# ORGANOMETALLICS

# Electronic Structure and Reactivity of the Carbyne-Bridged Dimolybdenum Radical $[Mo_2(\eta^5-C_5H_5)_2(\mu-CPh)(\mu-PCy_2)(\mu-CO)]^+$

M. Angeles Alvarez, M. Esther García, Daniel García-Vivó, Sonia Menéndez, and Miguel A. Ruiz\*

Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain

**Supporting Information** 

**ABSTRACT:** The unsaturated compound  $[Mo_2Cp_2(\mu-CPh) (\mu$ -PCy<sub>2</sub>) $(\mu$ -CO)] (1, Cp =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>) reacts with trace amounts of water in the presence of [FeCp<sub>2</sub>]BF<sub>4</sub> to give a mixture of the hydroxycarbyne complex  $[Mo_2Cp_2(\mu-COH)(\mu-CPh)(\mu PCy_2$ ]BF<sub>4</sub> (minor) and the hydroxo complex [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ - $CPh)(OH)(\mu - PCy_2)(CO)]BF_4$  (major product), with the latter rapidly rearranging to give the carbene isomer cis-[Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ - $\eta^{1}:\eta^{3}$ -CHPh)(O)( $\mu$ -PCy<sub>2</sub>)(CO)]BF<sub>4</sub> (Mo-Mo = 2.9435(3) Å). An analogous reaction takes place with phenol, to give selectively the related phenoxo complex  $[Mo_2Cp_2(\mu-CPh)-$ 



 $(OPh)(\mu$ -PCy<sub>2</sub>)(CO)]BF<sub>4</sub>. In contrast, the reactions of 1 with H<sub>2</sub>SiPh<sub>2</sub> or H<sub>3</sub>BNH<sub>2</sub><sup>4</sup>Bu in the presence of [FeCp<sub>2</sub>]BF<sub>4</sub> result in the selective H transfer to the O atom of the carbonyl ligand, to give the mentioned hydroxycarbyne complex. All the above reactions can be rationalized by assuming the initial formation of the radical cation  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(\mu-CO)]^+$  (2), a molecule displaying a somewhat weakened intermetallic bonding (Mo-Mo = 2.537 Å vs 2.493 Å in 1) and a linear semibridging carbonyl, with both the LUMO and most of the unpaired electron density being located at a single molybdenum atom, with a much smaller distribution over the oxygen atom of the carbonyl ligand, according to density functional theory calculations. As expected, the radical 2 adds rapidly a molecule of nitric oxide to give a diamagnetic product, but spontaneous decarbonylation also takes place to eventually give the 30-electron nitrosyl complex  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(\mu-NO)]BF_4$ . Deprotonation of cis- $[Mo_2Cp_2(\mu-\eta^1:\eta^3-CHPh)(O)(\mu-PCy_2)(CO)]BF_4$  gives the neutral carbyne complex cis- $[Mo_2Cp_2(\mu-CPh)(O)(\mu-PCy_2)$ (CO)] (Mo-Mo = 2.8024(5) Å), which upon protonation reverts to its carbene precursor, via the corresponding hydroxo complex. Related *trans* isomers can be prepared through protonation reactions of *trans*- $[Mo_2Cp_2(\mu-CPh)(O)(\mu-PCy_2)(CO)]$ (Mo-Mo = 2.8206(6) Å), a complex easily prepared by reacting the dicarbonyl  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(CO)_2]$  with air.

# INTRODUCTION

We have shown previously that binuclear cyclopentadienyl complexes with metal-metal multiple bonds are useful substrates to induce unusual bond formation and cleavage processes involving the ligands surrounding the coordinatively and electronically unsaturated dimetal center present in these molecules. The 30-electron benzylidyne complex  $[Mo_2Cp_2(\mu -$ CPh)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)] (1)<sup>1</sup> is one of these species (Cp =  $\eta^{5}$ - $C_5H_5$ ). For instance, it can be alkylated to give a cationic biscarbyne complex,  $[Mo_2Cp_2(\mu$ -COMe)( $\mu$ -CPh)( $\mu$ -PCy<sub>2</sub>)]- $(CF_3SO_3)$ , the latter undergoing C-C coupling between its carbyne ligands upon addition of simple donor molecules (L),  $C(OMe)CPh{(\mu-PCy_2)L_2](CF_3SO_3)}$  in a reversible way.<sup>2</sup> Interestingly, compound 1 undergoes a related redox-induced P-C coupling involving the carbyne and phosphide ligands. Thus, although 1 does not react itself with the secondary phosphine HPEt<sub>2</sub>, it reacts instantaneously in the presence of stoichiometric amounts of the ferrocenium salt [FeCp<sub>2</sub>]BF<sub>4</sub>, to give the phosphinocarbene derivative  $[Mo_2Cp_2(\mu-\eta^1:\eta^1,\kappa^1-\eta^1)]$  $CPhPEt_2)(\mu-PEt_2)(CO)(PHEt_2)]BF_4$  in high yield (Scheme 1).<sup>2</sup> More recently we have shown that 1 reacts with diphenyldisulfide (and also with HSPh) in the presence of Scheme 1



[FeCp<sub>2</sub>]BF<sub>4</sub> to give a thiolate derivative undergoing related P-C coupling upon carbonylation, now in a reversible way (Scheme 1).<sup>3</sup> The above reactions are themselves of interest

Received: October 22, 2012

since the coupling between  $PR_2$  and CR ligands at di- or polynuclear complexes to give bridging phosphinocarbene ligands has been observed only in a few instances,<sup>4,5</sup> and little is known about the reversibility of such processes.

Since compound 1 does not react itself with either PHEt<sub>2</sub> or S<sub>2</sub>Ph<sub>2</sub>, the reactions depicted in the Scheme 1 are likely to be initiated by the removal of one electron from 1 to give an extremely reactive 29-electron radical complex,  $[Mo_2Cp_2(\mu -$ CPh)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)]BF<sub>4</sub> (2), which would afterward react with the phosphine or disulfide reagents, respectively. It was thus of interest to examine in more detail the formation, structure, and chemical behavior of this putative paramagnetic species, in order to be able to further exploit its full synthetic potential. Organometallic radicals are quite elusive species, even if they are involved in many fundamental reactions such as ligand substitution, isomerization, atom transfer, electron transfer, and metal-metal bond formation, but most of work in this area has been devoted to the study of mononuclear species.<sup>6,7</sup> In contrast, the chemistry of binuclear radicals, particularly those having metal-metal bonds and electron counts below 34, has been comparatively little explored.8-10 Among the latter compounds, the 33-electron diiron and diruthenium complexes  $[Fe_2Cp_2(\mu$ -CSMe)( $\mu$ -CO)(CO)<sub>2</sub>] and  $[M_2Cp_2(\mu-CMe)(\mu-CO)(CO)_2]$  (M = Fe, Ru) are the only ones bearing carbyne ligands that appear to have been studied so far,<sup>9</sup> this adding more interest to the study of the reactivity of the dimolybdenum radical 2. Further interest in the chemistry of binuclear radicals stems from their use as synthetic analogues and models of the active centers of several naturally occurring enzymes such as the [FeFe]- and [NiFe]-hydrogenases.<sup>11</sup> We have shown previously that unsaturated binuclear radicals can be somewhat stabilized by using bridging P-donor ligands, thus allowing for a more controlled study of its chemical behavior. Such an approach is exemplified by the chemistry developed around the phosphide-bridged complex  $[Mo_2Cp_2(\mu-PPh_2) (CO)_{4}]^{12}$ and the diphosphine-bridged cations  $[M_2Cp_2(CO)_x(\mu-R_2PCH_2PR_2)]^+$  (M = Mo, W; R = Me, Ph; x = 2-4),<sup>13</sup> all of them displaying a metal-centered reactivity. In the case of compound 2, however, the presence of the bridging carbyne ligand might be the origin of some carbyne-centered reactivity, as it might be guessed from the behavior of the mentioned diiron complexes and also by that of some 17electron mononuclear carbyne complexes.<sup>7b</sup> In this paper we analyze the likely geometry and electronic structure of this paramagnetic complex in the light of density functional theory (DFT) calculations carried out on both the cation of 2 and its neutral precursor 1. This in turn will be useful to rationalize the reactivity of 2 toward simple molecules such as water, silanes, alcohols, or nitric oxide, among others. Moreover, complex 2 has been found to be very reactive toward a variety of bidentate ligands having E-H bonds (E = O, S, P), and the results of the latter reactions will be reported separately.

# RESULTS AND DISCUSSION

**Oxidation Reactions of the Carbyne Complex 1.** When no external reagents are added to a dichloromethane solution of the unsaturated compound 1, the addition of  $[FeCp_2]BF_4$  to this solution promotes a immediate reaction to give a mixture of up to three new species: the hydroxycarbyne complex  $[Mo_2Cp_2(\mu$ -COH)( $\mu$ -CPh)( $\mu$ -PCy<sub>2</sub>)]BF<sub>4</sub> (3), the hydroxo complex  $[Mo_2Cp_2(\mu$ -CPh)(OH)( $\mu$ -PCy<sub>2</sub>)(CO)]BF<sub>4</sub> (4), and the carbene complex *cis*- $[Mo_2Cp_2(\mu-\eta^{1}:\eta^{3}$ -CHPh)(O)( $\mu$ -PCy<sub>2</sub>)(CO)]BF<sub>4</sub> (*cis*-5) (Scheme 2). The relative ratio of Scheme 2



these compounds was found to be strongly dependent upon the precise experimental conditions, particularly the amount of water available (always present in trace amounts in the solvent, therefore proportional to the amount of solvent used) and the reaction time. Under the most anhydrous conditions used by us (reaction carried out in a CD<sub>2</sub>Cl<sub>2</sub> solution within an NMR tube), monitoring of the reaction mixture revealed that, just after the mixing of reagents, the ratio 3:4:cis-5 was around 3:10:1, but afterward the amounts of 3 and 4 gradually decreased, while that of cis-5 increased, so that the latter compound was the only species present in the solution after ca. 20 min. The presence of water greatly speeded these transformations: thus, the addition of a drop of water to the NMR tube just after mixing of reagents caused an immediate transformation to give *cis*-5 as the unique product detectable by <sup>31</sup>P NMR spectroscopy. The monitoring of this reaction when carried out in a Schlenk tube in dichloromethane solution (ca. 5 mL) gave similar results, except for the fact that, due to the greater amount of water available, the carbene cis-5 was the major species present even after the initial mixing of reagents. Of course, on-purpose addition of water causes the immediate full conversion into the carbene complex, which can be thus isolated in a conventional way (see the Experimental Section).

The unstable complexes 3 and 4 could be selectively generated through specific reactions (see later), and this allowed us to carry out some independent experiments to establish the role of water in the oxidation of 1 (Scheme 2). First we could observe that CD<sub>2</sub>Cl<sub>2</sub> solutions of the hydroxo complex 4 would slowly isomerize at room temperature to give cis-5, with this transformation being complete in ca. 20 min. However, when a drop of water was added to the NMR tube upon dissolution of 4, the transformation into the carbene complex was immediate, as determined by <sup>31</sup>P NMR spectroscopy. This suggests that the isomerization 4/cis-5 likely is an intermolecular process mediated by external reagents such as water or even the solvent. The external anion can be excluded as a possible proton vehicle since the oxidation of 1 with a ferrocenium salt having a less coordinating anion such as  $[FeCp_2](BAr'_4)$   $[Ar' = 3,5-C_6H_3(CF_3)_2]$  gave rapidly *cis-5*' (BAr'<sub>4</sub> - salt) without detectable amounts of the corresponding hydroxo complex. In any case, we note how different the above transformation is from that of the structurally related hydroxo complexes  $[M_2Cp_2(OH)(\mu-PPh_2)_2(CO)]BF_4$  (M = Mo, W), which at room temperature transform into the corresponding

Table 1. Sele	cted Bond	Lengths (A	) and Angles	(deg) for	the DFT-C	Computed	Structures of 1	1 and the	Cation in	2
---------------	-----------	------------	--------------	-----------	-----------	----------	-----------------	-----------	-----------	---

.

	$1^a$	1	2		1	2
Mo1-Mo2	2.464(1)	2.493	2.537	Mo1-P3-Mo2	61.2	62.0
Mo1-P3	2.402(3)	2.450	2.473	Mo1-C26-Mo2	77.3	78.6
Mo2-P3	2.403(2)	2.450	2.450	Mo1-Mo2-C5	54.1	64.6
Mo1-C26	1.99(1)	1.993	1.973	Mo1-Mo2-C26	51.2	49.7
Mo2-C26	1.97(1)	1.999	2.033	P3-Mo2-C5	88.6	92.5
Mo1-C5	2.09(1)	2.122	2.472	P3-Mo2-C26	89.9	91.4
Mo2-C5	2.11(1)	2.118	2.014	P3-Mo1-C5	88.5	81.8
C26-C31	1.46(2)	1.455	1.448	P3-Mo1-C26	90.1	92.1
C5-O4	1.18(1)	1.193	1.169	Mo2-C5-O4	144.1	166.9
				Mo1-C5-O4	143.8	124.7

<sup>a</sup>Experimental values determined by X-ray diffraction (see ref 2).

. . .

oxo hydride isomers  $[M_2Cp_2(\mu-H)(O)(\mu-PPh_2)_2(CO)]BF_4$ .<sup>14</sup> It is sensible to assume that the relatively high electron density at the bridgehead carbon of the carbyne ligand (see later) provides a driving force for the formation of the carbene (rather than hydride) isomer of the hydroxo complex 4.

The hydroxycarbyne complex 3 is analogous to the methoxycarbyne complex  $[Mo_2Cp_2(\mu$ -COH)( $\mu$ -COMe)( $\mu$ - $PCy_2$ ]BF<sub>4</sub>, a thermally unstable species rearranging at room temperature into the corresponding hydride isomer  $[Mo_2Cp_2(\mu$ -COMe)(H)( $\mu$ -PCy<sub>2</sub>)(CO)]BF<sub>4</sub>, before full decomposition takes place.<sup>15</sup> In contrast, the dichloromethane solutions of 3 are stable for a few hours at room temperature, although they eventually decompose, with no hydride isomer being detected during the process. An independent experiment revealed that compound 3 is rapidly deprotonated by water in dichloromethane solution, to cleanly regenerate the carbonyl complex 1. This is not unexpected after considering that hydroxycarbyne complexes have been previously generated through protonation reactions of carbonyl-bridged precursors.<sup>14a,15</sup> Not surprisingly either, the addition of 1 equiv of [FeCp<sub>2</sub>]BF<sub>4</sub> and a drop of water to a dichloromethane solution of 1 caused its immediate transformation into cis-5.

In all, the above data suggest that the radical complex 2 formed after removal, by the ferrocenium cation, of one electron from 1 would rapidly cleave the O–H bond of water molecules in two possible ways: either by capturing the OH group at the metal site (dominant path) or by abstracting an H atom at the oxygen of the bridging carbonyl (minor pathway). This is consistent with the observation of an irreversible oxidation wave at -0.14 V (vs the FeCp<sub>2</sub><sup>+</sup>/FeCp<sub>2</sub> couple) in the CV diagram of 1, when recorded in dichloromethane solution. In order to better understand this dual behavior of radical 2, we carried out some calculations and additional reactivity studies, to be discussed next.

**Geometric and Electronic Structure of the Paramagnetic Complex 2.** We have carried out DFT<sup>16</sup> calculations on both 1 and 2. Following the methodology previously used by us in the study of unsaturated carbyne complexes,<sup>15,17</sup> we have analyzed the electronic structure and bonding in these complexes through the properties of the relevant Kohn–Sham molecular orbitals (MO) and also by inspection of the topological properties of the electron density, as managed in the atoms in molecules (AIM) theory.<sup>18</sup>

The optimized bond lengths for the neutral substrate are in good agreement with the data measured through X-ray diffraction (Table 1),<sup>2</sup> although the computed values for lengths involving the metal atoms tend to be slightly longer (by less than 0.05 Å) than the corresponding experimental data.

This is a common trend with the functionals currently used in the DFT computations of transition metal compounds.<sup>16a,19</sup> We should stress that this neutral molecule displays essentially symmetrical bridging groups. It might have been expected that the removal of one electron from 1 would cause a generalized reduction in all interatomic distances, particularly those involving the metal atoms. Actually this was the observed effect upon removal of one electron from the singly bonded complex  $[Mo_2Cp_2(CO)_4(\mu-Ph_2PCH_2PPh_2)]$  (from ca. 3.27 to 2.99 Å)<sup>13b</sup> and more recently on the isolectronic complex  $[W_2Cp_2(CO)_4(PMe_3)_2]$  (from ca. 3.23 to 3.03 Å).<sup>10</sup> In contrast, the intermetallic length in 2 increases by some 0.05 Å, while the average Mo-CPh and Mo-P lengths remain almost unperturbed. The most dramatic change, however, takes place at the carbonyl ligand, which rearranges into a type II linear semibridging mode,<sup>20</sup> it being strongly bound to Mo2 (Mo-C = 2.014 Å) and only weakly bound to Mo1 (Mo-C = 2.014 Å)2.472 Å), while the Mo–C–O angle (166.9°) approaches linearity. The latter geometrical parameters are comparable to the experimental values measured for the semibridging carbonyls in the 30-electron complex  $[W_2Cp_2(CO)_2(\mu Ph_2PCH_2PPh_2)$ ] (average values W-C = 1.97 Å, W-C =2.44 Å,  $W-C-O = 167^{\circ})^{21}$  or in the isoelectronic dimers  $[M_2L_2(CO)_4]$  (M = Mo, W; L = Cp or related ligand).<sup>22</sup> Linear semibridging carbonyls of this type are favored for substrates with high intermetallic bond orders,<sup>23</sup> and this should be the case for the cation in 2. In all, however, the geometrical parameters suggest that the intermetallic bond order is somewhat reduced when going from 1 to 2, which is against simple predictions based on the effective atomic number (EAN) formalism, but consistent with the MO and AIM analysis to be discussed below.

The frontier MOs for 1 are comparable to those computed for the methoxycarbyne complex  $[Mo_2Cp_2(\mu$ -COMe $)(\mu$ - $PCy_2)(\mu$ -CO)],<sup>15</sup> except that the  $\delta$  component of the intermetallic bond having  $\pi$ -bonding character with respect to the metal-carbyne bond (MO 129) is much more stabilized in the benzylidyne complex. Apart from this, its triple M-M bond can be similarly described as having one  $\sigma$  (MO 131) and two  $\delta$ components, with the latter having some (MO 133) and significant (MO 129) bonding character to the bridging CO and CR ligands, respectively. Notably, the HOMO of the molecule is a bonding orbital having  $\sigma$  Mo-CO bonding character. Therefore, we can understand that the removal of one electron from this molecule might cause a significant weakening in the Mo-CO bond, which is consistent with the rearrangement (from bridging to linear semibridging) computed for the carbonyl ligand in 2.

The structural rearrangement occurring upon formation of 2 also modifies the intermetallic interactions in the cation, but in a less obvious way. Although the single-occupation MOs computed for 2 display considerable mixing, we can still identify pairs of  $\alpha$ - and  $\beta$ -spin orbitals accounting for the  $\sigma$ (MO 131 $\beta$  and MO 129 $\alpha$ ) and one  $\delta$  component (MO 134 $\alpha$ and MO 133 $\beta$ ) of the intermetallic bond. We notice that the latter component has considerable  $\pi$ -bonding character to the linear semibridging carbonyl, thus nicely reproducing the earlier interpretations that explain the prevalence of this type of carbonyl in complexes with multiple metal-metal bonds as derived from the stabilizing influence of these  $\pi$ -bonding interactions.<sup>20,22</sup> Steric effects have been proposed alternatively to explain the appearance of this sort of bridging ligand,<sup>23</sup> but obviously this is not the case for compound 2, which has the same steric constraints as those in its neutral precursor 1. Besides this, the second  $\delta$  component of the intermetallic bond present in 1 (the one involving  $\pi$  bonding to the carbyne ligand) can be clearly recognized in only a single orbital of the cation in 2 (MO 128 $\beta$ ). Thus, it appears that just three electrons would be clearly involved in  $\delta$ (Mo-Mo) bonding interactions, which is consistent with the moderate increase of the intermetallic distance (compared to 1) computed for 2.

On the other hand we note the presence, among the frontier orbitals, of one with a nonbonding character (MO  $132\alpha$ ), which therefore represents unpaired electron density largely located at the Mo1 atom, with a smaller contribution from the oxygen atom of the semibridging carbonyl. This is fully consistent with the distribution of the total spin density in the cation (Figure 3), which indeed is essentially located at the



**Figure 1.** DFT-optimized structure of the cation in compound **2**, with H atoms omitted for clarity.

Mo1 atom, with some participation of the oxygen atom and even smaller contributions from the Mo2 and C(carbyne) atoms. Moreover, the LUMO in the cation also is largely located at the Mo1 atom (MO134 $\beta$ , see the Supporting Information). Thus, from this orbital analysis we can conclude that the radical **2** should react preferentially at the Mo1 site, because of both the large concentration of unpaired electron density and the availability of an empty MO of low energy centered at this position, while the second site of attachment for an external radical should be the oxygen atom of the carbonyl. These conclusions are consistent with the outcome of reaction of **2** with water, which gives as the major product the hydroxo complex **4** (capture of an OH radical by the metal site), while the hydroxycarbyne complex 3 (following from the capture of a H radical by the oxygen site) is the minor product. We do not expect any primary reaction to take place at the carbyne C atom, in contrast to the chemical behavior observed for the paramagnetic  $Fe_2$  and  $Ru_2$  carbyne complexes mentioned in the Introduction.

The preceding orbital analysis does not give a full picture of the changes occurring at the carbyne and carbonyl ligands. These can be further analyzed by inspection of the topological properties of the electron density (Table 2). First we note that the electron density  $(\rho)$  at the intermetallic bond critical point (bcp) in 1 (0.624 e  $Å^{-3}$ ) is slightly higher than the one computed for its methoxycarbyne analogue  $[Mo_2Cp_2(\mu COMe)(\mu - PCy_2)(\mu - CO)]$  (0.609 e Å<sup>-3</sup>),<sup>15</sup> but in any case consistent with the triple intermetallic bond present in these molecules. Upon oxidation, that density is somewhat reduced to 0.553 e Å<sup>-3</sup>, a value still much higher than the values computed for related species having double metal-metal bonds (e.g., 0.444 e  $Å^{-3}$  for the 32-electron carboxycarbyne complex  $[Mo_2Cp_2{\mu-C(CO_2Me)}(\mu-PCy_2)(CO)_2])^{17}$  and actually comparable to the density computed for the 30-electron hydride  $[Mo_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_2]$  (0.582 e Å<sup>-3</sup>), a molecule with a triple intermetallic bond having one tricentric (Mo<sub>2</sub>H) and two bicentric (Mo-Mo) components.<sup>24</sup> Thus we conclude that the intermetallic bond in 1 is only moderately weakened upon oxidation, perhaps in part because of a larger delocalization of  $\delta$ -bonding electron density on the semibridging CO. As for the carbyne ligand, the average value of  $\rho$  at the Mo–C bcp (0.90 e  $Å^{-3}$ ) remains almost unchanged upon oxidation. In contrast, significant changes are computed for the carbonyl ligand. Thus, upon oxidation of 1, the density at the Mo2-C5 bond is increased from 0.72 to 0.80 e  $Å^{-3}$ , consistent with the appearance of a significant  $\pi$ -bonding contribution to that bond already noted, while no bcp could be located between the carbonyl and the Mo1 atom. At the same time, the density at the C–O bond is increased (from to 2.81 to 2.95 e  $Å^{-3}$ ), then approaching the values computed for terminal carbonyls.

Oxidatively Induced Reactions of 1 with Alcohols, Silanes, and Borane Adducts. To better understand the factors driving the reactions of the radical 2 to take place at the metal or oxygen sites, we investigated the oxidatively induced reactions of 1 with other reagents having E–H bonds, with E being a p-block element. We have noted above that the reaction with molecules having P–H and S–H bonds (reactions with PHEt<sub>2</sub> and HSPh) occur preferentially at the metal site to form the corresponding Mo–P and Mo–S bonds, respectively.<sup>2,3</sup> We have now examined some reactions with molecules having O– H, N–H, C–H, Si–H, and B–H bonds. Unfortunately, these reactions are seriously limited by kinetics, for if the added reagent reacts with 2 too slowly, then the reaction with water occurs preferentially to eventually give only *cis*-5.

No reaction other than the formation of *cis*-5 was observed when adding  $[FeCp_2]BF_4$  to dichloromethane solutions of 1 containing an excess of NH<sub>2</sub>(*p*-tol) or different 1-alkynes (HC=CR, with R = *p*-tol, CO<sub>2</sub>Me). However, in the presence of the silane SiH<sub>2</sub>Ph<sub>2</sub> or the borane adduct H<sub>3</sub>B·NH<sub>2</sub><sup>t</sup>Bu (molecules which are themselves unreactive toward 1), a fast reaction takes place to give the hydroxycarbyne complex 3, a result of the selective abstraction, by the oxygen site in the radical 2, of a hydrogen atom from the corresponding Si–H and B–H bonds (Scheme 3). In contrast, when the reaction was carried out in the presence of phenol, then the phenoxo complex  $[Mo_2Cp_2(\mu$ -CPh)(OPh)( $\mu$ -PCy<sub>2</sub>)(CO)]BF<sub>4</sub> (6) was



Figure 2. Selected molecular orbitals computed for 1 and the radical cation in 2, with their energies (in eV) and main bonding character indicated below.

formed selectively, this following from the selective abstraction of a phenoxyl group by the metal site in 2. Complex 6 is structurally related to the hydroxo complex 4 (see below) and also is rather unstable; it slowly undergoes hydrolysis upon manipulation, to eventually give cis-5 via compound 4.

From the above data we conclude that the outcome of the reactions of radical 2 are strongly influenced by the donor properties of the incoming molecule and obviously also by the strength of the E–H bond to be cleaved. We should recall here that the Mo1 atom not only bears most of the unpaired spin density but also is the greater contributor to the LUMO of the cation in 2. Therefore, H– $ER_n$  reagents with a significant donor

ability of the E atom would tend to bind first the metal site, then evolving through dehydrogenation (easier for the weaker E–H bonds), thus accounting for the formation of a new Mo– ER<sub>n</sub> bond. The silanes and borane adducts lack any lone electron pair and are therefore very poor donors, this precluding their efficient coordination at the metal site. Yet, the corresponding E–H bonds are relatively weak, with this now facilitating the H abstraction by the O atom of the carbonyl ligand, to generate a new and strong O–H bond. Under this view, the failure of 2 to react rapidly with amines and 1-alkynes would follow from a combination of two adverse



Figure 3. Total spin density for the radical cation in 2.

Table 2. Topological Properties of the Electron Density in Complexes 1 and  $2^a$ 

		1		
bond	ρ	$\nabla^2 \rho$	ρ	$ abla^2  ho$
Mo1-Mo2	0.624	1.85	0.553	1.62
Mo1-P3	0.502	3.31	0.484	2.87
Mo2-P3	0.500	3.33	0.500	3.33
Mo1-C(5)	0.715	6.04	not found	
Mo(2)-C(5)	0.720	6.10	0.800	9.45
Mo(1)-C(26)	0.909	9.50	0.946	9.37
Mo(2)-C(26)	0.895	9.44	0.829	8.92
C(5) - O(4)	2.807	23.83	2.952	28.64
C(26) - C(31)	1.954	-16.07	1.979	-16.44

<sup>*a*</sup>Values of the electron density at the bond critical points ( $\rho$ ) are given in e Å<sup>-3</sup>, and values of the Laplacian of  $\rho$  at these points ( $\nabla^2 \rho$ ) are given in e Å<sup>-5</sup>, with the labeling according to Figure 1; see the Experimental Section for details of the DFT calculations.

Scheme 3



circumstances: a relatively poor donor ability of these molecules and the relatively high strength of their N–H and C–H bonds.

Spectroscopic Characterization of Hydroxo, Alkoxo, and Hydroxycarbyne Complexes. The spectroscopic data available for the hydroxycarbyne complex 3 (Table 3 and Experimental Section) are similar to those of the isoelectronic hydroxy- and methoxycarbyne cations  $[Mo_2Cp_2(\mu-X)(\mu-COMe)(\mu-PCy_2)]BF_4$  (X = COH, CPh)<sup>15,2</sup> and, therefore, need no detailed analysis. We just note that all these 30electron cations are characterized by strongly deshielded <sup>31</sup>P NMR resonances at ca. 260 ppm and <sup>13</sup>C NMR resonances for

Table 3. Selected IR <sup><i>a</i></sup>	and <sup>31</sup> P{ <sup>1</sup> H} a	and <sup>13</sup> C{ <sup>1</sup> H}	NMR <sup>b</sup>	Data
for New Compounds				

compound	$\nu(\mathrm{XO})$	$\delta$ (P)	$\delta$ ( $\mu$ -C) [ $J_{\rm PC}$ ]
$\begin{bmatrix} Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO) \end{bmatrix}$ (1) <sup>c</sup>	1686 (s)	228.5	385.2 [15]
$\begin{bmatrix} Mo_2Cp_2(\mu\text{-COH})(\mu\text{-CPh})(\mu\text{-PCy}_2) \end{bmatrix}$ BF <sub>4</sub> (3)	$(w)^{d}$	254.8 <sup>e</sup>	401.4 [14] <sup>e</sup> 357.8 [14]
$\begin{bmatrix} Mo_2Cp_2(\mu\text{-}CPh)(OH)(\mu\text{-}PCy_2)(CO) \end{bmatrix} \\ BF_4 (4) \end{bmatrix}$	1965 (s)	302.4 <sup>d</sup>	413.1 <sup>d</sup>
$cis-[Mo_2Cp_2(\mu-\eta^{1}:\eta^3-CHPh)(O)(\mu-PCy_2)(CO)]BF_4$ ( $cis-5$ )	1944 (s)	236.4	
<i>cis</i> -[Mo <sub>2</sub> Cp <sub>2</sub> ( $\mu$ - $\eta$ <sup>1</sup> : $\eta$ <sup>3</sup> -CHPh)(O)( $\mu$ -PCy <sub>2</sub> )(CO)]BAr' <sub>4</sub> ( <i>cis</i> - <b>5</b> ')	1952 (s)	238.5	177.0
trans- $[Mo_2Cp_2(\mu-\eta^1:\eta^3-CHPh)(O)(\mu-PCy_2)(CO)]BF_4$ (trans-5)	1930 (s)	242.5	
$ \begin{array}{l} [Mo_2Cp_2(\mu\text{-CPh})(\text{OPh})(\mu\text{-PCy}_2) \\ (\text{CO})]BF_4 \ (6) \end{array} $	1962 (s)	277.3	
$\begin{array}{l} \textit{cis-}[Mo_2Cp_2(\mu\text{-}CPh)(O)(\mu\text{-}PCy_2)\\ (CO)] (\textit{cis-}7) \end{array}$	1915 (s)	195.8	360.0 [7]
$trans-[Mo_2Cp_2(\mu-CPh)(O)(\mu-PCy_2) (CO)] (trans-7)$	1895 (s)	187.4	
$ \begin{matrix} [Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}NO)]BF_4 \\ (8) \end{matrix} $	1511 (s)	267.9	404.5 [14]
$\begin{bmatrix} Mo_2Cp_2(\mu\text{-CHPh})(O)(\mu\text{-PCy}_2)(NO) \end{bmatrix} \\ BF_4 (9) \end{bmatrix}$	1610 (s)	181.0	132.3[4]

<sup>*a*</sup>Recorded in dichloromethane solution, with X–O (X = C, N) stretching bands ( $\nu$ (XO)) in cm<sup>-1</sup>. <sup>*b*</sup>Recorded in CD<sub>2</sub>Cl<sub>2</sub> solutions at 290 K and 162.00 MHz (<sup>31</sup>P) or 100.62 MHz (<sup>13</sup>C) unless otherwise stated;  $\delta$  in ppm relative to external 85% aqueous H<sub>3</sub>PO<sub>4</sub> or internal TMS, respectively; J<sub>PC</sub> in Hz. <sup>*c*</sup>Data from ref 1. <sup>*d*</sup>Recorded in Nujol mull. <sup>*e*</sup>Recorded at 233 K.

the bridgehead COR atoms at ca. 370 ppm. In the case of **3**, the <sup>13</sup>C NMR spectrum displays a second strongly deshielded resonance, which is therefore safely assigned to the benzylidyne ligand (401.4 ppm). We note that both carbyne resonances display a P–C coupling of 14 Hz, comparable to that measured in the starting complex **1**, in agreement with the similar P–Mo–C angles involving the carbyne ligands in all these molecules.<sup>25</sup> We also note that the Cp ligands give rise to single <sup>13</sup>C or <sup>1</sup>H NMR resonances, thus indicating that the hydroxycarbyne group undergoes fast rotation around its C–O bond, as previously observed for other hydroxycarbyne-bridged complexes.<sup>14a,15,26</sup> Unfortunately we could not identify the resonance of the OH group in the <sup>1</sup>H NMR spectrum of **3**, but its presence is supported by the appearance of a broad band at ca. 3400 cm<sup>-1</sup> in its solid-state IR spectrum, corresponding to the O–H stretch of this group.

The spectroscopic data for compounds 4 and 6 are similar to each other, suggesting that these asymmetric species share the same basic structural features. They display a high-frequency C-O stretch at ca. 1965 cm<sup>-1</sup>, indicative of the presence of a terminal carbonyl in a cationic complex.<sup>27</sup> Unexpectedly, both complexes display strongly deshielded <sup>31</sup>P NMR resonances at 302.4 and 277.3 ppm, respectively. This is a feature characteristic of  $Mo_2(\mu$ -PCy<sub>2</sub>) complexes having triple intermetallic bonds. Actually, such high values have been previously observed only for hydride complexes of the type  $[Mo_2Cp_2(H)(\mu-X)(\mu-PCy_2)(CO)]BF_4$  (X = COMe, PCy\_2),<sup>15,28</sup> which however display a *transoid* arrangement of their terminal hydride and semibridging carbonyls. We have recently shown that the related ditungsten complexes cis- $[W_2Cp_2(X)(\mu$ -PPh<sub>2</sub>)<sub>2</sub>(CO)]BF<sub>4</sub> display terminal hydroxo and thiolate ligands, which rather behave as three-electron donors due to strong  $\pi$  bonding to the metal atoms.<sup>29</sup> In contrast, the

dimolybdenum thiolate complex  $[Mo_2Cp_2(CPh)(\mu-PCy_2)(\mu-PCy_2)]$ SPh)(CO)]BF<sub>4</sub> seems to prefer a geometry with bridging thiolate (again a three-electron donor group) and essentially terminal benzylidyne ligands, according to DFT calculations. In all these previous cases, however, the corresponding cations are 32-electron complexes for which a double metal-metal bond can be formulated according to the EAN formalism. In line with this, the PR<sub>2</sub> ligands in all these species give rise to relatively shielded <sup>31</sup>P NMR resonances (around 110 ppm). This does not appear to be the case for compounds 4 and 6, which display strongly deshielded <sup>31</sup>P resonances characteristic of 30-electron complexes while keeping a bridging benzylidyne ligand ( $\delta_{\rm C}$  413.1 ppm for 4). From all these considerations we conclude that the Mo-OR binding in compounds 4 and 6 must be described as an essentially single bond, this leading us to propose a formal triple intermetallic bond for these molecules.

**Structure of the Carbene Complex** *cis*-5'. The structure of complex *cis*-5 was determined on a crystal of its  $BAr'_4^-$  salt *cis*-5'. The cation is built up from CpMo(CO) and CpMo(O) units placed in a *cisoid* arrangement and bridged by dicyclohexylphosphide and benzylidene ligands (Figure 4).



**Figure 4.** ORTEP diagram (30% probability) of the cation in compound *cis*-**5**', with H atoms (except H2) and Cy groups (except their  $C^1$  atoms) omitted for clarity.

The coordination of the carbene ligand is strongly asymmetric, it being strongly bound to the O-bearing metal atom (Mo–C = 2.083(3) Å) and more loosely to the CO-bearing metal (2.191(3) Å); additionally, the *ipso* carbon of the phenyl ring is clearly within bonding distance of the Mo1 atom (2.393(3) Å), while one of the *ortho* carbons might be viewed as weakly interacting with that metal atom (2.675(3) Å). Therefore, the carbene ligand can be formally viewed as a four-electron donor, bound to the metal center through the carbene atom and a double C–C bond of its aryl ring ( $\mu$ - $\eta^1$ : $\eta^3$  coordination mode). This coordination mode of arylcarbene ligands has been previously characterized crystallographically in a few instances,  $^{30,31}$  including the dimolybdenum complex [Mo<sub>2</sub>Cp<sub>2</sub>{ $\mu$ - $\eta^{1}:\eta^{3}-C(p-tol)_{2}$  ( $\mu$ -CO)(CO)<sub>3</sub>]. The coordination of the aryl ring in all these complexes seems to induce some localization effect on the ring (alternating long and short C-C bonds lengths) and some shortening in the carbene-aryl C-C bond, with these structural features also being observed in cis-5' (Table 4).

The Mo–O length in this cation is very short (1.689(2) Å), as usually found in organometallic complexes having terminal oxo ligands,<sup>32</sup> a feature indicative of the presence of

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *cis*-5'

Mo1-Mo2	2.9435(3)	C6-C7	1.417(5)
Mo1-P1	2.3958(8)	C7-C8	1.358(4)
Mo2-P1	2.4316(7)	C8-C3	1.436(4)
Mo2-C2	2.083(3)	Mo1-P1-Mo2	75.14(2)
Mo1-C2	2.191(3)	Mo1-C2-Mo2	87.0(1)
Mo1-C3	2.393(3)	Mo2-Mo1-C1	109.5(1)
Mo1-C4	2.675(3)	Mo1-Mo2-O2	106.4(1)
Mo1-C1	1.998(3)	P1-Mo1-C1	82.8(1)
Mo2-O2	1.689(2)	P1-Mo1-C2	97.9(1)
C2-C3	1.446(4)	P1-Mo2-O2	98.9(1)
C3-C4	1.421(4)	P1-Mo2-C2	99.8(1)
C4-C5	1.416(4)	С3-С2-Н2	115(2)
C5-C6	1.361(4)		

considerable multiplicity in that bond. Actually, the oxo ligand in *cis*-5' must be better considered as a four-electron donor, this leading to the electronic saturation of the dimetal center. As a result, a single metal—metal bond might be formulated for this 34-electron complex under the EAN formalism, which is in agreement with the relatively high intermetallic length of 2.9435(3) Å. For comparison, the intermetallic distance in the 32-electron carbyne complex  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)-(CO)_2]$  is only 2.666(1) Å.<sup>1</sup>

The spectroscopic data in solution for the salts cis-5 and cis-5' are comparable to each other, this revealing the presence of only moderate cation-anion interactions for the  $BF_4^-$  ion. Moreover they are fully consistent with the structure found in the crystal. Of particular interest concerning the description of the Mo-O and Mo-Mo bonds is the observation of a relatively deshielded <sup>31</sup>P NMR resonance at ca. 240 ppm, more than 100 ppm above the usual shifts observed for 32-electron complexes of the type  $[Mo_2Cp_2(\mu-X)(\mu-PCy_2)(CO)_2]$  (X = three-electron donor group; e.g.,  $\delta_{\rm P}$  117.6 ppm when X = CPh), thus supporting the formulation of this cation as a 34-electron complex with a single Mo-Mo bond. For comparison, the electron-precise tricarbonyls  $[Mo_2Cp_2(\mu-X)(\mu-PCy_2)(CO)_3]$  $(X = COMe, CHCH(p-tol), CHCH_2)$  display similarly deshielded <sup>31</sup>P NMR resonances in the range 220-250 ppm.<sup>17,33</sup>

The carbene ligand in *cis*-5 retains in solution the  $\mu$ - $\eta^{1}$ : $\eta^{3}$  coordination mode found in the solid state. Thus, the <sup>13</sup>C NMR spectrum of the complex displays, in addition to a resonance at 177.0 ppm consistent with the presence of a bridging carbene ligand,<sup>34</sup> six distinct resonances for the aryl ring, with the *ipso* (102.0 ppm) and one of the *ortho* resonances (101.2 ppm) being considerably shifted upfield (by some 60 and 30 ppm, respectively), thus denoting their coordination to a metal atom in solution. In line with this, the <sup>1</sup>H NMR spectrum of this complex reveals an unusual shielding for one of the *ortho* aryl resonances ( $\delta_{\rm H}$  ca. 4.6 ppm), while the carbene C–H resonance appears strongly deshielded ( $\delta_{\rm H}$  ca. 10 ppm). These spectroscopic features are common to previous binuclear complexes having  $\mu$ - $\eta^{1}$ : $\eta^{3}$  arylcarbene ligands.<sup>30c,35</sup>

Neutral Derivatives and *trans* lsomers of Compounds 4 and 5. The addition of a strong base such as 1,8diazabicycloundec-7-ene to dichloromethane solutions of either the hydroxo complex 4 or its carbene isomer *cis*-5 causes their immediate deprotonation to give the neutral oxo carbyne complex *cis*- $[Mo_2Cp_2(\mu$ -CPh)(O)( $\mu$ -PCy<sub>2</sub>)(CO)] (*cis*-7), which retains the *cisoid* arrangement of the MoCp fragments found in its cationic carbene precursor, as confirmed crystallographically (Scheme 4 and Figure 5). This neutral complex

#### Scheme 4



**Figure 5.** ORTEP diagram (30% probability) of *cis*-7, with H atoms and Cy groups (except their  $C^1$  atoms) omitted for clarity.

could be easily reprotonated upon reaction with  $\mathrm{HBF_4}\cdot\mathrm{OEt_2}$ , a process taking place selectively at the oxo ligand as expected, <sup>14</sup> to give the hydroxo complex 4, thus completing a loop connecting hydroxo carbyne, oxo carbene, and oxo carbyne complexes.

Taking into account the retention of stereochemistry observed in the above reactions, it could be anticipated that a whole set of trans isomers of compounds 4, 5, and 7 might be prepared, should a trans isomer of any of these compounds be available. Mays et al. have shown previously that the reaction of the dicarbonyl complex trans- $[Mo_2Cp_2(\mu-PPh_2)_2(CO)_2]$  with air gives the oxo derivative trans- $[Mo_2Cp_2(O)(\mu-PPh_2)_2(CO)]$ as the major product, whereas the same reaction with the carbonyl complex  $[Mo_2Cp_2(\mu-PPh_2)_2(\mu-CO)]$  instead leads preferentially to the cis isomer.<sup>36</sup> Similar selectivity was observed in the reactions of the methoxycarbyne complexes  $[Mo_2Cp_2(\mu$ -COMe $)(\mu$ -PCy<sub>2</sub> $)(CO)_x$  with air (x = 1, 2).<sup>37</sup> Thus, it was not surprising that we could prepare selectively the trans isomer of complex 7 by reacting the dicarbonyl  $[Mo_2Cp_2(\mu$ -CPh) $(\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] with air (Scheme 5). The neutral complex trans-7 thus obtained then reacts readily with  $HBF_4 \cdot OEt_2$ , but we could not detect a hydroxo complex in the reaction mixture; instead, the trans isomer of the carbene complex 5 was the only product present in the solution, a compound that reverts to its neutral precursor trans-7 upon reaction with a strong base. No doubt the protonation of trans-7 is initiated at the oxo ligand, but apparently the





corresponding hydroxo complex is just too unstable and rapidly rearranges into its more stable isomer *trans*-5.

The spectroscopic data available for *trans*-5 (Table 3 and Experimental Section) are comparable to those of its *cis* isomer and therefore deserve no detailed analysis. We just note that this isomer displays a C–O stretching band some 15 cm<sup>-1</sup> lower than that of its *cis* isomer, a difference also observed for the *cis* and *trans* isomers of the neutral oxo complexes 7. As for the carbene ligand, it gives rise to <sup>1</sup>H NMR resonances similar to those of *cis*-5, that is, a very deshielded C–H resonance ( $\delta_{\rm H}$  ca. 11 ppm) and five inequivalent aryl resonances, one of them quite shielded ( $\delta_{\rm H}$  ca. 4.6 ppm), thus indicating the  $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>3</sup> coordination of the arylcarbene ligand in this isomer.

**Structural Characterization of the Oxo Complexes 7.** The structures of the *cis* and *trans* isomers of the oxo carbyne complex 7 were determined through X-ray analysis (Figures 5 and 6 and Table 5). Both molecules are built up from



**Figure 6.** ORTEP diagram (30% probability) of *trans*-7, with H atoms and Cy groups (except their  $C^1$  atoms) omitted for clarity.

CpMo(CO) and CpMo(O) units bridged by dicyclohexylphosphide and benzylidyne ligands in a similar way, except for the relative conformation of the terminal ligands. In the *trans* isomer the central Mo<sub>2</sub>PC rhombus is nearly flat (dihedral P1– Mo1–Mo2–C2 angle 179.8°) and the terminal carbonyl is nearly normal to the intermetallic axis, while the oxo ligand points away from the intermetallic region (Mo–Mo–O ca. 110°). In the *cis* isomer, however, the central Mo<sub>2</sub>PC rhombus is significantly puckered (dihedral P1–Mo1–Mo2–C2 angle 155.6°), and the CO and O ligands are placed almost parallel to each other (Figure 5). The conformation of the *trans* isomer has been previous determined crystallographically in the related

Table 5.	Selected	Bond Len	oths (Å)	and Angles	(deg) fo	r the <i>cis</i>	and trans	Isomers o	f Compound 7
Table 5.	ociccica	Dona Len	guns (II)	and migics	(ucg) 10	i une cio	and name	130111013 0	i Compound /

	cis-7	trans-7		cis-7	trans-7
Mo1-Mo2	2.8024(5)	2.8206(6)	Mo1-P1-Mo2	70.89(4)	72.11(4)
Mo1-P1	2.363(1)	2.354(1)	Mo1-C2-Mo2	88.4(2)	89.1(2)
Mo2-P1	2.467(2)	2.437(1)	Mo1-Mo2-O2	103.6(1)	109.6(1)
Mo1-C1	1.962(6)	1.970(5)	Mo2-Mo1-C1	78.6(2)	87.7(2)
Mo1-C2	1.928(6)	1.920(5)	P1-Mo1-C1	91.7(1)	88.4(2)
Mo2-C2	2.089(5)	2.096(5)	P1-Mo1-C2	101.2(2)	103.3(2)
Mo2-O2	1.720(4)	1.704(4)	P1-Mo2-O2	105.5(1)	102.1(1)
C2-C3	1.465(8)	1.465(7)	P1-Mo2-C2	93.5(2)	95.5(2)
C1-O1	1.146(6)	1.154(6)	Mo1-C1-O1	174.0(4)	176.4(5)

oxo complexes *trans*- $[M_2Cp_2(\mu - X)(O)(\mu - PPh_2)(CO)]$  (M = Mo, X = PPh<sub>2</sub>,<sup>36</sup> CHCHPh;<sup>38</sup> M = W, X = CH<sub>2</sub>PPh<sub>2</sub>).<sup>21</sup> On the other hand, the conformation of the *cis* isomer can be related to those recently determined for several diphenylphosphide-bridged Mo<sub>2</sub> and W<sub>2</sub> complexes of the type  $[M_2Cp_2(\mu - PPh_2)_2(X)(CO)]^{n+}$  (n = 1, 0), with X being a terminal monodentate or chelate anionic ligand.<sup>14a,29,39</sup>

The above conformational differences, however, have little influence on the interatomic distances, which are comparable in both isomers of compound 7 but still deserve some analysis. The Mo–O lengths of ca. 1.71 Å are almost as short as that in *cis*-5, but the intermetallic lengths of ca. 2.81 Å are significantly longer, actually midway between the reference value for a double bond (cf. 2.666(1) Å in  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)-(CO)_2])^1$  and the value of 2.9435(3) Å measured for the "single" Mo–Mo bond in *cis*-5. We have previously interpreted this sort of intermediate situation as resulting from a diminished  $\pi(Mo-O)$  bonding interaction that can be visualized by using a mixture of canonical forms involving the oxo ligand acting as a two- or a four-electron donor, respectively.<sup>40</sup> This can be represented in the case of 7 through the forms *I* and *II* depicted in Chart 1, with the latter implying

# Chart 1



the asymmetric coordination of the bridging ligands, closer to the CO-bearing metal atom. Thus, although a form of type II would be dominant in the cation of *cis*-5 (and presumably also in the case of the mentioned complexes trans- $[M_2Cp_2(\mu X(O)(\mu$ -PPh<sub>2</sub>)(CO)], because of their large intermetallic lengths, in the range 2.89–2.95 Å), both canonical forms would contribute significantly to the bonding in compound 7. Incidentally we note that the trans isomer displays a slightly shorter Mo-O length of 1.704(4) Å, which correlates with a slightly longer Mo-Mo length of 2.8206(6) Å (greater contribution of the form II). In any case, the donor efficiency of the oxo ligand in 7 is much superior to that of the terminal CO, as concluded from the significant elongation of the Mo-P and Mo-C(carbyne) bonds involving the O-bearing metal atom (ca. 0.09 and 0.12 Å, respectively). This effect is so pronounced that the actual Mo-C lengths for the carbyne ligand of 1.92 and 2.09 Å approach the reference values for double and single bonds involving an sp<sup>2</sup> C atom even more

closely than anticipated for a situation intermediate between the extreme descriptions represented by the forms *I* and *II* (cf. 1.94(2) Å for the W=C bond in the carbene complex  $[W{\kappa^3-(NC_4HMe_2)_3BH}(CMePh)(CO)_2]BF_4)$ .<sup>41</sup>

The spectroscopic data in solution for the cis and trans isomers of complex 7 are consistent with the structural data just discussed. First we note that both isomers give rise to <sup>31</sup>P NMR resonances at ca. 190 ppm, a chemical shift much higher than the values expected for 32-electron complexes with double Mo-Mo bonds (cf. 117.6 ppm for  $[Mo_2Cp_2(\mu-CPh)(\mu PCy_2(CO)_2$ ), but still lower than the value of ca. 236 ppm recorded for the 34-electron complex cis-5. This again suggests a situation intermediate between those represented by the canonical forms I and II of Chart 1. In line with this, the  ${}^{13}C$ NMR resonance of the bridgehead atom of the carbyne ligand in cis-7 ( $\delta_{\rm C}$  360.0 ppm) appears significantly more shielded than the corresponding resonances in related dimolybdenum complexes having symmetrically bridging CPh ligands, with chemical shifts in the range 385-435 ppm.<sup>1,3</sup> We finally note that the *cis* isomer displays a C-O stretching frequency some 20 cm<sup>-1</sup> higher than its *trans* isomer, as noted already for the isomers of 5. A similar trend was found for the cis and trans isomers of the diphenylphosphide-bridged oxo complex  $[Mo_2Cp_2(O)(\mu-PPh_2)_2(CO)]$ .<sup>36</sup> It is tempting to attribute this effect to the slightly stronger Mo-O interaction apparent for the *trans* isomer, because that would increase the  $\pi$  backdonation of the metal center to the carbonyl, therefore reducing the stretching frequency of the latter ligand.

**Nitrosyl Derivatives of Complex 1.** Nitrogen monoxide is a stable radical expected to react readily with organometallic radicals to afford more stable diamagnetic products, <sup>12,13b</sup> and indeed this is the case of compound **2**. Thus, although the triply bonded complex **1** does not react rapidly with diluted NO (2000 ppm in N<sub>2</sub>), it does it instantaneously in the presence of [FeCp<sub>2</sub>]BF<sub>4</sub> to give the nitrosyl-bridged complex [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -CPh)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -NO)]BF<sub>4</sub> (**8**) in good yield. This reaction is presumably initiated by NO coordination to the radical **2**, to give an intermediate **A** having CO and NO ligands that would rapidly release CO to give **8** (Scheme 6). However, we have not identified such an intermediate upon monitoring of the above reaction.

Unsaturated binuclear complexes bridged by nitrosyl ligands are rather uncommon species,<sup>42</sup> but they can be involved in interesting reactions, particularly the cleavage of the N–O bond of the nitrosyl ligand, as observed for 32-electron complexes of the type  $[M_2Cp_2R_2(\mu-NO)_2]$  (M = Mo, W).<sup>43</sup> Interestingly, no complex with a nitrosyl ligand bridging a triple intermetallic bond appears to have been previously described in the literature. Unfortunately our attempts to grow X-ray quality crystals of **8** or its BAr'<sub>4</sub><sup>-</sup> salt were unsuccessful. Attempts to Scheme 6



purify the latter salts through column chromatography on alumina promoted instead a clean transformation on 8, to give the neutral carbone complex  $[Mo_2Cp_2(\mu-CHPh)(O)(\mu-PCy_2)-$ (NO)]BF<sub>4</sub> (9) in good yield (Scheme 6). Presumably, the formation of 9 involves the nucleophilic attack of surface hydroxide groups on the cation of 8, followed by a H migration from the coordinated OH to the carbyne ligand in the resulting intermediate B, a process analogous to the isomerization 4/cis-5 discussed above (Scheme 2). In agreement with this, a separate experiment confirmed that 9 can be obtained by stirring a dichloromethane solution of 8 with solid KOH. Actually, the latter reaction also gives a small amount of a second species (not isolated) that displays a <sup>31</sup>P NMR resonance at 180.8 ppm, quite close to that of 9 (181.0 ppm), therefore being proposed as a geometric isomer of the main product. In any case, the above transformation reveals that the unsaturated nitrosyl complex 8 is a highly electrophilic substrate, and further studies on the reactivity of this electrondeficient cation are now under way in our laboratory.

The structural characterization of 8 is straightforward on the basis of the available spectroscopic data. The presence of a symmetrically bridging carbyne ligand is denoted by the appearance of a strongly deshielded resonance at 405 ppm in its <sup>13</sup>C NMR spectrum, while the presence of the bridging nitrosyl is confirmed by the observation of a low-frequency N-O stretch at 1511 cm<sup>-1</sup> in its solid-state spectrum.<sup>42</sup> As a result, the cation in 8 is a 30-electron complex for which a triple intermetallic bond is to be formulated under the EAN formalism, which is in agreement with the strong deshielding of its <sup>31</sup>P nucleus ( $\delta_P$  ca. 270 ppm). In contrast, compound 9 gives rise to a <sup>31</sup>P NMR resonance comparable to those of the oxo complexes 7, while its solid-state IR spectrum establish unambiguously the presence of terminal nitrosyl ( $\nu_{\rm NO}$  1606 cm<sup>-1</sup>) and oxo ( $\nu_{\rm MoO}$  933 cm<sup>-1</sup>) ligands.<sup>32,42</sup> At the same time, its <sup>13</sup>C NMR spectrum shows the absence of any deshielded carbyne resonance, which has been instead replaced by a much more shielded CH resonance at 132.3 ppm, consistent with the presence of a bridging carbene ligand ( $\delta_{\rm H}$  8.70 ppm),<sup>34</sup> while the resonances of the phenyl ring are normal, indicating no

interaction with the metal atoms. From all the above data, however, we cannot establish the exact conformation of the molecule, although it likely corresponds to the *cis* isomer having the Ph group pointing away from the puckered central Mo<sub>2</sub>PC ring of the molecule, expectedly more favored on steric grounds.

# CONCLUDING REMARKS

One-electron oxidation by [FeCp<sub>2</sub>]BF<sub>4</sub> greatly increases the reactivity of the relatively inert 30-electron complex  $[Mo_2Cp_2(\mu$ -CPh $)(\mu$ -PCy<sub>2</sub> $)(\mu$ -CO)] (1), thus enabling it to rapidly react with many different molecules under mild conditions. According to DFT calculations, the radical species  $[Mo_2Cp_2(\mu$ -CPh)( $\mu$ -PCy\_2)( $\mu$ -CO)]<sup>+</sup> (2) formed after removal of one electron from 1 displays a somewhat weakened intermetallic bonding and a linear semibridging carbonyl, while both the LUMO and most of the unpaired electron density are located at a single molybdenum atom, with a much smaller distribution over the oxygen atom of the carbonyl ligand. As a result, the reactions of 2 with simple  $H-ER_n$ reagents (thiols, phosphines, alcohols, etc.) are expected to be initiated by the coordination of these donor molecules at the Mo site, followed by the cleavage of one H-E bond to eventually yield a new Mo-ER, bond. Molecules lacking a reasonable donor ability, but having relatively weak H-E bonds, instead might be involved in H transfer to the O atom of the carbonyl ligand of 2 to give the hydroxycarbyne complex  $[Mo_2Cp_2(\mu$ -COH)( $\mu$ -CPh)( $\mu$ -PCy<sub>2</sub>)]<sup>+</sup>, as observed in the reactions with silanes and borane adducts. Finally, molecules with poor donor properties and strong H-E bonds would fail to react with 2 fast enough to avoid the interaction of this reactive radical with trace water molecules. The latter reaction takes place at both the Mo and O sites, with the former being dominant and leading to the unstable hydroxo complex  $[Mo_2Cp_2(\mu$ -CPh)(OH)( $\mu$ -PCy\_2)(CO)]<sup>+</sup> rapidly rearranging into its carbene isomer cis-[Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>3</sup>-CHPh)(O)( $\mu$ - $PCy_2(CO)$ <sup>+</sup>, which in turn is reversibly deprotonated to give the corresponding oxo carbyne derivative *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ - $(CPh)(O)(\mu - PCy_2)(CO)]$ . The stereochemistry of these products is preserved along the pertinent transformations, a circumstance allowing the preparation of the corresponding trans isomers by starting from trans- $[Mo_2Cp_2(\mu-CPh)(O)(\mu PCy_2(CO)$ ]. As expected, the radical **2** adds rapidly a molecule of nitric oxide to give a diamagnetic product, but spontaneous decarbonylation also takes place to eventually give the 30electron nitrosyl complex  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(\mu-PCy_2)]$ NO]<sup>+</sup>, a cation that seems to have a strongly electrophilic character.

# EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen atmosphere (99.999%) using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.<sup>44</sup> Petroleum ether refers to that fraction distilling in the range 338– 343 K. Compounds  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(\mu-CO)]$  (1),<sup>1</sup>  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(CO)_2]$ ,<sup>1</sup>  $[FeCp_2]BF_4$ ,<sup>45</sup> Na[B{3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>}] (NaBAr'<sub>4</sub>),<sup>46</sup> and  $[FeCp_2](BAr'_4)^{47}$  were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was

mixed under nitrogen with the appropriate amount of water to reach the activity desired. Filtrations were performed using diatomaceous earth unless otherwise stated. IR C-O stretching frequencies were measured in solution, are referred to as  $\nu_{CO}$  (solvent), and are given in wavenumber units (cm<sup>-1</sup>). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 400.13  $(^{1}H)$ , 162.00  $(^{31}P{^{1}H})$ , or 100.62 MHz ( ${}^{13}C{}^{1}H{}$ ) at 290 K in  $CD_2Cl_2$  solutions unless otherwise stated. Chemical shifts ( $\delta$ ) are given in ppm, relative to internal tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or external 85% aqueous  $H_3PO_4$  solution  $(^{31}P)$ . Coupling constants (J) are given in hertz. Cyclic voltammetry (CV) experiments were performed in an airtight custom-made electrolytic cell using a Pt working electrode, an Ag wire reference electrode, and a Pt wire auxiliary electrode. [NBu<sub>4</sub>][PF<sub>6</sub>] was used as the supporting electrolyte (0.1 M solutions), and the analyte concentration was typically ca. 10<sup>-3</sup> M in dichloromethane. All the potentials were referenced versus the ferrocene/ferrocenium couple, used as internal reference in all the experiments.

Preparation of  $[Mo_2Cp_2(\mu-COH)(\mu-PCy_2)]BF_4$  (3). Diphenylsilane (0.025  $\mu$ L, 0.135 mmol) was added to a solution of compound 1 (0.030 g, 0.047 mmol) in dichloromethane (3 mL), and the mixture was stirred at room temperature for 3 min. Solid [FeCp<sub>2</sub>]BF<sub>4</sub> (0.013 g, 0.047 mmol) was then added to the solution, and the mixture was stirred for 2 min to give a yellow solution, which was filtered. Petroleum ether (10 mL) was then added to the filtrate, and the solvents were removed under vacuum. The resulting residue was then washed with petroleum ether  $(3 \times 5 \text{ mL})$  and dried under vacuum to give compound 3 as a reasonably pure yellow solid (0.028 g, 82%). Attempts to further purify this solid through crystallization resulted in its progressive decomposition. This reaction also can be performed directly in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) within an NMR tube and also by using tert-butylamine-borane adduct (0.030 g, 0.345 mmol) instead of diphenylsilane. IR (Nujol): 3400 (br,  $\nu_{OH}$ ), 1635 (br,  $\delta_{OH}$ ), 1304 (w,  $\nu_{\rm CO}$ ). <sup>1</sup>H NMR (233 K):  $\delta$  7.30 [false t,  $J_{\rm HH}$  = 7, 2H, H<sup>3</sup>(Ph)], 7.19  $[t, J_{HH} = 7, 1H, H^4(Ph)], 6.71$ [false d,  $J_{HH} = 7, 2H, H^2(Ph)], 6.12$ (s, 10H, Cp), 2.0-0.5 (m, 22H, Cy); the OH resonance could not be identified in this spectrum. <sup>13</sup>C{<sup>1</sup>H} NMR (233 K):  $\delta$  401.4 (d,  $J_{PC}$  = 14,  $\mu$ -CPh), 357.8 (d,  $J_{PC}$  = 14,  $\mu$ -COH), 160.1 [s, C<sup>1</sup>(Ph)], 128.0 [s, C<sup>4</sup>(Ph)], 127.4 [s, C<sup>3</sup>(Ph)], 122.3 [s, C<sup>2</sup>(Ph)], 98.4 (s, Cp), 41.7 [d,  $J_{\rm CP} = 18, \, {\rm C}^1({\rm Cy})$ ], 40.9 [d,  $J_{\rm CP} = 17, \, {\rm C}^1({\rm Cy})$ ], 33.0, 32.7 [2s,  ${\rm C}^2({\rm Cy})$ ], 26.9, 26.7 [2d,  $J_{CP} = 12$ ,  $C^{3}(Cy)$ ], 25.8, 25.7 [2s,  $C^{4}(Cy)$ ]

Preparation of cis-[Mo<sub>2</sub>Cp<sub>2</sub>(µ-CPh)(OH)(µ-PCy<sub>2</sub>)(CO)]BF<sub>4</sub> (4). Neat HBF4·OEt2 (12 µL, 0.087 mmol) was added to a dichloromethane solution (5 mL) of compound cis-7 (0.050 g, 0.076 mmol) at 233 K, and the mixture was stirred for 3 min at this temperature to give a green solution. Workup as described for 3 gave a green solid shown by NMR to contain compound 4 as the major species (0.048 g, 85%). All attempts to further purify this solid through crystallization resulted in its progressive transformation into its isomer cis-5 (see text). IR (Nujol): 3500 (vbr,  $\nu_{OH}$ ), 1954 (s,  $\nu_{CO}$ ). <sup>1</sup>H NMR (253 K):  $\delta$ 7.51 [false t,  $J_{\rm HH}$  = 7, 2H, H<sup>3</sup>(Ph)], 7.23 [t,  $J_{\rm HH}$  = 7, 1H, H<sup>4</sup>(Ph)], 6.63 [false d,  $J_{\rm HH}$  = 7, 2H, H<sup>2</sup>(Ph)], 5.96, 5.94 (2s, 2 × 5H, Cp), 2.4–1.2 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR (253 K):  $\delta$  413.1 (s,  $\mu$ -C), 233.1 (d,  $J_{PC}$ = 8, CO), 165.4 [s,  $C^{1}(Ph)$ ], 128.8 [s,  $C^{4}(Ph)$ ], 128.4 [s,  $C^{3}(Ph)$  and  $C^{2}(Ph)$ ], 105.2, 96.9 (2s, Cp), 47.8 [d,  $J_{CP}$  = 12,  $C^{1}(Cy)$ ], 46.4 [d,  $J_{CP}$ = 15,  $C^{1}(Cy)$ ], 33.2, 32.3, 30.8, 29.0 [4s,  $C^{2}(Cy)$ ], 26.6, 26.5, 26.5, 26.4 [4d,  $J_{CP} = 12$ ,  $C^{3}(Cy)$ ], 25.9, 25.8 [2s,  $C^{4}(Cy)$ ]

**Preparation of cis-[Mo<sub>2</sub>Cp<sub>2</sub>(μ-η<sup>1</sup>:η<sup>3</sup>-CHPh)(O)(μ-PCy<sub>2</sub>)(CO)]BF<sub>4</sub>** (cis-5). Solid [FeCp<sub>2</sub>]BF<sub>4</sub> (0.022g, 0.078 mmol) was added to a dichloromethane solution (5 mL) of compound 1 (0.050 g, 0.078 mmol) to give a green solution immediately. Then water (4 μL, 0.22 mmol) was added, whereupon the solution turned dark red, and the mixture was further stirred for 5 min. After removal of the solvent under vacuum, the residue was washed with petroleum ether (3 × 5 mL) and dried under vacuum to give compound *cis*-5 as a brown solid (0.048 g, 83%). Anal. Calcd for C<sub>30</sub>H<sub>38</sub>BF<sub>4</sub>Mo<sub>2</sub>O<sub>2</sub>P: C, 48.67; H, 5.17. Found: C, 48.35; H, 4.92. IR (Nujol): 1935 (vs, ν<sub>CO</sub>), 930 (s, ν<sub>MoO</sub>). <sup>1</sup>H NMR: δ 10.34 (s, 1H, μ-CH), 8.05, 7.64, 7.40, 7.33 (4m, 4 × 1H, Ph), 6.17, 4.78 (2s, 2 × 5H, Cp), 4.60 [d, J<sub>HH</sub> = 7, 1H, H<sup>2</sup>(Ph)], 2.2– 1.2 (m, 22H, Cy).

Preparation of cis-[Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>3</sup>-CHPh)(O)( $\mu$ -PCy<sub>2</sub>)(CO)]-BAr'<sub>4</sub> (cis-5''). Solid [FeCp<sub>2</sub>](BAr'<sub>4</sub>) (0.082 g, 0.078 mmol) and a droplet of water (4  $\mu$ L, 0.22 mmol) were added to a dichloromethane solution (5 mL) of compound 1 (0.050 g, 0.078 mmol) to give a red solution immediately, and the mixture was stirred for 5 min. The solvent was then removed under vacuum, and the residue was dissolved in a minimum amount of dichloromethane/petroleum ether (1:2) and chromatographed on alumina (activity IV) at 253 K. Elution with the same solvent mixture gave a brown fraction yielding, after removal of solvents, compound cis-5' as a red-brown microcrystalline solid (0.050 g, 80%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of toluene into a dichloromethane solution of the complex at 253 K. Anal. Calcd for C<sub>62</sub>H<sub>50</sub>BF<sub>24</sub>Mo<sub>2</sub>O<sub>2</sub>P: C, 49.10; H, 3.32. Found: C, 49.27; H, 3.43. IR (Nujol): 1942 (vs,  $\nu_{CO}$ ), 944 (s,  $\nu_{MoO}$ ). <sup>1</sup>H NMR:  $\delta$  9.80 (s, 1H,  $\mu$ -CH), 7.72 [s, 8H, H<sup>2</sup>(Ar')], 7.56 [s, 4H, H<sup>4</sup>(Ar')], 7.75, 7.64, 7.41, 7.36 (4m, 4 × 1H, Ph), 6.08, 4.63 (2s, 2 × 5H, Cp), 4.67 [d,  $J_{\rm HH}$  = 7, 1H,  $H^{2}(Ph)$ ], 2.6–1.2 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  234.2 (d,  $J_{PC}$  = 16, CO), 177.0 (s,  $\mu$ -CH), 162.1 [m,  $J_{CB} = 50$ , C<sup>1</sup>(Ar')], 135.2 [s,  $C^{2}(Ar')$ ], 137.3, 133.6, 131.7, 130.5 (4s, Ph), 129.3 [q,  $J_{CF} = 32$ ,  $C^{3}(Ar')], 125.0 [q, J_{CF} = 273, CF_{3}], 103.3, 91.3 (2s, Cp), 102.0 [s, C<sup>1</sup>(Ph)], 101.2 [s, C<sup>2</sup>(Ph)], 57.3 [d, J_{CP} = 18, C<sup>1</sup>(Cy)], 55.2 [d, J_{CP} = 9, C<sup>1</sup>(Cy)], 36.4, 35.0 [2d, J_{CP} = 6, C<sup>2</sup>(Cy)], 34.8, 33.4 [2d, J_{CP} = 4, C<sup>2</sup>(Cy)], 28.7 [d, J_{CP} = 11, C<sup>3</sup>(Cy)], 28.6 [d, J_{CP} = 10, C<sup>3</sup>(Cy)], 28.3, 001.6 [d, J_{CP} = 10, C<sup>3</sup>(Cy)], 28.4 [d, J_{CP} = 10, C<sup>3</sup>(Cy)], 28.5 [d, J_{CP} = 10, C<sup>3</sup>(CY)], 28$ 28.1 [2d,  $J_{CP} = 12$ ,  $C^{3}(Cy)$ ], 26.6, 26.5 [2s,  $C^{4}(Cy)$ ]

**Preparation of** *trans*-[**Mo**<sub>2</sub>**Cp**<sub>2</sub>(*μ*-*η*<sup>1</sup>:*η*<sup>3</sup>-**CHPh**)(**O**)(*μ*-**PCy**<sub>2</sub>)(**CO**)]-**BF**<sub>4</sub> (*trans*-5). Neat HBF<sub>4</sub>·OEt<sub>2</sub> (12 *μ*L, 0.087 mmol) was added to a dichloromethane solution (5 mL) of compound *trans*-7 (0.050 g, 0.076 mmol) at room temperature, and the mixture was stirred for 3 min to give a red solution. Workup as described for 3 gave compound *trans*-5 as a red solid (0.046 g, 82%). Anal. Calcd for  $C_{30}H_{38}BF_4Mo_2O_2P$ : C, 48.67; H, 5.17. Found: C, 48.30; H, 4.88. <sup>1</sup>H NMR: δ 11.00 (s, 1H, *μ*-CH), 7.82, 7.73, 7.63, 7.35 (4m, 4 × 1H, Ph), 5.49, 4.55 (2s, 2 × 5H, Cp), 4.62 [d, *J*<sub>HH</sub> = 7, 1H, H<sup>2</sup>(Ph)], 3.0–1.2 (m, 22H, Cy).

Preparation of  $[Mo_2Cp_2(\mu-CPh)(OPh)(\mu-PCy_2)(CO)]BF_4$  (6). Phenol (ca. 0.050 g, 0.53 mmol) was added to a solution of compound 1 (0.050 g, 0.078 mmol) in dichloromethane (3 mL), and the mixture was stirred at room temperature for 3 min. Solid  $[FeCp_2]BF_4$  (0.022g, 0.078 mmol) was then added to the solution, and the mixture was stirred for 5 min to give a green solution, which was filtered. Petroleum ether (10 mL) was then added to the filtrate, and the solvents were removed under vacuum. The resulting residue was then washed with petroleum ether  $(3 \times 5 \text{ mL})$  and dried under vacuum to give a green solid containing compound 6 as a major species, along with variable amounts of cis-5 (0.055 g, 85%). Attempts to further purify this solid through crystallization resulted in its progressive transformation into the mentioned complex (see Results and Discussion section). <sup>1</sup>H NMR:  $\delta$  7.55, 7.34 [2 false t,  $J_{\rm HH}$  = 7, 2 × 2H, H<sup>3</sup>(Ph)], 7.13, 6.90 [2t,  $J_{\rm HH}$  = 7, 2 × 1H, H<sup>4</sup>(Ph)], 6.83, 6.66 [2 false d,  $J_{\rm HH}$  = 7, 2H, H<sup>2</sup>(Ph)], 5.90, 5.70 (2s, 2 × 5H, Cp), 2.96–0.40 (m, 22H, Cy).

Preparation of cis-[Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -CPh)(O)( $\mu$ -PCy<sub>2</sub>)(CO)] (cis-7). Neat 1,8-diazabicycloundec-7-ene (12 µL, 0.08 mmol) was added to a dichloromethane solution (5 mL) of compound cis-5 (0.050 g, 0.067 mmol) at room temperature, and the mixture was stirred for 1 min to give a yellow solution. After removal of solvents under vacuum, the residue was chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1:4) gave a yellow fraction yielding, after removal of solvents, compound cis-7 as a yellow solid (0.037 g, 88%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for C<sub>30</sub>H<sub>37</sub>Mo<sub>2</sub>O<sub>2</sub>P: C, 55.22; H, 5.72. Found: C, 54.95; H, 5.53. <sup>1</sup>H NMR (300.13 MHz):  $\delta$  7.34 [false t,  $J_{\rm HH}$  = 7, 2H, H<sup>3</sup>(Ph)], 7.05 [t,  $J_{\rm HH}$  = 7, 1H, H<sup>4</sup>(Ph)], 6.81 [false d,  $J_{\rm HH}$  = 7, 2H, H<sup>2</sup>(Ph)], 5.47, 5.33 (2s, 2 × SH, Cp), 2.5–0.7 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  360.0 (d,  $J_{\rm PC}$  = 7,  $\mu$ -C), 238.5 (d,  $J_{PC}$  = 10, CO), 168.9 [s, C<sup>1</sup>(Ph)], 127.8 [s, C<sup>3</sup>(Ph)], 123.7 [s, C<sup>4</sup>(Ph)], 119.8 [s, C<sup>2</sup>(Ph)], 101.0, 92.4 (2s, Cp), 47.6 [d, J<sub>CP</sub> = 12,  $C^{1}(Cy)$ ], 44.1 [d,  $J_{CP}$  = 18,  $C^{1}(Cy)$ ], 36.3, 33.8, 32.5 [3s,

 $C^{2}(Cy)$ ], 33.4 [d,  $J_{CP}$  = 3,  $C^{2}(Cy)$ ], 28.6, 28.3, 27.8 [3d,  $J_{CP}$  = 12,  $C^{3}(Cy)$ ], 28.4 [d,  $J_{CP}$  = 8,  $C^{3}(Cy)$ ], 26.8, 26.7 [2s,  $C^{4}(Cy)$ ].

**Preparation of** *trans-*[Mo<sub>2</sub>Cp<sub>2</sub>(μ-CPh)(O)(μ-PCy<sub>2</sub>)(CO)] (*trans-*7). A dichloromethane solution (5 mL) of  $[Mo_2Cp_2(\mu$ -CPh)(μ-PCy<sub>2</sub>)(CO)<sub>2</sub>] (0.050 g, 0.075 mmol) was stirred in the open air for 5 min. The Schlenk tube was then closed, and the mixture was further stirred at room temperature for 8 h to give a yellow solution. Workup as described for *cis-*7 gave compound *trans-*7 as a yellow solid (0.035 g, 72%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for C<sub>30</sub>H<sub>37</sub>Mo<sub>2</sub>O<sub>2</sub>P: C, 55.22; H, 5.72. Found: C, 54.90; H, 5.48. <sup>1</sup>H NMR (300.13 MHz): δ 7.55 [false d, J<sub>HH</sub> = 7, 2H, H<sup>2</sup>(Ph)], 7.45 [false t, J<sub>HH</sub> = 7, 2H, H<sup>3</sup>(Ph)], 7.25 [t, J<sub>HH</sub> = 7, 1H, H<sup>4</sup>(Ph)], 5.42, 5.40 (2s, 2 × 5H, Cp), 2.2–0.8 (m, 22H, Cy).

**Preparation of [Mo<sub>2</sub>Cp<sub>2</sub>(μ-CPh)(μ-PCy<sub>2</sub>)(μ-NO)]BF<sub>4</sub> (8).** Nitric oxide (0.2% solution in N<sub>2</sub>) was bubbled through a solution of compound 1 (0.050 g, 0.078 mmol) in dichloromethane (10 mL) for 5 min. Solid [FeCp<sub>2</sub>]BF<sub>4</sub> (0.022 g, 0.078 mmol) was then added to the solution, and the mixture was stirred for 10 min while keeping the NO bubbling, to give an orange solution, which was filtered. Workup as described for 3 gave compound 8 as an orange solid (0.052, 91%). Anal. Calcd for C<sub>29</sub>H<sub>37</sub>BF<sub>4</sub>Mo<sub>2</sub>NOP: C, 48.03; H, 5.14; N, 1.93. Found: C, 47.70; H, 4.95; N, 1.75. <sup>1</sup>H NMR: δ 7.43 [false t, *J*<sub>HH</sub> = 7, 2H, H<sup>3</sup>(Ph)], 7.33 [t, *J*<sub>HH</sub> = 7, 1H, H<sup>4</sup>(Ph)], 6.82 [false d, *J*<sub>HH</sub> = 7, 2H, H<sup>2</sup>(Ph)], 6.41 (s, 10H, Cp), 2.6–1.2 (m, 18H, Cy), 0.72–0.50 (m, 4H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 404.5 (d, *J*<sub>PC</sub> = 14, μ-CPh), 159.1 [s, C<sup>1</sup>(Ph)], 130.9 [s, C<sup>4</sup>(Ph)], 128.8 [s, C<sup>3</sup>(Ph)], 123.6 [s, C<sup>2</sup>(Ph)], 103.6 (s, Cp), 43.9 [d, *J*<sub>CP</sub> = 15, C<sup>1</sup>(Cy)], 41.7 [d, *J*<sub>CP</sub> = 16, C<sup>1</sup>(Cy)], 33.7, 33.1 [2s, C<sup>2</sup>(Cy)], 27.0 [d, *J*<sub>CP</sub> = 15, C<sup>3</sup>(Cy)], 26.8 [d, *J*<sub>CP</sub> = 16, C<sup>3</sup>(Cy)], 25.7, 25.6 [2s, C<sup>4</sup>(Cy)].

**Preparation of [Mo<sub>2</sub>Cp<sub>2</sub>(μ-CHPh)(O)(μ-PCy<sub>2</sub>)(NO)] (9).** Compound 8 (0.030 g, 0.041 mmol) was dissolved in a minimum amount of dichloromethane/petroleum ether (1:1) and chromatographed on alumina (activity IV) at 253 K. Elution with the same solvent mixture gave a green fraction yielding, after removal of solvents, compound 9 as a green microcrystalline solid (0.022 g, 81%). Anal. Calcd for C<sub>29</sub>H<sub>38</sub>Mo<sub>2</sub>NO<sub>2</sub>P: C, 53.14; H, 5.84; N, 2.14. Found: C, 52.80; H, 5.61; N, 1.95. IR (Nujol): 1606 (vs,  $\nu_{NO}$ ), 933 (s,  $\nu_{MOO}$ ). <sup>1</sup>H NMR: δ 8.70 (s, 1H, μ-CH), 7.11 [false t,  $J_{HH}$  = 7, 2H, H<sup>3</sup>(Ph)], 6.85 [t,  $J_{HH}$  = 7, 1H, H<sup>4</sup>(Ph)], 6.33 [false d,  $J_{HH}$  = 7, 2H, H<sup>2</sup>(Ph)], 5.48, 5.44 (2s, 2 × 5H, Cp), 2.7–0.6 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 163.0 [s, C<sup>1</sup>(Ph)], 132.3 (d,  $J_{PC}$  = 4, μ-CH), 128.1 [s, C<sup>4</sup>(Ph)], 127.6 [s, C<sup>3</sup>(Ph)], 122.3 [s, C<sup>2</sup>(Ph)], 101.2, 96.2 (2s, Cp), 46.0 [d,  $J_{CP}$  = 15, C<sup>1</sup>(Cy)], 42.1 [d,  $J_{CP}$  = 13, C<sup>1</sup>(Cy)], 35.2, 33.7 [2d,  $J_{CP}$  = 2, C<sup>2</sup>(Cy)], 32.3 [d,  $J_{CP}$  = 12, C<sup>3</sup>(Cy)], 28.4 [d,  $J_{CP}$  = 10, C<sup>3</sup>(Cy)], 26.7, 26.6 [2s, C<sup>4</sup>(Cy)].

X-ray Structure Determination of Compounds cis-5' and cis-7. The X-ray intensity data were collected at 100 K on a Nonius KappaCCD single-crystal diffractometer, using graphite-monochromated Mo K $\alpha$  radiation. Images were collected at a 40 mm (*cis*-5') or 35 mm (cis-7) fixed crystal-detector distance, using the oscillation method, with 1° oscillation and 40 and 100 s exposure times per image, respectively. Data collection strategy was calculated with the program Collect,<sup>48</sup> and data reduction and cell refinements were performed with the programs HKL Denzo and Scalepack.<sup>49</sup> A semiempirical absorption correction was applied using the program SORTAV.<sup>50</sup> Using the program suite WinGX,<sup>51</sup> the structure was solved by Patterson interpretation and phase expansion using SHELXL97 and refined with full-matrix least-squares on  $F^2$  using SHELXL97.52 For compound cis-5' all non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically placed and refined using a riding model, except for H(2), which was located on the Fourier map and refined isotropically. A molecule of an unidentified solvent was found to be present in the asymmetric unit; therefore the SQUEEZE procedure,<sup>53</sup> as implemented in PLATON,<sup>54</sup> was used. Compound cis-7 was found to crystallize with a molecule of dichloromethane. Moreover one of the cyclopentadienyl ligands was found to be disordered over two positions, which were satisfactorily refined with 0.58/0.42 occupancies. All non-hydrogen atoms were

refined anisotropically, except the carbon atoms involved in the disorder. All hydrogen atoms were geometrically placed and refined using a riding mode.

X-ray Structure Determination of Compound trans-7. The Xray intensity data were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated Mo K $\alpha$  radiation at 100 K. The software APEX was used for collecting frames with the  $\omega/\phi$  scans measurement method.<sup>55</sup> The Bruker SAINT software was used for the data reduction,<sup>56</sup> and a multiscan absorption correction was applied with SADABS.<sup>57</sup> Structure solution and refinements were performed as described above, with all hydrogen atoms being geometrically placed and refined using a riding model. All non-H atoms were freely refined anisotropically except for C(12) and C(17), which were refined anisotropically in combination with the instructions DELU and SIMU. Moreover a highly disordered molecule of hexane placed on a symmetry element was found to be present in the asymmetric unit; therefore the SQUEEZE procedure, as described above, was used.

**Computational Details.** The computations for compounds 1 and 2 were carried out using the GAUSSIAN03 package, <sup>58</sup> in which the hybrid methods B3LYP (1) and UB3LYP (2) were applied with the Becke three-parameter exchange functional.<sup>59</sup> and the Lee–Yang–Parr correlation functional.<sup>60</sup> Effective core potentials and their associated double- $\zeta$  LANL2DZ basis set were used for the metal atoms.<sup>61</sup> The light elements (P, O, C, and H) were described with the 6-31G\* basis.<sup>62</sup> Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of 1, and frequency analyses were performed to ensure that a minimum structure with no imaginary frequencies was achieved in each case. Molecular orbitals and vibrational modes were visualized using the MOLEKEL program.<sup>63</sup> The topological analysis of the electron density was carried out with the Xaim routine.<sup>64</sup>

# ASSOCIATED CONTENT

# Supporting Information

A CIF file with full crystallographic data of compounds *cis*-5', *cis*-7, and *trans*-7. A PDF file containing data (complete ref 59, figures, selected bond distances and angles, selected molecular orbitals, atomic charges and topological properties of the electron density) for the DFT-optimized structures of 1 and 2, and a table with crystal data of compounds *cis*-5' and 7. This material is available free of charge via the Internet at http:// pubs.acs.org.

#### AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: mara@uniovi.es.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We thank the DGI of Spain for financial support (Project CTQ2009-09444) and the Consejería de Educación of Asturias for grants (to S.M. and D.G.-V.). We also thank the Universidad de Santiago de Compostela (Unidad de Rayos X) for the collection of the diffraction data.

### REFERENCES

(1) Alvarez, M. A.; García, M. E.; García-Vivó, D.; Martínez, M. E.; Ruiz, M. A. Organometallics **2011**, 30, 2189.

(2) Alvarez, M. A.; García, M. E.; Martínez, M. E.; Menéndez, S.; Ruiz, M. A. Organometallics **2010**, *29*, 710.

(3) Alvarez, M. A.; García, M. E.; García-Vivó, D.; Menéndez, S.; Ruiz, M. A. Organometallics **2012**, *31*, 7181.

(4) El Amin, E. A. E.; Jeffery, J. C.; Walters, T. M. J. Chem. Soc., Chem. Commun. 1990, 170. (5) (a) Davies, S. J.; Howard, J. A. K.; Pilotti, M. U.; Stone, F. G. A. J. Chem. Soc., Chem. Commun. 1989, 190. (b) Davies, S. J.; Howard, J. A. K.; Pilotti, M. U.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1989, 1855. (c) Davies, S. J.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1989, 1865.

(6) (a) Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis; Chanon, M.; Julliard, M.; Poite, J. C., Eds.; Kluwer Academic Publishers: Dordrecht, 1989. (b) Organometallic Radical Processes; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990. (c) Astruc, D. Electron Transfer and Radical Processes in Transition-Metal Chemistry; VCH: New York, 1995.

(7) (a) Geiger, W. E. Organometallics 2007, 26, 5738. (b) Pombeiro, A. J. L.; Guedes da Silva, M. F.; Lemos, M. A. N. D. A. Coord. Chem. Rev. 2001, 219–221, 53. (c) Torraca, K. E.; McElwee-White, L. Coord. Chem. Rev. 2000, 206–207, 469. (d) Astruc, D. Acc. Chem. Res. 1997, 30, 383. (e) Sun, S.; Sweigart, D. A. Adv. Organomet. Chem. 1996, 40, 171. (f) Connelly, N. G. Chem. Soc. Rev. 1989, 18, 153. (g) Connelly, N. G.; Geiger, W. E. Adv. Organomet. Chem. 1985, 24, 87.

(8) (a) Aubart, M. A.; Bergman, R. G. J. Am. Chem. Soc. 1996, 118, 1793. (b) Baker, R. T.; Calabrese, J. C.; Krusic, P. J.; Therien, M. J.; Trogler, W. C. J. Am. Chem. Soc. 1988, 110, 8392. (c) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. J. Am. Chem. Soc. 1976, 98, 7436. (d) Theopold, K. H.; Bergman, R. G. J. Am. Chem. Soc. 1983, 105, 464. (e) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakulski, M. J. Chem. Soc., Chem. Commun. 1985, 1267.

(9) (a) Schroeder, N. C.; Angelici, R. J. J. Am. Chem. Soc. **1986**, 108, 3688. (b) Aase, T.; Tilset, M.; Parker, V. Organometallics **1989**, 8, 1558.

(10) The intermetallic bond in these radicals is usually supported by bridging ligands. Very recently, Bullock, Yang, and co-workers have succeeded in isolating the unsupported 33-electron complexes  $[M_2Cp_2(CO)_4(PMe_3)_2][B(C_6F_5)_4]$  (M = Mo, W), which seem to be stabilized by the strong donor properties of the PMe<sub>3</sub> ligand, although no chemistry of these radicals has been reported so far: van der Eide, E. F.; Yang, P.; Walter, E. D.; Liu, T.; Bullock, R. M. Angew. Chem., Int. Ed. 2012, 51, 8361.

(11) For some recent work on this matter, see: (a) Schilter, D.; Rauchfuss, T. B.; Matthias, S. Inorg. Chem. 2012, 51, 8931. (b) Silakov, A.; Olsen, M. T.; Sproules, S.; Reijerse, E. J.; Rauchfuss, T. B. Inorg. Chem. 2012, 51, 8617. (c) Olsen, M. T.; Rauchfuss, T. B.; Zaffaroni, R. Organometallics 2012, 41, 3447. (d) Schilter, D.; Nilges, M. J.; Chakrabarti, M.; Lindahl, P. A.; Rauchfuss, T. B.; Stein, M. Inorg. Chem. 2012, 51, 2338. (e) Camara, J. M.; Rauchfuss, T. B. Nat. Chem. 2012, 4, 26. (f) Hsieh, C. H.; Erdem, O. F.; Harman, S. D.; Singleton, M. L.; Reijerse, E.; Lubitz, W.; Popescu, C. V.; Reibenspies, J. H.; Brothers, S. M.; Hall, M. B. J. Am. Chem. Soc. 2012, 134, 13089. (g) Darensbourg, M. Y.; Bethel, R. D. Nat. Chem. 2012, 4, 11. (h) Choufai, D.; Zampella, G.; Capon, J. F.; De Gioia, L.; Gloaguen, F.; Pétillon, J. F.; Scholhammer, P.; Talarmin, J. Inorg. Chem. 2011, 50, 12575. (i) Jablonslyte, A.; Wright, J. A.; Fairhurst, S. A.; Peck, J. N. T.; Ibrahim, S. K.; Oganesyan, V. S.; Pickett, C. J. J. Am. Chem. Soc. 2011, 133, 18606.

(12) García, M. E.; Riera, V.; Rueda, M. T.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. J. Am. Chem. Soc. **1999**, *121*, 4060.

(13) (a) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A.; Vaissermann, J. Organometallics 2003, 22, 456. (b) Alvarez, M. A.; Anaya, Y.; García, M. E.; Ruiz, M. A. Organometallics 2004, 23, 3950.
(c) Alvarez, M. A.; Anaya, Y.; García, M. E.; Ruiz, M. A.; Vaissermann, J. Organometallics 2005, 24, 2452.

(14) (a) García, M. E.; Riera, V.; Rueda, M. T.; Ruiz, M. A.; Halut, S. J. Am. Chem. Soc. **1999**, 121, 1960. (b) Cimadevilla, F.; García, M. E.; García-Vivó, D.; Ruiz, M. A.; Rueda, M. T.; Halut, S. J. Organomet. Chem. **2012**, 699, 67.

(15) García, M. E.; García-Vivó, D.; Ruiz, M. A.; Alvarez, S.; Aullón, G. Organometallics **2007**, *26*, 4930.

(16) (a) Koch, W.; Holthausen, M. C. A Chemist's Guide to Density Functional Theory, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2002.
(b) Ziegler, T. Chem. Rev. 1991, 91, 651. (c) Foresman, J. B.; Frisch, *Æ. Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburg, 1996.

(17) García, M. E.; García-Vivó, D.; Ruiz, M. A.; Alvarez, S.; Aullón, G. Organometallics **200**7, *26*, 5912.

(18) Bader, R. F. W. Atoms in Molecules-A Quantum Theory; Oxford University Press: Oxford, U. K., 1990.

(19) Cramer, C. J. Essentials of Computational Chemistry, 2nd ed.; Wiley: Chichester, U. K., 2004.

(20) Crabtree, R. H.; Lavin, M. Inorg. Chem. 1986, 25, 805.

(21) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Falvello, L. R.; Bois, C. Organometallics **1997**, *16*, 354.

(22) Winter, M. J. Adv. Organomet. Chem. 1989, 29, 101.

(23) Simpson, C. Q., II; Hall, M. B. J. Am. Chem. Soc. 1992, 114, 1641.

(24) García, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Marchio, L. Organometallics **2007**, *26*, 6197.

(25) A general trend established for  ${}^{2}J_{XY}$  in complexes of the type [MCpXYL<sub>2</sub>] is that it increases algebraically with the XMY angle, with absolute values in the order  $|J_{cis}| > |J_{trans}|$ . See, for instance: (a) Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 6. (b) Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. J. Organomet. Chem. **1990**, 399, 125.

(26) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A. Organometallics 1999, 18, 634.

(27) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, U. K., 1975.

(28) Alvarez, M. A.; García, M. E.; Martínez, M. E.; Ramos, A.; Ruiz, M. A.; Sáez, D.; Vaissermann, J. Inorg. Chem. **2006**, *45*, 6965.

(29) Cimadevilla, F.; García, M. E.; García-Vivó, D.; Ruiz, M. A.; Graiff, C.; Tiripicchio, A. *Inorg. Chem.* **2012**, *51*, 10427.

(30) (a) Jeffery, J. C.; More, I.; Razay, H.; Stone, F. G. A. J. Chem. Soc., Chem. Commun. 1981, 1255. (b) Fischer, H.; Schmid, J.; Riede, J. J. Organomet. Chem. 1988, 355, 219. (c) Tang, D.; Sun, J.; Chen, J. J. Chem. Soc., Dalton Trans. 1998, 931.

(31) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D.; Butler, W. M. J. Am. Chem. Soc. **1987**, 109, 3603.

(32) Bottomley, F.; Sutin, L. Adv. Organomet. Chem. 1988, 28, 339.

(33) (a) Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. Organometallics 2007, 26, 5454.
(b) Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A. J. Organomet. Chem. 2009, 694, 3864.

(34) Herrmann, W. A. Adv. Organomet. Chem. 1982, 20, 159.

(35) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Razay, H.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. **1984**, 1563.

(36) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. J. Chem. Soc., Dalton Trans. **1989**, 1555.

(37) García, M. E.; Melón, S.; Ramos, A.; Ruiz, M. A. Dalton Trans. 2009, 8171.

(38) Endrich, K.; Korswagen, R.; Zhan, T.; Ziegler, M. L. Angew. Chem., Int. Ed. Engl. 1982, 21, 919.

(39) Cimadevilla, F.; García, M. E.; García-Vivó, D.; Ruiz, M. A.; Graiff, C.; Tiripicchio, A. Inorg. Chem. **2012**, *51*, 7284.

(40) García, M. E.; García-Vivó, D.; Melón, S.; Ruiz, M. A.; Graiff, C.; Tiripicchio, A. Inorg. Chem. **2009**, *48*, 9282.

(41) Feng, S. G.; White, P. S.; Templeton, J. L. J. Am. Chem. Soc. 1992, 114, 2951.

(42) Ritcher-Addo, G. B.; Legzdins, P. Metal Nitrosyls; Oxford University Press: Oxford, U. K., 1992.

(43) Legzdins, P.; Young, M. A. Comments Inorg. Chem. 1995, 17, 239.

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

(45) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877.

(46) Yakelis, N. A.; Bergman, R. G. Organometallics 2005, 24, 3579.

(47) Chávez, I.; Alvarez-Carena, A.; Molins, E.; Roig, A.; Maninkiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manríquez, J. M. J. Organomet. Chem. **2000**, 601, 126.

(48) Collect; Nonius, B.V.: Delft, The Netherlands, 1997-2004.

- (49) Otwinowski, Z.; Minor, W. Methods Enzymol. 1997, 276, 307.
- (50) Blessing, R. H. Acta Crystallogr., Sect. A 1995, 51, 33.
- (51) Farrugia, L. J. J. Appl. Crystallogr. 1999, 32, 837.
- (52) Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112.
- (53) Van der Sluis, P.; Spek, A. L. Acta Crystallogr., Sect. A 1990, 46, 194.
- (54) (a) Spek, A. L. Acta Crystallogr., Sect. A **1990**, 46, C34. (b) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2010.
- (55) APEX 2, version 2.0-1; Bruker AXS Inc: Madison, WI, 2005.
- (56) SMART & SAINT Software Reference Manuals, version 5.051 (Windows NT version); Bruker Analytical X-ray Instruments: Madison, WI, 1998.
- (57) Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, 1996.
- (58) Frisch, M. J. et al. *Gaussian 03*, Revision B.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (59) Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
- (60) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785.
- (61) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.
- (62) (a) Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta 1973, 28,
- 213. (b) Petersson, G. A.; Al-Laham, M. A. J. Chem. Phys. 1991, 94,
- 6081. (c) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M.
- A.; Shirley, W. A.; Mantzaris, J. J. Chem. Phys. 1988, 89, 2193.
- (63) Portmann, S.; Lüthi, H. P. MOLEKEL: An Interactive Molecular Graphics Tool. CHIMIA 2000, 54, 766.
- (64) Ortiz, J. C.; Bo, C. Xaim; Departamento de Química Física e Inorgánica, Universidad Rovira i Virgili: Tarragona, Spain, 1998.