (d, $J_{\text{PH}} = 0.5$, Cp, 10H), 4.28, 3.98 (2 × m, OCH₂, 2 × 2H), 2.50–1.10 (m, Cy, 22H), 1.37 (t, $J_{\text{HH}} = 7$, CH₃, 6H).

4.2. Preparation of solutions of $[\text{Mo}_2\text{Cp}_2(\mu\text{-COSiPh}_3)(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**3a**)

Neat ClSiPh₃ (0.060 g, 0.20 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.06 mmol) in tetrahydrofuran (10 mL), and the mixture was stirred for 24 h to give a red-brown solution containing compound **3a** as the major species. This compound turned out to be very air- and moisture-sensitive, and it could not be isolated nor further purified.

4.3. Preparation of solutions of $[\text{Mo}_2\text{Cp}_2(\mu\text{-COSiMe}_3)(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**3b**)

Neat ClSiMe₃ (20 μL , 0.20 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL), and the mixture was stirred for 5 min to give a red-brown solution containing compound **3b** as the major species. This compound also turned out to be very air- and moisture-sensitive, and it could not be isolated nor further purified.

4.4. Preparation of $[\text{Mo}_2\text{Cp}_2(\mu\text{-SnPh}_3)(\mu\text{-PCy}_2)(\text{CO})_2]$ (**4a**)

Solid ClSnPh₃ (0.025 g, 0.07 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL), and the mixture was stirred for 20 h at room temperature to give a brown solution containing compound **4a** as the major species. After removal of the solvent under vacuum, the residue was chromatographed on an alumina column (activity IV) at 258 K. A brown-greenish fraction was eluted with dichloromethane–petroleum ether (1:8), this yielding, after removal of solvents under vacuum, compound **4a** as a brown-greenish solid (0.022 g, 46%). Spectroscopic data for this product were identical to those reported for the same species in the Ref. [10].

4.5. Preparation of solutions of $[\text{Mo}_2\text{Cp}_2(\mu\text{-SnClPh}_2)(\mu\text{-PCy}_2)(\text{CO})_2]$ (**4b**)

Solid Cl₂SnPh₂ (0.035 g, 0.10 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL) to give instantaneously a brown solution containing

compound **4b** as the major species. This compound turned out to be very unstable, and it decomposed rapidly upon the usual work-up (filtration, crystallization, etc.) so it could not be obtained as a pure material.

4.6. Preparation of solutions of $[\text{Mo}_2\text{Cp}_2(\mu\text{-COTiClCp}_2)(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**5a**)

Solid $[\text{TiCl}_2\text{Cp}_2]$ (0.015 g, 0.06 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL) and the mixture was stirred to give instantaneously a black solution containing compound **5a** as the major species. This compound turned out to be highly moisture-sensitive, rapidly reacting with trace amounts of water to give $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$ as the main decomposition product, so it could not be isolated as a pure material. $\nu(\text{CO})$ (THF): 1688 cm^{-1} .

4.7. Preparation of solutions of $[\text{Mo}_2\text{Cp}_2(\mu\text{-COZrClCp}_2)(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**5b**)

Solid $[\text{ZrCl}_2\text{Cp}_2]$ (0.040 g, 0.14 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL), and the mixture was stirred for 20 min to give a red-brown solution containing compound **5b** as the major species, along with variable amounts of $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$, the latter being formed by the hydrolysis of the former. This compound also is highly moisture-sensitive, so it could not be isolated as a pure material. $\nu(\text{CO})$ (THF): 1692 cm^{-1} .

4.8. Preparation of $[\text{AuMo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2\{\text{P}(\text{ptol})_3\}]$ (**6a**)

Solid $[\text{AuCl}\{\text{P}(\text{ptol})_3\}]$ (0.027 g, 0.05 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL) to give instantaneously a brown solution. After removal of the solvent under vacuum, the residue was extracted with toluene–petroleum ether (1:1) and the extract was filtered using a cannula. The solvents were then removed under vacuum to give a brown-greenish solid containing **6a** as the major product. All attempts to further purify this material resulted in its progressive decomposition. $^1\text{H NMR}$ (C_6D_6) δ 7.60 (dd, $J_{\text{PH}} = 11$, $J_{\text{HH}} = 8$, $\text{H}^2\text{-Ph}$, 6H), 6.91 (d, $J_{\text{HH}} = 8$, $\text{H}^3\text{-Ph}$, 6H), 5.09 (s, Cp, 10H), 2.65–1.20 (m, Cy, 22H), 1.97 (s, CH_3 , 9H).

4.9. Preparation of $[\text{AuMo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2\{\text{P}^i\text{Pr}_3\}]$ (**6b**)

Solid $[\text{AuCl}\{\text{P}^i\text{Pr}_3\}]$ (0.024 g, 0.06 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.06 mmol) in tetrahydrofuran (10 mL) to give instantaneously a brown solution. After removal of the solvent under vacuum, the residue was washed with petroleum ether ($2 \times 10\text{ mL}$) and extracted with toluene ($2 \times 7\text{ mL}$). The extracts were filtered using a cannula and the solvent was then removed from the filtrate to give a brown solid containing compound **6b** as the major product. All attempts to further purify this material resulted in its progressive decomposition. $^1\text{H NMR}$ (400.13 MHz, tol-d_8) δ 4.99 (s, Cp, 10H), 2.60–1.20 (m, Cy, 22H), 1.78 (m, CH, 3H), 0.98 (dd, $J_{\text{PH}} = 15$, $J_{\text{HH}} = 7$, CH_3 , 18H).

4.10. Preparation of $[\text{Au}_2\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2\{\text{P}(\text{ptol})_3\}_2][\text{PF}_6]$ (**7a**)

A solution of $[\text{Au}\{\text{P}(\text{ptol})_3\}(\text{THF})][\text{PF}_6]$ was prepared in situ by stirring a mixture of TIPF_6 (0.017 g, 0.05 mmol) and $[\text{AuCl}\{\text{P}(\text{ptol})_3\}]$ (0.027 g, 0.05 mmol) in tetrahydrofuran (5 mL) for 10 min. The solution was filtered using a cannula and added to a crude solution of **6a** (ca. 0.05 mmol, prepared as described above) in tetrahydrofuran (5 mL), and the mixture was then stirred for 5 min to give a green solution. The solvent was then removed under vac-

uum and the green residue was washed with petroleum ether ($3 \times 8\text{ mL}$), and extracted with THF–dichloromethane (1:10). The extracts were then filtered through alumina (activity IV) and the solvents were removed from the filtrate to give compound **7a** as a green solid (0.043 g, 50%). *Anal. Calc.* for $\text{C}_{66}\text{H}_{74}\text{Au}_2\text{F}_6\text{Mo}_2\text{O}_2\text{P}_4$ (**7a**): C, 46.01; H, 4.33. *Found*: C, 45.83; H, 4.17%. $^1\text{H NMR}$ (CDCl_3) δ 7.28 (dd, $J_{\text{PH}} = 12$, $J_{\text{HH}} = 7$, $\text{H}^2\text{-Ph}$, 12H), 7.15 (d, $J_{\text{HH}} = 7$, $\text{H}^3\text{-Ph}$, 12H), 4.86 (s, Cp, 10H), 2.80–1.20 (m, Cy, 22H), 2.39 (s, CH_3 , 18H).

4.11. Preparation of $[\text{Au}_2\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2\{\text{P}^i\text{Pr}_3\}_2][\text{PF}_6]$ (**7b**)

The procedure is identical to that described above for **7a** but using $[\text{AuCl}\{\text{P}^i\text{Pr}_3\}]$ (0.027 g, 0.06 mmol) instead, along with TIPF_6 (0.023 g, 0.07 mmol) and a solution of **6b** (ca. 0.06 mmol). In that way, compound **7b** was obtained as a green solid (0.057 g, 66%). *Anal. Calc.* for $\text{C}_{42}\text{H}_{74}\text{Au}_2\text{F}_6\text{Mo}_2\text{O}_2\text{P}_4$: C, 35.16; H, 5.20. *Found*: C, 35.03; H, 5.29%. $^1\text{H NMR}$ δ 4.94 (s, Cp, 10H), 2.75–1.25 (m, Cy, 22H), 2.53 (m, CH, 6H), 1.38, 1.37 ($2 \times$ dd, $J_{\text{PH}} = 16$, $J_{\text{HH}} = 7$, CH_3 , $2 \times 18\text{H}$).

4.12. Preparation of $[\text{HgMo}_4\text{Cp}_4(\mu\text{-PCy}_2)_2(\text{CO})_4]$ (**8**)

Solid HgI_2 (0.011 g, 0.024 mmol) was added to a solution (10 mL) of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL) to give instantaneously a brown suspension. After removal of the solvent under vacuum, the brown residue was extracted with dichloromethane–petroleum ether (1:1) and the extracts were filtered through alumina (activity IV). Removal of solvents from the filtrate gave compound **8** as a brown microcrystalline solid (0.030 g, 85%). *Anal. Calc.* for $\text{C}_{48}\text{H}_{64}\text{HgMo}_4\text{O}_4\text{P}_2$: C, 42.66; H, 4.77. *Found*: C, 42.95; H, 5.12%. $^1\text{H NMR}$ (CDCl_3) δ 5.18 (s, Cp, 20H), 2.50–1.00 (m, Cy, 44H).

4.13. Stoichiometric reaction of **1** with HgI_2

Solid HgI_2 (0.022 g, 0.048 mmol) was added to a solution of the lithium salt of the anion **1** (ca. 0.05 mmol) in tetrahydrofuran (10 mL) to give instantaneously a brown solution of the unstable cluster $[\text{Mo}_2\text{Cp}_2(\mu\text{-HgI})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**9**). After removal of the solvent under vacuum, the brown residue was extracted with toluene ($2 \times 10\text{ mL}$) and filtered through diatomaceous earth to give a green solution containing variable amounts of $[\text{Mo}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PCy}_2)(\text{CO})_2]$ [**2**] and $[\text{Mo}_2\text{Cp}_2(\mu\text{-HgI})(\mu\text{-PCy}_2)(\text{CO})_2]_2$ (**10**). All attempts to isolate compound **10** as a pure material were unsuccessful. *Data for compound 10*: $^1\text{H NMR}$ δ 5.04 (s, Cp, 20H); the resonances corresponding to the Cy groups were overlapped with those of $[\text{Mo}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PCy}_2)(\text{CO})_2]$. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.52 MHz): δ 255.6 (s, $\mu\text{-PCy}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF/ D_2O) δ 251.4 (s, $J_{\text{P-199Hg}} = 198$, $\mu\text{-PCy}_2$).

4.14. X-ray structure determination of compound **7b**

Crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of a layer of petroleum ether into a saturated solution of the compound in dichloromethane at room temperature. The X-ray intensity data were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation. The software APEX [32] was used for collecting frames with the omega/phi scans measurement method. The collected frames were then processed for integration by the software SAINT [33], and a multi-scan absorption correction was applied with SADABS [34]. Using the program suite WINGX [35] the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least squares on F^2 with SHELXL97 [36]. The cation of the compound was found to have all isopropyl groups attached to P(1) and the cyclopentadienyl ligand bound to Mo(2)

Table 3
Crystal data for compound **7b**.

Molecular formula	C ₄₂ H ₇₄ Au ₂ F ₆ Mo ₂ O ₂ P ₄
Molecular weight	1434.71
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Radiation (λ , Å)	0.71073
<i>a</i> (Å)	9.8068(2)
<i>b</i> , (Å)	14.5526(2)
<i>c</i> (Å)	17.6160(3)
α (°)	88.869(1)
β (°)	77.136(1)
γ (°)	83.474(1)
<i>V</i> (Å ³)	2435.04(7)
<i>Z</i>	2
<i>D</i> _{calc} , g cm ⁻³	1.957
Absorption coefficient (mm ⁻¹)	6.697
Temperature (K)	120
θ Range (°)	1.19–28.32
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	–12, 13; –19, 19; 0, 23
Reflections collected	66464
Independent reflections	12065 [<i>R</i> _{int} = 0.0410]
Reflection with <i>I</i> > 2 σ (<i>I</i>)	10610
<i>R</i> indexes (<i>I</i> > 2 σ (<i>I</i>)) ^a	<i>R</i> ₁ = 0.0219, <i>wR</i> ₂ = 0.0438 ^b
<i>R</i> indexes (all data) ^a	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0453 ^b
Goodness-of-fit (GOF)	1.063
Restraints/parameters	0/528
$\Delta\rho$ (maximum, minimum), e Å ⁻³	1.063, –1.186

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

^b $a = 0.0161$, $b = 1.1672$.

disordered in two positions. Occupancy factors of 0.5/0.5 and 0.65/0.35 gave a reasonable fit. All non-hydrogen atoms were refined anisotropically, except the disordered carbon atoms, which were refined isotropically. Hydrogen atoms were fixed at calculated positions and were given an overall isotropic thermal parameter. Crystallographic data and structure refinement details for **7b** are collected in Table 3.

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Appendix A. Supplementary data

CCDC 743404 contains the supplementary crystallographic data for compound **7b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via 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.2009.09.023](https://doi.org/10.1016/j.jorganchem.2009.09.023).

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