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Trapping of Hemiquinone Radicals at Mo and P Sites by Phosphide-Bridged Dimolybdenum Species: Chemistry of Complexes $[Mo_2(\eta^5\text{-}C_5H_5)_2(OC_6H_4OH)(\mu\text{-}PR_2)(CO)_4]$ and $[Mo_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}PR(OC_6H_4OH)\}(CO)_4]^-$ (R = Cy, Ph)

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The phosphide-bridged dimolybdenum complexes (H-DBU)$[Mo_2Cp_2(\mu\text{-}PR_2)(CO)_4]$ (R= Cy, Ph; DBU = 1,8-diazabicyclo[5.4.0.]undec-7-ene) react with *p*-benzoquinone to give the hemiquinone complexes $[Mo_2Cp_2(OC_6H_4\text{-}OH)(\mu\text{-}PR_2)(CO)_4]$. The latter experience facile homolytic cleavage of the corresponding Mo–O bonds and react readily at room temperature with HSPh or S_2Ph_2 to give the thiolate complexes $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SPh)(CO)_4]$ or $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}SPh)(CO)_2]$. In contrast, PRH-bridged substrates experience overall insertion of quinone into the P–H bond to give the anionic compounds (H-DBU)$[Mo_2Cp_2\{\mu\text{-}PR(OC_6H_4OH)\}(CO)_4]$, which upon acidification yield the corresponding neutral hydrides. The cyclohexyl anion experiences rapid nucleophilic displacement of the hemiquinone group by different anions ER^- (ER = OH, OMe, OC_4H_5, OPh, SPh) to give novel anionic compounds (H-DBU)$[Mo_2Cp_2\{\mu\text{-}PCy(ER)\}(CO)_4]$, which upon acidification yield the corresponding neutral hydrides. The structure of four of these hydride complexes [PPh(OC_6H_4OH), PCy(OH), PCy(OMe), and PCy(OPh) bridges] was determined by X-ray diffraction methods and confirmed the presence of cis and trans isomers in several of these complexes. In addition, it was found that the hydroxyphosphide anion $[Mo_2Cp_2\{\mu\text{-}PCy(OH)\}(CO)_4]^-$ displays in solution an unprecedented tautomeric equilibrium with its hydride-oxophosphinidene isomer $[Mo_2Cp_2(\mu\text{-}H)\{\mu\text{-}PCy(O)\}(CO)_4]^-$.

Introduction

Quinones are an important class of ubiquitous compounds that have widespread relevance in biology and chemistry.[1] Their fundamental role in the biochemistry of living cells is well established and evolves from their ability to play a pivotal role in electron- and proton-transfer reactions.[2] They serve as hormones and pigments and are used as pharmaceuticals, such as antibiotics and anticancer drugs.[3] Quinones are also suitable dehydrogenation agents for the aromatization of partially hydrogenated aromatic or heteroaromatic compounds.[4] The dual role of quinones as redox relays and proton shuttles has been the subject of numerous electrochemical studies.[5] In solution, quinones are reduced in two successive one-electron steps to form the radical anion ($\cdot Q^-$) and

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hydroquinone dianion (Q^{2-}). The anions thus formed couple easily with one or two protons to yield the radical hemiquinone (·QH) and the hydroquinone molecule (QH_2), respectively. These species can act as ligands by binding to metal centers either through their oxygen atoms (σ-coordination) or through their hydrocarbon rings (π-coordination). Both types of binding can be combined to achieve extended metal−organometallic coordination networks with potential applications as functional materials.[6] Recently, quinones have been found to experience interesting reactions, some of them in the vicinity of metal centers, such as insertion on S−S, P−C, or P−H bonds. Thus, Adams et al. have recently reported a heterodinuclear disulfide complex which reacts with *p*-benzoquinone to give a *p*-benzoquinonedithiolate ligand after S−S and C−H bond cleavages,[7] while Bertrand et al. have reported the insertion of an *o*-quinone into the P−C bond of an (amino)(phosphino)carbene.[8] Finally, Malisch et al. have reported the first example of hydrophosphination of *p*-benzoquinone, this occurring at a mononuclear iron phosphine complex.[9]

Recently we have found that the use of *p*-benzoquinone as oxidant toward the $[H\text{-}DBU]^+$ salt of the anionic complex $[MoCp(CO)_2\{P(O)R^*\}]^-$ ($R^* = 2,4,6\text{-}C_6H_2{}^tBu_3$, $Cp = \eta^5\text{-}C_5H_5$, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) results in hemiquinone incorporation at the P site of the oxophosphinidene ligand to give, after spontaneous H^+ transfer from the $(H\text{-}DBU)^+$ counterion, the neutral compound $[MoCp\{\kappa^2\text{-}OP(OC_6H_4OH)R^*\}(CO)_2]$, which is the first complex reported to have a P,O-bound phosphonite ligand.[10] This is in contrast with the result of the reaction with an innocent oxidant such as $[FeCp_2]^+$, which results in simple electron transfer and coupling of the neutral radicals thus generated.[10] We have shown previously that simple removal of electrons with $[FeCp_2]^+$ from suitable dinuclear complexes stabilized by diphosphine or phosphide bridging ligands can be an excellent synthetic route for highly reactive diamagnetic or paramagnetic binuclear species of Mo, W, or Fe.[11] We then considered the use of *p*-benzoquinone as oxidant on some of the above dinuclear substrates to explore the possibility of incorporating the hemiquinone radical to these binuclear substrates. In this paper, we report the preparation and reactions of the salts $[H\text{-}DBU][Mo_2Cp_2(\mu\text{-}PR_2)(CO)_4]$ and $[H\text{-}DBU][Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]$ with *p*-benzoquinone (R= Cy, Ph). The PPh_2-bridged anion has been recently reported to be electrochemically oxidized at quite low potentials to give first the 33-electron radical $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ and then the unstable unsaturated cation $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]^+$, a process that can be reproduced using the cation $[FeCp_2]^+$.[11a] As it will be shown, the oxidation reactions now being reported result in either O-coordination of the hemiquinone radical to the metal center or, if a P−H bond is present in the phosphide bridge, its incorporation at the phosphorus site. In both cases, the Mo- or P-bound hemiquinone group is easily replaced by other groups such as hydroxo, alkoxo, or thiolate groups, which adds synthetic value to the newly formed species.

Results and Discussion

Formation of Starting Anions and their Reactions with *p*-Benzoquinone. Hydride complexes of the type $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ are easily deprotonated by a variety of basic or reducing reagents to give the corresponding anions $[Mo_2Cp_2(\mu\text{-}PRR')(CO)_4]^-$.[11a,12,13] We have shown that a strong base such as DBU (DBU = 1,8-diazabicyclo[5.4.0.]-undec-7-ene) acts as an efficient deprotonating reagent for the hydride complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (**1b**) while at the same time providing a relatively large cation, $(H\text{-}DBU)^+$, which facilitates the manipulation of the resulting salt $(H\text{-}DBU)[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ (**3b**).[11a] Analogously, the hydride compounds $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**1a**)[14] and $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR)(CO)_4]$ [R = Cy (**2a**),[14] R = Ph (**2b**)[15]] react with DBU rapidly in THF to give the corresponding salts $(H\text{-}DBU)[Mo_2Cp_2(\mu\text{-}PCy_2)(CO)_4]$ (**3a**) and $(H\text{-}DBU)[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]$ [R = Cy (**4a**), R = Ph (**4b**)] in quantitative yield (Scheme 1), as shown by IR and ^{31}P NMR spectroscopy. These reactions are faster for PHR-bridged complexes, compared to the PR_2-bridged ones (see Experimental Section), which seems to point to some steric

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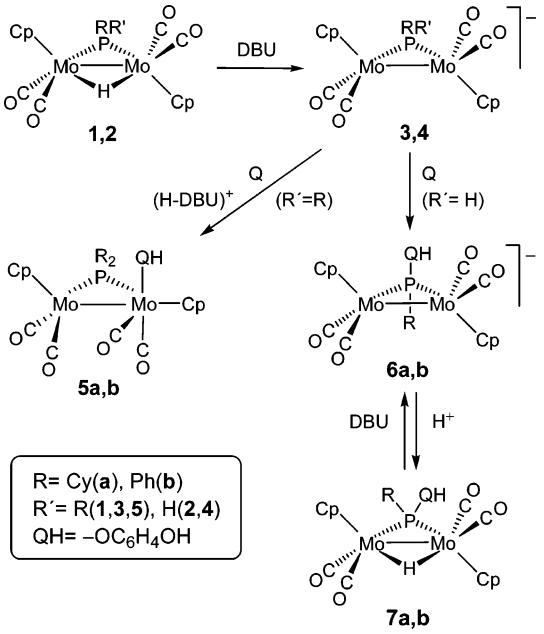
Scheme 1

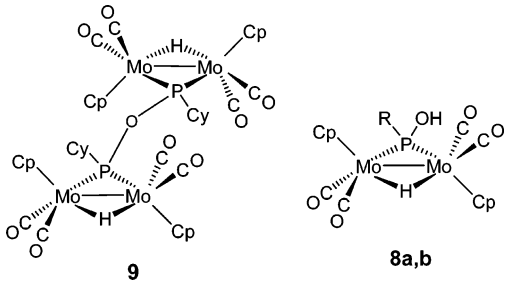


hindrance in the approach to the dimetal center of a relatively bulky base such as DBU. The structures of these anionic complexes are strongly related to those of their neutral derivatives and will be discussed later on.

Although the $(H\text{-}DBU)^+$ salts **3a**, **3b**, **4a**, and **4b** are easily generated in tetrahydrofuran solution, they are still quite air-sensitive, and no attempts were made to isolate these materials. Instead, their reactivity could be easily investigated using these solutions prepared in situ. Indeed, reactions with *p*-benzoquinone proceed rapidly at 243 K, the result being strongly dependent on the presence of P−H bonds in the phosphide ligand bridging the dimetal center (Scheme 1). Thus, the PR_2-bridged anions **3a** and **3b** give the neutral alkoxo complexes $[Mo_2Cp_2(OC_6H_4OH)(\mu\text{-}PR_2)(CO)_4]$ [R = Cy (**5a**), R = Ph (**5b**)], having a *p*-hydroxyphenoxo (hydroquinone) ligand terminally bound to a Mo atom. In contrast, the PHR-bridged anions **4a** and **4b** give the alkoxyphosphide anionic complexes $(H\text{-}DBU)[Mo_2Cp_2\{\mu\text{-}PR(OC_6H_4OH)\}(CO)_4]$ [R = Cy (**6a**), R = Ph (**6b**)]. The neutral complexes **5a** and **5b** are rather unstable, and only **5b** could be isolated as a reasonably pure solid. Interestingly, they decompose upon chromatography on alumina even at 253 K to give the corresponding radicals $[Mo_2Cp_2(\mu\text{-}PR_2)(CO)_4]$ (previously characterized by us when R = Ph),[11a] which is suggestive of the occurrence of an unexpected homolytic cleavage of the Mo−O bond, a matter to be discussed later.

For the anionic compounds, **6a** and **6b** are quite reactive species, and no attempts to isolate them were made. Instead, these complexes were converted in situ into the corresponding hydride derivatives $[Mo_2Cp_2(\mu\text{-}H)\{\mu\text{-}PR(OC_6H_4OH)\}(CO)_4]$ (**7a** and **7b**) through reaction with $[NH_4]PF_6$. Compounds **6** and **7** are formally derived from the insertion of *p*-benzoquinone into the P−H bond of a phosphide ligand. This is a very unusual reaction, and it has been observed previously only in a secondary phosphine ligand coordinated to an iron center,[9] as mentioned above. Moreover, it should be noted that free primary phosphines do not experience this

Chart 1



insertion process. Instead, they react with *p*-benzoquinone to give hydroquinone and biphosphines.[16]

Even when $[NH_4]PF_6$ is added to freshly prepared solutions of complexes **6**, some decomposition of these anions could not be avoided, which explains the appearance in the corresponding reaction mixtures of small and variable amounts of other products such as the hydroxyphosphide complexes $[Mo_2Cp_2(\mu\text{-}H)\{\mu\text{-}PR(OH)\}(CO)_4]$ (**8a** and **8b**) and the tetranuclear product $[\{Mo_2Cp_2(CO)_4(\mu\text{-}H)\}_2(\mu\text{-}Cy\text{-}POPCy)]$ (**9**) (Chart 1). These minor species could be isolated as pure materials after chromatography of the reaction mixture on alumina. The formation of compounds **8** is the result of the hydrolysis of the anions **6**. Indeed, a separate experiment showed that the addition of water to a basic solution of **6a** followed by acidification with $[NH_4]PF_6$ led to the hydride **8a** almost quantitatively; presumably, the phenyl compound **8b** is formed in a similar way. However, the origin of compound **9** is not so clear. Although this species might be derived either from **8a** by dehydration or directly from **6a** by reaction with oxygen, we have found no experimental conditions to prepare this compound in a selective way.

Reaction Pathways. The reaction of *p*-benzoquinone with the anionic complexes **3** and **4** are very fast even at 243 K, and no intermediate species could be detected. However, since the electrochemical oxidation of **3b** occurs at potentials as low as −0.53 V (PPN^+ salt, dichloromethane solution),[11a] it is likely that the reactions of compounds **3** and **4** with *p*-benzoquinone (Q in Scheme 2) are initiated by an electron-transfer step to yield the corresponding radicals $[Mo_2Cp_2(\mu\text{-}PRR')(CO)_4]$ (**A**) and the hemiquinonate anion ($\cdot Q^-$) because the redox potential for the $Q/\cdot Q^-$ couple is above 0 V (although this is significantly dependent on solvent and pH).[5a,b] The hemiquinonate anion then would be protonated by the $(H\text{-}DBU)^+$ cation despite unfavorable thermodynamics (the aqueous pK_a values for $(H\text{-}DBU)^+$ and for ·QH are ∼12 and 4, respectively)[17,5a] to give the hemiquinone radical (·QH, Scheme 2). Of course this is only possible if further reactions (with equilibrium constants above $\sim 10^8$) take place. On the basis of the products formed, we conclude that the evolution of the dimolybdenum radicals thus generated would be critically dependent on the presence of a P−H bond in the phosphide ligand. In the absence of such a bond (PR_2 bridges), the dimolybdenum radicals would just couple to

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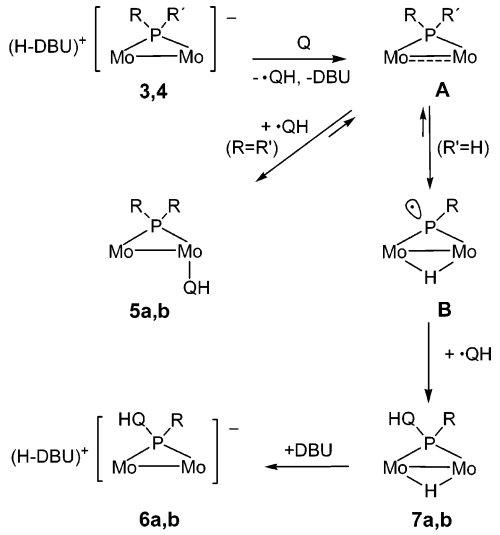
Scheme 2. Reaction Pathways Proposed for the Reactions of *p*-Benzoquinone (Q) with the Anionic Complexes **3** and **4** (QH = hemiquinone, Mo = $MoCp(CO)_2$)



the hemiquinone radical via the metal and oxygen atoms to give the hemiquinone complexes **5a** and **5b**. This is not surprising in view of the known chemistry and structural data of $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$, which are characteristic of a metal-centered radical.[11c,a] Interestingly, this coupling process seems to be reversible, since the attempted chromatography of compounds **5** on alumina columns gives the corresponding dimolybdenum radicals, as stated above. This in turn will be of help in understanding the dynamic behavior of these compounds in solution (see below).

When the starting substrate has a PHR bridge, we propose that the phosphide-bridged radical **A** would be in equilibrium with the corresponding hydride-phosphinidene tautomer **B**, this following from the oxidative addition of the P−H bond to the unsaturated metal center. As a result, the unpaired electron would be likely located at the bridging phosphorus atom, thus explaining the formation of alkoxyphosphide derivatives **7a** and **7b** by radical P−O coupling at this site. Finally, since DBU is present in the medium, deprotonation would then occur to give the anions **6a** and **6b**, as shown by independent experiments. Although there is no strict precedent in the literature for the proposed phosphide/hydrido-phosphinidene equilibrium at a paramagnetic substrate, we recall that a related P−H bond cleavage has been recently proposed by us to occur at the unsaturated dimolybdenum cations $[Mo_2Cp_2(\mu\text{-}PHR)(CO)_4]^+$ (here involving trigonal phosphinidene groups).[18] Interestingly, the reverse reaction (P−H reductive elimination) seems to be thermodynamically favored at anionic derivatives containing bent phosphinidene and hydride bridges, as observed for the cluster $[Os_3(\mu\text{-}H)(\mu_2\text{-}PPh)(CO)_{10}]^-$[19a,b] and proposed for the dimanganese anion $[Mn_2(\mu\text{-}H)(\mu\text{-}PCy)(CO)_8]^-$.[19c] On the other hand, the formation of a bent phosphinidene group bearing an unpaired electron is itself almost unprecedented. We note, however, the extensive studies performed on the diiron complexes $[Fe_2\{\mu\text{-}(R_2N)P(CO)P(NR_2)\}(CO)_6]$ which, upon CO extrusion are thought to generate phosphorus-centered phosphinidene diradicals $[Fe_2\{\mu\text{-}P(NR_2)\}_2(CO)_6]$, which are able to react with a great variety of single H−X and multiple C−X bonds (X= O, N, etc.).[20] Given the reversible character of the elementary steps proposed, the formation of the alkoxyphosphide compounds **7a** and **7b** instead of the corresponding isomeric alkoxocomplexes $[Mo_2Cp_2(OC_6H_4OH)(\mu\text{-}PHR)(CO)_4]$ (not detected) might have essentially a thermodynamic origin, since the generation of the latter requires the formation of a relatively weak Mo−O bond (soft/hard combination) compared to the strong P−O bond involved in the formation of hydrides **7a** and **7b**. Obviously this difference in not compensated by the distinct strengths of the respective Mo−H and P−H bonds.

Table 1. IR and $^{31}P\{^1H\}$ NMR Data for New Non-Hydride Compounds

compound	ν(CO)[a] (cm^{-1})	δ(P)[b]
$[Mo_2Cp_2(OC_6H_4OH)(\mu\text{-}PCy_2)(CO)_4]$ (**5a**)	1974 (vs), 1912 (vs), 1852 (m)	210.0
$[Mo_2Cp_2(OC_6H_4OH)(\mu\text{-}PPh_2)(CO)_4]$ (**5b**)	1981 (vs), 1922 (vs), 1862 (m)	182.5 (br)[c,d]
$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SPh)(CO)_4]$ (**10**)	1933 (s), 1854 (m)	−71.8
$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SPh)(CO)_2]$ (**11a**)	1882 (w, sh), 1844 (vs)	127
$[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_2]$ (**11b**)	1889 (w, sh), 1852 (vs)[e]	107.3

[a] Recorded in tetrahydrofuran solution, unless otherwise stated. [b] Recorded in CD_2Cl_2 solution at 290 K and 121.50 MHz unless otherwise stated; δ relative to external 85% aqueous H_3PO_4. [c] Recorded in tetrahydrofuran solution with external D_2O. [d] When recorded at 213 K and 162.0 MHz in CD_2Cl_2 solution, two resonances are present at 185.1 (isomer A) and 184.9 ppm (isomer B). [e] Recorded in dichloromethane solution.

Structure of the Hemiquinone Complexes 5. As stated above, compounds **5** are rather unstable species, and their structural characterization has been made only on the basis of spectroscopic data in solution. Their IR spectra (Table 1) exhibit C−O stretching bands very similar (both in frequency and intensity) to those of the chloro-complex $[Mo_2ClCp_2(\mu\text{-}PHPh)(CO)_4]$,[18] and therefore a similar structure is assumed for these alkoxocomplexes, with the hemiquinone ligand positioned cis with respect to the phosphide ligand, which in turn acts as the unique bridge between the inequivalent $MoCp(CO)_2$ moieties. In addition, compound **5b** was found to exhibit dynamic behavior in solution (no detailed spectroscopic data were collected for the less-stable dicyclohexyl compound **5a**). This is readily apparent because the ^1H NMR spectrum at room temperature exhibits just one broad cyclopentadienyl resonance at 5.1 ppm, inconsistent with the proposed structure. The analysis of the low-temperature NMR data (Table 1 and Experimental Section) reveals the presence of two isomers, **A** and **B**, interconverting

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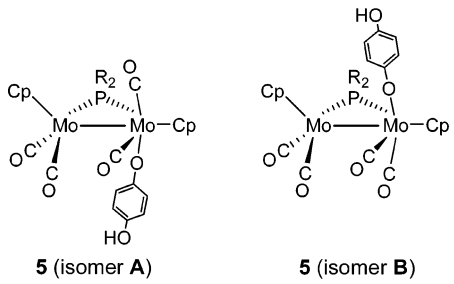
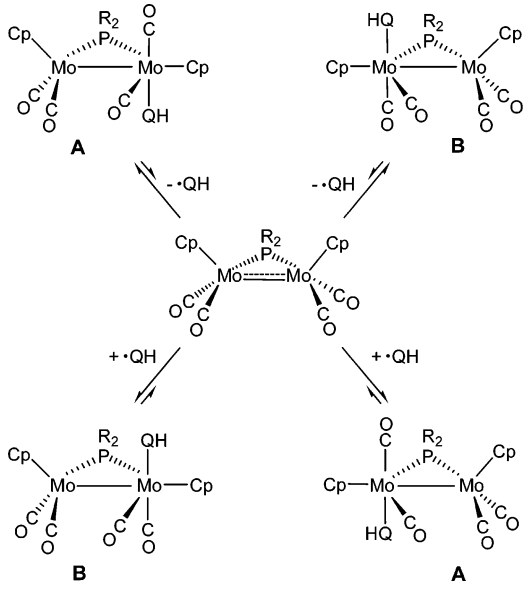
Chart 2



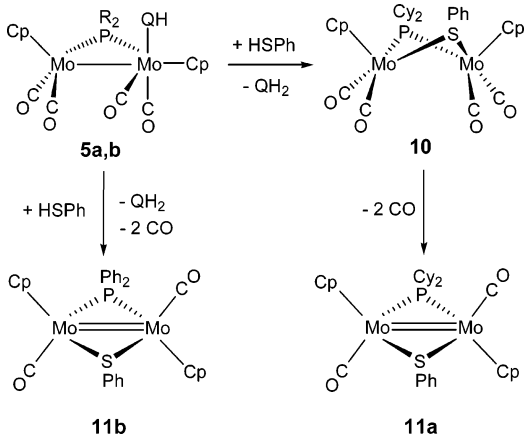
rapidly on the NMR time scale (Chart 2). Separate ^{31}P, ^{1}H, and ^{13}C NMR resonances could be observed at 243 K, (**A**/**B** ratio = 5 at this temperature), which revealed that both isomers display inequivalent cyclopentadienyl resonances, thus suggesting the terminal coordination of the hemiquinone ligand in both cases. In agreement with this, the ^{31}P chemical shifts of ∼180 ppm are the values expected for dicyclohexylphosphide ligands bridging single Mo−Mo bonds.[14,21] The ^{13}C NMR spectrum of the major isomer **A** is fully consistent with the crystal structure of the model complex $[Mo_2ClCp_2(\mu\text{-PHPh})(CO)_4]$, because it displays four distinct carbonyl resonances in the terminal region at 226.7 (s, br), 241.6 (s), 241.7 (d, J_{CP} = 20 Hz), and 248.8 (d, J_{CP} = 17 Hz) ppm, their multiplicity being consistent respectively with the presence of two ligands cis and two other trans with respect to the phosphorus atom.[18] From the available data for the minor isomer, we conclude that its structure would be quite similar to that of the major species. In fact, we propose that isomer **B** has the same structure as **A**, but with the hemiquinone ligand and the Cp group of the adjacent metal center placed on the same side of the Mo_2P plane (Chart 2). The presence of two asymmetric isomers, however, does not explain the appearance of just a single cyclopentadienyl resonance at room temperature for compound **5b**. Although we have not studied this process in detail, we propose that a homolytic cleavage of the P−O bond (actually, the reverse of the formation process) can take place in solution to a small extent (Scheme 3). This would generate small amounts of hydroquinone (·QH) and the tetracarbonyl radical $[Mo_2Cp_2(\mu\text{-PPh}_2)(CO)_4]$, shown previously to display a cisoid arrangement of its $MoCp(CO)_2$ metal fragments.[11a] Recombination of hemiquinone with that binuclear radical could happen at either of the molybdenum atoms, thus justifying the averaging of the inequivalent Cp resonances. In addition, recombination of hemiquinone could also take place on either side of the Mo_2P plane, thus justifying the interconversion between isomers **A** and **B** (the major isomer **A** is proposed to be the one involving minimum repulsions between hemiquinone and Cp groups, Chart 2). Although the above hypothesis is consistent with the chemical behavior of compounds **5** (decomposition on alumina columns and reactions with HSPh or S_2Ph_2), other possibilities such as intramolecular rearrangements cannot be excluded at this time.

(21) Carty, A. J.; MacLaughlin. S. A.; Nucciarone, D. In *Phosphorus 31 NMR Spectrscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 16.

Scheme 3. Dynamic Process Proposed for Hemiquinone Complex **5b** in Solution

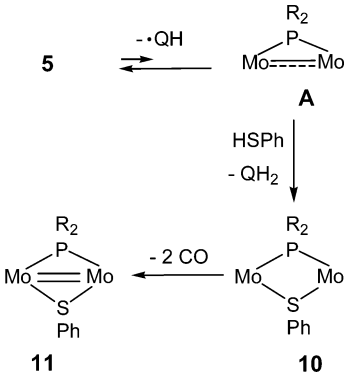


Scheme 4



Reaction of the Hemiquinone Complexes 5 with HSPh. Compounds **5a and 5b** react with an excess of HSPh at room temperature to give the red tetracarbonyl complex $[Mo_2Cp_2(\mu\text{-PCy}_2)(\mu\text{-SPh})(CO)_4]$ (**10**) and the green dicarbonyl complex $[Mo_2Cp_2(\mu\text{-PPh}_2)(\mu\text{-SPh})(CO)_2]$ (**11b**), respectively (Scheme 4). The formation of these products requires the elimination of hydroquinone (QH_2) and, in the case of the diphenylphosphide compound, the spontaneous loss of two CO molecules. Decarbonylation also occurs for the dicyclohexylphosphide compound **10** upon prolonged storage at room temperature under nitrogen or rapidly in toluene solution at 75 °C to cleanly give the analogous dicarbonyl $[Mo_2Cp_2(\mu\text{-PCy}_2)(\mu\text{-SPh})(CO)_2]$ (**11a**). From the distinct conditions required to form dicarbonyls **11a** and **11b**, we conclude that electron-releasing substituents on phosphorus, rather than bulky substituents at that position, favor in this case the decarbonylation of the corresponding tetracarbonyls, in agreement with previous findings by Mays et al. on mixed phosphide or phosphide-arsenide dimolybdenum complexes.[13] On the other hand, we note that **11b** can be also prepared in good yield by reacting **5b** with diphenyldisulfide (see Experimental Section); this presumably requires the

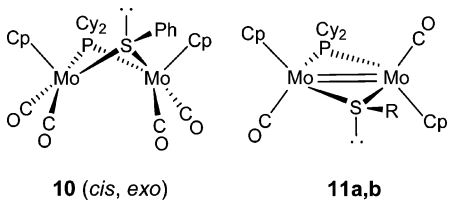
Scheme 5



formation of hydroquinone and quinone. Finally, we recall that compound **11b** was first prepared by us from the reaction of the 33-electron radical $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ with HSPh.[11c] All the above data clearly points to a radical mechanism for the reactions of these hemiquinone complexes (Scheme 5), which then seem to behave as effective sources of the corresponding dimolybdenum radicals. As proposed above to account for the dynamic behavior of compounds **5** in solution, it is thought that these hemiquinone complexes experience an homolytic cleavage of the Mo−O bond in solution, to a small extent, to give the corresponding radicals $[Mo_2Cp_2(\mu\text{-}PR_2)(CO)_4]$ and hemiquinone (·QH). The dimolybdenum radicals are themselves reactive toward HSPh and S_2Ph_2, as shown by independent experiments on the diphenylphosphide radical mentioned above,[11c] while hemiquinone is likely to be converted into hydroquinone by reaction with the sulfur reagent. The initial metallic product would be in any case a tetracarbonyl complex that, only in the case of the diphenylphosphide bridge, experiences fast decarbonylation to give the 32-electron derivative **11b**.

Structure of Thiolate Derivatives. Compound **10** displays a quite shielded ^{31}P resonance (−71.8 ppm) which suggests the absence of any metal−metal bond in the molecule.[21] According to the EAN rule, this is achieved if the thiolate ligand adopts a bridging position and then contributes with three electrons to the dimetal center. The latter can be accomplished in four different ways depending on the relative arrangement of the $MoCp(CO)_2$ moieties (cis or trans) and the position of the phenyl substituent on sulfur (endo or exo) with respect to the puckered SMo_2P ring. The IR spectrum of **10** in tetrahydrofuran solution displays two C−O stretching bands at 1933 (s) and 1854 (m) cm^{-1}, these being similar to those exhibited by related isoelectronic tetracarbonyls such as $[W_2Cp_2(\mu\text{-}SPh)_2(CO)_4]$,[22] *cis*-$[W_2Cp_2(\mu\text{-}SCHMe_2)_2CO)_4]$,[23] or *trans*-$[Mo_2Cp_2(\mu\text{-}PHPh)\{\mu\text{-}P(OEt)_2\}(CO)_4]$.[13] This suggests that the C−O stretching bands are little sensitive to the relative arrangement of the metal fragments in these molecules lacking a metal−metal bond. However, by considering that the Cp ligands in **10** give rise to single ^1H or ^{13}C resonances, we must assume a cisoid arrangement of both metal fragments. Finally, on the basis of minimum steric

Chart 3



repulsions, we propose for **10** the cis−exo geometry (Chart 3). Incidentally, this is the type of geometry found for the mentioned dithiolate complex of tungsten[23] and the related dimolybdenum complexes $[Mo_2Cp^*_2(\mu\text{-}ER)_2(CO)_4]$ [ER = SMe, SPh, SeMe, SePh].[24] Pyramidal inversion at the sulfur atom,[25] however, has been found to occur rapidly on related thiolate complexes;[26] therefore the possibility of fast interconversion between cis−exo and cis−endo isomers cannot be completely ruled out.

Dicarbonyl complexes **11a** and **11b** are isoelectronic to the dithiolate compounds $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$, which can display cis or trans geometries,[27] and to the bis(phosphide) complexes $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (M= Mo, W; R, R′= Ph, Cy, Et, etc),[14,29] for which analogous isomerism is possible. The spectroscopic data for compounds **11** (Table 1 and Experimental Section) are in fact quite similar to those of the bis(phosphide) *trans*-dicarbonyl complexes mentioned above,[14] characterized by a substantially shielded ^{31}P NMR resonance and C−O stretching bands of weak and strong intensities (in order of decreasing frequency), as expected for transoid $M_2(CO)_2$ oscillators.[30] Thus, a similar trans geometry is assumed for compounds **11** (Chart 3). In addition, the presence of the pyramidal phenylthiolate bridge now makes the carbonyl, cyclopentadienyl, and Cy (**11a**) or Ph (**11b**) groups inequivalent, as observed in the corresponding ^{13}C and ^1H NMR spectra (see Experimental Section).

Functionalization at Phosphorus by Hemiquinone Displacement in Compound 6a. The anionic (*p*-hydroxyphenoxy)phosphide complexes **6a** and **6b** are quite unstable and reactive species. Despite this, we have been able to show that the cyclohexyl complex **6a** can be an useful synthetic intermediate since it reacts with a variety of HER molecules (E = O, R = H, Me, Ph, C_4H_5; E = S, R = Ph) in the presence of DBU to give with good yields the corresponding anions $[Mo_2Cp_2\{\mu\text{-}PCy(ER)\}(CO)_4]^-$ [ER = OH (**12,** two tautomers), OMe (**13**), OC_4H_5 (**14**), OPh (**15**), SPh (**16**)], which follow from nucleophilic substitution of QH^- by ER^-

(22) Weinmam, D. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 2133.
(23) Shaver, A.; Lum, B. S.; Bird, P.; Livingstone, E.; Schweitzer, M. *Inorg. Chem.* **1990**, *29*, 1832.
(24) Schollhammer, P.; Pétillon, F. Y.; Pichon, R.; Poder-Guillou, S.; Talarmin, J. *Organometallics* **1995**, *14*, 2277 and references therein.
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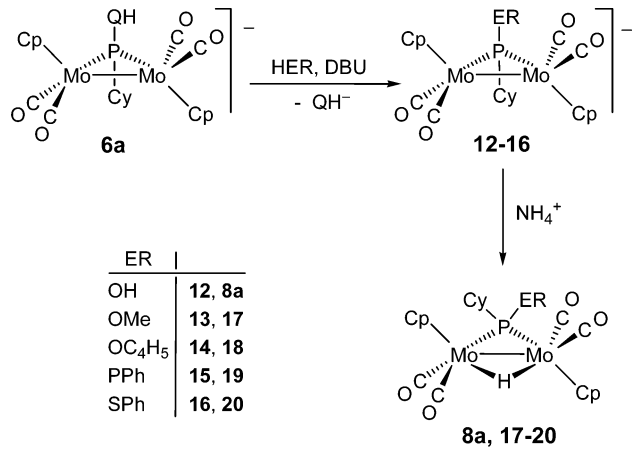
(26) Courtot-Coupez, J.; Guéguen, M.; Guerchais, J. E.; Pétillon, F. Y.; Talarmin, J. Mercier, R. *J. Organomet. Chem.* **1986**, *312*, 81.
(27) Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Coord. Chem. Rev.* **1998**, *178*−*180*, 203.
(28) (a) Abasq, M.-L.; Huger, D. L.; Pétillon, F. Y.; Pichon, R.; Pickett, C. J.; Talarmin, J. *J. Chem. Soc., Dalton Trans.* **1997**, 2279. (b) Benson, I. B.; Killops, S. D.; Knox, S. A. R.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1137.
(29) Adatia, A.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.
(30) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

Scheme 6



ER	
OH	**12**, **8a**
OMe	**13**, **17**
OC_4H_5	**14**, **18**
PPh	**15**, **19**
SPh	**16**, **20**

anions at the phosphorus site (Scheme 6). As expected, the latter complexes are readily protonated by $[NH_4]PF_6$ to give the corresponding hydrides $[Mo_2Cp_2(\mu\text{-H})\{\mu\text{-PCy(ER)}\}(CO)_4]$ [ER= OH (**8a**), OMe (**17**), OC_4H_5 (**18**), OPh (**19**), SPh (**20**)], which can be thus isolated in high yield and fully characterized.

The lability of the phosphorus−hemiquinone bond in compound **6a** is quite unexpected in view of the great strength of P−O bonds. Even more surprising is the formation of the thiolatephosphide complex **16**, since P−S bonds are considerably weaker than P−O bonds (201 vs 407 kJ).[31] Unfortunately, we have found in the literature no reactivity data to be used for comparative purposes. A phosphorus−hemiquinone bond is also present in the iron cations $[FeCpL_2\{PRH(OC_6H_4OH)\}]^+$, ($L_2$= $(CO)_2$ or diphosphine),[9] but no reactivity appears to have been reported for these complexes. Further studies must be carried out, in any case, to establish the synthetic use of this unexpected lability of the hemiquinone−phosphorus bond at metal-bound phosphide ligands.

Solid State Structure of Hydride Complexes $[Mo_2Cp_2(\mu\text{-H})\{\mu\text{-PR(ER′)}\}(CO)_4]$. Upon crystallization in different solvent mixtures, crystals of **7b**, **8a**·OC_4H_8, **17**, and **19** suitable for X-ray diffraction were formed. The molecular structures are shown in Figures 1−4. All of them exhibit $MoCp(CO)_2$ fragments bridged by phosphide and hydride ligands, and are placed in a transoid arrangement with respect to the average $Mo_2(\mu\text{-H})(\mu\text{-P})$ plane, except compound **17**, which exhibits two almost eclipsed $MoCp(CO)_2$ moieties (cis geometry). Out of the two possible cis isomers, the crystals of **17** correspond to the one with the bulkier group (Cy) close to the Cp ligands. While trans isomers are most commonly found for phosphide-hydride complexes of type $[M_2Cp_2(\mu\text{-H})(\mu\text{-PRR′})(CO)_4]$, the precedents for related cis complexes are restricted to $[Mo_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}(\mu\text{-H})(\mu\text{-PMe}_2)(CO)_4]$,[32] where the cis geometry is forced by the presence of the linked cyclopentadienyl ligands, and the mesitylphosphide complexes $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PXMes})(CO)_4]$, (X = H, F) recently reported by us.[18] However, related cis/trans

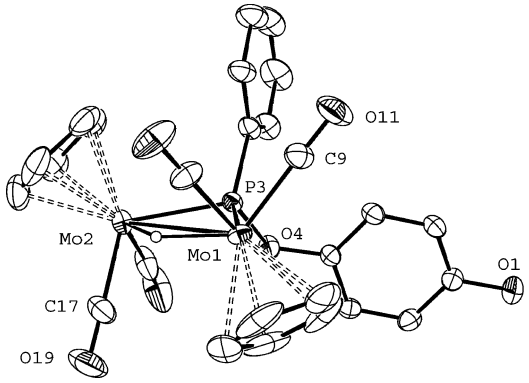


Figure 1. ORTEP diagram (30% probability) of compound **7b** with H atoms (except the hydride ligand) omitted for clarity.

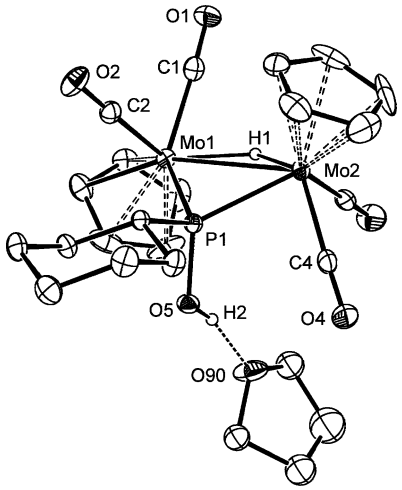


Figure 2. ORTEP diagram (25% probability) of compound **8a** and the tetrahydrofuran molecule H-bonded to it with H atoms (except the hydride and hydroxyl ones) omitted for clarity.

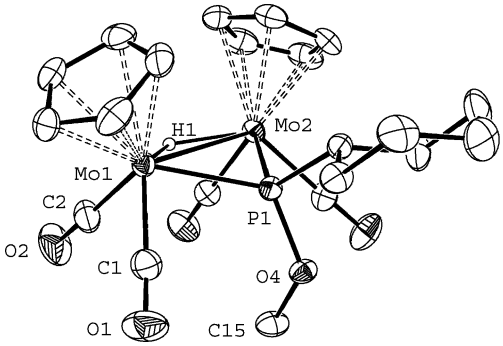


Figure 3. ORTEP diagram (30% probability) of compound **17** with H atoms (except the hydride ligand) omitted for clarity.

isomerism has been previously found and discussed in detail for the thiolate-bridged complexes $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-SR})(CO)_4]$ (R = Me, ^{t}Bu, Ph).[33]

The relevant bond lengths and angles in compounds **7b**−**19** are very similar to each other (Table 2), and they also comparable to those measured previously in related phosphide-hydride complexes,[18] thus deserving no special comment. The P−O lengths in the alkoxy- or hydroxyphosphide ligands have values consistent with single bonds, but they

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(32) Heck, J. *J. Organomet. Chem.* **1986**, *311*, C5.
(33) Muir, K. W.; Girdwood, S. E.; Pétillon, F. Y.; Pichon, R.; Poder-Guillou, S.; Schollhammer, P.; Talarmin, J. *J. Organomet. Chem.* **1995**, *486*, 183.

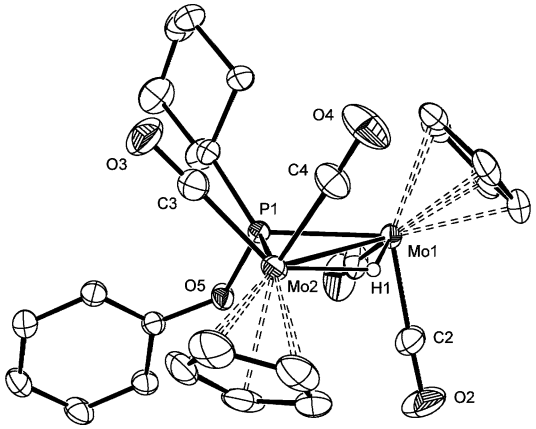
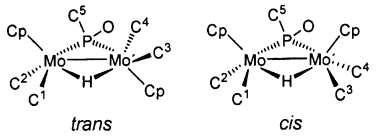


Figure 4. ORTEP diagram (30% probability) of compound **19** with H atoms (except the hydride ligand) omitted for clarity.

Table 2. Selected Bond Lengths and Angles for Compounds **7b**, **8a**, **17**, and **19**

parameter[a]	*trans*-**7b**	*trans*-**8a**	*trans*-**19**	*cis*-**17**
Mo−Mo′	3.2683(5)	3.2681(6)	3.2556(4)	3.2757(6)
Mo−H	1.95(4)	1.86(4)	1.85(3)	1.83(5)
Mo−P	2.395(1)	2.405(1)	2.411(1)	2.415(1)
Mo−C1	1.930(6)	1.955(4)	1.933(2)	1.966(4)
Mo−C2	1.926(6)	1.946(4)	1.957(2)	1.952(4)
Mo′−H	1.69(4)	1.87(4)	1.84(3)	1.82(5)
Mo′−P	2.395(1)	2.420(1)	2.404(1)	2.401(1)
Mo′−C3	1.951(5)	1.981(4)	1.961(2)	1.963(5)
Mo′−C4	1.957(5)	1.937(4)	1.949(2)	1.937(5)
P−O	1.661(3)	1.631(2)	1.661(1)	1.640(3)
P−C5	1.811(4)	1.841(3)	1.852(2)	1.847(3)
Mo−P−Mo′	86.05(3)	85.28(3)	85.10(2)	85.73(3)
C1−Mo−C2	77.3(3)	77.5(2)	78.7(1)	79.6(2)
P−Mo−C1	113.1(2)	112.0(1)	102.2(1)	108.1(1)
P−Mo−C2	78.5(2)	78.4(1)	76.1(1)	77.2(1)
C3−Mo′−C4	79.9(2)	77.6(2)	77.3(1)	79.3(2)
P−Mo′−C3	113.2(2)	122.1(1)	109.6(1)	112.6(1)
P−Mo′−C4	81.7(2)	81.5(1)	78.9(1)	80.7(1)
C5−P−O	100.8(2)	96.5(1)	101.0(1)	96.3(2)

[a] Bond lengths and angles in angstroms or degrees, respectively, according to the labeling shown in the figure below.



are slightly longer (by ∼0.02 Å) for those molecules having aromatic rings on oxygen (**7b** and **19**). This might be related to the experimental lability exhibited by the corresponding bond in the case of the hemiquinone compound **6a**.

Some of these complexes displayed H-bonding in the crystal. In the case of the hydroxyphosphide complex **8a**, the crystal contains a tetrahydrofuran molecule H-bonded to the hydroxyl group (Figure 2). The corresponding internuclear separations [P−O−H···O = 1.903 Å, P−O···O = 2.730 Å] are indicative of the presence of a hydrogen bond of medium strength.[34,35] The structure of hydroquinone compound **7b** features also some intermolecular hydrogen bonding, now of low strength (O···O= 3.03 Å), resulting in the formation of a 1-D supramolecular organometallic network running along the *c* axis. Here, the relevant interaction is established between the hydroxyl group of the hemiquinone and the oxygen atom of a carbonyl ligand in an adjacent molecule.

Solution Structure of Hydride Complexes [Mo_2Cp_2(μ-H){(μ-PR(ER′)}$(CO)_4$]. Spectroscopic data in solution for the title compounds (Table 3 and Experimental Section) are consistent with the solid-state structures discussed above and are also comparable to the data measured for related dialkyl- or diarylphosphide dimolybdenum complexes, which we have discussed in detail previously,[14,18] thereby needing no detailed discussion. The phenylphosphide compounds **7b** and **8b** exist in solution exclusively as trans isomers and exhibit a fluxional process rendering equivalent cyclopentadienyl and pairs of CO ligands, as found previously for other *trans*-[Mo_2Cp_2(μ-H)(μ-PRR′)$(CO)_4$] complexes.[14,15,18] The cyclohexyl products, however, display more complex IR spectra, which is suggestive of the presence of both cis and trans isomers in solution (Chart 4). From the previous IR data on cis and trans isomers in complexes [Mo_2Cp_2(μ-H)(μ-PRR′)$(CO)_4$][18] and [Mo_2Cp_2(μ-H)(μ-SR)$(CO)_4$],[33] we can safely conclude that compounds **17** and **18** (OMe and OC_4H_5 substituents on phosphorus) have the highest relative amount of the cis isomer (presumably, the same as that found in the crystals of **17**), characterized by two strong IR bands at frequencies ∼15−30 cm^{-1} above the strong bands of the trans isomers (Table 3). These isomers interconvert rapidly on the NMR time scale, so only averaged NMR parameters are obtained at room temperature. The products with phenoxy or thiophenoxy substituents on phosphorus, however, have a smaller proportion of the cis isomer. Indeed, the low-temperature NMR spectra of compounds **19** and **20** exhibited separate resonances for both isomers and yielded a trans/cis ratio of ∼8 in both cases, with no significant dependence on temperature. Finally, the weak additional bands present in the IR spectra of the products with hemiquinone (**7a**), hydroxyl (**8a**), and oxo (**9**) substituents on phosphorus, suggest the presence of only tiny amounts of the corresponding cis isomers in solution. In fact, the low-temperature NMR spectra of the hemiquinone compound **7a** failed to reveal separate resonances for any minor isomer. Moreover, we note that our structural proposal for the side product **9** is based on the strong similitude of its IR, ^{1}H NMR, and ^{13}C NMR spectra with those of the hydroxyphosphide complex **8a**, added to the absence of any OH proton resonance or O−H IR stretch.

The ^{31}P chemical shifts of the hydride compounds **7**−**19** are all above 300 ppm, as expected from the presence of an electron-withdrawing substituent (OR, OH) on the phosphide ligand. Although there is a limited number of phosphide complexes combining alkyl (or aryl) and alkoxy substituents on phosphorus, we note that similar shifts have been reported for related ligands, such as those present in the mononuclear complex [MoCp{P(OMe)Mes*}$(CO)_2$] (Mes*= 2,4,6-$C_6H_2^t$-

(34) (a) Dekock, R. L.; Gray, H. B. *Chemical Structure and Bonding*; Benjamin/Cummings: Menlo Park, CA, 1980; Chapter 7. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Butterworth-Heinemann: Oxford, U.K., 1997; Chapter 3.

(35) (a) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: Oxford, U.K., 1999; Chapter 3. (b) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.

Table 3. Selected IR and NMR Data for New Hydride $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PRR}')(CO)_4]$ Compounds

R	R′	compd	ν(CO)[a] (cm^{-1})	δ(P)[b] (ppm)	$\delta(\mu\text{-H})$[b] (ppm) [J_{PH}]
Cy	OC_6H_4OH	**7a**	1973 (vw), 1959 (vw), 1936 (vs), 1896(w, sh), 1872 (s).	356.3	−11.89 [39]
Ph	OC_6H_4OH	**7b**	1978 (w,sh), 1943 (vs), 1880 (s).	319.1	−11.37 [40]
Cy	OH	**8a**	1963 (vw), 1951 (vw), 1930 (vs), 1884 (w, sh), 1867 (s).	337.6	−10.83 [40]
Ph	OH	**8b**	1938 (vs), 1875(s).[c]	301.8[d]	−10.80 [40][d]
Cy	O	**9**	1962 (vw), 1947 (vw), 1926 (vs), 1862(s).	259	−11.12 [38]
Cy	OMe	**17**	1968 (vs),[e] 1933 (vs),1889 (s),[e] 1871 (s).	358.6[f]	−11.09 [41][f]
Cy	OC_4H_5	**18**	1968 (s),[e] 1934 (vs), 1889 (s),[e] 1871 (s)	352.0	−11.22 [41]
Cy	OC_6H_5	**19**	1974 (vw), 1959 (vw), 1937 (vs), 1897 (w, sh), 1874 (s)	358.3 (trans) 351.1 (cis)[g]	−10.90 [42] (cis) −11.99 [38] (trans)[g]
Cy	SPh	**20**	1968 (m), 1939 (vs), 1874 (s).	232.9 (trans) 217.7 (cis)[h]	−11.77 [38] (cis) −12.48 [35] (trans)[h]

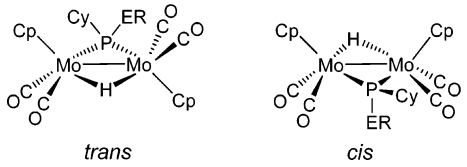
[a] Recorded in tetrahydrofuran solution, unless otherwise stated. [b] Recorded in CD_2Cl_2 solutions at 290 K and 300.13 (^{1}H) and 121.50 MHz (^{31}P) unless otherwise stated; δ in parts per million relative to internal TMS (^{1}H) or external 85% aqueous H_3PO_4; J in hertz. [c] In CH_2Cl_2 solution. [d] In $CDCl_3$ solution. [e] Bands assigned to the cis isomer. [f] Recorded at 200.1 (^{1}H) or 81.04 MHz (^{31}P). [g] Recorded at 233 K and 400.13 (^{1}H) or 162.0 MHz (^{31}P); when recorded at 290 K, only a broad resonance at 353.4 ppm (^{31}P) and at −11.82 ppm (d, J_{PH}= 39) (^{1}H) is observed. [h] Recorded at 243 K and 400.13 (^{1}H) or 162.0 MHz (^{31}P).

Table 4. IR and ^{31}P NMR Data for New Anionic Compounds (H-DBU)$[Mo_2Cp_2(\mu\text{-PRR}')(CO)_4]$

R	R′	compd	ν(CO)[a] (cm^{-1})	δ(P)[b] (ppm) [J_{PH}]
Cy	Cy	**3a**	1869 (w), 1840 (vs), 1777 (s), 1756 (m, sh)	248.3
Cy	H	**4a**	1878 (m), 1836 (vs), 1791 (s), 1768 (m)	180.6 [303][c]
Ph	H	**4b**	1882 (m), 1841 (vs), 1797 (s), 1774 (m)	143.0 [327][c]
Cy	OC_6H_4OH	**6a**	1881 (w), 1850 (vs), 1792 (s), 1770 (m, sh)	384.5
Ph	OC_6H_4OH	**6b**	1888 (m), 1850 (vs), 1805 (s), 1785 (m)	336.0
Cy	OH	**12**[d]	1903 (s), 1881 (w), 1836 (vs), 1786 (m), 1765 (w).	353.8 (**12A**) 314.8 [38] (**12B**)
Cy	OMe	**13**	1880 (m), 1848 (vs), 1839 (s), 1789 (s), 1770 (m sh)	376.8
Cy	OC_4H_5	**14**	1880 (w), 1848 (s), 1838 (vs), 1790 (s), 1768 (m, sh)	373.1
Cy	OPh	**15**	1884 (d), 1852 (vs), 1794 (s)	382.5[e]
Cy	SPh	**16**	1881 (m), 1846(vs), 1797(m), 1776(w).	257.3

[a] Recorded in tetrahydrofuran solution, unless otherwise stated. [b] Recorded in tetrahydrofuran solution with external D_2O at 290 K and 121.50 MHz, unless otherwise stated; δ relative to external 85% aqueous H_3PO_4. [c] Recorded in CD_2Cl_2 solution at 290 K and 81.04 MHz. [d] This compound appears in solution as a mixture of phosphide (tautomer **12A**) and hydride-oxophosphinidene isomers (tautomer **12B**, see text), in similar amounts. [e] Recorded at 81.04 MHz.

Chart 4



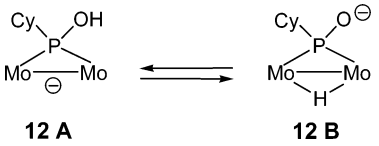
Bu_3, δ_P = 350.5)[36] or in the cluster anion $[FeCo_2(CO)_9\{\mu\text{-PPh(OMe)}\}]^-$ (δ_P = 320.0).[37]

As stated above, cis/trans isomerism in phosphide-hydride complexes related to compounds **7**−**20** has been only observed previously for the mesityl complexes $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PXMes})(CO)_4]$, (X = H, F).[18] By considering the observed cis/trans ratios, we find the following order: PCyOMe (∼1) > PMesH (0.5) > PCyOPh = PCySPh (∼0.15) > PCy(OC_6H_4OH) = PCyOH (∼0). Clearly, there is not a single electronic or steric parameter governing the relative amounts of the cis and trans isomers in these substrates. It rather seems that the cis isomers in these dimolybdenum complexes are favored by the combination of a relatively bulky group (Cy, Mes) with a small electron-withdrawing substituent (H, OMe).

Structure of Anionic Complexes (H-DBU)$[Mo_2Cp_2(\mu\text{-PRX})(CO)_4]$, (X = R, H, ER). It is generally assumed that the structures of anionic complexes of type $[M_2Cp_2(\mu\text{-PRR}')(CO)_4]^-$ are strongly related to those of the corresponding hydrides (mostly exhibiting trans geometries). Indeed, we note that retention of transoid geometries has been crystallographically verified in the pairs $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PR}_2)(CO)_4]$/$[Mo_2Cp_2(\mu\text{-PR}_2)(CO)_4]^-$, (R = Ph,[12b] Me[12c]). However, since cis and trans isomers in hydride complexes **17**−**20** are interconverting rapidly in solution (as previously found for the isomers in the mentioned complexes $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PXMes})(CO)_4]$),[18] it is clear that the structures of the anions and those of the corresponding hydrides may differ and cannot be deduced from each other. An inspection of the IR spectra of the new anionic complexes described in this work (Table 4) reveals that most of them exhibit the same pattern, with four bands at ∼1880 (m to w), 1840 (vs), 1790 (s) and 1770 (m) cm^{-1}. These spectra are thus similar to those of the diphenylphosphide complexes (H-DBU)$[M_2Cp_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_4]$ (M = Mo, W)[11a] and to that reported for the salt (PPN)$[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_4]$, which displays a transoid geometry in the solid state.[12b] Therefore, we deduce that anions having PCy_2 (**3a**), PCyH (**4a**), PPhH (**4b**), PCy(OC_6H_4OH) (**6a**), PPh(OC_6H_4OH) (**6b**), PCy(OPh) (**15**), and PCy(SPh) (**16**) bridges exist in solution essentially as trans isomers. We note that these are the anions whose hydride derivatives exhibit trans isomers as unique or very major species in solution. In contrast, anions with PCy(OMe) (**13**) and PCy(OC_4H_5) (**15**) bridges (hydride derivatives exhibiting the highest proportion of cis isomers) display different IR spectra, characterized by the presence of an additional strong band at ∼10 cm^{-1} below the usual strongest band (the relative intensities of the bands are also somewhat different).

(36) Alonso, M.; Alvarez, M. A.; García, M. E.; Ruiz, M. A.; Hamidov, H.; Jeffery, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 13610.
(37) Don, M.-J.; Richmond, M. G. *Inorg. Chem.* **1991**, *30*, 1703.

Scheme 7. Tautomeric Equilibrium Proposed for Compound **12** in Solution (Mo = $MoCp(CO)_2$)



12 A **12 B**

We interpret this as an indication of the presence of substantial amounts of the corresponding cis isomers in the solutions of these anions. In summary, the isomerism in anions **3**−**16** (except the hydroxyphosphide complex **12**) seems to follow the same general trends found for the corresponding hydride derivatives but with the trans isomers being more prevalent in the anionic substrates.

Tautomerism in the Hydroxyphosphide Complex 12. The anionic complex **12** exhibits unique structural features in solution. Its IR spectrum is completely different from the other anions since it displays, in addition to the usual C−O stretching bands, a strong band at quite high frequency (1903 cm^{-1}), while the relative intensities of the rest of bands are also somewhat modified. This is due to the presence in solution of a second isomer, which we propose to be the corresponding hydride-oxophosphinidene tautomer $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCyO})(CO)_4]^-$ (**12B**), resulting after proton migration from the oxygen atom up to the dimetal center (Scheme 7). This expectedly implies a shift of the electronic charge from the metal to the oxygen atom bound to phosphorus ($PCyO^-$ resonant form), thus explaining the increase of the C−O stretching frequencies. In agreement with this proposal, the $^{31}P\{^1H\}$ NMR spectrum of **12** displays two resonances of similar intensities. One of them appears at a chemical shift (354 ppm) comparable to alkoxyphosphide complexes **13** and **14** and is therefore assigned to the hydroxyphosphide tautomer **12A**. The other resonance is significantly lower in frequency (315 ppm) and splits into a doublet upon ^1H coupling, with the P−H coupling of 38 Hz being characteristic of the hydride-phosphide couplings in our substrates (Table 3). Therefore, this resonance is assigned to the hydride-oxophosphinidene tautomer **12B**. It should be noted that oxophosphinidene complexes are extremely rare species and their chemistry is virtually unexplored.[10,35,38] The anionic mononuclear complex (H-DBU)[MoCp{P(O)Mes*}$(CO)_2$] has been shown previously to react with hard electrophiles such as $(Me_3O)BF_4$ at the oxygen site of the oxophosphinidene ligand. Compound **12** behaves similarly and reacts rapidly with the same reagent to give the methoxyphosphide-hydride complex **17** as unique product (see Experimental Section). Anion **12**, therefore, may have a potential as synthetic intermediate in the same line as the hemiquinone compound **7a**, a matter to be explored in the future.

Concluding Remarks

The phosphide-bridged dimolybdenum complexes (H-DBU)$[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PRR}')(CO)_4]$ (R= Cy, Ph; R′= R, H) react readily with *p*-benzoquinone via electron-transfer followed by proton capture from the $(H\text{-DBU})^+$ cation to give hemiquinone and the corresponding 33-electron radicals $[Mo_2Cp_2(\mu\text{-PRR}')(CO)_4]$. The latter evolve differently depending on the nature of the phosphorus ligand. Thus, PR_2-bridged radicals just couple to hemiquinone at the metal site to give the hemiquinone complexes $[Mo_2Cp_2(OC_6H_4OH)(\mu\text{-PR}_2)(CO)_4]$, which exhibit facile homolytic cleavage of the corresponding Mo−O bonds; then they behave as a source of their paramagnetic precursors. In contrast, PHR-bridged substrates experience overall insertion of quinone into the P−H bond through a reaction sequence thought to involve an oxidative addition of the P−H bond to the metal center at the intermediate radicals $[Mo_2Cp_2(\mu\text{-PRH})(CO)_4]$, followed by coupling, at the phosphorus site, of hemiquinone and the resulting phosphinidene intermediate. The anions (H-DBU)$[Mo_2Cp_2\{\mu\text{-PR}(OC_6H_4OH)\}(CO)_4]$ thus formed also exhibit facile release of the hemiquinone group, now via the heterolytic cleavage of the P−O bond by reaction with ER^- anions (E = O, S; R = H, alkyl, aryl), to give derivatives bridged by novel PR(ER) phosphide ligands.

Experimental Section

General Comments. All manipulations and reactions were carried out using standard Schlenk techniques under an atmosphere of dry oxygen-free nitrogen (99.995%). Solvents were purified according to standard literature procedures[39] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range of 60−65 °C. Compounds $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_4]$ (**1a**),[14] $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PHCy})(CO)_4]$ (**2a**),[14] $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_4]$ (**1b**),[15a] $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PHPh})(CO)_4]$ (**2b**),[15a] and solutions of $[H\text{-DBU}][Mo_2Cp_2(\mu\text{-PPh}_2)(CO)_4]$ (**3b**),[11a] were prepared according to literature procedures. Other reagents were obtained from the usual commercial suppliers and used without further purification. Filtrations were carried out using a cannula or, more generally, through diatomaceous earth, and aluminum oxide (alumina) for column chromatography was deactivated by the appropriate addition of water to the commercial material (Aldrich, neutral, activity I). 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. NMR spectra were recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$), and 75.47 MHz ($^{13}C\{^1H\}$) on CD_2Cl_2 solutions at room temperature unless otherwise stated. Chemical shifts (δ) are given in parts per million, relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (*J*) are given in hertz.

Preparation of Solutions of $[H\text{-DBU}][Mo_2Cp_2(\mu\text{-PCy}_2)(CO)_4]$ (3a). Neat DBU (22 μL, 0.147 mmol) was added to a tetrahydrofuran solution (15 mL) of compound **1a** (0.060 g, 0.095 mmol) at 0 °C, and the mixture was stirred at that temperature for 30 min to give an orange solution of compound **3a** which was ready for further use.

Preparation of Solutions of $[H\text{-DBU}][Mo_2Cp_2(\mu\text{-PHCy})(CO)_4]$ (4a). Neat DBU (82 μL, 0.548 mmol) was added to a tetrahydrofuran solution (15 mL) of compound **1a** (0.200 g, 0.363 mmol) at 0 °C, and the mixture was stirred at that temperature for 5 min to give a cherry red solution of compound **4a** which was ready for further use.

(38) Alvarez, C. M.; Alvarez, M. A.; García, M. E.; González, R.; Ruiz, M. A.; Hamidov, H.; Jeffery, J. C. *Organometallics* **2005**, *24*, 5503.

(39) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, U.K., 2003.

Preparation of Solutions of [H-DBU][$Mo_2Cp_2(\mu$-PHPh)$(CO)_4$] (4b). Neat DBU (82 μL, 0.548 mmol) was added to a tetrahydrofuran solution (15 mL) of compound **1a** (0.200 g, 0.368 mmol) at 0 °C, and the mixture was stirred at that temperature for 5 min to give a violet solution of compound **4b** which was ready for further use.

Preparation of Solutions of [$Mo_2Cp_2(OC_6H_4OH)(\mu$-PCy_2)-$(CO)_4$] (5a). Solid *p*-benzoquinone (0.011 g, 0.102 mmol) was added to a tetrahydrofuran solution of compound **3a** (∼0.095 mmol), prepared as described above, and the mixture was stirred for 10 min to give a brown solution of compound **5a** which was ready for further use. All attempts to isolate this complex as a pure solid material resulted in its progressive decomposition.

Preparation of [$Mo_2Cp_2(OC_6H_4OH)(\mu$-PPh_2)$(CO)_4$] (5b). Neat DBU (6 μL, 0.040 mmol) was added to a tetrahydrofuran solution (6 mL) of compound **1b** (0.020 g, 0.032 mmol) and *p*-benzoquinone (0.007 g, 0.065 mmol) at 233 K, and the mixture was stirred at that temperature for 10 min to give a red-brown solution. The solvent was then removed under vacuum, the residue washed with petroleum ether (3 mL) and extracted with tetrahydrofuran (5 mL), and the extract was filtered using a cannula. The addition of cold petroleum ether (5 mL) to the filtrate and the removal of solvents under vacuum gave compound **5b** as a brown air-sensitive powder (0.021 g, 90%). ^{1}H NMR (293 K, averaged spectrum): δ 7.80−7.20 (m, 10H, Ph), 6.49 (d, J_{HH} = 8, 2H, C_6H_4), 6.00 (d, J_{HH} = 8, 2H, C_6H_4), 5.1 (br, 10 H, Cp). ^{1}H NMR (400.13 MHz, 243 K): δ 7.90−7.10 (m, 10H, Ph), 6.48 (d, J_{HH} = 8, 2H, C_6H_4, isomers *A* and *B*), 5.97 (d, J_{HH} = 8, 2H, C_6H_4, isomers *A* and *B*), 5.32, 4.88 (2 × s, Cp, isomer *A*), 5.31, 4.86 (2 × s, Cp, isomer *B*). Ratio *A*/*B* = 5. ^{13}C{^{1}H} NMR (100.63 MHz, 213 K, isomer *A*): δ 248.8 (d, J_{CP} = 17, CO), 241.7 (d, J_{CP} = 20, CO), 241.6 (s, CO), 226.7 (s, br, CO), 159.3 (s, C−OMo), 149.6 (s, C−OH), 142.7 [d, J_{CP} = 41, C^1(Ph)], 139.0 [d, J_{CP} = 31, C^1(Ph)], 136.5−126.5 (m, Ph), 118.4 [s, br, $C^{2,3}(C_6H_4)$], 116.4 [s, $C^{3,2}(C_6H_4)$], 95.0, 92.4 (2 × s, 2 × Cp).

Preparation of Solutions of [H-DBU][$Mo_2Cp_2\{\mu$-PCy$(OC_6H_4OH)\}(CO)_4$] (6a). Although impure solutions of **6a** can be prepared directly from **4a** and *p*-benzoquinone (see preparation of **7a**), pure solutions of this anionic complex have to be made from hydride **7a**. Neat DBU (28 μL, 0.187 mmol) was added to a tetrahydrofuran solution (5 mL) of compound **7a** (0.060 g, 0.091 mmol) at 0 °C, and the mixture was stirred at that temperature for 5 min to give a red solution of compound **6a** which was ready for further use.

Preparation of Solutions of [H-DBU][$Mo_2Cp_2\{\mu$-PPh$(OC_6H_4OH)\}(CO)_4$] (6b). Although impure solutions of **6b** can be prepared directly from **4b** and *p*-benzoquinone (see preparation of **7b**), pure solutions of this anionic complex have to be made from hydride **7b**. Neat DBU (15 μL, 0.100 mmol) was added to a tetrahydrofuran solution (5 mL) of compound **7b** (0.043 g, 0.065 mmol) at 0 °C, and the mixture was stirred at that temperature for 5 min to give a violet solution of compound **6b** which was ready for further use.

Preparation of [$Mo_2Cp_2(\mu$-H$)\{\mu$-PCy$(OC_6H_4OH)\}(CO)_4$] (7a). A tetrahydrofuran solution (1 mL) of *p*-benzoquinone (0.055 g, 0.509 mmol) was added to a tetrahydrofuran solution of compound**4a** (ca. 0.363 mmol), prepared as described above and cooled at 243 K, and the mixture was stirred at that temperature for 10 min to give a red solution of compound **6a**. Solid $[NH_4]PF_6$ (0.115 g, 0.706 mmol) was then added, and the mixture was stirred for 15 min and allowed to reach room temperature to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane and the extract chromatographed on an alumina column (activity IV) at 253 K. Elution with dichloromethane/petroleum ether (1:4) gave a yellow fraction yielding, after removal of solvents under vacuum, compound **9** as a yellow solid (0.020 g, 10%). Elution with tetrahydrofuran/toluene (1:12) gave an orange fraction yielding analogously compound **7a** as an orange powder (0.143 g, 60%). Finally, elution with tetrahydrofuran/toluene (1:6) gave a yellow fraction yielding compound **8a** as a yellow powder (0.51 g, 25%, see later). **Data for 7a.** Anal. Calcd for $C_{26}H_{27}Mo_2O_6P$: C, 47.43; H, 4.13. Found: C, 47.22; H, 4.30. ^{1}H NMR: δ 6.68 (s, 4H, C_6H_4), 5.12 (s, br, 10H, Cp), 5.47 (s, 1H, OH), 2.67−1.27 (m, 11H, Cy), −11.89 (d, J_{HP} = 39, 1H, μ-H). ^{13}C{^{1}H} NMR (100.63 MHz, 248 K): δ 243.8 (d, J_{CP} = 24, CO), 240.8 (d, J_{CP} = 21, CO), 232.9 (s, CO), 231.7 (s, CO), 151.8 (s, br, C−OH), 147.9 (s, C−OP), 121.4 [s, $C^{2,3}(C_6H_4)$], 115.8 [s, br, $C^{3,2}(C_6H_4)$], 89.7, 89.3 (2 × s, 2 × Cp), 50.8 [d, J_{CP} = 21, C^1-(Cy)], 30.1 [s, $C^{2,6}$(Cy)], 28.0 [s, $C^{6,2}$(Cy)], 26.5−25.8 [m, $C^{3,5}$-(Cy) and C^4(Cy)]. **Data for 9.** Anal. Calcd for $C_{40}H_{44}Mo_4O_9P_2$: C, 43.11; H, 3.98. Found: C, 43.32; H, 4.10. ^{1}H NMR (200.13 MHz): δ 5.18 (s, 10H, Cp), 1.90−1.26 (m, 11H, Cy), −11.12 (d, J_{HP} = 38, 1H, μ-H). ^{13}C{^{1}H} NMR: δ 243.1 (s, br, 2CO), 237.0 (s, br, 2CO], 90.7 (s, Cp), 31.1 [d, J_{CP} = 4, C^2(Cy)], 27.3 [d, J_{CP} = 12, C^3(Cy)], 26.4 [d, J_{CP} = 1, C^4(Cy)]. The resonance for the C^1(Cy) nucleus was hidden under that of the solvent, and it could be located at 57.7 ppm (d, J_{CP} = 24) in toluene-d_8 solution.

Preparation of [$Mo_2Cp_2(\mu$-H$)\{\mu$-PPh$(OC_6H_4OH)\}(CO)_4$] (7b). The procedure is similar to that described for **7a**, but it uses a tetrahydrofuran solution of **4b** (∼0.368 mmol), 0.040 g of *p*-benzoquinone (0.370 mmol), and 0.119 g of $[NH_4]PF_6$ (0.730 mmol). Elution with tetrahydrofuran/toluene (1:9) gave a orange fraction which yielded compound **7b** as an orange powder (0.149 g, 62%). Elution with pure tetrahydrofuran gave a yellow fraction yielding compound **8b** as a yellow powder (0.031 g, 15%). The crystals of **7b** used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at 253 K. **Data for 7b.** Anal. Calcd for $C_{26}H_{21}$-Mo_2O_6P: C, 47.87; H, 3.24. Found: C, 47.56; H, 3.15. ^{1}H NMR: δ 7.39−7.28 (m, 5H, Ph), 6.85, 6.70 (AB syst, J_{HH} = 9, 4H, C_6H_4), 4.94 (s, 10H, Cp), 4.78 (s, 1H, OH), −11.37 (d, J_{HP} = 40, 1H, μ-H]. ^{13}C{^{1}H} NMR: δ 241.6 (s, br, 2CO), 234.3 (s, br, 2CO), 151.8 (s, C−OH), 151.1 [d, J_{CP} = 12, C−OP), 149.0 [d, J_{CP} = 31, C^1(Ph)], 128.9 [d, J_{CP} = 12, $C^{2,3}$(Ph)], 128.6 [s, C^4(Ph)], 128.0 [d, J_{CP} = 12, $C^{3,2}$(Ph)], 120.7 [d, J_{CP} = 7, $C^{2,3}(C_6H_4)$], 115.8 [s, $C^{3,2}$-(C_6H_4)], 91.4 (s, Cp). **Data for 8b.** Anal. Calcd for $C_{20}H_{17}$-Mo_2O_5P: C, 42.88; H, 3.06. Found: C, 42.72; H, 3.15. ^{1}H NMR: δ 7.44−7.31 (m, 5H, Ph), 5.13 (s, br, 10H, Cp), 4.48 (s, 1H, OH), −10.80 (d, J_{HP} = 40, 1H, μ-H).

Preparation of [$Mo_2Cp_2(\mu$-PCy_2)$(\mu$-SPh$)(CO)_4$] (10). Neat HSPh (30 μL, 0.285 mmol) was added to a tetrahydrofuran solution (5 mL) of compound **5a** (∼0.095 mmol) prepared as described above, and the mixture was stirred at room temperature for 4 h. The solvent was then removed under vacuum; the residue was extracted with toluene/petroleum ether (1:1, 15 mL), and the extracts were filtered. Removal of the solvents from the filtrate gave a crude product which was recrystallized from toluene/petroleum ether to give compound **10** as red microcrystals (0.035 g, 50%). Anal. Calcd for $C_{32}H_{37}Mo_2O_4PS$: C, 51.90; H, 5.04. Found: C, 51.82; H, 5.13. ^{1}H NMR (200.13 MHz): δ 7.44−6.90 (m, 5H, Ph), 5.08 (s, 10H, Cp), 2.48−1.30 (m, 22H, Cy). ^{13}C{^{1}H} NMR (50.33 MHz, C_6D_6): δ 253.5 [d, J_{CP} = 20, CO], 252.8 (s, CO), 149.6 [s, C^1(Ph)], 95.0 (s, Cp), 50.3 [d, J_{CP} = 20, C^1(Cy)], 43.6 [d, J_{CP} = 17, C^1(Cy)], 34.7−26.6 (m, Cy).

Preparation of [$Mo_2Cp_2(\mu$-PCy_2)$(\mu$-SPh$)(CO)_2$] (11a). Compound **10a**, prepared as a crude solid as described above (∼0.095

mmol), was dissolved in toluene (10 mL) and heated at 75 °C for 4 h to give a green solution which was filtered. Removal of the solvent from the filtrate under vacuum gave a residue which was recrystallized by slow diffusion of a layer of petroleum ether into a dichloromethane solution of the product to yield complex **10** as dark-green microcrystals (0.058 g, 89%). Anal. Calcd for $C_{31}H_{39}Cl_2Mo_2O_2PS$ (**10**·CH_2Cl_2): C, 48.39; H, 5.11. Found: C, 48.80; H, 5.36. ^{1}H NMR (200.13 MHz): δ 7.26−7.13 (m, 5H, Ph), 5.45, 5.29 (2 × s, 2 × 5H, Cp), 2.26−1.28 (m, 22H, Cy). ^{13}C{^{1}H} NMR: δ 246.4 [d, J_{CP} = 13, CO], 241.7 [d, J_{CP} =14, CO], 148.3 [s, C^1(Ph)], 130.7, 127.5 [2 × s, C^{2,3}(Ph)], 125.4 [s, C^4(Ph)], 89.4, 89.2 (2 × s, Cp), 49.8 [d, J_{CP} = 21, C^1(Cy)], 42.6 [d, J_{CP} = 18, C^1(Cy)], 34.3, 33.5, 32.9, 32.0 [4 × s, C^{2,6}(Cy)], 28.0−27.7 [m, C^{3,5}(Cy)], 26.1, 25.9 [2 × s, C^4(Cy)].

Preparation of [$Mo_2Cp_2(\mu$-$PPh_2)(\mu$-SPh)$(CO)_2$] (11b). Neat HSPh (6 μL, 0.057 mmol, method A) or solid S_2Ph_2 (0.014 g, 0.063 mmol, method B) was added to a tetrahydrofuran solution (5 mL) of compound **5b** (∼0.032 mmol) prepared in situ as described above, and the mixture was stirred at room temperature for 4 h to give a green solution. The solvent was then removed under vacuum; the residue was extracted with dichloromethane, and the extracts were filtered through a silica gel column (230−400 mesh, 2 × 20 cm). Removal of the solvent from the filtrate gave compound **11b** as a green powder (method A 0.015 g, 70%; method B 0.012 g, 56%). Anal. Calcd for $C_{30}H_{25}Mo_2O_2PS$: C, 53.58; H, 3.75. Found: C, 53.45; H, 3.67. ^{1}H NMR (200.13 MHz): δ 7.90−7.00 (m, 15H, Cp), 5.52 (s, 10H, Cp). ^{13}C{^{1}H} NMR (50.33 MHz): δ 242.9 [d, J_{CP} = 14, CO], 239.0 [d, J_{CP} = 14, CO], 148.3 [s, C^1(SPh)], 145.5 [d, J_{CP} = 41, C^1(Ph)], 145.0 [d, J_{CP} = 39, C^1(Ph)], 135.5−126.0 (m, Ph), 90.9, 90.7 (2 × s, Cp).

Preparation of solutions of [H-DBU][Mo_2Cp_2{μ-PCy(OH)}$(CO)_4$] (12). A tetrahydrofuran solution (5 mL) containing ∼0.061 mmol of the salt **6a** and excess DBU was prepared in situ as described above. Water (4 μL, 0.22 mmol) was then added, and the mixture was stirred for 5 min to give a red solution shown (by NMR) to contain an equilibrium mixture of the anionic tautomers [Mo_2Cp_2{μ-PCy(OH)}$(CO)_4$]$^-$ (**12A**) and [$Mo_2Cp_2(\mu$-H){μ-PCy(O)}$(CO)_4$]$^-$ (**12B**) in similar amounts.

Preparation of [$Mo_2Cp_2(\mu$-H){μ-PCy(OH)}$(CO)_4$] (8a). Solid $[NH_4]PF_6$ (0.020 g, 0.122 mmol) was added to a tetrahydrofuran solution (5 mL) containing ∼0.061 mmol of compound **12**, prepared as described above, and the mixture was stirred for 10 min to give a yellow solution. The solvent was removed, and the residue was chromatographed on an alumina column (activity IV) at 253 K. Elution with tetrahydrofuran/toluene (1:9) gave a yellow fraction yielding, after removal of solvents, compound **8a** as a yellow powder (0.034 g, 88%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated tetrahydrofuran solution of the complex at 253 K. Anal. Calcd for $C_{24}H_{31}Mo_2O_6P$ (**8a**·OC_4H_8): C, 53.58; H, 3.75. Found: C, 53.45; H, 3.67. IR (Nujol mull): ν(OH) 3270 (br) cm^{-1}. ^{1}H NMR: δ 5.20 (s, 10H, Cp), 1.91−1.38 (m, 11H, Cy), −10.83 (d, J_{HP} = 40, 1H, μ-H). ^{13}C{^{1}H} NMR (50.33 MHz): δ 242.0 (sa, CO), 232.7 (sa, CO), 90.6 (s, Cp), 30.6 [s, C^2(Cy)], 27.1 [d, J_{CP} = 12, C^3(Cy)], 25.4 [s, C^4(Cy)]. The resonance for the C^1(Cy) nucleus was hidden under that of the solvent, and it could be located at 54.4 ppm (d, J_{CP} = 24) in $CDCl_3$ solution.

Preparation of Solutions of [H-DBU][Mo_2Cp_2{μ-PCy(OMe)}$(CO)_4$] (13). BuLi (190 μL of a 1.6 M solution in hexanes, 0.304 mmol) was added to a tetrahydrofuran solution (2 mL) of methanol (10 mL, 0.247 mmol) at 0 °C; the mixture was stirred for 1 min, and the solvent was then removed under vacuum to give a white residue of LiMeO which was washed with petroleum ether (5 mL). A tetrahydrofuran solution containing ∼0.106 mmol of **6a**, prepared as described above, was then added to this solid, and the mixture was stirred for 10 min to give a red solution of **13** which was ready for further use.

Preparation of Solutions of [H-DBU][Mo_2Cp_2{μ-PCy(OC_4H_5)}$(CO)_4$] (14). Neat 3-butyn-1-ol (14 μL 0.18 mmol) was added to a tetrahydrofuran solution containing ∼0.09 mmol of **6a**, prepared using an excess of DBU as described above, and the mixture was stirred for 10 min to give a red solution of **14** which was ready for further use.

Preparation of Solutions of [H-DBU][Mo_2Cp_2{μ-PCy(OPh)}$(CO)_4$] (15). The procedure is similar to that described for **14**, but with phenol (0.012 g, 0.128 mmol) instead, to give an orange solution of **15**.

Preparation of Solutions of [H-DBU][Mo_2Cp_2{μ-PCy(SPh)}$(CO)_4$] (16). The procedure is similar to that described for **14**, but with thiophenol (20 μL, 0.188 mmol) instead, to give an orange solution of **16**.

Preparation of [$Mo_2Cp_2(\mu$-H){μ-PCy(OMe)}$(CO)_4$] (17). Method A. The solvent was removed from a tetrahydrofuran solution containing ∼0.071 mmol of salt **12**, prepared as described above, and the residue was dissolved in dichloromethane (5 mL). Solid $[Me_3O]BF_4$ (0.012 g, 0.081 mmol) was then added, and the mixture was stirred for 1 min to give an orange solution. **Method B.** Solid $[NH_4]PF_6$ (0.050 g, 0.306 mmol) was added to a tetrahydrofuran solution containing ∼0.106 mmol of salt **13**, prepared as described above, and the mixture was stirred for 10 min to give an orange solution. In both cases the complex was purified by removal of the solvent and chromatography of the residue on an alumina column (2 × 15 cm, activity IV) at 243 K. A yellow fraction was collected in both cases using dichloromethane/petroleum ether (1:3) as eluant to give, after removal of solvents, compound **17** as an orange powder (method A 0.036 g, 88%; method B 0.042 g, 68%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{21}H_{25}Mo_2O_5P$: C, 43.47; H, 4.32. Found: C, 43.22; H, 4.32. IR (Nujol mull, *cis*-**17**): ν(CO) 1966 (s), 1921 (s), 1882 (vs), 1859 (s) cm^{-1}. ^{1}H NMR (200 MHz): δ 5.23 (s, 10H, Cp), 2.77 (d, J_{HP} = 14, 3H, OMe) 2.25−1.31 (m, 11H, Cy), −11.09 (d, J_{HP} = 41, 1H, μ-H).

Preparation of [$Mo_2Cp_2(\mu$-H){μ-PCy(OC_4H_5)}$(CO)_4$] (18). The preparation and purification of this complex was identical to that described for compound **17** (method B) but using a solution containing ∼0.090 mmol of salt **14** instead. This gave compound **18** as an orange solid (0.046 g, 82%). Anal. Calcd for $C_{24}H_{27}Mo_2O_5P$: C, 46.62; H, 4.40. Found: C, 46.22; H, 4.32. ^{1}H NMR: δ 5.25 (s, 10H, Cp), 2.92 (q, J_{HP} = J_{HH} = 7, 1H, CH_2), 2.43 (dt, J_{HH} = 7, 3, 1H, CH_2), 2.21−1.30 (m, 11H, Cy), 1.98 (t, J_{HH} = 3, 1H, CH), −11.22 (d, J_{HP} = 41, 1H, μ-H).

Preparation of [$Mo_2Cp_2(\mu$-H){μ-PCy(OPh)}$(CO)_4$] (19). The preparation and purification of this complex was identical to that described for compound **17** (method B) but with a solution containing ∼0.090 mmol of salt **15** instead. This gave compound **19** as an orange solid (0.036 g, 61%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{26}H_{27}Mo_2O_5P$: C, 48.62; H, 4.24. Found: C, 48.72; H, 4.27. ^{1}H NMR: δ 7.26−6.87 (m, 5H, OPh), 5.14 (s, br, 10H, Cp), 2.78−0.86 (m, 11H, Cy), −11.82 (d, J_{HP} = 39, 1H, μ-H). ^{1}H NMR (400.13 MHz, 233 K): isomer *trans*-**19** δ 7.30 (m, 2H, OPh), 7.08 (m, 1H, OPh), 6.95 (m, 2H, OPh), 5.37, 4.92 (2 x s, 2 × 5 H, Cp), 3.05−0.69 (m, 11H, Cy), −11.99 (d, J_{HP} = 38, 1H,

Table 5. Crystal Data for New Compounds

	7b	**8a**·OC_4H_8	**19**	**17**
mol formula	$C_{26}H_{21}Mo_2O_6P$	$C_{24}H_{31}Mo_2O_6P$	$C_{26}H_{27}Mo_2O_5P$	$C_{21}H_{25}Mo_2O_5P$
mol wt	652.30	638.34	642.33	580.26
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	*C*2/*c*	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
radiation (λ, Å)	0.71069	0.71073	0.71073	0.71073
a (Å)	30.009(7)	15.252(3)	9.0903(13)	8.1443(12)
b (Å)	8.680(9)	8.8714(15)	9.9522(15)	9.2872(14)
c (Å)	19.796(5)	18.616(3)	15.312(2)	15.368(2)
α (deg)	90	90	77.434(2)	85.330(2)
β (deg)	99.65(2)	90.517(3)	74.559(2)	76.400(2)
γ (deg)	90	90	80.305(2)	82.699(2)
V (Å^3)	5083(5)	2518.8(8)	1294.3(3)	1119.0(3)
Z	8	4	2	2
calcd density (g cm^{-3})	1.71	1.683	1.648	1.722
abs coeff (mm^{-1})	1.089	1.096	1.064	1.221
temp (K)	293	200(2)	292(2)	292(2)
θ range (deg)	1−28	1.72−26.44	1.40−26.40	1.37−26.42
index ranges (*h*, *k*, *l*)	0, 39; 0, 11; −26, 25	−19, 19; 0, 11; 0, 23	−10, 11; −11, 12; 0, 19	−9, 10; −11, 11; 0, 19
reflns collected	6664	21 567	14 771	10 779
independent reflns	6139	5503	5276	4532
reflns with $I > 2\sigma(I)$	3845 [$I > 3\sigma(I)$]	3765	4682	3454
R (data with $I > 2\sigma(I)$)	R1 = 0.0363	R1 = 0.035	R1 = 0.0191	R1 = 0.0295
	wR2 = 0.0439[a]	wR2 = 0.0757[b,c]	wR2 = 0.0511[b,d]	wR2 = 0.063[b,e]
GOF	1.093	1.088	1.112	1.060
restraints/params	0/317	0/298	0/311	0/266
$\Delta\rho$(max,min) (e Å^{-3})	0.85, −0.49	0.567, −0.456	0.316, −0.485	0.526, −0.456

[a] $w = w'[1 - ((||F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w'=1/\sum rArTr(X)$ with 3 coefficients 0.884, 0.367, and 0.507 for a Chebyshev Series, for which X is F_c/F_c(max). [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [c] a= 0.0345, b= 0.9836. [d] a = 0.0249, b = 0.3897. [e] a = 0.0238, b = 1.1099.

μ-H); isomer *cis*-**19** δ 5.24 (s, 10 H, Cp), −10.90 (d, J_{HP} = 42, 1H, μ-H); other resonances obscured by those of the major isomer. trans/cis ratio = 8.

Preparation of [Mo_2Cp_2(μ-H){μ-PCy(SPh)}$(CO)_4$] (20). The preparation and purification of this complex was identical to that described for compound **17** (method B) but with a solution containing ∼0.090 mmol of salt **16** instead. This gave compound **20** as an orange solid (0.043 g, 72%). Anal. Calcd for $C_{26}H_{27}Mo_2O_4PS$: C, 47.29; H, 4.31. Found: C, 47.43; H, 4.13. ^{1}H NMR (400.13 MHz, 243 K): isomer *trans*-**20** δ 7.63−7.24 (m, 5H, Ph), 5.35, 5.14 (2 × s, 2 × 5 H, Cp), 2.99−0.27 (m, 11H, Cy), −12.48 (d, J_{HP} = 35, 1H, μ-H); isomer *cis*-**20** δ 5.22 (s, 10 H, Cp), −11.77 (d, J_{HP} = 38, 1H, μ-H). The Ph and Cy resonances for the minor isomer could not been identified because they were hidden under those of the major isomer. trans/cis ratio = 8.

X-ray Structure Determination of Compound 7b. A suitable crystal of **7b** was stuck on a glass fiber and mounted on an Enraf-Nonius MACH-3 automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[40] Scattering factors and corrections for anomalous absorption were taken from ref 41. The structure was solved by direct methods (SHELXS),[42] completed by Fourier techniques and refined by full-matrix least-squares. An empirical absorption correction based on ψ-scan curve was applied (T_{min} = 0.95, T_{max} = 1). All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were introduced in calculated positions and were allocated an overall isotropic thermal parameter.

X-ray Structure Determination of Compounds 8a, 17, and 19. Data were collected at the University of Santiago de Compostela (Spain) on a Smart CCD-1000 Bruker diffractometer using graphite-monochromated Mo Kα radiation. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in 3 different ω regions and eventually refined against all reflections. The software SMART[43] 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,[43] and a multiscan absorption correction was applied with SADABS.[44] Using the program suite WinGX,[45] we solved the structures by Patterson interpretation and phase expansion, and they were refined with full-matrix least squares on F^2 with SHELXL97.[46] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the Fourier maps but were modeled on idealized positions except for the hydride atoms in all three compounds and the hydroxyl atom in **8a**, which were refined; all hydrogen atoms were given an overall isotropic parameter. In the case of **8a**, there is a tetrahydrofuran molecule H-bonded to the hydroxyl group but disordered over two positions (occupancies 0.60 and 0.40) sharing the same oxygen position. The corresponding carbon atoms were refined isotropically as the temperature factors were persistently nonpositive definites. For compound **17**, the hydrogens on the methoxy carbon atom were also found to be

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disordered over two positions (occupancies 0.5) related by rotation around the C−O bond.

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Supporting Information Available: Crystallographic data for the structural analysis of compounds **7b**, **8a**, **17**, and **19** in the CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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